

# ACARP TRACE ELEMENTS IN COAL

NO **02**

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BASED ON RESEARCH CARRIED OUT BY CSIRO ENERGY TECHNOLOGY

Australian thermal coals generally contain low levels of toxic trace elements in comparison to thermal coals from other countries traded on the international market.

Australian thermal coals contain substantially lower levels of arsenic, mercury and boron. These elements are of major environmental concern to power utilities.

## OVERVIEW

In an earlier study by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), the national Government body for scientific research in Australia, the levels of trace elements of environmental concern in Australian export thermal coals were compared with other internationally traded thermal coals (Dale, 1995). Representative samples of Australian product coals from major exporters and internationally traded coals obtained from a European distributor were used. The international coals were from the United States of America, South Africa, Indonesia, China, Poland, Colombia and Venezuela. The database was later substantially upgraded by CSIRO with additional samples of Australian and international thermal coals (Dale, 2000).

In two current research projects in the Australian Coal Association Research Program (ACARP) the database is being further expanded to include new Australian export coals and a wider range of international coals supplied by traditional and new suppliers. The database is the most comprehensive compilation available on the levels of environmental trace elements in internationally traded thermal coals.

**Australian thermal coals were generally found to contain significantly lower levels of arsenic, selenium, mercury and boron.** These four elements are of major environmental concern and are volatile resulting in their presence in flue gas. The levels of other environmentally sensitive trace elements were similar to international coals and the potential environmental impact would depend on their residence in waste products.

The radioactivity of all coals was low compared to the Earth's crust and the natural radionuclides arising from the decay of uranium and thorium present in the coals were considered to be of minimal environmental concern. The radioactivity of ash products from power stations was similar to that of the Earth's crust.

**The leaching of environmentally sensitive trace elements from stockpiles of Australian coals was found to be substantially below water quality guidelines.**

**The environmental impact of the utilisation of Australian thermal coals in relation to air emissions of trace elements and the leaching of trace elements from waste ash is considered to be minimal.**

## INTRODUCTION

There is increasing concern about the potential environmental impact of electricity generation from coal-fired power stations. Trace elements are becoming more important because of restrictions on the emission of air toxics and the disposal of waste ash. In many countries legislation has been introduced limiting the discharge of environmentally sensitive trace elements (Clarke and Sloss, 1992). **As a result more attention is being focussed on the levels of trace elements in power station feedstocks.** This is likely to have a significant impact on the world coal export market.

Australia is the world's largest exporter of thermal coal. However the international market is very competitive. Demonstration of the low levels of environmental trace elements in Australian export coals could provide a competitive edge in international coal trade.

Previous work (Swaine, 1990) demonstrated that Australian coals contain low levels of trace elements. However data in the literature on the levels in widely traded thermal coals is not readily available. A major problem is the uncertainties of the origin and nature of the samples for which data is presented. These data are therefore of questionable value. The use of non-standard methods of analysis places further doubt on the validity of the data.

**In order to make a valid comparison of the levels of trace elements in Australian export coals and those supplied to the international market by its competitors, it was necessary to characterise samples of local and foreign coals in the one laboratory using validated analytical methods.**

## COALS USED IN THE STUDY

The original database comparing the levels of trace elements in thermal coals was developed using representative samples of internationally traded coals obtained through a European importer of power station feedstocks and a selection of Australian export thermal coals from New South Wales and Queensland commonly supplied to the international market by Australia's major producers. The database has now been substantially upgraded by expanding the range of international coals supplied by the European importer and an Asian utility. The range of Australian coals has also been expanded to include all major suppliers to the international market. All samples analysed were representative of large shipments and were either superintending samples or power station laboratory control samples.

The current database includes trace element levels for up to 93 Australian export thermal coals. It contains data for 63 international coals from the USA (6 samples), South Africa (10), Indonesia (27), China (10), Poland (4), Colombia (5) and Venezuela (1).

Elements of major concern are arsenic, boron, cadmium, chromium, fluorine, mercury, molybdenum, lead and selenium. These elements have known adverse health effects at high levels of exposure. The compounds of these elements are mostly volatile and may be released to the atmosphere through gaseous emissions and in stack particulates. Their presence in aqueous process streams is also of concern.

