# Enrichment of trace element concentrations in coal and its combustion residues and their potential environmental and human health impact: Can Coal Basin, NW Turkey as a case study

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**Abstract:** In this study, the variation of trace element concentrations (total of 48 trace elements including rare earth elements) in coal, coal ash and fly ash were examined and compared with coal Clarke values. Results showed that the average concentrations of trace elements including As, B, Cu, Ce, Co, Cs, Gd, Hf, La, Lu, Mo, Nd, Nb, Pr, Pb, Sc, Sm, Ta, Tb, Th, U, V, W, Y, Yb, Zn and Zr in the Can Basin coals are higher than their respective Clarke values for world low-rank coals. The elements As, Cu, Co, Cs, Mo, Nb, Sc, Pb, Pr, Th, U, V, Zn and Zr are enriched in coal ashes, whereas As, Co, Nb, Sc, U and V are enriched in fly ashes. Among the elements, maximum enrichment in coal was observed for As, with the average concentration of 253.5 ppm As in the Can Basin coals, while the coal Clarke value is 14 ppm and world average value is 8.3 ppm. From the ecotoxicological point of view, combustion residues formed by indoor combustion of coal and/or in thermal power plants may be a hazard to the environment and to aquatic and terrestrial life including human beings, particularly As, trace elements and released radioactive elements.

**Keywords:** Can Basin coal; coal ashes; fly ash; trace elements; environmental impacts; Turkey.

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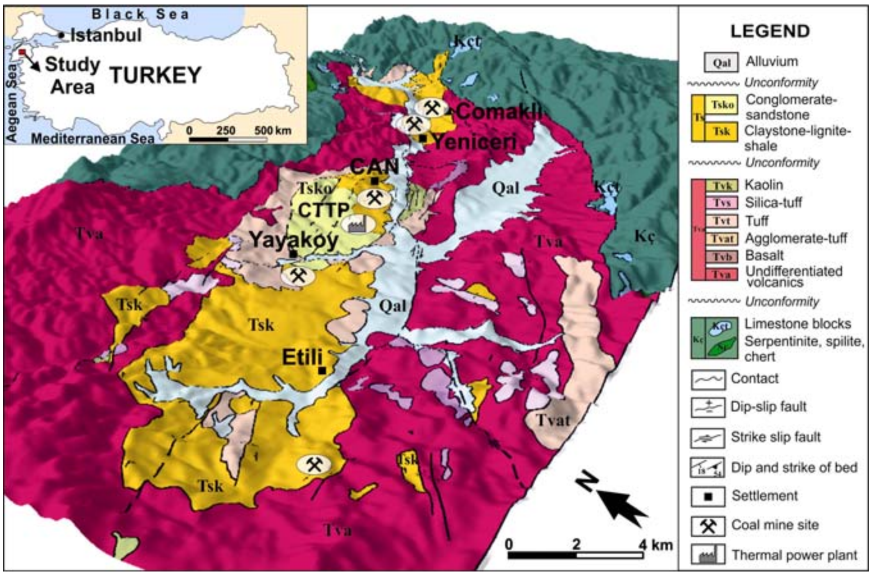
## 1 Introduction

Coal is a major energy source used in thermal power plants to generate electricity in most countries in the world. Coal combustion products associated with gaseous emissions and with the disposal of ash residues may cause serious environmental and health risks. In particular, the use of low quality lignite with high ash content results in huge quantities of fly ash which requires disposal (Baba and Turkman, 2001). Trace metals (e.g., As, B, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, V, Zn, U, Th and Cs) and even rare earth elements (REEs) present in coal as well as in fly ash are considered to be potential elements of environmental concern and possible health hazards (Swaine, 2000; Finkelman et al., 2002; Finkelman, 2004; Baba and Kaya, 2004; Mardon and Hower, 2004; Vassilev et al., 2005; Belkin et al., 2008; Bhangare et al., 2011; Dai et al., 2011; Sia and Abdullah, 2011; Singh et al., 2011). The disposal of ash and toxic elements released during coal combustion causes a contamination risk for soil, plants, and groundwater due to concentrations of potentially toxic heavy metals, soluble salts, acidity/alkalinity and radionuclides (Finkelman et al., 2002; Dai et al., 2005; Ram and Masto, 2010; Pandey et al., 2011; Singh et al., 2011). Several studies show that serious human health problems are caused by indoor combustion of coal in China, including endemic fluorosis, arsenosis, selenosis and lung cancer (Zheng et al., 1999, 2005; Finkelman et al., 2002; Liu et al., 2002; Belkin et al., 2008; Dai et al., 2011; Wang et al., 2011; Gurdal, 2011).

The distribution and concentration of trace elements in organic and inorganic components impact the quality of coal combustion by-products (Baba et al., 2008a, 2010; Finkelman, 1994a, 1994b, 1995; Swaine, 2000; Xu et al., 2003; Vassilev et al., 2005; Bhangare et al., 2011) and their concentration level and mobility determine their safe disposal and utilisation (Baba et al., 2010; Singh et al., 2011). Certain elements (e.g., Ge, Ga, U and REEs) that can potentially be of industrial value are concentrated in some coals and fly ashes (Seredin and Finkelman, 2008; Dai et al., 2011). The organically associated trace elements tend to be vaporised, either escaping to the atmosphere or being adsorbed on the fine fly ash particles, upon combustion in the furnace. The inorganically associated elements are generally non-volatile or have very low volatility, and tend to be retained in the bottom ash and in the fly ash particles upon combustion (Querol et al., 1995; Spears and Zheng, 1999; Vassilev and Braekman-Danheux, 1999; Huang et al., 2004; Liu et al., 2004, 2005; Dai et al., 2010; Vejahati et al., 2010; Sia and Abdullah, 2015).

Studies concerning the sensitive trace element (As, B, Ba, Be, Cd, Cu, Co, F, Hg, Mo, Ni, Pb, Sb, Se, Sn, Th, Tl, U, V, and Zn) geochemistry of Can coals (Gurdal, 2008; 2011) and leaching properties of Can fly ashes (Baba et al., 2010) have been previously reported. In this study, ten selected samples from the investigated Can coal samples were ashed and 48 trace elements measured in coal and coal-ashes were compared to coal and ash Clarke values (Yudovich et al., 1985), as well as to the world coal value (Ketris and Yudovich, 2009). Additionally, the concentrations of the studied elements were examined in fly ashes taken from Can Thermal Power Plant (CTPP). The results were evaluated in terms of the impact of the elements on the local environment and human health.

**Figure 1** Location and geological map of the Can Coal Basin (Bozcu et al., 2008) and coal mine sites (see online version for colours)

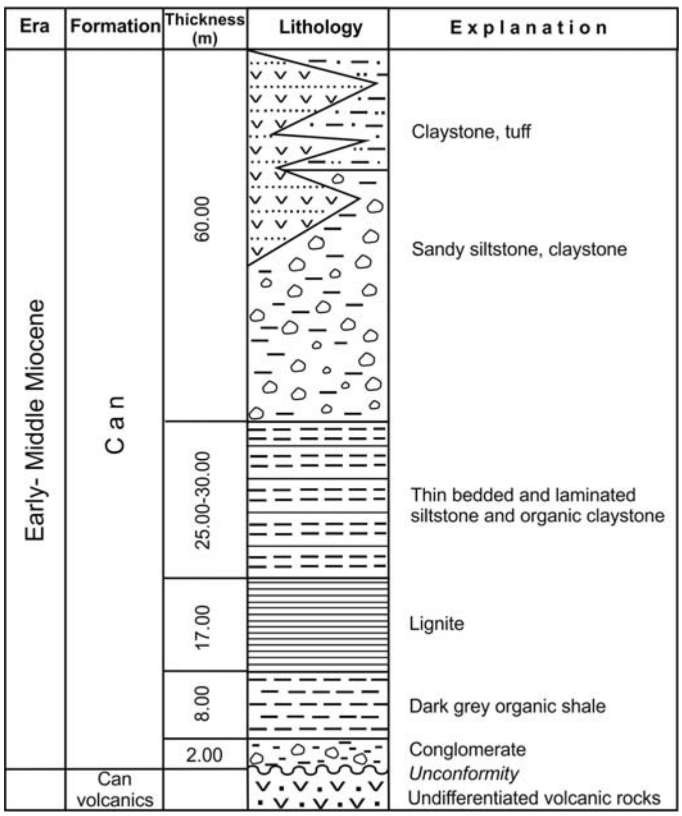



## 1.1 Geological background

The study area of the Early-Middle Miocene aged Can Coal Basin is located in the northwest of Turkey, to the north of the Kazdag Horst in the Biga Peninsula and consists of mainly volcano-clastics, fluviatile and lacustrine clastic sediments (Bozcu et al., 2008; Gurdal and Bozcu, 2011) (Figure 1). During the early to middle Miocene, the Can basin developed unconformably overlying the Oligocene-aged Can volcanic rocks. The sediments of the Can Coal Basin are composed of bituminous shale and claystone with intercalated lignite, sandstone, siltstone and tuff. Within the sequence of the Can formation, the lignite levels are commonly overlain by dark green or greenish-coloured well-laminated claystone. This claystone level contains rich organic matter and can be assumed to be a key horizon/reference layer in the field (Bozcu et al., 2008). In the basin, one main coal seam is mined which has a thickness ranging from 17 to 35 m and is contained in this claystone horizon (Figure 2). This organo-sedimentary level is interpreted as representing a low-energy lacustrine or lake-shore/swamp depositional environment. Depositional characteristics, lithological content and sedimentary structures of the Can formation indicate a change from a fluvial to lacustrine depositional environment. The basin resembles a caldera developed by volcanic and tectonic activity (Gurdal and Bozcu, 2011).

In the Can basin total coal reserves are over 100 Mt (Bozcu et al., 2008) and coal is exploited mainly by opencast mining and is consumed for domestic heating and as feed coals in the coal-fired CTPP with a 2 × 160 (320) MW capacity. The annual average lignite requirement of this plant is 1.82 million tons. A fluid coal-fired thermal power plant has been in operation since 2005 in Can County and currently it produces almost half a million tons of fly ash per year (Baba et al., 2010).

**Figure 2** The stratigraphical sequence of the Can formation




*Source:* Bozcu et al. (2008)

## 2 Materials and methods

### 2.1 Sample collection

The studied coal samples were a set of samples from previous studies performed by Baba et al. (2008b) and Bozcu et al. (2008). A total of ten coal samples were selected from Can Basin coals collected from drill cores (indicated by 'W', e.g., W06/4-3 and WYAY-SK2-2) or from seams in mines, namely Etili, Yayakoy, Can and Comakli mines (see Figure 1). Samples from open pit mines, namely Etili (Etili-3) and Comakli (Com-1), were collected using a channel-profile sampling strategy. The channel samples covered the whole thickness of the coal seam representing a volume between the roof and the floor of the seam at different locations. During the sampling process, freshly exposed faces were selected for sampling while mineral rich layers greater than 1 cm were excluded. Coal samples were air dried, crushed and blended before the analyses and the same coal samples were ashed at 600°C. In addition to the fly ash samples collected from the CTPP, samples which weighed 5 kg were collected under the electro filter. These fly ash samples were not subject to any preparatory processes at the plant.

### 2.2 Chemical analysis

Major and trace element concentrations in coals, coal ash and fly ashes were determined by inductively coupled-plasma mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using different analytical procedures at ACME Analytical Laboratories in Canada. The powdered solid samples and standard reference materials were digested using an acidic solution ($HCl:HNO_3:HF = 3:3:2$) in a microwave oven. After digestion, the concentrations of major and trace elements in the samples were analysed by ICP-MS and ICP-AES. The accuracy of most trace elements was determined using the standard reference material. The precision is within ±5 wt.% for most of the trace elements.

A thermogravimetric analyser (TGA-2000 A) was used to measure proximate analysis of coal according to ASTM D7582 at the Can Turkish Coal Enterprise Coal Laboratory. The moisture, ash yield, and volatile matter were determined by a LECO TGA 160 according to the ASTM D 3173, 3174, and 3175 procedures, respectively. The calorific values were determined by a LECO AC 350 instrument with ASTM D 5865 procedure and total sulphur analyses were carried out using LECO SC 132 (ASTM D 4239) at the accredited coal analysis laboratory of the General Directorate of Mineral Research and Exploration (MTA, in Turkish abbreviation) in Ankara.

### 2.3 Mineralogical analysis

X-ray diffraction (XRD) analysis of coal samples was performed by using Philips PW 1830 at the accredited mineralogy and petrography analysis laboratory of MTA in Ankara. The minerals in each sample were identified from the diffractograms by reference to the international centre for diffraction data (ICDD). The structure of fly ash was scanned with scanning electron microscopy (SEM) (FEI Philips XL30 sFEG, Oregon) coupled with energy dispersive X-ray spectrometry (EDX) carried out using SE and BSE detectors to determine surface features and local chemical contents in the Centre for Material Science (MAM) in Izmir Institute of Technology.

