ENVIROMENTAL STUDY OF COAL DEPOSITS OF SINDH, WITH SPECIAL REFERENCE TO HEAVY AND TRACE METAL STUDY IN THAR, SONDA AND METING-JHIMPIR COAL FIELD

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Dedicated to my Brother

HABIBULLAH SIDDIQUI

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ABSTRCT

Sindh is the second largest province of Pakistan in terms of population and physiographically known as the Lower Indus Basin. It is bounded by India in the east, Runn of Cutch and Arabian Sea in the south and the province of Punjab and Baluchistan in the north and west, respectively. This province is mainly composed of Western Highlands, Lower Indus Vally and Thar Desert. The Western Highland region includes the N-S crescent like hilly ranges of Kirthar, Pub, Laki and Kohistan area; the Lower Indus valley consists of monoclinal folds with adulatory plains in between and the Thar Desert is generally covering eastern part of the Sindh province. Stratigraphic succession of the Lower Indus Basin in Sindh region include the late Proterozoic magmatic rocks and Jurassics, Cretaceous / Paleocene and Neogene sedimentary sequences. These are covered with Quaternary marine coastal, offshore and aeolian deposits.

Recently, huge coal deposits are explored in the Sindh province and still the exploration of other coal resources are underway. The coal deposits explored so far include the Thar, Sonda, Meting-Jhimpir and Lakhra coalfields. These coal deposits occur in Bara Formation and in the Sonhari member of the Early Eocene Laki Formation. The Thar coalfield is the largest coalfield of Pakistan and is situated in the District Thar Parkar of south-east Sindh. It has the estimated resources of 175 billion tones. Coal in the Thar coalfield is present in the Bara Formation of Paleocene-Eocene age. The Sonda coalfield is located in the deltaic area of lower Indus and is lying in the east and northeast of Keenjhar lake

in District Thatta. Coal seams in the Sonda coalfield occur in the Bara Formation of Paleocene age and the Laki Formation of Eocene age. The total resources of 280 million tones of coal have been explored in the Sonda coalfield. The Meting-Jhimpir coalfield in the District Thatta is the second oldest coalfield after Lakhra explored in Sindh province. It is present in the Sonhari Member of the Laki Formation of Early Eocene age. About 161 million tones of coal resources are present in the Meting-Jhimpir coalfield.

There is greater potential for exploration of coal deposits in the Lower Indus Basin of Sindh. Among the recently explored coal deposits of Sindh, the Thar Sonda and Meting-Jhimpir coalfields are of greater importance because these coal deposits will be exploited and utilized in the power generation plants and in the other industries of Pakistan in near future. The present study has been carried out to investigate the geological and geochemical characterization and environmental assessment of the Sindh coalfields before their use in various types of industries. In this regard, the representative coal samples from the Sindh coalfields, especially Thar, Sonda and Meting-Jhimpir have been investigated for the heavy, trace and light elements, the proximate and ultimate parameters, the combustion properties, the leaching behavior and the mineralogy by using various techniques.

Among the heavy and trace elements, the average Pb contents are 34 ppm, 17 ppm and 23 ppm; average Zn contents are 48 ppm, 44 ppm and 40 ppm;

average Cu contents are 18 ppm, 14 ppm and 22 ppm; average Ni contents are 41 ppm, 34 ppm and 23 ppm; average Cr contents are 20 ppm, 11 ppm and 12 ppm; average Cd contents are 0.31 ppm, 0.27 ppm and 0.24 ppm; average Co contents are 12 ppm, 83 ppm and 0.25 ppm; average Fe contents are 5008 ppm, 5867 ppm and 4500 ppm and average Mn contents are 0.67 ppm, 0.27 ppm and 0.09 ppm in the Thar, Sonda and Meting-Jhimpir coalfields, respectively. Among the light elements, the average amounts of Ca are 250 ppm, 203 ppm and 241 ppm; Mg are 76 ppm, 43 ppm and 60 ppm; Na are 573 ppm, 414 ppm, and 515 ppm and K are 210 ppm, 289 ppm and 252 ppm in the Thar, Sonda and Meting-Jhimpir coalfields, respectively. Among the proximate parameters, the average contents of Fixed carbon are 40.44%, 41.20% and 40.11% and Ash contents are 5.165%, 5.77% and 10.77% in the Thar, Sonda and Meting-Jhimpir coalfields, respectively. Among the ultimate parameters, the average contents of Hydrogen are 6.89%, 6.90% and 6.82%; average Carbon contents are 62.10%, 61.43% and 60.20%; average Nitrogen contents are 0.35%, 0.31% and 0.32% and the average Sulfur contents are 1.17%, 4.33 % and 3.65 % in Thar, Sonda and Meting-Jhimpir coalfields, respectively. The average Calorific values for Thar, Sonda and Meting-Jhimpir coalfields are calculated as 10111 btu/lb, 10301 btu/lb and 10143 btu/lb, respectively. By comparing the heavy and trace elements of Sindh coals with the other coals of Pakistan and elsewhere in the world, it is noticed that Sindh coals are relatively enriched in the Pb, Zn, Ni, Co and Fe. The amounts of fixed carbon, ash hydrogen, carbon and nitrogen in Sindh coals are *within the permissible limit, however, the sulfur contents, especially in the Sonda and Meting-Jhimpir coals are above the permissible limit.*

Mineralogically the Sindh coals contain quartz and kaolinite as the dominant mineral phases with subordinate amount of calcite, dolomite, muscovite, illite and pyrite. The quartz and muscovite are generally detrital and the remaining phases are authigenic. The sequential leaching analyses suggest that most of the heavy and trace elements are associated with HCl – soluble compounds and also with the insoluble or organic shielded matters. However, the Fe is generally associated with the HNO_3 *– soluble disulfides. The leaching behavior of the Sindh coal suggests that there are chances of contamination of the underground water system due to acid mine drain water during the large scale coal mining in the region. The combustion of the Sindh coals may also pose threat to the environment of the region as far as the S, Pb, Zn and Ni contents of Sonda and Meting-Jhimpir coals are concerned. These coals, therefore need to be cleaned and also the particulate emission level of the power generation plants should be substantially reduced before the use of these coals in power generation plants and other industries of Pakistan.*

CHAPTER ONE

INTRODUCTION

Coal is a fossil fuel formed by the accumulation of organic material in sedimentary strata in the earth's crust. It undergoes *in situ* compaction with time to form various ranks of coal. The results of accumulation of in situ residues and important debris in swamps lead to the formation of peat. After the peat has accumulated for a period, it must be buried under mineral sediment, generally clay, silt, and sand. The peat forms beds of coal that range from a few centimeters to many meters in thickness. The coal is often inter bedded with shale, sandstone, and other sedimentary rocks. A single stratigraphic sequence may include several coal beds. Coal is known to have been deposited in shallow marine and fluviatile (lake) environment. These lakes have also received lithogenic fluxes from mineralized continental shield enriching the coal with heavy metals like Pb, Zn, Cu, Cd, Co, Ni, Mn etc. (Sahu,1990).

In coal, various metals or elements, hydrogen, carbon, nitrogen, sulfur, and oxygen are determined and reported in ultimate analytical sequence. More than 55 elements are commonly present in the organic and inorganic (mineral) form or part of the coal. Some of the elements found in coal represent only in mineral forms, other elements can be present both as constituents of minerals and in complex combination with the organic material of coal.

Coal is likely to remain an important part of the Pakistan energy supply, largely because it is the most abundant domestically available fossil fuel. One of the major concerns related to the use of coal for electricity production is the release of elements during combustion and the resulting coal combustion product (CCPs)- fly ash and bottom ash-to the environment. It is therefore, necessary to acquire an accurate, reliable and quantitative information about the concentration and modes of occurrence of chemical elements, especially heavy metals in feed coal and coal combustion product.

The extraction of coal is another cause of environmental degradation of the area, which results in the serious problems related to contaminated mine drainage. Acid mine drainage from closed and abundant mines (both surface and underground) has far reaching effects on water quality, on fish and wildlife.

Naturally occurring radioactive material released by coal combustion is accumulating in the environment along with elements such as mercury, arsenic, silicon, calcium, chlorine, lead and sodium as well as metals such as aluminum, iron, lead, magnesium, titanium, boron, chromium, nickel, zinc, copper which are collectively dispersed in millions of tons of coal combustion by-products. The potential threats of these released materials will someday be of such significance that they should not be ignored (Ahearne, 1993).

In Pakistan, the environmental laws were not enacted until 1960s but in 1975 the Environmental Ministry was established as a follow up of Stockholm Declaration of

1972. During 1977 to 1988 very few environmental laws were promulgated. In this period Environmental Protection Ordinance of 1983 and Environmental Protection Act of 1997 were established. But no specific laws have been constituted for the mining sector, especially coal mining; except few labor laws exist for the coal miners. However, the federal and provincial governments had promulgated following environmental laws for petroleum activities: (1) Petroleum (exploration and production) Rules 2001, and (2) Pakistan Petroleum (exploration and production) rules 1986 and (3) DGCPs guidelines for operational safety, health, and environmental management in Pakistan's Petroleum exploration and production sector. In this regard Sindh provincial government had also established sectoral guidelines for environmental protection in 1999 for off-shore oil and gas seismic surveys. However, no specific laws have been formulated for the mining sector so far.

Mining particularly coal mining has hazardous impact on environment. It can cause various types of lung diseases in the coal miners due to air pollution when fine coal dust particles spread in air as suspended particulate matter (SPM) during mining and transportation. This fine coal dust particles can cause bronchial or respiratory diseases. The problem of acid mine drainage water (AMD) is also well known that cause sulfurization of groundwater in coal mining areas. Coal mining accidents are also common in Baluchistan province due to methane gas accumulation in coalmines. Mine waste and blasting operation during mining activity also cause negative impact on environment. It is, therefore, considered important to draw attention of scientific and law making community for making some sectoral guidelines for environmental protection in the mining sector of Pakistan.

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Keeping in view the huge deposits of Sindh coal in Pakistan, their future threats to the environment need to be studied. This study is, therefore, proposed to evaluate the Sindh coal for its use in power generation and other industrial purposes.

COALFIELDS OF SINDH

Lower Indus Basin has number of coal basins (Fig. 1.1). These basins extend westward from Thar coalfield, through Tando Muhammad Khan, Badin to Lakhra-Sonda-Thatta area. The western part falls in the folded belt zone, where as most of the eastern part covers the Platform slope. Shelf platform and carbonate deposits ranging in age from Triassic to Recent overlie the basement slope.

Four major coalfields are named as (1) Sonda, (2) Meting-Jhimpir (both in Thatta district) (3) Lakhra (in Dadu district) and (4) Thar coalfield in Tharparkar have been explored (Fig. 1.1). These coal deposits occur in the Bara Formation (Middle Paleocene) and in the Sohnari Member of the Early Eocene Laki Formation. The Sohnari coal is restricted to the Meting-Jhimpir coalfield, consisting of about 30m thick Sohnari Member, having sandstone and lateritic clay. The coal in Lakhra and Sonda coalfield was deposited is in the Bara Formation, which is comformably overlian by the Lakhra Formation. The Bara Formation contains two main coal-bearing horizons, one is in the upper part and the other in the lower part. The lower one is known as Jheruck coalzone, found in Sonda coalfield. Sonda coal occurs relatively more persistently at three main horizons, named as Dadhuri, Sonda and Jherruck coal zone, and was deposited in the Bara Formation.

Meting-Jhimpir coal is found in the Sohnari Member of the Laki Formation of Eocene age, near the contact with Upper Paleocene of Lakhra Formation. There is only one workable coal bed, which is generally thin and lenticular and ranges in thickness from 0.3m to 1.0 meter. Thar coalfield is the largest coalfield of Pakistan and is located on the Indus Platform in Thar Desert in south-eastern corner of Pakistan. It covers an area of about 9,000 sq. kms.

The coal deposits of Sindh are developed at two different stratigraphic horizons; the lower one is associated with Bara formation (lower Ranikot) of middle Paleocene age and the upper zone is associated with the Sonhari member of the Laki formation of early Eocene age. Due to changes in facies and the depositional environment, the coal horizons at some places are represented by carbonaceous shale instead of lignitic to sub-bituminous coals.

The coal at Lakhra and Sonda-Thatta area is in the Bara formation, The upper formation consists of limestone, sandstone, siltstone and claystone. It is fossiliferous and has a thickness of 150 to 250 metres. At places, it thins out to less than 50 meters. The lower formation consists of sandstone with subordinate claystone, siltstone and coal. The main coal seams in Lakhra and Sonda area are named as Lailian bed and Sonda coal seam which normally lie about 80 to 100 metres below the top of the lower part of the lakhra formation. The coal in this formation appears to have been deposited in lacustrine conditions close to an oscillatory marine environment. Geological data are indicative of a fairly wide distribution of coal in Bara formation covering wide tracts of subsurface areas in the lower parts of Sind south and west of Hyderabad High. Regional geology of this extensive coal basin indicates that in the northern region in Lakhra, coal is formed in 'back barrier' environment, whereas in the southern region in Sonda and Sujawal the coal beds are deposited in lower deltaic plain (Waheeduddin et al., 1988). Much of this coal, outside the Lakhra and Sonda areas may lie at the depth of over 250 metres in the area lying to the east of the Indus river and in the Ranikot area where the part of the Bara formation is exposed.

