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Environmental aspects of selected heavy and trace elements of Cherat Coal deposits

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Abstract

Coal contains many toxic elements which become mobile during mining and combustion processes and contaminate the surface and ground-water quality. The main objective of this study was to assess the impact of coal mining on the degradation of the environment. For this purpose around 21 coal samples were collected randomly from six coal mining sites within Cherat area and analyzed for arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), lead (Pb) and zinc (Zn) using atomic absorption spectrophotometer (AAS). The results of the chemical analysis of coal samples revealed presence of trace elements i.e. Cu, Ni, Co, Pb, Cr, Zn, Cd, Fe, and As ranging from 5.62–28.12 mg/kg, 9.66–23.63 mg/kg, 4.47–30.96 mg/kg, 43.22–87.32 mg/kg, 20.51–72.4 mg/kg, 5.45–51.82 mg/kg, 1.23–2.58 mg/kg, 1240–2751.1 mg/kg and 3.51–5.77 mg/kg, respectively. It has been also observed that the sample collected from shakot-1(Sk-1) has got the highest concentration of Cu Ni, Co, Pb, Zn and Cd. While Fe and Cr contents were enriched mostly in the coal samples taken from Jabar tar (Jt), Arsenic was abundant in Bakhtai (Bk) coal mine. In comparison with rest of the country and worldwide, Cherat coals have higher concentration of Co, Pb, Cr and Cd but lower in Cu, Ni, Fe, As and Zn contents on the average. This paper presents an experimental investigation of heavy and trace elements of Cherat coal and may serve as a useful information about environmental risks associated with coal mining in Cherat area of Khyber Paktunkhwa.

Keywords: Experimental investigation; Degradation; Trace elements; Toxic; Environmental impact.

1. Introduction

Coal is a sedimentary rock largely comprised of remains of organic plant material. It is an important source of energy and is formed by the accumulation and burial of plant matter in a variety of depositional environments. In Pakistan, it is being commercially explored from the rocks of Hangu Formation and Patala Formation (Paleocene) in Khyber Pakhtunkhwa (KPK), and Punjab Province in north Pakistan (Warwick et al., 1995). Ghazij Formation (Eocene) contains coal bearing rocks in Balochistan, while Bara Formation (Paleocene) and Sonhari beds of Laki (Eocene) contain larger deposits of coal in Sindh (Thomas et al., 1993; Abbas and Atique, 2005; Sadiqui, 2008).

Coal is composed of complex mixtures of organic and inorganic compounds. The organic compounds in coal are due to the presence of decaying of plants remains. It may contain about 76 of the 90 naturally occurring elements of the periodic table. However, most of these elements generally occur in low concentrations (parts per million) and do not pose any threat to the environment (Finkelman and Brown, 1991). Some elements are known to have hazardous effect if their concentration exceeds permissible limits. The affinity of trace elements in coal for the organic compounds of the minerals affect the quality of the coal. In case the trace elements are organically bound, these may only be released either by burning, or by deep chemical leaching, causing environmental hazard and pollution. In order to meet the energy crises in Pakistan, coal can be exploited as an alternate energy source. Though it contains heavy and trace elements and not considered as a clean source of energy. During mining and combustion, these harmful metals may be released to the surrounding and thus affect human health (Finkelman et al., 2002; Wang, 2005).

In the present scenario, Cherat coal fields were selected as target area to look at the concentrations of heavy metals such as As, Cd, Co, Cr, Cu, Fe, Ni, Pb, and Zn which are coal combustion by-products (Van Oostdam, 1999). On coal combustion can volatilize heavy and trace elements, which may be inhaled or adsorbed on crops, taken up by livestock or bio-accumulated in animals.