## 3 Results and discussion

### *3.1 Characterisation of Can coals*

Properties (proximate, sulphur form, XRD and petrographic) of the studied coal samples are shown in Table 1. The Can Basin coals are humic coal and classified as lignite to sub-bituminous coal based on the random huminite reflectance (0.38–0.54 % Rr), volatile matter (45.50–62.25 wt.%, daf) and calorific value (3,419–6,479 kcal/kg, maf) (Gurdal and Bozcu, 2011). Moisture and ash content (on received basis) of the Can basin coals vary between 8.76–32.56 and 2.46–41.19 wt.%, respectively. The presence of high sulphur content (max: 14.36) may be attributed to the peat environment and regional volcanic activity (tuff deposits are interbedded in the coal-bearing sequences), as well as to alkaline depositional environments with intensive sulphide mineralisation (Gurdal and Bozcu, 2011). The results for sulphur form show that the sulphur contents are mainly of organic and pyritic sulphur.

The literature data (Gurdal and Bozcu, 2011; Gurdal, 2011) shows that Can coals have 74–95 vol.% huminite (mineral matter free, mmf), 2–19 vol.% (mmf) liptinite and 2–13 vol.% (mmf) inertinite (see Table 1) and the coals are rich in mineral matter (4–45 vol.%), which consists mostly of clay minerals and pyrite. XRD analysis results indicate that, in general, major mineral contents of Can basin coals are kaolinite, mixed layer clay minerals, quartz, illite/mica group minerals, pyrite, feldspar group minerals, gypsum and zeolite group minerals (see Table 1)

### *3.2 Characterisation of fly ash and leaching properties*

Coal combustion in CTPP has consumed low-quality lignite reserves from the Can Basin. At the CTPP approximately 5,000 tons of coal is burnt and approximately 1,500 tons of fly ash is produced per day. Chemical composition of fly ash varies considerably, depending upon the composition of host coal (Hajarnavis, 2000) and the operating conditions of the thermal power plant. The chemical composition of the fly ash from the CTPP contained less than 70% $SiO_2$+$Al_2O_3$+$Fe_2O_3$ values (average 53.27%) and CaO was more than 10% (average 22.95%) (Table 2). Based on these values, fly ashes were classified as C class, which has high calcareous and pozzolanic characteristics (Baba et al., 2010). When the ash concentration of $SiO_2$ + $Al_2O_3$ + $Fe_2O_3$ exceeds 70% and CaO is less than 10% it is classified as F class. Coal combustion in the CTPP uses fluidised bed combustion. This power generation produced F class ash one year. After 2007, a flue gas desulfurisation unit was placed inline and limestone was added, causing the composition of ash to completely change in the CTPP (Baba et al., 2010).

**Table 1** Some properties (proximate, sulphur form, XRD and petrographical) of the Can Basin coals

| *Sample ID* | *Moisture* | *Ash* | *Volatile matter* | *Fixed carbon* | *Gross calorific value* | *Total sulphur* |
|---|---|---|---|---|---|---|
| *Studied coal samples* | | *(wt.%, o)* | | | *(kcal/kg, o)* | *(wt.%, o)* |
| Etili-3 | 22.13 | 37.23 | 26.13 | 14.51 | 2,180 | 4.85 |
| WYAY-SK2-2 | 12.92 | 29.94 | 34.33 | 22.81 | 3,515 | 8.60 |
| WYAY-SK1-2 | 28.96 | 8.21 | 33.31 | 29.52 | 4,181 | 4.67 |
| WYAY-SK1-4 | 21.41 | 18.59 | 33.16 | 26.83 | 3,762 | 8.00 |
| W06/4-3 | 30.48 | 9.18 | 31.53 | 28.81 | 4,167 | 5.50 |
| W06/6-6 | 22.19 | 13.19 | 33.29 | 31.33 | 5,840 | 6.38 |
| W07/8-4 | 28.64 | 14.84 | 28.42 | 28.11 | 3,936 | 4.56 |
| W07/14-1 | 22.84 | 29.58 | 26.80 | 20.78 | 3,113 | 3.25 |
| W07/14-5 | 21.51 | 20.85 | 32.02 | 25.62 | 4,012 | 11.77 |
| Com-1 | 23.21 | 16.57 | 31.59 | 28.63 | 4,064 | 6.46 |
| Can Basins coal (min and max values, N = 81) | 8.76–32.56 | 2.46–41.19 | 22.67–47.62 | 14.31–46.14 | 2,176–6,312 | 0.21–14.36 |
| XRD | | | | | | |
| WYAY-SK1-4 | Kaolinite, opal-CT, quartz, pyrite, feldspar group minerals, mixed layer clay minerals, illite/mica group minerals, gypsum | | | | | |
| Etili-3 | Kaolinite, quartz, pyrite, gypsum, zeolite group minerals | | | | | |
| COM-1 | Kaolinite, pyrite, feldspar group minerals, mixed layer clay minerals, illite/mica group minerals, gypsum, zeolite group minerals | | | | | |

Notes: o, original basis; wt%, weight; total huminite (TH); total liptinite (TL); total inertinite (TI); total pyrite (TPy); clay (Cl); total mineral matter (TMM); nd (no data).

**Table 1** Some properties (proximate, sulphur form, XRD and petrographical) of the Can Basin coals (continued)

| *Sample ID* | *Pyritic sulphur* | *Sulphate sulphur* | *Organic sulphur* | *TH* | *TL* | *TI* | *MINERALS (vol.%)* | | |
|---|---|---|---|---|---|---|---|---|---|
| *Studied coal samples* | | *(%, o)* | | | *(vol.%, mmf)* | | *(TPy)* | *(Cl)* | *TMM* |
| Etili-3 | 1.04 | 1.08 | 1.80 | 89.3 | 6.0 | 4.8 | 4.00 | 12.00 | 16.00 |
| WYAY-SK2-2 | 3.13 | 1.20 | 4.04 | 89.6 | 6.5 | 3.9 | 9.00 | 14.00 | 23.00 |
| WYAY-SK1-2 | 0.45 | 0.67 | 2.79 | 89.0 | 6.1 | 4.9 | 5.00 | 13.00 | 18.00 |
| WYAY-SK1-4 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| W06/4-3 | nd | nd | nd | 92.1 | 5.3 | 2.6 | 4.00 | 20.00 | 24.00 |
| W06/6-6 | 0.87 | 1.79 | 4.41 | 86.7 | 10.0 | 3.3 | 1.00 | 9.00 | 10.00 |
| W07/8-4 | 0.89 | 0.74 | 0.90 | 86.1 | 6.9 | 6.9 | 6.00 | 22.00 | 28.00 |
| W07/14-1 | nd | nd | nd | 88.2 | 6.6 | 5.3 | 7.00 | 17.00 | 24.00 |
| W07/14-5 | 4.28 | 2.67 | 4.35 | 89.0 | 4.9 | 6.1 | 4.00 | 14.00 | 18.00 |
| Com-1 | 0.34 | 0.67 | 4.91 | 94.4 | 2.8 | 2.8 | 9.00 | 19.00 | 28.00 |
| Can Basins coal (min and max values, N = 81) | 0.22–6.34 | 0.35–2.67 | 0.9–6.07 | 74.0–95.0 | 2.0–19.0 | 2.0–13.0 | 1–20 | 3–37 | 4.0–45.0 |
| XRD | | | | | | | | | |
| WYAY-SK1-4 | Kaolinite, opal-CT, quartz, pyrite, feldspar group minerals, mixed layer clay minerals, illite/mica group minerals, gypsum | | | | | | | | |
| Etili-3 | Kaolinite, quartz, pyrite, gypsum, zeolite group minerals | | | | | | | | |
| COM-1 | Kaolinite, pyrite, feldspar group minerals, mixed layer clay minerals, illite/mica group minerals, gypsum, zeolite group minerals | | | | | | | | |

Notes: o, original basis; wt%, weight; total huminite (TH); total liptinite (TL); total inertinite (TI); total pyrite (TPy); clay (Cl); total mineral matter (TMM); nd (no data).

**Table 2** Major element oxides of Can Basin coal, coal ash and fly ash

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $MgO$ | $CaO$ | $Na_2O$ | $K_2O$ | $TiO_2$ | $P_2O_5$ | $MnO$ | $Cr_2O_3$ | *TOT/S* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | % | | | | | |
| COAL | | | | | | | | | | | | |
| Etili-3 | 19.58 | 14.83 | 5.24 | 0.26 | 0.83 | 0.37 | 0.33 | 0.39 | 0.05 | 0.01 | 0.004 | 4.85 |
| WYAY-SK2-2 | 11.62 | 9.61 | 7.95 | 0.14 | 0.98 | 0.41 | 0.09 | 0.30 | 0.03 | 0.01 | 0.002 | 8.60 |
| WYAY-SK1-2 | 2.19 | 1.96 | 2.18 | 0.16 | 1.32 | 0.52 | 0.09 | 0.06 | 0.02 | 0.01 | 0.001 | 4.67 |
| WYAY-SK1-4 | 6.12 | 4.82 | 6.05 | 0.15 | 0.96 | 0.42 | 0.10 | 0.16 | 0.01 | 0.01 | 0.003 | 8.00 |
| W06/4-3 | 27.57 | 20.35 | 8.38 | 0.15 | 0.48 | 0.04 | 0.49 | 0.77 | 0.09 | 0.02 | 0.003 | 7.99 |
| W06/6-6 | 2.74 | 2.83 | 2.40 | 0.11 | 0.79 | 0.44 | 0.05 | 0.08 | 0.04 | 0.01 | 0.004 | 5.50 |
| W07/8-4 | 9.95 | 2.99 | 2.56 | 0.12 | 0.65 | 0.51 | 0.06 | 0.11 | 0.01 | 0.01 | 0.001 | 4.56 |
| W07/14-1 | 3.96 | 3.01 | 4.65 | 0.04 | 0.34 | 0.12 | 0.05 | 0.09 | 0.01 | 0.02 | 0.001 | 7.55 |
| W07/14-5 | 23.26 | 7.72 | 3.35 | 0.24 | 0.66 | 0.43 | 0.11 | 0.25 | 0.03 | 0.01 | 0.002 | 3.25 |
| Com-1 | 5.60 | 2.82 | 14.12 | 0.09 | 0.57 | 0.41 | 0.17 | 0.07 | 0.02 | 0.02 | 0.007 | 13.77 |
| MEAN | 11.26 | 7.09 | 5.69 | 0.15 | 0.76 | 0.37 | 0.15 | 0.23 | 0.03 | 0.01 | 0.003 | 6.87 |
| COAL ASH | | | | | | | | | | | | |
| Etili-3 | 44.11 | 31.62 | 10.87 | 0.58 | 1.99 | 0.83 | 0.73 | 0.89 | 0.13 | 0.03 | 0.008 | 1.60 |
| WYAY-SK2-2 | 34.18 | 27.46 | 22.72 | 0.39 | 2.84 | 1.15 | 0.26 | 0.91 | 0.11 | 0.03 | 0.005 | 2.58 |
| WYAY-SK1-2 | 15.40 | 13.23 | 16.14 | 1.16 | 9.70 | 3.66 | 0.64 | 0.42 | 0.15 | 0.08 | 0.004 | 9.41 |
| WYAY-SK1-4 | 27.87 | 21.45 | 25.25 | 0.70 | 4.36 | 1.84 | 0.41 | 0.72 | 0.07 | 0.06 | 0.006 | 4.96 |
| W06/4-3 | 43.54 | 31.44 | 13.85 | 0.25 | 0.79 | 0.06 | 0.77 | 1.27 | 0.14 | 0.02 | 0.002 | 1.10 |
| W06/6-6 | 26.71 | 17.77 | 20.24 | 0.82 | 6.57 | 3.54 | 0.35 | 0.71 | 0.31 | 0.10 | 0.007 | 7.58 |
| W07/8-4 | 40.83 | 17.77 | 13.05 | 0.70 | 4.12 | 3.13 | 0.17 | 0.66 | 0.03 | 0.04 | 0.003 | 6.09 |
| W07/14-1 | 26.57 | 22.00 | 35.02 | 0.28 | 2.57 | 0.83 | 0.12 | 0.67 | 0.09 | 0.13 | 0.008 | 2.95 |
| W07/14-5 | 61.42 | 19.75 | 7.87 | 0.62 | 1.56 | 1.05 | 0.26 | 0.66 | 0.09 | 0.03 | 0.004 | 1.40 |
| Com-1 | 23.41 | 10.91 | 44.00 | 0.34 | 2.25 | 1.57 | 0.69 | 0.28 | 0.04 | 0.05 | 0.004 | 5.27 |
| MEAN | 34.40 | 21.34 | 20.90 | 0.58 | 3.68 | 1.77 | 0.44 | 0.72 | 0.12 | 0.06 | 0.005 | 4.29 |
| FLY ASH | | | | | | | | | | | | |
| 1 | 29.29 | 15.82 | 7.91 | 0.44 | 25.75 | 0.57 | 0.32 | 0.61 | 0.20 | 0.15 | 0.005 | 5.45 |
| 2 | 29.31 | 15.16 | 5.97 | 0.43 | 18.96 | 0.57 | 0.39 | 0.57 | 0.32 | 0.11 | 0.003 | 4.52 |
| 3 | 29.90 | 16.07 | 7.82 | 0.44 | 24.89 | 0.58 | 0.33 | 0.63 | 0.21 | 0.09 | 0.003 | 5.26 |
| 4 | 32.37 | 17.89 | 5.55 | 0.45 | 22.20 | 0.45 | 0.41 | 0.67 | 0.20 | 0.11 | 0.005 | 6.70 |
| MEAN | 30.22 | 16.24 | 6.81 | 0.44 | 22.95 | 0.54 | 0.36 | 0.62 | 0.23 | 0.12 | 0.004 | 5.48 |

