
Trace element emissions from coal

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Abstract

Trace elements are emitted during coal combustion. The quantity, in general, depends on the physical and chemical properties of the element itself, the concentration of the element in the coal, the combustion conditions and the type of particulate control device used, and its collection efficiency as a function of particle size. Some trace elements become concentrated in certain particle streams following combustion such as bottom ash, fly ash, and flue gas particulate matter, while others do not. Various classification schemes have been developed to describe this partitioning behaviour. These classification schemes generally distinguish between:

- Class 1: elements that are approximately equally concentrated in the fly ash and bottom ash, or show little or no fine particle enrichment, examples include Mn, Be, Co and Cr.
- Class 2: elements that are enriched in the fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size, examples include As, Cd, Pb and Sb.
- Class 3: elements which are emitted in the gas phase (primarily Hg (not discussed in this review), and in some cases, Se).

Control of class 1 trace elements is directly related to control of total particulate matter emissions, while control of the class 2 elements depends on collection of fine particulates. Due to the variability in particulate control device efficiencies, emission rates of these elements can vary substantially. The volatility of class 3 elements means that particulate controls have only a limited impact on the emissions of these elements.

Acronyms and abbreviations

AAS	atomic absorption spectrometry
APF	advance particle filtration
APIS	Air Pollution Information System (UK)
B/A	basic to acidic (ratio)
BAT	best available technology
CAAA	Clean Air Act Amendments (USA)
CAMR	Clean Air Mercury Rule (USA)
CCA	chromated copper arsenate
CCME	Canadian Council of Ministers for the Environment (Canada)
CCSD	Centre for Coal in Sustainable Development (Australia)
CCSEM	computer controlled scanning electron microscopy
CEM	continuous emission monitoring
CEN	Comité Européen de Normalisation (European Committee for Standardisation)
CRMs	certified reference materials
CSIRO	Commonwealth Scientific and Industrial Research Organisation (Australia)
CTB	Coal Trading Blog
EC	Elemental Coal Analyser
ECN	Energy Research Centre of the Netherlands
EDF	Électricité de France
EEl	Edison Electric Institute (USA)
EF	enrichment factor
EGUs	electric utility steam generating units (USA)
EPER	European Pollutant and Emissions Register (EU)
EPRI	Electric Power Research Institute (USA)
ESP	electrostatic precipitator
EU	European Union
FGD	flue gas desulphurisation
HAPs	hazardous air pollutants
HG	hydride generation
HGCU	hot gas cleaning unit
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
ICR	information collection request (USA)
IGCC	integrated gasification combined cycle
INAA	instrumental neutron activation analysis
IPPC	Integrated Pollution Prevention and Control (EU)
ISA	International Standards Organisation
KEMA-DAM	KEMA Dust Assessment Methodology (Netherlands)
LA	laser ablation
LCPD	Large Plant Combustion Directive (EU)
LFA	leached fly ash
LOI	loss on ignition
MACT	maximum available control technology (USA)
MAF	moisture-ash-free
MATS	Mercury and Air Toxics Standards (USA)
NRC	National Research Council (NRC)
OMB	Office of Management and Budget (USA)
PISCES	Power Plant Integrated Systems Chemical Emissions Studies
PFA	precipitator fly ash

PFBC	pressurised fluidised bed combustion
PFTNA	pulsed fast thermal neutron analysis
PGNAA	prompt gamma neutron activation analysis
PRB	Powder River Basin (USA)
QA/QC	quality assurance/quality control
RE	relative enrichment factor
REE	rare earth element
S&A	strategy and assessment
SCR	selective catalytic reduction
TRI	Toxics Release Inventory (USA)
TSP	total suspended particulates
UCDAVIS	University California Davis
UNECE	United Nations Economic Commission for Europe
US EPA	US Environmental Protection Agency
WFD	Water Framework Directive (EU)
WHO	World Health Organisation
XAFS	X-ray absorption fine structure
XRD	X-ray diffraction
XRF	X-ray fluorescence

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I Introduction

Combustion of coal is a potential source of several trace elements including heavy metal emissions to the atmosphere. Heavy metals is a general collective term which applies to the group of metals and metalloids with an atomic density greater than 4 g/cm³. Combustion processes are considered the most important sources of heavy metals – particularly power generation, smelting, incineration and the internal combustion engine. It is important that emissions of potentially toxic air pollutants from coal combustion, and biomass when co-fired with coal, are measured and, if necessary, controlled in order to limit any deleterious environmental effects. Increasing concern about the effects of trace pollutants in the environment has led to the introduction of emission standards for some of these elements. If standards are adopted they should be supported by commercially-available equipment, which can measure and monitor the emissions with accuracy in order to ensure compliance whilst using appropriate emission controls.

Various estimates have been published, which attempt to evaluate coal combustion as a source of potential air toxic emissions. Data indicate the importance of coal as a source of some trace elements on a global scale (Sloss and Smith, 2000). Global and regional budgets are difficult to estimate. There are two major approaches to determining emissions: estimation (based on emission factors) and measurement (based on actual monitoring of emissions at the source). An emission factor is a value which can be used to estimate emissions from a specific fuel and a specific source. Emission factors can be used to estimate emissions when direct monitoring is not possible. However, there are situations where emission factors are regarded as superior to direct emission measurements (Sloss, 2011). Emission factors are commonly based on a relatively small amount of actual measured data. The wide variation in the composition of coals, combustion conditions, and pollution control equipment must be taken into account when estimating emission factors. Furthermore, many of the techniques used for the measurement of emissions of trace elements, and thus for the estimation of emission factors, are under development and are known to have serious limitations.

A wide range of analytical techniques is available for trace element analysis. Some are destructive and require ashing and dissolution of the coal sample, while others allow nondestructive analysis. Some need standard reference materials that permit quantification of the data. The choice of the most suitable technique for an individual element may be relatively clear cut or there may be several apparently suitable techniques from which to choose. It is important that any technique used should have sufficient sensitivity to provide reliable data at the levels normally found in coals.

Trace elements are emitted during coal combustion in quantities which depend on:

- the physical and chemical properties of the element itself;
- the concentration of the element in the coal;
- the combustion conditions;
- the type of particulate control device used, and its collection efficiency as a function of particle size.

Some trace elements become concentrated in certain particle streams following combustion (for example: bottom ash, fly ash, and flue gas particulate matter) while others do not. Various classification schemes have been developed to describe this partitioning behaviour. These classification schemes generally distinguish between:

- **Class 1:** elements that are approximately equally concentrated in the fly ash and bottom ash, or show little or no small particle enrichment. Examples include manganese, beryllium, cobalt, and chromium.
- **Class 2:** elements that are enriched in the fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size. Examples include arsenic, cadmium, lead, and antimony.

- **Class 3:** elements which are emitted in the gas phase (primarily mercury (not discussed in this review) and, in some cases, selenium).

Mercury legislation, measurement, monitoring, emission and control have been reviewed in detail in several IEA Clean Coal Centre publications and hence are not included in this report (*see* Sloss, 2011, 2012). Visit www.iea.coal.org for more information.

Control of class 1 elements is directly related to control of total particulate matter emissions, while control of the class 2 elements depends on collection of fine particulates. Due to the variability in particulate control device efficiencies, emission rates of these elements can vary substantially. The volatility of class 3 elements means that particulate controls have only a limited impact on emissions of these elements.

In this report, occurrence of trace elements other than mercury in coal and biomass are discussed in Chapter 2. Measuring and legislation of such elements is presented in Chapter 3. In Chapter 4, the fate of these elements and their emission to air, water and soil is the topic under consideration while control techniques used to reduce emissions are discussed in Chapter 5.

2 Trace elements in coal and biomass

Coal, as the most abundant fossil fuel, accounts for ~40% of the electricity produced throughout the world. Coal-fired power plants release to the environment SO₂ and NO_x, as well as CO₂ and N₂O, particulate matter, mercury (Hg) and other trace element pollutants such as cadmium (Cd), arsenic (As), molybdenum (Mo), vanadium (V) and various acid gases. A recent trend in cofiring biomass in coal-fired power plants, which is expected to increase, also results in specific emissions to air. However, the cofiring of biomass with coal in utility power stations is considered a means of reducing air pollutant emissions, such as SO₂ and NO_x, as well as CO₂. In this chapter, trace elements in coal and biomass are discussed. Trace element emissions from coal combustion were the subject of a detailed review by Sloss and Smith (2000). For a compilation of emission factors and emission estimation techniques in coal combustion see US EPA (1995) and Environment Australia (1999).

According to Schweinfurth (2009, 2003), in an introduction to coal quality, coal may contain as many as 76 of the 90 naturally-occurring elements of the periodic table (*see* Figure 1). However, most of those elements are usually present in only trace amounts (in the order of parts per million, ppm). Some elements have the potential to be hazardous, such as Hg, Cd or Se, particularly if they are concentrated in more than trace amounts. Other trace elements may be concentrated in a specific coal bed, which may make the bed a valuable resource for elements such as silver (Ag), zinc (Zn) or germanium (Ge). Although as many as 120 different minerals have been identified in coal, only about 33 of those are commonly found in coal, and of these only about eight are abundant enough to be considered major constituents (*see* Table 1). The affinities of trace elements for either the organic compounds or the minerals in coal affect its quality. If trace elements are organically bound, then it is difficult to remove them from the coal by cleaning processes such as crushing and washing, which can remove mineral matter from coal before firing it. Organically-bound trace elements may be released only by burning or by deep chemical leaching, which is both very difficult and uneconomic according to Schweinfurth (2009). In contrast, trace elements associated with clays or pyrite may be removed to some extent from the coal by cleaning processes.

Schweinfurth (2009) concluded that although much is known about coal quality, much also remains to be understood. Therefore, research on coal quality continues both in the public and private sectors. Concerns about human health, the environment and energy demand and the supply of certain raw materials have broadened the concept of coal quality and have increased the need to know much more about its origins, nature and effects. Recent advances in analytical capabilities have made it easier to improve understanding of the complexities of coal quality. Schweinfurth (2009) considers that an extensive evaluation of coal quality must be central to its use, whatever that may be. Additional sophisticated multi-disciplinary research on coal quality remains a requirement for the future in order to benefit from the fuel whilst avoiding any detrimental effects that may result from its use. Expert systems can be used to assess coal quality and to understand and manage the effects of its variations. These include computer programs which can be used to assess the practical impact of changes in coal composition. The input to these programs can be based on empirical results and/or on modelling various aspects of the process. The challenge is always to validate the outcomes. The use of expert systems for assessing coal quality and its implications for power generation are discussed in detail by Nalbandian (2011).

According to Zevenhoven and Kilpinen (2001), the term ‘trace elements’ refers to chemical elements present in a natural material at concentrations <0.1% wt, besides the minor elements (0.1–1% wt) and the major elements (>1% wt). For coal, the ash forming elements, that is silicon (Si), aluminium (Al), iron (Fe), calcium (Ca), magnesium (Mg) and sometimes also the alkali elements, sodium (Na) and potassium (K), form the most important major elements. Trace elements cover roughly the whole periodic table of the elements after Ca (*see* Figure 1), although the elements beryllium (Be) and boron (B) should be included as well. The most important trace elements considered by Zevenhoven and



Figure 1 Periodic table of elements

Table 1 Common minerals found in coal and their elemental compositions (Schweinfurth, 2009)

Mineral name	Composition	Remarks
<i>Major constituents</i>		
Quartz	SiO ₂	–
Clay minerals: Kaolinite Illite-smectite	Al ₂ Si ₂ O ₅ (OH) ₄ Al, Si, K, Mg and Fe	–
Pyrite/marcasite	FeS ₂	May contain As, Cd, Co, Hg, Ni, Sb and Se
Calcite	CaCO ₃	–
<i>Minor constituents</i>		
Analcime	NaAlSi ₂ O ₆ ·H ₂ O	–
Apatite	Ca ₅ (PO ₄) ₃ (OH,F,Cl)	–
Barite	BaSO ₄	–
Chalcopyrite	CuFeS ₂	–
Clausthalite	PbSe	–
Crandallite group: Crandallite Florencite Gorceixite Goyazite	CaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O CeAl ₃ (PO ₄) ₂ (OH) ₆ BaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O SrAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O	–
Dolomite	CaMg(CO ₃) ₂	–
Feldspars	(Ca,K,Na)AlSi ₃ O ₈	–
Galena	PbS	–
Gypsum	CaSO ₄ ·2H ₂ O	–
Halite	NaCl	–
Marcasite	FeS ₂	May contain As, Cd, Co, Hg, Ni, Sb and Se
Monazite	(Ce,La,Y,Th,Nd)PO ₄	–
Rutile/anatase	TiO ₂	–
Siderite	FeCO ₃	May contain Mn.
Sphalerite	ZnS	May contain Cd
Xenotime	YPO ₄	–
Zircon	Zr(SiO ₄)	–
<i>Trace constituents</i>		
Chromite	FeCr ₂ O ₄	–
Gibbsite	Al(OH) ₃	–
Gold	Au	–
Magnetite	Fe ₃ O ₄	–
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	–
Although more than 120 different minerals have been identified in coal samples, only about 33 of these occur in most coal samples, of these only about eight are generally abundant enough to be considered as major constituents		

Kilpinen (2001) are marked by * in Figure 1. In addition, halogen compounds fluorine (F), chlorine (Cl) and bromine (Br) are often present in natural material as minor or trace elements. A sub-class of the trace elements are the ‘heavy metals’, with a density higher than 4000 kg/m³, such as cadmium (Cd), lead (Pb), mercury (Hg), zinc (Zn) and copper (Cu). Within the European community the thirteen elements of highest concern are arsenic (As), cadmium, cobalt (Co), chromium (Cr), copper, mercury, manganese (Mn), nickel (Ni), lead, antimony (Sb), tin (Sn), thallium (Tl) and vanadium (V). Emissions of these elements are regulated for waste incinerators and cement plants. For biomass, for example straw, the alkali metals Na and K are indicated with # in Figure 1. Zevenhoven and Kilpinen (2001) discuss in detail emission standards for trace elements and alkali metals as well as fuels, flue gases and control of such emissions.

The health impacts of trace elements in coal on human health and the environment is mentioned but not discussed in detail in this review. However, Finkelman and others (2006) and Finkelman (1999) discuss trace elements in coal and their environmental and health significance and impacts, and whether or not these should be of concern. Nelson (2007a) also discusses trace element emissions in fine particles from coal combustion and their health impacts.

2.1 Coal

Coal is a heterogeneous material of organic and mineral fractions. It contains a wide range of trace elements. The modes of occurrence of trace elements in coal are influenced by their depositional environment and the geologic processes prevailing during the formation of the coal beds. During coal combustion trace elements are released from their host environment and the more volatile elements such as Hg, Se and, to a lesser extent, As, enter the gas phase. Some elements may remain in the gas phase and be emitted to the atmosphere and others may recombine with the ash particles. The major issues relating to environmental impact of trace elements are their release to air and water. The partitioning of trace elements among the waste products has a major influence on the potential impact on the environment.

In a study by Xu and others (2003), elements present in coal are divided into three groups:

- 1 Major elements: carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S). These occur at >1000 ppm;
- 2 Minor elements: coal mineral matter: silicon (Si), aluminium (Al), calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), iron (Fe), manganese (Mn), titanium (Ti). These may be present in concentrations between 100 and 1000 ppm;
- 3 Trace elements which are the constituents with concentrations <100 ppm. These differ from one coal to another due to varying coalification processes but identifying them allows the prediction of their release following combustion. Table 2 shows the mean values of 38 trace element contents from 1500 samples from the USA, UK and Australian coals. Xu and others (2003) considered that although the trace element content seems to vary strongly with the coal type, four main groups of content level can be drawn showing that most trace elements are below concentrations of 50 ppm.

In 1992, the US Environmental Protection Agency (EPA) established the Center for Air Toxic Metals (CATM) at the University of North Dakota Energy & Environmental Research Center (EERC) to focus national research efforts on trace element emissions. Subsequently, the US EPA released a study on hazardous air pollutant emissions from electric utility steam generating units – final Report to Congress in 1998 (US EPA, 1998). According to the Coal Trading Blog (CTB, 2011), the US National Research Council (NRC), carried out a classification of trace elements which are of concern in coal in a study on ‘trace-element geochemistry of coal resource development related to environmental quality and health’. These were classified by level of concern based on known adverse health effects or because of their abundances in coal. In 2012, the US EPA published a final rule for national emission standards for hazardous air pollutants (HAPs) from coal-fired electric utility steam generating units and standards of performance for fossil fuel fired electric utility steam generating units. The final rule

Table 2 Concentrations of trace elements in 1500 bituminous and subbituminous coal samples from the US, UK and Australia. Data are based on numerous studies (arithmetic mean values, ppm) (Xu and others, 2003)

Element and chemical symbol	US coal	UK coal	Australian coal	For most coals	Element and chemical symbol	US coal	UK coal	Australian coal	For most coals
>50 ppm									
Barium (Ba)	150	70–300	70–300	20–1000	Antimony (Sb)	1.1–1.3	0.5–3.1	0.5	0.05–10
Boron (B)	50–102	30–60	30–60	5–400	Beryllium (Br)	1.6–2.0	1.5–1.8	1.5	0.1–15
Fluorine (F)	61–74	114–150	150	20–500	Cadmium (Cd)	1.3–2.5	0.08–0.4	0.08	0.1–3.0
Manganese (Mn)	49–100	84–130	130	5–300	Caesium (Cs)	–	1.3	1.3	0.3–5.0
Phosphorous (P)	71	–	–	10–3000	Cobalt (Co)	7–9.6	4.0	4.0	0.5–30
Strontium (Sr)	37–100	100	100	15–500	Gallium (Ga)	3.1	4.0	4.0	1.0–20
Titanium (Ti)	700–800	63–900	900	10–2000	Germanium (Ge)	6.6	5.1–6.8	6.0	0.5–50
Zinc (Zn)	39–272	25	25	5–300	Iodine (I)	2.0	–	–	–
10–50 ppm									
Arsenic (As)	14–15	1.5–18	1.5	0.5–80	Lanthanum (La)	6.9	16	16.0	–
Cerium (Ce)	11	–	–	–	Molybdenum (Mo)	3.0–7.5	1.5–<2.0	1.5	0.1–10
Bromine (Br)	15	–	–	–	Niobium (Nb)	3.0	–	–	1.0–20
Chlorine (Cl)	–	150	150	50–200	Scandium (Sc)	2.4–3.0	4.0	4.0	1.0–10
Chromium (Cr)	14–15	6–34	6.0	0.5–60	Selenium (Se)	2.1–4.1	0.8–2.8	0.8	0.2–4.0
Copper (Cu)	15–19	15–48	15	0.5–50	Thallium (Tl)	–	–	–	<0.2–1.0
Lead (Pb)	16–35	10–48	10	2–80	Thorium (Th)	2.0	2.7–3.9	2.7	0.5–10
Lithium (Li)	20	20	20	1–80	Uranium (U)	1.6–1.8	1.3–2.0	2.0	0.5–10
<1 ppm									
Nickel (Ni)	15–21	15–28	15	0.5–50	Mercury (Hg)	0.18–2.0	0.1–0.2	0.1	0.02–1.0
Rubidium (Rb)	14	–	–	2–50	Silver (Ag)	0.2	<0.1	<0.1	0.02–2.0
Vanadium (V)	20–33	20–76	20	2–100	Tantalum (Ta)	0.15	–	–	–
Zirconium (Zr)	30–72	100	100	5–200					

included a section on the health effects of HAPs from coal-fired electric utility generating units. The NRC classifications were as follows (CTB, 2011):

Major concern: *arsenic (As), boron (B), cadmium (Cd), lead (Pb), mercury (Hg), molybdenum (Mo) and selenium (Se).*

Arsenic, cadmium, lead and mercury are highly toxic to most biological systems at concentrations above critical levels. Selenium is an essential element but is also toxic above certain levels. High levels of molybdenum and boron in plants are of concern. Molybdenum affects the lactation of cows and boron is phytotoxic. Phytotoxicity is a term used to describe the degree of toxic effect by a compound on plant growth.

Moderate concern: *chromium (Cr), vanadium (V), copper (Cu), zinc (Zn), nickel (Ni) and fluorine (F).* These elements are potentially toxic and are present in coal combustion residues at elevated levels. Bio-accumulation is of some concern. Fluorine has an adverse effect on forage.

Minor concern: *barium (Ba), strontium (Sr), sodium (Na), manganese (Mn), cobalt (Co), antimony (Sb), lithium (Li), chlorine (Cl), bromine (Br) and germanium (Ge).*

These elements are of little environmental concern. They were classified mainly on the basis that they are present in residues.

Elements of concern but with negligible concentrations: *beryllium (Br), thallium (Tl), silver (Ag), tellurium (Te).*

These elements have known documented relationships to health but the low levels present are considered to have negligible impact.

Radioactive elements: *uranium (U) and thorium (Th).*

Uranium and thorium are radioactive and the products of their decay are the natural radionuclides present in the environment. Of the naturally-occurring radionuclides, radium (Ra), polonium (Po) and radon (Rn) are of some concern. Radium and polonium are alpha emitters with long half-lives. Radon is a gas with a short half-life and there has been some concern on the build-up of radon in underground coal mines.

Average values for trace elements in international coals are given in Table 3. Trace element distribution in different types of coal and wastes is shown in Table 4. Some trace elements are organically bound in coal and many are associated with the mineral matter. For example, trace elements in US bituminous coal were found mainly in the mineral matter fraction while Hg, As, Ni, Pb, Cu and Zn in Australian coals were predominantly associated with sulphide minerals and organic matter. According to Özbayoglu (2012), the amount of trace elements emission from coal combustion is strongly dependent on the modes of occurrence in the coal. Elements associated mostly with the coal organic and sulphide fractions tend to vaporise and then adsorb on the fine particles when the flue gas temperature drops. On the other hand, elements combined mainly with the other minerals remain in the ash. Özbayoglu (2012) considers that one option for controlling the release and distribution of these trace elements is to remove them prior to combustion. Özbayoglu (2012) discusses coal cleaning as an economic and effective technique in minimising the detrimental effect of trace elements on the environment. According to Zevenhoven and Kilpinen (2001), pre-cleaning (washing) the coal is a widely used method to reduce trace element emission.

A database comparing the levels of trace elements in thermal coals was developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) (Australia) using representative samples of internationally traded coals and a selection of Australian export thermal coals. This database was upgraded by expanding the range of coals and in 2006 included trace element levels for up to 93 Australian export thermal coals, 63 international coals, from the USA (six samples), South Africa (ten samples), Indonesia (27), China (ten samples), Poland (four samples), Colombia (five samples) and Venezuela (one sample) (Dale, 2006).

According to Dale (2006) environmental concern is based on the known toxic responses to high levels of trace elements. The responses to elements of major concern are summarised as follows (Dale, 2006):

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

Table 3 Average values for trace elements in international coals (Creelman, 2002)

Element	Average, mg/kg	Average range, mg/kg
Arsenic (As)	2.69	0.36–9.8
Boron (B)	47	11–123
Beryllium (Be)	1.0	0.1–2.0
Cadmium (Cd)	0.093	0.01–0.19
Cobalt (Co)	4.5	1.2–7.8
Mercury (Hg)	0.091	0.03–0.19
Lead (Pb)	7.0	1.1–22
Selenium (Se)	2.15	0.15–5.0
Chromium (Cr)	17.6	2.9–34
Copper (Cu)	10.8	1.8–20
Manganese (Mn)	40	8–93
Nickel (Ni)	11.1	1.5–21
Zinc (Zn)	12.7	5.1–18
Fluorine (F)	120	15–305
Chlorine (Cl)	440	25–1420

Table 4 Trace element distribution in coal as classified by the US National Research Council (Özbayoglu, 2012)

Affinity	Mineral group	Mineral type	Trace elements
Inorganic	clays, feldspars	kaolinite	Ba, Bi, Cr, Ce, Cu, Ga, Li, Ni, Pb, Sn, Sr, U, V, P, Rb, Th
	iron sulphides	pyrite	As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, Sb, Se, W, Ti, Zn, S
	carbonates	calcite, dolomite, ankerite	Ca, Co, Mn
	sulphates	–	Ba, Ca, Fe, S
	heavy minerals	tourmaline	B
Organic	N, S, Be, B, Ge, V, W (B in partial association with tourmaline in the heavy fraction, V with clays)		

- B-rich soils can limit plant growth resulting in decreased crop yields. Limits have been adopted on the permissible levels of B in wastewater and water for irrigation.
- Cd has no known biological function. It accumulates in the kidneys and liver. It is carcinogenic and can cause emphysema and fibrosis of the lung.
- Cr is also carcinogenic. It accumulates in the liver and spleen. Cr 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.
- F is readily absorbed in the body and concentrates in the same tissues as Ca, especially in bones and teeth. There is some evidence to suggest that F can cause genetic damage and disruption of the immune system. F causes leaf damage to plants.
- Exposure to Hg causes neural and renal damage, and cardiovascular disease. Organo-mercury compounds bio-accumulate, particularly in fish.
- Pastures containing high levels of Mo cause disease in cattle and sheep as well as poor growth and anaemia. The high Mo affects the absorption and metabolism of Cu which is an essential element.
- Pb causes anaemia and has cardiovascular, neurological and gastrointestinal effects. Some compounds are animal and possibly human carcinogens.
- Although Se is an essential element, the safe range is narrow. Elevated levels cause gastrointestinal disturbance, liver and spleen damage, and anaemia.

The coal samples were analysed with methods 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. According to Dale (2006), all methods are capable of determining, accurately, the concentrations of the trace elements at the levels normally present in thermal coal products. The results obtained showed that the most significant difference between the Australian and international coals was in the levels of As, Se, Hg and B, which are of major environmental concern. Australian coals contained significantly lower concentrations (up to 35% of the levels in the international coals) of these elements, which are volatile and therefore may be released to the atmosphere through gaseous emissions and in stack particulate matter. Figure 2 illustrates the average concentrations of these elements in Australian coals, relative to the average concentrations of international coals. The average value for As in Indonesian coals was high as in international coals. Significantly higher concentrations of B and Hg were noted in both the Indonesian and Chinese coals. The average value for Se in Chinese coals was similar to international coals. High levels of As were found in a number of international coals. These were coals from USA (up to 25 mg/kg), Colombia (5 mg/kg), Poland (5 mg/kg) and Indonesia (up to 5 mg/kg). B content was relatively high in some Indonesian and Chinese coals (100–150 mg/kg). Relatively high levels of Hg were present in some US, Indonesian and South African coals (>0.1 mg/kg). Se levels were about 5 mg/kg in some coals from USA, Indonesia, China and Colombia. The levels of other trace elements of major concern were generally similar in all coals. Levels of elements of less environmental concern in all coals were generally similar. So were the levels of U and Th (Dale, 2006). Dai and others (2012) presented the geochemistry of trace elements in Chinese coals in a review of abundances, genetic types, impacts on human health, and industrial utilisation.

2.2 Biomass

According to the Biomass Energy Centre (2012), although the levels of heavy metals in most virgin, untreated wood are extremely low, wood that has been treated with preservatives or coatings may potentially have high levels of heavy metals. The combustion of treated wood, therefore, is regulated under the EU Waste Incineration Directive. Wood used for outdoor applications, for example, might have been treated with chromated copper arsenate (CCA) which, if burned in unsuitable equipment, could allow the emission of As into the atmosphere, as well as Cu and Cr.

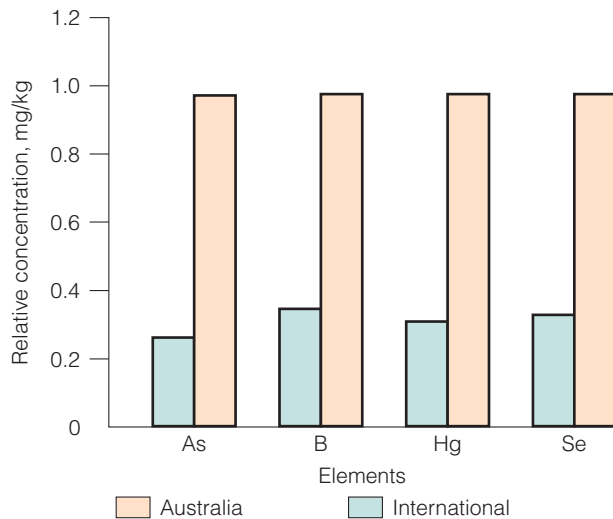


Figure 2 Comparison of the relative levels of As, Bo, Hg and Se in Australian and international coals (Dale, 2006)

CCA has now been replaced with less toxic alternatives within the EU. Significant levels of heavy metals can, exceptionally, build up in some kinds of virgin, untreated timber if it has grown on land in which they are present in high concentrations. This could potentially be on land remediation sites, or where sewage sludge or other effluent has been disposed of in the land (Biomass Energy Centre, 2012).

During coal combustion, trace elements are mobilised and fractionated among bottom ash and slag, heat exchanger deposits, fly ash, and atmospheric emissions. Additional fractionation involves fall-out and mobilisation by leaching from solid waste deposits such as in landfills. For example, a typical coal-fired power plant fly ash can be enriched with Se, I, As, Sb, Br, Zn, Cd, and Pb. The elements Br, Hg, and I are known to be partitioned into the gas phase and released into the atmosphere

through the stack. Studies of coal-fired power plants have mainly centred on understanding the size fractionation of trace elements between fly ash and bottom ash. Fewer studies have attempted to understand trace element partitioning in biomass-fired plants. The result is that little is known about trace elements and other environmentally critical pollutants associated with biomass combustion, although heavy metals, especially Pb and Zn, are known to influence the char reactivity and gasification rate for wood and other biomass waste. Trace metal mobilisation during combustion of biomass fuels was the subject of a detailed study by UCDAVIS (2008).

According to UCDAVIS (2008), the behaviour of the major and trace elements in biomass firing is controlled by the nature and composition of the solid components and by combustion temperature (among other possible factors). It is not possible to predict the trace element behaviour across the large temperature range encountered in biomass boilers from fuel ignition to partial or complete melting of ash and slag without direct experimental observations. It is plausible that elements in trace amounts, such as the halogens (F, I, Br) and alkalis (Be, Rb, Cs, Sr, Ba,) behave in a similar fashion as observed for their major element counterparts (Cl, K). Of particular interest are the trace elements (Cr, Co, Ni, Cu, Zn, Pb, Hg, As, Se, Sb, and Cd), which are toxic to many organisms. UCDAVIS (2008) concluded that:

- most major and trace elements can be analysed in ashes and slag using commonly available multi-element instrumental techniques (such as X-ray fluorescence, instrumental neutron activation analysis and inductively coupled plasma mass spectroscopy);
- trace element concentrations are distinctly dependent on fuel type;
- many major and trace elements are depleted with increasing firing temperature (Cl, Na, K, Rb, Ce, Ag, Cd, As, Se and Pb) due to release with volatile components;
- enrichment for some elements, including Ba, As, Cr and Pb, can cause concentrations in ash to approach, or even exceed, toxicity standards, such as those required by the US federal standards;
- fly ashes from controlled pilot- and full-scale experiments show very strong fractionation such that their trace element concentrations may bear little similarity to those observed in the original fuels;
- significant sources of contamination include plant construction materials, such as steel, and blended urban wood fuels;
- blending with straws poses few problems in terms of trace element abundances, due to their

generally low concentrations in straw ash, although major element effects on slag forming and fouling remain of concern.

According to van Loo and Koppejan (2008), all biomass contains heavy metals to some extent, most importantly Cu, Pb, Cd and Hg. These are either captured in the particulate control device with the particulate matter or emitted to the atmosphere as in coal. Contaminated biomass fuels such as impregnated or painted wood may contain significantly higher levels of heavy metals. The detrimental health impacts of these would be a result of their accumulation in the food chain. Some are toxic and some have carcinogenic effects. Table 5 shows the average concentrations of heavy metals in various ash fractions of bark, wood chips and sawdust incinerators. Concentrations of heavy metals in ash fractions of other types of biomass are discussed by van Loo and Koppejan (2008).

The concentrations of some trace elements can be significantly higher in certain biomass materials than in coal. However, there is no evidence that these elevated levels have led to compliance issues in existing plants that have switched to cofiring. However, as emissions standards worldwide are being tightened, the situation could arise that certain types of biomass have difficulties complying with future legislated limits, especially at high cofiring ratios (Sloss, 2011; Fernando, 2012).

Wood pellets are probably the largest traded solid biomass commodity used for energy production in terms of trade volume. In 2008, about 530 wood pellet plants produced about 8 Mt of pellets in 30 European countries. Imports from North America amounted to over 1 Mt. The market is booming and is expected to continue to do so due to the EU 2020 target for renewable energy. The EU Directive 2009/28/EG (adopted 23 April 2009) sets as its first objective the share of energy from renewable sources in gross final consumption of energy in 2020 at 20%. Sikkema and others (2009) discuss producers, traders and consumers of wood pellets.