2. Study area

The study area is located in Peshawar valley, situated in 33^0 45' to 34^0 0' N latitude and 71^0 45' to 72^0 0' East longitudes. Presently, six coal fields were identified in the Cherat area. These were; Otch Jaba (Jaba khushk), Tar or Lund Jaba, Shahkot-1, Shahkot-2, Bakhtai and Dag Ismael Khel areas as shown in the figure 1. The major rocks exposed near the coal mines are of Bakhtai Formation and Utch Khattak Formation which are composed of medium to dark grey limestones and inter-bedded slaty shale (Tahirkheli, 1970).The total numbers of mines, in the production and development stages, are more than hundred. The thickness of coal seams varies from 0.2 m to 1.6 m. Moisture level ranges from 1 to 5%, ash ranges from 21.7 to 45%, volatile matter 4.5 to 21%. The coal is mostly sub-bituminous with a calorific value varying from 6,400 to 9,000 BTU /lb (Akbar, 2001).

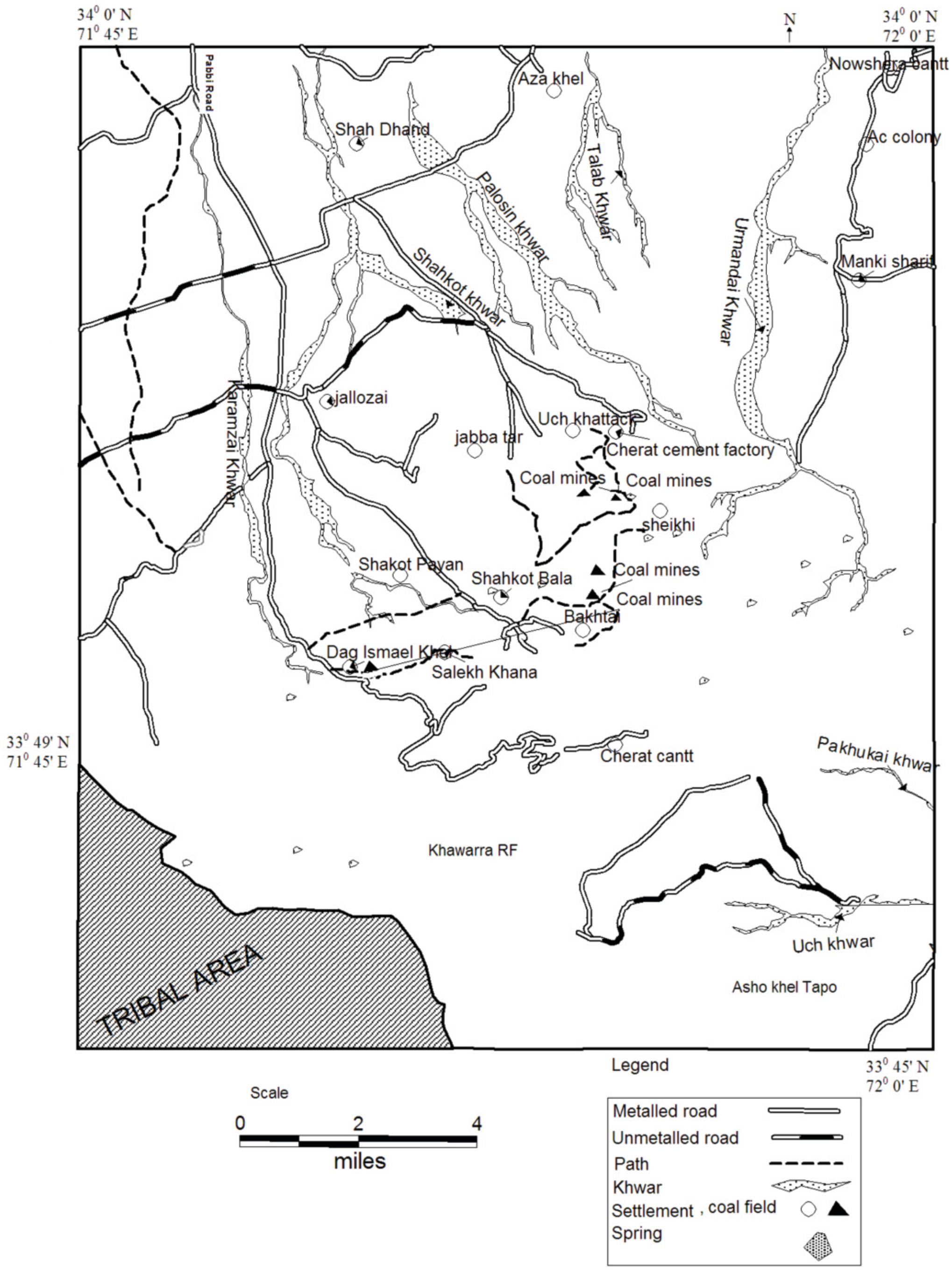

Fig. 1. Location map showing sample points of Cherat coal mines (adapted from Tahirkheli, 1970).

3. Methodology

Twenty one representative coal samples were collected from the study area as shown in figure 1. These samples were classified as Jaba tar (Jt), Jaba Khushk (Jk), Dag Ismail Khel (Dg), Bakhtai (Bk), Shakot-1 (Sk--1), Shakot-2 (Sk-2). Each sample was dried and pulverized to 200-mesh size. Heavy metals (AS, Cd, Cr, Cu, Fe, Ni, Pb, Zn, etc) analyses were carried out by AAS (Singh, 1988). The concentration of carbon (C), sulphur (S), hydrogen (H) and nitrogen (N) were determined on the CHNS elemental analyzer (Euro-EA3000) by using the powder pellets (Saddiqui, 2008). All the experimental investigations were performed using laboratory facilities of the National Centre of Excellence in Geology, University of Peshawar, Pakistan.

4. Results and discussion

