



COOPERATIVE RESEARCH CENTRE FOR COAL IN SUSTAINABLE DEVELOPMENT
Established and supported under the Australian Government's Cooperative Research Centres Program

**BACKGROUND INFORMATION FOR WEBSITE ON TRACE ELEMENTS
IN COAL**

RESEARCH REPORT 56

Author:

Ken Riley

CSIRO Energy Technology

August 2005



QCAT Technology Transfer Centre, Technology Court
Pullenvale Qld 4069 AUSTRALIA
Telephone (07) 3871 4400 Facsimile (07) 3871 4444
Email: Administration@ccsd.biz

This page is intentionally left blank

DISTRIBUTION LIST

CCSD

Chairman; Chief Executive Officer; Research Manager, Manager Technology; Files

Industry Participants

Australian Coal Research Limited	Mr Mark Bennetts
BHP Billiton Mitsubishi Alliance	Mr Ross Willims
.....	Mr Ben Klaassen
.....	Dr Andre Urfer
CNA Resources.....	Mr Ashley Conroy
CS Energy	Dr Chris Spero
Delta Electricity	Mr Greg Everett
Queensland Natural Resources & Mines	Mr Bob Potter
.....	Mr Ray Slater
Rio Tinto (TRPL).....	Mr David Cain
.....	Dr Jon Davis
Stanwell Corporation	Mr Howard Morrison
Tarong Energy	Mr Burt Beasley
The Griffin Coal Mining Co Pty Ltd	Mr Jim Coleman
Wesfarmers Premier Coal Ltd	Mr Peter Ashton
Western Power	Mr Keith Kirby
Xstrata Coal Pty Ltd.....	Mr Colin Whyte
.....	Mr Barry Isherwood

Research Participants

CSIRO	Dr David Brockway
Curtin University of Technology	Prof Barney Glover
Macquarie University	Prof Jim Piper
The University of Newcastle	Prof Adrian Page
The University of New South Wales	Prof David Young
The University of Queensland	Prof Don McKee

This page is intentionally left blank



*Cooperative Research Centre for
Coal in Sustainable Development*
QCAT Technology Transfer Centre
Technology Court
Pullenvale, Qld 4069
Telephone: (07) 3871 4400
Fax: (07) 3871 4444

Feedback Form

To help us improve our service to you may I ask you for five minutes of your time to complete this questionnaire. Please fax or mail it back to me, or, if you would prefer, give me a call.

ATTENTION **MANAGER TECHNOLOGY TRANSFER**

FAX NO **07 3871 4444** **DATE**

FROM **NAME:**
 COMPANY:.....

REPORT TITLE: **BACKGROUND INFORMATION FOR WEBSITE ON TRACE ELEMENTS IN COAL**
AUTHORS: **KEN RILEY**

Would you please rate our performance in the following areas by ticking the appropriate box:

The Research	Agree	Neutral	Disagree	Don't Know
This work has achieved its research objectives				
This work has delivered to agreed milestones				
This work is relevant to my organisation				
Communication of progress has been timely & useful				

The Report

The report is well presented				
The context of the report is clear				
The content of the report is substantial				
The report is clearly written and understandable				
This product is good value				

Any further comments which would assist us in better serving your future requirements?:

.....
.....

Are there any people you would like to add to our distribution list?:

.....
.....

Thank you for your response

This page is intentionally left blank

EXECUTIVE SUMMARY

The aim of this project was to develop a website that contains the essential information on the environmentally sensitive trace elements in Australian bituminous thermal coals and provides a comparison of the concentrations in the Australian coals with those of other thermal coals traded worldwide.

Information on Australian coals was sourced from the datasets available at CSIRO and ACIRL. The information on other coals was obtained from the reports to ACARP by Dale and colleagues, from other published reports and papers, as well as the world wide web.

This report also contains information on the behaviour of trace elements during combustion in power stations and the subsequent impacts on the environment.

Legislation relating to emissions of trace elements to the atmosphere and to water is also discussed in this report

Summary fact sheets are available from the CSIRO website; the URL address is http://www.det.csiro.au/science/researchservices/trace_elements.htm or <http://www.det.csiro.au/traceelements>

Note that the data in the website and this report on the concentration of trace elements are limited to the analyses completed in the laboratories of CSIRO Energy Technology. Data were obtained from the analysis of approximately 100 Australian coals and 60 coals traded from other nations. No claim is made that the data are representative of all internationally traded coals.

You must make your own assessment of the suitability for your purposes of this information. To the extent permitted by law, CSIRO excludes all liability arising directly or indirectly from use of this information.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	i
1 INTRODUCTION	1
2 SOURCES and COLLATION OF DATA.....	2
2.1 Concentrations of Trace Elements in Overseas Coals	2
2.2 Concentrations of Trace Elements in Australian Bituminous Coals.....	2
2.3 Discussion of Analytical Methods	3
2.4 Modes of Occurrence of Trace Elements in Bituminous Coals.....	6
3 BEHAVIOUR OF TRACE ELEMENTS DURING COMBUSTION	8
4 HEALTH AND ENVIRONMENTAL EFFECTS.....	9
5 INFORMATION ON THE KEY TRACE ELEMENTS	10
5.1 Antimony (Sb).....	11
5.2 Arsenic (As)	12
5.3 Barium (Ba).....	13
5.4 Beryllium.....	14
5.5 Boron (B).....	15
5.6 Cadmium (Cd).....	16
5.7 Chlorine (Cl)	17
5.8 Chromium (Cr).....	18
5.9 Cobalt (Co).....	20
5.10 Copper (Cu).....	21
5.11 Fluorine (F)	22
5.12 Iodine (I).....	23
5.13 Lead (Pb).....	24
5.14 Manganese (Mn)	25
5.15 Mercury (Hg)	26
5.16 Molybdenum (Mo).....	29
5.17 Nickel (Ni)	29
5.18 Radioactive Trace Elements.....	31
5.19 Selenium.....	32
5.20 Thorium.....	33
5.21 Uranium.....	34
5.22 Vanadium	35
5.23 Zinc.....	36
6 LEGISLATION WORLDWIDE	37
6.1 Emissions to the Atmosphere.....	37
6.2 Emissions to Water.....	37
6.3 Disposal of Coal Ash.....	37
7 CONCLUDING REMARKS	38
8 ACKNOWLEDGEMENTS	38
9 REFERENCES	38
9.1 Websites	45
10 APPENDIX: DATA FROM ACIRL LIMITED.....	46

List of Tables:

Table 1. Concentration of Antimony in Coal, Earth's Crust and Shales	11
Table 2. Concentration of Arsenic in Coal, Earth's Crust and Shales.....	12
Table 3. Concentration of Barium in Coal, Earth's Crust and Shales	13
Table 4. Concentration of Beryllium in Coal, Earth's Crust and Shales	14
Table 5. Concentration of Boron in Coal, Earth's Crust and Shales	15
Table 6. Concentration of Cadmium in Coal, Earth's Crust and Shales	16
Table 7. Concentration of Chlorine in Coal, Earth's Crust and Shales	17
Table 8. Concentration of Chromium in Coal, Earth's Crust and Shales	18
Table 9. Concentration of Cobalt in Coal, Earth's Crust and Shales.....	20
Table 10. Concentration of Copper in Coal, Earth's Crust and Shales	21
Table 11. Concentration of Fluorine in Coal, Earth's Crust and Shales.....	22
Table 12. Concentration of Iodine in Coal, Earth's Crust and Shales	23
Table 13. Concentration of Lead in Coal, Earth's Crust and Shales	24
Table 14. Concentration of Manganese in Coal, Earth's Crust and Shales	25
Table 15. Concentration of Mercury in Coal, Earth's Crust and Shales	26
Table 16. Concentration of Molybdenum in Coal, Earth's Crust and Shales.....	29
Table 17. Concentration of Nickel in Coal, Earth's Crust and Shales.....	30
Table 18. Concentration of Selenium in Coal, Earth's Crust and Shales	32
Table 19. Concentration of Thorium in Coal, Earth's Crust and Shales	33
Table 20. Concentration of Uranium in Coal, Earth's Crust and Shales	34
Table 21. Concentration of Vanadium in Coal, Earth's Crust and Shales.....	35
Table 22. Concentration of Zinc in Coal, Earth's Crust and Shales	36

1 INTRODUCTION

The objective of this research is the development of useful tool to assist the Australian coal producers. This report and associated website (<http://www.det.csiro.au/traceelements> or http://www.det.csiro.au/science/researchservices/trace_elements.htm) contain information on trace elements; this is readily accessible by the Australian coal industry.

Note that the data in the website and this report on the concentration of trace elements is limited to the analyses completed in the laboratories of CSIRO Energy Technology. Data were obtained from the analysis of approximately 100 Australian coals and 60 coals traded from other nations. No claim is made that the data are representative of all internationally traded coals.

You must make your own assessment of the suitability for your purposes of this information. To the extent permitted by law, CSIRO excludes all liability arising directly or indirectly from use of this information.

The website can obviously be easily updated as new data are acquired. The information supplied includes

- a) concentration and modes of occurrence of trace elements in internationally traded thermal coals
- b) discussion of techniques used for the determination of trace elements in coal
- c) fate of the environmentally significant trace elements following combustion
- d) environmental and health effects
- e) details on legislation (worldwide) on emissions

Data has been compiled on those trace elements identified by legislators as hazardous air pollutants or as elements of environmental concern. As well, trace elements of general interest have been included. The trace elements discussed in this report are: antimony, arsenic, beryllium, bismuth, boron, cadmium, chlorine, chromium, cobalt, copper, fluorine, lead, manganese, mercury, molybdenum, nickel, selenium, thorium, uranium, vanadium and zinc.

The United States Clean Air Act Amendments (1990) listed Hazardous Air Pollutants (HAPs); 11 of these HAPS are trace elements: arsenic (As), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb) and selenium (Se). These trace elements are found ubiquitously in nature and this obviously includes coal and associated mineral matter.

There are numerous publications on the general topic, “ trace elements in coal”. One of the most comprehensive is the monograph by Swaine (1990). Other essential sources of information are the IEA reports by Smith (1987), Clarke and Sloss (1992), Sloss and Smith (1994), Sloss and Smith (2000) on trace element emissions and also that by Davidson (2000) on the occurrences of trace elements in coal (details are available at the IEA Clean Coal Centre website: <http://www.iea-coal.org.uk/site/ieacc/home>). See also Swaine (2000).

Websites of interest are also listed in Section 9.1.

2 SOURCES AND COLLATION OF DATA

2.1 Concentrations of Trace Elements in Overseas Coals

There are datasets and journal publications on the occurrence and concentration of trace elements in coals from various locations in the world. There are also publications on the occurrence of trace elements in coals, worldwide. Many of these are reports of concentrations “in the ground” and not in product coals.

However, it is appropriate to mention some of these. For example, data on concentrations, stratigraphic occurrences, and geographic distributions of trace elements within West Virginia's coal beds is available at: <http://www.wvgs.wvnet.edu/www/datastat/te/index.htm>. The US Coal Quality Database of the National Coal Resources Data System contains information on the quality of US domestic coal reserves (The US Geological Survey Open-File Report 97-134, <http://energy.er.usgs.gov/products/databases/coalqual/intro.htm>); see also Ruppert et al, 2002; Eble and Hower (1997); Hower et al, 1997.

Reseachers have reported on the trace elements in coal seams worldwide including Canada (Gentzis and Goodarzi, 1997; Mukhopadhyay et al,1998; Pollock et al, 2000), the UK (Spears et al, 1999; Spears and Zhang, 1999), and Chile (Helle et al, 2000)

Data on the occurrences of trace elements in a number of Chinese coal mines have been reported by numerous researchers, for example Querol et al (1999), Zhuang et al (2000), Liu et al (2001), Zhang et al (2002: 2004). According to He et al (2002), some of these mines contain coal with unusually high levels of both arsenic (60-130 mg/kg) and selenium (up to 7 mg/kg).

As stated above, data on the concentrations of trace elements in “as-fired” or “as-traded” coals are more difficult to obtain. Such information is often regarded as commercial-in-confidence. However, there is some information in the public domain.

Mukhopadhyay et al (1996) and Goodarzi, and Huggins (2001) studied the trace elements in coals and ash products from Canadian power stations. Goodarzi (2002) also reports on the trace elements present in Canadian coals used in that country's power stations. Karayigit et al (2000) report on the trace elements in feed coals (lignites) to Turkish power stations.

The ranges expressed for overseas coals in this report were obtained from analyses completed in the laboratories of CSIRO at Lucas Heights. Although the number of samples is limited (65 coals were analysed), the identity of each of the coal samples is known unambiguously and the analytical data are accurate.

2.2 Concentrations of Trace Elements in Australian Bituminous Coals

The data on the trace elements in the product coals of Australia were obtained from the information held by CSIRO Energy Technology (see Dale, 2003) and the analytical results of ACIRL. Although the ACIRL results were not used in the final compilation of ranges and means for Australian coals, the data do confirm that the values quoted in this report and in the website fact sheets are consistent with the values reported generally within the industry (see Appendix 1). A total of 100 coals make up the dataset for Australian export coals. Fewer data are available for the trace elements of lesser importance i.e. barium and iodine.

2.3 Discussion of Analytical Methods

There are variations in methods used by laboratories both within Australia and the rest of the world. For a general summary of analytical procedures used for the analysis of coal for inorganic constituents, see Huggins (2002). Unlike the existing traditional methods used for the major components of coal such as carbon, hydrogen, nitrogen and sulfur and for the empirically defined properties such as moisture and ash, the development of standard procedures for the determination of trace elements has lagged.