**Figure 3** SEM images of fly ash, (a) irregular and spherical particles (b) irregular particles

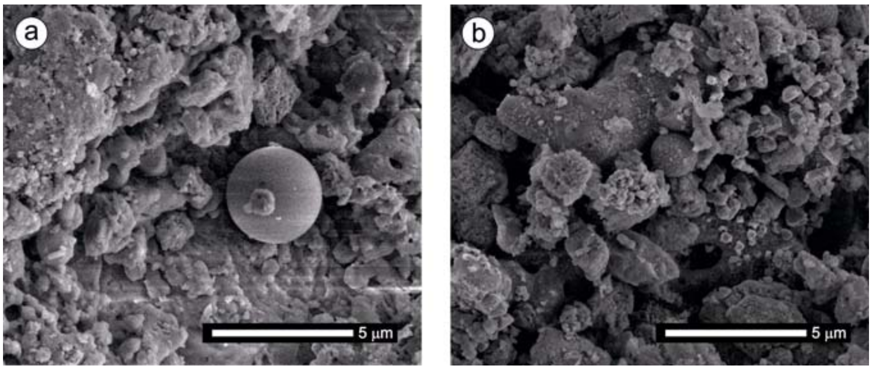
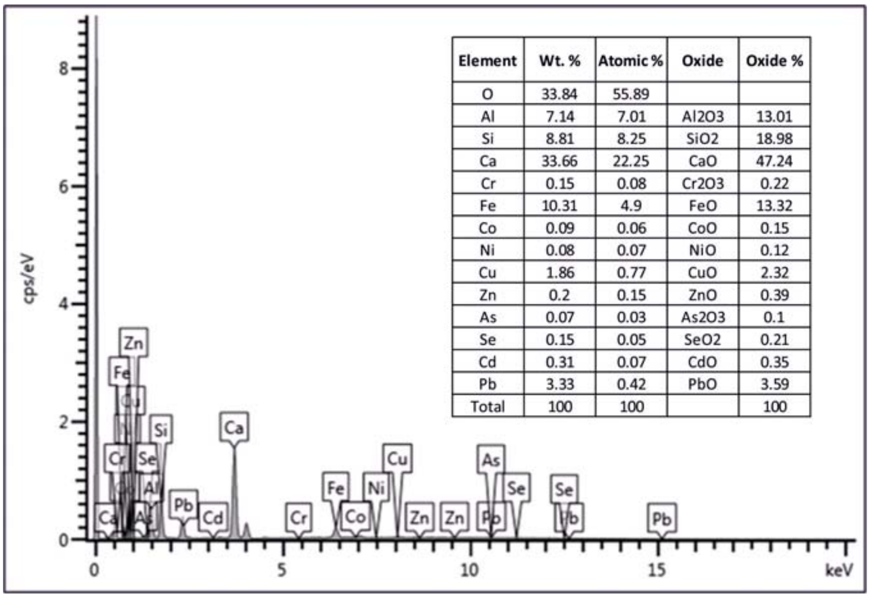



**Figure 4** EDX result of the fly ash




| Element | Wt. % | Atomic % | Oxide | Oxide % |
|---|---|---|---|---|
| O | 33.84 | 55.89 | | |
| Al | 7.14 | 7.01 | Al2O3 | 13.01 |
| Si | 8.81 | 8.25 | SiO2 | 18.98 |
| Ca | 33.66 | 22.25 | CaO | 47.24 |
| Cr | 0.15 | 0.08 | Cr2O3 | 0.22 |
| Fe | 10.31 | 4.9 | FeO | 13.32 |
| Co | 0.09 | 0.06 | CoO | 0.15 |
| Ni | 0.08 | 0.07 | NiO | 0.12 |
| Cu | 1.86 | 0.77 | CuO | 2.32 |
| Zn | 0.2 | 0.15 | ZnO | 0.39 |
| As | 0.07 | 0.03 | As2O3 | 0.1 |
| Se | 0.15 | 0.05 | SeO2 | 0.21 |
| Cd | 0.31 | 0.07 | CdO | 0.35 |
| Pb | 3.33 | 0.42 | PbO | 3.59 |
| Total | 100 | 100 | | 100 |

The scanning electron microscopy technique with energy-dispersive X-ray microanalysis was used to scan the size, shape and quantitative information on the local chemical composition of the particles. Generally fly ash was composed of mainly irregular particles; some ashes also contain spherical particles [Figure 3(a) and 3(b)]. Particles of fluidised bed combustion fly ash were very irregular in shape due to the combustion temperature. As the molten droplets of inorganic coal residues cool down, fly ash particles solidify and separate out as spheres, while solidifying around trapped hollow gas bubbles. Results of SEM analysis have shown those spherical fly ashes vary in size from 1 to 5 µm fly ashes of irregular shape are usually larger. EDX results show that typical components include Fe Ca Al-silicate with traces of As, Cd, Co, Cr, Cu, Ni, Pb, Se and Zn (Figure 4). Coal combustion fly ash was found to leach metals at concentrations inversely proportional to leachant pH and temperature in the study area. It can be concluded that the metal leaching increases with decreasing pH (Baba et al., 2010).

Consequently, even where pure water has been used in fly ash leaching studies, appreciable fractions of As and other elements were shown to leach from fly ash (Llorens et al., 2001). Therefore, the concentration of some heavy metals such as As may be enriched in fly ash deposited at the ash disposal site. In other words, the mobility of trace elements from fly ash depends not only on the element concentration, temperature and mode of occurrence, but also on the chemical conditions associated with the leaching process (Pandey et al., 2011).

### *3.3 Major and trace element concentrations in coal and its combustion residues*

The major and trace element concentrations of the studied coals, coal and fly ashes are given in Tables 2 and 3, respectively. Table 4 also lists ranges and average values of trace element concentrations in Can basin coals including Clarke (Yudovich et al., 1985) and world coal values (Ketris and Yudovich, 2009). Compared with the respective Clarke values for lignite, subbituminous coals and their ashes worldwide (Yudovich et al., 1985), the Can coals and ashes are enriched in As, B, Cu, Co, Cs, Mo, Pb, Th, U, V and Zn. Additionally, some elements such as Ce, Eu, Gd, Hf, Lu, Nd, Nb, Sc, Sm, Tb, W and Y have higher contents only in coal compared to the respective Clarke value for coals. Compared to world coals (Ketris and Yudovich, 2009), Can coals have higher values for most trace elements including As, B, Cu, Ce, Co, Cs, Eu, Er, Ga, Hf, La, Mo, Nd, Nb, Pb, Sc, Sm, Tl, Ta, Th, U, V, Y, Yb, Zr, and Zn. The fly ash data shows that As and V are significantly enriched, but Co, Sc, and U are slightly enriched in the samples studied.

Coals sometimes include high contents of natural radioactive elements (U, Th and their decay products) and, in some cases, concentrate considerable resources of uranium (Arbuzov et al., 2011). However, during the combustion process of such coals, the radioactive elements concentrate in the combustion products such as fly ash. The mean concentrations of U, Th and V in the selected Can coals (U = 10.6 ppm, Th = 9.79 ppm and V=173 ppm) increase two- or three fold in coal ashes (U = 29.1, Th = 31.03 ppm and V = 556.8 ppm) and when compared with world coal (Ketris and Yudovich, 2009) the element concentrations are extremely high. A similar enrichment of radioactive elements in coal combustion residues was reported by Mukhopadhyay et al. (1998) and Arbuzov et al. (2011). It was reported that uranium enrichment in coals and fly ashes can potentially have industrial value (Seredin and Finkelman, 2008; Dai et al., 2011; Gurdal, 2011).

Based on statistical analyses, most of the trace elements, except for U, show an affinity to ash yield. Elements including As, Cu, Mo and Zn show a possible association with pyrite; however, the elements B and Mo can have both organic and inorganic associations (Gurdal, 2011). The elements associated with sulphide minerals and organic matters are more volatile compared to those in different chemical forms like oxides (Bhangare et al., 2011). The behaviour of the elements during coal combustion includes two processes: the release stage (volatilisation) from the coal and the subsequent reaction stage (Zhang et al., 2003). Many elements can be volatilised during coal combustion depending on the modes of occurrence, concentrations, physical change, chemical reactions, and combustion technology (Querol et al., 1995; Hower et al., 1999; Pandey et al., 2011). The REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) in Can coals show an affinity to ash yield and REEs in coal are probably derived from clay minerals. Similar relationships have been reported by Ren et al. (2006) and Sun et al. (2007). It seems that REEs in Can coals rarely volatilise during combustion. Compared to world coals, reported by Ketris and Yudovich (2009), concentrations of some REEs in Can coals including La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Yb, Lu and Y are high. However, concentrations of Er and Tm elements are similar, while the mean content of Dy and Ho elements are less than world coal average. The results (see Table 4) show that the REE concentrations in coal ashes and fly ashes are within the range of Clarke values (Yudovich et al., 1985).

The relative enrichment index REI = ([X]a/[X]c) × (A/100) is used to describe the enrichment degree of elements in fly and coal ashes (Meij, 1994; Dai et al., 2010). [X]a is the mean content of elements in fly or coal ashes, and [X]c is the mean content of corresponding elements in coal. A is the ash yield of the coal. In order to determine the relative enrichment factor for fly ashes, A is accepted as 32% (this value is the maximum ash value accepted by CTPP) and the average element concentration of Can basin coals is used in the given equation. The REI values for coal ash and fly ash are given in Table 4. The results show that Ca has maximum enrichment among major oxides. The expected value is due to the fluidised bed combustion technology which uses $CaCO_3$. The composition of ash is highly calcareous and has pozzolanic characteristics due to the added limestone. This point may be important to control the quantity of As present in fly ash leachate since the leaching of As from high Ca-ash wastes is far less than from acid ones (Yudovich and Ketris, 2005). In the literature, the elements with REI values > 1.0 are accepted as non-volatile elements, whereas the elements with REI values < 0.7 are defined as volatile elements and the remaining elements between 0.7 and 1.0 have semi-volatile nature (Dai et al., 2010; Bhangare et al., 2011). If REI value > 0.7 the trace elements are regarded as enriched in ashes. The REI values are listed for both coal and fly ash in ascending order:

| | |
|---|---|
| REIflyash >1.0 | Ga > Rb > Sr > Ni > Tl > Ho > Gd |
| REIflyash 1.0–0.7 | Dy > Ba >Y > Er > Eu > La > Sc > Tm > Nb > Tb > Sw > Ce > Sm > Se > Be > Pr > Th > Pb > Nd > Yb > Cs > Lu > Hf > Cu > As > V |
| REIflyash <0.7 | Sb > U > Sn > Cu > Mo > Ta > Bi > Cd > Zn > Hg > Se > Ag > Au |
| REIcoalash >1.0 | Hf > Pb > Tl > F |
| REIcoalash 1.0–0.7 | Tm > Co > Hg > Eu > Ni > W > La > Nb > Tb > Er > Sr > Se > Ho > Nd > Pr > Ga> Mo > Ta > Th > B > Lu > Cd > Cu > Zr > Ba > Yb > Gd > Sm > Y >Cs > Dy > U > V > Zn > Rb |
| REIcoalash <0.7 | As > Bi > Be > Sn > Ag > Au > Sb > Se |

Although As is a typical highly volatile element, the REI value in coal ash is under < 0.7, whereas in fly ash the value is higher > 0.7. This result can be explained by its affinity to calcium which is used in CTTP (Querol et al., 1995; Senior et al., 2000). According to REI values (<0.7) for fly ash, Mo, Sb, Se and Zn are known as hazardous air pollutants among the volatile elements and are suspected to cause serious health effects such as cancer and birth defects. These elements vaporise during the combustion process and condense as the combustion gases cool (Senior et al., 2000).