The data of the six coal mines (Jt, Jk, Dg, Bk, Sk-1 and Sk-2) of the Cherat coal fields shows that the mean concentrations of the trace and heavy elements like As, Cd, Co, Cr, , Cu, Fe, Ni, Pb and Zn are present with mean concentrations ranges from 3.15–5.77 mg/kg, 1.23–2.58 mg/kg, 4.47–30.96 mg/kg, 20.51-72.4 mg/kg, 5.62–28.12 mg/kg, 1240.0–2751.1 mg/kg 9.66–23.63 mg/kg, 43.22–87.32 mg/kg, and 5.45–51.82 mg/kg, respectively as shown in the table 1.

Comparing the concentration of trace and heavy metals of various mines, it may be observed from Tables 1 and 2 that the concentration of Cu (7.6 mg/kg, 5.62 mg/kg, 12.66 mg/kg, 9.65 mg/kg, 28.12 mg/kg and 7.45 mg/kg) is highly variable in all the six coal mines of Cherat coalfields respectively. However, it was observed that Sk-1 has highest concentration of Cu (28.12mg/kg). Similarly, the mean concentration of Ni, Co, Pb, Zn and Cd was high in sample location Sk-1 (Table. 1). Coal mine Jt had maximum concentration (2751.1 mg/kg) and (72.4 mg/kg) for Fe and Cr (Table 1). However, As contents have highest level in samples location Bk and lowest level in location Sk-1 coal mine (Tables 1 and 2).

The mean concentrations of the heavy and trace elements of the investigated coals were also compared with the data obtained from various coals of Pakistan and worldwide (Table 2).

Arsenic (As)

Arsenic is naturally occurring element and extensively scattered in the biosphere and occurs in the air wherever coal is burnt. It is usually associated with the sulfide-rich fractions of pyrite and marcasite present in the coal. According to WHO, (2008) the permissible level of As in drinking water is 0.01 mg/l. The concentration of As in the water samples of study has 0.023 mg/l which is above the permissible limit as shown in the table 3.

Pillai (1983) and Gupta (1999) suggested that the trivalent form of As is more toxic than pentavalent form. Arsenic usually causes developmental disabilities, anemia, hyperpigmentation and heart diseases in humans (Asante-Duah, 1993).