Coal in Meting-Jhimpir area is present in the Sonhari beds at the base of the Laki formation of early Eocene age. The Sonhari beds are about 30 meters thick and mainly consist of sandstone and lateritic clay. The lateritic material was laid down on an old erosional surface marking an unconformity between Lakhra and Laki formations (Outerbridge et al., 1989). The Sonhari beds were deposited in lacustrine/fluviatile conditions near the coast. This environment prevailed on the Hyderabad arch during early Eocene prior to inundation by the sea and reversion of purely marine regime (Schweinfurth et al., 1988). Swamp vegetation which grew in the shallow, brackish water was buried by the later sediments and was source of coal (Outerbridge et al., 1989). Due to its origin and subsequent geological history and physiographic events the coal in the Sonhari beds are unlikely to have developed extensively within mineable depths.

Sonda coalfield

Sonda coalfield is situated close to the national highway linking Karachi with Hyderabad and covers an area of more than 600 sq.km. This field has the distinction to host both the coal horizons Lakhra coalfield and the Meting-Jhimpir coalfields. Its potential reserves, therefore, are fairly large. The lower coal horizon is associated with Bara formation of middle Paleocene age (as in Lakhra) and the upper horizon is found with the Sonhari member of Laki formation of early to middle Eocene (as in Meting-Jhimpir area).

Several coal seams are developed in the Bara formation but due to limited subsurface data, the lensoid nature of occurrence and quick facies changes, it is difficult to carry out the natural correlation. As coal outcrops are not exposed, all estimates of reserves for the coal are subsurface. The depth of the coal seams with a minimum thickness of one metre or more is generally between 80 to 250 metres.

The estimated of reserves are of 280 million tonnes in an area of 260 sq. km only (Kami et al., 1990).

Meting -Jhimpir coalfield

The Meting-jhimpir coalfield lies approximately 125 km to the east of Karachi in the vicinity of Jhimpir and Meting railway stations on the main railway line. The coalfield covers an area of about 90 sq.km. in Thatta District. The railway line between Jhimpir and Meting runs along the western limit of the coalfield.

According to Outerbridge et al. (1989) the coal in the Meting-Jhimpir area was deposited on the erosional surface of the Palcocene rocks. It is now grouped in the lower part of the Laki formation of early Eocene age. Only one workable coal seam is present which is generally thin and lenticular. Its thickness varies from 0.3 metre to 1.0 metre with an average thickness of about 0.5 metre. The coal is of lignite-A to sub-bituminous-B in rank. It is soft and friable and suffers from spontaneous combustion on exposure.

Total available resources of coal in the Meting-Jhimpir area are presently estimated as 25 million tonnes. These include 3 million tonnes proved reserves, 5 million tonnes probable reserves and 17 million tonnes possible reserves. Average annual production is of the order of 40,000 tonnes (Abbas and Atiq., 2005). This coal is used in brick kilns only located in Sindh.

Lakhra coalfield

Lakhra coal field is the second largest coal field of Pakistan, comprising an area of about 680 square kilometers. It is located 225 km north - east of Karachi in Dadu district of Sindh province. It lies between latitudes *25*°30' and *25°45' N* and longitudes *68*° 0' and *68*° 15' E and is covered in Survey of Pakistan topographic sheet Nos. 40 C/1 and 40C/2 (Fig. 1.1). Khanot is the nearest railway station, connected with Lakhra coalfield by a 19 km long metalled road up to Indus Coal mines.

The rocks exposed in the area belong to Ranikot group (Paleocene), Sonhrari member (Early Eocene), Laki limestone (Early Eocene) and Manchar formation (Pliocene). These units are composed of shallow marine and fluviatile sediments. The oldest exposed rocks, in the area belong to the Bara Formation of Early Paleocene. It is underlain by Lakhra Formation of Middle to Late Paleocene age which is unconformably overlain by the Laki Formation of Early Eocene age. The unconformity between the Lakhra and Laki formations is marked by a 38 to 63 cm thick laterite bed (Khan et al., 1988). Rocks of Middle Eocene to Miocene (intervening the Laki limestone and the Manchar Formation) are absent in the area, hence the Manchar Formation of Pliocene age directly overlies Laki Formation. A very thin cover of alluvium rests over the Manchar Formation. The thickness of the minable coal seam in the area varies between 1.5 to 3.35 meters (Khan et al., 1988).

The Lakhra coal is dull black and contains number of resin flakes. It could be extracted in large lumps, but dries to a moisture content of about 8% when brought to surface. It tends to crumble on longer exposure and is often susceptible to spontaneous combustion (Waheeduddin et al., 1986).

Thar coalfield

The Thar coalfield spread over 9100 sq km is located between latitudes 24°15'N & 25° 45' N and longitudes 69°45' E & 70° 45' E in the south eastern part of Sindh as shown in the Survey of Pakistan toposheet Nos. 40 L/2 to L/5. It is connected with a 667 km metalled road upto Islamkot from Karachi via Hyderabad-Mirpur khas-Naukot and the other route is from Thatta–Badin–Naukot. Islamkot town lies well within the western margin of this area, approximately 50 km east of Mithi, the district Headquarter of Tharparkar.

As the name implies, Thar Desert of Sindh is a vast tract of sand dunes and intervening sandy-silty plains merging imperceptibly with Indus plain in the east; in the west, it extends across the Rann of Kutch depression into Rajasthan in India. In the north, its part reaches east of Waheed ud dinpur in east Punjab and in the south, it edges the Rann of Kutch. Sand dunes are of varying height, rarely exceeding 50 m, and have a general north-south trend. The intervening sandy-silty plains are generally 40 to 50 m AMSL. In the extreme southeast corner of the Thar Desert is the tableland of Nagarparkar, an igneous and metamorphic complex (basement complex).

The climate of the area is broadly classed as hot and arid. The area lies in a region where monsoon rainfall is generally low, and the distinction between the summer and monsoon seasons, is not very well marked. Although it receives some monsoon rainfall, the rain's effect on temperature for instance is minimal. The drought years are common. The mean annual maximum and minimum temperatures are 19 to 35°C respectively. Maximum summer temperature commonly exceeds 40°C in April through June.

Sand dunes cover more than 56 percent of the area. The relief in the area varies between near sea level to more than 150 metres AMSL. The sand dunes are mostly longitudinal with a NE-SW trend and are stabilised by shrub vegetation and grass. Thar coalfield is located on the Indus Platform. The presence of coal in Thar desert of Sindh was first indicated in the drilling for fresh water by British Overseas Agency in 1988 near Khario Ghulam Shah village, about 15 km east of Islamkot. In 1992, USGS/GSP confirmed huge reserves of coal in the area, with a maximum thickness of 30 meters of coal. This coalfield is divided into following block (Fig.1.2):

1. Sinhar Vikian-varvai (Block-I) is southeast of Islamkot
2. Singharo-Bhitro (Block-II),
3. Saleh Jo Tar (Block-III) and
4. Sonalba (Block-IV) in the northeast of the area.

1. Sinhar Vikian-varvai or Block – I covers an area of 122.00 sq. km and has total reserves of 3,566 million tones in clastic rocks of Bara Formation.

2. The Singharo-Bhitro Block-II covering an area of 55 sq. kms falls in northern part of the Thar coal field and has coal resources of 1584 million tones in clastic rocks of Bara Formation. The measured reserves are 640 million tones. The

cumulative coal thickness varies from 7.52 to 30.89 meters. The coal beds range in thickness from 0.30 to 20.78 meters. The minimum depth at which the coal is present is 123.80 meters. 90 % of the coal can be extracted from unto -120 meters AMSL, whereas 75 % of the coal resource lies between -75 and -120 meters AMSL.

The maceral components indicate less maturity of coal formed from herbaceous plants in warm climate with rapid rise and fall in water table and environment of raised bogs (Fassett & Durrani., 1994). The quality of coal is lignite ‘B’. Claystone forms the roof as well as floor rock of coal benches (Jaleel et al., 2002).

3. The Saleh Jo Tar, Block-III, covers an area of 99.5 sq. km and falls in central part of the Southern Thar coalfield. The field area is covered by stabilized sand dunes trending longitudinally in northeast direction. It is approachable by all weather road upto 10 km. beyond Mithi and onwards by four-wheel driven vehicles through desert sand. It has coal resources of 2008 million tones in clastic sediments of Bara Formation. The measured reserves are 413 million tones. The cumulative coal thickness varies from 7.15 to 24.58 meters. The coal benches range in thickness from 0.20 to 14.65 meters. The minimum depth at which the coal is present is 114 meters. 90 % of the coal can be extracted upto -120 meters AMSL depth, whereas 85 % of the coal resources lie between -50 and -110 meters AMSL. The rank of coal is lignite ‘B’. Clay stone and loose sandstone beds form the roof

as well as the floor rock of coal benches. The palynological studies show that the Thar coals are Paleocene to Eocene in age and may have been deposited in a raised bog environment (Jaleel et al., 2002).

4. The Sonalba Block-IV covering an area of 82 sq. km falls in the northern part of the Thar coal field and has coal resources of 2559 million tones in clastic rocks of Bara Formation. The measured reserves are 637 million tonnes. The cumulative coal thickness varies from 10.74 to 30.88 meters. The coal seam range in thickness from 0.30 to 20.78 meters.

The Thar coalfield area is mainly covered by sand dunes. Its subsurface geology is obtained through drilling by the Geological Survey of Pakistan during 1994 to 2000. These studies show that coal bearing strata of Palaeocene–Eocene sediments unconformably overlie the Pre-Camberian basement rocks of igneous origin which are exposed at Nagar Parkar and form the only out crop in the area.

In Thar coalfield the Basement Complex is found at varying depths between 110 to 277 metres. The basement rock is generally granitic in composition which is highly altered to kaolinite. The Paleocene-Eocene coal bearing horizons, known as Bara Formation generally comprises of claystone, carbonaceous claystone, sandstone, siltstone with inter-laminated coal beds. The percentage of sand increases below the last coal beds. Claystone forms the dominant lithological unit of the formation. It is silty at places and also contains pockets of very fine sand

and scattered coal fragments. The claystone generally forms the floor as well as the roof rock. Pyrite is present as patches of fine of upto 2 mm size. Claystone also contains 3 to 30 cm thick sideretic bands and nodules.

Sandstone is very fine-to coarse-grained and consists dominantly of quartz and minor amounts of ferro-magnesian mineral grains. The lower 15-20 metres of the formation which consists the coal is saturated with brackish water.

The coal deposits of Sindh are yet to be explored fully before their large-scale exploitation and use in the power generation plants, which are going to be established in near future in the region. This study is, therefore, conducted to fully understand the geology of these coalfields and to carry out the environmental assessment of these coals deposits, which could help the planners for establishing the environmentally friendly mining activities and power generation plants in the region in future.

AIMS AND OBJECTIVES

Keeping in mind the importance of coal and its future use in power generation, environmental impact assessment of the investigated coalfield is needed in detail. For this purpose it is aimed:

- to determine the chemical (i.e., heavy, trace and light element analysis and proximate and ultimate analysis) and combustion (i.e., calorific values) properties of the Thar, Sonda and Meting-Jhimpir coalfields

- to evaluate the leaching behavior of the Sindh coal deposits which will help in predicting mine-drainage water quality.
- To compare and correlate the Sindh coal data with other known coal deposits of Pakistan and other countries of the world.
- to investigate the environmental impact in regard to heavy and trace elements concentration of the Sindh coal before its extensive utilization in power generation and also in the cement and other industries of Pakistan.

PREVIOUS WORK

The first book on Geology and Geography of Sindh was published by Lambrick (1825) in two volumes, giving details about physiographic and geological descriptions. Subsequently, in 1867, 1876, 1878 and 1879 Blanford published his research work on geology of coastal area of Sindh, Geology of Sindh, geology of eastern (Thar desert) Sindh western parts of Sindh and neighboring Punjab and Baluchistan. Gee (1940 & 1948) published his work on Geology of Indian coal, including Lakhra coal in Sindh.

Pithawala and Kaye (1946) published a book on Geology and Geography of Karachi and its neighborhood. In 1950 Khan conducted a general and geological survey to estimate the coal resources of Pakistan. Waheeduddin et al. (1954)

prepared the geological map of Sonda -Thatta coalfield. In 1980's a great work was initiated under coal reap program by Geological Survey of Pakistan and U. S. Geological Survey, and work was published by U. S. Geological Survey.

METHODOLOGY

The fresh bed coal samples were collected from thirteen coalmines at different depths operating in Metting-Jhimpir coalfield while the samples from Sonda and Thar coalfields were obtained from the Core Library of Geological Survey of Pakistan. These samples were numbered accordingly and packed in the polythene bags. The detail methodology along with instrumental standardizing conditions are given in the appendix-1, however, a brief analytical procedure adopted during this study is described bellow.