Boersma and others (2011) and Kiel and others (2009) reported on their findings on biomass cofiring

Table 5 Average concentrations of heavy metals in various ash fractions of bark, wood chips and sawdust incinerators, mg/kg (dry base) (van Loo and Koppejan, 2008)

Element	Bottom ash		Cyclone fly ash		Filter fly ash	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Cu	164.6	85.6	143.1	46.7	389.2	246.4
Zn	432.5	305.2	1870.4	598.5	12980.7	12195.9
Co	21.0	6.5	19.0	7.3	17.5	5.2
Mo	2.8	0.7	4.2	1.4	13.2	9.8
As	4.1	3.1	6.7	4.3	37.4	41.4
Ni	66.0	13.6	59.6	19.0	63.4	35.4
Cr	325.5	383.0	158.4	61.0	231.3	263.7
Pb	13.6	10.4	57.6	20.5	1053.3	1533.0
Cd	1.2	0.7	21.6	8.1	80.7	59.2
V	43.0	10.0	40.5	16.6	23.6	9.1
Hg	0.01	0.03	0.04	0.05	1.47	2.05

Ten samples were analysed from each ash fraction and each biomass fuel taken from representative test runs performed over 48 h in Austrian grate furnaces and under-feed stokers. Types of biomass used: wood chips and barks from spruce

in high percentages. The fate of trace elements from biomass cofiring is discussed in Chapter 4. The authors concluded that the concentration of trace elements in biomass, although lower than coal in all cases, can be significant when ash content is taken into consideration. Mn and Zn content of most biomass were found comparable with coal.

3 Current and future measurement and legislation for trace elements emission

Trace element emissions from coal combustion have not been an issue of major concern in international or worldwide legislation. The main exception is the USA, which has recently promulgated standards for mercury and other trace elements (*see* Section 3.2). There are a number of international and national agreements that aim to reduce trace element emissions, but very few of these have developed into limits on stack emissions in coal-fired power plants. Some countries have set stack emission limits for certain trace elements from coal combustion sources, but these are generally met with existing air pollution control devices. Emissions legislation, including Hg, and their impact on coal-fired power plants were reviewed by Sloss (2009). Trace element legislation was also reviewed by Sloss and Smith (2000). Challenges in international Hg legislation is discussed in detail by Sloss and others (2011). Therefore, Hg-specific legislation will be not discussed in this review. Zevenhoven and Kilpinen (2001) discuss emission standards for trace elements and alkali metals for waste incinerators and cement plants.

3.1 Measuring, modelling and analysis of trace elements

Sloss (2011) discussed in detail emissions monitoring and reporting from coal-fired plant including trace elements. The Comité Européen de Normalisation (European Committee for Standardisation) CEN 14385 is the European standard for the measurement of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl, and V. The US EPA Method 29 is the comparable multi-element sampling train used in the USA. Emphasis to date has been on the measurement and reporting of emissions of Hg. Currently there is no International Standards Organisation (ISO) or CEN standard specifically for measuring selenium or other trace element emissions from stationary sources. However, a new work item has been opened up on this issue by the ISO in 2011, which would suggest that there is growing interest in trace element emissions, especially selenium.

Mass balance calculations estimating flue gas pollutant emissions is useful for trace elements which may be a challenge to measure at the stack. By determining the amount of the element entering the plant via the coal and then measuring the amount of the element remaining in the fly ashes, the amount emitted may be calculated. The general approach for mass balance estimation is as follows (Sloss, 2011; CCME, 2007):

- annual average of the trace element content in the coal is determined from all coal samples analysed (ppm or g/t) in a year;
- total coal burned in the year is determined from records (t/y);
- annual average trace element emission in coal is multiplied by total coal burn to obtain total input (g/y);
- annual average for the ash trace element content is determined from all ash samples analysed (ppm or g/t) in a year;
- total ash is determined (t/y);
- annual average trace element in ash is determined from the trace element content and the total volume of ash (g/t);
- the total trace element in the ash is subtracted from the total trace element in the coal to obtain estimated emissions from the stack;
- the total trace element in the residue is divided by the total trace element in the coal to obtain the capture rate.

Emission limit values define a set maximum limit on stack emissions of pollutants. Measurement at the stack with a manual or automated device can confirm whether or not this limit value is exceeded. Continuous emission monitoring (CEM) systems are used for some pollutants. However, for more

challenging elements or elements for which CEM systems have not been commercialised, such as most trace elements, manual systems are used. During manual testing, a team of experts perform a one-off series of measurements to get a ‘snapshot’ of the emissions. This is less than optimal with respect to providing assurance that emission limits are not being exceeded at any time over an extended period. However, it is often the case that, on a plant which runs in a set manner, with well quantified performance and fuel characteristics, a minimum number of manual monitoring campaigns demonstrating that the emissions of a regulated pollutant are consistently well below the set emission limit value are considered adequate.

Manual monitoring methods are commonly defined within national and international standards. Most directives, such as the Large Combustion Plant Directive (LCPD) in the European Union (EU), specify a hierarchy of standards that must be used for monitoring emissions. In the EU this is:

CEN standards > ISO standards > National standards

The standards produced by CEN are prepared over an average of seven years through discussion with experts from all interested countries. Once approved and published, CEN standards are required to be used in all EU member states for any relevant monitoring under legislation monitoring regimes. ISO standards are produced in the same way as CEN standards but, once published, are considered more as recommendations or guidance on best practice than actual requirements. The ISO and CEN standards relevant to monitoring emissions from coal-fired plants are given by Sloss (2011).

In 2009, Meij and te Winkel reviewed trace elements in world steam coal and their behaviour in Dutch coal-fired power plants. In 1995, the contribution of coal to electricity production in the Netherlands amounted to 45% of total capacity. In 2006, 8.4 Mt of coal was used for centrally generated electricity. Since 1995, coal has been partially replaced with biomass. In 2006, 13.5% of the total fuel in coal-fired power plants on energy basis was biomass. All coal used for power generation in the Netherlands is imported – mainly from South Africa, Colombia, Indonesia, China, Poland, Australia, Russia, Eastern USA, Norway and Venezuela. Occasionally, coal is also imported from Egypt, New Zealand, Canada, India and Nigeria. The plants in the review utilise dry bottom boilers and are fitted with electrostatic precipitators (ESPs) for particulate control, wet lime(stone)/gypsum FGD systems and selective catalytic reduction (SCR) technology for NO_x reduction. Meij and te Winkel (2009), discuss coal characterisation as well as sampling and analysis techniques undertaken with several of the imported coals. Mass balance calculations were also carried out based on the relative enrichment factor (RE) (*see* Chapter 4) and trace element grouping. According to Meij and te Winkel (2009 and 2007), the behaviour of the elements during combustion of coal only (albeit from various origins) is similar to that during co-combustion. The authors discuss briefly using the KEMA TRACE MODEL[®] to predict the ash composition and the trace element emissions to air.

Boersma and others (2011) discussed the use of thermodynamic modelling and laboratory-scale measurement of trace elements in biomass cofiring. The objective of thermodynamic equilibrium calculations, carried out with the FactSage[™] software, was to predict the speciation of trace elements in the fly ash and to identify underlying mechanisms for biomass cofiring in conventional, ultra-supercritical and oxy-fuel boilers. According to Boersma and others (2011), this equilibrium approach is used often despite the fact that thermodynamic equilibrium is not likely to be reached due to the short residence times under investigation (1–4 s). However, an estimate is thus provided which gives an insight on the processes of the formation of trace element compounds. Calculations were performed with wood biomass and speciation were calculated for Ba, Cr, Mn, Co, Cu, Ni, Sb, Cd, Pb, Zn, Hg, Se, Te as well as sulphates. Figure 3 is an example of the calculated Cr speciation for different levels of cofiring in a conventional boiler. Boersma and others (2011) explain that the figure shows that the flux of all the selected phases containing Cr, formed in different temperature regimes, decreases when cofiring biomass, primarily because of the much lower Cr content of the biomass compared with typical hard coals. However, the authors noted that the temperature at which higher toxic hexavalent (6⁺) predominate, rather than trivalent (3⁺) Cr forms, shifts towards the lower end of the scale.

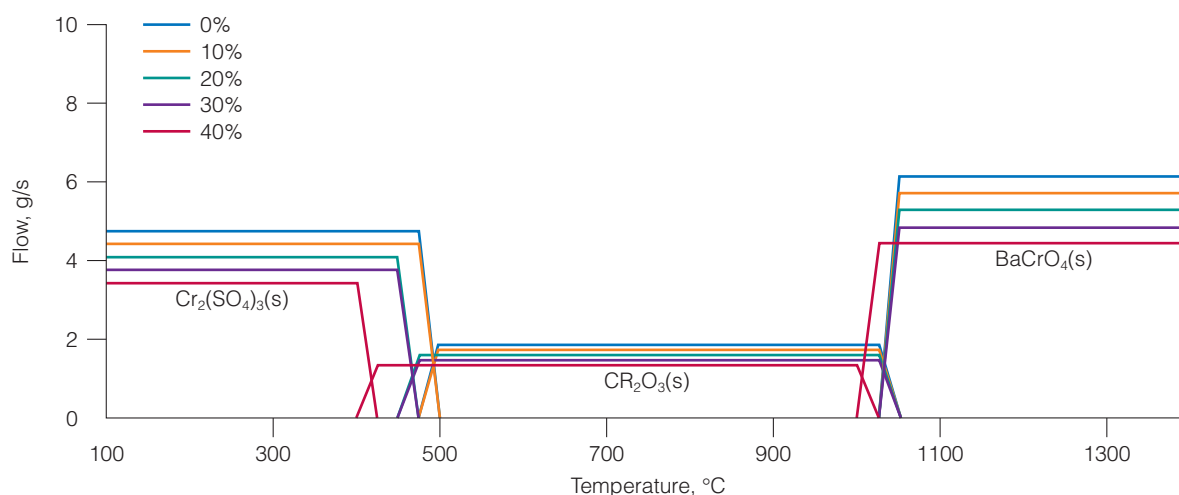


Figure 3 Result of thermodynamic equilibrium calculations: Cr speciation for 0–40% wood cofiring in conventional boilers (Boersma and others, 2011)

Based on the thermodynamic equilibrium calculations, Boersma and others (2011) concluded that speciation depends mainly on:

- the furnace exit gas temperature in ultra-supercritical boilers;
- fuel composition when cofiring biomass;
- recycling of the flue gas in oxy-fuel combustion.

However, they considered that the fuel (blend) composition is the parameter which has, by far, the greatest influence.

A full-scale measuring campaign was undertaken by KEMA Nederland B V and Energy Research Centre of the Netherlands (ECN) at unit 12 of the Borssele power station (BS-12). During the campaign, almost 30% (m/m) of coal was replaced with a mixture of three types of secondary fuel, all residues of vegetation origin corresponding to about 20% cofiring on energy basis (e/e). Sampling at all inlet and outlet stream was undertaken by KEMA whilst ECN carried out fly ash and flue gas measurement at intermediate points, before and after the NO_x control device, a selective catalytic reduction (SCR) system. A second full-scale measuring campaign was undertaken at the E.ON Benelux Maasvlakte 2 (MV2) power plant (Netherlands). In this campaign ~20% (m/m) of coal (corresponding to about 15% cofiring on energy basis (e/e)) was displaced with a mixture of different types of secondary fuel. The procedure followed was comparable to the campaign at Borssele BS-12 boiler. The results are discussed in detail by Eijk and te Winkel (2010) and Kalivodova (2010). As the results involved the air pollution control technologies, these are discussed in Chapter 5.

X-ray absorption fine structure (XAFS) is an analytical, spectroscopic technique capable of detecting the valency of an element and its complexation by bringing in atoms in close vicinity to the studied element. That is, it uses X-rays to probe the physical and chemical structure of matter at an atomic scale. XAFS analysis was undertaken in both campaigns at BS-12 and MV2. In BS-12, the speciation of Cr, V and Zn was determined in the ash, gypsum and sludge of the waste-water treatment plant. In gypsum, the levels were below the detection limits so no results were obtained. It appeared that in the ash, 6% of the Cr was present as Cr(VI), comparable to previous findings with full coal firing. In the sludge, only 1% of the total Cr was present as Cr(VI). The predominant form of V found had a valence of five (V) both in the ash and sludge. Results for Zn were less clear. In MV2, the speciation of Cr, V, Zn, As and Se was determined in the bottom ash, fly ash (ESP) and fly ash (before the SCR system). Results obtained for As indicate that >90% is present as As(V) in arsenate complexes.

Results showed that the only significant Se species present was Se(IV) in selenite complexes. The results for Cr show that it is mainly present as Cr³⁺ in aluminosilicate glass. For Zn, the results indicated that much of it was present in four-fold coordination by oxygen. Laboratory-scale experiments and pH-static extraction were also undertaken in the project (Boersma and others, (2011). Huggins and others (1999) studied the direct speciation of chromium in coal combustion by-products by X-ray absorption fine structure.

Samuilov and others (2010) discuss the development of a simulation model that combines geochemistry, chemical thermodynamics, phase analysis and chemical kinetics to calculate the distribution of As, Cu, Ni, Be and Sb in the combustion products of coals near Moscow. Martello and others (2008) discuss the apportionment of ambient primary and secondary fine particulate matter at the Pittsburgh National Energy Laboratory particulate matter characterisation site using positive matrix factorisation and a potential source contributions function analysis.

In recent years, online analysers have been used in coal-fired power plant for elemental analysis (*see* Nalbandian, 2005). The main technique used to measure elemental composition of the coal is excitation (for example, prompt gamma neutron activation analysis – PGNAA). In PGNAA, a field of neutrons is used to raise the energy levels of the various atoms present. As these return to a stable condition, the different atoms lose energy by emitting gamma-rays of characteristic energy and intensity. These gamma-rays can, with suitable detectors, be used to determine the amount of various elements present in the coal mineral matter and chemically combined in the organic matter. X-ray fluorescence (XRF) is the emission of characteristic ‘secondary’ (or fluorescent) X-rays from a material that has been excited by bombarding it with high-energy X-rays or gamma rays. It is a technique used to determine the elemental composition of a sample, including major, minor and trace elements. Although XRF spectrometry has the potential to be very sensitive in measuring trace elements, it has the disadvantage in that it requires 15–30 minute sample collection and pre-concentration. Elemental analysis based on XRF was the subject of studies by Landsman and Bachmann (2002), Klein and Ritter (2004) and Andrés and others (2004). Most samples of XRF are either pressed to a pellet (disc shaped) or are converted to a homogeneous glass disc (bead) by fusion with lithium tetraborate. The fused bead technique overcomes heterogeneity effects and is generally required for obtaining highest analytical accuracies for minors and majors, in particular for silicon oxide and iron oxide. On the other hand, pressed pellets are more suitable for trace analysis. The pellets are either pressed in undiluted form or are first mixed with a binder. A small dilution still ensures high X-ray intensities as required for trace analysis. Unlike fusion, the volatile elements remain in the prepared specimen, the pressed pellet (van Kroonenberg, 1996):

Analytical methods relating to mineral matter in coal and ash from coal combustion are discussed in detail by Creelman (2002). Elemental online analysis is considerably more difficult to undertake (and/or less accurate) where the coal comes from a number of sources, as is the case in many coal-fired power plants today. The assumptions on which PGNAA analysers rely, that is coal characteristics which can vary considerably in different coals, can cause problems necessitating the development and application of different calibration curves. These assumptions are the bound moisture, the moisture-ash-free (MAF) calorific value and the fraction of the ash not measurable by PGNAA. The pulsed fast thermal neutron analysis (PFTNA) technique is similar to the PGNAA in that a source of neutrons is utilised to excite a target nucleus. The excited nucleus then decays radioactively by the emission of prompt and delayed gamma rays and other radiation such as beta particles. The emitted radiation is characteristic for the particular target nucleus and can be used to identify it. Today, online elemental analysers can be used on conveyor belts and to divert coal with different qualities to different stockpiles for subsequent blending. The instruments can be used to control blending of higher and lower quality coals to produce a feedstock of consistent properties, for example sulphur content. Early elemental analysers relied on PGNAA and they analysed sample streams rather than full process flow. More recently, through- or cross-belt PGNAA analysers have been developed in order to reduce the cost and complexity of installation of these systems. Several cross-belt PGNAA analysers have already been installed in the USA and Australia. The US Thermo Gamma-Metrics Company

developed and has already installed at commercial scale a number of their cross-belt Elemental Coal Analyser (ECA) (Nalbandian, 2005).

QEMSCAN is an automated electron beam image analysis technique, originally developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) (Australia), Division of Minerals and now by the CSIRO spin-off company Intellection Pty Ltd. The technology has been widely applied in the minerals industry. However, according to French and others (2008), its use in the coal and related industries has been limited. QEMSCAN has the potential to provide quantitative mineralogical and textural data for assessing coal behaviour during preparation, combustion in power generation, coking and steel production, gasification and the management and utilisation of coal by-products and residue (French and others, 2008). Liu and others (2005, 2007) studied the capabilities of QEMSCAN to characterise mineral matter in pulverised coal in terms of mineralogy composition, chemistry composition, size, shape, included/excluded association and mineral-mineral association. The authors found that QEMSCAN analysis can be interpreted to predict ash impacts in pulverised coal furnaces by two methods, observation of QEMSCAN images and comparison of coals by statistical means, and prediction after conversion to an equivalent computer controlled scanning electron microscopy (CCSEM) analysis and use of an ash effect predictor. Liu and others (2007) concluded that the QEMSCAN technique and data based mechanistic ash prediction models require further development before the ash impact predictions are fully automated. French and Ward (2009) investigated the use of quantitative XRD and QEMSCAN to evaluate the nature, mode of occurrence, distribution and relative abundance of the different minerals in a range of coal combustion by-products. The authors recommended the two techniques are used in conjunction with each other and with other techniques, such as chemical analysis and electron microprobe investigation. They concluded that further work is required in specific areas, such as relative identification of the clay minerals in coal and better discrimination of glass compositions in coal utilisation products (French and others, 2009).

Traditional measurement of trace elements is based on extractive systems. Typically, this consists of a heated inert extraction probe, with a cyclone and/or filter to remove particulate matter entrained in the flue gas stream and a series of liquid-filled ‘bubblers’ containing a range of oxidising agents designed to trap the trace elements in the solution. Whilst the techniques are reliable, they can suffer from a number of practical limitations. In general, they require significant volumes of flue gas to sample in order to build up concentrations of the elements in the liquid phase and this requires sampling times of the order of one hour. Hence, the method gives poor temporal definition and is effectively suitable only for time average measurements. Preparation of each sampling train is also time consuming and therefore costly. Finally, as the period required to analyse the collected solution is typically of the order of a day or more, such methods are not usable for online, real time measurement and control (Irons and others, 2000).

According to Irons and others (2000) the only methods that appear to be capable of direct trace element measurement in the gas phase involve a spectroscopic approach including:

- mass spectroscopy: conventional mass spectrometers are not considered suitable for online plant use due to size, complexity and cost of equipment. Portable instruments have not been used to measure the elements of interest in coal-firing plant and are likely to be ‘not sufficiently’ sensitive;
- atomic emission spectroscopy: as the atomic vapours of many elements emit light at characteristic wavelengths when heated in a flame, these, theoretically, can be measured (at the relevant wavelengths) in the high temperature zones of a furnace. However, the intensity of the emission is proportional to the fourth power of the absolute temperature and therefore a very accurate measurement of the temperature at the measurement point is required to allow quantitative measurements. Also, the intensity of the atomic emission would be very small and impossible to distinguish from the general background radiation from the flame;
- atomic fluorescence spectroscopy: the atomic vapours of many elements absorb radiation at a particular wavelength to produce excited atoms. A fraction of these excited atoms lose energy

and emit radiation, often at a different wavelength to that of the excitation source. In this process, which is called atomic fluorescence, the fluorescence can be measured by a suitable detector located at right angles to the light source beam. The elements in the case of coal firing fluoresce in the ultraviolet region of the spectrum and so the fluorescence signal is not temperature dependent and can be very sensitive. However, this method is not usable in the furnace section of a combustor as the small fluorescence signal would be swamped by background radiation from the flame. Although it may be possible to use this approach in the cooler sections of a boiler, this would necessitate filtering of the flue gas stream as reflection of light from the particles would add to the detected signal. The technique requires a light source that emits an intense and very narrow spectral peak at the required wavelength. Producing such a narrow peak using a broad band light source and filters or monochromators is not possible. According to Irons and others (2000), hollow cathode lamps that produce light by application of a high voltage between an anode and a cylindrical cathode coated with the element of interest produce the necessary sharp peaks and are commercially available;

- atomic absorption spectroscopy: the atomic vapours of many elements absorb light at characteristic wavelengths for the element. At low levels of absorption, the concentration of elemental vapour is proportional to the amount of light absorbed. The light sources used in atomic absorption spectroscopy are the same as those used in atomic fluorescence. However, where a sufficiently sensitive detector is used, the intensity of the sources need not be so high for atomic absorption. The detector is located so as to receive the light from the source directly and the atomic vapour generated between the source and detector. The atomic vapours of the elements in pulverised coal combustion also absorb in the ultraviolet region of the spectrum. The technique is suitable for use in the cooler sections of a boiler. However, the method is less sensitive to particulate matter in the gas stream than atomic fluorescence;
- laser induced breakdown spectroscopy: in this technique a laser beam is focused at a point in a gas stream where measurements are to be made. Rapid pulsing of the laser generates a high intensity spark which results in the formation of a high temperature plasma at the measurement point. The temperature is sufficient to break down many gaseous and solid species to form an atomic vapour, from which the emissions can be measured with a detector coupled to a spectral analyser. The laser does not require tuning to any particular wavelength as it is only used to generate the spark. The technique also produces strong emissions due to the high temperatures generated. However, in practice, the noise generated in the spark reduces the sensitivity to below the levels required to measure the species of interest at the concentrations likely to be present in the flue gas;
- tunable diode laser absorption spectroscopy: in this technique, the laser wavelength is tuned to the infrared absorption wavelength of the target atoms and molecules and the laser beam passed through the measurement area. By tuning the laser beam wavelength to the desired gas absorption line and by precise measurement of the absorption level of that beam it is possible to determine the concentration of the gas. Resolution of the measurement is generally expressed in ppm.

Atomic absorption spectroscopy is one of the most common types of analyser used for Hg measurement in coal-fired plant as it is well developed, sensitive, relatively inexpensive and can analyse a gas stream directly. Online and conventional methods for trace element measurement in the gas phase are discussed by Irons and others (2000). Atomic spectroscopy is discussed in detail by Bings and others (2004) while plant and environmental monitoring using state-of-the-art laser diagnostics is presented by Deguchi and others (2005) and Duret (2004). The use of flue gas CEM data to determine coal analysis is the subject of a paper by Munukutla and Craven (2004). For detailed reviews on CEM techniques and application visit www.iea-coal.org.

3.2 Legislation

The Dangerous Substances Directive of the European Union (76/464/EEC) defines dangerous

chemicals as those which are toxic, persistent and/or bio-accumulative. As they are elements, they cannot be broken down, therefore trace elements will persist in the environment. They will tend to accumulate in the environment, especially in water (lake, estuarine or marine sediments) and can be transported from one media to another (APIS, 2012). The information in the UK Air Pollution Information System (APIS) is primarily focused on elements which are transported via the atmosphere. According to APIS (2012), whether the source of trace elements is natural or anthropogenic, the concentrations in terrestrial and aquatic organisms are determined by the size of the source and adsorption/precipitation in soils and sediments. The extent of adsorption depends on the element, the absorbent, the physio-chemical characteristics of the environment (for example: pH, water hardness and redox potential) and the concentrations of other elements and complex chemicals present in the soil or water.

Critical levels and loads are tools for assessing the risk of air pollution impacts to ecosystems. The APIS provides critical loads and levels for different pollutants in the UK. Although some critical levels have been developed, there are currently no critical loads for heavy metals. However, researchers have started to develop effects-based critical levels and critical loads for some heavy metals in soils and fresh waters.

Most critical levels derive from the European Union's Dangerous Substances Directive (76/464/EEC), the US EPA for water, the EU Air Quality Framework Directive (96/62/EEC) and the World Health Organization for air. The first Air Quality Daughter Directive sets critical levels for Pb and another in preparation will set limits for Cd, As, Ni and Hg. The general aim of the Air Framework and Daughter Directives is to avoid, prevent and reduce harmful effects of air pollutants on human health and the environment as a whole. The EU sludge to land directive (86/278/EEC) sets critical levels for heavy metals in agricultural soils that receive sewage sludge. Critical levels and loads for heavy metals are expected to be available in Europe in a few years and they should be well-founded, effects-based standards which aim to protect target organisms in terrestrial and freshwater ecosystems. There are four current developments which should lead to the production of critical levels and loads for heavy metals. These include the Dangerous Substances Directive, the proposed European Union Water Framework Directive, the Bad Harzburg Workshop in 1997 (UN ECE Convention on Long-range Transboundary Air Pollution, Task Force on Mapping 1998) and the United Nations Economic Commission for Europe adopted Protocol on Heavy Metals in 1998 (APIS, 2012).

Within Europe, the Integrated Pollution Prevention and Control (IPPC) Directive is applicable to coal-fired power plants with thermal input exceeding 50 MWth. The directive covers 'metals and their compounds' and requires the use of Best Available Technology (BAT) to reduce emissions to air. The Directive also provided for the setting up of the European Pollutant and Emissions Register (EPER), which reports annually on emissions of many species to air, land and aqueous systems. The Large Combustion Plant Directive (LCPD) recognises that many trace elements are associated with dust emissions and sets limits for total dust emissions of $<50 \text{ mg/m}^3$ for plant $\geq 50 \text{ MWth}$. In December 2005 the Commission submitted a report to the European Parliament assessing the amounts of heavy metals emitted by large combustion plant, the cost-effectiveness of further emission reductions for combustion plant and the need for further measures (Nalbandian, 2007; DTI 2004). In general, emission regulation is in accordance with permits and other European Union (EU) directives, such as the EU LCPD, which when firing coal, regulates only the emissions of particulate matter, SO_2 and NO_x . However, when cofiring with a secondary fuel, such as biomass, limits are set for other elements and their release to the environment (air, water and soil (by-products)). Such elements and the media they are released to in the Netherlands (as an example) are shown in Table 6. National limits can be more stringent (Meij and te Winkel, 2009).

On an international level, the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (LRTAP) on Heavy Metals, was implemented on 29 December 2003. The 1998 Aarhus Protocol on Heavy Metals, as it is also known as, was ratified by 31 countries as of 14 May 2012. This protocol targeted three metals; cadmium

Table 6 Varying regulations for trace element emissions and regulated elements in coal (in the Netherlands) (Meij and te Winkel, 2009)

Relevancy		Elements
Emission to air	Permits, LCPD*, WID†	S, N, F, Cl, Hg, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Tl, V.
Emission to surface water	Permits, WID†	As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, Tl.
By-products	Technical aspects Application as building materials Environmental aspects Leaching, EWC‡ Occupational health aspects and radiological aspect TLV§ or PEL¶ values	Al, Si, Fe, Ca, Na, K, P, C, Cl, S (and performance characteristics).S, F, Cl, Ba, Be, Br, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, U, V, Zn.Ca, As, B, Ba, Be, Cd, Co, Cr, Cu, F, Hf, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Te, Tl, Th, U, V, W.
* European Union Large Combustion Plants Directive † European Union Waste Incineration Directive ‡ European Waste Catalogue § Threshold Limit Values ¶ Personal Exposure Limits		

Table 7 The eleven trace elements and their compounds commonly found in coal identified by the US 1990 Clean Air Act Amendments (CAAA) as potentially 'hazardous air pollutants' (HAPs)

Element	Concentration, µg/g	Ranges
Beryllium (Be)	2	0.1–15
Chromium (Cr)	20	0.5–60
Manganese (Mn)	70	5–300
Cobalt (Co)	5	0.5–30
Nickel (Ni)	20	0.5–50
Arsenic (As)	10	0.5–80
Selenium (Se)	1	0.2–10
Cadmium (Cd)	0.5	0.1–3
Antimony (Sb)	1	0.05–10
Mercury (Hg)	0.1	0.02–1
Lead (Pb)	40	2–80

(Cd), lead (Pb) and mercury (Hg) and committed parties to reduce emissions below 1990 levels through the application of BAT to fossil-fuel, stationary industrial sources, combustion processes and waste incineration.

In the USA, the Clean Air Act Amendments (CAAA) of 1990 identified eleven trace elements and their compounds commonly found in coal as potentially 'hazardous air pollutants' (HAPs). These elements are listed Table 7. Potential ppm in coal of some trace elements are listed in the 1990 CAAA as As 24, Be 2.2, Cd 0.5, Cl 600, Co 6, Cr 15, F 100, Hg 02, Mn 43, Ni 14, Pb 11, Sb 1.2, Se 2.8 and U 2.1. The emphasis on introducing trace element legislation began with Hg control. The 1990 CAAA required the US Environmental Protection Agency (EPA) to conduct an assessment of health and

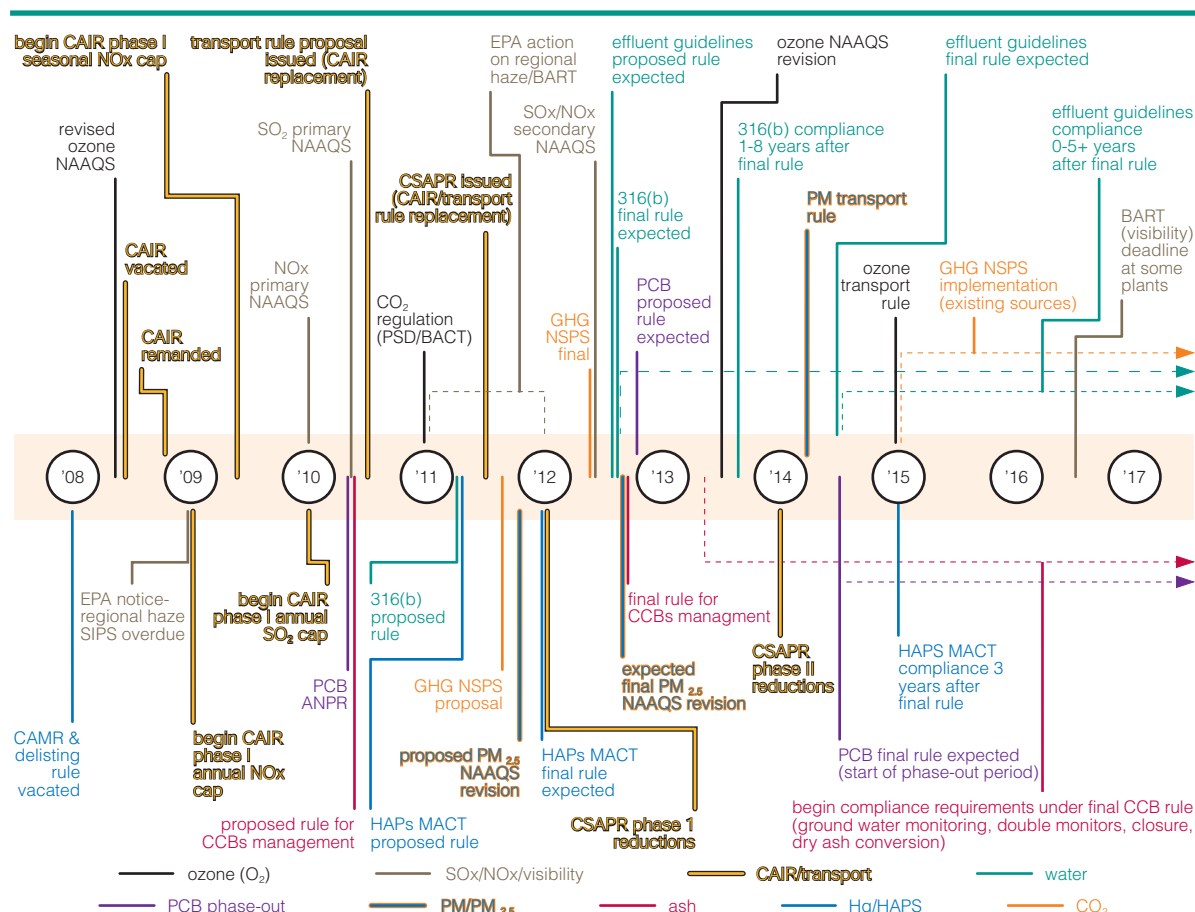


Figure 4 Possible timeline for environmental regulatory requirements for the utility industry in the USA (Rossler, 2011)

environmental effects posed by the emission of a range of trace chemicals from coal-fired power plant. Two reports to congress were published, the Mercury Report and the Utility Air Toxics Study. Prior to 1990 there were few data available on trace element concentrations and behaviour in the combustion system, and the US EPA authorised an Information Collection Request (ICR) in 1999. The resultant database contains information on all US coal-fired utility boilers, coal analyses for mercury, chlorine, sulphur, moisture, ash and calorific value for 1143 US generating units, as well as air pollution control device inlet and outlet flue gas analysis for total and speciated mercury for 84 of the above units. Rossler (2011) discussed the recent history of HAPS regulatory effort within the environmental regulatory requirements for the utility industry in the USA (*see* Figure 4). In August 2011, the Edison Electric Institute published a history (*see below*) of the US EPA efforts to regulate Hg and other HAPs from coal-and oil-based power plants (EEI, 2011). Thiry and Crosby (2012) discussed the compliance of biomass plants with the PM_{2.5} and maximum available control technology (MACT) emission limits and the risks of emission testing.