**Table 3** Trace elements concentrations of Can Basin coal, coal ash and fly ash

| *Elements* | *Ag* | *Au* | *As* | *Ba* | *Be* | *Bi* | *B* | *Cd* | *Cu* | *Ce* | *Co* | *Cs* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *(ppm, on a whole coal basis)* | | | | | | | | | | | |
| COAL | | | | | | | | | | | | |
| Etili-3 | 0.09 | 2.00 | **115.40** | **716.10** | 3.0 | 0.5 | **435.0** | **0.1** | **30.1** | 76.2 | **9.2** | 3.3 |
| WYAY-SK2-2 | 0.09 | 3.00 | **5,180.40** | **53.50** | 2.0 | 0.3 | **147.0** | **0.2** | **44.3** | 68.5 | **11.8** | 9.5 |
| WYAY-SK1-2 | 0.09 | 1.00 | **772.70** | **45.30** | 1.0 | 0.1 | **210.0** | **0.1** | **8.3** | 13.7 | **2.1** | 1.6 |
| WYAY-SK1-4 | 0.09 | 1.40 | **1,841.30** | **44.90** | 2.0 | 0.2 | **147.0** | **0.2** | **23.0** | 31.2 | **9.7** | 4.3 |
| Com-1 | 0.09 | 2.10 | **102.40** | **169.70** | 2.0 | 0.2 | **409.0** | **0.3** | **45.9** | 54.2 | **74.2** | 7.3 |
| W06/4-3 | 0.09 | 2.00 | **567.50** | **122.20** | 1.0 | 0.1 | **222.0** | **0.1** | **10.2** | 6.1 | **3.0** | 0.8 |
| W06/6-6 | 0.09 | 0.70 | **417.30** | **21.00** | 1.0 | 0.1 | **252.0** | **0.1** | **9.9** | 8.8 | **1.5** | 2.9 |
| W07/8-4 | 0.09 | 1.60 | **90.40** | **80.30** | 1.0 | 0.1 | **441.0** | **0.1** | **12.8** | 8.5 | **3.0** | 1.0 |
| W07/14-1 | 0.09 | 1.40 | **23.00** | **101.30** | 1.0 | 0.2 | **451.0** | **0.1** | **24.3** | 24.6 | **6.1** | 2.6 |
| W07/14-5 | 0.09 | 1.40 | **218.90** | **87.20** | 0.9 | 0.2 | **366.0** | **0.1** | **10.7** | 12.5 | **15.4** | 0.6 |
| *MEAN* | *0.09* | *1.66* | *932.93* | *144.15* | *1.49* | *0.20* | *308.00* | *0.13* | *21.95* | *30.43* | *13.60* | *3.39* |
| COAL ASH | | | | | | | | | | | | |
| Etili-3 | 0.10 | 3.40 | 219.00 | 1,618.60 | 5 | 1.1 | 882 | 0.2 | 66.4 | 157.9 | 21.9 | 6.3 |
| WYAY-SK2-2 | 0.20 | 3.80 | 10,000.00 | 146.80 | 4 | 0.6 | 414 | 0.6 | 114.2 | 189.8 | 37.1 | 24 |
| WYAY-SK1-2 | 0.10 | 1.70 | 5,505.90 | 237.70 | 3 | 0.4 | 1,573 | 0.3 | 55.7 | 93.4 | 19.5 | 10.6 |
| WYAY-SK1-4 | 0.20 | 1.20 | 6,666.70 | 151.70 | 6 | 0.4 | 539 | 0.5 | 89.4 | 123.2 | 43.1 | 14.9 |
| Com-1 | 0.09 | 1.20 | 103.40 | 264.40 | 2 | 0.2 | 693 | 0.5 | 77.6 | 88.4 | 117.8 | 10.8 |
| W06/4-3 | 0.10 | 5.90 | 3,681.50 | 1,028.90 | 7 | 1.7 | 1,905 | 0.9 | 80.6 | 56.3 | 31.1 | 5.6 |
| W06/6-6 | 0.10 | 1.90 | 3,392.30 | 120.80 | 4 | 0.4 | 1,761 | 0.1 | 79.1 | 63 | 13.8 | 18.5 |
| W07/8-4 | 0.10 | 1.20 | 270.50 | 390.40 | 4 | 0.3 | 2,635 | 0.2 | 69.3 | 31.1 | 24.7 | 3.8 |
| W07/14-1 | 0.09 | 1.30 | 52.80 | 233.50 | 2 | 0.3 | 979 | 0.1 | 50.7 | 60.8 | 16.1 | 5.9 |
| W07/14-5 | 0.10 | 2.10 | 466.70 | 420.30 | 2 | 0.4 | 1,149 | 0.6 | 32.7 | 45 | 75 | 3.3 |
| *MEAN* | *0.12* | *2.37* | *3,035.88* | *461.31* | *3.90* | *0.58* | *1,253.00* | *0.40* | *71.57* | *90.89* | *40.01* | *10.37* |
| FLY ASH | | | | | | | | | | | | |
| 1 | 0.09 | 0.70 | 827.30 | 294.00 | 4.0 | 0.3 | nd | 0.3 | **40.8** | 71.9 | 22.9 | 5.2 |
| 2 | 0.09 | 0.49 | 445.60 | 273.00 | 4.0 | 0.3 | nd | 0.3 | **32.8** | 85 | 18 | 5.1 |
| 3 | 0.09 | 1.40 | 806.80 | 311.00 | 4.0 | 0.3 | nd | 0.2 | **40.1** | 75.4 | 22.7 | 5.6 |
| 4 | 0.09 | 1.90 | 249.20 | 333.00 | 3.0 | 0.3 | nd | 0.2 | **30.3** | 79.5 | 20.9 | 5.6 |
| *MEAN* | *0.09* | *1.12* | *582.23* | *302.75* | *3.75* | *0.30* | *nd* | *0.25* | *36.00* | *77.95* | *21.13* | *5.38* |

Note: Hazardous elements are given as bold character.

**Table 3** Trace elements concentrations of Can Basin coal, coal ash and fly ash (continued)

| *Elements* | *Dy* | *Eu* | *Er* | *F* | *Gd* | *Ga* | *Hf* | *Ho* | *Hg* | *La* | *Lu* | *Mo* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *(ppm, on a whole coal basis)* | | | | | | |
| COAL | | | | | | | | | | | | |
| Etili-3 | 2.0 | 1.0 | 0.9 | **180.0** | 3.07 | 15.50 | 3.30 | 0.31 | **0.29** | 38.3 | 0.1 | **4.9** |
| WYAY-SK2-2 | 2.6 | 1.1 | 1.4 | **60.0** | 3.35 | 9.00 | 2.40 | 0.45 | **0.10** | 27.7 | 0.2 | **3.3** |
| WYAY-SK1-2 | 0.7 | 0.2 | 0.4 | **20.0** | 0.80 | 1.70 | 0.50 | 0.12 | **0.05** | 6.0 | 0.1 | **1.1** |
| WYAY-SK1-4 | 1.9 | 0.7 | 1.1 | **20.0** | 2.19 | 4.50 | 1.20 | 0.32 | **0.12** | 15.6 | 0.2 | **3.1** |
| Com-1 | 2.6 | 1.1 | 1.5 | **50.0** | 3.21 | 18.10 | 3.80 | 0.43 | **0.08** | 33.8 | 0.3 | **1.0** |
| W06/4-3 | 0.5 | 0.2 | 0.3 | **30.0** | 0.60 | 2.20 | 0.40 | 0.10 | **0.04** | 3.6 | 0.1 | **3.2** |
| W06/6-6 | 0.5 | 0.2 | 0.3 | **30.0** | 0.66 | 3.40 | 0.60 | 0.10 | **0.05** | 5.2 | 0.1 | **2.9** |
| W07/8-4 | 0.7 | 0.2 | 0.4 | **9.0** | 0.75 | 2.90 | 0.60 | 0.13 | **0.04** | 4.1 | 0.1 | **6.7** |
| W07/14-1 | 1.6 | 0.5 | 0.9 | **20.0** | 1.88 | 6.40 | 1.50 | 0.27 | **0.11** | 13.5 | 0.1 | **3.1** |
| W07/14-5 | 0.7 | 0.2 | 0.3 | **9.0** | 0.62 | 2.30 | 0.80 | 0.12 | **0.06** | 5.1 | 0.1 | **41.6** |
| *MEAN* | *1.38* | *0.54* | *0.76* | *42.80* | *1.71* | *6.60* | *1.51* | *0.24* | *0.09* | *15.29* | *0.12* | *7.09* |
| COAL ASH | | | | | | | | | | | | |
| Etili-3 | 4 | 2.26 | 2.2 | 240 | 5.88 | 32.1 | 7.5 | 0.68 | **0.009** | 87.8 | 0.31 | 10.4 |
| WYAY-SK2-2 | 7.06 | 3.42 | 4.35 | 150 | 9.01 | 25 | 6.1 | 1.29 | **0.009** | 84.9 | 0.66 | 9.5 |
| WYAY-SK1-2 | 4.27 | 1.78 | 2.85 | 210 | 5.02 | 12.3 | 3.2 | 0.91 | **0.009** | 43.9 | 0.44 | 15 |
| WYAY-SK1-4 | 7.58 | 3.11 | 4.7 | 180 | 8.87 | 20.8 | 4.5 | 1.44 | **0.009** | 68 | 0.72 | 12.5 |
| Com-1 | 4.06 | 2.05 | 2.51 | 90 | 5.17 | 27.6 | 6.2 | 0.76 | **0.009** | 60.3 | 0.44 | 1.2 |
| W06/4-3 | 4.53 | 1.62 | 3.17 | 60 | 5.06 | 15.3 | 3.2 | 0.95 | **0.009** | 31.7 | 0.47 | 26.5 |
| W06/6-6 | 3.26 | 1.43 | 2.26 | 100 | 4.03 | 19.8 | 4.3 | 0.64 | **0.009** | 40.3 | 0.37 | 29.6 |
| W07/8-4 | 2.97 | 1 | 2.07 | 120 | 3.03 | 15.5 | 3.3 | 0.66 | **0.009** | 20.1 | 0.33 | 18.2 |
| W07/14-1 | 3.41 | 1.5 | 2.14 | 120 | 4.32 | 16.3 | 4 | 0.69 | **0.009** | 35.2 | 0.32 | 5.3 |
| W07/14-5 | 2.3 | 0.96 | 1.5 | 70 | 2.8 | 10.9 | 2.7 | 0.44 | **0.009** | 23.7 | 0.25 | 130.2 |
| *MEAN* | *4.34* | *1.91* | *2.78* | *134.00* | *5.32* | *19.56* | *4.50* | *0.85* | *0.01* | *49.59* | *0.43* | *25.84* |
| FLY ASH | | | | | | | | | | | | |
| 1 | 5.4 | 1.7 | 2.9 | nd | 6.39 | 27.5 | 3.9 | 1.01 | **0.18** | 35.9 | 0.4 | **8.5** |
| 2 | 6.5 | 1.8 | 3.8 | nd | 7.26 | 24.3 | 3.4 | 1.26 | **0.09** | 37.6 | 0.5 | **6.0** |
| 3 | 5.3 | 1.7 | 3.0 | nd | 6.28 | 24.4 | 3.8 | 1.01 | **0.23** | 36.9 | 0.4 | **8.9** |
| 4 | 4.4 | 1.6 | 2.5 | nd | 5.67 | 23.6 | 3.8 | 0.85 | **0.009** | 40.5 | 0.4 | **2.9** |
| *MEAN* | *5.38* | *1.68* | *3.01* | *nd* | *6.40* | *24.95* | *3.73* | *1.03* | *0.13* | *37.73* | *0.43* | *6.58* |

Note: Hazardous elements are given as bold character.