As a consequence, many laboratories in Australia have developed procedures independently of any formal methods generation from within the committee structure of Standards Australia. Indeed the process of standardisation is difficult where there are frequent advances in instrumental techniques. Alternatives to the prescriptive procedures of the past are required. The Australian Standard AS 1038.10.0 – Guide to the determination of trace elements in coal (Standards Australia) was developed with the assistance of funding from ACARP (Dale and Riley, 1997). One aim was the removal of prescriptive procedures from a standard. In this document, suitable methods for the determination of the trace elements are discussed but a given method is not prescribed for a particular trace element. The scheme of analysis, shown in Figure 1 is taken from this Guide.

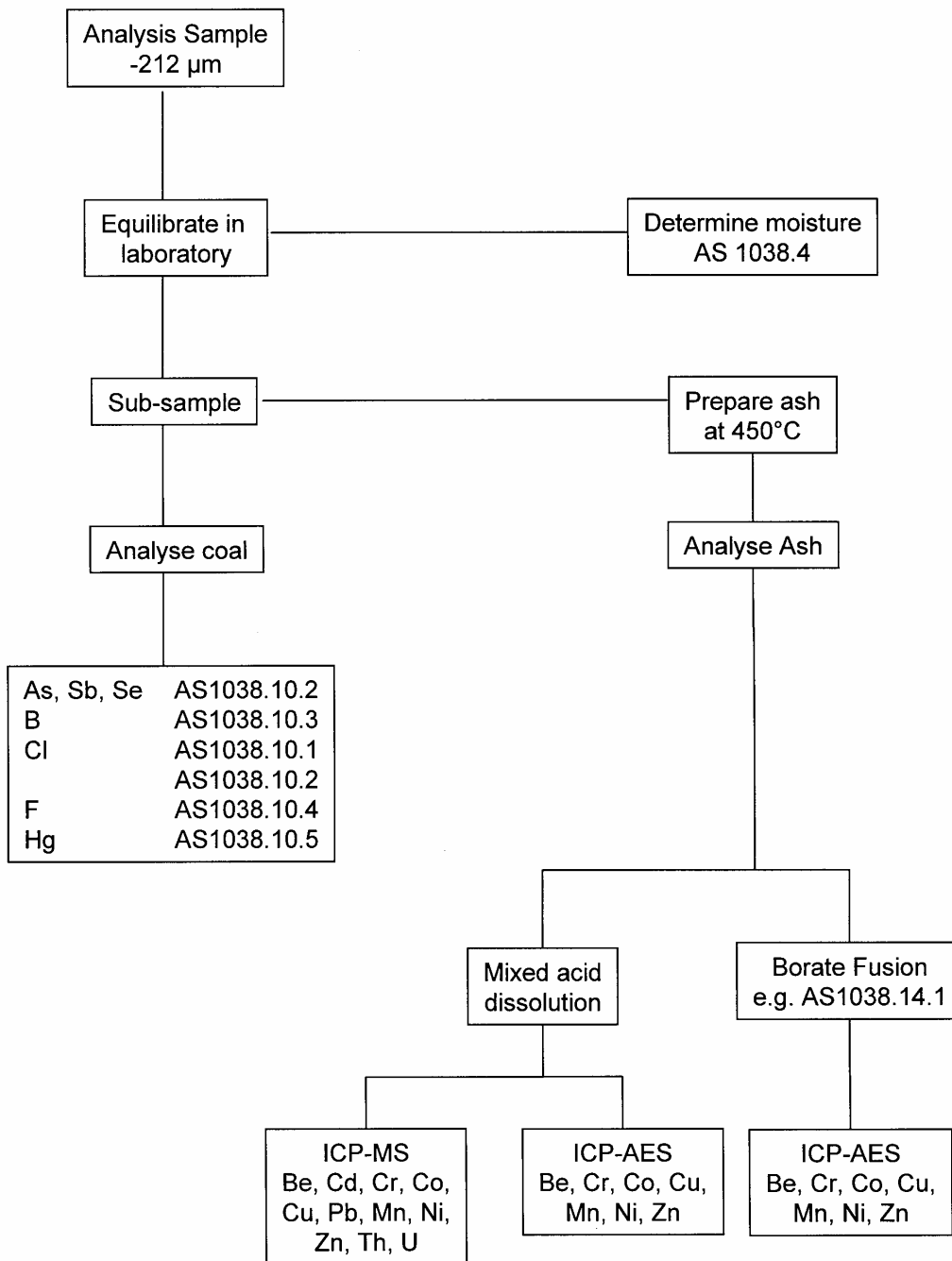


Fig 1. Recommended Scheme of Analysis for Trace Elements in Coal

To comply with this Standard, the laboratory is required to report the analytical results on a Standard Reference Material (SRM) or Certified Reference Material (CRM). It is to be accepted that laboratories may use methods that differ from the Australian Standards and recommended procedures listed in Figure 1 but that these methods follow the general scheme of analysis described in the Standard. However it is also mandatory that laboratories report the results of the analyses of suitable reference materials together with the certified values of

these materials. These data provide a necessary and transparent check on the performance of the laboratory and also on the accuracy of the results.

It is important that clients of analytical laboratories insist that appropriate SRMs or CRMs are analysed in the same work batches as their samples and that the results are reported with the analyses of the client's samples.

Reference materials of coal and ashes are commercially available from international institutes. For example the US National Institute of Standards and Technology (NIST: <http://www.nist.gov/>), an agency of the US Dept of Commerce produces a comprehensive range of reference materials including NIST 1632c, a bituminous coal and NIST 1633b, a coal fly ash. South African reference coals (SARM 18, 19 and 20) are available from Mintek, <http://www.mintek.co.za/newwebsite/> ; the price list and catalogue are available at http://www.mintek.co.za/newwebsite/downloads/Mintek_ASD_PriceList_SARM.pdf

Details of reference materials are available from a number of databases. The International Atomic Energy Agency has compiled The IAEA Database of Natural Matrix Reference Materials at <http://www-aweb.iaea.org/nahu/nmrm/nmrm2003/descript.htm> . This contains a listing of reference materials and suppliers. The European Commission's Institute for Reference Materials and Measurements also have compiled a catalogue. It is available at http://www.irmm.jrc.be/html/reference_materials_catalogue/catalogue/index.htm.

2.4 Modes of Occurrence of Trace Elements in Bituminous Coals

Different approaches have been used by researchers to identify the modes of occurrences (or mineralogical residences) of trace elements in coal.

Physical separation uses column separation or heavy liquids to separate the coaly (organic) matter from the mineral matter and also to separate the mineral phases of differing density. Analysis of the separated phases enables the various trace elements to be assigned to these phases. Its accuracy is very much dependent upon the ability to effectively separate the different phases.

Sequential leaching procedures are schemes using solvents that target specific mineral types. The reagents and extraction conditions can vary from laboratory to laboratory. An example may be:

- 1) extraction with deionised water to remove trace elements in pore fluids and soluble salts
- 2) extraction with ammonium acetate to remove loosely bound ions on clays or organic matter (i.e. particularly those cations bound to carboxylic acid groups present in low rank coals)
- 3) extraction with dilute hydrochloric acid to dissolve carbonates and monosulfides
- 4) extraction with dilute nitric acid to dissolve disulfides (i.e. pyrite predominantly)
- 5) extraction with hydrofluoric acid to dissolve silicates
- 6) residual trace elements deemed to be organically associated

Some laboratories do not extract with water or ammonium acetate and thus do not assign trace elements to the “soluble” or “loosely-bound” categories. Some laboratories reverse the order of steps 4 and 5, i.e. the extraction with hydrofluoric acid is done before that with nitric acid. One laboratory’s practice is to destroy the organic matter by extracting with hot nitric acid before extracting with hydrofluoric acid (i.e. acid extraction at step 6 before step 5). As indicated above, the concentration of the dilute acids can vary from laboratory to laboratory as well as the time and temperature of extraction.

Davidson (2000) reported on an inter-laboratory study on the occurrences of trace elements in coal. Laboratories from five countries (Australia, Canada, Spain, UK and the USA) participated and used physical separation and/or different sequential leaching techniques to assign trace elements to mineral groupings. Davidson (2000) concluded that the results from both techniques must be interpreted with caution.

There are other techniques that have been applied to the assessment or estimation of modes of occurrence of trace elements in coals. Of particular importance is the work of Huggins and his colleagues (Huggins et al, 1997, 1999, 2002; Huggins and Huffman, 1995, 1996 and 2004; Goodarzi and Huggins, 2001), who have used the non-destructive technique, X-ray absorption edge spectroscopy (XAFS) and X-ray absorption near edge spectroscopy (XANES). Although the technique is non-destructive and does not rely on chemical or physical separations, there are limitations. It is not suitable for B, Be, Bi, Hg, Sb, Cd, Mo, Th and U because the concentrations in coal are too low; it may be useful for Se, As, Co, and Pb and is generally useful for Cr, Mn, Ni, V, and Zn (Huggins, personal communication, 2004).

A major disadvantage of XAFS is that its application requires access to a synchrotron facility, thus the technique may be limited by availability and cost. The other disadvantage is that the detection limit is not adequate for the many of the trace elements of interest.

As can be seen from the preceding discussion, there is a variety of techniques used worldwide and often a combination of the techniques is required to provide an “estimate” of the occurrence or mineralogical association of trace elements in coal. Thus, there is continuing discussion of the uncertainties of the assignment of trace elements’ occurrence in coal.

3 BEHAVIOUR OF TRACE ELEMENTS DURING COMBUSTION

There are key reviews and scientific papers on the fate of trace elements during, and following the combustion of coal. IEA Coal Research has produced comprehensive reviews (Smith, 1987; Clarke and Sloss, 1992). There are also special issues of the journal, Fuel Processing Technology devoted to the transformations of trace elements in coal-fired systems (see Benson 2004; Benson and Brown, 2000). There are also key individual research papers, in particular the papers by Swaine (2000), Huggins et al (2000) and Senior et al (2000).

Meij from KEMA (The Netherlands) has published extensively and continues to do on the transformation and fate of trace elements in Dutch power stations (Meij, 1994; 1995).

Based on their apparent volatility during combustion, trace elements have been classified by researchers into three groups. The summary in below is taken from Clarke and Sloss (1992). The elements discussed in the following sections of this report are highlighted in bold:

Group 1: with low volatility, equally distributed between bottom ash and fly ash
Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, **Th**, Ti

Group 2: volatile, enriched in the flyash.

Meij (1994) separates the elements of Group 2 into three classes: IIc, IIb and IIa. The more volatile elements are in IIa, the least in IIc. Meij bases this separation on the relative concentration of the trace element in the fine fuel ash and “flyash” defined by the author as the particulate matter emitted through the stack (Meij, 1994).

IIc: Ba, **Cr**, **Mn**, Na, Rb;
IIb: **Be**, **Co**, **Cu**, **Ni**, P, U, **V**, W;
IIa: **As**, **Cd**, Ge, **Mo**, **Pb**, **Sb**, Tl, **Zn**

Group 3: highly volatile, at least partially present in the gas phase and not enriched in the flyash
B, Br, **Cl**, **F**, **Hg**, I, S, **Se**

4 HEALTH AND ENVIRONMENTAL EFFECTS

The emissions of trace elements from coal-fired power stations during combustion and the mobilisation of trace elements from ash-handling systems have been studied by researchers worldwide.

The Australian Government's National Pollutant Inventory (NPI) has made available handbooks on the calculation of emissions of pollutants from various industries. The handbook for coal-fired power stations provides guidance on the estimation of emissions to air, land and water. It is available at http://www.npi.gov.au/handbooks/approved_handbooks/pubs/elec-supply.pdf.

There are general publications of the health and environmental impacts of trace elements in coal. Swaine and Goodarzi (1995) edited a book on health and environmental impacts of trace elements in coal. Particularly relevant chapters include those by Swaine (1995), Meij (1995), Godbeer and Swaine (1995) and Jones (1995). A list of the data considered necessary to assess the environmental and health impacts of coal utilisation has been prepared by Finkelman and Gross (1999).

Finkelman et al (2002) have discussed the health impacts of coal mining and use. The authors' particular concerns are the inappropriate mining practices and use of coal in some regions of the world. Highly mineralised coal enriched in some trace elements has led to chronic illness; this is particularly so, where these coals are used as domestic fuels in poorly ventilated dwellings. The authors have identified particular examples of adverse impacts in regions of China (see also Querol et al, 1999; Zheng et al, 1999; He et al, 2002; Liu et al, 2002; Sun, 2004). It must be stressed that these health problems are not evident where coals are burnt in modern power stations.

The two trace elements that have gained the most interest by researchers or legislators are selenium (emissions to water from ash repositories) and mercury (emissions to the atmosphere from power stations). These two elements are discussed in fuller detail in the following section.

5 INFORMATION ON THE KEY TRACE ELEMENTS

The following information on each of the trace elements (antimony, arsenic, barium, beryllium, boron, cadmium, chlorine, chromium, cobalt, copper, fluorine, lead, manganese, mercury, molybdenum, nickel, selenium, thorium, uranium, vanadium and zinc) has been summarised and is in the form of individual fact sheets available at the URL: <http://www.det.csiro.au/traceelements> or http://www.det.csiro.au/science/researchservices/trace_elements.htm.

This section of the report contains references to the relevant publications where appropriate. These references are not listed in the fact sheets on the website.

Note that in this section and in the fact sheets, “Australian Domestic Coals” refers to those bituminous coals burnt in Australian power stations. The Figure associated with each Table in a depiction of the ranges and means of the trace elements in export coals from Australia and “Other” trading nations

It should also be noted that although the data from the analyses of approximately 100 Australian coals and 60 coals exported from overseas is used in the compilation, not every coal was analysed for every trace element discussed in this section. Thus there are few data points for some trace elements e.g. barium and iodine.