In the **CAAA of 1990** Congress established a framework for evaluating whether to further regulate HAPs emitted from different industrial source categories. Congress specifically treated electric utility steam generating units (EGUs) differently from other stationary source categories that emit HAPs, which were subject to MACT standards outlined in the CAA. A separate section in the CAA was created that directed the US EPA not to regulate EGUs until it completed a study of the hazards to public health ‘reasonably anticipated to occur’ as a result of EGU HAP emissions, after all other provisions of the CAA were implemented. The US EPA was allowed to regulate EGUs with MACT standards only if the agency found such regulation ‘appropriate and necessary’ after considering the results of the Utility Study. The Mercury Report was completed in 1997 and the Utility Study in 1998.

The Utility Study identified mercury emissions from coal-based EGUs as ‘the HAP of greatest potential concern and merits additional research and monitoring’.

The National Emission Standards for Hazardous Air Pollutants (NESHAPS) are stationary source standards for hazardous air pollutants. Hazardous air pollutants (HAPs) are those pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. The NESHAPS promulgated after the 1990 Clean Air Act Amendments are found in 40 CFR Part 63 standards (www.epa.gov). These standards require application of technology-based emissions standards referred to as MACT. Consequently, these post-1990 NESHAPS are also referred to as MACT standards. The NESHAPS are delegated to the states but both the US EPA and the States implement and enforce these standards.

The Subsequent US EPA Regulations were developed (EEI, 2011):

December 2000

The US EPA issued a ‘regulatory determination’ under the CAA that it is ‘appropriate and necessary’ to regulate mercury emissions from coal-based power plants and nickel emissions from oil-based power plants, and that certain other HAPs pose a ‘potential concern for carcinogenic effects...[and] public health.’ This regulatory determination listed coal- and oil-based EGUs as a source category under the CAA, the first step to setting MACT standards.

30 January 2004

The US EPA published a proposed rule that included two alternative control plans: a two-phase market-based cap-and-trade approach and a MACT approach that would establish separate emission limits for mercury and nickel for new and existing coal- and oil-based EGUs. EPA also proposed to reverse the regulatory finding it made on 20 December 2000.

15 March 2005

The US EPA finalised the Clean Air Mercury Rule (CAMR), which established standards of performance for new and existing coal-based EGUs under the CAA and capped emissions with a first phase cap of 38 tons in 2010, and a second phase cap of 15 tons in 2018. The US EPA determined that regulation of nickel emissions from oil-based plants is not ‘appropriate and necessary.’ It reversed the December 2000 finding and removed coal- and oil-based EGUs from the list. The agency concluded that its December 2000 notice ‘lacked foundation’ and was legally and factually in error.

8 February 2008

The US Court of Appeals for the District of Columbia Circuit issued an opinion regarding the US EPA’s final mercury rules. The Court held that the de-listing was unlawful, vacated both the De-listing Rule and CAMR, and sent CAMR back to the US EPA for reconsideration.

Utility MACT Rule-making

6 February 2009

The Federal Administration indicated it would accept the Court of Appeals’ decision and would develop new MACT standards for the utility industry of the CAA.

2 July 2009

The US EPA proposed a detailed ICR to obtain fuel and emission data to inform the Utility MACT rule-making.

October 2009

The US EPA agreed to a proposed consent decree with various public health and environmental groups, which required it to propose standards addressing mercury and other HAPs by 16 March 2011, and finalise standards by 16 November 2011. In response, utility interests commented to the

court that the deadlines provided inadequate time for the US EPA to fully analyse the data utilities provided to it.

December 2009

On 24 December the Office of Management and Budget (OMB) approved the ICR, and letters were sent to all EGUs on 31 December, requesting the data.

15 April 2010

The consent decree was approved.

October 2010

The electric utility industry completed the US EPA's data request and associated emissions sampling, at a cost of about US\$100 million.

16 March 2011

The US EPA issued the Utility MACT proposal as per the consent decree. The Utility MACT proposal included MACT standards for mercury and other HAPs for coal- and oil-based EGUs.

3 May 2011

The proposal was published in the Federal Register.

4 August 2011

Comments on the proposed Utility MACT due to the US EPA.

16 November 2011

Under the consent decree, the US EPA was obliged to issue a final rule by this date.

7 December 2011

The US EPA published the reconsidered boiler MACT rule.

21 December 2011

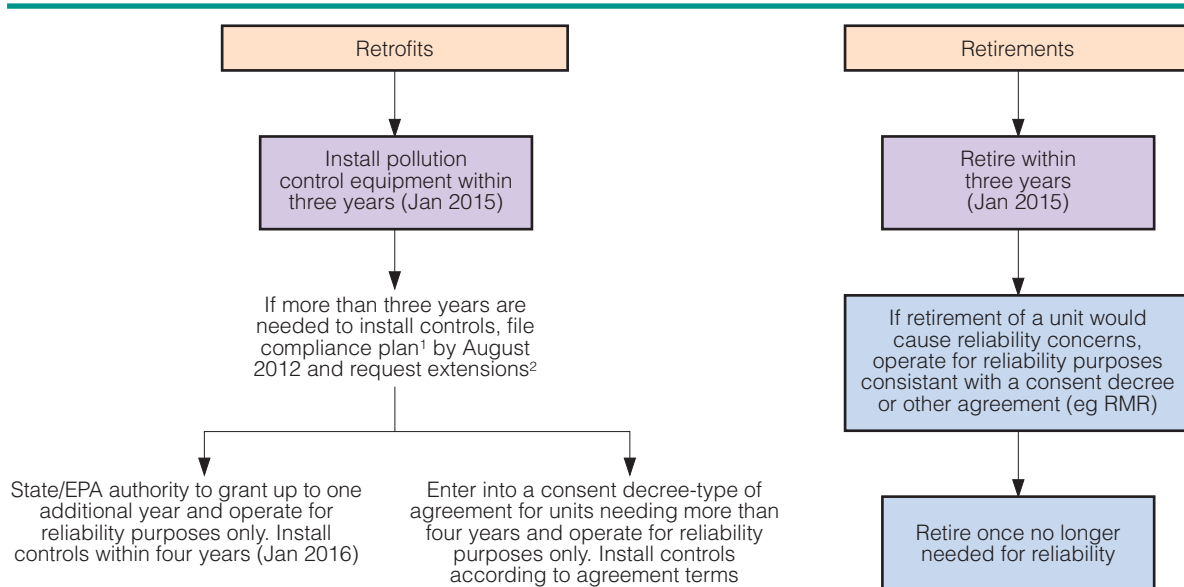
The US EPA finalised the Air Toxics Rule and promulgated the Mercury and Air Toxics Standards (MATS) which imposes limits on the air emissions of mercury and other trace elements from coal- and oil-fired power plants.

3 July 2012

Amendments to the EPA rule were published which include final limits for filterable particulate matter or total non-Hg HAP metals or individual HAP metals limits for antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), manganese (Mn), nickel (Ni) and selenium (Se).

It is postulated that the MATS rule will require a minimum of 40% of all coal-fired power plants in the USA to deploy pollution control technologies to curb emissions of mercury and other air pollutants such as arsenic, chromium, nickel and cyanide within three years. However, a further one year extension, and in some cases more, will be considered by the US EPA 'where there is a well-defined pathway to address any localised reliability problems, should they arise'. According to POWERnews (2011), the regulation has been called the 'most expensive order' aimed at companies that has been considered by the Federal Administration. In early 2011, The US EPA estimated the rule would cost US\$11 billion per year but in a new review on the regulatory impact analysis for the final MATS rule, the agency findings indicate that the projected annual incremental private cost to the power sector will be in the region of US\$ 9.6 billion in 2015 (in 2007 US\$) (POWERnews, 2011).

The affected facilities include approximately 1200 coal-fired units. These represent ~45% of the US electricity generation. Of these ~50% fire bituminous coals, ~45% subbituminous coals and ~5%



¹ In order to facilitate market responses and ensure reliability, companies requesting additional time beyond three years should be required to submit a fleet-wide compliance plan that identifies which units will retire and which units will be retrofitted, explains the need for any additional time beyond three years to install controls, and that includes appropriate milestones for compliance

² Although the existing regulatory and enforcement discretion tools should mitigate the need for Presidential extensions, if the technology is not available and it is in the interests of national security, the President has the authority to grant two-year extensions

Figure 5 Suggested compliance options for the toxics rule and existing authority for extensions for plants in the utility industry in the USA (Allen, 2011)

lignites. The units include those that burn coal, coal refuse, a synthetic gas derived from coal, solid oil-derived fuel (for example, petroleum coke) either exclusively, in any combination together, or in any combination with other supplemental fuels that are not solid wastes. For trace elements, the rule introduces numeric emission limits for total particulate matter (PM) as a surrogate, with an alternate surrogate for total metal air toxics (Culligan, 2011; Hendricks, 2011). For coal-fired units, the Utility MACT limits emissions for hydrogen chloride (as a surrogate for acid gas hazardous air pollutants, filterable particulate matter (as a surrogate for non-mercury metals), mercury, and organic hazardous air pollutants. The limits vary, based on type of coal burnt and whether the units are new or were already in operation when the final rule was published. Total non-mercury hazardous air pollutant metals and individual non-mercury metals limits can be used as an alternative to the filterable PM limits. Coal-fired EGUs with flue gas desulphurisation (FGD) units can use SO₂ limits as an alternative to the hydrogen chloride limits. The rule also creates a variety of new work practice standards. For example, units must burn natural gas or distillate oil during periods of start-up. Relevant emissions control systems must be operated during periods of start-up and shut-down. In addition, optimisation of NO_x and CO, combined with 'best practices' efforts to maximise fuel efficiency must be demonstrated and documented for the EPA. Staudt (2011) reviewed control technologies to reduce conventional and hazardous air pollutant from coal-fired power plants. Allen (2011) suggested compliance options for the toxics rule and existing authority for extensions (*see* Figure 5).

4 Fate of trace elements from coal combustion

Trace element emissions from a conventional coal-fired power plant can vary by 3–4 orders of magnitude from day to day. This variability is due to many factors including process conditions such as the coal characteristics and furnace temperature as well as sampling and analytical variability. A conventional 1000 MW pulverised coal fired power plant consumes over an average 12,000 t of coal per day and produces about 1 Mt of waste per year (Llorens and others, 2001). The quantity of trace elements emitted from coal combustion, in general, depends on:

- the concentration of the element in the coal;
- the physical and chemical properties of the element itself;
- the combustion conditions;
- the type of emissions control device used, and its collection efficiency as a function of particle size.

Coal is an abundant fuel that continues to play an important role as a world energy resource. The pollutant trace element emissions from coal utilisation can have a detrimental impact on the environment and human health. Therefore, greater understanding of trace elements behaviour with coal combustion including classification, characterisation, partitioning, modelling, environmental impacts and emissions control is necessary.

4.1 Classification

Some trace elements become concentrated in certain particle streams following combustion (for example: bottom ash, fly ash, and flue gas particulate matter) while others do not. Various classification schemes have been developed to describe this partitioning behaviour. Partitioning of trace elements in coal combustion is discussed by Nelson (2007b). The classification schemes generally make the following distinction between the elements:

- **Class 1:** elements that are approximately equally concentrated in the fly ash and bottom ash, or show little or no small particle enrichment. Examples include manganese (Mn), beryllium (Be), cobalt (Co), and chromium (Cr).
- **Class 2:** elements that are enriched in the fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size. Examples include arsenic (As), cadmium, (Cd) lead (Pb), and antimony (Sb).
- **Class 3:** elements which are emitted in the gas phase (primarily mercury (Hg) (not discussed in this review, see www.iea-coal.org) and, in some cases, selenium (Se)).

Classification of trace elements is connected to the concept of enrichment. The relative enrichment factor (RE) of an element in ash is defined as:

$$RE = \frac{\text{element concentration in ash}}{\text{element concentration in fuel}} \times \frac{\% \text{ ash in fuel}}{100}$$

Based on pulverised coal combustion, dry bottom and electrostatic precipitation (ESP) for particulate control (Zevenhoven and Kilpinen (2001):

- for Class 1 elements RE is ~1 for bottom ash and fly ash;
- for Class 2 elements RE is <0.7 for bottom ash and ~1.3–4 for fly ash;
- for Class 3 elements RE is <<1 for bottom ash and >>10 for fly ash.

Control of class 1 trace elements is directly related to control of total particulate matter emissions, while control of the class 2 elements depends on collection of the fine particulates. Due to the variability in particulate control device efficiencies, emission rates of these elements can vary

Table 8 Classification of elements based on their behaviour during combustion and their relative enrichment factor (RE) (Meij and te Winkel, 2009)					
Classification	Furnace bottom ash	Precipitator fly ash	Fly ash*	Behaviour in installation	Classified elements
1	~1	~1	~1	Not volatile	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th and Ti
2a	<0.7	~1	1.3<...≤2	Volatile in boiler but complete condensation in the precipitator on the ash particles	Ba, Cr, Mn, Na and Rb
2b	<0.7	~1	2<...≤4		Be, Co, Cu, Ni, P, U, V and W
2c	<0.7	~1	>4		As, Cd, Ge, Mo, Pb, Sb, Tl and Zn
3	<<1	<<1		Very volatile: some to hardly any condensation on ash particles in the precipitator	B, Br, C, Cl, F, Hg, I, N, S, and Se
* Fly ash present in the flue gas downstream of the electrostatic precipitator (ES) and precipitator fly ash from the last hopper of the ESP (finest fraction).					

substantially. The volatility of class 3 trace elements means that particulate controls have only a limited impact on emissions of these elements. Table 8 shows the mass balance calculations carried out by Meij and te Winkel (2009), based on the relative enrichment factor (RE) and trace element grouping.

4.2 Partitioning

According to Attalla and others (2004), in order to minimise the potential risks these trace elements pose to human health and the environment, it is essential to understand and predict their behaviour in a coal combustion process. This involves characterisation, quantification and modelling of the physical and chemical mechanisms that govern the fate of these elements both during and after the combustion process. Figure 6 shows ash formation mechanisms during coal combustion and Figure 7 shows a general model of fine ash formation mechanisms for trace elements which involves a series of complex processes. Factors that influence the fate of trace element in coal combustion include (Attalla and others, 2004):

- combustion system design: this determines the fraction split between bottom ash/slag and fly ash;
- coal ranks and composition: this determines the mode of occurrence of the trace element species and their interaction with mineral matter transformations and partitioning mechanisms;
- firing conditions and level of equipment maintenance.

The following are some of the conclusions drawn by Attalla and others (2004) in relation to previous studies on trace element release during combustion:

- the elemental form of trace species has an influence on its final partitioning;
- the more volatile elements seem to vaporise independently of mode of occurrence and the char particle temperature determines the degree of volatilisation;
- elements that are more refractory show a greater dependence on mode of occurrence and char particle temperature on vaporisation;
- some post combustion zone transformations have been identified which affect trace element partitioning. For example, the interaction of Ca with As, Se and Cd dictates that for coals, which contain significant CaO, the partitioning behaviour of these elements is controlled by surface reactions rather than condensation.

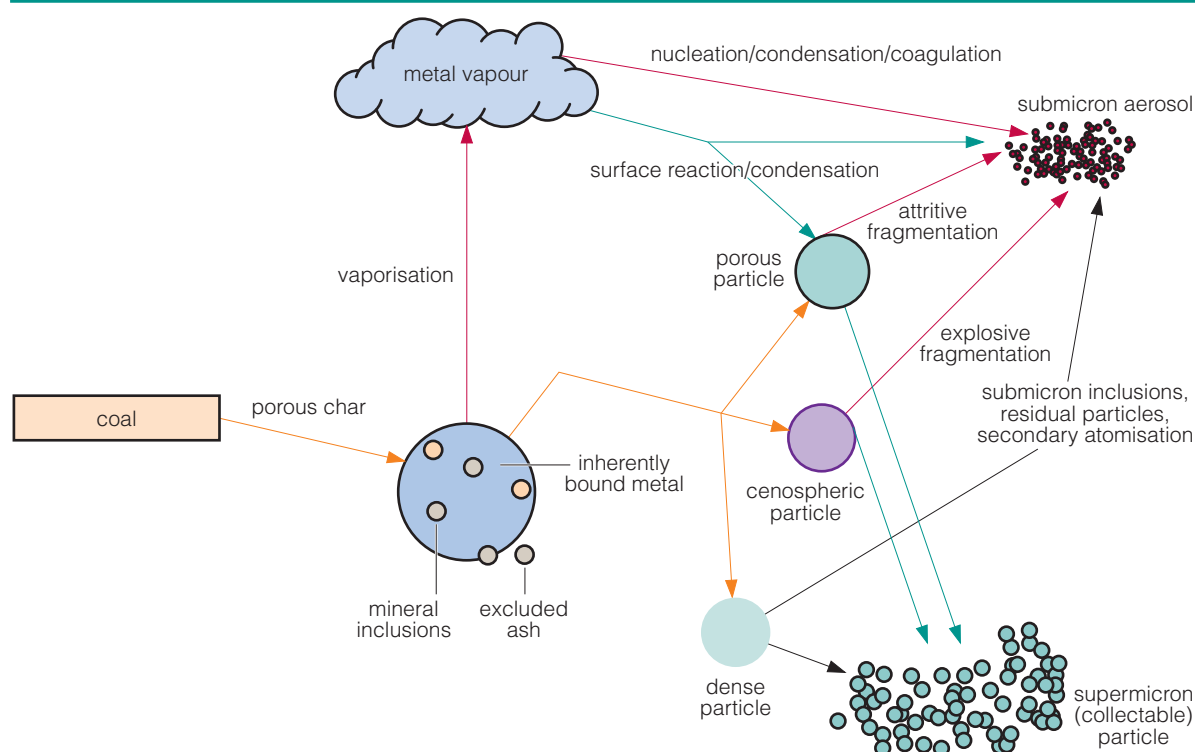


Figure 6 Ash formation mechanisms for trace elements (Attalla and others, 2004)

Attalla and others (2004) discussed the development of a model to predict the vaporisation and subsequent partitioning of trace elements during the combustion of Australian coals. The model is based on theoretical thermodynamic equilibrium, theoretical trace element vaporisation, experimental data and data correlation. The release and partitioning of trace elements from the combustion of seven Australian coals was examined during experimentation under varying furnace temperatures (1600°C to 2500°C) and oxygen environments to produce a range of particles and carbon burnout rates. Observations made by Attalla and others (2004) from the experimental results include:

- release of Se during the experiments was found to lie in the range of 60–80% of the Se in coal, based on ‘percentage retention’ on the cyclone ash or char. A similar broad range of Se release was observed for all coals at all combustion conditions. Further examination indicated an ultimate low mass balance closure for Se with losses encountered (that is, Se unaccounted for) in the experimental system or post combustion capture apparatus;
- the other trace elements examined in the study showed a broad range of release. The release of Pb from the tested coals was found to be in the range 10–90%. The release of Cd was found to be low overall in comparison to the other trace elements, with a level release ranging predominantly from 0% to 70%. The lowest level of release was found to be Ni which ranged from 0% to 50%;
- Ca interaction appeared to play an important role in the heterogenous transformation of As from the vapour phase to the sub-micron particles.

Zevenhoven and Kilpinen (2001) consider that for a typical coal combustion plant the most important gaseous species are As as AsO , As_4O_6 , and As_2O_5 , Cd as Cd^0 (that is elemental Cd) and CdO , Cr as CrOOH , CrO_2OH , CrO_2OH and $\text{CrO}_2(\text{OH})_2$, Hg as Hg^0 (elemental Hg), Pb as Pb^0 (elemental Pb) and PbO , Sb as SbO , Se as SeO_2 , V as VO_2 , and Zn as Zn^0 (element Zn). Co, Cu, Ni and some of the Cr are not volatilised and found in $\text{PM}_{2.5}$ fly ash particles as ferrite spinels AB_2O_4 with $\text{A}^{2+} = \text{Fe, Mg, Ni}$, Co, Cu, $\text{B}^{3+} = \text{Al, Fe, Cr}$. It was found that temperature and not particle size dictates whether a certain trace element or trace element compound is volatile. For example, due to the lower temperatures in pressurised fluidised bed combustion (PFBC) and integrated gasification combined cycle (IGCC),

fewer trace elements are released compared to pulverised coal combustion. However, a higher system pressure allows for a higher temperature for effective trace element removal by the particulate control device: at 1 bar, ~500°C gives sufficient removal, whilst at 20 bar, ~600°C is allowed. Studies have shown that higher particulate removal temperatures result in lower concentrations of trace elements in the fly ash. Stoichiometry (air factor) also plays an important role in trace element release as many species are more volatile in a reducing atmosphere than under oxidising conditions. The presence of halogens, especially chlorine, can also affect trace element volatilisation.

- development of a database of pollutant emissions (gas, particulate and trace toxic compounds) from Australian power stations, utilising validated sampling and analytical procedures;
- measurement of trace elements release and transformations from selected Australian coals;

- development of techniques (correlations, predictors and models) which relate emissions to coal properties, furnace design and operating conditions;
- use of the acquired data and techniques to develop strategies for the environmental impacts of pollutant emissions to land, air and water from coal utilisation in current power plants where this is assessed as being required;
- assess the policy settings which may be necessary to achieve improvements in the sustainability of coal combustion.

Trace element enrichment evaluation, at full scale, was carried out and size-dependent emission factors were developed. The results obtained were for two power plants that have a common coal supply but one utilises an ESP and the other a fabric filter system. Although the coal is sourced from the same mine, there are temporal variations in its composition which led to variations in the trace element species, As, Be, Cd, Mo, Sb and Se. This was the case during the sampling procedure. Nelson and others (2010) noted that the concentration of the elements Cd, Sb and Be remained relatively constant over the course of the sampling campaign. However, the data suggest that the elements As, Mo, and Se increased overall in concentration. These variations demonstrate the importance of collecting samples of coal feed in conjunction with the emissions sampling and they also potentially result in variations in amount of trace elements emitted. Further sampling and analysis showed that reliable assessment of the potential environmental impacts of trace gaseous and particulate emissions from coal-fired power plants requires detailed data on emission fluxes, particle size distributions, trace element concentrations as a function of particle size, and speciation of the trace elements. Nelson and others (2010) summarise their findings as follows:

- particle capture efficiency in ESPs is significantly less than in fabric filters, particularly for submicron particulate matter where penetration of 10% or so was observed for ESP equipped power station;
- for many of the most toxic elements, significant enrichment was observed in the finer particle sizes emitted from both ESPs and fabric filter system;

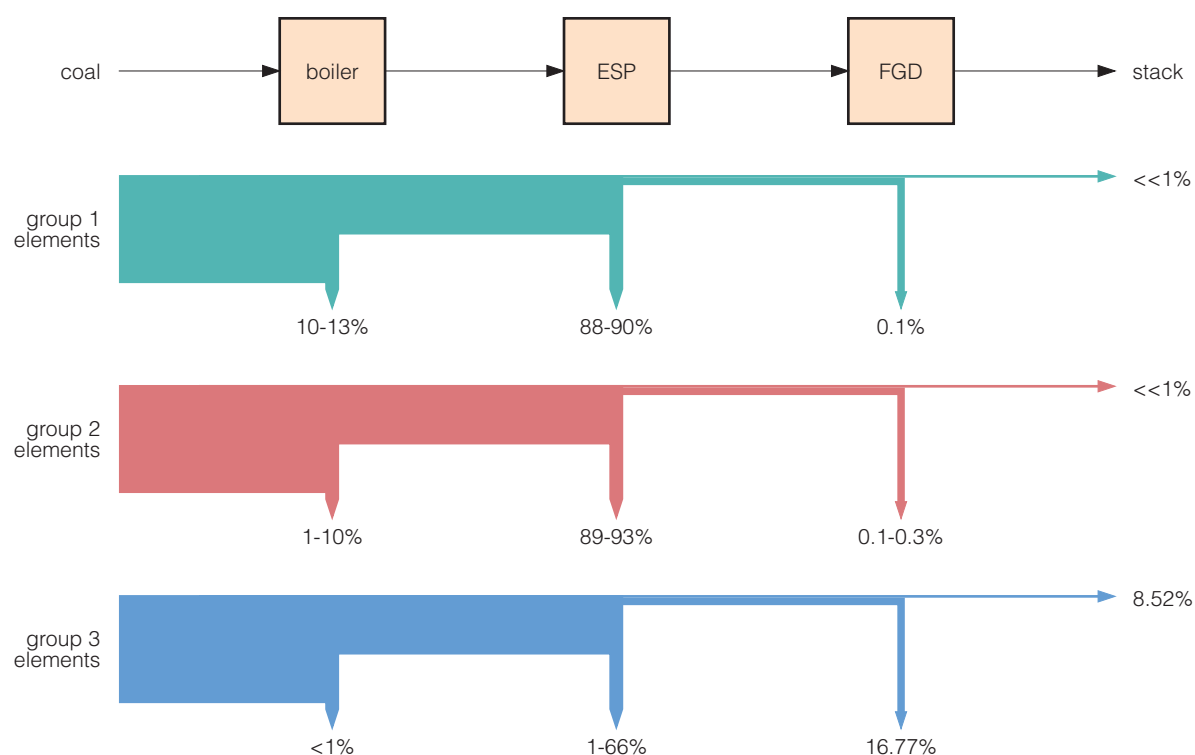


Figure 8 Partitioning of trace elements in a pulverised coal combustion plant (Zevenhoven and Kilpinen, 2001)

- the majority of Cr in fly ash was present in the less toxic Cr^{3+} form; Cr^{6+} was not detected in the bottom ash;
- speciation of As in feed coals was variable but the dominant form of As in the fly ash was the less toxic As^{5+} .

Zevenhoven and Kilpinen (2001) illustrated an example of the partitioning of trace elements in a pulverised coal fired plant with ESP and spray dry scrubber flue gas desulphurisation (FGD) *see* Figure 8. The figure shows that ~90% of Classes 1 and 2 trace elements are collected in the fly ash and that a significant part of the Class 3 trace elements (~17%) is captured in the FGD system. A closer analysis for eight trace elements is given in Figure 9, which shows that gaseous emissions of Hg, Pb and Cd can be significant. In this figure a wet FGD scrubber was in operation capturing a considerable amount of Hg, B and Se. As, Cr and Ni behave similarly and are mainly captured in the fly ash. The investigation demonstrated that not all trace elements enter the system with the fuel. Some B was introduced in the water used to slurry the FGD sorbent. The FGD limestone introduced not only considerable amounts of Pb and other trace elements such as As, Cd, Mn but also Fe, Mg, Si and Ti. Zevenhoven and Kilpinen (2001) considered that in conventional pulverised coal fired combustion with particulate control and a wet FGD system, the only species of concern are Hg^0 , HgCl_2 , SeO_2 , B_2O_3 and As_2O_3 , the remainder (90–99%) which is mainly Class 2 trace elements are captured with the particulate control device.

As stated above, during coal combustion trace elements are released. The more volatile elements such as Hg, Se and As enter the gas phase. While some elements may remain in the gas phase and be

emitted to the atmosphere, others recombine with the ash particles and are captured in particulate control devices then either used in other areas or disposed of. The issues relating to environmental impact of trace elements and their release to air, soil and water are discussed in this chapter.

Llorens and others (2001) studied the fate of trace elements in a Spanish 1050 MW power plant that uses a homogenised mixture of 95% subbituminous coal and 5% bituminous coal as fuel. The local subbituminous coal had high contents of sulphur and mineral matter and a major proportion of clay minerals (kaolinite and illite), iron sulphides, calcium and iron sulphates, quartz, feldspars and calcite. Following seven days of sampling of the coal feed and combustion by-products, the concentration of Al, Ca, Fe, K, Mg, Na, P and Ti was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Concentration of trace elements in the coal feed and combustion by-products was determined by inductively coupled plasma mass spectrometry (ICP-MS). Analysis of the trace elements Hg, Se and As was carried out with atomic absorption spectrometry (AAS) with cold vapour and ICP-AES with hydride generation (HG). Leaching tests were also conducted by means of ICP-MS to analyse trace element concentrations in the leachates.

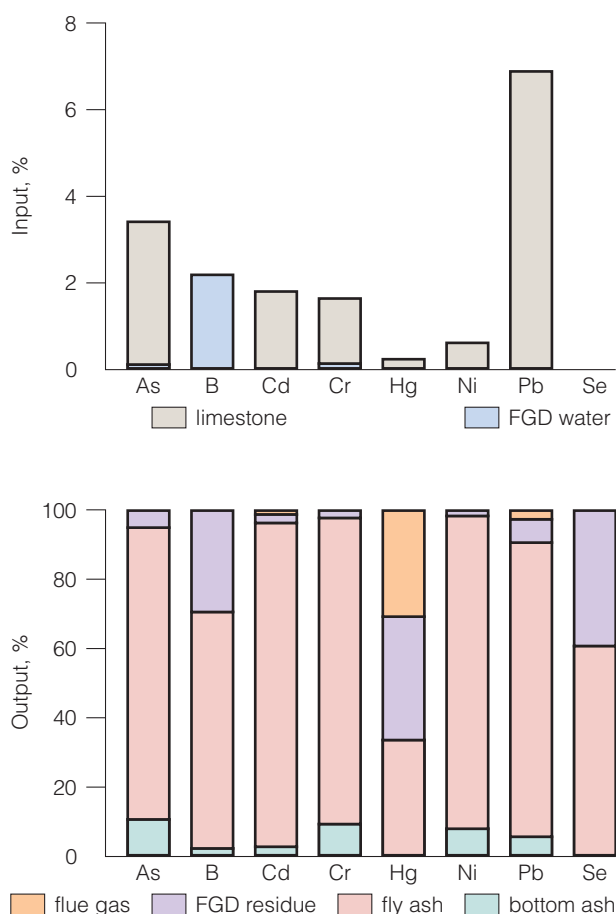


Figure 9 Trace element partitioning at a Danish pulverised coal combustion plants (Studstrup 3) (Zevenhoven and Kilpinen, 2001)

Trace elements are released to the environment following coal combustion either via atmospheric emissions of trace elements in volatile phases or through leaching of solid combustion by-products during disposal, whether in ponds or landfills or after deposition on the soil of the surrounding area from the atmospheric emissions. A power plant mass balance and the leachability of trace elements have been used to quantify the transfer of trace elements from the power plant to the environment. The partitioning of trace elements between fly ash, bottom ash and combustion flue gas depends on their particular geochemical occurrence in the feed coal as well as the technical features, that is operating conditions, of a power plant. The mass balance, in a given period of time, according to Llorens and others (2001), can be expressed according to the following equation:

$$[TE]_c = [TE]_c TEK_{fa} + [TE]_c TEK_{ba} + [TE]_c TEK_{afa} + [TE]_c TEK_v \quad (1)$$

where $[TE]_c$ is the concentration of a trace element TE in the input coal c; $^{TE}K_{fa}$, $^{TE}K_{ba}$, $^{TE}K_{afa}$, $^{TE}K_v$ are the partition coefficients of the trace element TE in the combustion by-products generation at the power plant (fa, fly ash; ba, bottom ash; afa, fly ash emitted to the atmosphere; v, volatiles).

A partition coefficient $^{TE}K_i$ of the trace element TE in the combustion by-products i is defined as:

$$^{TE}K_i = \frac{[TE]_i X_i}{[TE]_c}$$

where $[TE]_c$ and $[TE]_i$ are the concentrations of the trace element TE in the input coal and combustion by-product i respectively, and X_i is the mass fraction of the combustion by-product i.