The air-dried coal samples were crushed and pulverized to 200 mesh. A known weight of the powdered coal sample was decomposed by concentrated hydrofluoric acid (HF), concentrated nitric acid (HNO_3) and 3N hydrochloric acid (HCl) in the teflon beaker and the final stock solution of 50 ml volume was prepared by using the method of Jeffery and Hutchison (1986). After preparing the stock solutions of all the coal samples, various heavy, trace and light elements (i.e., Cu, Pb, Zn, Ni, Cr, Co, Cd, Fe, Mn, Ca, Mg, Na, K) were determined in these solutions by the Perkin Elmer atomic absorption spectrophotometer.

For determining the leaching behavior of these colas, four different types of leachates were prepared by leaching the representative mixture of all the three coals of Sindh with IN ammonium acetate, 3N hydrochloric acid, concentrated hydrofluoric acid and 2N nitric acid seperately by using the method of Finkelman et al. (1900) and Palmer et al. (2000). The heavy and trace elements in these leachates were then determined by atomic absorption spectrophotometer.

The proximate analyses (i.e., fixed carbon and ash contents) were performed by using the method of Harker (1981) whereas the ultimate analyses (carbon, hydrogen, nitrogen and sulfur contents) were determined by EuroVector Elemental analyzer.

All the above experiments were carried out by using the facilities of the Geochemistry Laboratory of the National Centre of Excellence, University of Peshawar, Pakistan.

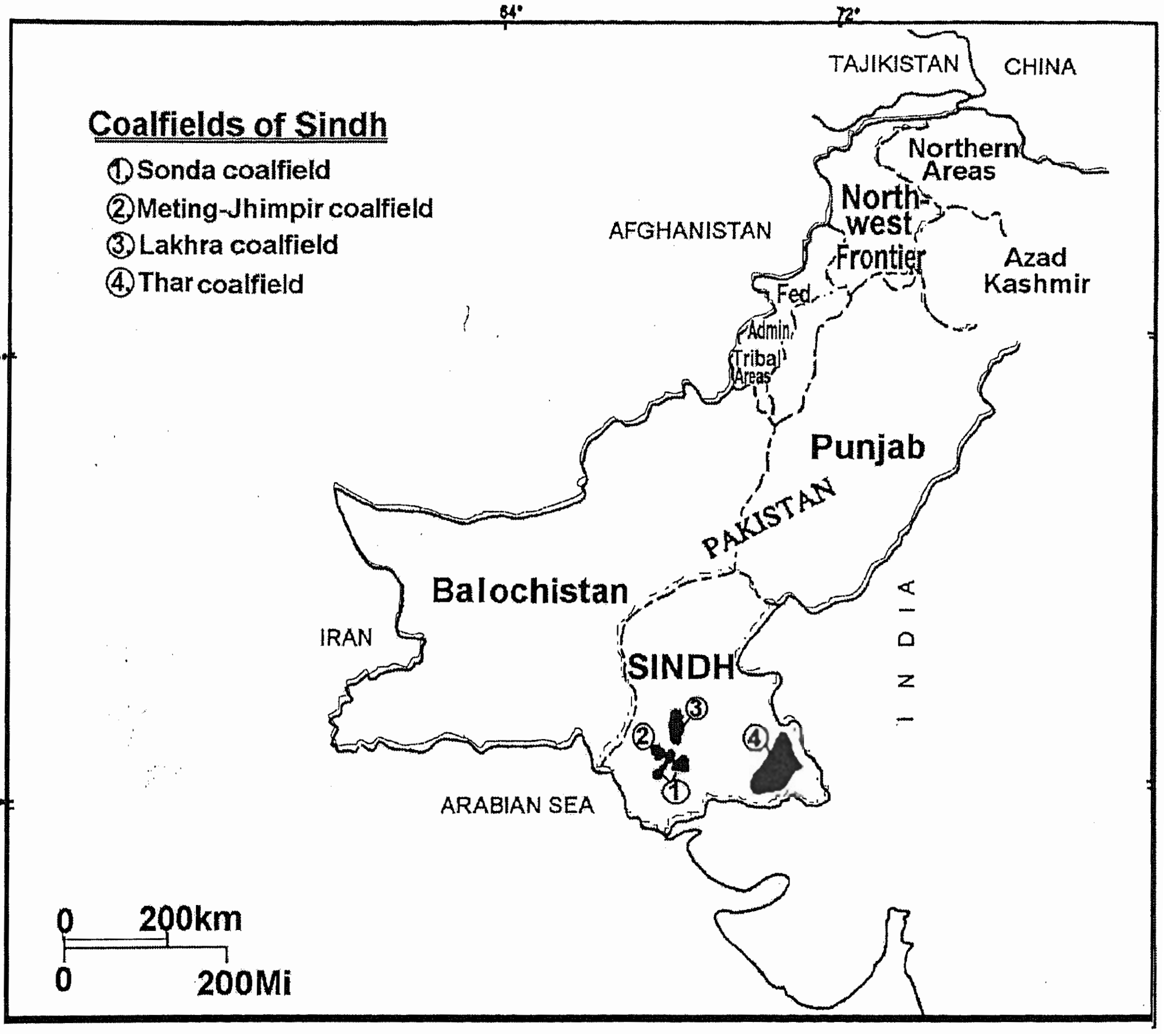


Fig. 1.1 Map showing various coalfields of Sindh province, Pakistan.

CHAPTER TWO

PHYSIOGRAPHY, TECTONICS AND STRATIGRAPHY OF SINDH

GENERAL

Sindh is the second largest province of Pakistan, lying at latitudes 23° 35'- 28° 30' N and longitudes 66° 42'- 71° 1' E. It is bounded in north and west by the provinces of Baluchistan and Punjab, in east by Rajisthan (India), in south by the Runn of Cutch and the Arabian Sea (Fig. 2.1). Sindh has 240 kilometres of coastal strip in the Southwest along the Arabian Sea. It is physiographically known as the "Lower Indus Basin" which forms the southern part of Pakistan with N-S extension of about 580 km and maximum breadth of 442 kms. The province of Sindh has been sustained by River Indus for centuries. River Indus has length of 2,880 km and a third of that (about 944 kms) traverses the Sindh province. The extreme west of Sindh is generally mountainous consisting of Kohistan section of the barren Khirthar mountains. To the east is the sandy belt stretching from the borders of Bhawalpur to the Run of cutch. Between these tracts lies the Indus valley terminating in the deltaic area in the southwest. Except for the western mountainous region of Pab-Kirthar ranges and a small hilly tract in the South East corner of the Tharparkar District (Nagar Parkar), Sindh is mainly comprised of plain area (Fig. 2.1). Eastern Sindh is delimited by Rajputana desert. The Arabian

Sea forms the southern boundary of Sindh whereas it extends to the foot of the Sulaiman range in the north (Rehman, 1997).

The province of Sindh can be divided into three major physiographic divisions named as:

1) Western Highlands
2) Lower Indus valley
3) Desert

Western Highlands

This region includes the N-S crescent like hilly ranges of Khirthar, Pab, Laki, and Kohistan area. Rocks of these ranges consist of folded sedimentary strata that are severely folded, jointed, deeply ravined and fissured. Khirther Range has a simple anticlinal structure with flanks gently dipping towards west and south. There is no vegetation or soil due to scanty rainfall. The highest altitude in the Khirther range is 2072.64 meters named as Kutai-ji-Kabar i.e. Dog's grave (Pithawala, 1939).

Lower Indus Valley (Delta Area)

The lower ranges of Kohistan consist of monoclinal folds with undulatory plains in between. There is considerable subaerial denudation because of relatively high rainfall. Laki Ranges are mainly composed of Tertiary rocks and a large number of thermal springs are found here.

A large part of Sindh lies in the deltaic plain of Lower Indus valley. This region includes plains mostly overlain by alluvium, old and new, trenched with river channels in some places and overridden by raised terraces in others. A few isolated low limestone hills are the only outcrops in the plains, which are otherwise quite levelled. The Lower Indus valley may be subdivided into three parts namely (1) Western valley (2) Eastern valley and (3) Deltaic area. The western valley section is distinguished from eastern valley by the presence of old alluvium and seasonal springs flowing from Khirthar mountain into Manchar Lake (Khan, 2003).

The Deltaic area largely consists of mangrove swamps, and sandbars. The chief characteristic of the region is the changing outlets of the Indus, which act as the inlet of the sea. The deltaic area is of recent growth and is still growing. The lowland plain of Indus merges into it. The changes in the delta are caused by the mouth of the river itself and by the stormy nature of the sea during the monsoon season (Khan, 2003).

Desert

The eastern part of Sindh is covered by Thar Desert that extends into Rajputana in India. Thar desert is the 9th largest and the most densely populated desert of the world, with over 91 thousand people inhabiting in it. The origin of the Thar Desert is a controversial. Some consider it to be 4000 to 10,000 years old, whereas others state that aridity started in this region much earlier. Another theory states that area turned to desert relatively recently, perhaps around 2000-1500 BC; around this time the Ghaggar ceased to be a major river. It now terminates in the desert. It has been observed that Late Quaternary climatic changes and neotectonics have played a significant role in modifying the drainage courses in this part and a large number of palaeo channels exist Gupta & Prakash, 1975). The name Thar is derived from Thul the general term for the region and ridges. The land area of Thar is spread over about 22,000 sq. km.

The Thar desert lies between latitudes 24° 10' to 25°45' N and longitude 69' 04' to 71°06'E. It is bounded on the north by Mirpurkhas and Umerkot districts, on east by Barmer and Jaisselmir districts of India, on west by district Badin and on south by Rann of Cutch. Thar is covered by sand dunes up to an average depth of >80 meters.

Physical Features of Thar Parkar

The Thar region forms part of the bigger desert of the same name that spread over a vast area of Pakistan and India from Cholistan to Nagar Parkar in Pakistan. The Thar is mostly desert and consists of barren tracts of sand dunes covered with thorny bushes. The ridges are irregular and roughly parallel, they often enclose sheltered valleys above which they rise to a height of some forty six meters.

There are three principal landforms in the Thar desert region (i.e., the predominantly sand covered Thar, Pat or plains and Parkar). These are explained in the following section.

The desert fringe zone and aeolian sand deposits or Thar Sands: It is a barren region where sand is piled up into huge wind blown dunes. The sand dunes are of three types (i.e., longitudinal parabolic, transverse and barchans). The first type, running NNE-SSW, i.e. parallel to the prevailing winds, occurs to the south and west of the Thar. The transverse dunes, aligned across the wind direction to the east and north of Thar and barchans with the concave sides facing the wind in the interior, predominant in Central Thar. On the whole the Thar Desert slopes imperceptibly towards the Indus plain and surface unevenness is mainly due to sand dunes. The dunes in the south are higher rising sometimes to 152 m whereas in the north they are lower and rise to 16 m above the ground level (Kazmi, 1985). (Fig. 2.2).

Pat or Plains: Along the margin of the zone of longitudinal dunes, there is a relatively small zone of active and moving barchan dunes. Barchan dunes, with their two pointed crescentic ends directed northeastwards, are arranged along narrow sand ridges. Their height varies from 14 to 93 meters and the larger ones are as much as 117 to 160 meters. Southwestwards, these moving dunes are directly in contact with the longitudinal stabilized dunes. The southern margin of this zone of barchans is in the form of a straight line parallel to the margin of the Indus flood plain. In the past, at the time of the formation of the longitudinal dunes, the southwesterly winds may have been less strong and it may be expected that there were in addition strong, relatively short cross-winds from the northwest. The northwesterly wind at present affects the northern part of the desert, but does not reach as far south as the Lower Thar Desert (Kazmi, 1985). (Fig. 2.2).

It also extends from near Nawabshah, northeastward up to Bahawalpur, and is characterized by sand dunes in the form of parallel transverse ridges. The continuity of the transverse ridges is frequently broken by the moving sand, in the form of barchan dunes or at some places in the form of small longitudinal dunes. Northeastward the dunes become more complex (Pithawala, 1946).

Parkar: The Parkar area of Nagarparkar has a rock outcrop in the center having an altitude of 400 meters which is known as Karoonjhar Hills. Hill is surrounded by plain valley of about 50,000 hectares containing alluvial deposits with granite out crop at some places. The whole Parkar area has the alluvial deposits, the soil is fertile, having high clay and silt in it (Pithawala, 1946).

The only hills in the Thar Parkar are at Nagarparkar on the northern edge of the Rann of Kutch which belongs to Precambrian age. It consists of granitic rocks of the Aravalli range. The Aravalli series belongs to Archaen system, which constitutes the oldest rocks. The principal range of Karunjhar is 19 kilometers in length and attains a height of 305 meters (Kazmi, 1985).

The climate of Sindh is extremely hot in summer and relatively cold in winters. Drought years are common. The mean annual maximum and minimum temperatures are 35°C and 19°C, respectively. The maximum daily temperature commonly exceeds 45°C in April through June. The average annual rainfall varies between 200 and 300 mm, which occur during the monsoon season of June to September (Khan, 2003).