5.1 Antimony (Sb)

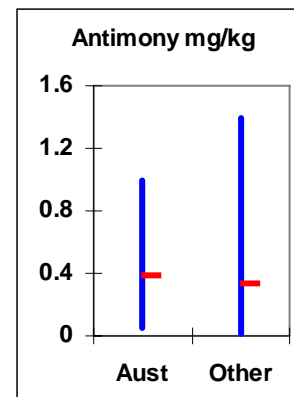
5.1.1 Concentration and Occurrence of Antimony in Coal

Antimony concentrations are generally very low in most coals. Typical concentrations in coal, the earth's crust and shales are listed in Table 1.

Table 1. Concentration of Antimony in Coal, Earth's Crust and Shales

Concentration of Antimony in:	mg /kg
Australian Export Coals	0.05 – 1.0 (0.39) #
Other Internationally Traded Coals	0.02 – 1.4 (0.33) #
Australian Domestic Coals	0.06 – 1.0 (0.55) #
Earth's Crust	0.2
Earth's Shales	1.0

values in parentheses are averages



Antimony is likely to be associated with the sulphide minerals (Finkelman, 1995) and possibly the organic matter. However there is significant uncertainty about the occurrence of this trace element in coals (Swaine, 1990).

5.1.2 Behaviour of Antimony during Combustion

Antimony is volatile and condenses on the fly ash and is enriched on the finer ash particles. Thus it is classified as belonging to Group I (Meij, 1994; Clarke and Sloss, 1992).

5.1.3 Environmental and Health Effects of Antimony from Coal Combustion

There appears to be no reports on any adverse environmental or health effects of the emission of antimony from coal combustion.

5.2 Arsenic (As)

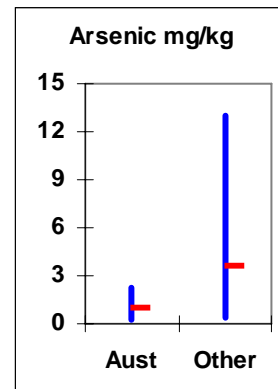
5.2.1 Concentration and Occurrence of Arsenic in Coal

Typical concentrations of arsenic in coal, the earth's crust and shales are listed in Table 2.

Table 2. Concentration of Arsenic in Coal, Earth's Crust and Shales

Concentration of Arsenic in:	mg /kg
Australian Export Coals	0.2 – 2.2 (1.05)#
Other Internationally Traded Coals	0.3 – 13.0 (3.6) #
Australian Domestic Coals	0.4 – 7.0 (1.6)#
Earth's Crust	1.8
Earth's Shales	15

values in parentheses are averages



Both Finkelman (1994) and Dale et al (1999) report that arsenic is most likely present in the pyrite in coal. Finkelman (1994) also suggests that a minor amount may be organically bound. Swaine (1990) suggests that some arsenic may be present as arsenate in clays or phosphate minerals. See also Kolker et al (2000) and Huggins et al (2002).

5.2.2 Behaviour of Arsenic during Combustion

According to Meij (1994), arsenic is not classified as a Group 3, highly volatile element as it is generally not found in the flue gases past the electrostatic precipitator (ESP). Rather it is in Group IIa. It appears that volatile As_2O_3 is produced during combustion (see also Clarke and Sloss, 1992) and if calcium is present in the mineral matter, calcium arsenate is formed.

5.2.3 Environmental and Health Effects of Arsenic from Coal Combustion

Arsenic is extremely low in most bituminous coals (<1-2 mg/kg in most Australian coals) and when these coals are used in modern PF-fired power stations, there have been no reports of adverse health effects. However, as mentioned in Section 4., adverse health effects have been reported in regions of China, where highly mineralised coal is utilised as a fuel in poorly ventilated dwellings (see Sun, 2004).

5.3 Barium (Ba)

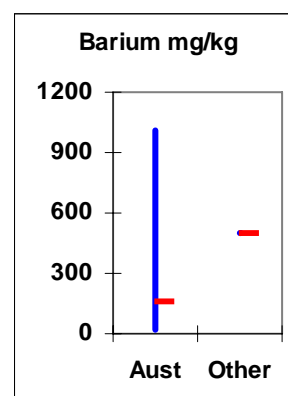
5.3.1 Concentration and Occurrence of Barium in Coal

Typical concentrations of barium in coal, the earth's crust and shales are listed in Table 3. Few data are available for coals traded internationally. The mean value for internationally traded coals is taken from Swaine (1990).

Table 3. Concentration of Barium in Coal, Earth's Crust and Shales

Concentration of Barium in:	mg /kg
Australian Export Coals	16 – 1010 (180) [#]
Other Internationally Traded Coals	(500) [#]
Australian Domestic Coals	15 – 250 (115) [#]
Earth's Crust	425
Earth's Shales	700

[#] values in parentheses are averages



The most likely occurrences of barium in coal are as sulfate i.e. barite (Swaine, 1990) and as other barium minerals i.e. phosphates and carbonates (Finkelman, 1994; 1995).

5.3.2 Behaviour of Barium during Combustion

Barium exhibits some volatility and is slightly enriched in the fly ash. It is in Class IIb (Meij, 1994).

5.3.3 Environmental and Effects of Barium from Coal Combustion

There are no reports of environmental or health effects from barium present in coal.

5.4 Beryllium

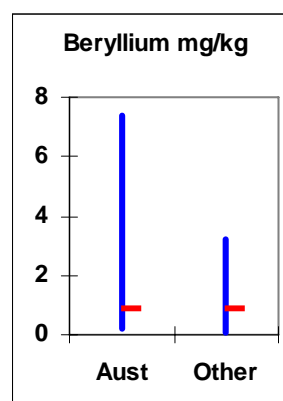
5.4.1 Concentration and Occurrence of Beryllium in Coal

Typical concentrations of beryllium in coal and the earth's crust and shales are listed in Table 4.

Table 4. Concentration of Beryllium in Coal, Earth's Crust and Shales

Concentration of Beryllium in:	mg /kg
Australian Export Coals	0.2 – 7.4 (0.9) [#]
Other Internationally Traded Coals	0.1 – 3.2 (0.9) [#]
Australian Domestic Coals	0.4 – 2.5 (1.2) [#]
Earth's Crust	1.8
Earth's Shales	15

[#] values in parentheses are averages



Swaine (1990) and Finkelman (1994; 1995) suggest that beryllium is associated with the organic matter and with some beryllium present in clays. Dale et al (1999) report that in the Australian coals studied in their research that beryllium is present in the silicates (clays).

5.4.2 Behaviour of Beryllium during Combustion

Beryllium appears to be partly volatilised and according to Meij (1994), the element is slightly enriched in the flyash, i.e. it is in Class IIb.

5.4.3 Environmental and Health Effects of Beryllium from Coal Combustion

Typically, beryllium is present at low concentrations (typically about 1 mg/kg) in coal and beryllium emissions from coal-fired power stations are not regarded as likely to have adverse environmental or health impacts. There does not appear to be any reports of adverse health or environmental impacts.

5.5 Boron (B)

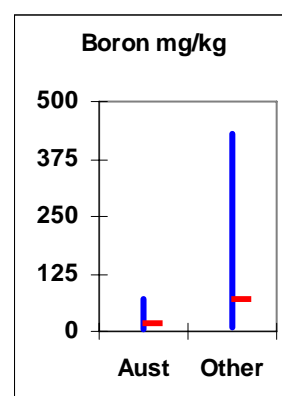
5.5.1 Concentration and Occurrence of Boron in Coal

In a study of Australian and Canadian coals, Goodarzi and Swaine (1994) reported that the concentration of boron in coals reflects the influence of marine incursions during the early stages of coalification. The authors suggest that concentrations of < 50 mg/kg indicate formation in freshwater, 50-110 mg/kg, indicate mildly brackish water and > 100 mg/kg indicate brackish water. Typical concentrations in coal, the earth's crust and shales are listed in Table 5.

Table 5. Concentration of Boron in Coal, Earth's Crust and Shales

Concentration of Boron in:	mg /kg
Australian Export Coals	5 – 70 (19) [#]
Other Internationally Traded Coals	11 – 430 (72) [#]
Australian Domestic Coals	7 – 141 (32) [#]
Earth's Crust	10
Earth's Shales	100

[#] values in parentheses are averages



It appears that most of the boron is organically associated in coal (Swaine, 1990; Finkelman, 1994; 1995).

5.5.2 Behaviour of Boron during Combustion

Boron is regarded as being highly volatile i.e. in Class III (Meij, 1999). Approximately 50% of the element is found in the flyash. It is depleted in the bottom ash. Clarke and Sloss (1992) state that B₂O₃ is the likely volatile species.

5.5.3 Environmental and Health Effects of Boron from Coal Combustion

For those power stations not equipped with scrubbers, a significant proportion of boron in the coal is released to the atmosphere. Boron is enriched in coal ash and can be leached into the environment, if the ash is not appropriately stored. There have been studies on the uptake of boron by plants grown in ash-amended soils or on landfill sites (for example, see Clarke et al, 1999; Woodbury et al, 1999; Wong et al, 1998). There does not appear to be any studies reporting adverse health effects resulting from the atmospheric emissions of boron from power stations.

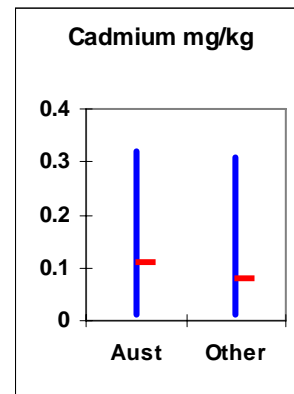
5.6 Cadmium (Cd)

5.6.1 Concentration and Occurrence of Cadmium in Coal

Typical concentrations of cadmium in coal, the earth's crust and shales are listed in Table 6.

Table 6. Concentration of Cadmium in Coal, Earth's Crust and Shales

Concentration of Cadmium in:	mg /kg
Australian Export Coals	0.01 – 0.32 (0.11) [#]
Other Internationally Traded Coals	0.01 – 0.31 (0.08) [#]
Australian Domestic Coals	0.03 – 0.38 (0.15) [#]
Earth's Crust	0.2
Earth's Shales	0.2



[#] values in parentheses are averages

Both Swaine (1990) and Finkelman (1994; 1995) state that cadmium is predominantly associated with the monosulfide, sphalerite (ZnS), but that it may be found in other sulfides. Similarly, Dale et al (1999) report that cadmium is present in the monosulfides and pyrite but the authors indicate the cadmium can also be found in the silicates.

5.6.2 Behaviour of Cadmium during Combustion

Cadmium is volatile and is enriched in the flyash; it is a Class IIa element (Meij, 1994).

5.6.3 Environmental and Health Effects of Cadmium from Coal Combustion

Cadmium is typically present at low concentrations in most bituminous coals. However, it must be stated that cadmium is a trace element of general environmental concern particularly as it can bioaccumulate in the food chain. There does not appear to be any health effects nor significant environmental impacts from cadmium from the utilisation of coal in power stations.

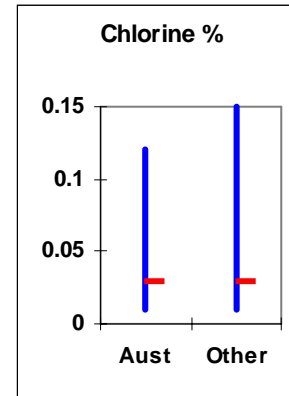
5.7 Chlorine (Cl)

5.7.1 Concentration and Occurrence of Chlorine in Coal

The concentrations of cadmium in coal, the earth's crust and shales are listed in Table 7.

Table 7. Concentration of Chlorine in Coal, Earth's Crust and Shales

Concentration of Chlorine in:	%
Australian Export Coals	<0.01 – 0.12 (0.03) [#]
Other Internationally Traded Coals	<0.01 – 0.15 (0.04) [#]
Australian Domestic Coals	<0.01 – 0.14 (0.03) [#]
Earth's Crust	0.01
Earth's Shales	0.02



[#] values in parentheses are averages

Swaine (1990) suggests that chlorine is likely present in some form of organic association in bituminous coals. Finkelman (1994;1995) suggests that chlorine is present as chloride in pore water or adsorbed onto the coal macerals. Huggins and Huffman (1995) report that chlorine is present in higher rank coals as chloride anions in the moisture on the surface of micropores in coal macerals and that there is no evidence for organic chlorine in coal.

5.7.2 Behaviour of Chlorine during Combustion

There is an IEA publication on halogen emissions from coal combustion (Sloss, 1992); this is a comprehensive review of the research on the behaviour of the halogens during coal combustion. Researchers are of the opinion that almost all (>90%) of the chlorine is emitted as hydrogen chloride (Sloss, 1992, p.24). The amount of chlorine present in the coal as fired is an important factor in the nature of the mercury compounds formed during combustion (see Sliger et al, 2000; Senior et al, 2000;).

See also the IEA report by Davidson (1996).

5.7.3 Environmental and Health Effects of Chlorine from Coal Combustion

In power station without wet scrubbers, chlorine is emitted to the atmosphere as hydrogen chloride. The low levels present in most bituminous coals are unlikely to cause adverse health effects and environmental impacts.

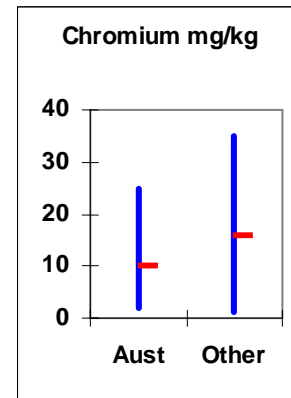
5.8 Chromium (Cr)

5.8.1 Concentration and Occurrence of Chromium in Coal

The concentrations of chromium in coal, the earth's crust and shales are listed in Table 8.