In addition, the ingestion of high concentration of As causes muscle weakness and aching, skin pigmentation especially of the neck, skin and liver cancers, bladder and kidney cancers (Klaassen, 1991; Centano et al., 2000). Recent reports show that long-term exposure to As may be carcinogenic to humans and teratogenic to animals.

In table 2 the concentration of As in coal mines varies around the world. In Pakistan, the largest coal mines are in Sindh. Sadiqui (2008) reported that in Thar coal (Sindh) As content was 2.01 mg/kg. Warwick (1995) reported that As content in Surghar range (Punjab) coal mine was 5.88 mg/kg. Arsenic content in the world coal mine was 5 mg/kg (Valkovic, 1983; Papanicolaou, et al., 2004). This study shows that As in Cherat coal mines was 4.45 mg/kg and was same as was in world coal mines. Nonetheless As content was high in Cherat coal mines of Khyber Pakhtunkhwa than Thar coal mines in Sindh.

Cadmium (Cd)

Cadmium emitted during coal combustion was accumulated in different tissues of plants (Keller, 1992). Cadmium may further be concentrated in the food chain and biomagnifications may takes place. It occurs in nature in the form of sulfide in Zn-Pb ores as impurities (Michael, 1982). Cadmium can cause toxicity in animals, whether ingested, injected, or inhaled. It has been observed that Cd effect the kidneys, liver, gastrointestinal tract, reproductive system, pancreas, and blood system. WHO (2008) has reported permissible limit for Cd as 0.003 mg/l. The coal samples of this study have 0.111 mg/l, and was greater than the permissible limit for Cd as reported by WHO (2008) (Table 3).

Table 1. Trace and minor elements concentration (mg/kg) in Cherat coal fields.

Elements	R/M	Jt	Jk	Dg	Bk	Sk-1	Sk-2	Average
As (mg/kg)	Range	(1.40-9.67)	(1.77-8.08)	(3.087-5.4)	(1.65-12.77)	(2.24-3.99)	(2.85-6.15)	(1.65-12.77)
	Mean	4.47	4.83	4.28	5.77	3.15	4.23	4.45
Cd (mg/kg)	Range	(0.25-3.55)	(2-2.7)	(0.5-4.1)	(0.20-4.3)	(1.1-5.2)	(0.9-1.45)	(0.20-5.2)
	Mean	1.95	1.67	2.37	1.59	2.58	1.23	1.89
Co(mg/kg)	Range	(1.55-31.5)	(2.1-14.05)	(7.85-15.75)	(1.8-24.1)	(8.9-59.1)	(3.25-6.5)	(1.8-59.1)
	Mean	14.01	7.85	15.47	10.5	30.96	4.47	13.87
Cr (mg/kg)	Range	(17.8-186.2)	(10.55-36.7)	(31-72.35)	(19.5-68.3)	(24.4-113.1)	(26.65-63.65)	(10.55-113.1)
	Mean	72.4	20.51	54.08	37.3	59.35	46.33	48.33
CU (mg/kg)	Range	(3.5-15.4)	(3.35-9.5)	(3.9-21.45)	(1.3-28.85)	(4-74.5)	(2.1-16.6)	(1.3-74.5)
	Mean	7.6	5.62	12.66	9.65	28.12	7.45	11.85
Fe (mg/kg)	Range	(687.5-4765)	(1207.5-3495)	(745-2306)	(295-3325)	(1115-3522.5)	(1140-3125)	(1207-3522.5)
	Mean	2751.1	2119.6	1295.3	1240	2044	1801.7	1875.28
Ni (mg/kg)	Range	(9.45-26.35)	(10-14)	(9.45-26.45)	(5.35-20.75)	(6.5-53.4)	(6.5-17.45)	(5.35-53.4)
	Mean	14.86	11.56	15.01	9.66	23.63	11.13	14.31
Pb (mg/kg)	Range	(44.1-65.05)	(40-48.05)	(46.25-71)	(48.85-119.85)	(59.7-117.7)	(33.75-105.95)	(33.75-119.85)
	Mean	54.74	43.22	56.46	67.19	87.32	65.76	62.45
Zn (mg/kg)	Range	(6.2-44.4)	(5.4-10.4)	(3.2-13.8)	(2.8-12.65)	(5.7-139.25)	(2.8-12.65)	(2.8-139.25)
	Mean	18.63	7.42	7.46	5.45	51.82	5.45	21.25