**Table 3** Trace elements concentrations of Can basin coal, coal ash and fly ash (continued)

| *Elements* | *Ni* | *Nd* | *Nb* | *Pb* | *Pr* | *Rb* | *Sc* | *Se* | *Sn* | *Sr* | *Sb* | *Sm* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *(ppm)* | | | | | | |
| COAL | | | | | | | | | | | | |
| Etili-3 | **9.30** | 27.90 | 10.10 | **27.70** | 7.80 | 12.3 | 7.0 | **1.4** | **2.00** | 209.5 | **0.30** | 4.15 |
| WYAY-SK2-2 | **7.90** | 24.60 | 4.70 | **24.30** | 6.41 | 4.2 | 10.0 | **1.3** | **1.00** | 132.5 | **0.30** | 4.13 |
| WYAY-SK1-2 | **2.40** | 5.60 | 0.80 | **3.90** | 1.30 | 3.0 | 2.0 | **0.8** | **0.90** | 151.3 | **0.10** | 0.86 |
| WYAY-SK1-4 | **7.10** | 14.60 | 3.10 | **11.90** | 3.61 | 4.0 | 6.0 | **1.2** | **0.90** | 124.3 | **0.30** | 2.68 |
| Com-1 | **21.00** | 26.80 | 6.80 | **19.40** | 7.16 | 15.1 | 15.0 | **1.1** | **1.00** | 96.7 | **0.40** | 4.65 |
| W06/4-3 | **3.70** | 2.90 | 0.80 | **3.70** | 0.75 | 1.5 | 2.0 | **1.1** | **0.90** | 81.8 | **0.30** | 0.60 |
| W06/6-6 | **2.40** | 4.30 | 2.00 | **4.10** | 1.06 | 2.0 | 3.0 | **1.1** | **0.90** | 56.6 | **0.20** | 0.64 |
| W07/8-4 | **3.40** | 3.80 | 1.40 | **3.10** | 0.95 | 2.6 | 3.0 | **3.1** | **0.90** | 94.0 | **0.30** | 0.77 |
| W07/14-1 | **5.40** | 11.50 | 3.70 | **9.40** | 2.99 | 5.4 | 7.0 | **0.9** | **0.90** | 128.0 | **0.10** | 2.19 |
| W07/14-5 | **5.00** | 4.50 | 1.50 | **7.90** | 1.24 | 5.1 | 2.0 | **7.0** | **0.90** | 97.5 | **1.50** | 0.83 |
| *MEAN* | *6.76* | *12.65* | *3.49* | *11.54* | *3.33* | *5.52* | *5.70* | *1.90* | *1.03* | *117.22* | *0.38* | *2.15* |
| COAL ASH | | | | | | | | | | | | |
| Etili-3 | 32.3 | 59.9 | 22.8 | 101.4 | 17.03 | 27.4 | 15 | 0.5 | 3 | 476.4 | 0.1 | 8.67 |
| WYAY-SK2-2 | 24.2 | 70.7 | 13.5 | 165.7 | 18.47 | 12.9 | 29 | 0.5 | 2 | 401.5 | 0.1 | 11.3 |
| WYAY-SK1-2 | 16.3 | 37.7 | 6.6 | 234.3 | 9.42 | 21.4 | 14 | 1.8 | 2 | 1,128.2 | 0.5 | 5.82 |
| WYAY-SK1-4 | 28.7 | 62 | 11.9 | 146.9 | 14.87 | 16.1 | 28 | 0.49 | 2 | 509.8 | 0.4 | 9.58 |
| Com-1 | 35.8 | 47.7 | 12 | 46.8 | 12.32 | 25.2 | 24 | 0.49 | 1 | 164.3 | 0.1 | 7.16 |
| W06/4-3 | 24.5 | 27.8 | 7.5 | 398.9 | 6.91 | 13.9 | 17 | 0.6 | 2 | 703 | 0.9 | 4.92 |
| W06/6-6 | 22.3 | 28.3 | 13.6 | 158.3 | 7.85 | 8.3 | 20 | 1.2 | 2 | 419.6 | 0.5 | 4.56 |
| W07/8-4 | 17.5 | 16.2 | 9.1 | 744.3 | 4.24 | 8.7 | 21 | 1.3 | 2 | 546.3 | 0.2 | 2.87 |
| W07/14-1 | 15.4 | 28.7 | 9.9 | 74.4 | 7.68 | 13.8 | 17 | 0.49 | 1 | 289.3 | 0.1 | 5.18 |
| W07/14-5 | 17 | 20.9 | 5.9 | 388 | 5 | 25.2 | 7 | 0.8 | 1 | 414.8 | 2.5 | 3.2 |
| *MEAN* | *23.40* | *39.99* | *11.28* | *245.90* | *10.38* | *17.29* | *19.20* | *0.82* | *1.80* | *505.32* | *0.54* | *6.33* |
| FLY ASH | | | | | | | | | | | | |
| 1 | **19.00** | 32.10 | 11.4 | **28.9** | 8.45 | 15.6 | 16.0 | **2.0** | **2** | 366.1 | **0.6** | 6.17 |
| 2 | **31.00** | 37.50 | 9.9 | **23.9** | 9.43 | 19.3 | 16.0 | **1.4** | **2** | 295.8 | **0.3** | 7.16 |
| 3 | **19.00** | 31.40 | 11.6 | **27.5** | 8.49 | 17.1 | 15.0 | **1.6** | **2** | 358.2 | **0.4** | 6.35 |
| 4 | **19.00** | 33.80 | 10.1 | **22.8** | 9 | 18.3 | 15.0 | **0.5** | **2** | 334.9 | **0.4** | 6.14 |
| *MEAN* | *22.00* | *33.70* | *10.75* | *25.78* | *8.84* | *17.58* | *15.50* | *1.37* | *2.00* | *338.75* | *0.43* | *6.46* |

Note: Hazardous elements are given as bold character.

**Table 3** Trace elements concentrations of Can basin coal, coal ash and fly ash (continued)

| *Elements* | *Tl* | *Ta* | *Th* | *Tb* | *Tm* | *U* | *V* | *W* | *Y* | *Yb* | *Zr* | *Zn* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (ppm) | | | | | | | | | | | |
| COAL | | | | | | | | | | | | |
| Etili-3 | **0.30** | 0.50 | **28.30** | 0.42 | 0.12 | **7.3** | **109.0** | 2.3 | 11.80 | 0.99 | 132.0 | **35.0** |
| WYAY-SK2-2 | **1.20** | 0.40 | **20.50** | 0.52 | 0.22 | **5.3** | **94.0** | 1.2 | 17.10 | 1.63 | 79.3 | **81.0** |
| WYAY-SK1-2 | **0.10** | 0.10 | **4.50** | 0.13 | 0.06 | **1.3** | **31.0** | 0.3 | 5.60 | 0.44 | 17.7 | **16.0** |
| WYAY-SK1-4 | **0.90** | 0.20 | **8.30** | 0.34 | 0.16 | **2.9** | **94.0** | 0.8 | 13.70 | 1.22 | 41.0 | **75.0** |
| Com-1 | **0.30** | 0.50 | **15.10** | 0.50 | 0.22 | **18.0** | **228.0** | 0.6 | 13.80 | 1.81 | 134.3 | **381.0** |
| W06/4-3 | **0.60** | 0.09 | **2.50** | 0.10 | 0.03 | **2.2** | **64.0** | 0.7 | 4.70 | 0.38 | 13.8 | **22.0** |
| W06/6-6 | **0.10** | 0.10 | **4.10** | 0.10 | 0.04 | **5.4** | **60.0** | 0.7 | 3.40 | 0.35 | 23.3 | **12.0** |
| W07/8-4 | **0.10** | 0.10 | **1.90** | 0.12 | 0.05 | **33.9** | **459.0** | 1.1 | 6.00 | 0.51 | 23.7 | **20.0** |
| W07/14-1 | **0.20** | 0.20 | **8.00** | 0.29 | 0.12 | **3.5** | **100.0** | 0.7 | 9.50 | 0.88 | 59.7 | **22.0** |
| W07/14-5 | **0.50** | 0.10 | **4.70** | 0.12 | 0.04 | **29.4** | **491.0** | 1.4 | 4.30 | 0.37 | 30.4 | **41.0** |
| *MEAN* | *0.43* | *0.23* | *9.79* | *0.26* | *0.11* | *10.92* | *173.00* | *0.98* | *8.99* | *0.86* | *55.52* | *70.50* |
| COAL ASH | | | | | | | | | | | | |
| Etili-3 | 1.3 | 1.3 | 61.8 | 0.98 | 0.34 | 16.3 | 234 | 5.8 | 24 | 1.94 | 282.4 | 89 |
| WYAY-SK2-2 | 4.6 | 1 | 58.2 | 1.56 | 0.62 | 16.1 | 273 | 3.4 | 46.2 | 4.21 | 213.7 | 193 |
| WYAY-SK1-2 | 0.6 | 0.4 | 31.3 | 0.92 | 0.42 | 8 | 216 | 2.8 | 36.4 | 2.75 | 123.3 | 88 |
| WYAY-SK1-4 | 2.8 | 0.8 | 39.9 | 1.51 | 0.64 | 11.9 | 345 | 3 | 52.6 | 4.65 | 156.7 | 220 |
| Com-1 | 0.8 | 0.7 | 23.9 | 0.88 | 0.4 | 29.9 | 337 | 1 | 21.5 | 2.85 | 218.2 | 579 |
| W06/4-3 | 5.2 | 0.6 | 19.5 | 0.93 | 0.46 | 18.8 | 539 | 5.5 | 36.8 | 3.21 | 119.3 | 103 |
| W06/6-6 | 2.3 | 1 | 31 | 0.73 | 0.37 | 39.5 | 406 | 6.8 | 24.4 | 2.39 | 152.4 | 86 |
| W07/8-4 | 0.7 | 0.4 | 9.9 | 0.58 | 0.32 | 53 | 1,209 | 6.4 | 24.9 | 2.19 | 122.7 | 101 |
| W07/14-1 | 1.2 | 0.6 | 19.7 | 0.76 | 0.32 | 8.5 | 215 | 2 | 22.8 | 2.24 | 141.3 | 70 |
| W07/14-5 | 1.7 | 0.4 | 15.1 | 0.51 | 0.23 | 89.3 | 1,794 | 4.5 | 17.4 | 1.53 | 110.6 | 111 |
| *MEAN* | *2.12* | *0.72* | *31.03* | *0.94* | *0.41* | *29.13* | *556.80* | *4.12* | *30.70* | *2.80* | *164.06* | *164.00* |
| FLY ASH | | | | | | | | | | | | |
| 1 | **1.3** | 0.5 | **21.7** | 0.96 | 0.43 | **18.7** | **333.0** | 3.5 | 32.5 | 2.70 | 138.2 | **65.0** |
| 2 | **0.8** | 0.6 | **19.9** | 1.09 | 0.5 | **16.9** | **256.0** | 3.0 | 39.7 | 3.35 | 117.7 | **67.0** |
| 3 | **1.2** | 0.6 | **21.9** | 0.92 | 0.42 | **18.0** | **344.0** | 3.5 | 32.2 | 2.72 | 137.6 | **69.0** |
| 4 | **0.9** | 0.7 | **22.9** | 0.82 | 0.35 | **15.4** | **210.0** | 2.5 | 25.6 | 2.31 | 131.2 | **69.0** |
| *MEAN* | *1.05* | *0.60* | *21.60* | *0.95* | *0.43* | *17.25* | *285.75* | *3.13* | *32.50* | *2.77* | *131.18* | *67.50* |

Note: Hazardous elements are given as bold character.

**Table 4** Ranges and average values of trace element concentrations of the Can Basin coals, compared with the Clarke values for lignite and subbituminous coals and their ashes and the average world coal values, according Yudovich et al. (1985) and Ketris and Yudovich (2009), respectively

| *Element* | | *Can Basin coals*[a] *(N = 81)* | | *Can Basin Selected Coals (n = 10)* | | | | | *Fly ash (from CTTP)* | | | *Clarke*[b] | | *World*[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *Coal* | *Coal ash* | | | | *Fly ash* | | | | | |
| | | *Range* | *AM* | *AM* | *AM* | $REI_{coalash}$ | $EDF_{coal}$ | $EDF_{coalash}$ | *AM* | $REI_{flyash}$ | $EDF_{flyash}$ | *Coal* | *Ash* | |
| $SiO_2$ | % | 0.47–45.23 | 11.53 | 11.26 | 34.4 | 0.8 | nd | nd | 30.22 | 0.84 | nd | nd | nd | nd |
| $Al_2O_3$ | | 0.40–29.55 | 6.37 | 7.09 | 21.34 | 0.79 | 4.73 | 1.86 | 16.24 | 0.82 | 1.41 | 1.5[d] | 11.5[d] | nd |
| $Fe_2O_3$ | | 0.05–14.12 | 2.94 | 5.69 | 20.9 | 0.99 | 4.38 | 2.11 | 6.81 | 0.74 | 0.69 | 1.3[d] | 9.9[d] | nd |
| MgO | | 0.03–0.49 | 0.16 | 0.15 | 0.58 | 0.03 | 1.36 | 0.73 | 0.44 | 0.88 | 0.55 | 0.11[d] | 0.8[d] | nd |
| CaO | | 0.13–1.73 | 0.64 | 0.76 | 3.68 | 0.22 | 1.65 | 1.05 | 22.95 | 11.48 | 6.54 | 0.46[d] | 3.51[d] | nd |
| $Na_2O$ | | 0.02–1.13 | 0.34 | 0.37 | 1.77 | 0.1 | 4.63 | 2.9 | 0.54 | 0.51 | 0.89 | 0.08[d] | 0.61[d] | nd |
| $K_2O$ | | <0.04–0.82 | 0.11 | 0.15 | 0.44 | 0.02 | 0.83 | 0.32 | 0.36 | 1.05 | 0.26 | 0.18[d] | 1.37[d] | 0.133 |
| $TiO_2$ | | 0.02–1.32 | 0.2 | 0.23 | 0.72 | 0.03 | nd | 0.31 | 0.62 | 0.99 | nd | 500 (ppm) | 2,600 (ppm) | 0.011 |
| $P_2O_5$ | | <0.01–0.16 | 0.03 | 0.03 | 0.12 | 0.01 | 2.31 | 1.2 | 0.23 | 2.45 | 2.3 | 0.013[d] | 0.1[d] | 0.053 |
| MnO | | <0.01–0.03 | 0.01 | 0.013 | 0.057 | nd | nd | nd | 0.115 | 3.68 | nd | 100 (ppm) | 510 (ppm) | nd |
| $Cr_2O_3$ | | <0.001–0.012 | 0.002 | 0.003 | 0.005 | nd | nd | nd | 0.004 | 0.64 | nd | 12 (ppm) | 70 (ppm) | 16 (ppm) |
| TOT/S | | 0.06–14.36 | 4.12 | 6.87 | 4.29 | 0.05 | 3.82 | 0.31 | 5.48 | 0.43 | 0.4 | 1.8[d] | 13.7[d] | nd |
| Ag | ppm | <0.1–0.1 | 0.09 | 0.09 | 0.12 | 0.31 | nd | nd | 0.09 | 0.32 | nd | nd | nd | nd |
| Au | | 0.05–4.20 | 1.46 | 1.66 | 2.37 | 0.3 | nd | nd | 1 | 0.22 | nd | nd | nd | nd |
| As | | 1.4–6,413.8 | 253.5 | 932.93 | 3,035.88 | 0.64 | 66.64 | 50.6 | 582.23 | 0.73 | 9.7 | 14 | 60 | 8.3 |
| Ba | | 12.2–735 | 99 | 144.15 | 461.31 | 0.76 | 1.20 | 0.52 | 302.75 | 0.98 | 0.34 | 120 | 890 | 150 |
| Be | | <1.0–5.0 | 1.4 | 0.49 | 3.9 | 0.54 | 0.20 | 0.35 | 3.8 | 0.87 | 0.35 | 2.4 | 11 | 1.6 |
| Bi | | 0.09–0.7 | 0.18 | 0.2 | 0.58 | 0.61 | 0.20 | 0.08 | 0.3 | 0.53 | 0.04 | <1.0[d] | <7.6[d] | 0.97 |
| B | | 97–1,186 | 328 | 308 | 1,253 | 0.78 | 3.62 | 2.24 | nd | nd | nd | 85 | 560 | 52 |
| Cd | | <0.10–2.00 | 0.18 | 0.1 | 0.4 | 0.77 | 0.33 | 0.13 | 0.25 | 0.44 | 0.08 | 0.3 | 3 | 0.22 |