Table 8. Concentration of Chromium in Coal, Earth's Crust and Shales

Concentration of Chromium in:	mg/kg
Australian Export Coals	2 – 25 (10) [#]
Other Internationally Traded Coals	1 – 35 (16) [#]
Australian Domestic Coals	2 – 23 (10) [#]
Earth's Crust	100
Earth's Shales	100



[#] values in parentheses are averages

According to Finkelman (1994), there “are insufficient data to specify the modes of occurrence of Cr in coal”, although the researcher states that it is possibly associated with the clays or organic matter (Finkelman, 1995). Some organic association is suspected (Swaine, 1990). Dale et al (1999) report that chromium is present in the oxide/carbonate/monosulfide group but that it may also be present in the silicates (clays) and associated with the organic matter. The organic association may well be correct, however it should be borne in mind that residual chromium following extraction during the stages of the speciation procedure may in fact have an association with resistant minerals.

Huffman et al (1994) and Huggins et al (2000) determined the valency of the chromium and concluded that the chromium was present as Cr³⁺ in the coal. It is to be expected that chromium would be in the reduced state in coal and associated minerals.

The valency of chromium in the ash after combustion is of interest. Huggins et al (1999) used XAFS spectroscopy to determine the valency of the chromium in coal ash. The researchers concluded that chromium was predominantly present as Cr³⁺ in the ash from power stations.

5.8.2 Behaviour of Chromium during Combustion

Chromium is in Class IIc and is regarded as an element that can be vapourised and then condensed on the flyash. However Meij (1994) shows Cr to be evenly distributed between the bottom ash and flyash.

5.8.3 Environmental and Health Effects of Chromium from Coal Combustion

The adverse health and environmental effects of chromium in waste are a consequence of its presence in the chromate form, i.e. Cr(VI). As indicated in the preceding sections, chromium is present in coal and coal ash predominantly in the Cr(III) form. In this form and at the low concentrations present in both coal and ash, it is not likely to have any adverse health or environmental impacts.

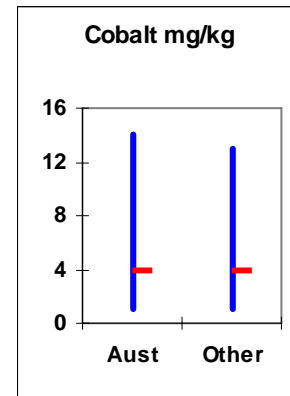
5.9 Cobalt (Co)

5.9.1 Concentration and Occurrence of Cobalt in Coal

Typical concentration ranges of cobalt are shown in Table 9.

Table 9. Concentration of Cobalt in Coal, Earth's Crust and Shales

Concentration of Cobalt in:	mg/kg
Australian Export Coals	1 – 14 (4) [#]
Other Internationally Traded Coals	<1 – 13 (4) [#]
Australian Domestic Coals	1 – 12 (4) [#]
Earth's Crust	25
Earth's Shales	20



[#] values in parentheses are averages

Swaine (1990) indicates that cobalt is associated with both the mineral matter and organic matter. According to Finkelman (1994; 1995), cobalt is most likely associated with sulfide minerals but is found in clays and in the organic matter. Dale et al (1999) found that cobalt was associated with the silicates (i.e. clays) rather than with the sulfides in the Australian coals studied; this finding may well be a consequence of the low concentration of sulfides in most Australian coals.

5.9.2 Behaviour of Cobalt during Combustion

Cobalt is slightly volatile (Class IIb) and condenses on the fly ash particles. Some enrichment in the finer particles of ash is expected (Meij, 1994).

5.9.3 Environmental and Health Effects of Cobalt from Coal Combustion

There does not appear to be any reports of adverse health nor environmental impacts from cobalt emissions from the combustion of coal in power stations

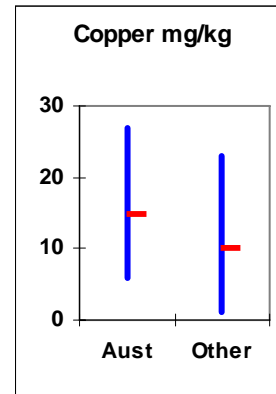
5.10 Copper (Cu)

5.10.1 Concentration and Occurrence of Copper in Coal

Typical concentrations of copper are shown in Table 10.

Table 10. Concentration of Copper in Coal, Earth's Crust and Shales

Concentration of Copper in:	mg/kg
Australian Export Coals	6 – 27 (15) [#]
Other Internationally Traded Coals	<1 – 23 (9) [#]
Australian Domestic Coals	1 – 12 (4) [#]
Earth's Crust	55
Earth's Shales	50



[#] values in parentheses are averages

Swaine (1990) states that copper is likely present in coal as chalcopyrite or other sulfides and possibly as organically bound species in coal. Finkelman (1994;1995) states copper occurs primarily in chalcopyrite in coal. Dale et al (1999) agree that copper is present in the monosulfides and pyrite and add that some copper is present in the silicates.

5.10.2 Behaviour of Copper during Combustion

Copper is in Class IIb and is moderately enriched on the fine particles of flyash (Meij, 1994).

5.10.3 Environmental and Health Effects of Copper from Coal Combustion

There are not likely to be any health impacts from the emissions of copper from the combustion of coal. The presence of copper at extremely low levels in the discharge waters of power stations may cause adverse environmental impacts, if not treated or disposed of appropriately. This trace element may be leached from coal ash but its presence may also be a consequence of corrosion within the power plant.

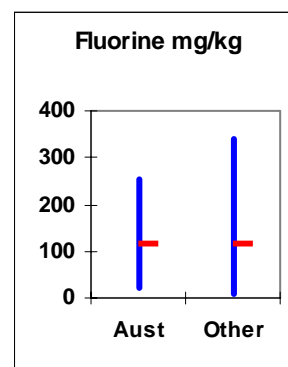
5.11 Fluorine (F)

5.11.1 Concentration and Occurrence of Fluorine in Coal

The concentration ranges of fluorine are shown in Table 11.

Table 11. Concentration of Fluorine in Coal, Earth's Crust and Shales

Concentration of Fluorine in:	mg/kg
Australian Export Coals	20 – 255 (114) [#]
Other Internationally Traded Coals	<20 – 340 (115) [#]
Australian Domestic Coals	<20 – 200 (127) [#]
Earth's Crust	625
Earth's Shales	740



[#] values in parentheses are averages

Fluorine apparently occurs in a variety of minerals the associated with coal; the likely minerals include the clay minerals, micas, fluorapatite and possibly fluorite (Swaine, 1990; Finkelman, 1994; 1995).

It is appropriate to make some comment on the procedures used to determine fluorine in coal. Techniques based on bomb combustion procedures are not considered accurate by many researchers who report low recoveries (see Godbeer and Swaine, 1987). Methods based on pyrohydrolysis procedures (Doolan, 1987; Godbeer and Swaine, 1987) or those based on proton induced gamma ray emission (PIGME or PIGE) are accurate (Roelandts et al, 1996). Some fusion procedures can also give reliable results (e.g. see Wood et al, 2003).

5.11.2 Behaviour of Fluorine during Combustion

Fluorine is vaporised during combustion and may be emitted to the atmosphere. There is little condensation on fine ash particles (Meij, 1994).

5.11.3 Environmental and Health Effects of Fluorine from Coal Combustion

There appears to be no reports of adverse health effects from fluoride emissions from modern power stations burning typical coals. Some stations in horticultural regions (e.g. grape growing areas) are set emission limits. There have been reports of health effects in China where high fluoride coals (or briquettes containing clay) have been used for heating and cooking (Finkelman et al, 1999; Dai et al, 2004; Ando et al, 2001; Luo et al, 2004).

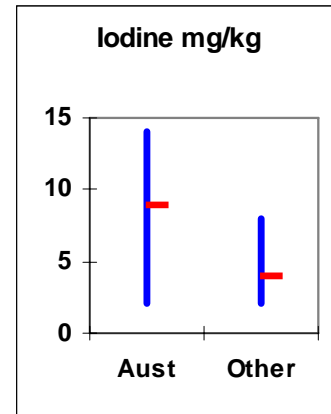
5.12 Iodine (I)

5.12.1 Concentration and Occurrence of Iodine in Coal

The concentration ranges of iodine in coal are shown in Table 12. It should be noted that there are few data available on the concentrations of iodine present in coal.

Table 12. Concentration of Iodine in Coal, Earth's Crust and Shales

Concentration of Iodine in:	mg/kg
Australian Export Coals	2 – 14 (9) [#]
Other Internationally Traded Coals	2 – 8 (4) [#]
Australian Domestic Coals	few data available
Earth's Crust	0.5
Earth's Shales	2.2



[#] values in parentheses are averages

Iodine is likely to be organically bound in coal although it is thought that some may be associated with the clays (Swaine 1990).

5.12.2 Behaviour of Iodine during Combustion

Iodine probably as hydrogen iodide or elemental iodine is volatilised during combustion (i.e. it is in Class III, Meij, 1994). It is released to the atmosphere or captured in wet scrubbers (where fitted to power stations).

5.12.3 Environmental and Health Effects of Iodine from Coal Combustion

The iodine released to the atmosphere from coal combustion is not regarded as having a significant environmental or health impact. Where the exhaust gases are scrubbed in those stations equipped with wet DeSO_x systems, the iodide can accumulate in the discharge waters of scrubbers. This can interfere with the determination of COD (chemical oxygen demand), however the iodide itself is not regarded as having a significant environmental impact.

5.13 Lead (Pb)

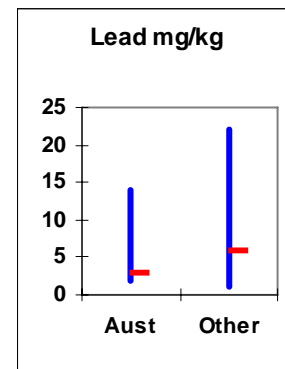
5.13.1 Concentration and Occurrence of Lead in Coal

The concentration ranges of lead are shown in Table 13.

Table 13. Concentration of Lead in Coal, Earth's Crust and Shales

Concentration of Lead in:	mg/kg
Australian Export Coals	2 – 14 (3) [#]
Other Internationally Traded Coals	<1 – 22 (6) [#]
Australian Domestic Coals	3 – 18 (10) [#]
Earth's Crust	12
Earth's Shales	20

[#] values in parentheses are averages



Lead is present predominantly associated with sulfide minerals in bituminous coals (Swaine 1990; Finkelman, 1994; 1995). There are also reports of lead selenide occurring in bituminous coals (Hower and Robertson, 2003; Finkelman, 1994; 1995).

5.13.2 Behaviour of Lead during Combustion

Lead is volatile and condenses on the fly ash particles (Class IIA, Meij, 1994). It is enriched in the finer particles; a small percentage of these fine particles are emitted to the atmosphere from modern power stations.

5.13.3 Environmental and Health Effects of Lead from Coal Combustion

Although lead is a trace element of environmental concern, there is unlikely to be any significant adverse health or environmental impacts at the low levels present in most coals.

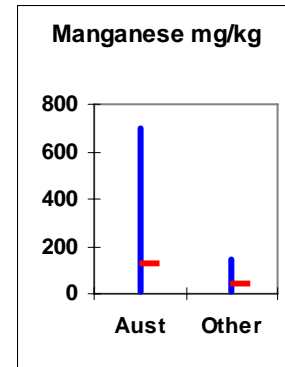
5.14 Manganese (Mn)

5.14.1 Occurrence of Manganese in Coal

The concentrations of manganese in coal, the earth's crust and shales are listed in Table 14.

Table 14. Concentration of Manganese in Coal, Earth's Crust and Shales

Concentration of Manganese in:	mg/kg
Australian Export Coals	5 – 700 (125) [#]
Other Internationally Traded Coals	7 – 117 (40) [#]
Australian Domestic Coals	19 – 430 (160) [#]
Earth's Crust	950
Earth's Shales	850



[#] values in parentheses are averages

Swaine (1990) states that manganese is associated with carbonate minerals and clays. Dale et al (1999) found manganese present in the oxide/carbonate/monosulfide group. Certainly, carbonate minerals are likely a major source of manganese (Finkelman, 1994; 1995).

5.14.2 Behaviour of Manganese during Combustion

Manganese exhibits limited volatility and may be slightly enriched in the finer ash particles. It is a Class IIc element (Meij, 1994).

5.14.3 Environmental and Health Effects of Manganese from Coal Combustion

No significant adverse health nor environmental impacts from the manganese present in most coals are likely.

5.15 Mercury (Hg)

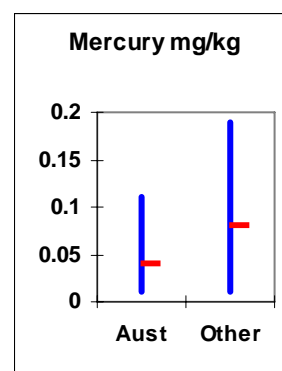
Of the trace elements emitted to the atmosphere from coal combustion, mercury is the trace element of paramount interest to the legislators and environmentalists.

5.15.1 Concentration and Occurrence of Mercury in Coal

Typical concentrations of mercury in coal, the earth's crust and shales are given in Table 15.