TECTONIC FRAMEWORK OF SINDH

In the global tectonic perspective, Pakistan is situated at the junction of three lithospheric plates, the Indian Plate, Arabian Plate and Eurasian Plate. The Indus Basin is situated on the north-western corner of the Indian Plate (Fig. 2.3).

The Indian Plate started drifting in the northeastern direction during Jurassic to Early Cretaceous time and collided with the Eurasian Plate in Paleocene to Early Eocene. During Lower to Middle Cretaceous the Lower Indus Basin was subjected to extensional tectonics and block-faulting followed by volcanic activity, as witnessed in the southern Sindh in Pakistan and Kutch region in India (Fig.2.3). The impact of collision combined with large-scale transform movement in the west is manifested in the form of fold and thrust belts and development of sub-basins (Malik et al., 1988).

Pakistan contains two sedimentary basins, the Indus basin and the Baluchistan Basin. These basins separated by a major fracture zone, the exial belt, collectively occupy an area of about 828,000 sq. km (Fig.2.4). The Indus Basin belongs to the class Extra Continental Down Warp Trough. The basin has elongated shape and is oriented in northeast-southwest direction. The main tectonic features of the Indus Basin are the platform, the foredeep comprising depressions, an inner folded zone and outer folded zone ((Memon et al., 1999).

The Platform known as Indian Platform coincides with the present Indus Plain and is sub-divided into the Punjab Monocline, Sukkur Rift Zone and Sindh monocline. The foredeep includes, from north to south, the Potwar, Kohat, Sulaiman, Sibi, Khirthar and Karachi Depressions. The Inner folded zone includes Zinda Pir, Mari-Bugti, Sanni and Mazarani, whereas the outer folded zones are Sulaiman and Khirthar Folded Zones (Fig 2.2) (Memon et al., 1999).

The province of Sindh is situated in the Lower Indus Basin and includes Sukkur Rift Zone comprising Kandhkot-Mari Horst, Panno Aqil Graben and Jacobabad – Khairpur Horst, Sindh Monocline, a part of Khirthar Depression, Karachi Depression and Mazarani Folded zone (Fig 2.5).

STRATIGRAPHY

The following stratigraphic succession, of the Lower Indus Basin has been established by various workers:

Precambrian

In Sindh Late-Proterozoic magmatic rocks of Precambrian age are found in southeastern Desert named as Nagar Parkar, that may be an extension of similar rocks in Rajsitan, India. A basement of Late Proterozoic rocks, surrounded by sandy desert at the southeastern corner of Sindh exists at latitude 24° 22′ 18″ N, and longitude 70° 43′ 14″ E. The Rocks of this basement are exposed at the edge of Thar Desert in the northeastern margin of Rann of Cutch (Wynne, 1967; Kazmi & Khan et al., 1973; But et al., 1994; Jan et al., 1997). Rocks of the area have been divided into three major groups, namely the Nagar Parkar igneous complex which crops out in the form of small hillocks and forms the basement; the overlying marine sedimentary rocks; and the surfacial alluvial and aeoline deposits. The igneous rocks of Nagar Parker can be classified into basement rocks, grey granite and pink granite.

The Basement rocks: The basement rocks are mainly composed of granites and amphibolites. Granites are containing xenoliths of basic rocks, both of plutonic and volcanic origin.

Grey Granite: The grey granite is the main variety of the area. It occurs in Karunjhar and forms the largest outcrop of plutonic igneous rocks of granitic composition (Butt et al., 1994; Muslim et al., 1997).The Grey granites are the second oldest rocks in the complex after the amphibolites (Jan et al., 1997).

Pink Granite: The outcrops of the pink granites are best seen along the northeastern margin of the Karunjhar hill directly below the grey granite. The largest body of this granite is characterized by a typical pink colour (Kazmi & Jan, 1997).

The rocks are generally medium- to coarse and fine-grained. There are several acidic dykes exposed in this area, the fine- grained granite is greyish pink in color. The rocks may be a part of the basement rocks, as they also occur as xenoliths in the coarse-grained granite (Jan et al., 1997).

Jurassic

The Jurassic sedimentary rocks largely constitute a thick (820m-3000m) sequence of marine pericratonic shelf deposits consisting of limestone, shale, and sandstone with subordinate dolomite and ferruginous beds. They form a platform cover in the entire Indus basin/area (Kazmi & Jan, 1997).

Cretaceous

The Cretaceous sediments belonging to Lower Indus Basin (particularly Sindh) which has various lithology ranging from shale deposited in deep depressions which in turn are overlain by shallow marine limestones and thick sandstones in the upper part. Cretaceous sedimentary rocks are exposed in the Kirthar region of the lower Indus Basin. Except for local disconformities there is a complete sequence of the upper cretaceous rocks ranging from Maestrichtian. The sequence comprises vast amount of fossiliferous shale, carbonates and clastic sediments Pab sandstone (Farshori, 1972).

i. Mughal Kot Formation: The term Mughal kot Formation has been applied to the rocks developed between the Parh limestone and Pab sandstone on the border of Baluchistan (Sulaiman Range) and Sindh (Williams, 1959). This Formation largely consists of grey, silty, calcareous shale in the Kirthar area, In Sindh near Dhabbo creek, basalt has been found in this Formation. The basal part of the Mughal Kot Formation exposed at the Bara Nala section is creamy in colour, hard, compact, fosiliferous, and crystalline. In most of the areas, the Mughal Kot Formation overlies the Parh Limestone unconformably but in Karachi a conformable contact has been observed by Fatmi (1977). On the basis of Omphalocyclus sp., Orbitoides sp.Campanian, Early Maestrichtian age has been assigned to this Formation (Williams, 1959; Marks, 1962).

ii. Pab Sandstone: Vredenburg (1909) and Williams (1959) named this formation as Pab sandstone. It is exposed in the Kirthar region, resting conformably on the Fort Munro Formation, but in some localities overlies Parh limestone unconformably (Shah, 1987). It consists mainly of white, cream or brown thick bedded to massive cross-bedded, medium-coarse-grained quartoze sandstone, with intercalations of subordinate argillaceous limestone and shale. The type section is west of Wirahab Nai in Pab Range, and its thickness ranges from 240 m (Mughal kot) to 1000 m in Pab Range (Kazmi & Jan, 1997). The Pab sandstone at places is unconformably overlain by Paleocene Khadro Formation (Fatmi, 1977). On the basis of Maestrichtian foraminifera, the Pab sandstone has been assigned a Late Cretaceous age (Vredenburg, 1909).

Cenozoic/ Paleocene

Ranikot Group: In the Kirthar area of the Indus Basin, the Paleocene succession consists of the Rani kot Group (Blandford, 1876; 1879, Vredenburg, 1909). This group has a basal marine sequence of sanstone and shale with interbeds of limestone and basaltic lava flows (Khadro Formation), a middle fluviatile to paralic sequence of sandstone and shale with coal and carbonaceous beds (Bara Formation), and an upper sequence consisting of marine limestone and some estuarine sandstone and shale (Lakhra Formation).

Khadro Formation: Khadro Formation is widely distributed in the Kirthar and adjacent region. It lies unconformably on the Late cretaceous Pab sandstone. At the type locality (Bara Nai in the Laki Range), the basal part of the Formation consists of limestone containing oysters and reptile bones. This is followed by a series of olive-grey to brown gypsiferous medium grained fossliferous limesone. A number of basaltic lava flows are also present in it. The thickness of the Formation is 140m as revealed by a test hole at Lakhra coalfield (Williams, 1959). Fossils in Khadro Formation include Cardita beaumonti (Blanford, 1878).Globigerina pseudobulloides and G. triloculinoids (Nagappa, 1959). The Formation has thus been considered to be Early Paleocene in age.

Bara Formation: This Formation conformably overlies the Khadro Formation and is widely distributed in the Kirthar Range and adjacent areas. The type section is in Bara Nai in Laki Range and adjacent areas. The Formation consists of interbedded sandstone and shale. The sandstone is fine to coarse grained, calcareous, ferruginous and at places glauconitic, ripple marked and cross-bedded. Beds range in thickness from a few centimeters to 3 m (Kazmi & Jan, 1997). The shale is soft, earthy, gypsiferous and commonly carbonaceous. Oyster shale, some reptile remains and abundant leaf impressions have been found. Ostraea Talpur has been reported from the base (Vredenburg, 1909). The Formation has been given Middle Paleocene age (Cheema, 1977.

Lakhra Formation: Lakhra Formation overlies the Bara Formation and crops out in the Kirthar and adjacent areas. The type section is southern part of the Lakhra anticline (Cheema et al., 1977). It consists mostly of grey, thin to thick bedded, nodular, sandy, and in places argillaceous, fossilifereous limestone, with interbeds of sandstone, shale in the upper part. Its thickness ranges from 50 m to about 242 m (Kazmi & Jan, 1997). The Formation contains rock assemblage of foraminifera. On the basis of Corals, mollusks, Miscellanea miscella, M. stampi, Lockhartia haimei, Lepidocyclina etc. and echnoids, Late Paleocene age has been assigned to the Lakhra Formation (Davies, 1926; Nuttal, 1931; Duncan, 1881; Vredenburg, 1909, 1928; Duncan, 1835; Cheema et al., 1977).

Laki Formation: The term Laki Formation has been proposed by Hunting Survey Corporation (HSC) (1960). It overlies the Ranikot Group unconformably and is exposed mainly in the southern Kirthar Range. The type locality is near Meting and near Mari Nai in the northern Laki Range. The Formation comprises cream coloured to grey limestone, with subordinate marl, calcareous shale, sandstone and lateritic clay. It contains a rich fossil assemblage of foraminafera, gastropods, bivalves, echinoderms and algae. The lower part of the Formation has been divided into the Sonhari Member and Meting limestone and Shale member by HSC (1960). The Sonhari Member contains lateritic clay, shale, pockets of limonite and ochre, coal beds, sandstone and locally developed yellow, arenaceous limestone. The Sonhari Member is overlain by Meting limestone and Shale Member (Vredenburg 1906), which consists of thin-bedded creamy white, fossiliferous, nodular limestone followed by a sequence of interbedded limestone and shale with subordinate sandstone. The age of the Laki Formation is Early Eocene (Noetling, 1903; HSC 1960).

Sonhari Formation: The Sonhari Member of HSC (1960) has been excluded from the Laki and renamed as Sonhari Formation because it is distinct from the overlying Laki and Lakhra limestone and it comprises a distinct non-marine to brackish water deposits (Outerbridge et al., 1989).

Tiyon Formation: The term Tiyon Formation has been proposed by HSC (1959), to the upper beds of Late Lower Eocene in Sindh. These rocks were included by Vredenburg (1909) with Kirthar Series. The type section is exposed along the Tiyon Nai, (Lat. 26° 8’ 30’’ E, 67° 7’ 15”) south of Manchar Lake. The Formation mainly consists of shale, marl, and limestone. The shale is bluish green, greenish brown, yellowish grey in colour and is calcareous and gypsiferous. The marl is gently nodular, and weathers yellow, reddish brown and cream white. The limestone is thin bedded, nodular and marly, it is cream in colour and contains ferruginous nodules. The Formation is highly fossiliferous containing foraminifera. Generally Tiyon Formation is exposed on the western flank of Laki range and can be found at Thano Bula Khan, Kalu Kuhar and west of Bara nala. It is exposed near Kotdijji and Rohri, where it is underlying Kirthar limestone. It is absent on the east of Laki range. The Tiyon Formation is conformable with underlying Laki Formation and overlying Kirthar Formation. The Formation has been deposited in shallow marine environment on the shelf. Alveolina oblonga, Ovicula, Ovoidea, Assiilina exponens fossils are found in this Formation, indicating an age of Late Ypresian to Early Lutetian (Farshori, 1972).

Kirthar Formation: Kirthar Formation overlies the Laki Formation conformably in Kirthar area. The type area is in the Kithar Range (Gaj River section) (Blandford, 1876; Noetling, 1903). The Formation is mainly fossiliferous limestone interbedded with subordinate shale and marl. The limestone is thick-bedded to massive, nodular in some areas, grey to white in colour and locally contains algal and coralline structures. In some localities the upper half of the Formation is massive cliff-forming limestone. The shale is olive orange, yellow or grey, soft, earthy and calcareous. The thickness of the Formation ranges from 15m to 30m in western Kirthar Range and in Gaj River type section it is 1270 m thick (Cheema et al., 1977). The Formation contains abundant foraminifera, gastropods, bivalves, echinoids and vertebrate remains The age of Kirthar Formation is Middle Eocene to Early Oligocene. (Oldham, 1890; Vredenburd, 1906, 1909; Pilgrim, 1940; Eames, 1952; HSC, 1960).