The focus on the trace elements of most environmental concern is based on their known adverse health and ecological effects and has been driven by designations introduced by the United States National Research Council (1980), amendments to the United States Clean Air Act (1990) and by the National Pollutant Inventory established by Environment Australia in 1998. The classifications and designations are shown in Table 5 on the back page of this Newsletter.

From these designations, together with air emission regulations and water quality guidelines, a suite of 23 trace elements, considered to be of most environmental concern, was selected. They are antimony, arsenic, boron, beryllium, bromine, cadmium, chlorine, cobalt, chromium, copper, fluorine, iodine, mercury, manganese, molybdenum, nickel, lead, selenium, sulphur, thorium, uranium, vanadium and zinc.

Environmental concern is based on the known toxic responses to high levels of trace elements. The responses to elements of major concern are summarised below:

#### **ARSENIC**

Arsenic is carcinogenic and can cause damage to peripheral nerves and blood vessels. It can also cause anaemia and gastric disturbance. Arsenic is accumulated in the food chain, especially in seafood. Concentrations exceeding 50 µg/L in drinking water are considered hazardous.

#### **BORON**

Boron-rich soils can limit plant growth resulting in decreased crop yields. Limits exist on the levels of boron in wastewater and water for irrigation.

#### **CADMIUM**

Cadmium has no known biological function. It accumulates in the kidneys and liver. It is carcinogenic and can cause emphysema and fibrosis of the lung.

#### **CHROMIUM**

Chromium is carcinogenic. It accumulates in the liver and spleen. Chromium exists in the non-toxic form Cr(III) and tends to be absorbed onto clays, sediments and organic matter. It is therefore not very mobile in the environment. Cr(VI) is more mobile and more toxic.

#### **FLUORINE**

Fluorine is readily absorbed in the body and concentrates in the same tissues as calcium, especially the bones and teeth. There is some evidence to suggest that fluorine can cause genetic damage and disruption of the immune system. Fluorine causes leaf damage to plants.

#### **MERCURY**

Exposure to mercury causes neural and renal damage, and cardiovascular disease. Organo-mercury compounds bio-accumulate, particularly in fish.

#### **MOLYBDENUM**

Pastures containing high levels of molybdenum cause disease in cattle and sheep as well as poor growth and anaemia. The high molybdenum affects the absorption and metabolism of copper which is an essential element.

#### **LEAD**

Lead causes anaemia and has cardiovascular, neurological and gastrointestinal effects. Some compounds are animal and possible human carcinogens.

#### **SELENIUM**

Although selenium is an essential element, the safe range is narrow. Elevated levels cause gastrointestinal disturbance, liver and spleen damage, and anaemia.

## ANALYTICAL METHODS

Samples were analysed by the CSIRO using standard methods accredited by Standards Australia (SA), the American Society for Testing Materials (ASTM) and the International Organisation for Standardisation (ISO). Many of the methods used were developed in work undertaken within ACARP. The analysis scheme used was according to AS 1038.10.0 – Coal and coke – analysis and testing, Part 10.0: Determination of trace elements – Guide to the determination of trace elements (2002). The exceptions were iodine, bromine and fluorine for which CSIRO methods were used.

The methods are based on modern instrumental techniques including inductively coupled plasma mass spectrometry, inductively coupled plasma atomic

emission spectrometry, hydride generation and cold vapour atomic fluorescence spectrometry, X-ray fluorescence spectrometry and proton induced gamma emission. All are capable of accurately determining the concentrations of the trace elements at the levels normally present in thermal coal products.

All chemical analyses included quality control and assurance procedures using certified reference materials obtained from the National Institute for Standards and Technology (NIST), USA and the South African Council for Mineral Technology (MINTEK).

## RESULTS AND DISCUSSION

The suite of priority trace elements was selected from the designations introduced by the United States National Research Council (1980) which classified trace elements by level of concern and was based on the potential hazards of these elements to biological systems arising from coal combustion. Amendments to the US Clean Air Act designated a number of trace elements as hazardous air pollutants associated with the operation of industrial plant which included coal-fired power plants. The National Pollutant Inventory (2005) designated a range of trace elements which are of concern as potential emissions to the environment.