Table 2. Comparison of the heavy and trace elements of Cherat caol with Pakistan and world average coal.

Elements	Cherat Coal	Thar coal Sind[a]	Sorghar-Range Coal[b]	Degari coal[c]	World wide range
CU	(1.3-74.5) 11.85	(7-38) 18	(63-140) 111	8	(0.5-50)[d] 15[e]
Ni	(5.35-53.4) 14.31	(9-75) 41	(150-51) 112	NR[f]	(0.5-50)[d] 15[e]
Co	(1.55-59.1) 13.87	(2-25) 12	(4.72-1.76) 2.75	NR	(0.5-30)[d] 5[e]
Pb	(33.75-119.85) 62.45	(7-65) 34	(22-120) 69	9	(2-80)[d] 25[e]
Cr	(10.55-186.2) 48.33	(8-35) 20	(34.4-11) 20.7	NR	(0.5-60)[d] 10[e]
Zn	(2.8-139.25) 21.25	(8-116) 48	(39-180) 130	16	(5-300)[d] 50[e]
Cd	(0.20-5.2) 1.89	(0.1-0.4) 0.31	(0.28-0.60) 0.38	NR	(0.1-3)[d] 0.3[e]
Fe	(1240-2751.1) 1875.28	320-8762 5005	(304100-107800) 237600	5580	Nd[d] 1000
As	(1.40-12.77) 4.45	(0.8-4.1) 2.01	(8-2.44) 5.88	NR	(0.5-80)[d] 5[e]

Sadiqui, (2008)
b. Warwick, et al. (1995)
c. Ahmad et al. (2004) Siddiqui, (2008)
d. Ren et al. (1999)
e. Valkovic (1983), Papanicolaou, et al. (2004)
f. Not reported

The concentration of cadmium (Cd) in Thar coal, (Sindh) was 0.31 mg/kg as reported by Sadique (2008), Warwick, (1995) reported 0.38 mg/kg in Surghar range Punjab, no data available for Degari coal Baluchistan. Valkovic (1983) and Papanicolaou et al. (2004) reported Cd concentration in world average coal as 0.3 mg/kg. While chemical analysis for heavy and trace elements of Cherat coal reveals that investigated coals have highest contents of Cd (1.89 mg/kg) as compared to other coal fields of the country and world average as shown in the Table 2.

Cobalt (Co)

Cobalt is essential for humans, plants and animals because it is responsible for the synthesis of vitamin B12 (Krishnan, 1996). Co is also associated with sulphides of silver, Ni, Pb, Cu and Fe. In drinking water the maximum tolerance limits for cobalt is not available. It has been reported by Krishnan, (1995) and Gupta, (1999) that continual exposure to Co at elevated concentrations causes a disease called goiter.

Table 2 shows the concentration of Co in different coal mines in Pakistan and world wide. In Thar coal (Sindh) Co was 12 mg/kg (Sadique, 2008), Surghar range (Punjab) was 2.75 mg/kg (Warwick, 1995), no data was available for Degari coal mines (Baluchistan), in world average coal it was reported 5 mg/kg by Valkovic (1983) and Papanicolaou, et al. (2004). While chemical analysis for heavy and trace elements of study area reveals that Cherat coals have lowest contents of Co (13.87) mg/kg. Cobalt average content in Cherat coal mine was less than the reported value of cobalt in other coal mines in Pakistan and world.