Nari Formation: Nari Formation is exposed extensively in the Kirthar region as scattered outcrops. In Kirthar province it conformably overlies the Kirthar Formation except in Hyderabad anticlinorium where it oversteps and unconformably overlies the Kirthar and Lakhi Formations (Blanford, 1876; Williams, 1959). The type section is in the Gaj river gorge in the Kirthar Range

(Kazmi & Jan, 1997). The upper part of the Nari Formation is mostly brown, fine to coarse-grained sandstone with interbeds of shale. The lower part consists of interbedded grey to brown, fossiliferous sandy limestone, calcareous sandstone and shale. At many places/localities the lower part of the Formation is gray to brown shelly, nodular, thick-bedded to massive limestone, which has been named as the Nal Member (HSC, 1960). The thickness of Nari Formation ranges from 1045 m to 1820m in the Kirthar area. It contains a rich fauna including echinoids, mollusks, corals, foraminifera and algae. Some of the significant large foraminifera include ummulites intermedius, N. Vascus, . fichtele, N. Clipens and Lepidocyclina dilatata (Duncan et al., 1834; Khan, 1968; Iqbal, 1969). The age of the Nari Formation is Oligocene to Early Miocene (Latif, 1964; Khan, 1968).

Neogene

Gaj Formation: In the Kirthar Range, the lower part of the Neogene consists of near shore marine to estuarine sediments of the Gaj Formation. The type locality is at the Gaj River (Blanford, 1876; Williams, 1959; Pascoe, 1964; Cheema et al., 1977). The Formation rests conformably and transitionally over the Nari Formation (Kazmi & Jan, 1997). The Gaj Formation is mostly shale, which is variegated, grey and gypsiferous and cross-bedded sandstone and fossiliferous brownish, argillaceous limestone. However, in the southern part of the Kirthar range in the Kirthar area, the Formation predominantly consists of yellowish brown sandstone and cream coloured or pinkish white argillaceous limestone. Its maximum thickness is about 600m in the Kirthar area. The Formation contains foramininfera, mollusks, echinoids and corals (Nuttal 1931; Vredenburg 1906, Hunting Survey Corporation 1960; Khan 1968; Cheema et al., 1977). The Gaj Formation is Early Miocene (Aquitanian to Burdigalian) in age but in places may extend into Middle Miocene (Pascoe, 1964; Khan, 1968).

Siwalik Group: In the Kirthar range, the Gaj Formation is overlain by the Siwalik Group, which is composed of molasse type sediments. It overlies the Gaj Formation conformably (Middlecott, 1864; Pilgrim, 1913; Lewis, 1937; Cheema et al., 1977). The term Siwalik group now includes the Manchar series of Blanford (1876) and Vredenburg (1906). Manchar Formation was named after the Manchar Lake (Lat. 26° 08' N, Long. 67° 34' E) It is chiefly composed of sandstone, shale, clay and subordinate conglomerate and is well developed in Sindh. It occupies large area of Laki Range particularly in the synclinal valley in the north and west of Laki Range. In the Gaj river section the contact between the Manchar Formation and underlying Gaj Formation is gradational/transitional drawn above the gypsum bed. Near Manchar Lake and east of Laki Range, i.e. Bara Nala, Ranikot, Laki shah Saddar and Sehwan the lower contact is disconformable. In most of the areas the formation is overlain by Recent to subrecent deposits. The Siwalik Group consists of (a) Nagri Formation (b) Dhok Pathan Formation (Kazmi & Jan, 1997).

Nagri Formation: The type locality of Nagri Formation is Nagri village at Gaj River. This Formation overlies the Gaj Formation in the Kirthar Range. At some places an angular unconformity may be observed (Cheema et al., 1977). The

Formation is largely thick bedded to massive, greenish grey, medium to coarse grained calcareous sandstone, interbedded with subordinate brown to reddish sandy clay and conglomerate. The Formation has yielded a rich vertebrate fauna including proboscideans, rhinoceratides, crocodiles, chelonians and aniodactyles. The age of Nagri Formation is Early Pliocene/Pontian (Pilgrim, 1913; 1926; Lewis, 1937; Cheema et al., 1977).

Dhok Pathan Formation: The type section of Dhok Pathan Formation is at Dhok Pathan village. It has transitional contact with the underlying Nagri Formation and consists of thick pile of interbedded sandstone and clay. The sandstone is thick-bedded, grey to brown, calcareous and cross-bedded; the clay is brown, orange to red. Lenses of conglomerate are present in the upper part (Blanford, 1876;, Griesbach, 1893; Pilgrim, 1913; Cheema et al., 1977). It is less fossiliferous in the Kirthar Ranges. However, Hipperion punjabiense, Rhinoceros sivalensis and Pachyportax latidens have been found (Cheema et al., 1977). The age of the Formation is Early to Middle Pliocene (Kazmi & Jan, 1997).

Quaternary

Quaternary stratigraphic sequence in Sindh represents marine, coastal deposits, shore and offshore deposits, the aeolian deposits of the Thar, evaporates of Salt lakes and flood plain and delta of the Indus River. The Thar Desert along the eastern margin of Indus plain, is largely covered with longitudinal and complex seif type established sand dunes. Some of the longitudinal sand dune ridges have a relief of as much as 100 m and are more than 40 km long (Kazmi, 1977; 1985). The aeolian deposits of Thar Desert range in age from Pleistocene to Recent.

Lei/Dada Conglomerate: In the Kirthar foredeep on the western side of the Lower Indus plain, the Lei conglomerate (Dada conglomerate of Hunting Survey Corporation, 1960) overlies Siwalik Group and earlier formations with a sharp angular unconformity (Gill, 1952). It is composed of thick beds of boulder, conglomerate and subordinate coarse, cross-bedded sandstone. This may be piedmont out wash deposit in the foothill region and in the piedmont plain; it is overlain by younger unconsolidated piedmont deposits. Towards the Indus plain it interfingers with silt and clays of Larkana Formation. Lei/Dada conglomerate is unfossiliferous and its age has been inferred as Early to Middle glaciation (Kazmi, 1984).

Nabisar Formation: South of Nawabshah, a subsurface sequence of more than 125m thick deltaic hard clay, interbedded with lenses of very fine sand, overlies the Eocene bed-rock and Siwaliks (Manchar Formation of Blanford, 1876). The clay is laminated and ranges in colour from dark grey, brown to greyish white. It is calcareous and at places contains abundant mollusc shells, resembling the deltaic deposits. The oil wells at Nabisar, and other ground water test holes in Mirpur Khas and Nabisar and farther northwards, encountered a thick sequence of this Formation, which has been named after the town of Nabisar. This deep inland position of deltaic deposits is due to the rise in sea level and consequent inland encroachment of delta during the last and earlier interglacial stages (Kazmi & Jan, 1984).

Larkana Formation: The name Larkana Formation has been proposed by Kazmi (1966, 1974) and Kazmi and Jan (1997), It is composed of siltstone and clay with interbeds of very fine sand ranging in thickness from 20 m to more than 120 m. The Formation has been encountered in boreholes upstream of Sehwan. Near Khairpur it overlies the Eocene limestone, where as west of the Indus it interfingers and correlates with the Lei/Dada conglomerate and is overlain by piedmont deposits that were interpreted as an ancient sub piedmont deposit and correlated with the lie/Dada conglomerate. Its age varies from Early Middle to Late Middle glacial periods (Kazmi, 1966).

Tando Jam Formation: The term Tando Jam formation has been proposed by Kazmi (1966), Kazmi and Jan (1997), for the coarse sand of channel to the lower Indus Plain at the depth of 130-200 m depths and about 50 km wide buried channel of Indus. The channel is filled with very fine to coarse sand with pebbles and cobbles. The sand has been named as Tando Jam where the Formation was first recognised and is well developed. This Formation is comprised of an upper fine sand member of ~70m of uniformaly deposited fine to very fine sand similar to the sand presently deposited by the Indus.

The lower gravelly coarse sand member occurs below the depth of 80 m and is largely comprised of medium to coarse-sand with pebbles and large cobbles.

The facetted pebbles and cobbles indicate a cold glacial regime during ice rifting. In the eastern part of the lower Indus plain, the Tando Jam Formation overlies Nabisar and Larkana Formation. In the western part it overlies the Larkana Formation and the piedmont and sub-piedmont deposits. The age of lower member of the Tando Jam Formation is Early Holocene and the upper member of this formation is Late Holocene (Kazmi & Jan, 1997).

Table 2.1. Stratigraphic succession of Sindh (after Farshori, 1972 and Kazmi and Jan., 1997).

AGE	FORMATION/GROUP	THICKNESS (IN METERS)
Quaternary	Tando Jam Formation	130m-200m?
	Larkana Formation	20m-120m
	Nabisar Formation	125 m
	Lie/Dada conglomerate	?
Upper Miocene to Pliocene	Siwalik Group: Dhok Pathan Formation	1330-2000m
	Nagri Formation	200m -3000m
Lower to Middle Miocene	Gaj Formation	600 m
	Disconformity	
Oligocene	Nari Formation	1045-1820m
	Disconformity	
Eocene	Kirthar Formation	15m- 270m
	Tiyon Formation	350-500 ??
	Laki Formation	40m-100 m
	Disconformity	
Paleocene	Ranikot Group: Lakhra Formation	50 m –242m
	Bara Formation	3 m
Paleocene	Khadro Formation	67m-180 m
	Disconformity	
Upper Cretaceous	Pab Sandstone	240m-1000m
	Mughal kot Formation	150m-170m
Precambrian	Nagar Parkar igneous complex	

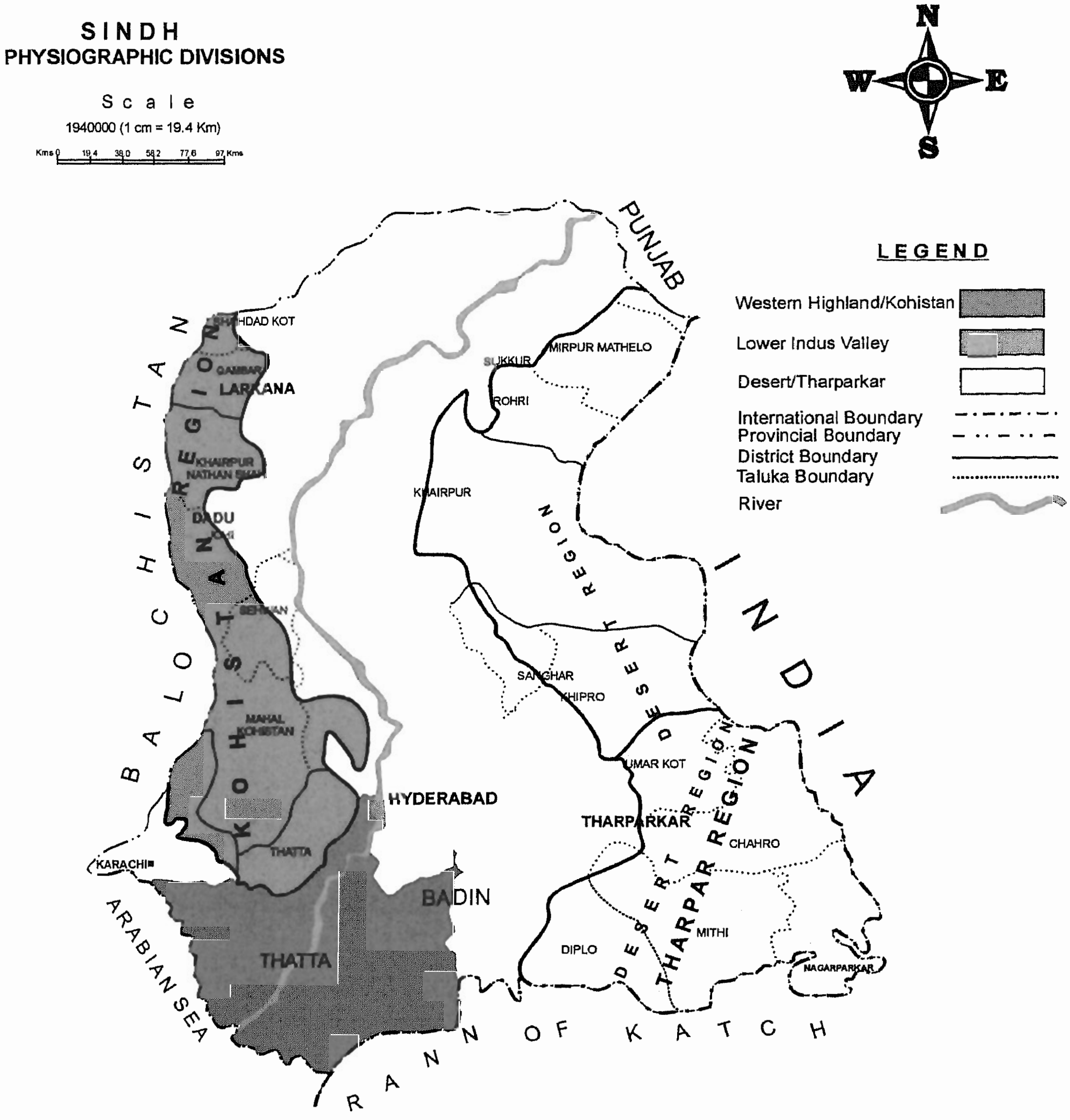


Fig. 2.1 Map showing physiographic divisions of Sindh province, Pakistan.

