

## Trace element emissions from coal

Combustion of coal is a potential source of several trace element emissions to the atmosphere, including heavy metals. Heavy metals is a general collective term which applies to the group of metals and metalloids with an atomic density greater than 4 g/cm<sup>3</sup>. 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.

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 SO<sub>2</sub> and NO<sub>x</sub>, as well as CO<sub>2</sub> and N<sub>2</sub>O, particulate matter, mercury (Hg) and other trace element pollutants such as cadmium (Cd), arsenic (As), molybdenum (Mo), vanadium (V) and various acid gases. Average values for trace elements in international coals are given in the table. 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 SO<sub>2</sub> and NO<sub>x</sub>, as well as CO<sub>2</sub>.

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 as follows:

**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, thallium, silver, tellurium. 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, polonium and radon 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.

Following coal combustion, some trace elements become concentrated in certain particle streams (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:

### Average values for trace elements in international coals

| 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              |

- **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).

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). Fine particles tend

to carry more of the semi-volatile trace elements due to their larger surface area on an equal mass basis. 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. NOx 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.

Trace elements that are vaporised during high-temperature coal combustion cannot be measured easily by available methodologies. Instrumental techniques have and continue to be developed to measure trace element concentrations online and in the gas phase. 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.

Each issue of *Profiles* is based on a detailed study undertaken by IEA Clean Coal Centre, the full report of which is available separately. This particular issue of *Profiles* is based on the report:

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CCC/203, ISBN 978-92-9029-523-5,

89 pp, September 2012, £255\*/£85†/£42.50‡

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† member countries

‡ educational establishments within member countries



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