Thus, equation 1 can also be expressed as (Llorens and others, 2001):

$$[TE]_c = [TE]_{fa} X_{fa} + [TE]_{ba} X_{ba} + [TE]_{afa} X_{afa} + [TE]_v X_v \quad (2)$$

where $[TE]_c$, $[TE]_{fa}$, $[TE]_{ba}$, and $[TE]_v$ are the concentrations of trace element TE in the input coal, fly ash, bottom ash and volatile fraction respectively, and X_{fa} , X_{ba} , X_{afa} and X_v are the mass fractions of the combustion by-products generated at the power plant (fly ash, bottom ash and fly ash emitted to the atmosphere and volatile fraction respectively).

Llorens and others (2001) consider that equation 2 allows the estimation of atmospheric emissions by calculating the imbalance between the feed coal and the solid wastes. Using equation 2, the authors infer X_{fa} and X_{ba} for two non-volatile elements, which is selected among those that are not partitioned in the volatile phase during combustion and show a low analytical error. In the specific study undertaken by Llorens and others (2001), the two elements were cerium (Ce) and lanthanum (La), which remained primarily in the solid wastes and their analytical error by ICP-MS was lower than 2%. In the case of Ce and La, Llorens and others (2001) estimated their value for X_{fa} and X_{ba} at 15.4% and 9.6% respectively (that is, a total solid waste content of 25% in weight in relation to the feed coal). X_{afa} is determined as a function of X_{fa} and the efficiency of the ESP (99.892% in the power plant in the study), that is 0.02% in weight with respect to the feed coal. Once X_{fa} , X_{ba} and X_{afa} were determined, the partition coefficients $^{TE}K_i$ for the solid wastes can be calculated taking into account equation 1 (Llorens and others, 2001):

$$^{TE}K_v = 1 - (^{TE}K_{fa} + ^{TE}K_{ba} + ^{TE}K_{afa})$$

The estimated partition coefficients $^{TE}K_i$ are shown in Figure 10. The authors found that some trace elements (such as Ba, Cu, Dy, Lu, Sr, Yb and Zr) presented experimental values of $^{TE}K_v$ lower than, but near, zero. This was attributed to analytical error and assumed as zero in the figure, that is these are elements that are totally retained in the solid waste. Llorens and others (2001) concluded that the trace elements retained in the solid wastes were Ba, Ce, Co, Cs, Cu, Dy, Ga, La, Lu, Mn, Ni, Rb, Sr, Tb, Th, Y, Yb, Ge, Zn and Zr as their partition coefficient K_v ranged between zero and 0.10% (see Figure 10). These elements show a low degree of mobility since they are mainly non-volatile elements

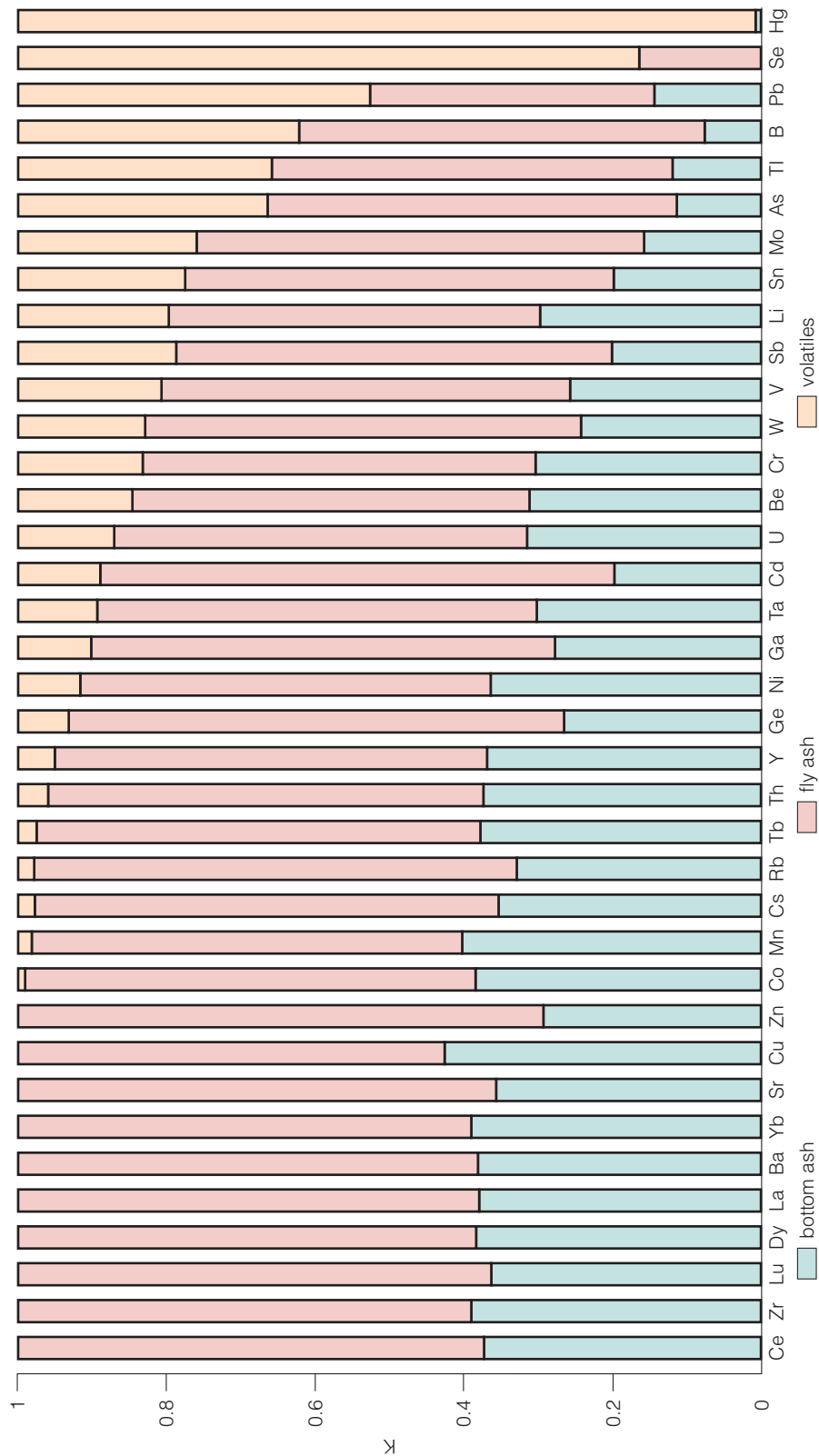


Figure 10 Trace element partition coefficients in the combustion by-products generated at a 1050 MW coal-fired power plant (Llorens and others, 2001)

included in the matrix of solid wastes (aluminosilicate glass and iron oxides). Trace elements partially retained in solid wastes include As, B, Be, Cd, Cr, Li, Mo, Pb, Sb, Sn, Ta, Tl, U, V and W ($0.01 < K_v < 0.80$). These are present in phases (for example, sulphates) which can easily be leached in natural environmental conditions. Trace elements primarily emitted to the atmosphere are Hg and Se ($K_v > 0.80$). The authors considered that in order of magnitude, the transfer of trace elements from the power plant in this case study to the surrounding environment exceeded 10 t/y of As, Cr, Pb, V, Li and B through atmospheric emissions, while >1 t/y of Li, Ba, Cr, Sr, V, Mo and B from fly ash and Sr and B from bottom ash could have been potentially mobilised by leaching of the solid combustion by-products (Llorens and others, 2001).

The fate of trace elements in pulverised coal combustion was the subject of a project reviewed by Irons and others (2000). The project was undertaken to improve the understanding of trace elements behaviour in coal combustion as a function of combustion conditions, coal type and coal cleaning as well as to develop new methods for determining real-time in-site trace element concentrations. The specific aims of the project were (Irons and others, 2000):

- to improve the understanding of the distribution and partitioning of trace elements in coals and the changes which take place during coal preparation and cleaning;
- to develop novel techniques for the on-line measurement of significant trace elements;
- to correlate trace element distribution and partitioning data for cleaned and uncleaned coals and in-furnace and post-combustion pollutant concentrations to allow prediction of trace pollutant emissions;
- to assess the combustion performance of cleaned coals to identify the effects of coal cleaning strategies.

The combustion testing of coals from the UK, Colombia and Indonesia was carried out at a 1 MW combustion rig scale. The coals from the UK and Colombia were tested in both raw and cleaned forms whilst the Indonesian coal, with low ash content, was tested in raw form only. Irons and others (2000) concluded that:

- pilot-scale combustion results demonstrated that operational O_2 levels can have a profound effect on the partitioning of Hg and Se between the fly ash and gas phases;
- although the washing of coals was successful in removing a significant proportion of the bulk ash material, the result of the cleaning process was largely to wash out the inert (alumino-silicate) fractions of the mineral matter, rendering the remaining material more pernicious (in terms of slagging potential). The washing process had little impact on the levels of gaseous trace element emissions;
- the occurrence of trace elements in coals as ‘organic’ and ‘included’ or ‘excluded’ mineral matter was achieved by analysing a range of coal sub-samples of varying densities ash contents;
- concentration ranges of seven trace elements including Co, Cr, Cu, Ga, Ni, V and Zn in the major minerals from samples of all the coals, ash samples and deposits were determined using computer controlled scanning electron microscopy (CCSEM) which is a technique that provides a measurement of coal mineralogy;
- an analytical technique using the principle of atomic absorption was used to obtain online measurements of the concentration of Hg and Cd in the flue gas from the 1 MW pilot-scale coal combustion test rig.

Xu and others (2003) discussed trace element partitioning following coal combustion. The partitioning referred to the dispersion of trace elements among different emission streams including bottom ash, fly ash, ash in scrubber waste and the flue gas (*see* Figure 11). According to the figure, the main proportion of almost all trace elements is bound with the fly ash and collected in the particulate control device, in this case the ESP. B and Se are partially discharged in the vapour phase and Hg is almost fully released with the flue gas. According to Xu and others (2003), most trace elements that are partially or fully vaporised during coal combustion, tend to condense and enrich in the submicron particles with a significant surface-to-volume ratio. These particles have a greater detrimental impact on human health and can only be captured by highly efficient particulate control devices. In their

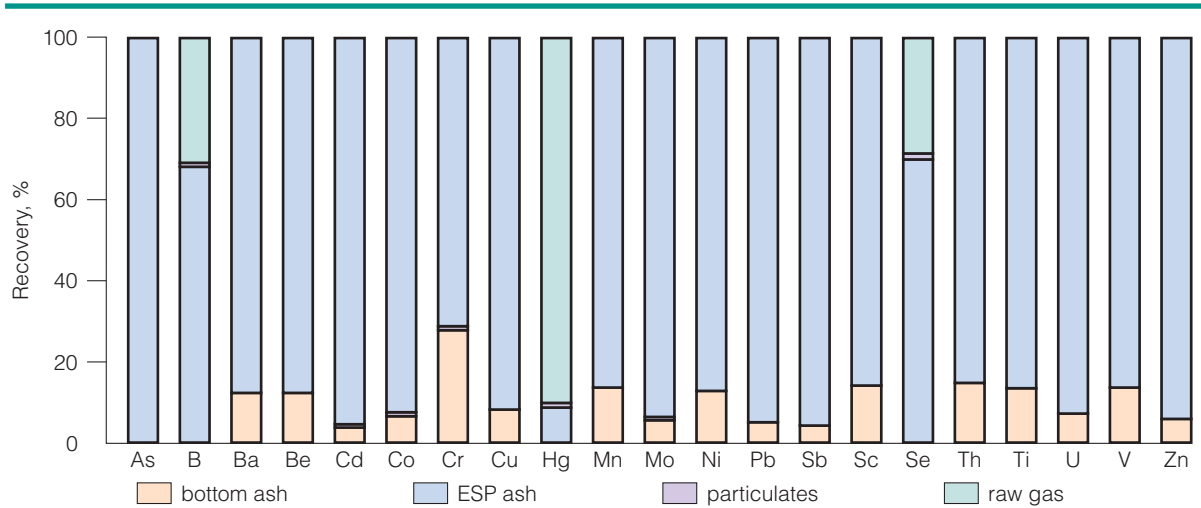


Figure 11 Relative distribution of trace elements between bottom ash, ESP ash, particulate emission and the raw gas based on data from a coal-fired power station in the Netherlands (Xu and others, 2003)

review, the authors found that although the fraction of submicron fly ash particles before the particulate control device contained <5% of the total mass, it represented approximately 50% of the total mass following the particulate control device. Based on partition and enrichment behaviour of trace elements, three basic classes of trace elements were defined by Xu and others (2003):

- Class 1: elements distributed, approximately equally, between the bottom ash and the fly ash, or show no significant enrichment or depletion in the bottom ash;
- Class 2: elements enriched in the fly ash and depleted in the bottom ash, or show increasing enrichment with decreasing fly ash particle size;
- Class 3: elements totally emitted in the vapour phase.

Xu and others (2003) noted that as data show that most trace elements are enriched in submicron particles, these should be subject to regulatory concern due to the greater risks they have on the environment and human health.

4.3 Emissions to air

In 1990, the Electric Power Research Institute (EPRI) (USA) developed and maintains, with annual upgrades with new data, a large multimedia database of historical and recent data for trace species/hazardous air pollutants measurements in all process media associated with coal, oil and gas-fired power plants. The database is known as the Power Plant Integrated Systems Chemical Emissions Studies (PISCES) database. It is a multimedia database containing primary information on the concentration and fate of substances in power plant process and discharge streams. Power plant owners must report emissions of specific compounds to state and federal regulators and they have to maintain records of regulatory reporting to defend assumptions made in estimating emissions if questions are raised by regulators (EPRI, 2012). A customised online web query interface has also been developed which EPRI members can use to retrieve data for many purposes including permitting, Toxics Release Inventory (TRI) Program reporting/analyses, control system removal performance and plant mass balances for trace species (Orr, 2012).

In mid-2009, URS Corporation (USA) began a project with EPRI to evaluate data collected by utilities as part of the US Environmental Protection Agency (EPA) information collection request (ICR) (Orr, 2012). Phase I (2009) of the project involved detailed review of data quality, for about

50% of the data, prior to final submittal to the US EPA. The project also involved other tasks such as the review of data anomalies, quality assurance/quality control (QA/QC) and strategy and assessment (S&A) methods with feedback reports sent to each individual utility to use prior to final data submittal to the US EPA. In Phase II (2010), URS Corporation carried out: a detailed analysis of the ICR data released by the US EPA over the course of their environmental rule-making process, evaluated possible scenarios for maximum achievable control technology (MACT) limits and identified data quality issues, identified potential errors in the US EPA MACT analyses and the ICR data sets used to support their analyses, and assisted EPRI in providing technical comments to the docket on the proposed rule. Phase III (2011), involved the development of guidance for utilities on the emissions performance of boiler type/control technology configurations tested as part of the ICR and providing data and information to assist utilities in evaluating options for complying with the proposed limits (*see* Chapter 3) for new and existing electric utility steam generating units (Orr, 2012).

The vaporisation of As, Se and Sb during coal combustion was studied by Zeng and others (2001). Experiments for the study were performed to find distributions of the As, Se and Pb after devolatilisation/combustion. Three bituminous coals from the eastern US were selected and segregated into varying size cuts with different densities. The coal was then devolatilised and burnt under well-defined conditions. Char and ash samples were analysed by using a neutron activation analysis method. A quantitative model was established and used to predict vaporisation rates for As, Se and Sb during coal combustion. The experimental results showed that vaporisation rate is proportional to elemental concentration. More elements were vaporised at higher pyrolysis temperatures and at higher combustion oxygen concentrations. Although the thermodynamic properties, such as the volatility for the As, Se and Sb were very different, the fractions present in the vaporised or submicron particles were of the same order of magnitude. Zeng and others (2001) attributed this to the association of the elements with the pyrite in coals. The vaporisation processes for the three elements studied consisted of three consecutive processes: diffusion through the pyrrhotite (FeS) melt, vaporisation from liquid to vapour at the interface of melt and gas, and transport through the pores of the char. The controlling step for vaporisation of arsenic is diffusion through the melt. Diffusion processes in the melt and within the char pores together determine the vaporisation rates for Se and Sb (Zeng and others, 2001). The fate of Se in coal combustion, that is the volatilisation and speciation of Se in the flue gas was studied by Yan and others (2001).

Furuta and others (2005) reported on the concentrations, enrichment and predominant sources of Sb and other trace elements in size classified airborne particulate matter collected in Tokyo from May 1995 to 2004. The authors found that the concentration of trace elements was seasonal and that the atmosphere in Tokyo was ‘seriously’ polluted with toxic heavy metal elements, with Sb found to be the highest. However, the authors concluded that the fly ash from the combustion of plastic products and brake pads of automobiles were likely to be the contributors to the greater Sb concentration in the air as these products are treated with antimony sulphide to be flame and heat resistant.

Xie and others (2006) studied the concentrations of As and Se in particulate matter from coal combustion in Taiyuan (Shanxi Province, China), where one quarter of Chinese raw coal is produced. The annual coal consumption of Taiyuan, which covers 1500 km² and has a population of 2.7 million, is ~25 million tons (~23 Mt). About 9.7 million tons (8.8 Mt) is for energy use accounting for 95% of total energy production. The city is surrounded by mountains favouring the build-up of pollutants in the area. Particulate samples <10 µm (PM₁₀) in aerodynamic diameter were collected and multi-element analyses were performed by inductively coupled plasma atomic emission spectrometry (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS). The results obtained for the elemental concentration in the samples are listed in Table 9. Xie and others (2006) regard As and Se of particular interest. The As concentrations ranged from 12 to 83 ng/m³, with the arithmetic average of 43 ng/m³, far exceeding the World Health Organisation (WHO) guidelines for Europe (WHO, 2001) which is 0.7 ng/m³. The authors consider As one of the most toxic elements which is expected to be in high concentration in the Taiyuan air due to the large quantity of coal consumption. Se concentrations

Table 9 Elemental concentrations in air for PM₁₀ collected in Taiyuan City (Shanxi Province, China) in March 2004 (Xie and others, 2006)

Element	Unit	Minimum	Medium	Maximum	Median	σ sigma
Al	$\mu\text{g}/\text{m}^3$	9.94	26.28	55.13	26.69	13.12
Ca	$\mu\text{g}/\text{m}^3$	15.11	38.60	76.93	41.92	19.81
Fe	$\mu\text{g}/\text{m}^3$	7.43	17.55	34.43	19.13	8.47
K	$\mu\text{g}/\text{m}^3$	2.52	8.45	17.11	8.45	4.64
Mg	$\mu\text{g}/\text{m}^3$	3.21	6.62	17.74	8.60	4.70
Na	$\mu\text{g}/\text{m}^3$	1.46	4.60	11.17	5.08	3.12
Mn	$\mu\text{g}/\text{m}^3$	0.27	0.69	1.21	0.69	0.37
Pb	$\mu\text{g}/\text{m}^3$	0.17	0.63	1.34	0.63	0.38
Ti	$\mu\text{g}/\text{m}^3$	0.59	1.43	2.85	1.55	0.69
Zn	$\mu\text{g}/\text{m}^3$	0.35	1.02	2.44	1.30	0.86
As	ng/m^3	11.98	31.57	82.55	43.36	27.61
Ni	ng/m^3	6.96	41.59	123.90	43.62	41.64
Sb	ng/m^3	2.85	9.57	19.57	11.08	9.57
Se	ng/m^3	9.50	44.41	126.36	58.21	44.41
Sn	ng/m^3	2.41	6.96	33.75	11.77	9.49
V	ng/m^3	13.59	33.78	62.72	36.90	16.13

Table 10 Comparison of As and Se concentration (all in PM₁₀) from different parts of the world (Xie and others, 2006)

Location	Mean As, ng/m^3	Mean Se, ng/m^3	Time-frame
Downtown Los Angeles (LA), USA	6.9	8.1	1987
Birmingham, UK	6.7	4.9	Winter 1992
Birmingham, UK	5.65	3.05	Summer and Winter 1992
Coimbra, Portugal	2.35	0.79	1992-93
Macao, China	17	21	2001
Shanghai, China	42.1	19.5	Winter 2001
Taiyuan, China	43	58	March 2004

ranged between 9.5 and 126 ng/m^3 , with an arithmetic average of 58 ng/m^3 . In general, the concentration of urban particulate Se is in the range of 1 to 10 ng/m^3 . The concentrations of As and Se recorded in the study were then compared to results from PM₁₀ studies in other urban areas (*see* Table 10).

Xie and others (2006) summarised that the heavy coal consumption in Taiyuan resulted in elevated concentrations of trace elements, especially the volatile elements, such as As and Se. The authors reasoned that this was because these elements are easily released into the gas phase at high temperature and then condense on to fly ash particles. As and Se are recognised as coal combustion

markers. Correlation analysis conducted during the study revealed that As and Se are highly correlated, which indicated a dominant source of pollution. Fairly high concentrations of As and Se with Al were noted, Al being a lithophilic element. This suggested that they were from the same source, that is, coal combustion. Furthermore, Xie and others (2006) concluded that high correlations of Al and Se with PM_{10} identified coal combustion as a dominant source of particulate pollution in Taiyuan. Volatility and mobility of trace elements in the Shizuishan power plant also in China is discussed by Song and others (2011).

A study by Widory and others (2010) assessed the use of coupling Lead ($^{206}Pb/^{204}Pb$) and strontium ($^{87}Sr/^{86}Sr$) isotope systematics to help determine the origin of aerosols (total suspended particulates (TSP) and $PM_{2.5}$) in the atmosphere in Beijing (China). According to Widory and others (2010), isotope compositions have proved to be reliable tracers of the origin of aerosols in the atmosphere, including urban air. Cement factories, coal combustion and Pb refining were identified as potential sources of pollution in the area. These were chemically and isotopically characterised, then, through the isotopic characterisation of ambient aerosols, the major sources of pollution were recognised and, where possible, their respective contribution to particulate matter emissions was apportioned.

Widory and others (2010) concluded that:

- unique identification of the sources of Pb and Sr, the concentrations of which in different size fractions were relatively high (up to 2500 and 1000 ppm respectively), were not possible;
- lead ($^{206}Pb/^{204}Pb$) isotopes identified emissions from Pb refining plants as the major emitter in Beijing's atmosphere followed by coal-fired power stations;
- strontium ($^{87}Sr/^{86}Sr$) isotopes indicated that emissions of Sr in the atmosphere in Beijing are mainly from coal combustion;
- coupling the Pb and Sr isotope systematics gave a greater insight into the sources responsible for the emission levels of Pb and Sr in the measured aerosols.

The authors finish by stating that the results confirm the major role played by coal combustion in Pb and Sr emissions to air in Beijing. Also, that while the study of the Pb and Sr concentrations may have considered a correlation between the source(s) involved and the size fraction of the particles, that is, each size fraction being influenced by a specific pollution source, use of the multi-isotope approach showed that TSP and $PM_{2.5}$ are both from the same source of pollution.

According to Xu and others (2003), the most volatile trace elements Hg, Se and As remain mostly in the vapour phase as they pass through the heat transfer sections of a boiler. The percentages of the total in-stack concentrations of these trace elements in vapour phase are reportedly:

Cl up to 99% as HCl
 F up to 90% as HF
 Br 25–98% as HBr
 Hg up to 98% as Hg, HgO and CH_3Hg
 Se up to 59% as Se and SeO_2
 As 0.7–52% as As_2O_3
 I 90–99% as HI

Based on three basic classes of partition and enrichment behaviour of trace elements defined by Xu and others (2003) *above*, Figure 12 categorises trace elements based on their volatility (for example, boiling point) and indicates the potential for their intermediate behaviour. Figure 12 shows that (Xu and others, 2003):

- elements, minor and trace, not vaporised during combustion compose the matrix of both fly ash and bottom ash in the form of a homogenous 'melt' as well as crystalline phases;
- elements, partially or fully, vaporised undergo additional transformation and partitioning downstream, as the flue gas cools down in the upper furnace and heat recovery section of the combustion system. The conversion of trace elements is determined by three complex and interrelated processes including adsorption, condensation and chemical transformation.

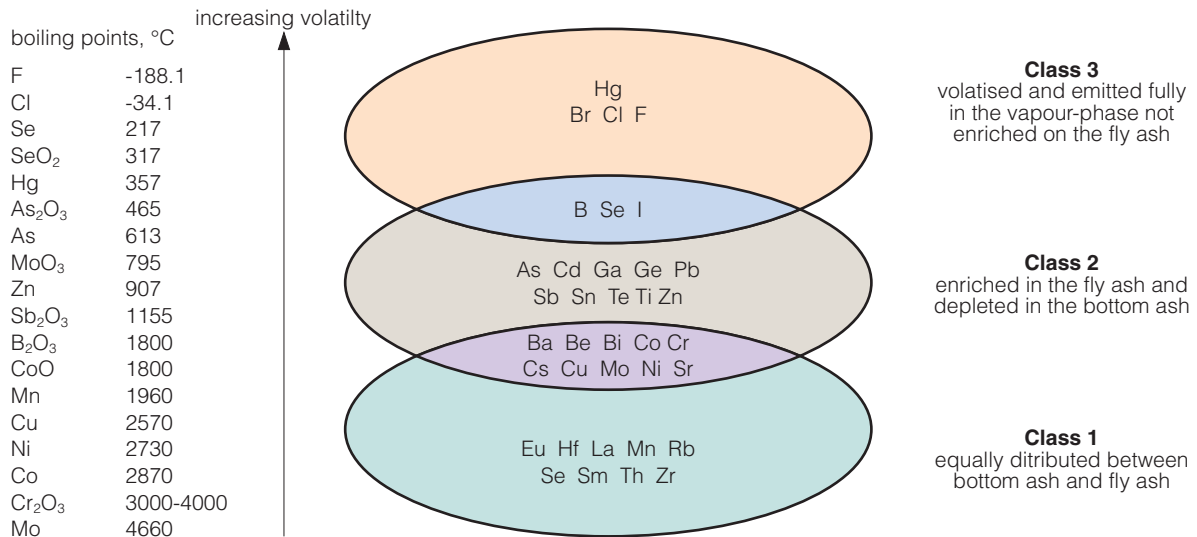


Figure 12 Categorisation of trace elements based on volatility behaviour (Xu and others, 2003)

Table 11 Details of the six boilers in a study to assess trace elements during pulverised coal combustion in the Czech Republic (Danihelka and others, 2003)

Type of boiler	Particulate control device	Nominal output, MW	Coal type
Natural circulation, vertical tube, slag tap furnace	ESP	160	bituminous
Dry bottom	ESP	49	bituminous
Dry bottom	ESP	64	brown coal
Hot water	ESP	58	bituminous
Forced circulation, dry bottom	ESP	55	bituminous
Vertical tube, dry bottom	fabric filter	258	bituminous

Emission of the trace elements As, Se, Cd, Co, Cr, Cu, Zn, Hg, Tl, Pb, Ni, Sn, Sb, V, Mn and Fe from six pulverised coal combustion plants in the Czech Republic, ranging in size from 49 to 258 MW, was investigated by Danihelka and others (2003). Details of the boilers in the study are given in Table 11. The distribution of the elements in the combustion products was obtained using the relative enrichment factor (RE) (*discussed above*). The results based on RE calculations, give an indication of how trace elements are enriched or depleted in different fractions. From the results obtained, Danihelka and others (2003) classified the trace elements as follows:

- **Class 1** elements are distributed in bottom and fly ash, with RE 0.7–1.3. These are defined as elements with no significant enrichment or depletion in the fly ash.
- **Class 2** elements enriched in fly ash, RE factors for bottom ash <0.7 and ~1 for fly ash and larger RE for the smallest particles which are included in air emissions (sampled from the stack). This class included V, Cr, Co, Ni, Cu, Zn, As, Se, Cd, Sn, Sb, Tl and Pb.
- **Class 3** elements that are volatilised and have RE <1 in the bottom ash and fly ash, that is they are not enriched in these fractions.

According to Danihelka and others (2003), the calculation of an enrichment factor (EF) provides additional insight where:

$$EF = \frac{C_x \text{ in fraction} / C_{Mn} \text{ in fraction}}{C_x \text{ in coal} / C_{Mn} \text{ in coal}}$$

where C_x is the concentration of trace element in the coal, fly ash, bottom ash or solid particles of the stack emissions and C_{Mn} is the concentration of a normalising element in the coal or combustion products. Mn was chosen as the normalising element in the study as it is relatively non-volatile and its concentration was analysed in all fractions unlike the other non-volatile elements, for example Fe. After comparing the RE and EF, Danihelka and others (2003) divided the trace elements into four groups:

- **Group 1** Mn and Fe, which have similar enrichment in fly ash and bottom ash and are low in the stack particulate emissions.
- **Group 2** Cd, Sn, Zn, Pb, Sb, Cu are more enriched in the fly ash and in particulate emissions.
- **Group 3** Hg, Se and As are notably enriched in the fly ash (with a ratio of bottom ash/fly ash up to 0.3) and therefore are higher in stack particulate emissions.
- **Group 4** Co, Cr, V, Tl and Ni are more enriched in the fly ash but they have no significant enrichment in the stack particulate emissions.

Danihelka and others (2003) consider that, based on the assumption that the ratio between bottom ash and fly ash in pulverised coal combustion plant being 80/20, the mass flow of the trace elements in the same said plant can be obtained and presented as a percentage average values of retained elements in different fractions (*see* Figure 13). Based on this partitioning, the authors concluded that it is typical that ~20% of Fe and Mn, which belong to Group 1, are retained in bottom ash. Up to 80% of Cd, Sn, Zn, Pb, Sb and Cu (Group 2) are retained in fly ash and about 5–10% of their amount is retained in the bottom ash. As for the trace elements from Group 3, Hg, Se and As, the authors consider that it is obvious that a relatively large amount of these elements is emitted to air with the flue gas compared to the other elements. About 15% of Se and 2% of As is retained in the solid particles and only 5% of the same elements is retained in the bottom ash. Up to 85% of Hg is either emitted to the atmosphere or captured in solid fly ash particles and a negligible amount is retained in the bottom ash. According to Danihelka and others (2003), the mass balance of Tl was poor and therefore concluded that up to 80% of Tl seemed to be ‘lost’. However, the authors note that there are very small amounts of Tl in coal and combustion products and that concentrations of Tl are usually below detection limits. Regarding the other elements in Group 4 including Co, Cr, V and Ni, the conclusion was that typically about

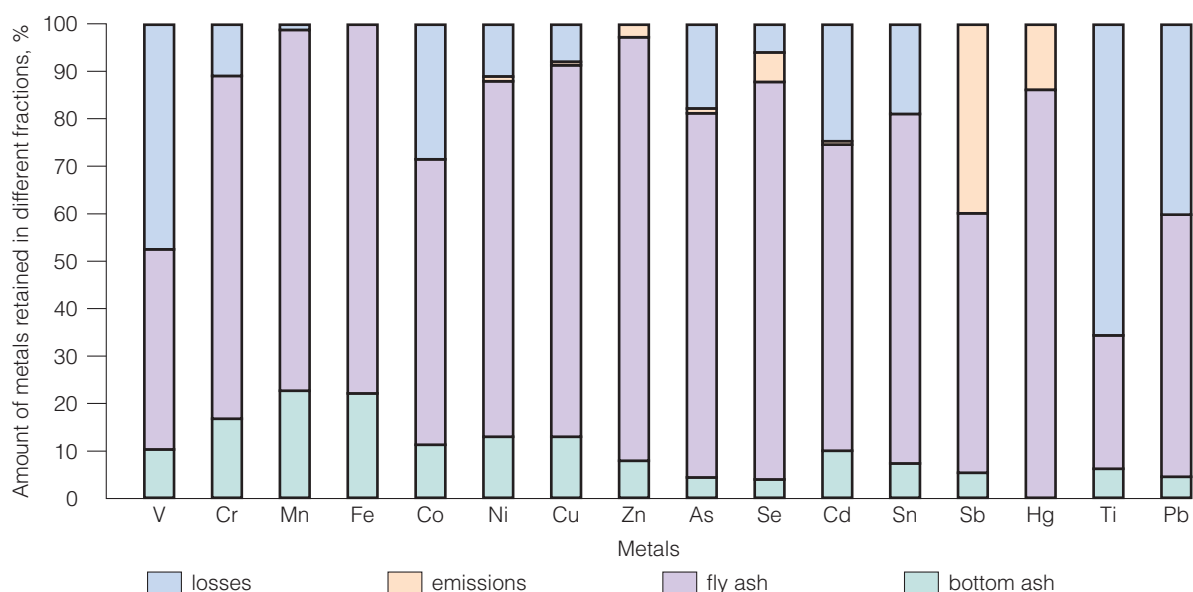


Figure 13 Distribution of trace elements between bottom, fly ash and emission during pulverised coal combustion (average values) (Danihelka and others, 2003)

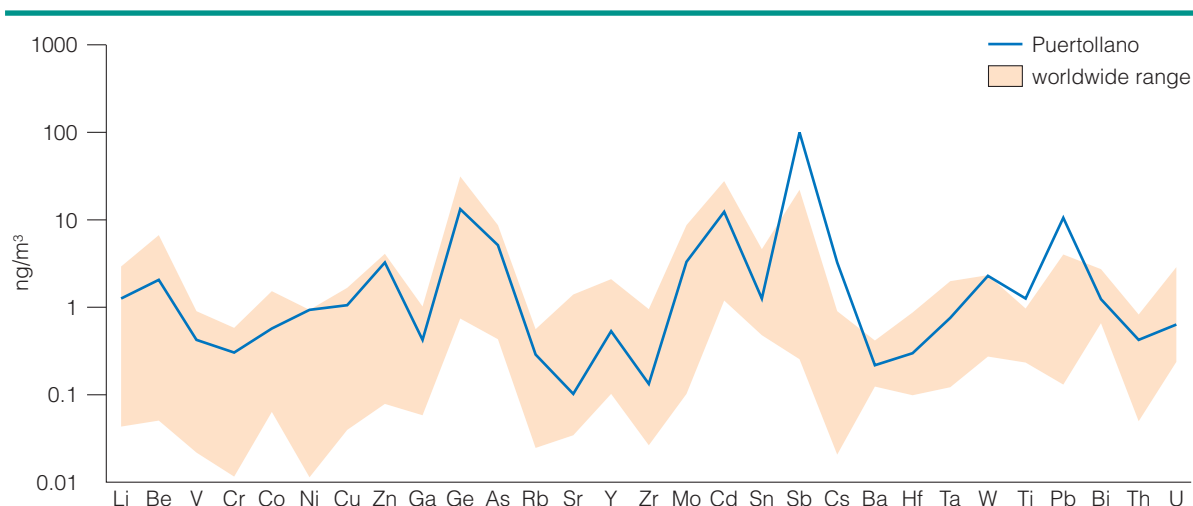


Figure 14 Concentrations of trace elements in Puertollano coals normalised to upper continental crust values compared with values from its compositional range for worldwide coal (Moreno and others, 2007)

10–15% of these elements is retained in the bottom ash and about 70% remains in the fly ash. The influence of Cl content in the coal was also investigated. Danihelka and others (2003) found that the amount of Cl in coal has a considerable influence in the volatilisation of some elements such as Zn, Cu, Pb, Hg and Tl. The affinities for Cl followed the order $Tl > Cu > Zn > Pb > Co > Mn > Sn > Hg$.