Iodine and bromine are of no environmental concern. However since iodine is volatile it reports to the scrubber water in power stations fitted with FGD units. The presence of iodine interferes with the measurement of chemical oxygen demand. This parameter is a measure of the amount of free oxygen in water and impacts on marine life when discharged into natural water systems. Bromine is of no significant concern and is included because of its volatility.

The radioactive elements uranium and thorium have been included because of concerns relating to their redistribution in the environment and the use of waste ash as an additive in construction materials.

The presence of trace elements in coal does not imply a health risk. Rather it takes into account the potential for these elements to impact on the environment through their distribution in the waste products from combustion.

The concentrations of the trace elements of environmental concern in the Australian export and international coals are given in Table 1. Also included is the data for Indonesian and Chinese coals which has been extracted from the international coals database. Table 1 gives the average values and ranges. For the Australian coals typical values are also provided. These are the median values. The column headed “n” indicates the number of coals sampled for each element.

### TRACE ELEMENTS OF MAJOR CONCERN

As is evident from Table 1 the most significant difference between the Australian and international coals was in the levels of arsenic, selenium, mercury and boron. **Australian coals contained substantially lower concentrations (up to 35 percent of the levels in the international coals) of these elements which are of major environmental concern.** These elements are volatile and therefore may be released to the atmosphere through gaseous emissions and in stack particulates (Clarke, 1993). The comparison of the average concentrations of these elements in Australian coals, relative to the average concentrations of the international coals, is shown in Figure 1.

For the Indonesian coals the average value for arsenic was high and similar to the international coals. Significantly higher levels of boron and mercury were present in both the Indonesian and Chinese coals. The average value for selenium in Chinese coals was similar to the international coals.

In a survey of the levels of trace elements in 137 Chinese coals from the main coal fields (Deyi Ren *et al.*, 1999) the average values for arsenic, selenium, mercury, lead and molybdenum were substantially higher than Australian coals. The levels of chromium, copper, fluorine, antimony, zinc, vanadium, uranium and thorium were also significantly higher.

A number of international coals had relatively high levels of arsenic. These were coals from USA (up to 25 mg/kg), Colombia (5mg/kg), Poland (5mg/kg) and a number of coals from Indonesia (up to 5mg/kg). Some Indonesian and Chinese coals had

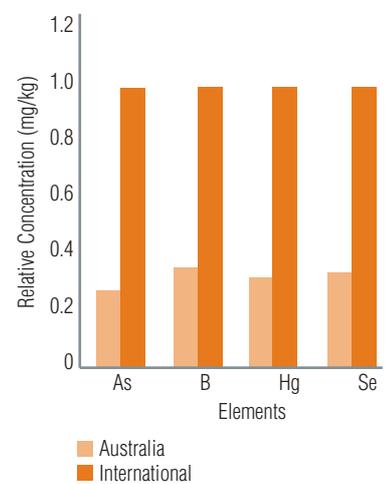
relatively high boron contents in the range 100-150mg/kg. Relatively high levels of mercury (>0.1 mg/kg) were present in some USA, Indonesian and South African coals. Some coals from USA, Indonesia, China and Colombia contained selenium at levels of around 5mg/kg.

The high levels of individual trace elements in coals from some countries may simply be as a consequence of factors affecting the depositional environment. Fortunately, in Australia, the depositional environment has been relatively benign.

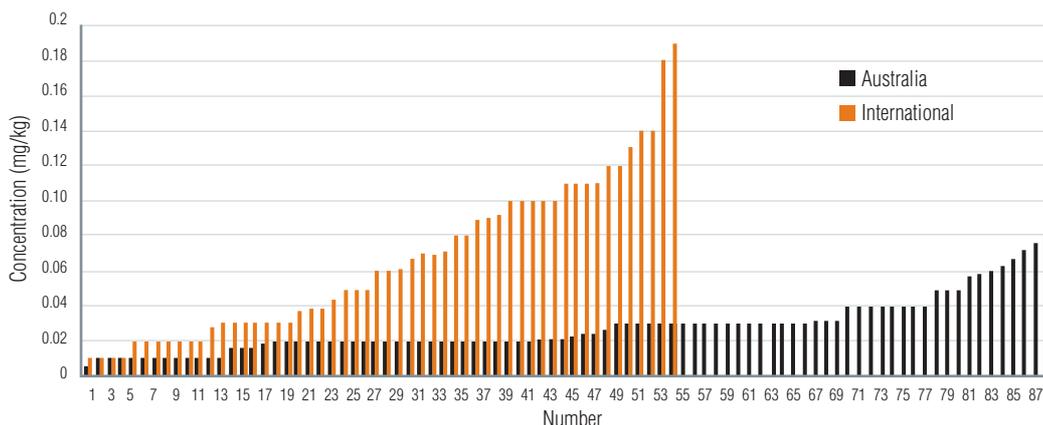
The levels of other elements of major concern were generally similar.