Chromium (Cr)

The presence of Cr in water is mostly due to combustion of fossil fuels like coals and municipal incineration. Hexavalent (Cr^{+6}) form of chromium is 100 times more toxic than it's trivalent (Cr^{+3}) form (Krishnan, 1995; Gupta, 1999). The USEPA (1994) and WHO (2008) had Suggested a tolerance limit of Cr (0.1 mg/l and 0.05 mg/l) respectively in drinking water while surface and ground water of Cherat have 0.213 mg/l which were found above the desirable limit (Table. 3). Intake of Cr^{+6} causes gastrointestinal ulcers, skin irritations, irritation to mucous membranes and dermatitis (Dara, 1993; Gupta, 1999).

Table 2 shows the concentration of Cu in different coal mines in Pakistan and world widely. In Thar coal (Sindh) Cu was 18 mg/kg (Sadique, 2008), Surghar range (Punjab) was 111 mg/kg (Warwick, 1995), Degari coal (Baluchistan) have 8 mg/kg (Ahmad et al., 2004; Sadiqui, 2008) and in world average coal it was reported 15 mg/kg by Valkovic (1983) and Papanicolaou et al. (2004). While chemical analysis for heavy and trace elements of study area reveals that Cherat coals have lower contents of Cu (11.85) mg/kg as compared to other parts of the country and world average coal.

Iron (Fe)

Fe is believed to be the fourth abundant element in the earth crust (Sadiqui, 2008). Fe is the most used of all the metals, comprising 95% of all the metal tonnage produced worldwide. Steel is the common and well-known alloy of Fe. According to Moore (1973) Fe is an essential nutrient for all organisms, except for a few bacteria. Fe distribution is heavily regulated in mammals. Symptoms of Fe toxicity are nausea, fatigue, dizziness, vomiting, weight loss, headache and shortness of breath. Excessive ingestion of iron in the body causes spoiling of liver and kidney called haemochromatosis. Some Fe compounds are carcinogenic (Greaney, 2005).

Table 2 shows the concentration of Fe in different coal mines in Pakistan and world widely. In Thar coal (Sindh) Fe was 5005 mg/kg (Sadique, 2008), Surghar range (Punjab) was 237600 mg/kg (Warwick, 1995), Degari coal (Baluchistan) have 5580 mg/kg (Ahmad et al., 2004; Sadiqui, 2008) and in world average coal it was reported 1000 mg/kg by Valkovic (1983), Papanicolaou et al. (2004) and Swaine and Goodarzi (2013). While chemical analysis for heavy and trace elements of investigated coal reveals that Cherat coals have lower contents of Fe (1875.28) mg/kg as compared to other parts of the country.

Nickel (Ni)

Nickel is an essential nutrient for some microorganisms and animals, but not essential to plants. It is also responsible for the synthesis of vitamin B12 and toxic when taken at higher concentrations (Dara, 1993). It causes Asthma, effects central nervous system, gastrointestinal diseases, headache and lung cancer (Asante-Duah, 1993). The guideline value as recommended by the WHO (2008) for Ni in drinking water is 0.07 mg/l and Cherat water has 0.577 mg/l (Table 3).

Ni contents in Pakistani coals were reported by many workers. Sadique, (2008) reported 41 mg/kg in Thar coal (Sindh), Surghar range have 112 mg/kg (Warwick P.D. 1995), no data available for Degari coal, world average coal have 15 mg/kg Ni contents as reported by Valkovic (1983) and Papanicolaou et al. (2004). while in Cherat coal Ni contents has been found as 14.31 mg/kg which shows that studied coal have less contents of Ni as shown in the table 2.