Moreno and others (2007) discussed the identification of metallic elements in airborne particulate matter from fossil fuel fired plants as well as petrochemical and fertiliser complexes in the Puertollano industrial centre in Spain. The conventional coal-fired facility utilises locally-mined coal.

Concentrations of trace elements in the coal compared with values from a compositional range of worldwide coals are shown in Figure 14. Mean trace element concentrations (bulk coal dry basis) in these coals show notable enrichments in Zn (234 ppm), Ge (19 ppm), As (25 ppm), Sb (44 ppm), Pb (185 ppm) and Cs (16 ppm). Additional sources of emissions are local traffic (minor) and domestic heating (with wood, coal or oil). The study reported trace element data of airborne particulate matter $<10\ \mu\text{m}$ and $<2.5\ \mu\text{m}$ in size collected over a 57-week period during 2004 and 2005.

Maximum, minimum and mean concentration values of 20 trace elements were collected over the study period. Figure 15 compares the results obtained with those recorded from five other towns in Spain including Burgos (suburban), Badajoz (urban), Huelva and Tarragona (urban-industrial) and Barcelona (urban, traffic). The figure shows that average levels of airborne trace element-bearing particles at Puertollano were mostly within the typical range for the other Spanish cities listed above. Moreno and others (2007) consider that, due to the amount of heavy industry based in Puertollano which has a relatively small population (~50,000), higher-than-average levels of metals and metalloids such as Ti, V, Cr, Co, Ni, Zn, As and Sb were present, although not in exceptional amounts. Factor analysis indicated the presence of five main element groupings in the particulate matter $<10\ \mu\text{m}$. Two of these were attributed to natural sources, one being silicate-rich and derived from the erosion of rocks and soils and the other of lesser importance, according to Moreno and others (2007), being sea spray (Cl^- , Na^+ and Mg^{2+}). The remaining three groups are given in Table 12. These are all from anthropogenic sources. One is characterised by ammonium sulphates and nitrates associated with V and Ni (source 2 in Table 12). The remaining two groups are metalliferous, one linking Sb with Pb (source 1 in Table 12) and the other linking V with Ni but without the link with sulphates and nitrates (source 3 in Table 12). Moreno and others (2007) consider that whereas both sources 1 and 2 are also clearly identifiable in the $\text{PM}_{2.5}$ fraction, source 3 is not, which indicates the presence of this association only within the coarser aerosol fraction.

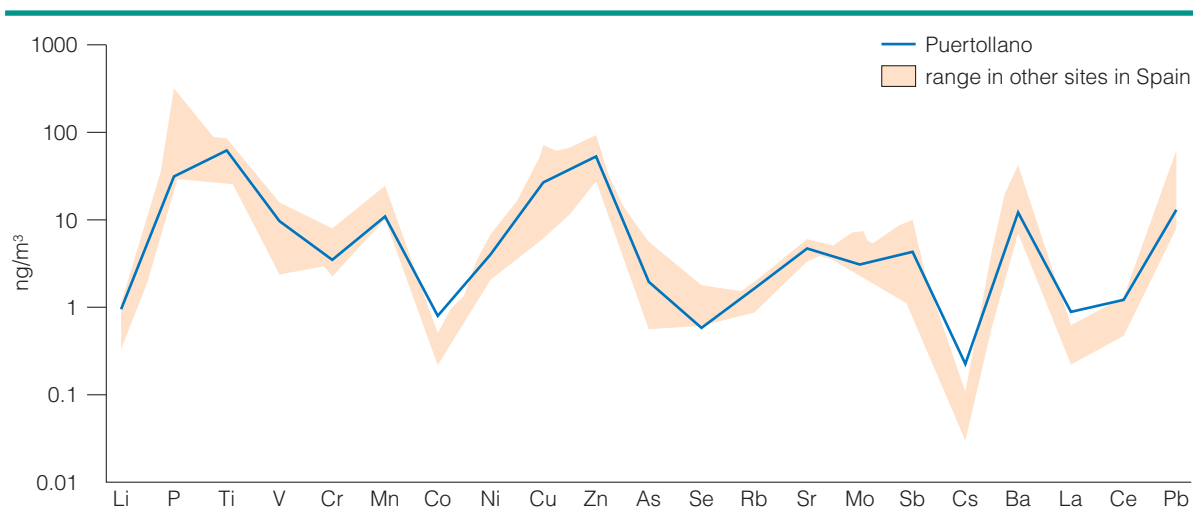


Figure 15 Concentrations (ng/m³) of selected trace elements in Puertollano compared with the range of these elements recorded from air pollution monitoring sites in five Spanish cities: Huelva, Badajoz, Burgos, Tarragona and Barcelona (Moreno and others, 2007)

The authors conclude that the results of the study show that elemental concentrations in the feed coal can be used as markers and combined with statistical analysis of the chemistry of particulate matter that may be inhaled, can be used to identify likely atmospheric contamination sources. Moreno and others (2007) consider that this is particularly relevant for the more toxic elements such as trace metals and metalloids. During the 2004-05 study period at Puertollano, atmospheric annual average concentrations of trace elements regulated by the European Union limit of 500 ng/m³ Pb and target 6, 20 and 4 ng/m³ for As, Ni and Cd values respectively, were significantly below those levels. The average values measured at Puertollano of 12 and 4.2 ng/m³ of Pb and Sb respectively in PM₁₀ and 9.3 and 3.2 ng/m³ of Pb and Sb in PM_{2.5} are mostly linked to the combustion of local coals. The results offer a step toward identifying and reducing the primary sources of such pollution (Moreno and others, 2007).

The distribution of trace elements from a bituminous coal that was fired at two different Spanish power plants installed with ESPs for particulate control was studied by López-Antón and others (2011). The comparative study aimed to assess the influence of operational variables on the characteristics of the fly ash when firing the same supply of coal. Assessment of the results obtained during experimental work at both plants was based on a comparison of the distribution and mass balances of Hg, Sb, As, Be, Cd, Co, Pb, Mn, Ni, Se, U, Ag, V, Zn, Mo and Cu in the two power plants and the RE enrichment factors of the elements in the ashes with a special focus on the fly ash fractions taken from each ESP hopper. In addition, a leachability test was performed on the fly ash. López-Antón and others (2011) observed no significant differences, especially in the case of Hg, which was mainly emitted in the gas phase, nor in the case of Be, which was concentrated in bottom ash, nor in the rest of the trace elements, which were concentrated in the fly ash. However, fly ash fractions taken from the hoppers of the ESPs revealed that some operational variables, especially the different performances of the mills, may affect/modify the composition of the fly ash significantly. Heterogeneity in the coal feed at one of the plants led to greater enrichment in the fine fly ash particles of some of the elements, such as Sb, As and Se, resulting in generally lowering their emissions to air. López-Antón and others (2011) concluded that all by-products evaluated from both facilities were considered to be inert waste suitable for disposal since their leaching concentration did not exceed the limits beyond which the waste was considered hazardous.

The effects of loss on ignition (LOI) and particle size on the concentration of trace elements in fly ash were discussed by Vervynckt and others (2007). LOI is a measure of the unburnt carbon in the ash.

Table 12 Component analysis results for Puertollano particulate matter (10 µm and 2.5 µm) samples (ng/m³) (Moreno and others, 2007)

Particulate matter (10 µm) PM ₁₀		Particulate matter (2.5 µm) PM _{2.5}	
Source 1	Source 2	Source 3	Source 1
Coal	Industrial 1	Industrial 2	Coal
Component	Concentration	Concentration	Concentration
Sb	0.93	0.93	0.67
Pb	0.89	0.84	0.67
As	0.70	0.80	0.62
Zn	0.62	0.74	0.56
Co	0.53	0.67	0.69
		Ni	0.61
		V	0.50
% Var. = 9		% Var. = 11	
Components with a loading factor <0.50 are excluded. PM = particulate matter OM-EC = organic matter and elemental carbon		% Var. = 35	

Fly ash samples from three different coal types: bituminous, powder river basin (PRB) and lignite were grouped and categorised based on LOI and particle size. Each sample was then run for LOI, Hg, As and Se concentrations, BET surface area and average pore size determination. The BET method is based on adsorption of gas on a surface. The principle of the method is that the amount of gas adsorbed at a given pressure can be used to determine the surface area. Figure 16a shows the graph of the As concentrations compared to LOI. The figure shows that as the LOI values increased, As values decreased. This was especially prominent at lower tested LOI values between 0% and 10% for all three coal types. Eventually, with LOI values >10% the trend appeared to level off for PRB coals although a downward trend was still the case. Figure 16b shows the graph of values for Se concentration as compared to LOI values. The trends for Se were not as clear as for As and appear to be more coal dependent. A very slight increase is noted for Se concentration in the fly ash from bituminous and lignite coals as LOI values increase, and Se concentrations decrease as LOI values decrease in fly ash from PRB coal. Average pore size analysis compared to LOI values showed a downward trend for each coal type indicating an inverse relationship for average pore size and LOI values. According to Vervynck and

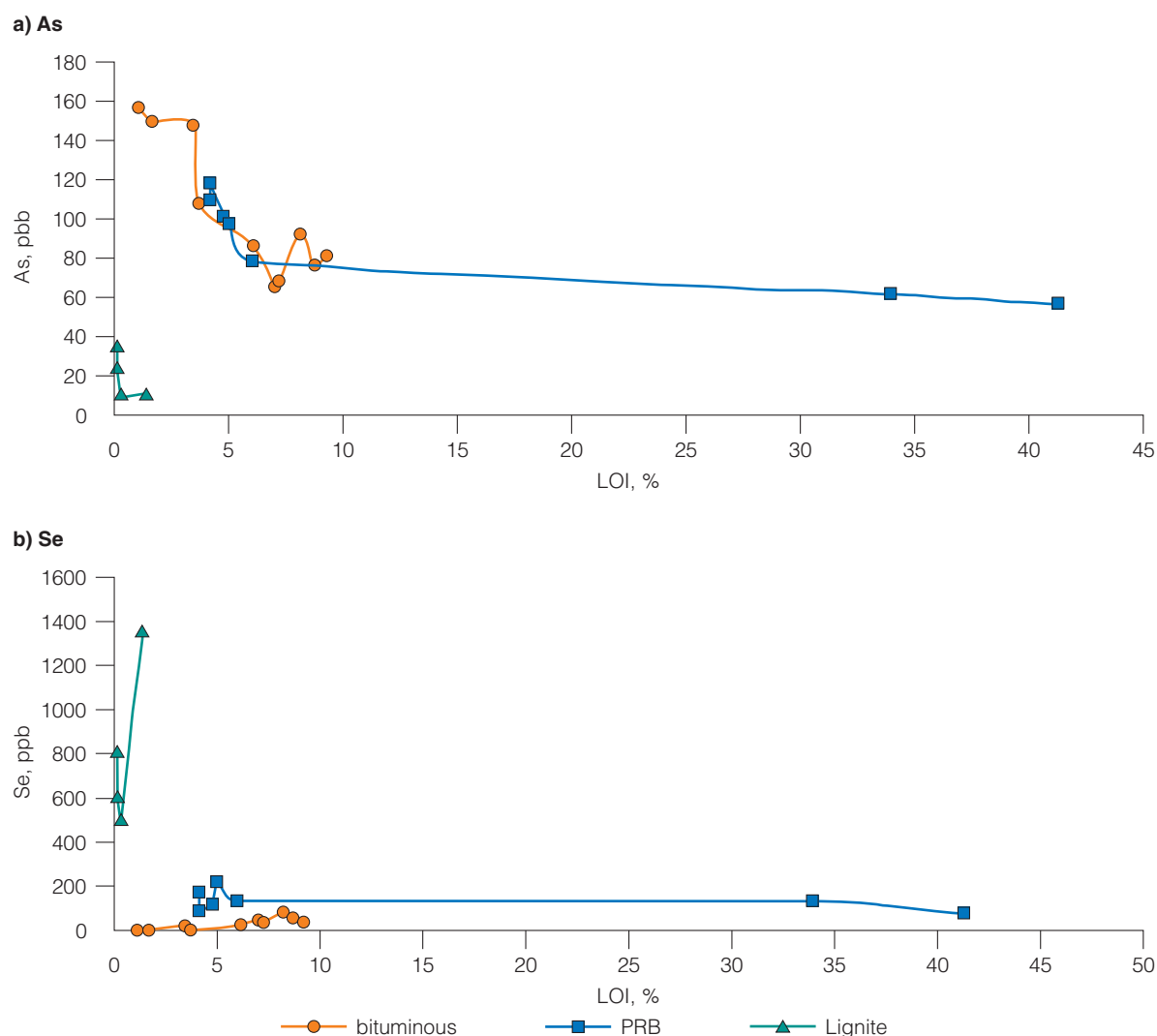


Figure 16 Concentration of As and Se plotted against LOI (Vervynckt and others, 2007)

others (2007), it can be assumed that average pore size will also have an inverse relationship to the individual elements as compared to LOI. BET surface area analysis showed that as BET surface area values increase, the corresponding LOI values also increase for all three coal types suggesting a direct relationship between the two values. Vervynckt and others (2007), conclude that BET surface area will have relationships to the individual elements that are analogous to the relationships the elements have with the LOI values.

Lecuyer and others (2004) discussed the assessment and uncertainties regarding heavy metal atmospheric emissions from Électricité de France (EDF) coal-fired power plants. A computerised tool was developed to carry out the assessment. The heavy metal partitioning factors within each plant unit were determined according to the type of unit and the coal characteristics. Heavy metals emissions, especially to air, were then deduced from the actual coal consumption and chemical composition. A first inventory of the emissions was obtained for the year 2001. Results indicated accuracy within $\pm 40\%$ for the non-volatile elements (Cr, Cu, Co, Mn, Ni and V) and for PM_{10} and $PM_{2.5}$. The uncertainty was greater at $\pm 80\%$ for the volatile elements (As, Pb and Zn). Excess values were obtained for elements which are both volatile and at low concentration in coal including Hg, Se and Cd (Lecuyer and others, 2004).

Trace elements in atmospheric particulate matter over a coal (lignite) firing power generation area of

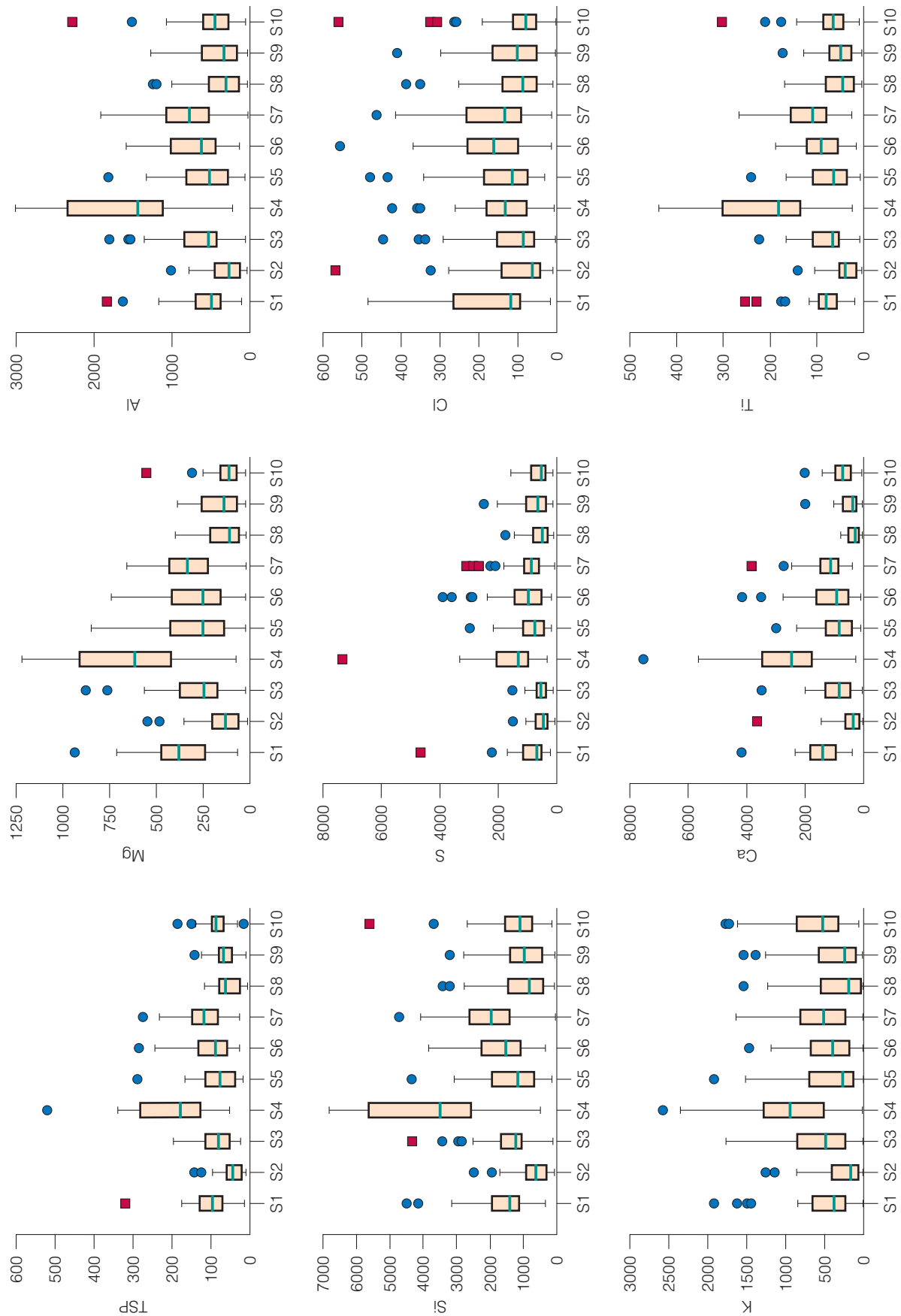
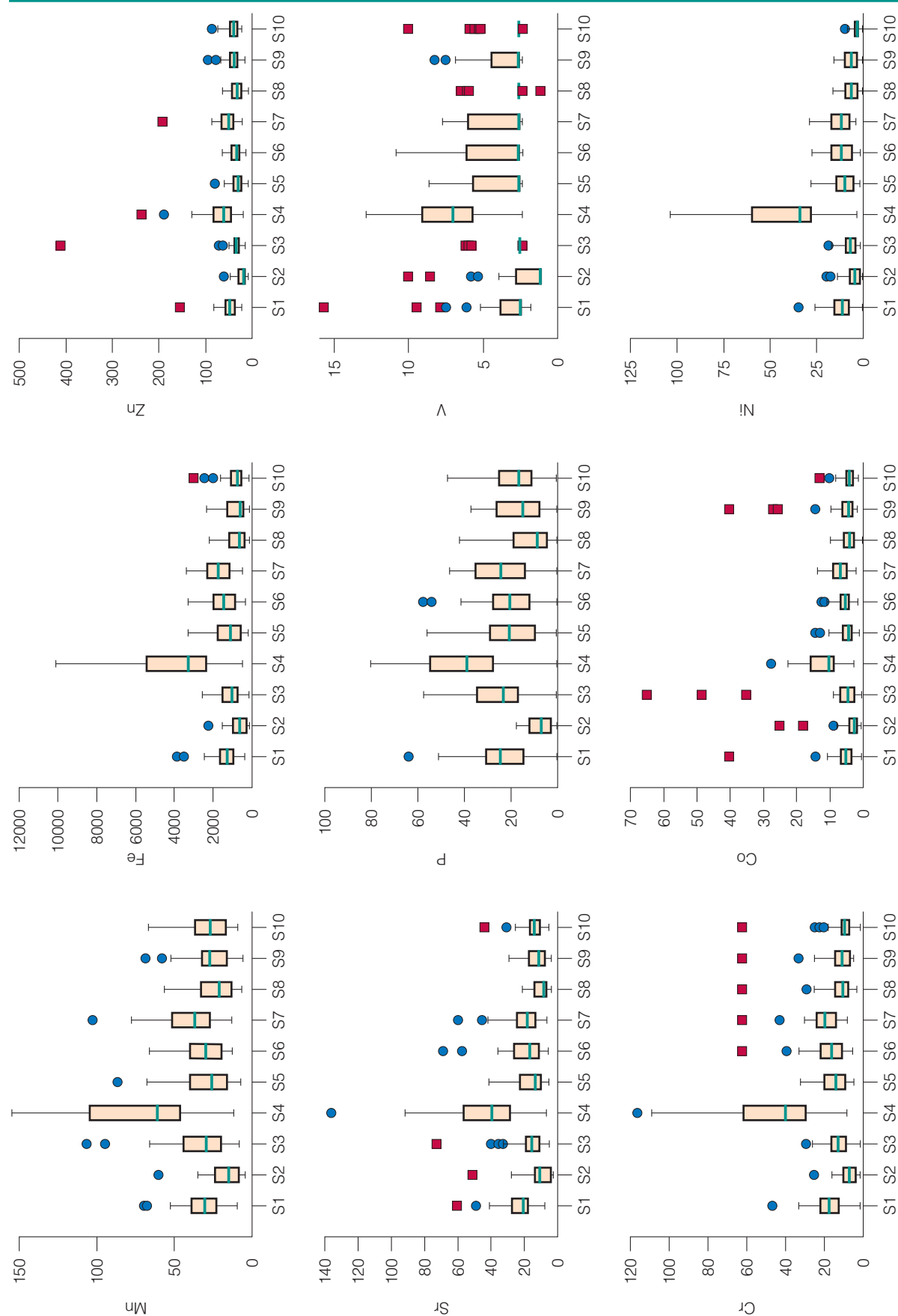
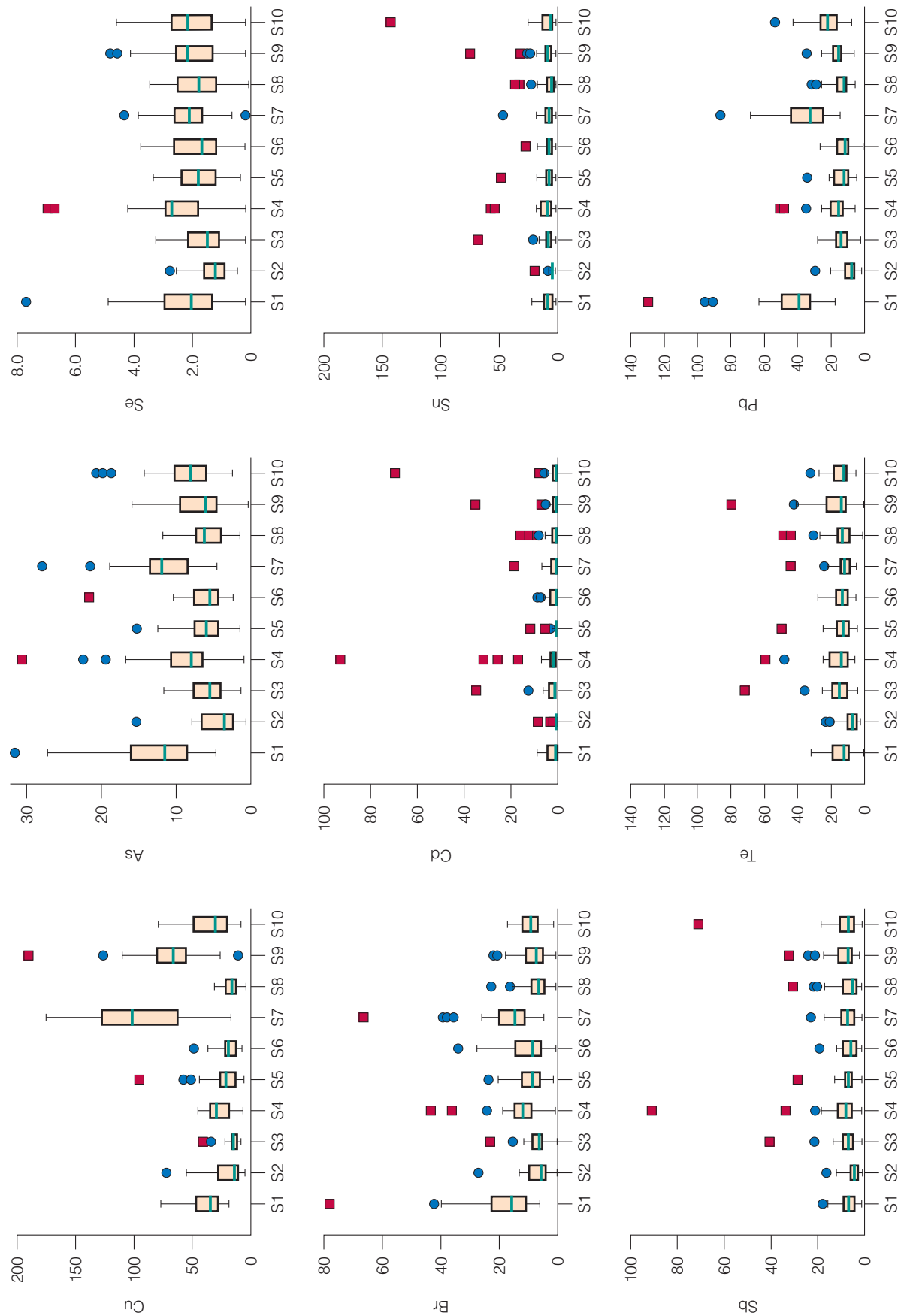


Figure 17 Concentrations of TSP ($\mu\text{g}/\text{m}^3$) and associated elements (ng/m^3) at the ten sampling sites in the Eordea basin (western Macedonia, Greece) (Petaloti and others, 2006)





Western Macedonia (Greece) was the subject of a study by Petaloti and others (2006). The study was conducted over a one-year period (November 2000 to November 2001) at ten sites located at variable distances from the power plants. A total of 336 (24-hour) particulate matter samples were analysed for 27 major, minor and trace elements. Figure 17 shows the concentrations of particulate matter ($\mu\text{g}/\text{m}^3$) and associated elements (ng/m^3) at the ten sampling sites. Box plots show the median, inter-quartile range, outliers (for example, cases with values between 1.5 and 3 box length from the upper and the lower edge of the box) and extreme values (for example, cases with values more than 3 box lengths from the upper and the lower edge of the box) of individual variables. Figure 18 shows the profiles of the total suspended particulate matter at the same sites. These show that almost all elemental components (except Cd, Sn and Sb) exhibited significant differences among sites. The differences are attributed to the variable distance from the emission sources and the prevailing weather conditions. The EC annual emission limits for particulate matter of $15 \mu\text{g}/\text{m}^3$ were exceeded only at one of the sites. The site was located closest to the power stations and the lignite conveyor belts. Enrichment factor (EF) calculations showed that at all sites, the most enriched elements ($\text{EF} > 100$) were S, Cl, Cu, As, Se, Br, Cd and Pb suggesting that their atmospheric concentrations are primarily due to emissions released directly into the atmosphere. Major sources of these elements are considered to be automotive emissions and coal firing. Low EF values (<5) were found for Mg, Al, Si, K, Ca, Ti, Mn, Sr, P, V, Cr, Ni at all the sampling sites indicating that these elements originate mainly from soil or road dust suspension.

Petaloti and others (2006) concluded that statistical analysis indicated insignificant seasonal variation for the total suspended particulate matter concentrations at all the sites. However, significant seasonality was found for some elements including Cl, As, Pb, Br, S, Se and Cd at some sites. The highest concentrations were recorded during the cold period suggesting more intense emissions from traffic, domestic heating and other combustion sources. Concentrations significantly higher during the warm period of the year were found at other sites for the crustal and traffic-related elements Ti, Mn, P, Cr, K, Al, Te, Mn, Fe, Sr, P and Cu. The authors consider that this suggests stronger influence from soil and road dust resuspension in the warm months. Finally, influences from power generation were considered likely at the sites located nearest to the power plants and mining activities.

4.4 Discharge to soil and water

The leaching behaviour of cadmium (Cd), arsenic (As), zinc (Zn) and chlorine (Cl) in the ash from coal-fired plant was investigated by Zhao and others (2006). According to the authors, 74% of the fuel and energy in China comes from coal and 64% of chemical materials are coal-derived products. Coal-combustion residues produced in China in 2000 amounted to 153 million tons (139 Mt). The residue is often used as insulation or construction material or for soil enrichment. As in other countries, the potential leaching of these and other trace elements to water and soil are of concern to the authorities and hence resulted in a number of investigations on the subject.

Zhao and others (2006) collected samples from a Chinese coal-fired plant. Phase composition of the collected samples was carried out using optical microscopy and X-ray diffraction (XRD) techniques. The concentrations of minor and trace elements in the samples were determined by instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS). Sequential extraction experiments were used to characterise the occurrences or phases of the As, Cd and Zn in the samples studied. The investigation involved the utilisation of column leaching under different pH conditions varying from 2.0, 4.0, 6.0 and 7.5 during various leaching durations (up to 80 h).