Table 15. Concentration of Mercury in Coal, Earth's Crust and Shales

Concentration of Mercury in:	mg/kg
Australian Export Coals	0.01 – 0.11 (0.04) [#]
Other Internationally Traded Coals	0.02 – 0.19 (0.09) [#]
Australian Domestic Coals	0.02 – 0.13 (0.04) [#]
Earth's Crust	0.08
Earth's Shales	0.50



[#] values in parentheses are averages

Mercury is associated with the sulfides in coal i.e. it occurs in the pyrite (Finkelman, 1994; 1995) or the monosulfides. Selective leaching has indicated that mercury is also associated with the coal organic matter. Swaine (1990) states that Hg is “probably associated with pyrite and sometimes sphalerite, with organically bound Hg still an uncertainty”. It should be considered that all the fine-grained mineral matter such as pyrite may not be selectively removed by the leaching stages. As a consequence, the mercury residing in the residual pyrite may be identified as being organically bound. Dale et al (1999) agree that Hg is associated with the pyrite and that there is residual Hg present after acid extractions and that this mercury is likely to be associated with framboidal pyrite that is protected by coaly matter during acid leaching.

Tewalt et al (2001) of the US Geological Survey have produced a factsheet on the occurrence of mercury in US coals (<http://pubs.usgs.gov/fs/fs095-01/fs095-01.pdf>). Mercury is generally believed to present in the sulfide minerals (i.e. predominantly pyrite) present in coal. Quick et al (2003) have pointed out that the concentrations of mercury reported for “insitu” coals do not correspond to the concentrations in the “as fired” coals reported to the USEPA as part of its Information Collection Request (ICR).

Similarly, Feng et al (2002) have stated that this is also true for the coals from Guizhou, China. Wang et al, (2000) have reported the averages and ranges of mercury levels in the 14 principal coal-producing provinces of China; the concentration range is 0.02-2.67 mg/kg. This upper range is usually high.

There is a recent review of the occurrence of mercury in coal (see Yudovich and Ketris, 2005).

5.15.2 Behaviour of Mercury during Combustion

Mercury is totally vaporised during the combustion of coal (i.e. Class III, Meij, 1994). Its behaviour depends on its chemical form in the vapour phase. Some of the mercury condenses on the flyash whilst a significant proportion (in some cases the major proportion) may be released to the atmosphere.

Studies indicate that somewhere between 20-80% of the mercury present in coal is released to the atmosphere in power stations equipped with ESPs or bag filters. In those stations equipped with ESPs and wet scrubbers (DeSOx units), the mercury release may be less. This depends upon the forms of mercury present in the gas stream. Ionic mercury (principally, either mercuric chloride or sulfate) is trapped in the DeSOx wash.

The behaviour of the mercury appears to be related to a number of factors but the nature (occurrence) of the mercury in the coal is not one of them as it is to be expected that almost all the mercury in coal is vaporised at the temperature of combustion. The formation of ionic mercury is related to the amount of chloride in coal (see Sliger et al, 2000; Senior et al, 2000; Gibb et al, 2000; Galbreath and Zygarlicke, 2000); this is one important factor in the proportion of mercury emitted to the atmosphere.

5.15.3 Environmental and Health Effects of Mercury from Coal Combustion

The estimate of total mercury release from the Australian electricity supply industry, reported in The National Pollutant Inventory (<http://www.npi.gov.au/>) is 1.1 tonne of mercury for the year 2003-2004. Unlike in the US, in Australia, power stations are not the major industrial source of mercury emissions.

Never the less, mercury release is a concern to regulatory and environmental agencies worldwide. Newman-Sutherland et al (2001) review the impacts of mercury (from coal combustion), the technologies to control the emissions and the legislative scenarios in a number of countries.

Worldwide, coal combustion is the largest single source of anthropogenic mercury. Pacyna and Pacyna (2002) estimated the global emissions of mercury from stationary fossil fuel combustion in 1995 to be almost 1500 tonnes. However the estimate given by the authors for Australia and Oceania is 99.9 tonnes; this estimate is almost two orders of magnitude too high.

A quick calculation illustrates the scale of this error. In Australia, coal-fired power stations consume approximately 55 million tonne of bituminous coal and 65 million tonne of brown coal per annum. If it is assumed that almost all of the mercury emitted to the atmosphere from stationary fossil fuel combustion in Oceania, comes from the major power stations in Australia, then the coal fired would have to contain mercury at a concentration of at least 0.9 mg/kg (1.8 mg/kg if half the mercury present is emitted etc.). These concentrations are

nonsensical. Typically, Australian coals contain less than 0.05 mg/kg of mercury. For further discussion, see Peterson et al, 2004.

However mercury emissions from coal-fired power station has been identified by the USEPA as the single largest industrial source of atmospheric emissions in that country. On March 15, 2005, the USEPA issued the Clean Air Mercury Rule; the intent of this rule is to cap and reduce mercury emissions from coal-fired power plants. The US is the first country to regulate mercury emissions from power stations (see <http://www.epa.gov/air/mercuryrule/> and http://www.epa.gov/mercury/control_emissions/index.htm).

It is possible that other nations may follow this precedent. Canada has indicated its intention (http://www.ccme.ca/assets/pdf/mercury_epg_notice_9june03_e.pdf) to adopt similar regulations.

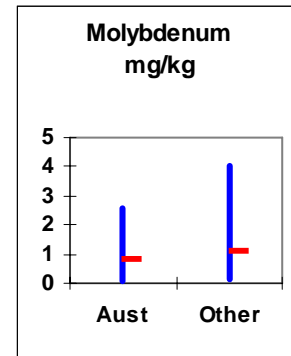
5.16 Molybdenum (Mo)

5.16.1 Concentration and Occurrence of Molybdenum in Coal

The concentrations of molybdenum in coal, the earth's crust and shales are listed in Table 16.

Table 16. Concentration of Molybdenum in Coal, Earth's Crust and Shales

Concentration of Molybdenum in:	mg/kg
Australian Export Coals	0.1 – 2.6 (0.8) [#]
Other Internationally Traded Coals	0.1 – 4.0 (1.2) [#]
Australian Domestic Coals	<0.1 – 1.9 (0.9) [#]
Earth's Crust	1.5
Earth's Shales	3.0



[#] values in parentheses are averages

The occurrence of molybdenum is uncertain (Finkelman, 1994; 1995). According to Swaine (1990), “the mode of occurrence of Mo in coals ranges from mostly inorganic to mostly organic”. Dale et al (1999) report that Mo is present in the monosulfides, pyrite and possibly associated with organic matter; it is possible that this residual molybdenum may be present in minerals (e.g. framboidal pyrite) that are protected during the chemical leaching used to estimate “occurrence” or “association”.

5.16.2 Behaviour of Molybdenum during Combustion

Molybdenum is in Class IIa (Meij, 1994); it is volatile and is enriched on the finer particles of flyash.

5.16.3 Environmental and Health Effects of Molybdenum from Coal Combustion

There are few reports of detrimental health or environmental effects from the emission of molybdenum compounds from power stations. However molybdenum can be leached from ash in ash deposits or where ash is used a soil conditioner (e.g. see Woodbury et al, 1999) and can accumulate in plants and cause molybdenosis in grazing animals (see Swaine, 1990).

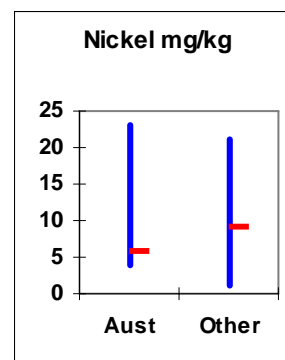
5.17 Nickel (Ni)

5.17.1 Occurrence of Nickel in Coal

The concentration ranges of nickel in coal and geological materials are listed in Table 17.

Table 17. Concentration of Nickel in Coal, Earth's Crust and Shales

Concentration of Nickel in:	mg/kg
Australian Export Coals	4 – 23 (6) [#]
Other Internationally Traded Coals	2 – 22 (10) [#]
Australian Domestic Coals	2 – 18 (6) [#]
Earth's Crust	75
Earth's Shales	70



[#] values in parentheses are averages

There is a high level of uncertainty about the occurrence of nickel in bituminous coals. It is thought to be associated with pyrite and the organic matter (Finkelman, 1994; 1995). Although nickel is apparently also present in the clays and carbonates (Swaine, 1990). There has been a study of the occurrence of nickel in Canadian feed coals and the ash produced. (Goodarzi and Huggins, 2001; 2004).

5.17.2 Behaviour of Nickel during Combustion

Nickel is volatile and condenses on the fly ash particles (Class IIB, Meij, 1994).

5.17.3 Environmental and Health Effects of Nickel from Coal Combustion

There does not appear to be any reports of harmful effects from the presence of the low concentrations of nickel in coal and its combustion products.

5.18 Radioactive Trace Elements

Some trace elements in coal are radioactive. These elements occur naturally in coal and include uranium, thorium and their products of radioactive decay e.g. radium and the gas, radon. The concentrations of these trace elements are generally no higher in the mineral matter in coal than occurs naturally in other geological materials. During combustion, radon gas is released into the atmosphere. The other radioactive trace elements are retained in the ash. The levels in the coal ash are similar to those levels occurring in rocks, soils and sediments in the earth's crust.

There have been many studies on the radioactivity emitted from coal-fired power stations. None have reported any health effects caused by the natural radioactivity of coal from most locations in the world.

The radioactive trace elements, uranium and thorium in Australian coals are present at the low levels seen in most bituminous coals (see Tables 19 and 20).

Information is readily available from The United States Geological Survey (Radioactive Elements in Coal and Fly Ash, USGS Factsheet 163-97, <http://greenwood.cr.usgs.gov/energy/factshts/163-97/FS-163-97.html>)

5.19 Selenium

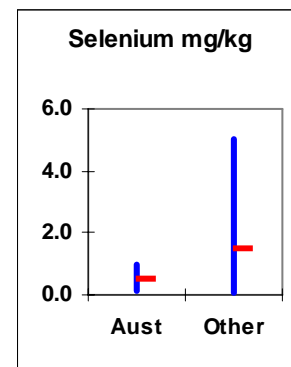
5.19.1 Concentration and Occurrence of Selenium in Coal

The concentrations of selenium in coal, the earth's crust and shales are listed in Table 18.

Table 18. Concentration of Selenium in Coal, Earth's Crust and Shales

Concentration of Selenium in:	mg/kg
Australian Export Coals	0.1 – 1.0 (0.5) [#]
Other Internationally Traded Coals	0.1 – 5.0 (1.5) [#]
Australian Domestic Coals	0.3 – 1.1 (0.6) [#]
Earth's Crust	0.05
Earth's Shales	0.60

[#] values in parentheses are averages



Selenium is thought to be associated with sulfides including pyrite, the organic matter and maybe clays in bituminous coals (Swaine, 1990). The presence of lead selenide has been reported (Hower and Robertson, 2003; Finkelman, 1994; 1995).

5.19.2 Behaviour of Selenium during Combustion

Selenium is vaporised during combustion and is partly condensed on the fly ash particles. Coal combustion is one of the major anthropogenic sources of selenium emitted to the atmosphere.

5.19.3 Environmental and Health Effects of Selenium from Coal Combustion

Selenium is an important trace element in biological functions. Insufficient and conversely too much can be detrimental. There are reports of situations where selenium leached from flyash has had adverse impacts on species in wetlands and inland waterways e.g. see Crutchfield, 2000; Lemly, 2002; Peters, et al, 1999; Kirby et al, 2001). Again, the inappropriate use of coal (containing elevated levels of selenium) in domestic situations in China has resulted in health problems (Zheng et al, 1999).

5.20 Thorium

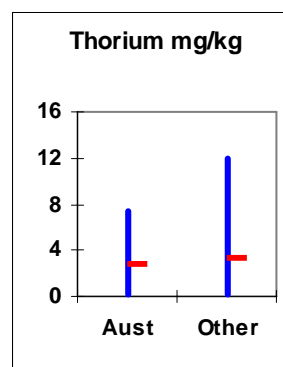
5.20.1 Concentration and Occurrence of Thorium in Coal

The concentrations of thorium in coal, the earth's crust and shales are listed in Table 19.

Table 19. Concentration of Thorium in Coal, Earth's Crust and Shales

Concentration of Thorium in:	mg/kg
Australian Export Coals	0.1 – 7.3 (2.8) [#]
Other Internationally Traded Coals	0.3 – 12.0 (3.8) [#]
Australian Domestic Coals	1.2 – 5.5 (2.9) [#]
Earth's Crust	10
Earth's Shales	12

[#] values in parentheses are averages



According to Swaine (1990), thorium is present in the minerals, likely monazite and to a lesser extent in zircon and xenotime; small amounts could be present in iron oxides and clays.

5.20.2 Behaviour of Thorium during Combustion

Thorium appears not to be volatile during combustion; it is not enriched on the finer ash particles.

5.20.3 Environmental and Health Effects of Thorium from Coal Combustion

Thorium is radioactive and is consequentially of interest. There is no evidence that the small concentrations present in most coals have any adverse health or environmental impacts (see Section 5.18, above).

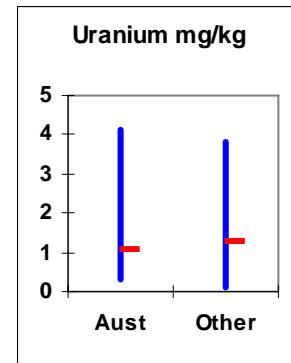
5.21 Uranium

5.21.1 Concentration and Occurrence of Uranium in Coal

The concentrations of uranium in coal, the earth's crust and shales are listed in Table 20.