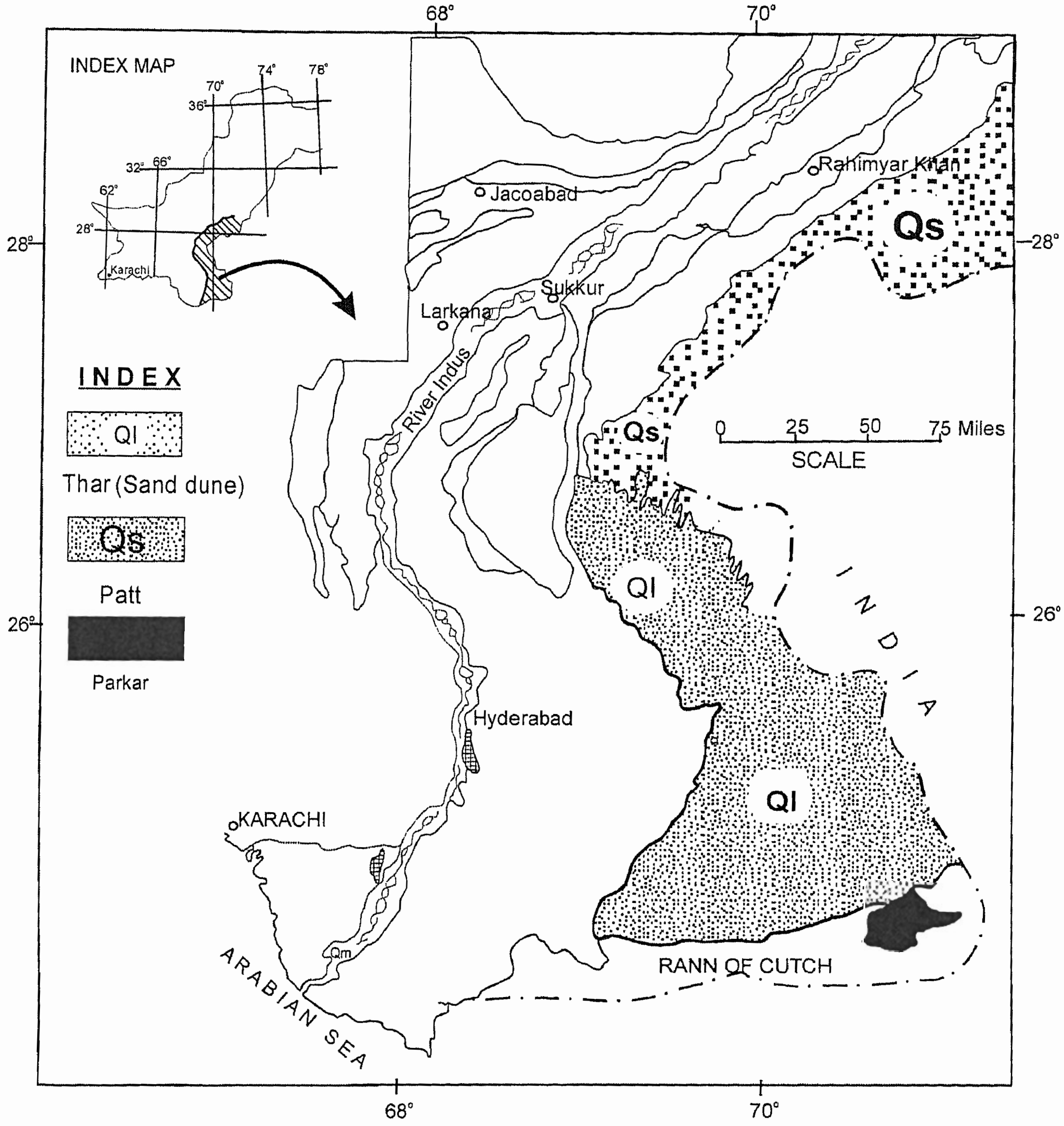


Fig. 2.2 Map showing Physiographic divisions of Thar desert, Sindh province, Pakistan (after Kazmi, 1985).

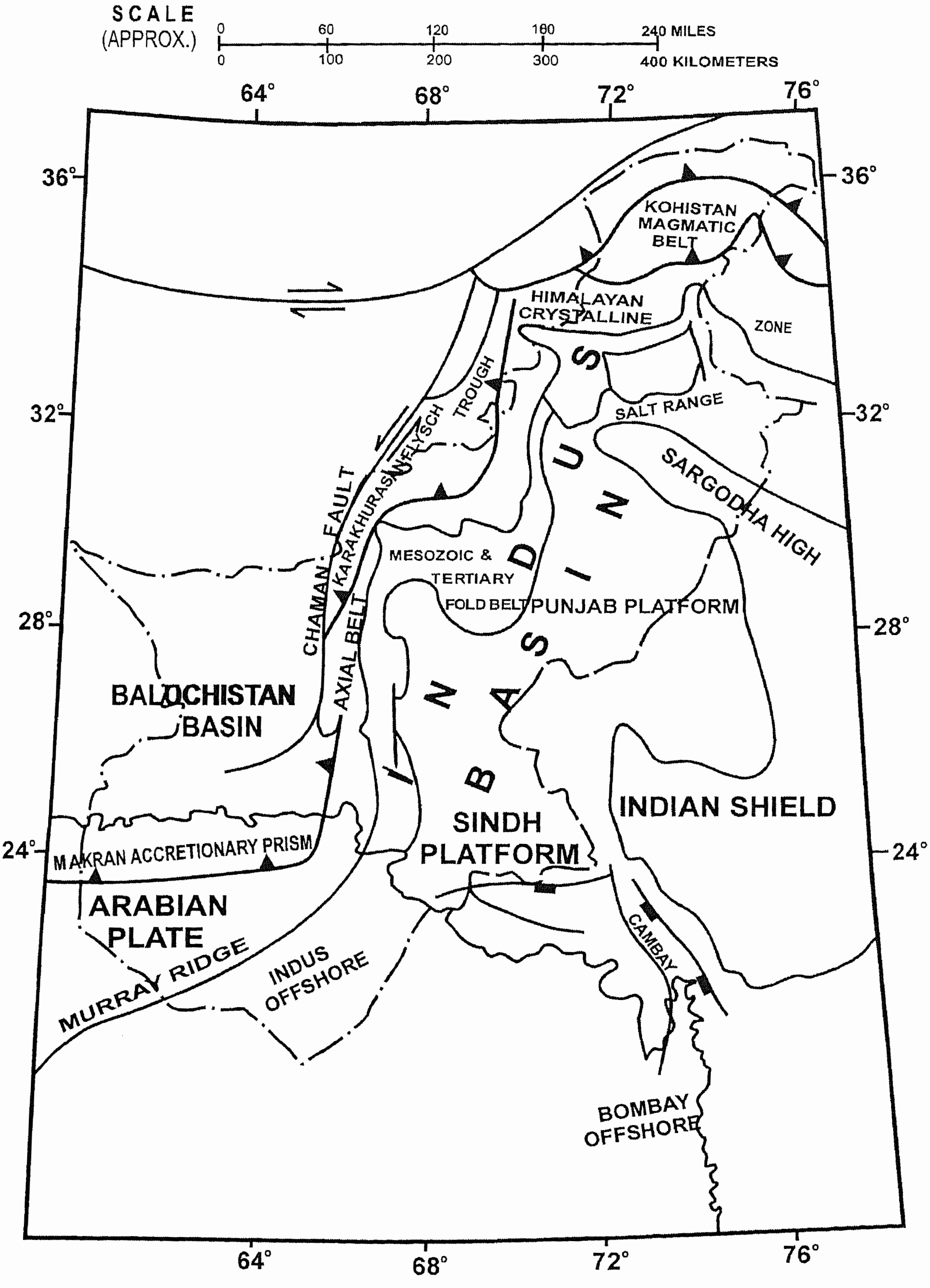


Fig 2.3 Map showing tectonic divisions of Pakistan, and sedimentary basins of Pakistan (Raza et al., 1989).

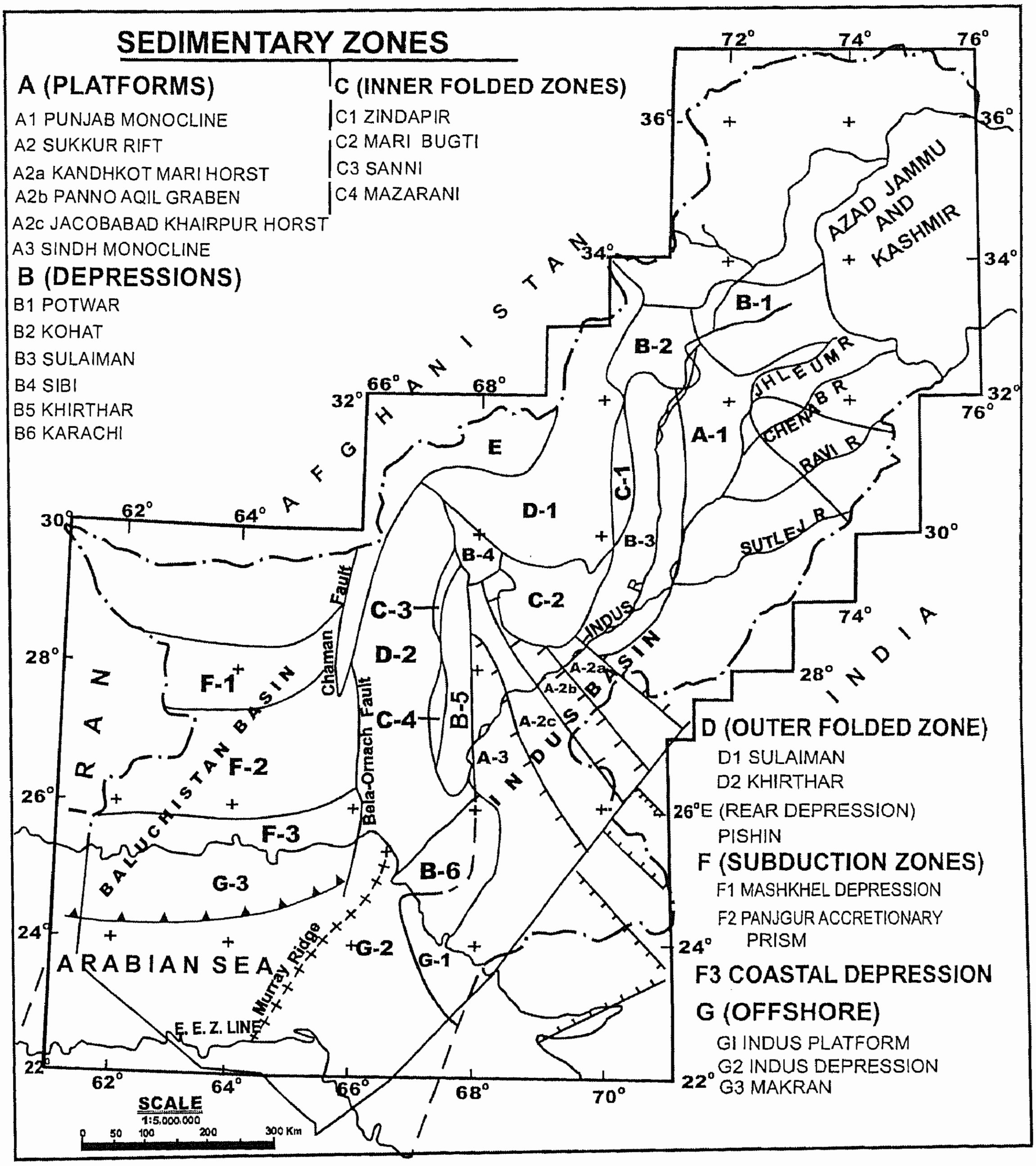


Fig. 2.4 Map showing details of Sedimentary Zones of Pakistan (after Raza et al., 1989).