Selenium and boron are of particular concern to Japanese utilities because these elements are volatile during combustion and report to the discharge streams of FGD units. Water and soil regulations imposed by the Japan Ministry of the Environment place limits on the discharge of trace elements from wet FGD units for a number of trace elements including arsenic, boron, cadmium, chromium, mercury, fluorine, copper, lead, selenium and zinc. Limits are also imposed on the leaching of trace elements from fly ash and include arsenic, cadmium, lead, chromium, mercury and selenium. These limits apply to both the leaching of landfill and water at landfill sites.

**Australian coals had narrower range values than international coals for elements of major concern.** This is demonstrated in Figure 2 which shows the individual values for mercury in the Australian and international coals.



**Figure 1:** Comparison of the relative levels of arsenic, boron, mercury and selenium in Australian and international coals.



**Figure 2:** Distribution of mercury in Australian and international thermal coals.

## RESULTS AND DISCUSSION CONT.

### OTHER TRACE ELEMENTS

The levels of elements of less environmental concern in Australian and international coals were generally similar. Their potential impact would depend on the nature and characteristics of the waste products generated during combustion.

### RADIOACTIVE ELEMENTS

The levels of uranium and thorium in Australian and international coals were similar and are considered to be of no environmental concern. **The total radioactivity arising from the natural decay of these elements was very low compared to the Earth's crustal abundance and common garden soil** (Dale, 2003). This is shown in Table 2.

**Table 2:** Total Radioactivity (Bq/kg) of Australian and International Coals

Australia	370
International	440
Earth's crust	1430
Common garden soil	1480

1 Bq = 1 disintegration per second

**Table 3:** Average Total Radioactivity (Bq/kg) of Coal and Ash Products from Power Stations

Coal	400
Coal ash (laboratory prepared)	1530
Fly ash	1680
Bottom ash	1410

Previous CSIRO research on trace element mass balances on New South Wales and Queensland power stations has shown that **the radioactivity of waste ash is similar to that of the Earth's crust**. This is shown in Table 3.

There was no significant difference between the radioactivity of the ashes, the Earth's crustal abundance (1430 Bq/kg) and garden soil (1480 Bq/kg).

### LEACHING OF TRACE ELEMENTS FROM COAL STOCKPILES

There has been some concern about the potential for trace elements to be leached from coal stockpiles. Research undertaken in ACARP (Riley, 2003) demonstrated that **the levels of environmental trace elements in waste water from three coal ports in New South Wales and Queensland were considerably lower than water quality guidelines for irrigation water set by ANZECC (1992) and the National Effluent Standards of the Japan Ministry of the Environment (2001)**. This is shown in Table 4 where the ranges of levels leached are compared with the guidelines.

Selenium was the only element of environmental concern that approached the ANZECC guideline value.

**Table 4:** Concentrations ( $\mu\text{g/L}$ ) of Trace Elements Leached from Coal Stockpiles

ELEMENT	RANGE	IRRIGATION*	EFFLUENT*
As	2-8	100	100
B	80-320	6000	10000
Be	<0.1	100	
Cd	<0.1	10	100
Co	0.3-3	50	
Cr	<0.1-0.6	1000	500
Cu	<0.1-0.6	200	
F	0.2-1.2	1000	8000
Hg	<0.01	2	5
Mn	0.1-74	2000	
Mo	3-39	10	
Ni	1-21	200	
Pb	<0.1-0.6	200	100
Sb	<0.1-2.4		
Se	0.2-11.8	20	100
Th	<0.1		
U	0.7-11	10	
V	<0.1-3.6	100	
Zn	<2-59	2000	

\* ANZECC •Japan Ministry of the Environment

**This study has shown that Australian export coals contain significantly lower levels of trace elements of major environmental concern compared to coals produced by major international competitors.**

Specifically the average values of the key environmental elements arsenic, selenium, mercury and boron were substantially lower in the Australian coals studied than most of the international coals. Some international coals contained relatively high levels of arsenic and selenium and, to a lesser extent, boron. These elements are volatile and contribute to air emissions.