In their conclusions, Zhao and others (2006) found that elements enriched on the surface of the ash samples and occurring in water-soluble and ion-exchangeable phases as well as the Fe-Mn oxide phase are easily leached, whereas elements enriched inside the sample particles and occurring in the organic matter and silicates phases are less likely to be leached. The authors also concluded that, the cumulative percentage of Zn, As, Cl and Cd leached in C and ash increase with decreasing pH values,

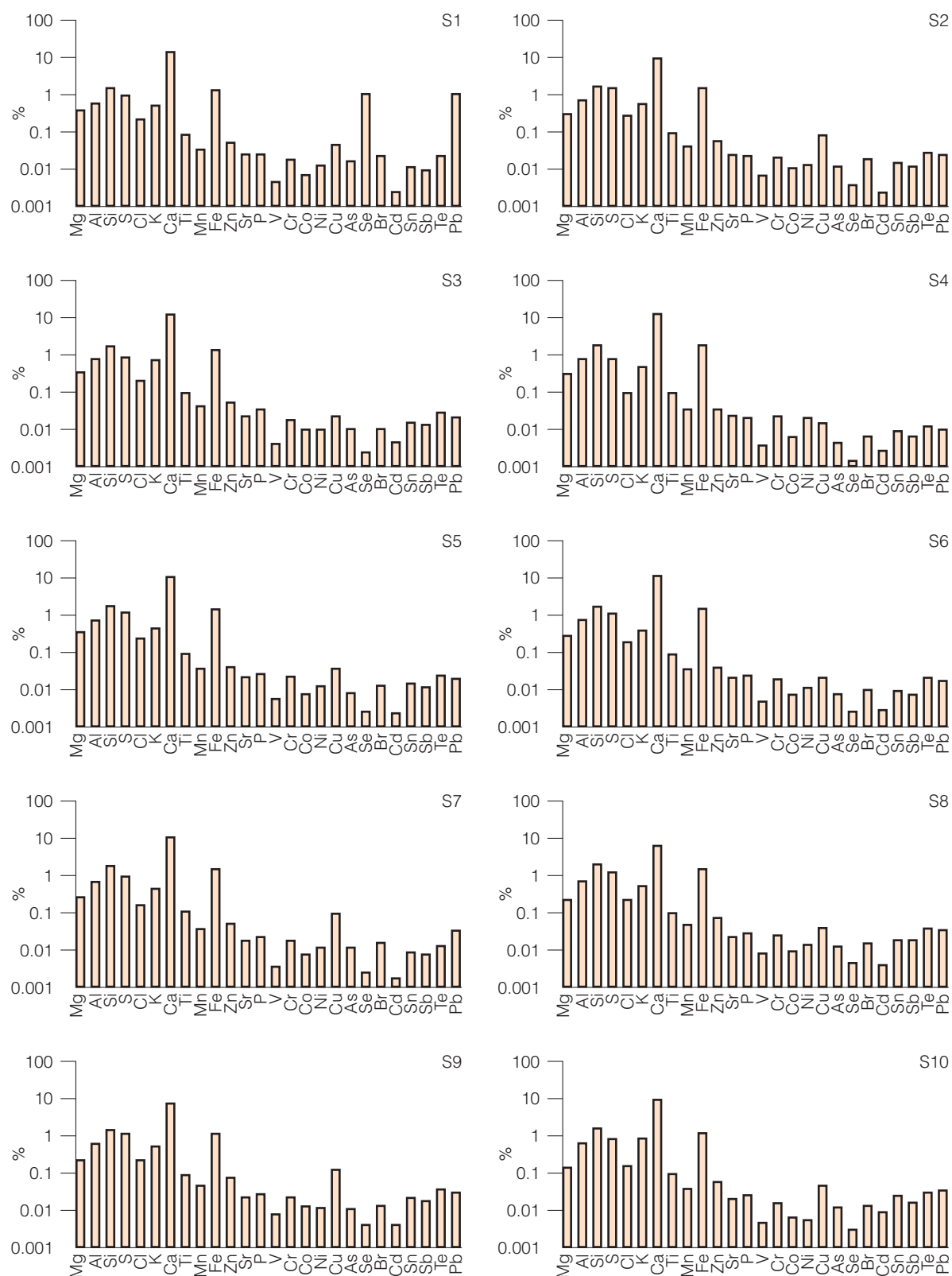


Figure 18 Elemental profiles of TSP at the ten sampling sites in the Eordea basin (western Macedonia, Greece) (Petaloti and others, 2006)

that is, the more acidic the leaching solution, the higher the leaching rate. The leaching rates of As and Cl in C and ash samples were found to be higher in comparison with those of Zn and Cd. However, the maximum concentrations of Cd in the leachate from the feed coals were in excess of or close to their standard concentrations permitted in the Chinese Standards for Drinking Water and Surface Water. In the leaching process, the concentration of Cd, Cl and As in the leachates changed continuously during the experimentation timescale of 80 h, and no equilibrium condition was reached. Zhao and others (2006) therefore consider that a longer time for leaching experimentation is necessary for the evaluation of the impact of these trace elements on aqueous environments. The authors also stated that it is difficult to establish models for the leaching behaviour of Cd, Zn, As and Cl in coal and coal ash.

Stankova and others (2011) studied the use of nanosecond laser ablation (LA) techniques for the analysis of some trace elements in fly ash. LA is used for the characterisation of fly ash. The technique is highly sensitive and relatively flexible with respect to the physicochemical properties of a solid matrix. However, it has a drawback in that it lacks accuracy and therefore its use is mainly in research and not as a routine analytical tool in laboratories. In the study, six reference materials were investigated. These included fly ash from coal combustion in Poland, the USA, Germany, Hungary and the Czech Republic. The study also included fly ash from some incinerators. Difficulties arose from the fly ash analysis mainly due to pellet preparation. The samples had no self-bonding properties so several binders were evaluated to convert the fly ash material into pellets. Addition of a binder was thus necessary to obtain compact and mechanically-stable pellets resistant to the LA process. However, this led to sample dilution into the binder. A chromophore, added to the binder, increased sensitivity but did not fully compensate for the 1:1 ratio dilution. The LA techniques used allowed the detection and quantification of V, Cr, Mn, Ni, Cu, Zn, Sr, Ba, As and Pb. However, Stankova and others (2011) concluded that the difficulty with this procedure was to adapt the calibration range to the determined concentrations, noting that a careful selection of the certified reference materials (CRMs) employed for calibration have to be made. The authors consider that, for instance, a semi-quantitative analysis of the sample should be made first to adapt the selection of calibration standards.

Element mobility, that is element leaching, from stored fly ash in Australia was the subject of a field study by Ward and others (2009). Potential barriers to the use of fly ash from coal combustion have focused primarily on concerns about leaching of trace elements from the fly ash. In addition to the total metals content of the fly ash, the potential for leaching is influenced by the crystallinity of the ash. This is because crystallinity determines whether the metals are incorporated within the glass phase or within crystalline compounds which hydrate. The leachability of the trace metals therefore depends on the boiler design and remains relatively constant for a given source of ash. The benefits and barriers to land uses of coal-fly ash were researched by Smith (2005). The purpose of the in-depth study by Ward and others (2009) in part was to compare the results of laboratory leaching tests to ash behaviour and element release under field conditions. It also intended to evaluate any changes in leaching behaviour of key elements in the ash associated with long-term storage. The installed capacity of coal-fired power generation in Australia during 2005 was ~29 GW and produced approximately 14.55 Mt of ash. As no flue gas desulphurisation (FGD) technology was utilised due to the use of low-sulphur coals, most of the waste product (85–90%) was fine fly ash and the remainder mainly coarser bottom ash. Around 2 Mt/y of the ash is sold mainly for use in the cement and concrete industries. A further 4 Mt/y is used for other purposes such as structural fill, road construction and mine backfill. The remaining ~7 Mt/y is stored as a resource for possible future use, either under water in ash ponds (lagoons) or above the water table in dry disposal sites.

Ward and others (2009) found that leaching of many of the trace elements in the acid fly ash evaluated in the study depends on the pH of the ash-water system. Partly as a result of pH changes and partly due to loss of material from the ash into solution, leaching of many trace elements from water-stored ash is different to that of the same elements from dry fresh fly ash samples. The authors concluded that the concentrations of most elements in the laboratory test leachates are of a similar order of magnitude to the concentrations of the same elements in the water in the actual ash pond. This

increased the confidence in the use of laboratory tests to provide guidance on the expected behaviour of the ash when exposed to water in field situations. The influence of coal fly ash application on trace element mobility and distribution in soil, plant and leachate was also the subject of a review by Manohara and others (2007).

Adnadjevic and others (2009) studied the prevention of trace and major element leaching from coal combustion products by treating the coal ash hydrothermally. Coal ash is the most widely examined raw waste material for obtaining ion-exchanging materials, particularly zeolites. A zeolite may be defined as a crystalline hydrated aluminosilicate whose framework structure encloses cavities (or pores) occupied by cations and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration. A zeolite is commonly used as commercial adsorbent. Methods for converting portions of coal ash into zeolites usually comprise heating coal ash with alkaline solutions. Concentrations of reactants, reaction time, temperature and composition of the coal play an important role in zeolite synthesis. Zeolites obtained hydrothermally may be used as sorbents for heavy metals. The goals of experiments carried out by Adnadjevic and others (2009) were to develop zeolite material from coal combustion ash from the Nikola Testa A, coal-fired power plant located near Belgrade, Serbia. The purpose of the study was also to establish potential application of the resultant ion exchange material in order to prevent leaching of selected trace and major elements from deposited coal ash. Adnadjevic and others (2009) concluded that the amorphous phase of coal ash (that of meta-kaoline nature) can be effectively and entirely transformed, hydrothermally, into zeolite material. In the experiments, when the zeolite obtained from coal ash was added in moderate proportion (5%) to the coal ash itself, a significant decrease (>10%) was noted in the amounts of some extracted elements, for example, adsorbed Zn and ion-exchangeable Cr from samples of both power plants and ion-exchangeable Cu from another power plant ash. Concentrations of the majority of the other examined elements remained the same or there was no significant decrease of leached concentrations. The authors consider that this proved that simple adding of limited amounts of coal-ash-originated zeolites cannot prevent leaching of some trace and major elements from the waste disposal site. Concentrations of water- and ammonium-acetate extracted Fe and Mn increased after the samples were spiked with the hydrothermally treated coal ash. Adnadjevic and others (2009) attribute this to the formation of additional leachable fractions of these elements during the hydrothermal treatment of ash itself. Finally, the authors state that treatment of coal ash leachates with zeolites from coal ash is an effective method to reduce toxic trace and major elements release to the environment.

The reduction of trace element leaching in brown coal fly ash using geopolymers was studied by Bankowski and others (2004). Geopolymers, according to the authors, are used for waste stabilisation. They function in terms of encapsulation, which may be physical or chemical, and provide acid resistance, compressive strength, durability and thermal resistance. Synthesis of geopolymers involves using material with silica and alumina in the correct ratios and activated by an alkali metal hydroxide to produce a three-dimensional inorganic amorphous structure. According to Bankowski and others (2004), who discuss geopolymerisation in detail, the principles of geopolymers involve the synthesis of aluminosilicate oxides (Al^{3+} in four-fold co-ordination) with alkali polysilicates to give polymeric Si-O-Al bonds. It can be carried out with clay or pozzolanic material that dissolves partially in alkali solution and is therefore a source of geopolymeric precursors. The alkali solutions dissolve the alumina and silica precursors and hydrolyse the surface of particles, allowing reactions to occur between already-dissolved silicate species and the particle surface. Materials such as kaolinite, black coal fly ash and waste slags as well as alumino-silicate minerals can be used as a basis for geopolymerisation. Bankowski and others (2004) consider that geopolymers, as a means of stabilising waste, have shown great potential. The aim of their study was to determine the effectiveness of stabilising brown coal fly ash against leaching by using geopolymer material.

The geopolymer material used in the study was blended with fly ash. Bankowski and others (2004) found that the formation of the geopolymer is reduced as the percentage of the added fly ash is increased. In matrices containing 60 wt% precipitator fly ash (PFA), collected from the hoppers of the

ESPs, there was insufficient geopolymer to provide adequate stabilisation. Leached fly ash (LFA) was collected from ash disposal ponds. The addition of PFA (over 60 wt%) and LFA (over 70 wt%) failed to produce matrices that cured into geopolymeric materials, placing the maximum loading at these values. Based on experimental work involving scanning electron microscopy imaging, the authors determined the mechanism of particle encapsulation based on the interaction between fly ash and the geopolymer. For lower percentage fly ash (20 wt%) images showed that fly ash is completely dissolved and encapsulated by the geopolymer. At 40 wt% fly ash, the geopolymer was diluted by the fly ash and it appeared that surface reactions bind the waste particles together. At 60 wt% fly ash, the geopolymer was unable to stabilise the waste due to dilution by the fly ash. Bankowski and others (2004) considered that the formation of gypsum and calcium sulphate hydrates could have led to the consolidation of the waste but not stabilisation.

Bankowski and others (2004) concluded that leaching of Ca and K was reduced by the geopolymer. Lower leaching rates were noted with the LFA which had been in contact with water prior to stabilisation compared to the PFA. Heavy metal stabilisation was greater in PFA than LFA for the same reason. Significant reductions in leaching were found for Ca, As, Sr, Se and Ba. The geopolymer was found to be effective at stabilising low percentages of fly ash, but less effective when the percentage of fly ash increased. The authors stated that there appeared to be potential in using this type of stabilisation, however further research is required into optimising geopolymer formation for this type of fly ash.

Wen-dong and others (2005) reported on the distribution and environmental impact of Se in wastes from a coal-fired power plant. The authors collected and studied samples of the coal, fly ash (coarse and fine) and slag. They found that Se tends to be enriched in fly ash particles $>19.0\ \mu\text{m}$ in size. They considered that the particle distribution was determined by the volatility and organic occurrence of Se in the coal, the residence time in the flue gas and the morphology of particles (that is the holes on the surface of the particles $>19.0\ \mu\text{m}$ which may result in greater adsorption of Se). Wen-dong and others (2005) also carried out a sequence leaching test which indicated that Se is mainly bonded organically in coal, ~69.7%. Mass balance calculations of the coal fired at the plant showed that ~16.5% of the Se in the coal may be released to air directly. Wen-dong and others (2005) concluded that the environmental impact of releasing Se to air is minor and releasing it into soil lacking in Se, may be beneficial.

The mass balance of major and trace elements in the Soma coal-fired power plant in western Turkey, which consists of six 165 MW units firing local coal from two different mines was the subject of a study by Karayigit and others, (2006). A total of 48 samples, feed coal, fly ash and bottom ash were collected and evaluated for major and trace elements including Al, Ca, Fe, K, Mg, Mn, Na, Ti, S, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Cs, Ga, Ge, Hf, Hg, Li, Mo, Nb, Ni, P, Pb, Rb, Sb, Sc, Se, Sn, Sr, Ta, Th, Tl, U, V, Y, Zn, Zr and the rare-earth-elements (REEs), to obtain knowledge on their behaviour during coal combustion. Comparison between fly ash and bottom ash using their ratios of relative enrichment factor for fly ash to relative enrichment factor of bottom ash showed the following (Karayigit and others, 2006):

- elements indicating enrichment in the fly ash ≥ 1.2 are Hg, Bi, Cd, As, Pb, Ge, Tl, Sn, Zn, Sb and B;
- elements showing enrichments in bottom ash ≤ 0.8 are Ta, Mn and Nb. Enrichment of Se, Ca, Mg, Na, Fe and Cu was also noted in bottom ash relative to the fly ash;
- the remaining elements investigated in the study had no clear segregation between the fly ash and the bottom with enrichment ratios between 0.9 and 1.1.

Turkish coal reserves are estimated to be in the order of 8.3 Gt of lignite and 1.4 Gt of bituminous coal. Total annual lignite production in 2002 was ~52 Mt of which 82% was used for power generation. The total power generation capacity from coal in Turkey is approximately 6.4 GW, 95% of which is generated from lignite-subbituminous coal and 5% from bituminous coals (Karayigit and others, 2006).

The potential impact on fly ash derived coagulants with regard to the heavy metal content of these ashes was the subject of a study by Fan and others (2006). Experimental research was carried out analysing the distribution of 15 trace elements (including As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Ti, Ag, Co, Mo, Mn, Zn and Sr) in 32 samples of fly ash collected from Australia, Canada, China and the USA. The authors found that the concentrations of trace elements in fly ash can vary by more than one order of magnitude. The concentration distribution ranges were As: 1~100 ppm, Ba: 10~500 ppm, Cd: 0~5 ppm, Cr: 40~400 ppm, Cu: 30~250 ppm, Hg: 0~0.6 ppm, Ni: 20~400 ppm, Pb: 1~30 ppm, Ti: 5~40 ppm, Ag: 0~0.7 ppm, Co: 15~170 ppm, Mo: 1~35 ppm, Mn: 10~410 ppm, Zn: 150~470 ppm and Sr: 5~750 ppm. The concentration of trace elements was found not only to differ from country to country but also from plant to plant. According to Fan and others (2006), the expected maximum dosage of heavy metals during coagulation can be estimated from the ratio of Al and Fe to each of the 15 elements above. However, the authors consider that the assumptions made would grossly exaggerate heavy metals remaining in the wastewater. Fan and others (2006) concluded that because the range of trace elements in the tested fly ash samples varied greatly and the potential risk of introducing heavy metals into the wastewater, fly ash and wastewater coagulated with coagulants produced from fly ash, should be thorough analysed before use of these coagulants.

The fate of arsenic (As) in coal ash in India was investigated by Pandey and others (2011). In 2011, India with 3.4% share of global energy consumption, ranked sixth in the world as an energy consumer. Total demand for electricity is expected to exceed 950 GW by 2030. Electricity generation in the country is mainly dependent on coal. In 2005-06 fly ash from coal combustion in India reached 112 Mt and is expected to increase to 150–170 Mt/y by the end of 2012. The coal fired in the majority of the plants is domestic. It is characterised by low S, high ash (35–50%), refractory nature of its ash, low Cl content, low toxic trace elements, high ash fusion temperature and low Fe content in the ash. The waste ash by-product is disposed of, in general, in ash ponds.

According to Pandey and others (2011), there are three dominant forms of As that are found in coal. These are sulphides, organic and arsenate forms, the most common form being sulphides. Other possible forms in clay include arsenopyrite. Pyrite is considered a main carrier of As, while arsenopyrite can be a minor host. As may be present in the coal in organic and inorganic forms. The authors highlight that the first case of As poisoning occurred in Inner Mongolia, an autonomous region of China, in 1990. Also, that Guizhou in China is the only known arsenocosis endermic area caused by As contaminated coal. In eastern India, coal combustion is considered one of the major source of anthropogenic As emission in the biosphere.

Following coal combustion, As is concentrated in particles as well as in volatile form. The concentrations of As species in the flue gas depend to a large extent on temperature and chemical interactions with the fly ash. A significant amount of As is captured in the fly ash. However, the fate of As is dependent not only on temperature but also on condensation-vaporisation processes, the presence of Ca, as well gaseous S and Cl compounds in the flue gas. Elemental As and As oxide form, As_2O_3 , are considered the most probable As species in the oxidising flue gas environment in a coal combustion process. However, as the latter, As_2O_3 , is much more volatile, researchers concluded that As could only be present in the flue gas in the form of an oxide. Thermodynamic modelling shows that 6.6% As is captured in combustion wastes (slag) at temperatures lower than 926°C. As escapes in the gas phase in the form of AsO and As_2O_3 during combustion temperatures ranging from 1000°C to 1200°C. At higher temperatures, 1200°C to 1600°C, only the As_2O_3 species is released. However, As concentration in the combustion residues varies widely and depends on several factors including coal quality, flue gas temperature at particulate collection point, pH of the ash and ignition conditions. The values range from 2 to 240 ppm in the fly ash and from 0.02 to 168 ppm in the bottom ash. According to Zevenhoven and others (2007), the combustion of coal and biomass fuels can result in As emissions, ranging from 0.1 to 8.0 mg/kg (dry), to the atmosphere.

Pandey and others (2011) found that there is a lack of studies on the fate of As in ash from coal combustion. Due to the high amounts of ash disposed of in ponds and utilised in industry in India,

which continues to increase, the authors question the effects on human health, agriculture and the natural ecosystems. Over 38% of Indian fly ash was utilised in recent and current years mainly in civil construction, building materials and some in agro-forestry. The presence of trace elements, mostly As, has become a subject of concern due to worries about contamination of soil as well as surface and ground water and potentially inhibits more widespread utilisation of these ashes on a sustainable basis. The authors concluded that measures should also be taken to check the release of As, as well as other trace elements, from the ash ponds and subsequent mixing with ground water. Means of reducing trace element release to all media include firing quality coal and temperature control during the combustion process as the latter is a key factor for minimising As and other trace element formation. Underground lining in ash ponds can be used to prevent direct contact of the ash pile with top soil and the local drainage system. Use of lime (CaO) and sorbents such as activated carbon as flue gas scrubbing agents can also be used to capture As and other trace elements. Analysis of fly ash heavy metal content and disposal in three coal-fired power plants in north India was the subject of a study by Sushil and Batra (2006). Experimental chemical treatment of coal fly ash to reduce the mobility of priority trace elements such as As, B, Cr, Mo, Ni, Se, Sr and V was the subject of a study by Bhattacharyya and others (2009). A long-term risk assessment management option for the bulk utilisation of fly ash from coal-fired power plants for horticulture in India was the subject of a study by Ansari and others (2011).

The leaching characteristics of heavy metals in fly ash from a coal-fired power plant in China, that fires Inner Mongolian lignite, was the subject of a study by Gong and others (2010). The heavy metals considered in the study were Cd, Cr, Pb and V. Fly ash from each hopper of a three-field ESP was used in long-term batch leaching tests. The samples were collected from each hopper and prepared for analysis. These are represented by particle size and distribution in Figure 19 as FA1, FA2 and FA3. Particle size in FA1 was found to be significantly higher than particles in FA2 and FA3 with the volume average particle size being 87.79 μm , 18.11 μm and 9.32 μm respectively. Elemental analysis results of the fly ash are given in Table 13. The data show that Si and Al are dominant elements in the samples. With decreasing particle size, Al, Mg, Ni and Cr also decreased but S, Ca, Cd, Pb, Cu and Zn increased significantly. Leaching tests were undertaken with leaching solutions prepared in the laboratory. Each sample was tested three times and the standard deviation for all the tests results were <2%. Gong and others (2010) show the relationship between the sample pH value and leaching time in Figure 20. As the figure shows that after 15 minutes the leachate sample is alkaline in both acidic (pH = 4) and alkaline (pH = 10) conditions, the authors consider that FA1, FA2 and FA3 are all alkaline fly ash. After approximately two hours of leaching, the pH value tended to be stable. The leachate of FA3 was found to have a relatively high pH value which stabilised at about pH 11.0 while FA1 and FA2 were stable at about pH 10.0. Gong and others (2010) concluded that the leachability of the trace elements in the fly ash is affected by the time of leaching. The leachability of Cd, Cr and Pb

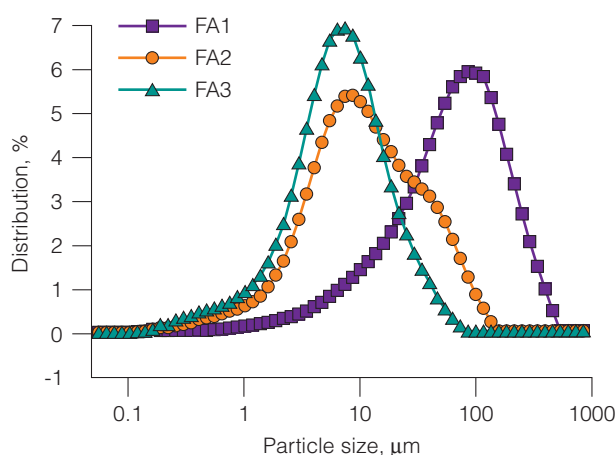


Figure 19 Particle size distribution of fly ash
(Gong and others, 2010)

continued to increase after a week of experimentation. The leachability of Cr was found to be higher with the leaching in acidic solution (pH = 4) and the leachability of Pb was found to be higher with the leaching in alkaline solution (pH = 10).

Marrero and others (2007) discussed the characterisation and determination of 28 major, minor and trace elements in fly ash collected from the hoppers of the ESP of the San Nicolás thermal only coal-fired, 1200 MW, power plant near Buenos Aires (Argentina). The subbituminous coal fired at the facility is imported from Australia, Colombia or South-Africa. The trace elements to be characterised and determined included

Table 13 Trace element analysis of fly ash from a Chinese lignite-fired power plant (mg/kg)
(Gong and others, 2010)

Element	FA1	FA2	FA3
Al	206,400	191,500	176,200
Ca	72,450	76,550	104,100
Cd	4	9	11
Cr	86	77	71
Cu	34	48	67
Fe	133,100	79,450	79,350
K	20,650	25,650	23,750
Mg	12,450	11,570	5,686
Mn	9,13.0	7,52.8	1,076
Na	6,167	6,782	4,774
Ni	648	501	266
Pb	143	159	197
S	4,000	8,000	10,550
Si	531,300	568,200	554,300
Ti	11,750	12,200	11,750
V	1,821	2,430	2,330
Zn	111	223	265

As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, V and Zn. No attempt was made during the study to characterise the coal itself. Seven samples of fly ash were collected during seven consecutive days and as in previous studies chemical and physical characteristics of the ash were tested as well as enrichment factors and element concentrations in fly ash. The results showed that the use of different techniques to characterise complex combustion by-products such as fly ash provides morphological information as well as chemical composition (metals, metalloids and rare earth elements). Marrero and others (2007) concluded that the use of inductively coupled plasma optical emission spectrometry (ICP OES) is a fully adequate technique for the multi-elemental determination of metals and metalloids in fly ash. Instrumental neutron activation analysis (NAA) is particularly suited for the determination of many trace elements in fly ash mainly because of its high sensitivity and selectivity. However, the authors noted that a nuclear reactor and a special laboratory are required and radioactive waste is produced with NAA. Table 14 summarises the mean, maximum and minimum concentrations of the 28 elements in the fly ash samples. Finally, the study shows that Fe (41,870 µg/g) >> V (1137 µg/g) > Ni (269 µg/g) > Mn (169 µg/g) are the main components in the fly ash and that As > V >> Sb > Sc > Pb exhibited the highest enrichment factor (Merrero and others, 2007).

4.5 Cofiring with biomass

Energy Research Centre of the Netherlands (ECN), KEMA Nederland B.V. and TU Delft formed a research and development consortium, with the collaboration of the Dutch power generating sector, to address biomass cofiring issues. The fate of trace elements in biomass cofiring was part of the project.

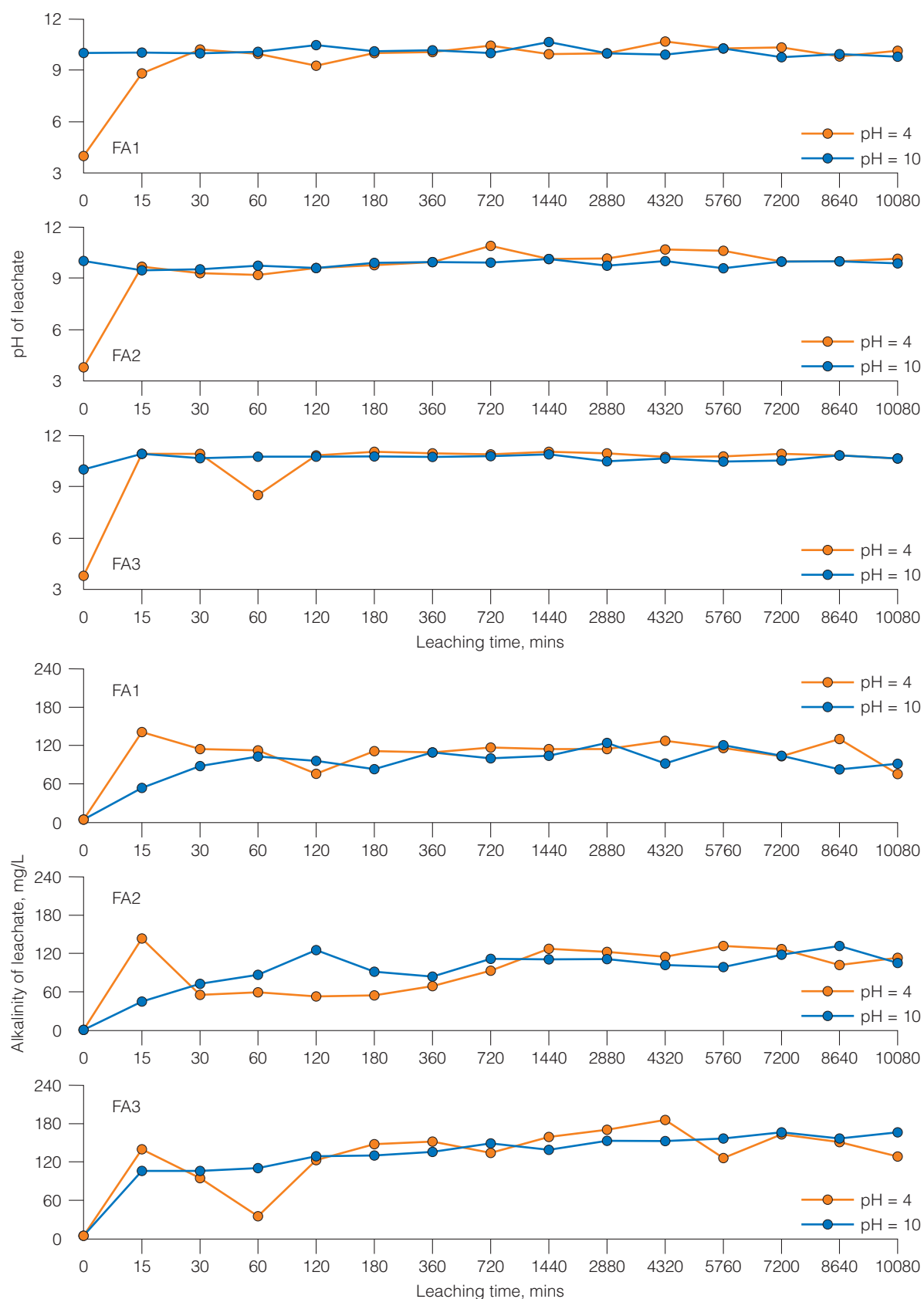


Figure 20 Leachates pH value and leachates alkalinity (Gong and others, 2010)

Table 14 Metals and metalloids in fly ash from the San Nicolás thermal, 1200 MW, coal-fired power plants near Buenos Aires (Argentina), determined by inductively coupled plasma optical emission spectrometry (ICP OES) or neutron activation analysis (NAA) (Marrero and others, 2007)

Element	Minimum, µg/g	Mean, µg/g	Maximum, µg/g
As	23.3	23.7	24.3
Ba	250	303	390
Ce	72.6	98.0	104
Cd	–	not detected	–
Co	24.4	30.4	32.8
Cr	43.3	59.8	65.6
Cs	2.16	2.94	3.20
Cu	60.3	61.3	66.6
Eu	2.22	3.08	3.41
Fe	30,920	41,870	44,290
Gd	6.15	8.53	10.0
Hf	7.6	10.4	10.8
La	34.2	44.4	46.7
Lu	0.82	1.14	1.18
Mn	262	269	281
Ni	270	278	297
Pb	87.4	91.6	93.5
Rb	24.0	28.5	33.0
Sb	1.49	1.82	1.98
Sc	27.8	37.4	38.9
Sm	9.41	12.7	13.6
Ta	0.78	1.30	1.66
Tb	1.29	1.94	2.09
Th	10.8	14.6	15.1
U	4.70	5.18	5.50
V	1128	1137	1163
Yb	5.12	6.97	7.41
Zn	60.3	66.1	76.7

Boersma and others (2011) reported on the findings which included studying all aspects of biomass cofiring including the fate of trace elements. The trace elements considered in the study included F, Br, As, B, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Te, Ti, V and Zn. The overall objectives of the project were (Boersma and others, 2011):

- setting up a knowledge database on the behaviour of trace elements at biomass cofiring percentages (>5–10% on energy basis) and for advanced ultra-supercritical and oxy-fuel,

- coal-fired power plants. The database would include knowledge on the mechanisms of formation and speciation of trace elements under such conditions;
- formulation of design and operating guidelines to control the emission of critical trace elements. Particular attention would be given to upgraded flue gas desulphurisation (FGD) units and the ultra-supercritical and oxy-fuel combustion in combination with flue gas cleaning and CO₂ removal.

A combination of three differing approaches was taken to obtain data on the speciation of trace elements. These included thermodynamic equilibrium calculations (modelling), measuring campaigns at full-scale power generating plants (full-scale measuring campaigns) and laboratory-scale experiments. The approaches are considered complementary by Boersma and others (2011) and according to the authors, each have their merits and their limitations. By combining these, greater understanding of speciation can be derived. Moreover, modelling and laboratory-scale experimentation allow the conditions to be extended to advanced clean coal technologies such as ultra-supercritical and oxy-fuel combustion. The three approaches and the trace element speciation within each approach are shown in Table 15.

Boersma and others (2011), based on the availability of the biomass for energy use and suitability for cofiring, concluded that the main biomass products to be considered are woody biomass, oils and residues from the food industry. However, new types of biomass such as torrefied biomass, aquatic biomass and residues from bio-fuel production may also play a prominent role in cofiring. This depends on developments in such biomass and biofuel markets. Torrefaction of biomass can be described as a mild form of pyrolysis at temperatures typically in the range 200–320°C. During torrefaction the biomass properties are changed to obtain a much better fuel quality for combustion and gasification applications. Torrefaction combined with densification leads to an energy dense fuel carrier of 20–25 GJ/t (*see* Figure 21; Mitchell and others, 2007). Torrefied biomass can lead to an enrichment in trace elements due to partial devolatilisation.