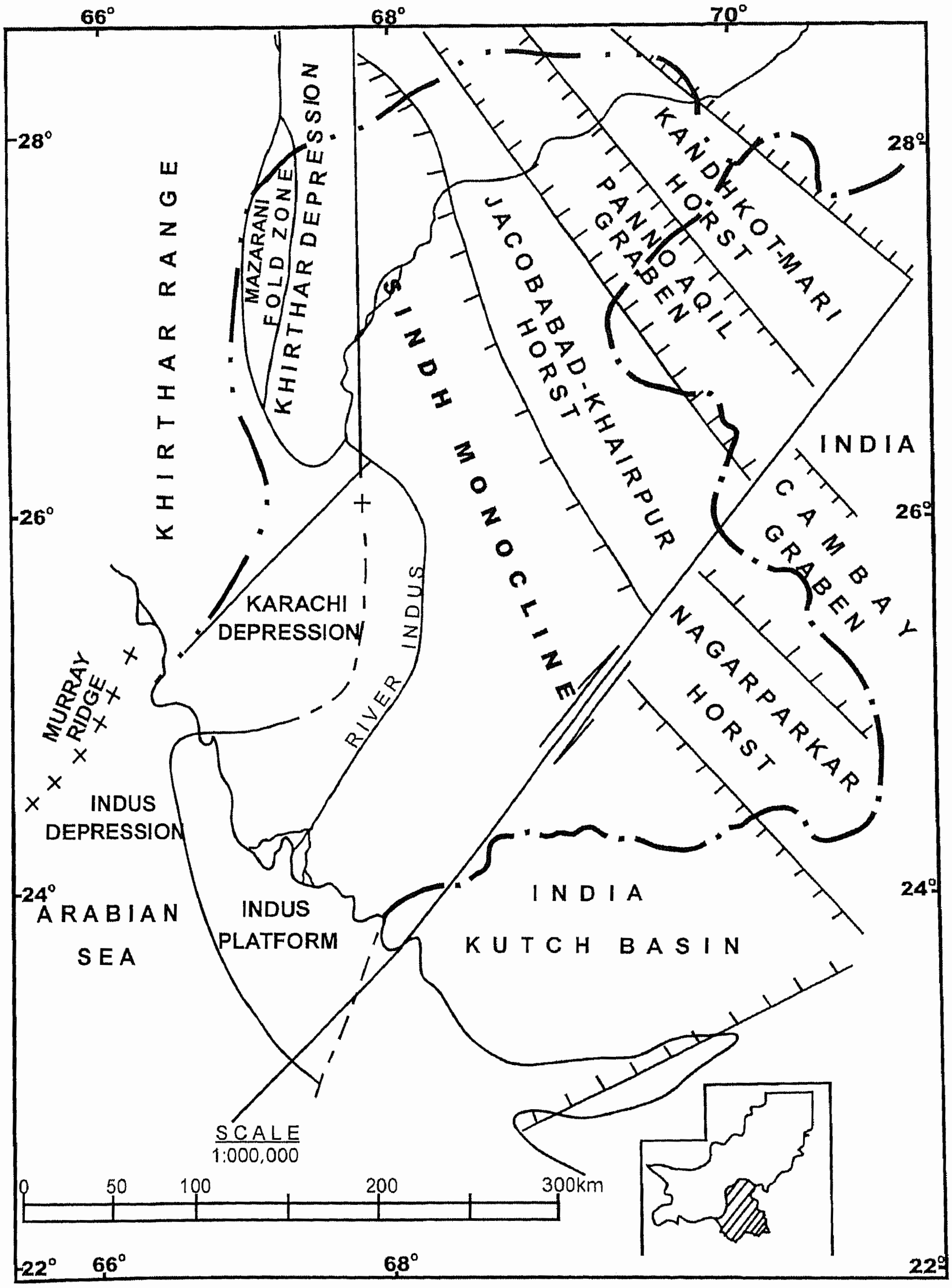


Fig. 2.5 Map showing Tectonic Map of Lower Indus Basin, Sindh province, Pakistan (after Raza 1989).

CHAPTER THREE

THAR COALFIELD

INTRODUCTION

The Thar coalfield of Thar desert (located between latitudes 24°15' *N* and 25 ° 45' N and longitudes 69° 45' E and 70° 45' E; see Survey of Pakistan topo-sheet Nos. 40 L/2, 5 and 6) situated in District Tharparkar of south-eastern Sindh, is the largest coalfield of Pakistan having an area of about 9000 square kilometres. It has north-south length of 140 km and east-west width of 65 km. It is connected with a 410 km. metalled road that leads upto Mithi from Karachi via Hyderabad, Mirpur Khas, Naukot, and Thatta, Badin and Naukot-Mithi-Islamkot. From Mithi onwards sandy jeepable tracks lead to the area. Furthar, a rail link from Karachi via Hyderabad reaches upto Naukot, which is about 50 km from Mithi (Fig. 3.1).

The resource potential of this single coalfield is estimated about 175 billion tonnes. The landscape is sandy and rough with sand dunes forming the topography. Sand dunes cover more than 56 percent of the area. The relief in the area varies between near sea level to more than 150 metres above mean sea level. The sand dunes are mostly longitudinal with a NE-SW trend and are stabilised by shrub vegetation and grass. The drainage system is lacking in the area.

The climate is extremely hot in summer and relatively cold in winters. The average annual rainfall varies between 200 and 300mm, which occur during the monsoon season of June to September. Drought years are common. The mean annual maximum and minimum temperatures are 35°C and 19°C, respectively. The maximum daily temperature commonly exceeds 45°C in April through June (Khan, 2003).

GEOLOGY

The Thar coalfield is covered by thick sand dunes with an average depth of over 80 meters resting upon the structural platform in the eastern part of the desert, underlain by relatively shallow granitic basement rocks (Fig. 3.2). This granite complex dips down abruptly beneath the western part of the Thar Desert and is highly faulted (Fasset & Durrani, 1994). An over 3000 meters thick sedimentary sequence occurs at a distance of 60 kms north of Singharo-Bhithro Block of Thar coalfield and consists of Triassic-Jurassic, Cretaceous, Paleocene, Eocene, and post Eocene age rocks. This sedimentary sequence thins from west to east across the Thar Desert and in the Thar coalfield area has an average thickness of 250 meters (Khan & Khan, 1994).

An unconformity at the base of underlying sedimentary sequence eastward to the point where the Paleocene/Eocene rocks rest directly on the basement granite is present. The geological investigation has proved that coal-bearing strata of Paleocene-Eocene sediments unconformably overlie the Pre-Cambrian basement igneous rocks exposed at Nagar Parkar (Fasset & Durrani, 1994).

The basement rocks are represented by granite and granodiorite at the depth of 110 to 277 meters. The granite is of white, pinkish grey to very light grey in colour and coarse grained, having feldspar altered kaolinite (Jaffery, 1999). The metabasites are medium to coarse-grained volcanics and plutonic rocks that have been metamorphosed to epidote amphibolites and contain acidic dykes of rhyolite to quartz trachyte composition (Jan et al., 1997).

The grey granite found at large scale intruded with metabasite and pink granite. Medium- to coarse - grained equigranular to subporphyritic origin with perthite, albite, quartz and aegerine and minor biotite occurs commonly with accessories of Zircon, apathite, allamite, titamite alongwith epidote (Jan et al., 1997). The granite is pink homogeneous medium to coarse grained and equigranular to sub-equigranular. It is leucocratic, comprising perthite and quartz. Some exposed veins contain plagioclase as adamallite, biotite, opaques, zircon, titanite, apatite, and fluorite, are found as accessory minerals in it (Jan et al., 1997).

The Coal bearing Horizon of the Paleocene-Eocene sediments above the basement complex is designated as the Bara Formation. The name 'Bara Formation' is derived from the section at Bara Nai near Amri, District Dadu, where the rocks are best exposed.

Bara Formation

Coal in the Thar coalfield (as in Lakhra, Sonda, and Meting-Jhimpir) is found in Bara Formation of Paleocene-Eocene age. In Thar coalfield the Bara Formation has an unconformable contact with the underlying Basement complex and overlying Sub-Recent deposits (Fig. 3.3). The contact with overlying unit varies between 54 and 230 meters depth. The Formation comprises of claystone, carbonaceous claystone, sandstone, siltstone, kaolin, underclay (a 0.15 to 2.70 meters thick olive grey colored clayey material present under or in between the coal beds, containing coal fragments, carbonaceous material and pyretic grains) with interlaminated coal beds underclay and with sandstone. The following units of Bara Formation have been encountered at various locations in Thar coalfield:

Claystone: Claystone forms the dominant lithological unit of the formation. It is medium grey to dark grey, greyish black, olive green, light grey, brownish grey and brownish black in colour. At some places it is silty and contains pockets of very fine sand and scattered coal fragments. The floor and roof of the coal bed is formed by the clay stone (Fig. 3.3). The clay stone below the coal beds contain lamination of carbonaceous fragments and resin globules. Fine- grains of pyretic crystals are also present that have developed upto 2 mm in size. Claystone also contains 3 to 30 cm thick siderite bands and nodules.

Sandstone: Sandstone is very fine to coarse grained, with sub-angular to sub-rounded, consisting of dominantly quartz, and minor amount of ferromagnesian mineral grains (Fig. 3.3).

Coal: The coal found in Thar coalfield is brownish black and greyish black in colour, it is compact and well to poorly cleave. The resins are brown to greenish yellow in colour and chunks of 1cm size resins have been observed (Jaleel et al., 2002). The beds of coal range in thickness from 0.20 to 22.81 meters; at some places its maximum thickness is 36 meters (Thomas et al., 1994). Clay stone invariably forms the roof and floor of the coal beds (Fig. 3.3).

Siltstone: It is light brownish grey to brownish grey in color. Compact siltstone beds of 0.10 to 3.02 meters thickness with abundant coaly streak are also found at some places (Fig. 3.3). It is sometimes clayey with sandy partings.

Kaolin: Chalky white to grey kaolin with conchoidal fracture has been deposited as a result of weathering and alteration of granite of Indian shield rocks. Reworkable kaolin is found above and bellow the coalbeds within the Bara Formation, where as residual Kaolin is confined to the base of the formation (Fig. 3.3). The transported kaolin was met in two horizons at the depth of 55 to 75 meters and 115 to 135 meters below the sea level as lenses and lenticles of maximium thickness of 7.1 meters (Jaffery, 1997).

The dirty coal beds of 10-30 cm thickness containing interlaminated sand and clay streaks and lamination with little yellow and orange coloured resin beds have been struck at some places. Clay material has also been found under or in between the coal beds. These clays are olive grey in colour containing coal fragments. Carbonacous material and pyretic grains have also been found in it (Jaleel et al., 2002).

Carbonaceous claystone: Carbonaceous claystone is dark grey, and greyish black and brownish black in colour. Carbonaceous material and resin in the form of globules and chunks have been found along the bedding planes. Some of the carbonaceous fragments show poorly preserved wooden structures and claystone bands of 15 cm thickness (Fig. 3.3).

Sub-Recent deposits: The sub-recent deposits have unconformable contact with the overlying sand dune. The lower contact with the coal-bearing Bara Formation is also unconformable. The lithology of the deposits consists of dominant sandstone and siltstone with minor claystone beds and granite wash/kaolin. The units of Sub-Recent deposits vary from 11 to 209 meters (Fig. 3.3). These units are described as follows:

Sandstone: Sandstone is pale orange to pale yellowish orange, light gray, light bluish grey and pinkish grey in colour. It is often silty or clayey, compact, very fine-to-fine-grained. The grains are mostly well sorted, at few places moderately and poorly sorted or angular to sub-rounded, and highly oxidized with yellow, brown, dark-brown and red iron oxide patches. Some times it also contains dark-brown and black iron stone concretions (Fasset & Durrani, 1994).

Siltstone: Siltstone is light grey, and dark yellowish orange in colour. It is usually compact and clayey or sandy. The grains vary from fine through fine, medium and coarse grains in size. At places it contains dark brown and black ironstone concretions. It is yellow, brown, dark brown, with red iron oxide patches indicating a high degree of oxidation (Fasset & Durrani, 1994).

Claystone: Claystone is yellowish brown and pinkish grey in colour. It is spotted with yellow, brown, dark brown and red iron oxide patches. The clay stone is usually silty and sandy.

Kaoline/granite wash: It is gritty, coarse-grained, whitish light grey to grey material, containing fine to coarse angular to sub-angular quartz and feldspar grains in white kaolinitic matrix. Granite wash also contains a few black, very fine grains of ferromagnesian minerals. In some places at the basement, it also occurs at the base of the Bara Formation.

Recent deposits: Recent deposits consist sand dunes of predominantly fine sand and also contain a few thick bands of silt and clay. Sand consists mostly of quartz that is fine to medium and coarse-grained, sub-angular to sub-rounded and moderate to well-sorted grains with scattered mica flakes and grains of ferromagnesian minerals. The thicknesses of dune sands of recent deposits vary in size from 14 to 93 meters (Fig. 3.3). Sand is pale yellowish brown, yellowish grey, greyish orange and pinkish grey (Thomas et al., 1994).

The Thar coalfield has been divided into four blocks, adjacent to each other, which are located east of Islamkot. Following are the details of each block:

Sinhar Vikian Varvai, Block-I: This block is located between latitude 24°35'N to 24°44' N and longitudes 70°12'E to 70°18'E, and about 15 km east of Islamkot (Fig. 3.1) This block covers an area of about 122 sq. km. The thickness of the coal seams in this block varies from 0.20 to 22.81 meters. The coal zone more than 20 meters thick is in between and to the east of Sinhar Vikian and Varvai villages. This block has 1, 028.43 million tones of inferred reserves of coal.

Singharo Bhitro, Block-II: This block is located between latitude 24° 44'N to 24° 51' N and longitudes 70° 18'E to 70° 25'E. It is about 25 km north east of Islamkot, measuring 55.00 sq. km. 'Thar coal seams' have an average thickness of 15.50 meters. The coal is found at the depth of 164 to 123.80 meters.

The thickest coal seam has an average thickness of 15.50 meters and varies between 8.19 meters to 20.78 meters. The minimum depth at which the first coal bed was hit is 123.80 meters and maximum depth at first coal bed hit is 164.70

meters (Fig. 3.3). The coal here is generally over 17.5 meters thick. The coal covers about 85% area of this block. This block has total reserves of 1584.00 million tones (Abbas & Atiq, 2005).