Table 20. Concentration of Uranium in Coal, Earth's Crust and Shales

Concentration of Uranium in:	mg/kg
Australian Export Coals	0.3 – 4.1 (1.1) [#]
Other Internationally Traded Coals	<0.1 – 3.8 (1.3) [#]
Australian Domestic Coals	0.5 – 2.1 (0.9) [#]
Earth's Crust	2.7
Earth's Shales	4.0



[#] values in parentheses are averages

Uranium is associated with clays, zircon and phosphates and may also be organically bound in coal (Swaine, 1990). Finkelman (1994; 1995) indicates that most of the uranium is organically bound with a “substantial proportion” in higher rank coals present in minerals such as zircon and rare-earth phosphates.

5.21.2 Behaviour of Uranium during Combustion

Uranium exhibits some volatility during combustion. It is slightly enriched on the finer ash particles (Meij, 1994).

5.21.3 Environmental and Health Effects of Uranium from Coal Combustion

Uranium because of its radioactivity is of interest. However, it is low in most coals and there are studies that indicate that at the concentrations present, there are no adverse impacts (see Section 5.18, above).

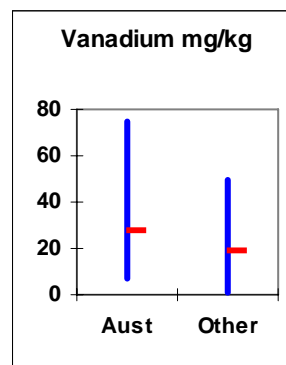
5.22 Vanadium

5.22.1 Occurrence of Vanadium in Coal

The concentrations of vanadium in coal, the earth's crust and shales are listed in Table 21.

Table 21. Concentration of Vanadium in Coal, Earth's Crust and Shales

Concentration of Vanadium in:	mg/kg
Australian Export Coals	7 – 75 (28) [#]
Other Internationally Traded Coals	1 – 50 (19) [#]
Australian Domestic Coals	few data available
Earth's Crust	135
Earth's Shales	130



[#] values in parentheses are averages

According to Swaine (1990), vanadium is thought to be present in both the organic and mineral phases (clays, especially illite), however there is a high uncertainty with the assignment of vanadium to particular phases (Finkelman, 1994; 1995).

5.22.2 Behaviour of Vanadium during Combustion

Vanadium exhibits some volatility during combustion. It is slightly enriched on the finer ash particles (Meij, 1994).

5.22.3 Environmental and Health Effects of Vanadium from Coal Combustion

As vanadium is present at low concentrations, there are apparently no reports of adverse health or environmental impacts.

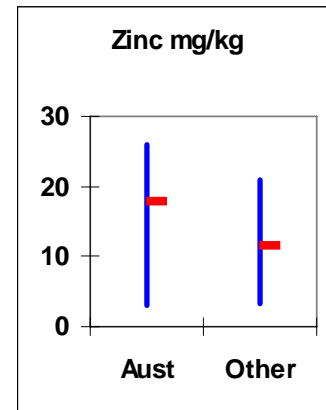
5.23 Zinc

5.23.1 Concentration and Occurrence of Zinc in Coal

The concentrations of zinc in coal, the earth's crust and shales are listed in Table 22.

Table 22. Concentration of Zinc in Coal, Earth's Crust and Shales

Concentration of Zinc in:	mg/kg
Australian Export Coals	3 – 26 (18) [#]
Other Internationally Traded Coals	4 – 23 (11) [#]
Australian Domestic Coals	<0.01 – 0.14 (0.03) [#]
Earth's Crust	70
Earth's Shales	100



[#] values in parentheses are averages

Zinc is likely present as sphalerite, ZnS (Swaine, 1990; Dale, 1999) and to a lesser extent in pyrite (Finkelman, 1994; 1995).

5.23.2 Behaviour of Zinc during Combustion

Zinc is a volatile trace element (Class IIA) that is enriched in the finer particles of flyash (Meij, 1994).

5.23.3 Environmental and Health Effects of Zinc from Coal Combustion

There are apparently no reports of harmful effects from zinc emissions from the utilisation of coal in power stations.

6 LEGISLATION WORLDWIDE

Sloss and Smith (2000) have reported on the legislative regime worldwide that may apply to the emissions of trace elements from coal-fired power stations. Legislation that is relevant to the use of coal and disposal of the ash and associated effluent streams does not generally address or target the masses of trace elements emitted to the environment in the gas phase (with the exception of mercury, the emissions of which are coming under scrutiny) or in the particulate matter to the atmosphere. However the concentrations of the trace elements in the ash may come under some regulations and certainly the concentrations of the trace elements in any water discharge do come under specific regulations.

6.1 Emissions to the Atmosphere

General environmental laws cover the emissions of trace elements from coal-fired power stations.

Trace elements are either emitted to the atmosphere associated with the particulate matter passing through the electrostatic precipitators (ESPs) or baghouses or as volatile species in the gas phase. The significant volatile trace elements are the halogens (chlorine, fluorine, with lesser amounts of bromine and iodine), boron, selenium and mercury. Many power stations are equipped with wet DeSO_x scrubbers to remove sulfur dioxide and these scrubbers may also attenuate the emissions of fly ash and also volatile gaseous species of the trace elements including compounds of mercury. However the emissions of DeSO_x particulate material or aerosol may occur and the trace elements present in the lime or limestone or in the water will be emitted.

The emission of mercury to the atmosphere is of interest and in the future, laws in the US will cap the emissions of mercury from power stations (see Section 5.15).

6.2 Emissions to Water

The disposal of ash and DeSO_x sludge leads to the possibility of leaching trace elements into surface and ground waters. Most emissions of trace elements to surface and groundwaters are a consequence of the ash handling systems (this includes the ultimate disposal of ash to a pond or landfill).

6.3 Disposal of Coal Ash

There are international agreements on the shipment of hazardous materials such as the Basel Convention administered by the United Nations (UN). The Basel Convention (<http://www.basel.int/>) seeks to control the transboundary movements and disposal of hazardous wastes. The text of Basel Convention, 1989 is available at the URL: <http://www.basel.int/text/con-e.pdf>. Annex I of the Convention is a list of “Categories of wastes to be controlled”. This list includes wastes having as constituents, “compounds of beryllium, hexavalent chromium, copper, zinc, arsenic, selenium, cadmium, antimony, tellurium, mercury, thallium and lead”. Compounds of these trace elements are present at very low levels in coal ash and according to the Basel Convention, fly ash is not a “hazardous

waste” unless it or its leachate contains a toxic substance or substances at such concentrations, that it or its leachate exhibits a “hazardous characteristic”. There have been occurrences where leachate from ash disposal sites has had a detrimental impact; in particular, the impact of selenium on aquatic species in lakes and ponds. There are examples of this in both the US and Australia (see for example, Crutchfield, 2000; Lemly, 2002; Peters, et al, 1999; Kirby et al, 2001.)

The Australian legislation on ash disposal has been reviewed by Aynsley et al (2003) for the Ash Development Association of Australia (ADAA) and the Cooperative Research Centre for Coal in Sustainable Development (CCSD). The report lists the relevant legislation of the Commonwealth and States that applies or could apply to the use or disposal of coal ash. Most legislation does not specifically mention ash but applies to waste generally. The Hazardous Waste Act 1989, the implementation of the Basel Convention is the most relevant legislation of the Commonwealth of Australia.

7 CONCLUDING REMARKS

This report does not contain an exhaustive listing or review of the information published on the general topic “trace elements in coal”; rather it provide key references. The background information contained in this report should be of interest to those who wish to obtain further details from the original reports and papers that were used to prepare the website on trace elements in coal at http://www.det.csiro.au/science/researchservices/trace_elements.htm or <http://www.det.csiro.au/traceelements>

The website will be undated at regular intervals and should continue to provide relevant information to coal producers and others associated with the industry.

8 ACKNOWLEDGEMENTS

The Australian Coal Association is thanked for its financial contribution through its research program, ACARP. Jim Craigen of ACARP is acknowledged and thanked for his advice during the project. The assistance of Les Dale (CSIRO), Glenn Devir (ACIRL), Anthony Williams (ACIRL) and Don Holcombe (ACIRL) is gratefully acknowledged. Jon Davis (Rio Tinto Australia Pty Ltd) is thanked for reviewing the work and for his critical comments.

9 REFERENCES

Ando, M., Tadano, M., Yamamoto, S., Tamura, K., Asanuma, S., Watanabe, T., Kondo, T., Sakurai, S., Ji, R., Liang, C., Chen, X., Hong, Z. and Cao, S. (2001), Health effects of fluoride pollution caused by coal burning, *The Science of the Total Environment*, 271 (1-3), 107-116

Aynsley, D., Porteous, M., Heidrich, C. and Zhang D-k. (2003), “COAL ASH: a review of legislation and regulations within Australia”, Ash Development Association of Australia, PO Box 1194 Wollongong, NSW 2500, Australia.

Benson, S. A. (2004), Air quality III: mercury, trace elements, and particulate matter, *Fuel Processing Technology*, 85(6-7), 423-424.

Benson, S. A. and Brown, T. D. (2000), Editorial, Special Issue: Air Quality, Trace Elements and Particulate matter, *Fuel Processing Technology*, 65-66, 1-3.

Clarke, L.B. and Sloss, L.L. (1992), Trace elements - emissions from coal combustion and gasification, IEACR/49, IEA Clean Coal Centre, London, UK.

Clark, R.B., Zeto, S.K., Ritchey, K.D. and Baligar, V.C. (1999), Boron accumulation by maize grown in acidic soil amended with coal combustion products, *Fuel*, 78 (2), 179-185.

Crutchfield Jr, J. U. (2000), Recovery of a power plant cooling reservoir ecosystem from selenium bioaccumulation, *Environmental Science & Policy*, 3, Supplement 1, S145-S163.

Dai, S., Ren, D. and Ma, S. (2004), The cause of endemic fluorosis in western Guizhou Province, Southwest China, *Fuel*, 83(14-15), 2095-2098.

Dale, L.S. (2003) Review of Trace Elements In Coal, CSIRO Energy Technology Investigation Report ET/IR599 ACARP Project C11020, End Of Grant Report Prepared for Australian Coal Association Research Program.

Dale, L.S., Chapman, J.F., Buchanan, S.J. and Lavrencic, S.A. (1999), Mechanisms for Trace Element Partitioning in Australian Coals, Project 4.2, Final Report to CRC for Black Coal Utilisation, Australian Black Coal Utilisation Research Limited 2002.

Dale, L.S. and Riley, K.W. (1997), Standard analytical methods for trace elements in coal. ACARP Project C5063, Australian Coal Association Research Program.

Davidson, R.M. (1996), Chlorine and other halogens in coal, IEAPER/28, IEA Clean Centre, London UK.

Davidson, R., (2000), Modes of occurrence of trace elements in coal - results from an international collaborative programme, CCC/36, IEA Clean Centre, London UK.

Doolan, K.J. (1987), A pyrohydrolytic method for the determination of low fluorine concentrations in coal and minerals, *Analytica Chimica Acta*, 202, 61-73.

Eble, C.F. and Hower, J.C. (1997), Coal quality trends and distribution of potentially hazardous trace elements in Eastern Kentucky coals, *Fuel*, 76(8), 711-715.

Feng, X., Sommar, J., Lindqvist, O. and Hong, Y. (2002), Occurrence, Emissions and Deposition of Mercury during Coal Combustion in the Province Guizhou, China, *Water, Air, and Soil Pollution*, 139(1/4), 311-324.

Finkelman, R.B. (1994), Modes of occurrence of potentially hazardous trace elements in coal: levels of confidence, *Fuel Processing Technology*, 39, 21-34.

Finkelman, R.B. (1995), Modes of Occurrence of Environmentally-sensitive Trace Elements in Coal, Chapter 3, pp 24-50, in: Swaine, D.J. and Goodarzi, F. (Eds), Environmental Aspects of Trace Elements in Coal. Kluwer, Dordrecht, The Netherlands, 312 pp.

Finkelman, R.B. and Gross, P.M.K. (1999), The types of data needed for assessing the environmental and human health impacts of coal, *International Journal of Coal Geology*, 40(2-3), 91-101.

Finkelman, R.B., Belkin, H.E. and Zheng, B. (1999), Health impacts of domestic coal use in China, *Proceedings of the National Academy of Sciences of the United States of America*, 96(7), 3427-3431.

Finkelman, R.B., Orem, W., Castranova, V., Tatu, C.A., Belkin, H.E., Zheng, B., Lerch, H.E., Maharaj, S.V. and Bates, A. L. (2002), Health impacts of coal and coal use: possible solutions, *International Journal of Coal Geology*, 50(1-4), 425-443.

Galbreath, Kevin C.; Zygarlicke, Christopher J. (2000), Mercury transformations in coal combustion flue gas, *Fuel Processing Technology*, 65-66, 289-310.

Gentzis, T. and Goodarzi, F. (1997), Trace element geochemistry of the Obed Mountain deposit coals, Alberta, Canada, *Fuel*, 76(14-15), 1491-1501.

Gibb, W.H., Clarke, F. and Mehta, A.K. (2000), The fate of coal mercury during combustion, *Fuel Processing Technology*, 65-66, 365-377.

Godbeer, W.C. and Swaine, D.J. (1987), Fluorine in Australian coals, *Fuel*, 66(6), 794-798..

Godbeer, W.C. and Swaine, D.J. (1995), The Deposition of Trace Elements in the Environs of a Power Station, Chapter 10, pp 178-203 in: Swaine, D.J. and Goodarzi, F. (Eds), Environmental Aspects of Trace Elements in Coal. Kluwer, Dordrecht, The Netherlands, 312 pp.

Goodarzi, F. (2002), Mineralogy, elemental composition and modes of occurrence of elements in Canadian feed-coals, *Fuel*, 81(9), 1199-1213.