Notes: [a]Content of elements from Can Basin (Gurdal, 2011).
[b]Clarke for lignite and subbituminous coals and their ashes (Yudovich et al., 1985).
[c]From Ketris and Yudovich (2009).
[d]Clarke for USA coals and ashes (Finkelman, 1994a).
REI: the relative enrichment index, EDF: enrichment/depletion factor – a ratio of the mean element content in coal, coal ashes and fly ash samples to the respective Clarke value in coal and or coal ashes, AM: arithmetic mean.

**Table 4** Ranges and average values of trace element concentrations of the Can Basin coals, compared with the Clarke values for lignite and subbituminous coals and their ashes and the average world coal values, according Yudovich et al. (1985) and Ketris and Yudovich (2009), respectively (continued)

| *Element* | | *Can Basin coals*[a] *(N = 81)* | | *Can Basin Selected Coals (n = 10)* | | | | | *Fly ash (from CTTP)* | | | *Clarke*[b] | | *World*[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *Coal* | *Coal ash* | | | | *Fly ash* | | | | | |
| | | *Range* | *AM* | *AM* | *AM* | $REI_{coalash}$ | $EDF_{coal}$ | $EDF_{coalash}$ | *AM* | $REI_{flyash}$ | $EDF_{flyash}$ | *Coal* | *Ash* | |
| Cu | ppm | 1.9–67.5 | 20 | 22 | 71.57 | 0.77 | 2.93 | 1.49 | 36 | 0.58 | 0.75 | 7.5 | 48 | 16 |
| Ce | | 1.7–120.30 | 28.36 | 30.4 | 90.89 | 0.77 | 1.45 | 0.57 | 77.95 | 0.88 | 0.49 | 21[d] | 160[d] | 23 |
| Co | | <0.5–74.2 | 9 | 13.6 | 40.01 | 0.95 | 4.00 | 2 | 21.13 | 0.75 | 1.06 | 3.4 | 20 | 5.1 |
| Cs | | 0.01–10.0 | 2.13 | 3.4 | 10.37 | 0.74 | 3.09 | 1.23 | 5.4 | 0.81 | 0.64 | 1.1[d] | 8.4[d] | 1 |
| Dy | | 0.05–9.74 | 1.74 | 1.4 | 4.344 | 0.73 | 0.74 | 0.3 | 5.4 | 0.99 | 0.37 | 1.9[d] | 14.5[d] | 2.1 |
| Eu | | 0.05–2.87 | 0.58 | 0.5 | 1.913 | 0.88 | 1.25 | 0.62 | 1.7 | 0.94 | 0.55 | 0.4[d] | 3.1[d] | 0.47 |
| Er | | 0.05–5.82 | 1.01 | 0.8 | 2.775 | 0.83 | 0.80 | 0.37 | 3 | 0.95 | 0.39 | 1.0[d] | 7.6[d] | 0.93 |
| F | | <10–730 | 64 | 42.8 | 134 | 1.08 | nd | nd | nd | nd | nd | nd | nd | 88 |
| Gd | | 0.05–12.52 | 2.05 | 1.71 | 5.319 | 0.75 | 0.95 | 0.39 | 6.4 | 1 | 0.47 | 1.8d | 13.7d | 2.7 |
| Ga | | 0.49–32.00 | 5.96 | 6.6 | 19.56 | 0.79 | 0.94 | 0.54 | 24.95 | 1.34 | 0.69 | 7 | 36 | 5.8 |
| Hf | | 0.30–6.70 | 1.53 | 1.51 | 4.5 | 31.67 | 2.16 | 0.8 | 3.73 | 0.78 | 0.67 | 0.7[d] | 5.6[d] | 1.2 |
| Ho | | 0.05–1.73 | 0.32 | 0.24 | 0.846 | 0.81 | 0.32 | 2.7 | 1.03 | 1.03 | 0.38 | 0.35[d] | 2.7[d] | 0.54 |
| Hg | | 0.01–0.29 | 0.1 | 0.01 | 0.01 | 0.94 | nd | nd | 0.13 | 0.41 | nd | nd | nd | 0.1 |
| La | | 0.70–49.90 | 13.3 | 15.3 | 49.59 | 0.85 | 1.28 | 0.54 | 37.7 | 0.91 | 0.41 | 12[d] | 92[d] | 11 |
| Lu | | 0.01–0.89 | 0.16 | 0.1 | 0.431 | 0.78 | 0.71 | 0.39 | 0.4 | 0.8 | 0.36 | 0.14[d] | 1.1[d] | 0.2 |
| Mo | | 0.1–41.6 | 3.7 | 7.1 | 25.84 | 0.79 | 2.96 | 1.99 | 6.6 | 0.57 | 0.51 | 2.4 | 13 | 2.2 |
| Ni | | 0.8–40.1 | 6.3 | 6.76 | 23.4 | 0.87 | 0.85 | 0.46 | 22 | 1.12 | 0.43 | 8 | 51 | 13 |
| Nd | | 0.70–72.00 | 12.9 | 12.65 | 39.99 | 0.81 | 1.33 | 0.55 | 33.7 | 0.84 | 0.46 | 9.5[d] | 73[d] | 12 |
| Nb | | 0.49–15.50 | 3.86 | 3.49 | 11.28 | 0.84 | 3.49 | 2.26 | 10.75 | 0.89 | 2.15 | 1 | 5 | 3.7 |
| Pb | | 0.7–97.0 | 9.7 | 11.54 | 245.9 | 7.54 | 4.62 | 4.64 | 25.78 | 0.85 | 0.49 | 2.5 | 53 | 7.8 |

Notes: [a]Content of elements from Can Basin (Gurdal, 2011).
[b]Clarke for lignite and subbituminous coals and their ashes (Yudovich et al., 1985).
[c]From Ketris and Yudovich (2009).
[d]Clarke for USA coals and ashes (Finkelman, 1994a).
REI: the relative enrichment index, EDF: enrichment/depletion factor – a ratio of the mean element content in coal, coal ashes and fly ash samples to the respective Clarke value in coal and or coal ashes, AM: arithmetic mean.

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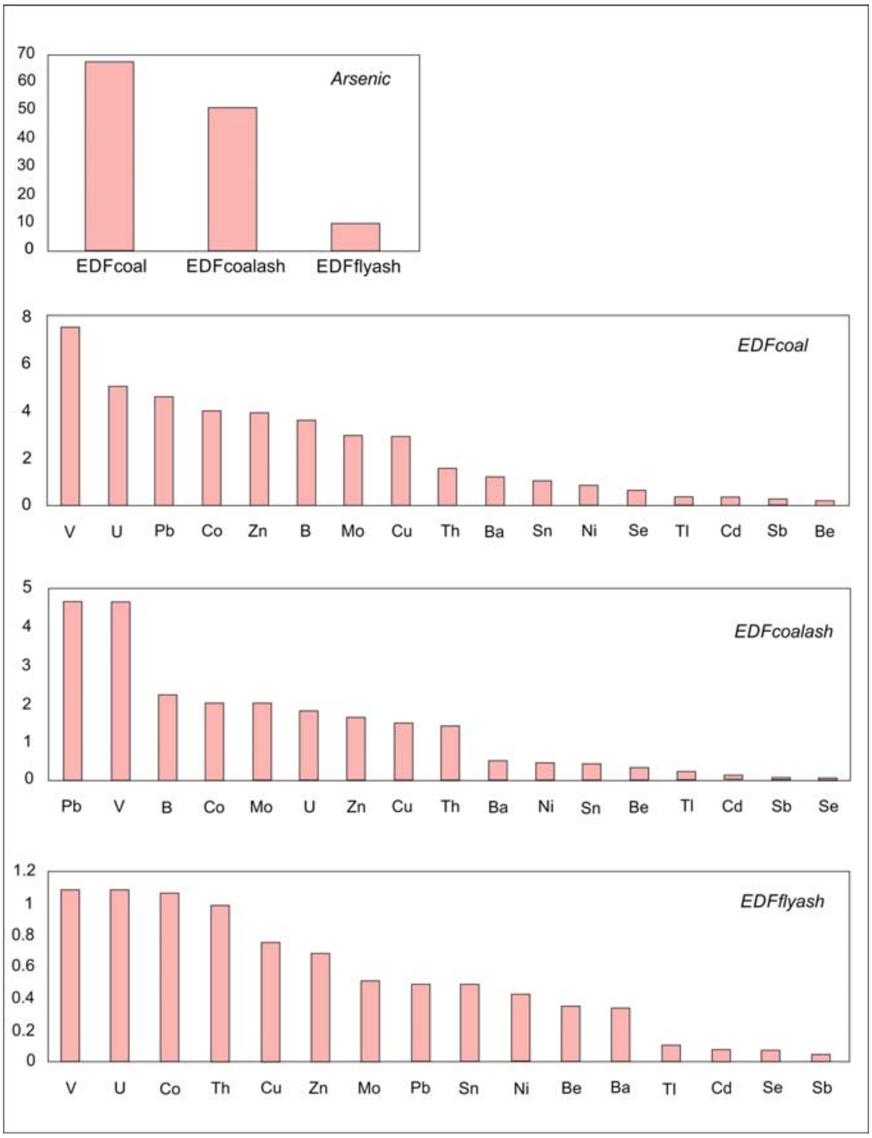
| *Element* | | *Can Basin coals*[a] *(N = 81)* | | *Can Basin Selected Coals (n = 10)* | | | | | *Fly ash (from CTTP)* | | | *Clarke*[b] | | *World*[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *Coal* | *Coal ash* | | | | *Fly ash* | | | | | |
| | | *Range* | *AM* | *AM* | *AM* | $REI_{coalash}$ | $EDF_{coal}$ | $EDF_{coalash}$ | *AM* | $REI_{flyash}$ | $EDF_{flyash}$ | *Coal* | *Ash* | |
| Pr | ppm | 0.20–16.99 | 3.3 | 3.33 | 10.379 | 0.81 | 1.39 | 0.57 | 8.84 | 0.86 | 0.48 | 2.4[d] | 18.3[d] | 3.5 |
| Rb | | 0.49–18.60 | 4.66 | 5.5 | 17.29 | 0.71 | 1.10 | 0.38 | 17.6 | 1.21 | 0.38 | 5 | 46 | 14 |
| Sc | | 0.9–26.00 | 5.44 | 5.7 | 19.2 | 0.82 | 2.85 | 1.28 | 15.5 | 0.91 | 1.03 | 2 | 15 | 3.9 |
| Se | | <0.5–7.0 | 1.1 | 1.9 | 0.8 | 0.12 | 0.63 | 0.04 | 1.3 | 0.38 | 0.07 | 3 | 20 | 1.3 |
| Sn | | <1.0–4.0 | 1.05 | 1.03 | 1.8 | 0.37 | 1.03 | 0.44 | 2 | 0.61 | 0.49 | 1 | 4.1 | 1.1 |
| Sr | | 15.80–289.80 | 92.21 | 117.2 | 505.3 | 0.83 | 0.90 | 0.46 | 338.8 | 1.18 | 0.31 | 130 | 1,100 | 110 |
| Sb | | <0.1–1.5 | 0.2 | 0.38 | 0.54 | 0.24 | 0.29 | 0.07 | 0.43 | 0.68 | 0.05 | 1.3 | 8 | 0.92 |
| Sm | | 0.10–14.06 | 2.36 | 2.15 | 6.33 | 0.75 | 1.26 | 0.49 | 6.46 | 0.88 | 0.5 | 1.7[d] | 13.0[d] | 2 |
| Ta | | 0.09–1.30 | 0.34 | 0.24 | 0.72 | 0.79 | 1.09 | 0.42 | 0.6 | 0.56 | 0.35 | 0.22[d] | 1.7[d] | 0.28 |
| Tb | | 0.02–1.90 | 0.34 | 0.26 | 0.94 | 0.84 | 0.87 | 0.41 | 0.95 | 0.89 | 0.41 | 0.30[d] | 2.3[d] | 0.32 |
| Th | | 0.3–35.2 | 8 | 9.79 | 31.03 | 0.79 | 1.55 | 1.41 | 21.6 | 0.86 | 0.98 | 6.3 | 22 | 3.3 |
| Tl | | <0.1–3.4 | 0.32 | 0.43 | 2.12 | 1.28 | 0.36 | 0.23 | 1.05 | 1.05 | 0.11 | 1.2[d] | 9.2[d] | 0.63 |
| Tm | | 0.03–0.87 | 0.15 | 0.11 | 0.41 | 0.98 | 0.73 | 0.34 | 0.43 | 0.91 | 0.35 | 0.15[d] | 1.2[d] | 0.31 |
| U | | 0.5–64.5 | 8.7 | 10.6 | 29.1 | 0.73 | 5.05 | 1.82 | 17.3 | 0.64 | 1.08 | 2.1[d] | 16.0[d] | 2.4 |
| V | | 26–491 | 128 | 173 | 556.8 | 0.72 | 7.52 | 4.64 | 285.8 | 0.71 | 2.38 | 23 | 120 | 25 |
| W | | 0.09–5.80 | 1.11 | 1 | 4.1 | 0.86 | 1 | 0.54 | 3.1 | 0.89 | 0.41 | 1.0[d] | 7.6d | 1.1 |
| Y | | 0.7–52.20 | 10.73 | 8.99 | 30.7 | 0.75 | 1.28 | 0.83 | 32.5 | 0.97 | 0.88 | 7 | 37 | 8.4 |
| Yb | | 0.05–6.43 | 1.06 | 0.86 | 2.8 | 0.76 | 0.96 | 0.56 | 2.77 | 0.84 | 0.55 | 0.9 | 5 | 1 |
| Zr | | 4.30–233.90 | 55.98 | 55.5 | 164.1 | 0.77 | 1.85 | 1.03 | 131.2 | 0.75 | 0.82 | 30 | 160 | 36 |
| Zn | | 3–524 | 50 | 70.5 | 164 | 0.72 | 3.92 | 1.64 | 67.5 | 0.43 | 0.68 | 18 | 100 | 23 |