The radioactivity of all coals was similar due to the low

levels of uranium and thorium. The radioactivity of waste ash was similar to the levels in the Earth's crust and common garden soil.

**The leaching of trace elements from coal stockpiles was very low and substantially less than water quality guidelines.**

This study on power station feedstocks is the most comprehensive compilation of the levels of trace elements of environmental concern in Australian export coals and internationally traded coals available. Continual upgrading of the database ensures up-to-date information on the characterisation of internationally traded thermal coals.

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### ACKNOWLEDGEMENT

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**Table 1:** Trace Elements (mg/kg) in Australian and International Thermal Coals

Element	Australian Export					International				Indonesian				Chinese			
	Average	Typical	Low	High	n	Average	Low	High	n	Average	Low	High	n	Average	Low	High	n
As	0.93	0.86	0.1	2.7	89	3.4	0.32	26	63	2.9	0.43	13	27	1.4	0.32	4.1	10
H	21	17	4	36	77	62	6	143	63	87	12	146	27	83	25	95	10
Be	0.82	0.6	0.2	2.1	52	0.91	0.1	3.2	36	0.53	0.09	1.8	27	1.2	0.6	2.1	10
Br	5	5	2	17	33	6	2	38	35	3	2	7	27	17	2	38	10
Cd	0.09	0.07	0.01	0.28	89	0.08	0.01	0.19	63	0.05	0.02	0.19	27	0.06	0.01	0.15	10
Cl	320	240	10	1500	57	330	10	1470	63	130	50	480	27	280	50	670	10
Co	3.7	3.0	1.2	12	44	5.0	1	13	63	4.0	1	9	27	5.0	1	13	10
Cr	9	7	2.9	24	77	12	2	34	63	7	2	22	27	7	3	13	10
Cu	14	13	6.2	32	77	10	1	28	63	7	2	19	27	8	4	12	10
F	98	85	35	340	57	95	15	305	63	63	11	340	27	100	35	155	10
Hg	0.021	0.021	0.006	0.08	88	0.065	0.01	0.19	63	0.050	0.01	0.18	27	0.065	0.01	0.19	10
I	6	4	2	14	28	3	2	7	63	3	2	7	27	3	2	6	10
Mn	99	42	4	700	62	45	8	123	63	28	13	57	27	70	17	123	10
Mo	0.85	0.66	0.1	2.7	77	1.1	0.07	4.2	63	0.58	0.06	1.7	27	0.95	0.20	2.3	10
Ni	8.6	7.5	1.4	31	77	10	1	22	63	8	3	21	27	7	2	14	10
Pb	5.8	5.6	2.2	14	92	7.0	0.5	22	63	0.6	0.5	18	27	11	4	22	10
S(%)	0.60	0.465	0.21	0.95	42	0.67	0.12	3.0	63	0.58	0.11	1.1	27	0.51	0.30	0.95	10
Sb	0.46	0.40	0.05	1.2	72	0.36	0.02	1.4	63	0.13	0.01	0.35	27	0.36	0.16	0.67	10
Se	0.47	0.42	0.12	1.1	90	1.4	0.1	5.3	63	0.52	0.09	3.8	27	1.5	0.17	4.4	10
Th	2.6	2.4	0.5	6.9	76	3.0	0.1	12.2	63	1.3	0.10	2.0	27	4.7	0.88	12	10
U	0.93	0.82	0.27	2.5	76	1.3	0.02	5.5	63	0.68	0.04	9	27	2.1	0.36	5.5	10
V	23	22	7	62	77	21	1.5	54	63	17	2	60	27	14	4	55	10
Zn	14	11	4	51	77	12	4	55	63	9	5	17	27	14	4	55	10

From the results obtained on the certified reference materials a variation of approximately 10 percent relative from the reference value is typical for most trace element measurements. When comparing the concentrations of elements in Table 1, variations of less than 10 percent are therefore not considered to be significant.

**Table 5:** Designations of Trace Elements of Environmental Concern