Goodarzi, F. and Huggins, F. E. (2001), Monitoring the species of arsenic, chromium and nickel in milled coal, bottom ash and fly ash from a pulverized coal-fired power plant in western Canada, *Journal of Environmental Monitoring*, 3(1)

Goodarzi, F. and Huggins, F. (2004), Speciation of nickel in Canadian subbituminous and bituminous feed coals, and their ash by-products, *Journal of Environmental Monitoring*, 6(10), 787 – 791.

Goodarzi, F and Swaine, D.J. (1994), The influence of geological factors on the concentration of boron in Australian and Canadian coals, *Chemical Geology*, 118 (1-4), 301-318.

He, B., Liang, L. and Jiang, G. (2002), Distributions of arsenic and selenium in selected Chinese coal mines, *The Science of the Total Environment*, 296(1-3), 19-26.

Helle, S., Alfaro, G., Kelm, U., and Tascón, J.M.D. (2000), Mineralogical and chemical characterisation of coals from Southern Chile, *International Journal of Coal Geology*, 44(1), 85-94.

Hower, J.C. and Robertson, J. D. (2003), Clausthalite in coal, *International Journal of Coal Geology*, 53(4), 219-225.

Hower, J.C., Robertson, J. D., Wong, A.S., Eble, C.F. and Ruppert, L.F. (1997), Arsenic and lead concentrations in the Pond Creek and Fire Clay coal beds, eastern Kentucky coal field, *Applied Geochemistry*, 12(3), 281-289.

Huffman, G.P., Huggins, F.E., Shah, N., Shah, J. and Zhao, J. (1994), Speciation of arsenic and chromium in coal and combustion ash by XAFS spectroscopy, *Fuel Processing Technology*, 39, 47-62.

Huggins, F.E. (2002), Overview of analytical methods for inorganic constituents in coal, *International Journal of Coal Geology*, 50(1-4), 169-214.

Huggins, F.E. and Huffman, G.P. (1995), Chlorine in coal: an XAFS spectroscopic investigation, *Fuel*, 74(4), 556-569.

Huggins, F.E. and Huffman, G.P. (1996), Modes of occurrence of trace elements in coal from XAFS spectroscopy, *International Journal of Coal Geology*, 32(1-4), 31-53.

Huggins, F.E. and Huffman, G. P. (2004), How do lithophile elements occur in organic association in bituminous coals?, *International Journal of Coal Geology*, 58(3), 193-204.

Huggins, F.E., Huffman, G.P., Kolker, A., Mroczkowski, S.J., Palmer, C.A. and Finkelman, R.B. (2002), Combined Application of XAFS Spectroscopy and Sequential Leaching for Determination of Arsenic Speciation in Coal, *Energy & Fuels*, 16(5), 1167-1172.

Huggins, F.E.; Najih, M. and Huffman, G.P. (1999), Direct speciation of chromium in coal combustion by-products by X-ray absorption fine-structure spectroscopy, *Fuel*, 78(2), 233-242.

Huggins, F.E., Shah, N., Huffman, G.P. and Robertson, J. D. (2000), XAFS spectroscopic characterization of elements in combustion ash and fine particulate matter, *Fuel Processing Technology*, 65-66, 203-218.

Huggins, F.E.; Srikantapura, S., Parekh, B. K.; Blanchard, L. and Robertson, J. D. (1997), XANES Spectroscopic Characterization of Selected Elements in Deep-Cleaned Fractions of Kentucky No. 9 Coal, *Energy & Fuels*, 11(3), 691-701.

Jones, D.R. (1995), The Leaching of Major and Trace Elements from Coal Ash, Chapter 12, pp 221-262 in: Swaine, D.J. and Goodarzi, F. (Eds), *Environmental Aspects of Trace Elements in Coal*. Kluwer, Dordrecht, The Netherlands, 312 pp.

Karayigit, A.I., Gayer, R.A., Querol, X. and Onacak, T. (2000), Contents of major and trace elements in feed coals from Turkish coal-fired power plants, *International Journal of Coal Geology*, 44(2), 169-184.

Kirby, J., Maher, W. and Harasti, D. (2001). Changes in Selenium, Copper, Cadmium, and Zinc Concentrations in Mullet (*Mugil cephalus*) from the Southern Basin of Lake Macquarie, Australia, in Response to Alteration of Coal-Fired Power Station Fly Ash Handling Procedures, *Archives of Environmental Contamination and Toxicology*, 41(2), 171 – 181.

Kolker, A., Huggins, F.E., Palmer, C.A., Shah, N., Crowley, S.S.; Huffman, G.P. and Finkelman, R.B. (2000). Mode of occurrence of arsenic in four US coals, *Fuel Processing Technology*, 63(2-3) 167-178.

Lemly, A. D. (2002). Symptoms and implications of selenium toxicity in fish: the Belews Lake case example, *Aquatic Toxicology*, 57(1-2), 39 – 49.

Liu, D., Yang, Q., Tang, D., Kang, X. and Huang, W. (2001), Geochemistry of sulfur and elements in coals from the Antaibao surface mine, Pingshuo, Shanxi Province, China, *International Journal of Coal Geology*, 46(1), 51-64.

Liu, J., Zheng, B.S., Aposhian, H.V., Zhou, Y.S. Chen, M.L., Zhang, A.H. and Waalkes, M.P. (2002), Chronic Arsenic Poisoning From Burning High-Arsenic-Containing Coal In Guizhou, China, *Environmental Health Perspectives*, 110, 119–122.

Luo, K., Ren, D., Xu, L., Dai, S., Cao, D., Feng, F. and Tan, J. (2004), Fluorine content and distribution pattern in Chinese coals, *International Journal of Coal Geology*, 57(2), 143-149.

Meij, R. (1994), Trace element behaviour in coal-fired power plants, *Fuel Processing Technology*, 39, 199-217.

Meij, R. (1995), The Distribution of Trace Elements during the Combustion of Coal, Chapter 7, pp 111-126 in: Swaine, D.J. and Goodarzi, F. (Eds), *Environmental Aspects of Trace Elements in Coal*. Kluwer, Dordrecht, The Netherlands, 312 pp.

Mukhopadhyay, P.K., Goodarzi, F., Crandlemire, A.L., Gillis, K.S., MacNeil, D.J. and Smith, W.D. (1998) Comparison of coal composition and elemental distribution in selected seams of the Sydney and Stellarton Basins, Nova Scotia, Eastern Canada, *International Journal of Coal Geology*, 37(1-2), 113-141.

Mukhopadhyay, P.K., Lajeunesse, G. and Crandlemire, A.L (1996), Mineralogical speciation of elements in an eastern Canadian feed coal and their combustion residues from a Canadian power plant, *International Journal of Coal Geology*, 32(1-4), 279-312.

Newman-Sutherland, E., Nunez, R.A., Davis, J. and Narelle Burns, N. (2001), Mercury and Coal-fuelled Power Plants: Emissions, Technologies and Legislation, Technology Assessment Report 19, CRC for Coal in Sustainable Development, Pullenvale, Qld, Australia.

Pacyna, E. G. and Pacyna, J. M. (2002), Global Emission of Mercury from Anthropogenic Sources in 1995, *Water, Air, and Soil Pollution*, 137(1/4), 149-165.

Peters, G.M., Maher, W.A., Jolley, D., Carroll, B.I., Gomes, V.G., Jenkinson, A.V. and McOrist, G.D. (1999). Selenium contamination, redistribution and remobilisation in sediments of Lake Macquarie, NSW. *Organic Geochemistry*, 30, 1287-1300.

Peterson, C., Nelson, P. and Morrison, A. (2004), Quantifying Natural and Anthropogenic Sourced Mercury Emissions from Australia in 2001, Research Report 46, CRC for Coal in Sustainable Development, Pullenvale, Qld, Australia.

Pollock, S.M., Goodarzi, F. and Riediger, C.L. (2000), Mineralogical and elemental variation of coal from Alberta, Canada: an example from the No. 2 seam, Genesee Mine, *International Journal of Coal Geology* Volume: 43(1-4), 259-286.

Querol, X., Alastuey, A., Lopez-Soler, A., Plana, F., Zeng, R., Zhao, J. and Zhuang, X. (1999), Geological controls on the quality of coals from the West Shandong mining district, Eastern China, *International Journal of Coal Geology*, 42(1), 63-88.

Quick, J. C., Brill, T. C. and Tabet, D. E. (2003), Mercury in US coal: observations using the COALQUAL and ICR data. *Environmental Geology*, 43(3), 247 – 259.

Roelandts, I., Robaye, G., Delbrouck-Habaru, J.M. and Weber, G. (1996), Determination of total fluorine in five coal reference materials by proton-induced gamma-ray emission spectrometry, *Talanta*, 43(3), 439-449.

Ruppert, L.F., Kirschbaum, M.A., Warwick, P.D., Flores, R.M.; Affolter, R. H. and Hatch, J.R. (2002), The US Geological Survey's national coal resource assessment: the results, *International Journal of Coal Geology*, 50(1-4), 247-274.

Senior, C.L., Sarofim, A.F., Zeng, T., Helble, J.J. and Mamani-Paco, R. (2000), Gas-phase transformations of mercury in coal-fired power plants, *Fuel Processing Technology*, 63(2-3), 197-213.

Sliger, R. N., Kramlich, J.C. and Marinov, N.M. (2000). Towards the development of a chemical kinetic model for the homogeneous oxidation of mercury by chlorine species, *Fuel Processing Technology*, 65-66, 423-438.

Sloss, L. and Smith, I. (1994), Trace elements in coal, IEAPER/21, IEA Clean Coal Centre, London, UK.

Sloss, L. and Smith, I. (2000), Trace element emissions, IEA CCC/34, IEA Clean Coal Centre, London, UK.

Smith, I. (1987), Trace elements from coal combustion: emissions, IEA Coal Research Report IEACR/01, IEA Clean Coal Centre, London, UK.

Spears, D.A., Manzanares-Papayanopoulos, L.I. and Booth, C.A. (1999), The distribution and origin of trace elements in a UK coal; the importance of pyrite, *Fuel*, 78(14), 1671-1677.

Spears, D.A. and Zheng, Y. (1999), Geochemistry and origin of elements in some UK coals, *International Journal of Coal Geology*, 38(3-4), 161-179.

Sun, G. (2004), Arsenic contamination and arsenicosis in China, *Toxicology and Applied Pharmacology*, 198(3), 268-271.

Swaine, D. J. (1990), *Trace Elements in Coal*, Butterworth & Co. Ltd, London, 278 pp.

Swaine, D.J. (1995), The Contents and Some Related Aspects of Trace Elements in Coals, Chapter 2, pp 5-23 in: Swaine, D.J. and Goodarzi, F. (Eds), *Environmental Aspects of Trace Elements in Coal*. Kluwer, Dordrecht, The Netherlands, 312 pp.

Swaine, D. J. (2000), Why trace elements are important, *Fuel Processing Technology*, 65-66, 21-33.

Swaine, D.J. and Goodarzi, F. (Eds), (1995), *Environmental Aspects of Trace Elements in Coal*. Kluwer, Dordrecht, The Netherlands, 312 pp.

Tewalt, S.J., Linda J. Bragg, L.J. and Robert B. Finkelman, R.B. (2001), U.S. Geological Survey Fact Sheet 095-01, Mercury in U.S. Coal -- Abundance, Distribution, and Modes of Occurrence, <http://pubs.usgs.gov/fs/fs095-01/fs095-01.pdf>

Wong, J. W. C., Jiang, R. F. and Su, D. C. (1998), The Accumulation of Boron in *Agropyron elongatum* grown in Coal Fly Ash and Sewage Sludge Mixture, *Water, Air, and Soil Pollution*, 106(1-2), 137-147.

Wood, R. A., Dale, L. S. and Riley, K. W. (2003), A borate fusion method for the determination of fluorine in coal, *Fuel*, 82, (13), 1587-1590.

Woodbury, P. B., Rubin, G., McCune, D. C., Weinstein, L.H. and Neuhauser, E. F. (1999), Assessing Trace Element Uptake by Vegetation on a Coal Fly Ash Landfill, *Water, Air, and Soil Pollution*, 106(1-2), 137-147.

Yudovich, Y.E. and Ketris, M.P. (2005), Mercury in coal: a review: Part 1. Geochemistry, *International Journal of Coal Geology*, 62(3), 107-134.

Zeng, T., Sarofim, A. F. and Senior, C. L. (2001), Vaporization of arsenic, selenium and antimony during coal combustion, *Combustion and Flame* Volume: 126(3),1714-1724.

Zhang, J., Ren, D., Zheng, C., Zeng, R., Chou, C.-L. and Liu, J. (2002), Trace element abundances in major minerals of Late Permian coals from southwestern Guizhou province, China, *International Journal of Coal Geology*, 53(1), 55-64.

Zhang, J.Y., Zheng, C.G., Ren, D.Y.; Chou, C.-L., Liu, J., Zeng, R.S., Wang, Z.P., Zhao, F.H. and; Ge, Y.T. (2004), Distribution of potentially hazardous trace elements in coals from Shanxi province, China, *Fuel*, 83(1), 129-135.

Zheng, B., Ding, Z., Huang, R., Zhu, J., Yu, X., Wang, A., Zhou, D. et. al. (1999), Issues of health and disease relating to coal use in southwestern China, *International Journal of Coal Geology*, 40(2-3), 119-132.

Zhuang, X., Querol, X., Zeng, R., Xu, W., Alastuey, A., Lopez-Soler, A. and Plana, F. (2000), Mineralogy and geochemistry of coal from the Liupanshui mining district, Guizhou, south China, *International Journal of Coal Geology*, 45(1), 21-37.

9.1 Websites

The following websites are sources of information of the topic of “trace elements” in coal. All websites both in this listing and mentioned in the body of the report were assessed in July, 2005.