Boersma and others (2011) concluded that, based on the thermodynamic modelling and laboratory-scale and direct measurement of ashes from the BS-12 operating coal-fired power plant (discussed in Chapter 3), the speciation of some trace elements depends on the type and composition of the biomass, for example a high amount of Ca in woody biomass. The redox conditions in the boiler as well as during the flue gas cleaning processes also play a role leading to the formation of higher valent species. Redox (reduction-oxidation) conditions refer to all chemical reactions in which atoms have their oxidation state changed. This can be either a redox process in which the oxidation of carbon

Table 15 The three approaches undertaken to investigate trace element speciation in biomass cofiring (Boersma and others, 2011)

Approach	Modelling	Full-scale measuring campaigns	Laboratory-scale experiments
Conditions	Theoretical variable input	Real fixed input	Semi real variable input
Boiler	Ultra-supercritical, oxyfuel combustion	Supercritical	Ultrasupercritical, oxyfuel combustion
Analysis/results	Calculated	Direct measurement (XAFS)	Direct/indirect measurements (LeachXS, CCSEM)
Elements	Ba, Cr, Mn, Co, Cu, Ni, As, Sb, Cd, Pb, Zn, Hg, Se, Te	Cr, V, Zn, As, Se	15 toxic metals
Partner involved	KEMA Nederland B.V.	KEMA Nederland B.V. & ECN	ECN

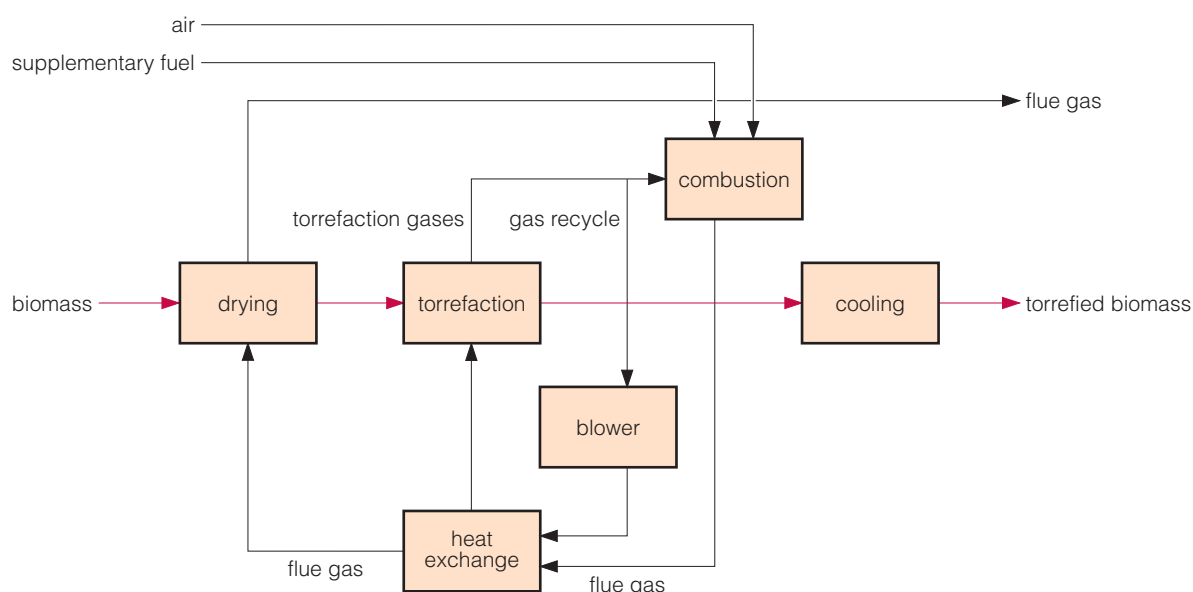


Figure 21 Energy Research Centre of the Netherlands (ECN) torrefaction technology (Mitchell, 2007)

takes place to yield carbon dioxide (CO_2) or the reduction of carbon by hydrogen to yield methane (CH_4). Valency is the combining power of an element, as measured by the number of hydrogen atoms it can displace or combine with, for example, carbon always has a valence of 4. When compared to conventional boilers, the authors considered that oxy-fuel conditions may be expected to influence trace elements speciation due to a different gas phase composition and the resulting redox conditions. They also stated that ultra-supercritical conditions may also influence speciation due to the changes in furnace exit temperature but to a lesser degree.

The sampling and measuring campaign at MV2 (*see* Chapter 3) showed that most trace elements leave the installation mainly with the fly ash. Effluent output included Cl, Na, Br, I and Mg. The gypsum contained Ca, S, F, I and Se, while the sludge of the wastewater treatment plant was found to be a significant output-route for F, B, Hg and Se. The campaign also showed that the flue gas contained mainly C and to a much lesser extent B, Hg, I, Se and S.

Initial ash leaching test results indicate that computer-aided, pH-static extraction techniques may be used to study the oxidation state and complex analysis of trace elements. The techniques used in the study showed clear differing behaviour of trace elements contained in the ashes from different conversion conditions and technologies including gasification, grate firing and pulverised coal fired combustion.

KEMA Nederland B.V. investigated the health aspects of ash from cofiring. These involved tests on a 1 MWth test boiler in which secondary fuels were cofired up to a cofiring ratio of 10% on a mass basis followed by tests on seven Dutch coal-fired plant with cofiring ratios of up to 40% (mass). The ash was used as raw material to make concrete test cubes which were subjected to leaching and other tests. The exercise demonstrated that fly ash generated by high percentage cofiring can meet European standards. The health effects were also assessed using the KEMA Dust Assessment Methodology (KEMA-DAM) which determines whether, in case of fly ash dust exposure, the threshold limited values or health limit values of particular substances in the dust can be exceeded. The KEMA-DAM procedure was applied to calculate the ash compositions at cofiring ratios of 10%, 30% and 50% (mass) for five secondary fuels. The results showed that up to 50% cofiring ratios of paper sludge,

sewage sludge, residual wood, chicken manure and refuse derived fuel of average composition did not lead to individual occupational exposure limits being exceeded at an inhalable dust exposure of 10 mg/m³. The sum of the average concentrations of the potentially carcinogenic trace elements As, Be, Cd, Co, Cr and Ni in the fly ash in all cases was less than 40% of the limit value for carcinogenic components and mixtures of 1000 mg/kg. The overall conclusions were that ash from cofiring biomass with coal did not pose any increased health risk for the ashes tested which were up to a cofiring ratio of 40%, and that the ash could be regarded as ‘non dangerous substances’ according to the European Waste Catalogue (te Winkel, 2010; Fernando, 2012).

Singh and others (2011) carried out a comparative evaluation of minerals and trace elements in the ash from lignite, coal refuse, and biomass-fired power plants. Fly ash from coal combustion in thermal power plants in India is approximately 160 Mt/y. This is expected to increase to 300 Mt/y by 2016-17. Safe handling and disposal is considered an important issue due to the potential toxic element content in the ash. Representative feed and ash samples were collected from three facilities firing lignite, coal refuse and biomass. Following sampling and analyses of these ashes the authors found that the lignite ash, coal refuse ash and biomass ash have 90% of their particles with sizes of <36 µm, 182 µm and 135 µm respectively. The abundance of the smaller particles in the lignite was attributed to the fact that lower rank coals typically contain substantial proportions of organically-bound inorganic elements, such as Ca, Mg and Na, which are likely to form finer sized ash particles. The concentrations of 39 elements analysed in all the ashes (As, Ba, Co, Cr, Cs, Cu, Ga, Hf, Hg, Mn, Mo, Nb, Ni, Pb, Rb, Se, Sr, Ta, Th, U, V, Zn, Zr, Sc, Y, Ce, Dy, Er, Eu, Cd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm and Yb) are given in Table 16. Concentration of the elements in the ashes follows the order (Singh and others, 2011): Sr>Ba>Zn>Ce>Mn>Nd>Ni>Cr>La>V>Rb>Cu>Co>Pb>Sm>Sc>Dy>Th>Gd>Cs>Mo>Yb>Eu>U>Ho>>Tb>As>Hf>Tm>Se>Pr>Lu>Er>Y>Nb>Ta>Ga>Zr. Excluding the high concentration of Ba at 721 mg/kg in the coal refuse ash and Sr at 885 mg/kg in the biomass ash, the range of values for the lignite, coal refuse and biomass ashes, which was 0.19 to 391 mg/kg, 0.31 to 722 mg/kg and 0.14 to 885 mg/kg respectively, was reduced to 0.14 to 391 mg/kg. Hg was below detection limits at <0.1 mg/kg in all ashes, As and Se were also <0.1 mg/kg in the biomass ash.

According to Singh and others (2011), the concentrations of Sc, V, Cr, Co, Ni, As, Hf, Pb and the rare earth elements (REEs) were significantly higher in the lignite ash, Sc, Se, Mn, Zn, Rb, Cs, B, Pb, Th and U were higher in the coal refuse ash and Mo, Cu, Zn, Rb, Sr and Ba were higher in the biomass ash. The ash with high concentration of trace elements were lignite ash (V<La<Mn<Cr<Ni<Nd<Ba<Ce<Zn<Sr), coal refuse ash (Cr<Ce<V<Rb<Mn<Sr<Zn<Ba) and biomass ash (Cu<Zn<Ba<Sr). Thus, the lignite ash had the highest total concentration of trace elements followed by the coal refuse ash and the biomass ash (*see* Table 16). The lignite ash had high proportions of SiO₂, CaO, MgO, Al₂O₃ and SO₃; the coal refuse ash had high SiO₂ and Fe₂O₃; the biomass ash contained high SiO₂ (but low Al₂O₃) and high CaO, MgO, K₂O, Na₂O, SO₃ and P₂O₅. Quartz and aluminosilicate were found in all the ashes. Singh and others (2011) consider that the ratio of basic to acidic oxides (B/A ratios) in the ashes suggest that biomass is more prone to slagging than lignite or coal refuse. The substantial presence of Cl in the biomass ash (2.1%) may also result in fouling and corrosion in the furnace. The authors conclude that, based on enrichment factorisation and association of the trace elements with the minerals in the ashes shows that the ash characteristics, in respect of mineral and elemental content, are strongly influenced by the feed composition as well as the volatility of the trace element, depending on combustion temperature. Potentially toxic elements enriched in the lignite ash were As, Se, Mo and Pb, in the refuse ash these were Se, Mo and Pb and in the biomass ash were Mo, Pb and Cu (Singh and others, 2011).

4.6 Future challenges

Research needs on trace element emissions from coal combustion include (Xu and others, 2003):

- Trace element speciation and enrichment in coal and coal ash: the relationship between associated elements and coal macerals with mineral matter should be investigated by systematic

Table 16 Trace elements in lignite, coal refuse and biomass fly ash (Singh and others, 2011)

Elements	Lignite ash, mg/kg	Refuse ash, mg/kg	Biomass ash, mg/kg
Sc	28	297	10
V	131	120	59
Cr	137	102	61
Co	77	15	7
Ni	140	49	35
As	1.2	0.4	<0.1
Se	2.4	2.3	<0.1
Mo	3.0	3.3	10
Hg	<0.1	<0.1	<0.1
Mn	135	226	77
Cu	64	86	113
Zn	298	377	161
Ga	0.5	0.5	0.2
Rb	4.5	129	87
Sr	391	258	885
Y	1.2	0.3	0.2
Zr	0.4	0.3	0.2
Nb	0.5	0.9	0.3
Cs	0.2	13	4.5
Ba	210	722	376
Hf	2.8	2.2	0.9
Ta	0.7	0.4	0.4
Pb	40	36	26
Th	9.1	22	11
U	3.5	5.3	1.7
La	134	58	32
Ce	295	114	61
Pr	2	0.54	0.3
Nd	152	43	25
Sm	33	9.3	5.2
Eu	8.1	1.8	1
Gd	20.2	5.8	3.2
Tb	3.7	1	0.6
Dy	22.8	6.2	3.3
Ho	4.6	1.2	0.6
Er	1.3	0.3	0.2
Tm	2.6	0.7	0.4
Vb	9.4	2.6	1.2
Lu	1.5	0.4	0.2

testing of trace element speciation and enrichment in typical coals and their fly ash. The quantitative relationship between trace elements partitioning in the fine particulate matter with trace element content, from coal and other compositions with coal, should be studied.

- Trace element partitioning in the combustion process: a thermodynamic equilibrium model including equilibrium calculation of interactions between trace elements should be developed based on the chemical equilibrium principle. The model can be used to predict the status of trace elements in the combustion process and their partitioning following a cooling process in the flue gas. Thus, the reaction mechanisms of trace elements and the interaction between trace elements and other pollutants in the combustion process can be obtained.
- Mechanisms of transformation and control technologies for easily vaporised trace elements during combustion: a relatively effective model should be developed using heterogeneous chemical kinetics to describe the transformation and mobility characteristics of the easily vaporised trace elements in the combustion process. The vaporisation, nucleation mechanisms of trace elements, their retention by fly ash and the reaction mechanisms of solid sorbents with trace elements should be investigated further with an objective to develop multi-pollutant control technologies for trace elements and other pollutants with high efficiency and low investment cost.

In summary, trace elements are released during coal combustion and can pose an environmental and human health risk. The emissions depend on the concentration of the element in the coal, the physical and chemical properties of the element itself, combustion conditions and the type and efficiency of the particulate control device used. Trace element partitioning begins at the burner front and continues in the high-temperature radiant section of the furnace. Many trace elements are captured in the fly ash and bottom ash and some are emitted to the atmosphere in the combustion flue gas. The partitioning depends upon the degree of volatilisation of the particular element geochemical modes of occurrence within the coal and the extent to which they may be physically or chemically bound to the carbon matrix or the primary aluminosilicate minerals. The key factors that influence the behaviour of the trace elements in the flue gas are the conversion of the vaporised components into solid forms and their collection with the fly ash. This is determined by three complex processes: adsorption, condensation and chemical transformation. Collection of these trace species in an ESP or fabric filter depends to a large extent on the size fractionation of the particles. Research has shown that the most volatile trace elements, Hg, Se and As, remain mostly in the vapour phase as they pass through the heat transfer sections of a boiler and are emitted to air. For example, heavy coal consumption in Taiyuan resulted in elevated concentrations of these trace elements in the atmosphere. However, investigative work in Beijing confirmed the major role played by coal combustion in Pb and Sr emissions to air.

Assuming that the ratio between bottom ash and fly ash in a pulverised coal combustion plant is 80/20, the mass flow of the trace elements in the plant can be obtained and presented as a percentage average values of retained elements in different fractions. Based on partitioning (as shown in Figure 13), it may be concluded that, typically, 20% of Fe and Mn are retained in bottom ash, up to 5–10% of Cd, Sn, Zn, Pb, Sb and Cu are retained in bottom ash and about 80% is retained in the fly ash. As for the trace elements Hg, Se and As, a relatively large amount is emitted to air with the flue gas compared to the other elements. About 15% of Se and 2% of As is retained in the solid particles and only 5% of the same elements is retained in the bottom ash. Up to 75% of Hg is either emitted to the atmosphere or captured in solid particles and a negligible amount is retained in the bottom ash.

Coal-combustion produces large amounts of residue, which is sometimes stored in ponds or often used in other industries, for example as construction or insulation material or for soil enrichment. The potential leaching of trace elements to water and/or soil is of major concern to authorities throughout the world and hence has resulted in a number of investigations on the subject. Leaching of many trace elements from water-stored ash is different to that of the same elements from dry fly ash. Although some research noted that the cumulative percent of As, Cd, Cl and Zn leached in C and ash, increased with decreasing pH values (that is, increasing acidity), other studies show that the leachability of the trace elements in the fly ash is affected by the time of leaching. The leachability of, for example, Cd,

Cr and Pb continued to increase after a week of experimentation in one study. The leachability of Cr was found to be higher with the leaching in acidic solution ($\text{pH} = 4$) while the leachability of Pb was found to be higher with the leaching in alkaline solution ($\text{pH} = 10$). Coal may be hydrothermally treated to prevent trace and major element leaching from coal combustion. Geopolymers, a technique for waste stabilisation using material with silica and alumina in the correct ratios and activated by an alkali metal hydroxide to produce a three-dimensional inorganic amorphous structure, shows potential as a means of stabilising residue from coal combustion.

5 Trace element emission reduction

Trace elements are released from both natural sources and human activities. Currently the trace element emissions considered to be of major concern are arsenic (As), Boron (B), cadmium (Cd), lead (Pb), and mercury (Hg), molybdenum (Mo) and selenium (Se). Of these, mercury and lead are the trace element of most concern with respect to emissions to the atmosphere from coal-fired power stations. The IEA Clean Coal Centre has published numerous reports on mercury emissions and control in coal-fired power plant. Hence, mercury emissions and control will not be discussed further in this section. Visit www.iea-coal.org for more information. Staudt (2011) also reviewed control technologies to reduce conventional and hazardous air pollutants from coal-fired power plants. Moritomi (2001) discussed trace element emission control technologies in a coal combustion process.

5.1 Particulate control

As discussed in Chapter 4, trace elements can be grouped in three classes: Class 1 trace elements that are easily captured in the bottom ash and fly ash through a particulate control device such as an electrostatic precipitator (ESP) or fabric filter (examples include Mn, Be, Co and Cr); Class 2 elements that are enriched in the fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size (examples include As, Cd, Pb and Sb); and Class 3 elements that are emitted in the gas phase (primarily Hg (not discussed in this review) and Se).

Efficient particulate control devices capture the majority of trace elements in the fly ash. Table 17 gives trace element emissions from several coal- and peat-fired power plants and the particulate control device efficiency. According to Zevenhoven and Kilpinen (2001), ESP and fabric filter removal efficiencies are of the order of 99–99.9% for most trace elements, especially class 1. For some class 2 elements the removal efficiency is somewhat lower at around 95–99% and even less for class 3 trace elements. Trace elements that are not captured in the ESP or fabric filter device may be removed by a downstream FGD system for SO₂ control. Typical data for removal of some trace elements from pulverised coal fired power plant with wet scrubbing downstream of a particulate control device are given in Table 18 (Zevenhoven and Kilpinen, 2001).

ESPs capture particles by ionising the incoming flue gas in high-voltage coronas. This charges the particles. An applied electric field is then used to move the particles onto large, earthed, planar electrodes (flat collecting surfaces). A series of discharge electrodes are spaced along the centre line of the adjacent collection electrodes. Collection plates are large steel sheets, which may have a variety of shapes to help retain the particles. The collected fly ash is then dislodged and moved, vertically, from the collecting plates, at suitable intervals, by rapping. Vertical movement is resisted by viscous and mechanical effects. Rapping is carried out by mechanical hammer and anvil arrangement or pneumatic/electromagnetic impulse. Re-entrainment can take place during the rapping procedure. Regular inspection for build-up of fly ash, frequent emptying and maintenance of the heater systems for the hoppers minimise problems that may arise at the final stage of this particulate control system. ESPs are the particulate emissions control technology which is most widely used in coal-fired power generating facilities. Fabric filters can achieve an overall collection efficiency of 99.95% across all particle sizes and >99% collection efficiency for fine particles. In recent years there has been a vast increase in the type of filter media available for different applications. The developments of new filter media materials, special coating and finishing techniques have resulted in fabric filter media that have extended life, improved performance with lower energy consumption and can operate in a wide temperature range. The choice between ESP and fabric filtration generally depends on coal type, plant size and boiler type and configuration. Both technologies are highly efficient particulate removal devices with design efficiencies in excess of 99.9%. Conditioning the fly ash in the flue gas is an established technique used to restore the performance of an ESP in coal-fired power plants with high-

Table 17 Trace elements emission from several coal- and peat-fired power plants
(Zevenhoven and Kilpinen, 2001)

Process	Pulverised coal combustion	Pulverised peat combustion	Circulating fluidised bed peat combustion
Particulate control system efficiency, %	95.6–99.5	98.7–99.5	99.5–99.8
Emissions, µg/MJ			
Hg	0.12	0.11	0.03
As	2–39	<1.5–2.3	<0.1–1.6
Be	5	0.05	0.01–0.3
Cd	0.5–1.8	<0.002–0.13	0.1–0.4
Co	1–22	0.3–1.2	0.3–4
Cr	8–230	3–79	0.7–1.3
Mn	2–230	10–26	0.6–6
Mo	<1–41	<1–11	<1.5–2.3
Ni	<15–170	<33–54	9–13
Pb	20–120	3–4	1–11
V	10–88	4–6	9
Zn	20–220	<6–12	1–11

Table 18 Typical removal efficiency for volatile trace elements by wet FGD scrubbing downstream of a particulate control device (Zevenhoven and Kilpinen, 2001)

	Removal efficiency, %	Outlet concentration µg/m ³
Hg	~50	~1.5
Se	~60	~10
Be	~80	~250
Fly ash	90~99	1000~10000

resistivity fly ash resulting from burning low sulphur coals. For details on the efficiency, effectiveness and issues with ESP and fabric filtration *see* Zhu (2003) and Soud and Mitchell (1997). A summary of emission control technologies is presented by Sen (2010).

For trace elements associated with particles, the capture efficiency for any given particulate control technology should relate directly to the particulate collection efficiency of the system. Modern ESP and fabric filters in use today achieve efficiencies of 99.9% or more. However, conventional (older) ESP can have poor capture efficiency for 0.1–1.0 µm particles. Fine particles tend to carry more of the semi-volatile trace elements due to their larger surface area on an equal mass basis. ESPs have lower capture efficiencies for ultra-fine particles as smaller particles are more difficult to charge to a sufficient level for electrostatic collection. The problem is exacerbated with high resistivity fly ash. Trace elements associated with smaller particles will have similarly reduced collection efficiencies. Particle agglomeration systems may provide an economical solution to fine particulate control from

ESPs as well as fabric filters (Zhu, 2003). Table 19 shows the average removal efficiency for trace elements across a conventional ESP on an unspecified boiler (Sloss and Smith, 2000).

According to Staudt (2011), toxic metals, other than Hg, are normally in the particle form and are therefore captured in the particulate control devices, that is ESPs and fabric filters. The most recent air toxics rule in the USA set numerical particulate matter emission limits as a surrogate for non-mercury metal emission limits. Table 20 lists particulate matter emission control technologies in coal-fired power plant that include the capture of some hazardous air pollutants. Depending on performance of a particular ESP, further controls to remove some trace elements to achieve compliance may not be

Table 19 Trace element removal example in an ESP from an unspecified boiler
(Sloss and Smith, 2000)

Element	Removal efficiency, %
Antimony	81.0
Arsenic	99.1
Barium	99.8
Beryllium	97.4
Cadmium	99.2
Chromium	99.2
Cobalt	99.3
Copper	99.6
Manganese	99.6
Mercury	<20.0
Molybdenum	96.0
Nickel	98.2
Phosphorus	98.0
Vanadium	99.6

necessary. However, upgrading an existing ESP by addition of new electric fields, use of new high frequency transformer rectifier technology or other advanced modifications could result in greater capture of trace elements. Replacing an existing ESP with fabric filters is another option as the capture of the finer particles in fabric filtration is greater compared with ESP. In fabric filters, the fly ash is removed from the flue gas stream by passing through some kind of filtration media that is porous. Initially, the fly ash forms a porous cake on the surface of the fabric. Thereafter, this dust-cake actually does the filtration. In some cases, the filtration material is coated with appropriate dust-cake prior to installation in order to accelerate the cake forming stage. However, the costs entailed may be prohibitive. Another option is the installation of a polishing fabric filter downstream of an existing ESP which would result in a higher efficiency in the capture of the finer particulate matter. Yi and others (2008) discuss fine particle and trace element emissions from an anthracite coal-fired power plant equipped with a fabric filter system in China.

Table 20 Most widely used particulate matter emission control methods in power plant
(Staudt, 2011)

Electrostatic precipitator (ESP)	Method: electrostatic capture of particulate matter with high capture efficiency. Reagent: none Typical fuel: solid Capital costs: high Co-benefits: capture of particulate-bound trace elements
Fabric filter	Method: filtration of particulate matter with highest capture efficiency Reagent: none Typical fuel: gaseous Capital costs: high Co-benefits: high capture of hazardous air pollutants
	A co-benefit of flue gas desulphurisation (FGD) where fitted downstream of a particulate control device is further particulate matter capture

In 2007, Zevenhoven and others discussed As flows in the environment in the EU. Following investigative work at two coal-fired power plants in Finland firing approximately 60 t/h pulverised bituminous Polish coal, the authors found that ~94% (mass) of the As in coal was captured in the ESP and ~6% in the spray dry FGD scrubber. As concentrations in the bottom ash and the flue gas were below 1%. With a concentration of ~5 mg/kg As in the coal, the As input to the plant was about 300 g/h of which approximately 1.5 g/h (that is, ~0.58%) is emitted through the stack to the atmosphere. As concentration in the bottom ash/fly ash and the FGD residues was about 5 and 30 mg/kg respectively. According to Pandey and others (2011), analysis of fly ash from coal combustion shows that As is enriched, as with other trace elements, in the finest fractions which may not be captured by some particulate control devices.

5.2 Flue gas desulphurisation (FGD)

FGD technologies are discussed in details in several IEA CCC reviews including Nalbandian Soud (2000). The most widely used FGD system is the wet scrubber technology followed by spray dry scrubbing and to a lesser extent sorbent injection. Xu and others (2003) note that the high volatility and existence in the vapour phase makes trace elements control a difficult task to accomplish. In principle, trace elements in vapour phase can be condensed by lowering the flue gas temperature. However, the resulting loss in buoyancy of the flue gas would require the reheating of the said flue gas, which would not be economical. Furthermore, the resulting particulate matter may be in the fine, submicron particle sizing, thus making their capture difficult in conventional particulate control devices.

Trace element capture is achieved in electrostatic or ionising wet scrubber technologies by flue gas cooling and collection of the condensed fine particulate matter. Electrostatic or ionising advanced wet scrubbers or the condensing wet scrubbers are the most commonly used technologies in waste incineration plants for trace element capture. According to Xu and others (2003), the electrostatically enhanced wet scrubbers capture the condensed fine particles by imparting a charge to the incoming particulate matter and then collecting these on neutral packing material or negatively charged collection electrodes. In condensing wet scrubbers, the flue gas is cooled to below its adiabatic saturation temperature. This results in the condensation of a larger fraction of the vapour phase elements. In addition, the cooling induces water vapour to condense forming a large number of droplets to aid in the collection of the fine particulate matter (Xu and others, 2003).

Spray dry scrubbing is the FGD technology of choice in waste incineration plants to reduce trace element emissions. The system usually utilises hydrated lime as the reagent. According to Xu and others (2003), spray dry scrubbing may also be suitable for the reduction of trace elements from coal combustion. Trace element removal in the dust collection device, which in spray dry scrubbing is usually fabric filtration, is enhanced by the cooling of the inlet flue gas temperature from 2000°C to ~150°C as it passes through the spray drying system. Due to the cooling process, some vaporised trace elements condense to form fine particulate matter, which increase in size through impaction and agglomeration with the high number of lime droplets produced by the atomisation devices. The particles are thus easily captured in the particulate collection device. In general, the lower the spray dry scrubber outlet temperature, the higher the efficiency of the acid gas absorption and the vaporised toxic metal removal. According to Xu and others (2003), the minimum reliable operating temperature depends on the spray dry scrubber and particulate collection design and on the composition of the dry fly ash reaction product. Meanwhile, the spray dry scrubber outlet temperature must be maintained high enough to ensure complete reagent evaporation and the production of a free-flowing product.

The capture of fine (submicron) particulate matter on sorbents by physical, chemical or a combination of physical and chemical means, as well as the interaction between trace elements and various sorbents, has been the subject of many studies including Xu and others (2003). For example, pilot-scale investigation on the effectiveness of high-temperature furnace sorbent injection for the capture

of trace elements showed that mineral sorbents, such as hydrated lime, limestone and kaolinite, can be effective for As, Cd and Pb capture at 1000–1300°C. Other sorbents, such as fly ash and activated carbon have shown to be able to capture As, Cu, Mo, Pb and Zn. Activated carbon was also found to be effective in capturing As oxides. Xu and others (2003) found that other studies indicated that trace element absorptive capacity is related to the qualities of the absorbents (type, amount and particle size) as well as the combustion temperature. Results from refuse-derived char ash from municipal solid waste utilisation indicate that kaolinite and montmorillonite or coals enriched in these minerals play a role in the retention of the most volatile Pb, Sb and Cu. Dry sorbent injection for in situ capture of trace elements as well as SO₂ and NO_x from hot flue gas was the subject of many studies aiming to develop a potential multi-pollutant control technique. These indicated that activated carbon is a viable sorbent in the low temperature range in capturing SO₂ and Hg. However, there is a lack of investigative work in studying the use of activated carbon to capture other trace elements (Xu and others, 2003).

According to Attalla and others (2004), particulate control devices and FGD technologies have shown additional benefits in trace element removal from hot gas streams. Pandey and others (2011), for example, stated the effective removal of most of As from the flue gas in FGD systems. Table 21 summarises the performance of such technologies with regard to trace element removal. Cleaning systems associated with the table include ESP and fabric filters for conventional pulverised coal combustion, venturi scrubber, zinc titanate sorbent associated with hot gas cleaning unit (HGCU), water scrubber for integrated gasification combined cycle (IGCC), and two-stage cyclone/ESP and cyclone/barrier filter advance particle filtration (APF) system for pressurised fluidised bed combustion (PFBC) (Attalla and others, 2004).

Table 21 Trace element control efficiencies achieved in conventional pulverised coal plant
(Attalla and others, 2004)

Trace element	Conventional pollution control			Advanced pollution control	
	ESP	Fabric filter	FGD	APF	HGCU
Sb	96	97	99	65	88
As	98.5	98.5	98.5	99	74
Ba	99.5	98	99.5	100	79
Be	98.5	98.5	98.5	99.5	36
B	68	97	63	ND	ND
Cd	83	94	96	100	70
Cr	97.5	99.5	99.5	89	77
Co	98	99	99	99	36
Cu	89	99.5	99	99.5	38
Pb	98	98.5	99	100	92
Mn	97	99.5	99.5	98	58
Hg	30	60	20	10	30
Mo	96	100	99	63	–51
Ni	96	99	99	77	38
Se	21	65	60	20	89
V	98	100	99.5	99.5	91

The use of sorbents is an area where research continues to find the most effective reactants to capture not only air pollutants but also as many trace elements as possible. These sorbents have been used either where they were in a fixed or fluidised bed and the flue gas was passed through the bed or by direct injection of the sorbent as a powder in the flue gas. Solid materials such as clay minerals, fly ash, metal oxide mixtures and hydrated lime have been tested for retaining trace elements including As. Chemical-sorption of trace elements is considered to be one of the probable retention mechanisms. Activated carbon, which is commonly used for Hg capture, is considered a potentially viable sorbent that would also capture As as well as other trace elements in the flue gas (Pandey and others, 2011).