Lead (Pb)

Due to its insolubility the diffusion of Pb is somewhat limited. According to WHO, (2008) and USEPA, (2004) the maximum permissible limit for lead in drinking water 0.01 mg/l and in study area the concentration has been found 0.155 mg/kg (Table. 3). Exposure to Pb affects pregnancy, lactation and menopause and damaged kidneys (Gupta, 1999).

Table 2 shows the concentration of Pb in different coal mines in Pakistan and world widely. In Thar coal (Sindh) Pb was 34 mg/kg (Sadique, 2008), Surghar range (Punjab) was 69 mg/kg (Warwick, 1995), Degari coal (Baluchistan) have 9 mg/kg (Ahmad et al., 2004; Sadiqui, 2008) and in world average coal it was reported 25 mg/kg by Valkovic (1983) and Papanicolaou et al. (2004). While chemical analysis for heavy and trace elements of Cherat coals 62.45 mg/kg Pb contents was found. Hence it was observed that on the average studied coals have highest contents of Pb as compared to other parts of the country and world wide coals.

Zinc (Zn)

Zinc is an essential metal (Swaine, 1990), and is distributed throughout human tissues. The most abundant sources of Zn are minerals like sphalerite (ZnS) and wlutzite (Zn. Fe) S, and to a lesser extent smithsonite (ZnO_3), willemite (Zn_2SiO_4), and zincite (ZnO) (Reimann and deCaritat, 1998). High contents of Zn from a diet may cause anemia. The Zn concentration in the water sample of study area were found to be 26.73 mg/l, which is above the recommended safe limits of WHO (2008) and USEPA (2004) (Table. 3).

Table 2 shows the concentration of Zn in different coal mines in Pakistan and world widely. In Thar coal (Sindh) Zn was 48 mg/kg (Sadique, 2008), Surghar range (Punjab) was 130 mg/kg (Warwick, 1995), Degari coal (Baluchistan) was 16 mg/kg Zn contents (Ahmad et al., 2004 and Sadique, 2008), in world average coal it was reported 50 mg/kg by Valkovic, (1983) and Papanicolaou et al. (2004). While chemical analysis for heavy and trace elements of study area reveals that Cherat coals have lowest contents of Zn (21.25) mg/kg as compared to other parts of the country and world average coal except surghar-range coal mines.

The above discussion demonstrates a number of health problems linked to the concentrations of various heavy and trace elements. When trace elements are present at high concentration in soil may accumulated in plants and enters in human body through food chain. Similarly when trace elements enters in drinking water may cause risk to human health.

Table 3. Comparison of water quality of the study area with the international standards.

Metals	Cherat coal mg/kg	USEPA* mg/kg	WHO** mg/kg
As	0.023	0.05	0.01
Cd	0.111	0.01	0.003
Co	0.367	Not known	Not known
Cr	0.213	0.05	0.05
CU	0.525	1.3	2
Fe	-	0.3	2
Ni	0.577	Not known	0.07
Pb	0.155	0.01	0.01
Zn	26.73	5	3

United States environmental protection Agency*
World health organization**

5. Conclusion

The results of this study revealed the presence of trace elements such as As, Cd, Co, Cr, Cu, Fe, Ni, Pb, and Zn in the study area. The continuous mining and combustion of coal disperse these elements into the environment and thus pollute the surface and ground-water resources of the area. The concentrations of Cr, Cu, Ni, and Zn were found above the respective limits in some of the surface and ground-water samples. The variation in the concentrations of these elements may be due to many factors like solubility of various ions under various chemical conditions. During inhalation or oral intake of these elements accumulate in the body, and its cumulative effect over a long time exposure may create gastric disorder, cardiovascular disease, carcinogenic, teratogenic and mutagenic effects and other diseases as described above in future.

6. Recommendations

- Water treatment plant / water purification unit should be installed near the affected area.
- The mining activities may be reduced and conducted in environment friendly way to control environmental degradation.
- Safety measures should be strictly followed at the work places to safe guard the workers as well as locals of the area.
- Hazardous wastes treatment must be an integral part of the mining activity

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