Notes: [a]Content of elements from Can Basin (Gurdal, 2011).
[b]Clarke for lignite and subbituminous coals and their ashes (Yudovich et al., 1985).
[c]From Ketris and Yudovich (2009).
[d]Clarke for USA coals and ashes (Finkelman, 1994a).
REI: the relative enrichment index, EDF: enrichment/depletion factor – a ratio of the mean element content in coal, coal ashes and fly ash samples to the respective Clarke value in coal and or coal ashes, AM: arithmetic mean.

**Figure 5** The variation of EDF value in coal, coal ash and fly ash for hazardous trace elements (see online version for colours)




## 3.4 Environmental and health considerations

The enrichment/depletion factor (EDF) for coal and coal combustion products is calculated as the ratio of the mean element content in coal and coal ash samples to the respective Clarke value in coal and/or coal ashes (Table 4). From these elements, As, B, Co, Cu, Mo, Pb, Th, U, V and Zn are defined as potential environmentally hazardous trace elements by Finkelman (1995). The European Pollutant Emission Register (EPER) requires the reporting of As, Cd, Cu, Cr, Hg, Ni, Pb and Zn (Gibb et al., 2003), and the USA Clean Air Act Amendments Bill of 1990 lists 11 elements of potential concern, namely: As, Cd, Cr, Hg, Ni, Pb, Sb, Be, Mn, Se and Co (Wagner and Tlotleng, 2012). The variation of EDF values in coal, coal ash and fly ash for potential hazardous trace elements are shown in Figure 5. According to the results, the maximum enrichment was observed for As in coal and in coal and fly ashes. The enrichment in coal ash is probably related to the low-temperature ignition (600°C) since maximum arsenic passes into gaseous phase in the forms of $As_2$, $As_3$ and AsS at temperatures higher than 600°C (Belkova et al., 2000; Pandey et al., 2011). The form of As residence in fly ash is influenced by the composition of the parent coal and the conditions during coal combustion, particularly during cooling. Arsenic is initially volatilised at the temperature of coal combustion, but will partition between the vapour phase and fly ash particles in the cooler portions of the flue gas stream (Pandey et al., 2011). Compared to other trace elements in coal and fly ash, As shows particularly strong enrichment (approximately ten times). Similar results for fly ash have been reported in the literature (Smith, 1980). They concluded that compared to other trace elements in fly ash, As shows strong enrichment (5–10 times) in the finest (<10 μm diameter) size fractions due to the high surface area.

Arsenic is classified as one of the prime environmentally sensitive elements (Swaine and Goodarzi, 1995). Arsenic is also the most volatile element which can lead to serious environmental and health problems (Zheng et al., 1999; Ding et al., 2001; Liu et al., 2002; Finkelman, 2004; Goodarzi et al., 2008; Bhangare et al., 2011; Dai et al., 2011). U.S. Public Health Service (2000) reported that most As compounds can easily dissolve in water, and so As can enter water bodies such as rivers, lakes, ponds and surface runoff (Pandey et al., 2011). The literature data indicate that As exposure may affect organs of the human body, skin and immune system (Duker et al., 2005), and even at low concentrations may damage the blood circulatory system as well as injuring the nervous system and other vital organs (USPHS, 2000). Arsenic is associated with skin damage, increased risk of cancer, and problems with the circulatory system (Scragg, 2006; Wuana and Okieimen, 2011). Using good quality coal and temperature control during coal combustion is a key factor to control As release into the environment (Pandey et al., 2011). Additionally, spontaneous combustion of coal (Pone et al., 2007) is another mechanism which causes the release of As (Finkelman and Gross, 1999; Pone et al., 2007; Goodarzi et al., 2008), especially in summer conditions.

The abundance of sulphur minerals in Can coals present some environmental and human health concerns. The mine wastes cover approximately 1 $km^2$ around Etili open pit coal mine in Can coal basin (Yucel and Yucel, 2016; Yucel and Turan, 2016) and active and abandoned coal mining areas contain variable amounts of sulphide minerals, especially pyrite. After being exposed to air and water, oxidation of these minerals within the surrounding rock and mine waste generates acid mine drainage (Yucel and Baba, 2013, 2016; Yucel et al., 2014). Acid mine drainage/lakes near agricultural fields and villages with low pH (<3) and high concentration of metals and trace elements create environmental problems in the Etili coal mine (Yucel and Baba, 2013; Okumusoglu and Gunduz, 2013; Yucel et al., 2014, 2016). Yucel and Baba (2013) stated that As concentration in acid mine lakes reaches 17.7 μg/L in the Can coal basin. Yucel and Yucel (2016) further analysed the impact of mine waste effluents on the quality of water resources downstream of the disposal sites as some of these compounds can dissolve in water and enter waterways and impact humans and wildlife. In addition, Baba et al. (2008b) found that according to biological samples collected from local inhabitants in Can coal basin, As and Pb levels in blood and hair are higher than in other regions of the

Biga Peninsula. This indicates that high trace element concentrations in water resources, soil and atmosphere have negative effects on people's health.

## 4 Conclusions

The concentration of trace elements may change in coal seams in different open-pit mining sites of the Can Basin. Concentrations of trace elements are different in the Can coal samples compared to ash yields and sulphur contents. In general, the values of trace element concentrations are within the world average values. Note that the average concentrations of the trace elements, including As, B, Cu, Co, Mo, Pb, Th, U, V, and Zn, are higher in Can Basin coals than the world average value. The results show that some toxic elements such as As, B, Cu, Co, Pb, Th, U, V and Zn are also extremely enriched in coal ashes when compared to the world average value and the concentration of elements including Dy, Er, Gd, Ga, Ho, Hg, Se, Sn, Sm and Y in fly ash was higher than that of coal ash. The study shows that the toxic effects of As may become a critical issue in the Can basin. Coal combustion can mobilise trace elements by introducing them to terrestrial, aquatic and atmospheric environments, and if leached, these elements have a potential to contaminate soil and water resources. Therefore, these elements may become a hazard to the environment because of their contribution to the formation of toxic compounds if the ash is not utilised or disposed of properly. This possible contamination could lead to health, environmental and land-use problems. It is recommended that water resources and soil be monitored regularly in the Can coal basin.

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## References

Arbuzov, S.I., Volostnov, A.V., Rikhvanov, L.P., Mezhibor A.M. and Ilenok, S.S. (2011) 'Geochemistry of radioactive elements (U, Th) in coal and peat of Northern Asia (Siberia, Russian Far East, Kazakhstan, and Mongolia)', *International Journal of Coal Geology*, Vol. 86, No. 4, pp.318–328.

Baba, A. and Kaya, A. (2004) 'Leaching characteristics of solid wastes from thermal power plants of western Turkey and comparison of toxicity methodologies', *Journal of Environmental Management*, Vol. 73, No. 3, pp.199–207.

Baba, A. and Turkman, A., (2001) 'Investigation of geochemical and leaching characteristics of solid wastes from Yenikoy (Mugla-Turkey) Power Plant', *Turkish Journal of Engineering and Environmental Science*, Vol. 25, No. 1, pp.321–328.

Baba, A., Gurdal, G. and Sengunalp, F. (2010) 'Leaching characteristics of fly ash from fluidized bed combustion thermal power plant: case study: Can (Canakkale-Turkey)', *Fuel Process Technology*, Vol. 91, No. 9, pp.1073–1080.

Baba, A., Gurdal, G., Sengunalp, F. and Ozay, O. (2008a) 'Effects of leachant temperature and pH on leachability of metals from fly ash. A case study: Can thermal power plant, province of Canakkale, Turkey', *Environmental Monitoring Assessment*, Vol. 139, No. 1, pp.287–298.

Baba, A., Save, D., Gunduz, O., Gurdal, G., Bozcu, M. and Sulun, S. (2008b) *The Assessment of Mining Activities from Medical Geology Perspective: Biga Peninsula (Can-Canakkale),* TUBITAK, 106Y041/REP.

Belkin, H.E., Zheng, B., Zhou, D. and Finkelman, R.B. (2008) 'Chronic arsenic poisoning from domestic combustion of coal in rural China: a case study of the relationship between earth materials and human health', *Environmental Geochemistry*, pp.401–420, Elsevier, Netherlands.

Belkova, V.A., Bychinsky, I.M.T. and Kotelnikov, N.V. (2000) 'The behaviour of trace elements at the Cheremkhovo coal combustion', *Ugol Coal*, Vol. 5, No. 1, pp.43–70.

Bhangare, R.C., Ajmal, P.Y., Sahu, S.K., Pandit, G.G. and Puranik, V.D. (2011) 'Distribution of trace elements in coal and combustion residues from five thermal power plants in India', *International Journal of Coal Geology*, Vol. 86, No. 4, pp.349–356.

Bozcu, M., Akgun, F., Gurdal, G., Yesilyurt, S.K. and Karaca O. (2008) *Sedimentologic, Petrologic, Geochemical and Palinologic Examination of Can Yenice Bayramic (Canakkale) lignite Basin*, TUBITAK, 105Y114/REP.

Dai, S., Ren, D., Chou, C.L., Finkelman, R.B., Seredin, V.V. and Zhou, Y. (2011) 'Geochemistry of trace elements in Chinese coals: a review of abundances, genetic types, impacts on human health, and industrial utilization', *International Journal of Coal Geology*, Vol. 94, No. 1, pp.3–21.

Dai, S., Ren, D., Tang, Y., Yue, M. and Hao, L.M. (2005) 'Concentration and distribution of elements in Late Permian coals from western Guizhou Province, China', *International Journal of Coal Geology*, Vol. 61, No. 1, pp.119–137.

Dai, S., Zhou, Y., Peng, S., Chou, C.L., Wang, X. and Zhang, Y. (2010) 'Abundances and distribution of minerals and elements in high alumina coal fly ash from the Jungar Power Plant, Inner Mongolia, China', *International Journal of Coal Geology*, Vol. 81, No. 4, pp.320–332.

Ding, Z.H., Zheng, B.S., Long, J.P., Belkin, H.E., Finkelman, R.B. and Chen, C.G. (2001) 'Geological and geochemical characteristics of high arsenic coals from endemic arsenosis areas in Southwestern Guizhou Province, China', *Applied Geochemistry*, Vol. 16, Nos. 11–12, pp.1353–1360.

Duker, A.A., Carranza, E.J.M. and Hale, M. (2005) 'Arsenic geochemistry and health', *Environment International*, Vol. 31, No. 5, pp.631–641.