Cooperative Research Centre for Coal in Sustainable Development (CCSD)
<http://www.ccsd.biz/>

Europa, European Commission, DG Energy and Transport, COAL
http://europa.eu.int/comm/energy/en/fa_13_en.html

European Environmental legislation
http://europa.eu.int/comm/energy/en/environmental_legislation_en.html

IEA Clean Coal Centre <http://www.iea-coal.org.uk/>

IEA: Cleaner Coal Technology related websites <http://www.iea-coal.co.uk/site/links/cct1.htm>

National Pollutant Inventory (of Australia) <http://www.npi.gov.au/>

USEPA <http://www.epa.gov>

USEPA CLEAR SKIES <http://www.epa.gov/air/clearskies/>

USEPA Mercury <http://www.epa.gov/mercury/>

US National Coal Resources Data System - Coal Quality Database
<http://energy.er.usgs.gov/products/databases/coalqual/intro.htm>

West Virginia Coals: <http://www.wvgs.wvnet.edu/www/datastat/te/index.htm>

10 APPENDIX: DATA FROM ACIRL LIMITED

The following information was supplied by Anthony Williams of ACIRL. Researchers at ACIRL were unable to unambiguously identify product coals (both export and domestic) from their database. Most samples in ACIRL's laboratory systems lacked the necessary descriptors. The obvious bore core samples were removed before processing the data. Outliers were removed using a statistical approach:

An outlier was identified if the Trace element concentration [TE] was greater than the addition of

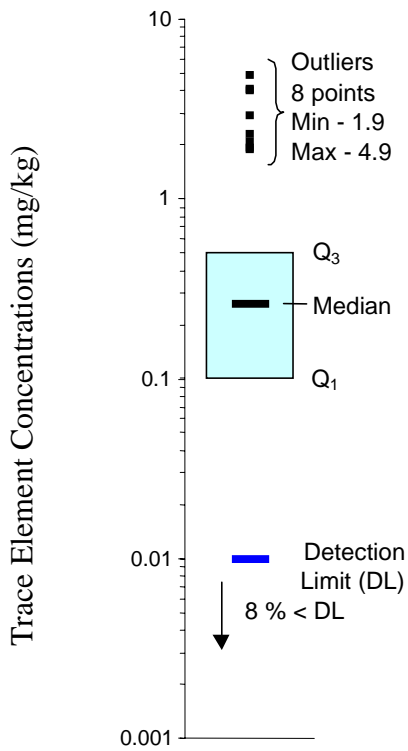
- 3 times the difference between the third quartile (Q_3) and the first quartile (Q_1),
- and the third quartile (Q_3)

or

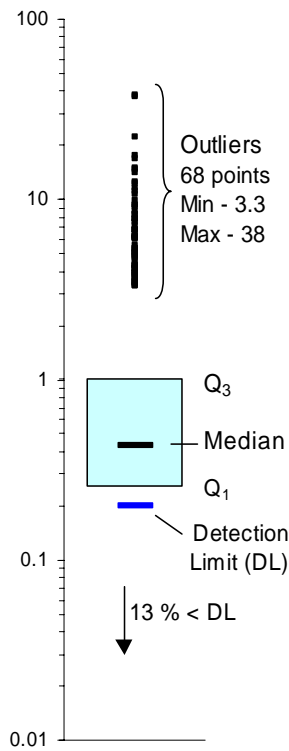
$$[TE] > Q_3 + 3.(Q_3 - Q_1)$$

The data has been arranged in the three Tables below:

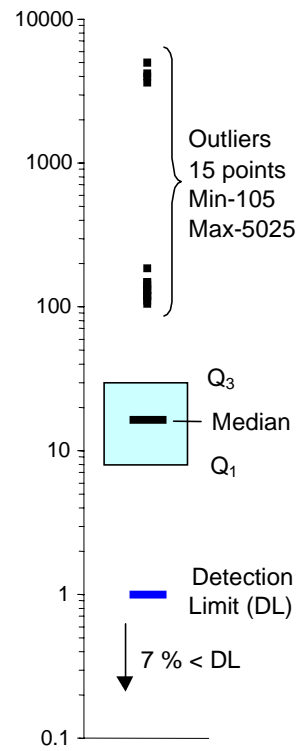
- a) Table 1A: Outliers, Median, 3rd quartile (Q_3), 1st quartile (Q_1), and detection limits for Antimony, Arsenic, Boron, Cadmium, Chlorine, and Chromium
- b) Table 2A: Outliers, Median, 3rd quartile (Q_3), 1st quartile (Q_1), and detection limits for Cobalt, Copper, Fluorine, Lead, Mercury, and Molybdenum
- c) Table 3A: Outliers, Median, 3rd quartile (Q_3), 1st quartile (Q_1), and detection limits for Nickel, Selenium, Vanadium, and Zinc



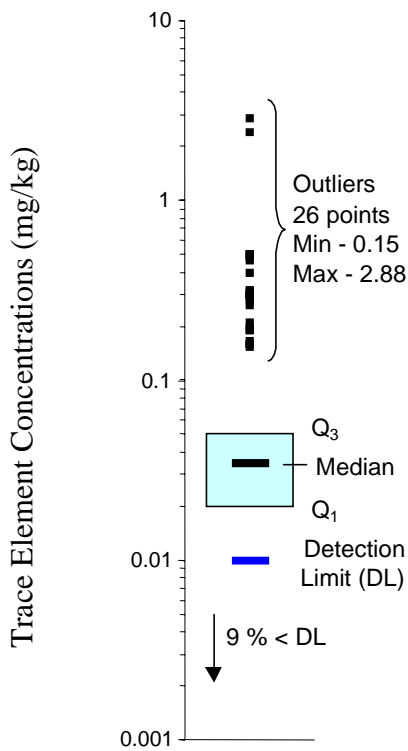
Antimony



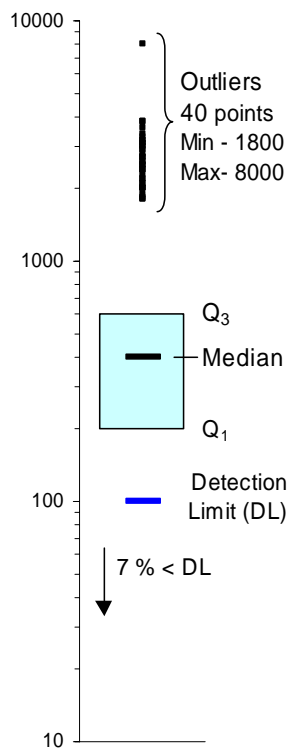
Arsenic



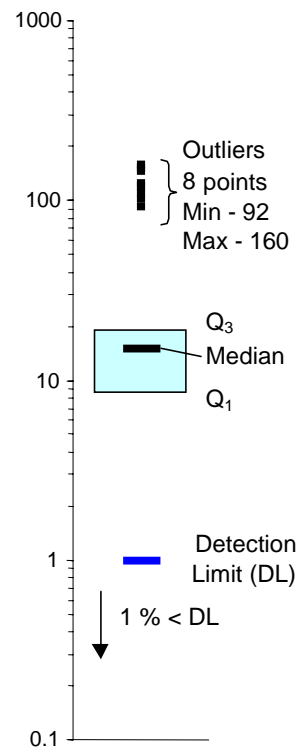
Boron



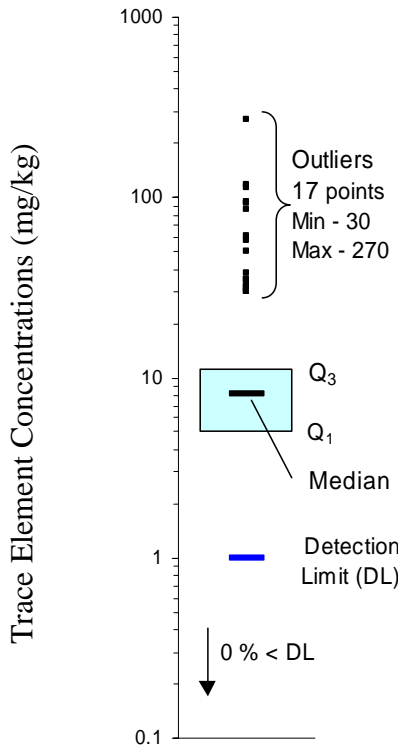
Cadmium



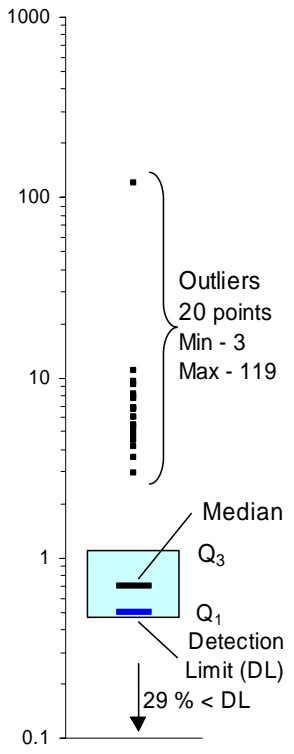
Chlorine



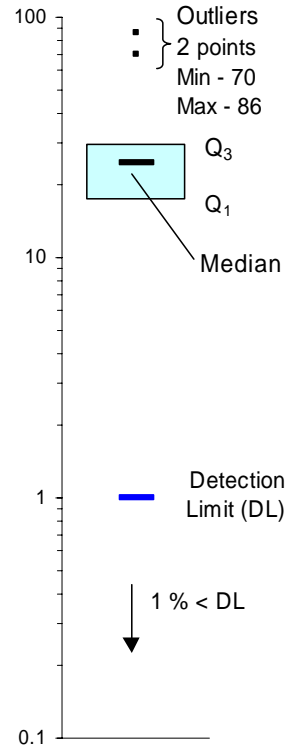
Chromium



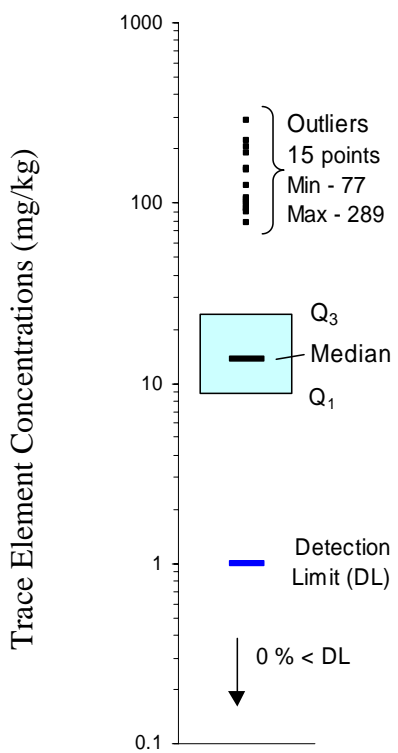
Nickel



Selenium



Vanadium



Zinc

Table 4A contains a summary of the data.

Note that outliers have been removed and a value of half the detection limit was assumed for concentration less than the detection limit.

Table 4A. Summary of ACIRL Data Base of Coal Results

Trace Element	Min	Max	Average	Trim* Mean	Std dev	Q ₁	Median	Q ₃
Antimony	0.005	1.69	0.33	0.32	0.32	0.09	0.26	0.46
Arsenic	0.1	3.2	0.62	0.59	0.60	0.25	0.38	0.72
Boron	0.5	70	18.6	18.4	14.4	7.92	15.4	27.9
Cadmium	0.005	0.14	0.04	0.04	0.03	0.02	0.03	0.05
Chlorine	50	1700	411	402	278	200	400	600
Chromium	0.5	49	14.9	14.7	8.6	8	14.2	18.3
Cobalt	0.5	14.2	4.3	4.27	2.33	2.87	3.81	5.32
Copper	0.5	49	20.1	20.0	8.41	15	18.2	25.8
Fluorine	5	365	101.9	100.4	59.2	58.2	97	140
Lead	0.5	21.6	6.93	6.84	3.68	4.58	6.1	8.62
Mercury	0.005	0.241	0.07	0.07	0.04	0.05	0.061	0.09
Molybdenum	0.5	2.6	0.87	0.86	0.57	0.5	0.5	1.02
Nickel	1	26.1	7.81	7.68	4.78	4.65	7.44	9.72
Selenium	0.25	2.94	0.77	0.76	0.51	0.25	0.67	1.04
Vanadium	0.5	61	25.1	25.0	11.3	17.5	24.3	29
Zinc	1.82	65	16.12	15.9	11.8	8.62	12.6	19

* - trimmed 5 percent of the values

Table 5A. Comparison of ACIRL Data with CSIRO Data for Export Australian Coals (concentrations are in mg/kg).

Trace Element	ACIRL	ACIRL	ACIRL		CSIRO	CSIRO	CSIRO
	Min	Max	Average		Min	Max	Average
Antimony	0.005	1.69	0.33		0.05	1.0	0.39
Arsenic	0.1	3.2	0.62		0.2	2.2	1.05
Boron	<5	70	19		5	70	19
Cadmium	0.005	0.14	0.04		0.01	0.32	0.11
Chlorine	50	1700	400		100	1200	300
Chromium	0.5	49	15		2	25	10
Cobalt	0.5	14	4		1	14	4
Copper	0.5	49	20		6	27	15
Fluorine	5	365	102		20	255	114
Lead	0.5	22	7		2	14	3
Mercury	0.005	0.241	0.07		0.01	0.11	0.04
Molybdenum	0.5	2.6	0.9		0.1	2.6	0.8
Nickel	1	26	8		4	23	6
Selenium	0.2	2.9	0.8		0.1	1.0	0.5
Vanadium	0.5	61	25		7	75	28
Zinc	1.82	65	16		3	26	18