The analysis of Se data from the US 2010 utility ICR (*see* Chapter 3) and slipstream testing of sorbents for Se adsorption was the subject of a paper by Dombrowski and others (2011). As discussed in Chapter 3, EPRI is conducting a programme to improve the understanding of the factors affecting

Table 22 Coal-to-stack Se removal and Se emissions for MACT units firing subbituminous coal (Dombrowski and others, 2011)

Configuration	Se removal			Se emissions (lb/TBu)		
	Average, %	Range, %	Unit count	Average, lb/TBtu (~ppb)	Range, lb/TBtu (~ppb)	Unit count
ESPc	93.9	89–97	6	9.2 (3.49)	2.0–20 (0.76–7.58)	8
ACI ESPc	95.3	94–96	2	4.0 (1.52)	3.0–5.0 (1.18–1.89)	2
SNCR ESPc	88.2	86–89	3	11.9 (4.51)	6.3–23 (2.39–8.72)	3
SNCR DSI ESPc	94.2	92–96	2	5.5 (2.08)	5.0–6.0 (1.89–2.27)	2
SCR ESPc	65.5	43–89	2	15 (5.69)	6.3–23 (2.39–8.72)	2
SCR ESPc FGDw	70.7	70.7	1	14.5 (5.50)	14.5 (5.50)	1
FF	94.1	84–99	6	3.0 (1.18)	1.3–7.0 (0.49–2.65)	8
ACI FF	89.8	77–97	5	6.3 (2.39)	1.5–12.9 (0.57–4.89)	5
FGDd FF	98.7	98.7	1	1.4 (0.53)	1.4 (0.53)	1
SCR FGDd FF	99.4	99+	5	0.4 (0.15)	0.08–0.8 (0.03–0.30)	5
ACI FGDd FF	NA	NA	NA	0.2 (0.08)	0.2 (0.08)	1
SCR ACI FGDd FF	98.4	97–99+	3	1.4 (0.53)	0.5–1 (0.19–0.38)	3
FF FGDw	98.3	98–99	2	1.2 (0.45)	0.7–2.0 (0.27–0.76)	3
ACI FF FGDw	99.9	99+	2	0.2 (0.08)	0.1–0.3 (0.04–0.11)	4
SCR ACI FF FGDw	99.3	99+	2	1.0 (0.38)	0.6–1.3 (0.23–0.49)	2
ESPc = electrostatic precipitator, cold side ACI = activated carbon injection SNCR = selective non catalytic reduction DSI = dry sorbent injection SCR = selective catalytic reduction FGDw = flue gas desulphurisation, wet FF = fabric filtration FGDd = flue gas desulphurisation, spray dry						

Table 23 Coal-to-stack Se removal and Se emissions for MACT units firing bituminous coal (Dombrowski and others, 2011)

Configuration	Se removal			Se emissions		
	Average, %	Range, %	Unit count	Average, lb/TBtu (~ppb)	Range, lb/TBtu (~ppb)	Unit count
ESPc	66.3	33–93	7	85.4 (32.37)	14.0–140 (3.56–53.06)	8
SCR ACI ESPc	36.0	36	1	92 (34.87)	92 (34.87)	1
SNCR ESPc	39.1	39	1	154.2 (58.44)	117–190 (44.34–72.01)	2
SNCR ESPc FGDw1	94.2	94.26	3	31.6 (11.98)	14.0–84 (5.31–31.84)	4
SNCR FGDd ESPc (FBC)	99.8	99+	2	0.8 (0.30)	0.7–0.9 (0.27–0.34)	2
ESPc FGDw	69.6	33–90	4	25.3 (9.59)	16.0–34 (6.06–12.87)	4
DSI ESPc FGDw	64.1	64–99	1	54 (20.47)	54 (20.47)	1
SCR ESPc FGDw	88.7	80–99	7	28.8 (10.92)	3.0–83.9 (1.14–31.80)	9
ASI SCR ESPc FGDw	90.4	90–91	3	14.3 (5.42)	9.0–19 (3.41–7.20)	6
FF2	94.9	84–99	7	4.6 (1.74)	0.2–11 (0.08–4.17)	7
FGDd FF	99.5	98–99+	4A	0.6 (0.23)	0.05–2.0 (0.02–0.76)	10
SCR FGDd FF	99.9	99+	5	0.13 (0.05)	0.02–0.5 (0.01–0.02)	6
SCR FGDd ACI FF	99.4	99.49	1	0.52 (0.20)	0.5–2.0 (0.02–0.76)	1
ACI FF	NA	NA	NA	8.7 (3.30)	7.0–10 (2,65–3.79)	1
ACI FGDd FF	99.4	99+	1	0.5 (0.19)	0.5 (0.19)	1
SNCR FGDd FF (FBC)	99.6	99+	9	0.6 (0.23)	0.05–1.8 (0.02–0.68)	10
SNCR FGDd FF	99.3	99+	2	1.5 (0.57)	1.3–1.7 (0.49–0.64)	2
FF FGDw3	90.5	74–99	4	11.4 (4.32)	3.6–23.0 (1.36–8.72)	4
SCR FF FGDw	92.7	92.7	1	17.3 (6.56)	17.3 (6.56)	1
SNCR FF FGDw	95.2	95.2	1	9.4 (3.56)	9.4 (3.56)	1
ESPc = electrostatic precipitator, cold side SNCR = selective non catalytic reduction SCR = selective catalytic reduction FF = fabric filtration FGDd = flue gas desulphurisation, spray dry				FBC = fluidised bed combustion ACI = activated carbon injection DSI = dry sorbent injection FGDw = flue gas desulphurisation, wet		
1 Three of four units fed a common stack. As per ICR instructions, the stack was samples and the same emissions were repeated for all three un its 2 Average Se emissions and Se removal for FF does not include two units that had outlier emission values of 239 (~90.58 ppb) and 331 lb/TBtu (~125.45 ppb). In both cases, Se emissions were higher than the coal Se concentrations, indicating an error in the data 3 Se data for one unit (74%, 23 lb/TBtu (~8.72 ppb)) of the four FF FGDw units was markedly different from the other three units, but is not a statistical outlier based on 95% Q-test. If data from this unit are dropped, the average Se removal becomes 96% and the average Se emissions becomes 7.4 lb/TBtu (~2.8 ppb)						

trace elements emissions, especially Se, from coal-fired power plants. In the first phase of the programme, EPRI evaluated the 2010 US EPA utility ICT data in order to identify trends in Se removal based on coal type, particulate and FGD control devices as well as sorbent injection techniques. In the second phase of the programme, slipstream tests were conducted to evaluate the ability of various sorbents to adsorb the Se in the flue gas. Laboratory validation of the measurement method proposed for use in evaluating sorbents as well as evaluation of sorbents at a Texas lignite-fired power plant have been carried out. The sorbents evaluated were carbon-, alkaline- and mineral based. Tables 22 and 23 show Se removal (coal-to-stack) and Se emissions for a variety of ICT unit configurations for subbituminous and bituminous coals, respectively. These are units fitted with maximum available control technology (MACT) and most recently installed particulate control devices, and thus are not representative of all plants in the USA. Units from the random 50 data set are not included in the ICT MACT data (Dombrowski, and others, 2011).

The effects of coal type, the air pollutant control technologies including ESP, fabric filters, FGD wet and spray dry systems as well as the effects of dry activated carbon sorbent injection, and finally boiler type on Se emissions were discussed by Dombrowski and others (2011, 2010). The following trends were observed from the data on effects of coal and control type (Dombrowski and others, 2011):

- units firing bituminous coal had higher average Se emissions than those firing subbituminous coal;
- units firing bituminous coal installed with fabric filters had lower average Se emissions and higher average Se removal than units firing bituminous coal with ESPs;
- for both types of coal, units with FGD had lower average Se emissions and higher average Se removal than comparable units without FGD.

Factors that have been identified as possible reasons for lower Se emissions from units firing subbituminous coals included lower sulphur content, higher alkalinity ash and lower Se concentrations in subbituminous coals compared to bituminous coals.

Sorbents for gas-phase Se capture were chosen and tested based on literature reviews and choosing sorbent material that is already known to be effective for gas-phase Hg adsorption. These were categorised as follows (Dombrowski and others, 2011):

- activated carbon sorbents including brominated carbon, iodinated carbon, sulphonated carbon and carbon mixed with zinc granules;
- alkaline sorbents including hydrated lime and Sofnolime® (a mixture of NaOH, Ca(OH)₂, and KOH);
- mineral sorbents such as iron pyrite.

Experimental results given in Table 24 show the Se concentrations measured for each sorbent and the percentage Se captured compared to Method 29 results. The US EPA Method 29 measures hazardous air pollutant (HAP) emissions from stationary sources. Elements to be tested include Hg, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Tl, and Zn. In Method 29, a stack sample is withdrawn isokinetically from the source, particulate emissions are collected in a probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analysed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analysed only for Hg). The recovered samples are digested, and appropriate fractions are analysed using an analytical method with a sufficient detection limit to demonstrate compliance. All carbon sorbents demonstrated good Se capture at 350°F (176.7°C). Brominated carbon, at 300°F (148.9°C), captured only 67% of the Se in the gas phase. Hydrated lime, at 500°F (260°C) demonstrated poor capture and the iron pyrite, at 350° (176.7°C) had no affinity for adsorbing gas-phase Se. Dombrowski and others (2011) found that the carbon sorbents are likely to have more reactivity for Se than the alkaline sorbents. This was attributed to possible sorbent chemical properties and/or differences in size/shape of the sorbent granules. The reactivity of the carbon sorbents for Se remains unknown. Without the reactivity of the sorbent, Dombrowski and others (2011) consider that it is not possible to predict how effective the

Table 24 Se captured by sorbents at various temperatures (Dombrowski and others, 2011)

Sorbent	Sorbent temperature, °F (°C)	Average Se, first bed, µg/g	Se captured based on first bed based on M29 results*	Average Se, second bed, µg/g
Brominated carbon	350 (176.1)	151.8	121	<1.7
Brominated carbon	300 (148.9)	148.8	67	<1.8
Iodinated carbon	350 (176.1)	141.6	109	<3.7
Zinc granules with carbon	500 (260.0)	149.5	91	<1.0†
Zinc granules with carbon	350 (176.1)	111.9†	129	<3.1†
Sulphonated carbon	350 (176.1)	130.6	114	<0.9
Sofnolime®	350 (176.1)	140.6	118	18.1‡
Hydrated lime	350 (176.1)	135.5	113	37.7
Hydrated lime	500 (260.0)	84.5	39	33.3
Iron pyrite	350 (176.1)	<32.3	21	<28.7
<p>* Percentage Se capture calculated on a run-by-run basis using M29 data collected during each sorbent trap test</p> <p>† Background corrections were performed on results for Zn/Carbon because the background was approximately 10% of the sample result</p> <p>‡ Indicates the average has at least one value below and one value above the detection limit</p>				

sorbent would be in capturing Se when injected as a powder into the flue gas. The behaviour of Se in coal-fired power plants and the implications for multi-media emissions was studied by Senior and others (2010). Se speciation and partitioning in wet FGD systems was also discussed by Blythe and others (2010). Partitioning of Hg, As, Se, B and Cl in a full-scale coal-fired, 795 MW, power plant equipped with ESP, SCR and a wet FGD system was the subject of a field-study by Cheng and others (2009).

The trace elements Se and B are of particular concern for Japanese utilities because they are volatile during combustion and report to the discharge stream of FGD units. Water and soil regulations imposed by the Japan Ministry of the Environment set limits on the discharge of trace elements from wet FGD scrubbing units for a number of trace elements including As, B, Cd, Cr, Hg, F, Cu, Pb, Se and Zn. Limits are also imposed on the leaching of trace elements from fly ash and include As, Cd, Pb, Cr, Hg and Se. These limits apply to both the leaching of landfill and water at landfill sites (Dale, 2006).

The fate of trace pollutants in a 1200 MW, pulverised coal fired Spanish power plant installed with ESP for particulate control and FGD for SO₂ reduction was a main objective of a study by Font and others (2009). Experimental results showed that the FGD system captured 0.3–39% of the volatile trace elements Hg, B, As and Se as well as S, Cl and F. The FGD gypsum retained 76–100% of P, Ca, Nd, Ti, Ce, Zr, La, Y, Al, Nb, Fe, Pb, Li, Sr, Ga, Rb, Ba, V, Sn, Cr, Cu, K, U and Ni. The water effluent contained >60% of Mg, Na, Mn, Co, Sc, Cd, Zn and Mo. The volatile fraction of B and Cl before the ESP was reduced significantly after the FGD system due to the high water solubility of most of the B and Cl species (95–97% for B and 91% for Cl) in the effluent. The prevalent sources of Se in the FGD unit were attributed to the flue gas exiting the ESP and the water streams. A relatively high fraction of the Se was retained in the FGD gypsum (28–41%). However, 28–29% of the pollutant is released as particulate matter out of the FGD system. Low amounts of Se were emitted as gaseous species (2.2–2.8%). In this experiment, most of the As entering the FGD system came from the limestone

(78–88%) (2 mg/kg) which was fed to the system at the rate of 32.5 t/h. As also entered the FGD scrubber in the fly ash. A high fraction of the trace element was retained in the gypsum. The authors consider that this was most probably as Ca arsenate ($\text{Ca}_3(\text{AsO}_4)_2$). Only 0.3% of As-bearing species were emitted through the stack to the atmosphere. Font and others (2009) concluded that the use of additives seems to be a major parameter in affecting the partitioning of trace elements in FGD systems. The addition of Al in the scrubber accounted for modifying the partitioning of F in the FGD plants and therefore its speciation and capture. Finally, the authors consider that the efficiencies can vary between samples in a given power plant. The enrichment of trace pollutants in FGD water streams was also discussed by Córdoba and others (2010). The fate of trace elements in a coal combustion power plant fitted with wet limestone FGD was also studied by Álvarez-Ayuso and others (2006).

5.3 NO_x control

Selective catalytic reduction (SCR) is the most widely used technology to reduce NO_x emissions following combustion in coal-fired plant. These systems have been found to influence Hg emissions. This is discussed in detail in several IEA CCC publications (*see* www.iea-coal.org for more information on Hg control in coal-fired power plant). According to Zevenhoven and Kilpinen (2001), NO_x control systems have little influence on trace element behaviour or removal. However, catalyst poisoning is a major issue in SCR systems, especially when firing coal with low Ca/As ratio, which may cause rapid catalyst deactivation (Pandey and others, 2011). Catalyst poisoning is also discussed in details in several IEA CCC publications. Please visit www.iea-coal.org for reviews and further information on NO_x abatement and control.

5.4 Biomass cofiring

In 2011, Boersma and others (2011) published a review of biomass cofiring which included a full-scale sampling and measurement of trace elements from unit 12 Borselle power station (BS-12) in the Netherlands. In the campaign, ~30% (m/m) (corresponding to about 20% e/e) of coal was displaced with a mixture of different types of vegetation-based biomass. Figure 22 shows the BS-12

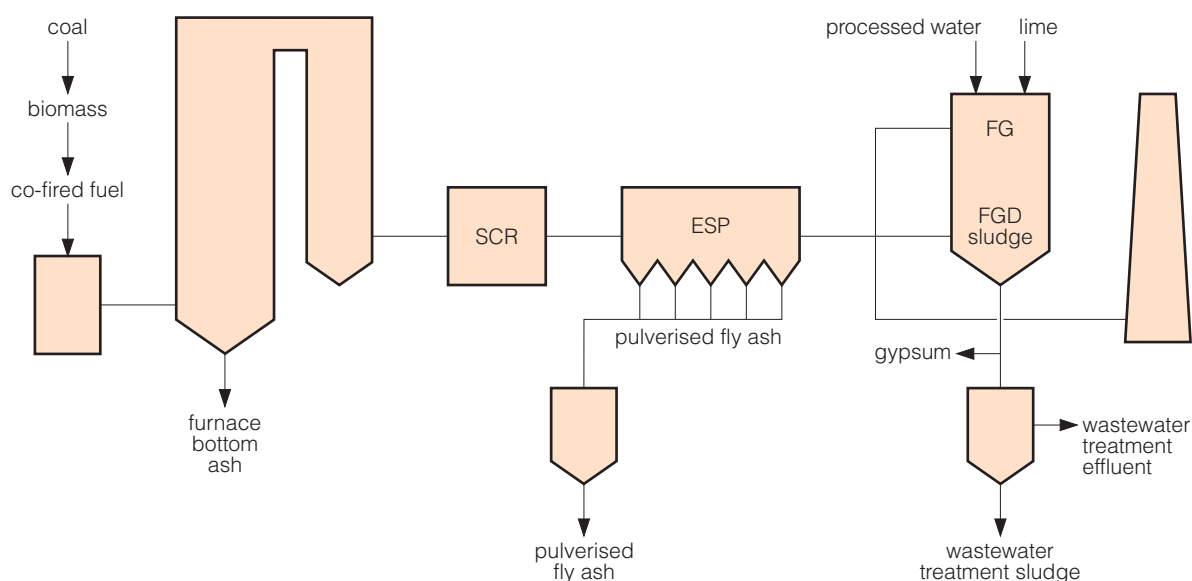


Figure 22 Borselle 12 (BS-12) power plant layout including sampling points during the first measuring campaign (Boersma and others, 2011)

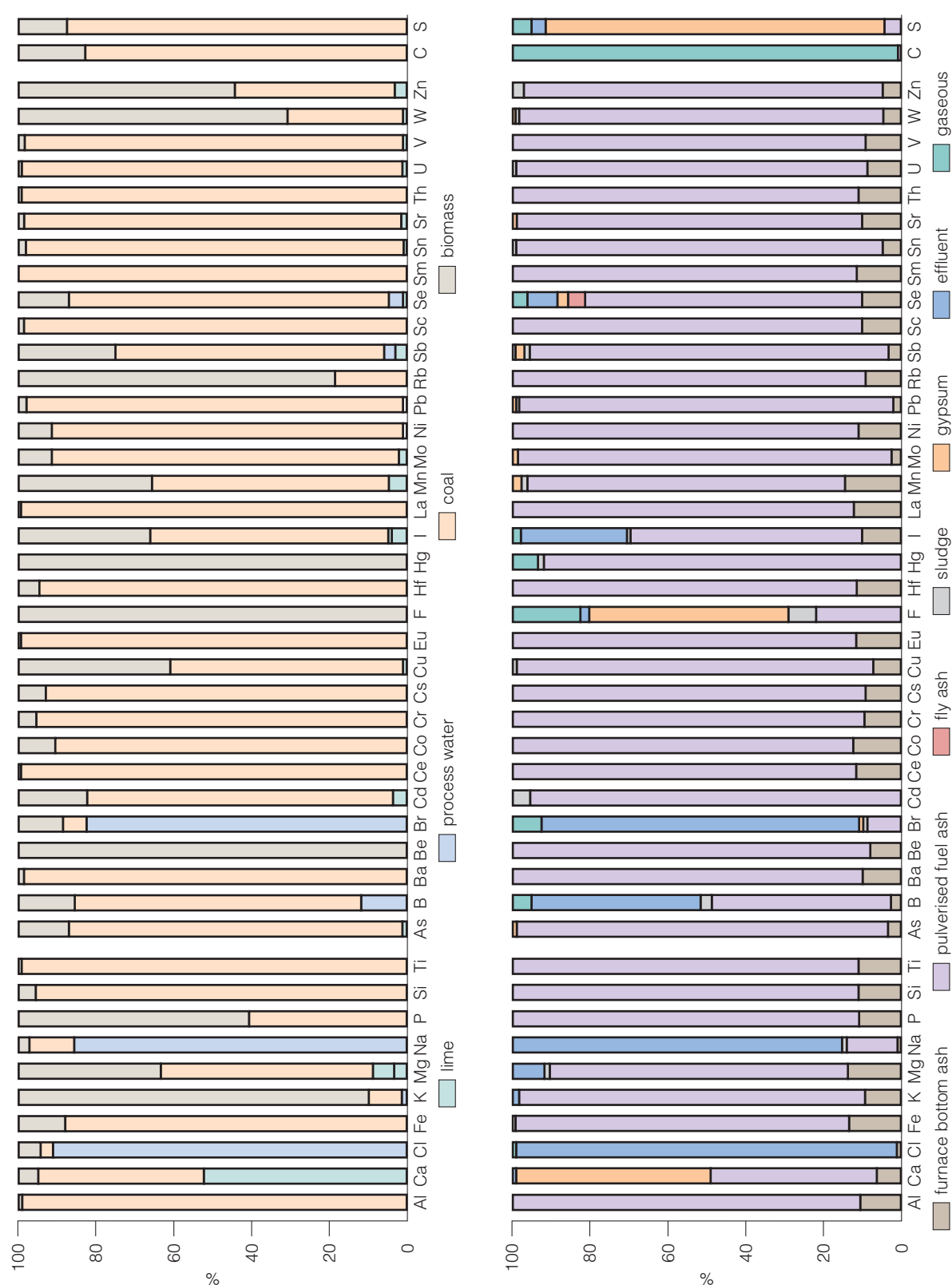


Figure 23 Borssele 12 (BS-12) full-scale campaign: distribution of the elements over input and output streams on the first day (Boersma and others, 2011)

power plant. Sampling of the inlet and outlet stream was undertaken by KEMA whilst ECN carried out fly ash and flue gas measurement at two intermediate points (before and after the SCR system). Cascade impactors were used for fly ash collection at both locations. Sampling obtained over two days were then analysed at ECN. The analysed streams included: indirectly cofired fuel; coal;

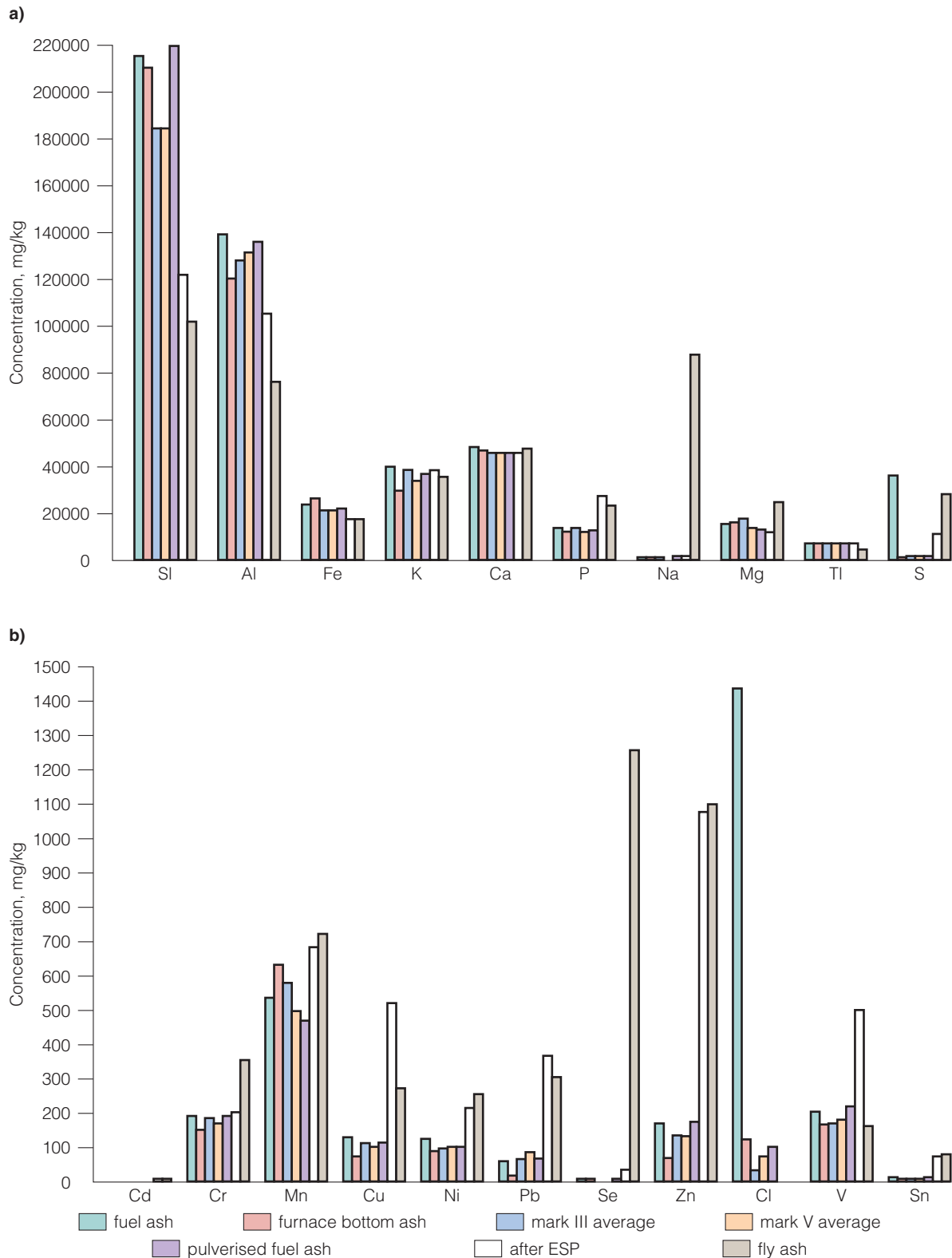


Figure 24 Main (a) and trace (b) element concentrations in fuel, ash and emitted dust throughout the Borssele 12 (BS-12) power plant (Boersma and others, 2011)

biomass; lime; process water; furnace bottom ash; pulverised fly ash; wastewater treatment sludge; wastewater treatment effluent; FGD sludge; gypsum (*see* Figure 22). Figure 23 illustrates the distribution of the elements over the input and output streams on the first day of the procedure.

Boersma and others (2011) noted a small increase in the concentration of some volatile elements in the fly ash downstream of the SCR system, Pb and V in particular (*see* Figure 24). This was accompanied by a significant increase in Cl load with no such increase for common alkalis. A small but significant increase was also noted with S, which was considered to be an indication of the complexation of the condensing metals. Complexation is the formation of a group of compounds in which a part of the molecular bonding between compounds is of the co-ordinate type. It is known that there is a strong oxidation potential in an SCR system which can lead to the formation of Cl_2 and SO_3 both of which are strong oxidative agents for the free, volatile metals. Catalyst poisoning with As, as discussed above, is an issue in SCR NO_x control. Boersma and others (2011) found that, with cofiring, As on SCR catalyst was for the greater part deposited on the catalyst layers in the form of arsenates. Furthermore, the authors found that P might play an active role in the arsenate-induced catalyst poisoning as molar levels of P correlate with those of As for the most exposed materials. This was attributed to the fact that As and P have by nature quite similar thermochemical characteristics and therefore may interfere with one another leading to the formation of a common phase which constitutes a higher overall mass fraction than arsenates alone and thus enhancing deactivation. Boersma and others (2011) concluded that this could also mean that the introduction of biomass, which is characterised by fairly high P levels compared with coals, may lead to an increase in the As-induced catalyst poisoning in SCR. Further investigative work with laboratory-scale experiments and pH-static extraction on biomass effects on the SCR catalyst is presented by Boersma and others (2011).

6 Conclusions

Coal combustion results in the release of trace elements to the environment. Some trace elements become concentrated in certain particle streams following combustion (for example: bottom ash, fly ash, and flue gas particulate matter) while others do not. Modes of occurrence, physical and chemical characteristics of trace elements in coal are main controlling factors to trace element volatility. The volatilisation of trace elements rises with furnace temperature. Various classification schemes have been developed to describe this partitioning behaviour. These classification schemes generally make the following distinction between the elements:

- **Class 1:** elements that are approximately equally concentrated in the fly ash and bottom ash, or show little or no small particle enrichment. Examples include manganese (Mn), beryllium (Be), cobalt (Co), and chromium (Cr).
- **Class 2:** elements that are enriched in the fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size. Examples include arsenic (As), cadmium (Cd), lead (Pb), and antimony (Sb).
- **Class 3:** elements which are emitted in the gas phase primarily mercury (Hg) (not discussed in this review), and in some cases, selenium (Se).

Classification of trace elements of environmental concern related to coal utilisation are:

- | | |
|---|----------------------------|
| ● elements of greatest concern | As, B, Cd, Hg, Pb, Se |
| ● elements of moderate concern | Cr, Cu, Ni, V, Zn |
| ● elements of minor concern | Ba, Co, Ce, Li, Mn, Sb, Sr |
| ● elements of concern but present in very small amounts | Be, Sn, Te, Tl |

The elements of greatest concern, As, B, Cd, Hg, Pb, Se as well as Zn, are semi-volatile. Their significance is due to their potentially detrimental impact on human health and the environment. In coal combustion, these elements are known to be volatile in the hot zones of the process and to condense on the fly ash particles in the cooler zones downstream of the combustion process.

Concentration of trace elements in the fly ash depends on several factors including type of coal feed, coal source(s), occurrence of significant elements and their association with the organic and inorganic components of the coal, combustion conditions, volatilisation-condensation mechanisms and the particle size of the ash. The fine ash particles, which have the relatively larger surface areas, are in general enriched in trace elements. Different enrichment patterns have been observed. These depend on the specific trace element deposition mechanism. Understanding the mechanisms and factors that influence the partitioning of trace elements in coal combustion is necessary in order to develop tools and techniques to predict and mitigate the release of these trace elements into the environment. The mechanisms of trace element partitioning between the vapour and particle phases during coal combustion are not well understood and therefore remain an area where more research is required.

During coal combustion, trace elements are mobilised and fractionated among bottom ash and slag, heat exchanger deposits, fly ash, and atmospheric emissions. Additional fractionation involves fall-out and mobilisation by leaching from solid waste deposits such as in landfills. For example, a typical coal-fired power plant fly ash can be enriched with Se, I, As, Sb, Br, Zn, Cd, and Pb. The elements Br, Hg, and I are known to be partitioned into the gas phase and released into the atmosphere through the stack. Studies of coal-fired power plants have mainly centred on understanding the size fractionation of trace elements between fly ash and bottom ash. Fewer studies have attempted to understand trace element partitioning in biomass-fired plants. The result is that little is known about the trace elements, including heavy metals, and other environmentally critical pollutants associated with biomass combustion, although heavy metals, especially Pb and Zn, are known to influence the char reactivity and gasification rate for wood and other biomass waste.

Many studies agree in general that in coal combustion, analysis of bottom ash and fly ash shows that

the trace elements Ba, Ce, Co, Cs, Cu, Dy, Ga, Ge, La, Lu, Mn, Ni, Rb, Sr, Tb, Th, Y, Yb, Zn and Zr are usually retained in the combustion by-products while As, B, Be, Cd, Cr, Li, Mo, Pb, Sb, Sn, Ta, Tl, U, V and W may be only partially retained in the solid wastes whilst Hg and Se, can be primarily emitted to the atmosphere.

Conventional efficient particulate control devices, such as ESP or fabric filters in general capture the particulate phase elements As, Cd, Cr, Ni and (Pb). For trace elements associated with particles, the capture efficiency for any given particulate control technology should relate directly to the particulate collection efficiency of the system. Modern, efficient ESP, and fabric filters achieve efficiencies of 99.9% or more. However, older, inefficient ESP have poor capture efficiency for 0.1–1.0 µm particles. Fine particles tend to carry more of the semi-volatile trace elements due to their larger surface area on an equal mass basis. Upgrading an existing ESP by adding new electric fields, using new high frequency transformer rectifier technology or other advanced modifications could result in greater capture of trace elements. Replacing an existing ESP with fabric filters is another option as the capture of the finer particles in fabric filtration is greater compared with ESP.

A combination of particulate control technology and FGD may assist in capturing further trace elements. However, some trace elements, including Hg, Cl, Se, B and As can be emitted as these are not consistently captured by the existing conventional air pollutant control devices. Wet, spray dry and sorbent injection FGD technologies have been used successfully in waste incineration plants for the capture of trace elements. In coal combustion some FGD systems, in some cases in combination with SCR for NO_x control, have been proven to increase the capture of Hg emissions. The use of sorbents is an area where research continues to find the most effective reactants to capture not only air pollutants but also as many trace elements as possible. Solid materials such as clay minerals, fly ash, metal oxide mixtures and hydrated lime have been tested for retaining trace elements including As. Chemical-sorption of trace elements is considered to be one of the probable retention mechanisms. Activated carbon, which is commonly used for Hg capture, is considered a potentially viable sorbent that would also capture As as well as other trace elements in the flue gas. The trace elements Se and B may be of particular concern due to their volatility during combustion and their discharge in stream of FGD units. Water and soil regulations limits are set in some countries for the discharge of trace elements from wet FGD scrubbing units for a number of trace elements including As, B, Cd, Cr, Hg, F, Cu, Pb, Se and Zn. Limits may also be imposed on the leaching of trace elements from fly ash and include As, Cd, Pb, Cr, Hg and Sel.

NO_x control systems have little influence on trace element behaviour or removal. However, catalyst poisoning is a major issue in SCR systems, especially when firing coal with low Ca/As ratio, which may cause rapid catalyst deactivation. When cofiring with biomass, a small increase in the concentration of some volatile metals in the fly ash downstream of the SCR system, Pb and V in particular has been observed along with a significant increase in Cl load with no such increase for common alkalis. A small but significant increase was also noted with S, which was considered to be an indication of the complexation of condensing metals. Catalyst poisoning with As is an issue in SCR NO_x control. With cofiring, As on SCR catalyst was for the great part deposited on the catalyst layers in the form of arsenates. The introduction of biomass, which is characterised by fairly high P levels compared with coals, may also lead to an increase in the As-induced catalyst poisoning in SCR.

Trace elements that are vaporised during high-temperature coal-combustion cannot be measured easily by available methodologies. Instrumental technique have and continue to be developed to measure trace element concentrations online and in the gas phase. Research continues and, in recent years more so, to improve understanding of partitioning between solid and gaseous residues of various trace pollutants, for both cleaned and uncleaned coals, during combustion. There is also increased emphasis on understanding and resolving the leaching issues of trace elements to water and/or soil from the coal fly ash stored in landfills and/or by-products, such as gypsum, used in other industries.

Areas that continue to require further understanding include trace element speciation and enrichment

in coal and coal ash and the relationship between associated elements and coal macerals with mineral matter. The quantitative relationship between trace elements partitioning in the fine particulate matter with trace element content, from coal and other compositions with coal, should be studied further. Development of thermodynamic equilibrium modelling can assist in predicting the status of trace elements in the combustion process and their partitioning following the cooling process in the flue gas. Modelling the mechanisms of transformation and control technologies for easily vaporised trace elements during combustion could also be useful to describe the transformation and mobility characteristics of the easily vaporised trace elements in the combustion process. The vaporisation, nucleation mechanisms of trace elements, their retention by fly ash and the reaction mechanisms of solid sorbents with trace elements should be investigated further with an objective to develop multi-pollutant control technologies for trace elements and other pollutants with high efficiency and low investment cost.

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