Finkelman, R.B. (1994a) 'Modes of occurrence of potentially hazardous elements in coal: levels of confidence', *Fuel Process Technology*, Vol. 39, Nos. 1–3, pp.21–34.

Finkelman, R.B. (1994b) 'The use of modes of occurrence information to predict the removal of the hazardous air pollutants', *International Journal of Coal Geology*, Vol. 12, No. 1, pp.132–134.

Finkelman, R.B. (1995) 'Modes of occurrence of environmentally-sensitive trace elements of coal', in Swaine, D.J. and Goodarzi, F. (Eds.): *Environmental Aspects of Trace Elements of Coal*, pp.24–50, Kluwer Academic Publishers, Netherlands.

Finkelman, R.B. (2004) 'Potential health impacts of burning coal beds and waste banks', *International Journal of Coal Geology*, Vol. 59, No. 1, pp.19–24.

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

Finkelman, R.B., Orem, W., Castranova, V., Tatu, C.A., Belkin, H.E. and Zheng, B. (2002) 'Health impacts of coal and coal use: possible solutions', *International Journal of Coal Geology*, Vol. 50, Nos. 1–4, pp.425–443.

Gibb, W., Quick, W. and Salisbury, M. (2003) *Technology Status Review: Monitoring & Control of Trace Elements*, Coal R249 REP.

Goodarzi, F., Huggins, F.E. and Sanei, H. (2008) 'Assessment of elements, speciation of As, Cr, Ni and emitted Hg for a Canadian plant burning bituminous coal', *International Journal of Coal Geology*, Vol. 74, No. 1, pp.1–12.

Gurdal, G. (2008) 'Geochemistry of trace elements in Can Coal (Miocene), Canakkale, Turkey', *International Journal of Coal Geology*, Vol. 74, No. 1, pp.28–40.

Gurdal, G. (2011) 'Abundances and modes of occurrence of trace elements in the Can coals (Miocene), Canakkale-Turkey', *International Journal of Coal Geology*, Vol. 87, No. 2, pp.157–173.

Gurdal, G. and Bozcu, M. (2011) 'Petrographic characteristics and depositional environment of Miocene Can coals, Canakkale-Turkey', *International Journal of Coal Geology*, Vol. 85, No. 1, pp.143–160.

Hajarnavis, M.R. (2000) 'Studies of trace metals in acidic fly ash', *Journal of Scientific and Industrial Research*, Vol. 59, No. 1, pp.381–388.

Hower, J.C., Robl, T.L. and Thomas, G.A. (1999) 'Changes in the quality of coal combustion by-products produced by Kentucky power plants 1978 to 1997: consequences of clean air act drives', *Fuel*, Vol. 78, No. 1, pp.701–712.

Huang, Y., Jin, B., Zhong, Z., Xiao, R., Tang, Z. and Ren, H. (2004) 'Trace elements (Mn, Cr, Pb, Se, Zn, Cd and Hg) in emissions from a pulverized coal boiler', *Fuel Processing Technology*, Vol. 86, No. 1, pp.23–32.

Ketris, M.P. and Yudovich, Y.E. (2009) 'Estimations of Clarkes for carbonaceous biolithes: world average for trace element contents in black shales and coals', *International Journal of Coal Geology*, Vol. 78, No. 2, pp.135–148.

Liu, G., Vassilev, S.V., Gao, L., Zheng, L. and Peng, Z. (2005) 'Mineral and chemical composition and some trace element contents in coals and coal ashes from Huaibei coalfield, China', *Energy Conversion and Management*, Vol. 46, Nos. 13–14, pp.2001–2009.

Liu, G., Yang, P., Peng, Z. and Chou, C.L. (2004) 'Petrographic and geochemical contrasts and environmentally significant trace elements in marine-influenced coal seams, Yanzhou mining area, China', *Journal of Asian Earth Sciences*, Vol. 23, No. 4, pp.491–506.

Liu, J., Zheng, B., Aposhian, H.V., Zhou, Y., Chen, M. and Zhang, A. (2002) 'Chronic arsenic poisoning from burning high-arsenic-containing coal in Guizhou, China', *Environmental Health Perspectives*, Vol. 110, No. 2, pp.119–122.

Llorens, J.F., Fernández-Turiel, J.L. and Querol, X. (2001) 'The fate of trace elements in a large coal-fired power plant', *Environmental Geology*, Vol. 40, No. 4, pp.409–416.

Mardon, S.M. and Hower, J.C. (2004) 'Impact of coal properties on coal combustion by-product quality: examples from a Kentucky power plant', *International Journal of Coal Geology*, Vol. 59, No. 3, pp.153–169.

Meij, R. (1994) 'Trace element behavior in coal-fired power plants', *Fuel Processing Technology*, Vol. 39, Nos. 1–3, pp.199–217.

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

Okumusoglu, D. and Gunduz, O. (2013) 'Hydrochemical status of an acidic mining lake in Can-Canakkale, Turkey', *Water Environment Research*, Vol. 85, No. 7, pp.604–620.

Pandey, V.C., Shankar, J., Singh, R.P., Singh, N. and Yunus, M. (2011) 'Arsenic hazards in coal fly ash and its fate in Indian scenario', *Resources, Conservation and Recycling*, Vol. 55, Nos. 9–10, pp.819–835.

Pone, J.D.N., Hein, K.A.A., Stracher, G.B., Annegarn, H.J., Finkelman, R.B. and Blake, D.R. (2007) 'The spontaneous combustion of coal and its by-products in the Witbank and Sasolbug coalfields of South Africa', *International Journal of Coal Geology*, Vol. 72, No. 2, pp.124–140.

Querol, X., Fernandes-Turiel, J.L. and Lopez-Soler, A. (1995) 'Trace elements in coal and their behaviour during combustion in a large power station', *Fuel*, Vol. 74, No. 3, pp.331–343.

Ram, L.C. and Masto, R.E. (2010) 'An appraisal of the potential use of fly ash for reclaiming coal mine spoil', *Journal of Environmental Management*, Vol. 91, No. 3, pp.603–617.

Ren, D.Y., Zhao, F.H., Dai, S.F., Zhang, J.Y. and Luo, K.L. (2006) *Geochemistry of trace elements in Coal*, Science Press, Beijing.

Scragg, A. (2006) Environmental Biotechnology, 2nd ed., Oxford University Press, Oxford UK.

Senior, C.L., Bool, E.L. and Morency, J.R. (2000) 'Laboratory study of trace element vaporization from combustion of pulverized coal', *Fuel Processing Technology*, Vol. 63, Nos. 2–3, pp.109–124.

Seredin, V. and Finkelman, R.B. (2008) 'Metalliferous coals: a review of the main genetic and geochemical types', *International Journal of Coal Geology*, Vol. 76, No. 4, pp.253–289.

Sia, S.G. and Abdullah, W.H. (2011) 'Concentration and association of minor and trace elements in Mukah coal from Sarawak, Malaysia, with emphasis on the potentially hazardous trace elements', *International Journal of Coal Geology*, Vol. 88, No. 4, pp.179–193.

Sia, S.G. and Abdullah, W.H. (2015) 'Mercury and chlorine in the Balingian coal from Sarawak, Malaysia', *Natural Resources Research*, Vol. 24, No. 2, pp.197–207.

Singh, S., Ram, L.C., Masto, R.E. and Verma, S.K. (2011) 'A comparative evaluation of minerals and trace elements in the ashes from lignite, coal refuse, and biomass fired power plants', *International Journal of Coal Geology*, Vol. 87, No. 2, pp.112–120.

Smith, R.D. (1980) 'The trace element chemistry of coal during combustion and the emissions from coal-based plants', *Progress in Energy and Combustion Science*, Vol. 6, No. 1, pp.53–119.

Spears, D.A. and Zheng, Y. (1999) 'Geochemistry and origin of elements in some UK coals', *International Journal of Coal Geology*, Vol. 38, No. 1, pp.161–179.

Sun, Y.Z., Lin, M.Y., Qin, P., Zhao, C.L. and Jin, K. (2007) Geochemistry of the barkinite liptobiolith (Late Permian) from the Jinshan Mine, Anhui Province, China', *Environmental Geochemistry and Health*, Vol. 29, No. 1, pp.33–44.

Swaine, D.J. (2000) 'Why trace elements are important', *Fuel Processing Technology*, Vol. 65, No. 66, pp.21–33.

Swaine, D.J. and Goodarzi, F. (1995) *Environmental Aspect of Trace Elements in Coal*, Kluwer Academic Publishers, Netherlands.

US Department of Health and Human Services (2000) *Toxicological Profile for Arsenic*, Atlanta, Georgia.

Vassilev, S.V. and Braekman-Danheux, C. (1999). 'Characterization of refuse-derived char from municipal solid waste 2. Occurrence, abundance and source of trace elements', *Fuel Processing Technology*, Vol. 59, Nos. 2–3, pp.135–161.

Vassilev, S.V., Vassileva, C.G, Karayigit, A.I., Bulut, Y., Alastuey, A. and Querol, X. (2005) 'Phase-mineral and chemical composition of composite samples from feed coals, bottom ashes and fly ashes at the Somapower station, Turkey', *International Journal of Coal Geology*, Vol. 61, No. 1, pp.35–63.

Vejahati, F., Xu, Z. and Gupta, R. (2010) 'Trace elements in coal: associations with coal and minerals and their behavior during coal utilization: a review', *Fuel*, Vol. 89, No. 4, pp.904–911.

Wagner, N.J. and Tlotleng, M.T. (2012) 'Distribution of selected trace elements in density fractionated Waterberg coals from South Africa', *International Journal of Coal Geology*, Vol. 94, No. 1, pp.225–237.

Wang, X., Dai, S., Sun, Y., Li, D., Zhang, W. and Zhang, Y. (2011) 'Modes of occurrence of fluorine in the late Paleozoic No. 6 coal from the Haerwusu Surface Mine, Inner Mongolia, China', *Fuel*, Vol. 90, No. 1, pp.248–254.

Wuana, R.A. and Okieimen, F.E. (2011) 'Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation', *ISRN Ecology*, No. 1, pp.1–20.

Xu, R., Yan, R., Zheng, C. and Qiao, Y. (2003) 'Status of trace element emission in a coal combustion process: a review', *Fuel Processing Technology*, Vol. 85, No. 2, pp.215–237.

Yucel, D.S. and Baba, A. (2013) 'Geochemical characterization of acid mine lakes and their effect on the environment, NW of Turkey', *Archives of Environmental Contamination and Toxicology*, Vol. 64, No. 3, pp.357–376.

Yucel, D.S. and Baba, A. (2016) 'Prediction of acid mine drainage generation potential of various lithologies using static tests: Etili coal mine (NW Turkey) as a case study', *Environmental Monitoring and Assessment*, Vol. 188, No. 8, p.473, doi:10.1007/s10661-016-5462-5.

Yucel, D.S. and Yucel, M.A. (2016) 'Determining hydrochemical characteristics of mine lakes from abandoned coal mines and 3D modelling of them using unmanned aerial vehicle', *Pamukkale University Journal of Engineering Sciences*, Vol. 23, No. 2, pp.1–8, doi:10.5505/pajes.2016.37431.

Yucel, D.S., Balci, N. and Baba, A. (2016) 'Generation of acid mine lakes associated with abandoned coal mines in Northwest Turkey', *Archives of Environmental Contamination and Toxicology*, Vol. 70, No. 4, pp.757–782.

Yucel, D.S., Yucel, M.A. and Baba, A. (2014) 'Change detection and visualization of acid mine lakes using time series satellite image data in geographic information systems (GIS): Can (Canakkale) County, NW Turkey', *Environmental Earth Sciences*, Vol. 72, No. 11, pp.4311–4323.

Yucel, M.A. and Turan, R.Y. (2016) 'Areal change detection and 3D modeling of mine lakes using high resolution unmanned aerial vehicle image', *Arabian Journal for Science and Engineering*, Vol. 41, No. 12, pp.4867–4878.

Yudovich, Y.E. and Ketris, M.P. (2005) 'Arsenic in coal: a review', *International Journal of Coal Geology*, Vol. 61, Nos. 3–4, pp.141–196.

Yudovich, Y.E., Ketris, M.P. and Merts, A.V. (1985) *Impurity Elements in Coals*, Nauka Press, Leningrad.

Zhang, J., Han, C.L. and Xu, Y.Q. (2003) 'The release of the hazardous elements from coal in the initial stage of combustion process', *Fuel Processing Technology*, Vol. 84, No. 1, pp.121–133.

Zheng, B., Ding, Z., Huang, R., Zhu, J., Yu, X. and Wang, A. (1999) 'Issues of health and disease relating to coal use in southwestern China', *International Journal of Coal Geology*, Vol. 40, No. 2, pp.119–132.

Zheng, B., Wang, B., Ding, Z., Zhou, D., Zhou, Y. and Zhou, C. (2005) 'Endemic arsenosis caused by indoor combustion of high-As coal in Guizhou Province, P.R. China', *Environmental Geochemistry and Health*, Vol. 27, No. 5, pp.521–528.