Saleh Jo Tar, Block-III: This block is located between latitude 24° 49'N to 24° 58' N and longitudes 70°12'E to 70° 18' E, measuring 99.50 sq. km. In this block there are 3 to 12 coal seams. The thickness of the coal seams varies from 0.30 to 14.65 meters. The thickest coal bed "Thar Coal Seam" has an average thickness of 9.27 meters. The coal is more than 16 meters thick having maximum thickness of 24.58 meters at one place (Fig. 3.2). This block has total reserves of 2008.04 million tones (Abbas & Atiq, 2005).

Sonalba, Block-IV: This block is located between the latitude 24°41'N to 24°48' N and longitudes 70°12'E to 70°20'E. It is situated at the distance of 25km north-northwest of Islamkot, measuring 82.50 sq. km. The coal seams in this block are from 0.20 to 21.50 meters thick. This thickest coal bed (Thar coal seam) has a average thickness of about 17.47 meters. The minimum depth of the first coal seam is 117.30 meters and the maximium depth of coal seam is 165.50meters. This block has total reserves of 2471.51 million tones (Abbas & Atiq, 2005).

HEAVY AND TRACE ELEMENTS IN THAR COAL

Coal is a heterogeneous solid originating from the plant material. It contains, in varying amount, essentially all elements of the periodic table combined into nearly all of the minerals normally found in the earth's crust. It contain diverse amount of trace elements in their over all composition. Those predominantly associated with organic fraction are boron, beryllium, germanium, gallium, phosphorous, antimony, titanium and vanadium; those predominantly associated with inorganic fraction include arsenic, cadmium, manganese, molybdenum, lead, zinc, zirconium, cobalt, chromium, nickel and selenium (Swaine, 1990). Boron can be a useful index in indicating the paleo salinity of the depositional conditions of coal (Valkovic, 1983). Certain trace and minor elements such as lead, arsenic, cadmium, chromium and mercury, if present in high amounts, could prevent the coal from being used in environmentally sensitive situations. Others including boron, titanium, vanadium, and zinc have detrimental effects on the metallurgical industry (Thomas, 2002).

The metals like Pb, Zn, Cd, Cr, Cu, Fe and Ni are commonly classified as heavy metals (i.e. metals having densities above 5 g/cm^3). These six metals are a subset of a larger group of trace elements that occur in low concentration in the Earth's crust (Callender, 2004).

A total of fifty six drill core samples of the Thar coal were obtained from the core library of Geological Survey of Pakistan, Sindh regional office in Karachi. Their locations are shown in Figure 3.4. Among these, thirteen samples are from Block-I, thirty one from Block-II and twelve from the Block-III of the Thar coalfield.

Due to the limited facilities for the chemical analysis in the Geochemistry Laboratory of the National Centre of Excellence in Geology, University of Peshawar, Pakistan, the coal samples were analyzed for heavy, trace and light elements including Pb, Zn, Cd, Cr, Co, Cu, Ni, Fe, Mn, Ca, Mg, Na, and K. (see appendix-I). The chemical data is presented in Table 3.2, and graphically shown in Figure 3.5 to 3.7.

Lead (Pb)

Lead having atomic number 82 is a bluish-white metal of bright luster. It is soft, very malleable, ductile, and a poor conductor of electricity. Because of these properties and also its low melting point (327.5^{O}C), and resistance to corrosion, Pb has been used in the manufacturing of metal products for thousands of years. Pb has atomic weight of 207.2 and density of 11.342 g cm^{-3}, hence finds extensive use as a shield for radiation. It has two oxidation states, $^{+}$2 and $^{+}$4. The tetravalent state is a powerful oxidizing agent but is not common in the earth's sarfacial environment; the divalent state, on the other hand, is the most stable oxidation level and most Pb^{2+} salts with naturally occurring common anions are slightly soluble. It is composed of four stable isotopes (^{208}Pb= 52%) and several radioisotopes whose longest half-life is 15 M. years (Reimann & deCaritat, 1998). Lead belongs to group IVA of the periodic table which classifies it as a heavy metal whose geochemical affinity is chalcophilic (associated with sulfur). The average concentration of Pb in the lithosphere is about 14 ppm and the most abundant sources of the metal are minerals galena ($PbSO_4$) and cerussite ($PbCO_3$). The most important environmental sources of Pb are gasoline (Petrol) combustion (presently a minor source, but in the past 40 years a major contributor to Pb pollution), Cu-Zn-Pb smelting, battery factories, sewage sludge, coal combustion, and waste incineration (Callender, 2004).

It is clear from the Table 3.2 and Figure 3.5a that the concentration of lead is highly variable in all three Blocks of the Thar coalfield. The Block-I has maximum lead contents of 36 ppm, Block-II has 56 ppm, and Block-III has 65 ppm with an average lead content of 20 ppm, 33 ppm and 49 ppm respectively (Table 3.2; Fig. 3.5a). It is, therefore, observed that the Block-III has relatively the highest lead concentration on average basis.

Zinc (Zn)

Zinc (atomic no. 30) is a bluish-white, relatively soft metal with a density of 7.133g cm^{-3}. It belongs to group (II B) of the periodic table, which classifies it as a heavy metal whose geochemical affinity is chalcophilic. It has an atomic weight of 65.39, a melting point of 419.58°C, and a boiling point of 907°C. Zinc is divalent in all compounds and is composed of five stable isotopes (^{64}Zn = 49%) and a common radioisotope, ^{65}Zn, with a half-life of 245 days. (Callender, 2004). The average Zn content of the lithosphere is ~ 80 ppm and the most abundant sources of Zn are minerals sphalerite (ZnS) and wurtzite (Zn, Fe) S, and to a lesser extent smithsonite (ZnO_3), willemite (Zn_2SiO_4), and zincite (ZnO) (Reimann & deCaritat, 1998). The smelting of nonferrous metals and burning of fossil fuels and municipal wastes are the major Zn sources contributing to air pollution (Reimann & deCaritat, 1998; Callender, 2004).

The concentration of Zn varies from 10ppm to 36ppm in Block-I, 8ppm to 71ppm in Block-II and 25ppm to 116ppm in Block-III of the Thar coalfield (Table 3.2, Fig. 3.5b). The average concentration of Zn is 22 ppm, 38 ppm and 85 ppm in Block-I, II, and III respectively (Table 3.2, Fig. 3.5b). It is clear from the data that the Block-III of the Thar coalfield has relatively high concentration of Zinc.

Copper (Cu)

Copper has atomic number 29, an atomic weight of 63.546, having two stable isotopes (^{63}Cu = 69.2%, ^{65}Cu = 30.8%), and a density of 8.94g cm^{-3} (Webelements, 2002). Metallic Cu compounds (sulfides) are brassy yellow in color while the carbonates are a variety of green and yellow-colored. It is some what malleable with a melting point of 1084.87°C. It belongs to group I B of the transition metals and in aqueous solution Cu exists primarily in the divalent oxidation state although some univalent complexes and compounds of Cu do occur in nature (Leckie & Davis, 1979). Copper is moderately abundant heavy metal with a concentration in the lithosphere of about 39μg g^{-1} (Li, 2000).

The most common Cu minerals, from which the element is refined into the metal, are Chalcocite (Cu_2S), Covellite (CuS), Chalcopyrite ($CuFeS_2$), Malachite (Cu_2CO_3 $(OH)_2$ and Azurite $2[Cu_3 (OH)_2 (CO_3)_2]$. The source of Cu pollution is smelters that contribute vast quantities of Cu—S particulates to the atmosphere. The burning of fossil fuels and waste incineration are the major sources of Cu in the atmosphere and the application of sewage sludge, municipal composts, poultry wastes are the primary sources of anthropogenic Cu contributed to the land surface (Alloway, 1995).

The concentration of Cu varies from 8 ppm to 17 ppm in the block-I, 10 pm to 38 ppm in Block-II and 12 ppm to 31 ppm in the Block-III of the Thar coalfield (Table 3.2; Figure 3.5c). The average concentration of Cu in Block-I (12 ppm), in Block-II (21 ppm) and Block-III (21 ppm) suggest that the coal of Block-II is relatively high in Copper.

Nickel (Ni)

Nickel has an atomic number of 28, an atomic weight of 58.71 and a density of 8.9 g cm^{-3}. It has five stable isotopes of which ^{58}Ni (67.9%) and ^{60}Ni (26.2%) are the most abundant (National Science Foundation, 1975). Nickel is silvery white, malleable metal with a melting point of 1453°C. It has poor ductility, good thermal conductivity, moderate strength and hardness. It can be fabricated easily by the procedure, which are common to steel (Nriagu, 1980). Ni belongs to group VIIIa and is classified as a transition metal (the end of first transition series) whose prevalent valence states are 0 and 2^+. However, the majority of nickel compounds are of the Ni^{II} species.

The concentration of Ni in the lithosphere is 55 ppm . Natural emissions of Ni to the atmosphere are dominated by windblown dusts while anthropogenic sources that represent 65% of all emission sources are dominated by fossil-fuel combustion, waste incineration and nonferrous metal production (Nriagu, 1980). Major use of Ni includes its metallurgical use as alloy (stainless steel and corrosion-resistant alloys), plating and electroplating, as a major component of Ni—Cd batteries, and as a catalyst for hydrogenating vegetable oils (National Science Foundation, 1975).

The concentration of Ni in the Thar coalfield varies from 9ppm to 32ppm (average 22 ppm) in Block-I, from 13 ppm to 65 ppm in (average 41 ppm) in Thar coalfield Block-II and from 13ppm to 75ppm (average 60 ppm) in Block-III (Table 3.2; Fig. 3.5d). It is clear from the Table 3.2 that the Block-II and III are relatively enriched in Nickel.

Chromium (Cr)

Chromium has an atomic number of 24, an atomic weight of 51.996, density of 7.14 gcm^{-3} and is having four stable isotopes (^{52}Cr) = 84%). Crystalline Cr is steel-grey in color, luster, hard metal that has a melting point of 1863°C. It belongs to group VI B of the transition metal. Chromium, as well as Zn, are the most abundant of the "heavy metals" with a concentration of about 69 ppm in the lithosphere.

Chromium occurs in nature mainly in the mineral chromite; Cr also occurs in small quantities in many minerals in which it replaces 3^+ and Al 3^+ (Faust and Aly, 1981). The metallurgical industry uses the highest quality of chromite ore whilst the lower-grade ore is used for refractory bricks in melting furnaces. Major atmospheric emissions are from the chromium alloy and metal producing industries. Smaller emissions come from coal combustion and municipal incineration. In aquatic environment, the major sources of Cr are electroplating and metal finishing industries. Hexavalent Cr^{VI} is a potent carcinogen and trivalent Cr^{III} is an essential trace element (Krishnamurthy & Wilkens, 1994).

It is clear from Table 3.2 and Figure 3.5e that the Thar coalfield is having Cr up to 21ppm (average 15 ppm) in Block-I, up to 35 ppm (average 18 ppm) in Block-II and 47 ppm (average 26 ppm) in Block-III. It suggests that the Block-III of the Thar coalfield is relatively more enriched in chromium.

Cadmium (Cd)

Cadmium has atomic number of 48, an atomic weight of 112.40 consisting of eight stable isotopes ($^{112.114}$Cd are most abundant), and a density of 8.65 g cm^{-3} (Nriagu, 1980). In several aspects Cd is similar to Zn; in fact it is almost always associated with Zn in mineral deposits and other earth materials. Cadmium is soft, silvery white, ductile metal with a faint bluish tinge. It has a melting point of 321°C. It belongs to group IIB of elements in the periodic table and in aqueous solution has the stable 2^+ oxidation state. Cadmium is a rare element (67th element in order of abundance) with a concentration of 0.1 ppm in the lithosphere and is strongly chalcophilitic, like Zn (Callender, 2004).

Among the heavy metal in Thar coal the concentration of cadmium is the lowest and is ranging from 0.1ppm to 0.4ppm in all three Blocks- (Table 3.2; Fig. 3.5f). However, the Block-I has the highest average (0.34ppm) concentration of cadmium.

Arsenic (AS)

Arsenic is a naturally occurring element widely distributed in the earth's crust. It combines with oxygen and other elements to form inorganic arsenic compounds. Inorganic arsenic compounds have various industrial purposes, including the smelting of other metals such as lead, manufacture of some types of glass, and formulation of pesticides and fungicides. Inorganic arsenic compounds also can be used in pressure-treated wood (Wikipedia., 2006).

Inorganic arsenic compounds can dissolve in water, get into food, or blow on the wind in arsenic-containing soil. Organic arsenic compounds are less toxic than inorganic arsenic compounds.

Arsenic is associated with sulfide-rich fractions of the coal and most likely is in the solid solution in the ferrous disulfides in coal; pyrite and marcasite. According to Gloskoter (1977) Arsenic is more strongly associated with the mineral matter fraction of the coal than is chromium. It is assumed to be present in solid solution than iron sulfide minerals.

High levels of Arsenic exposure can cause nausea and vomiting, diarrhea, anemia, and low blood pressure. These symptoms may be followed by a feeling of "pins and needles" in the hands and feet (neuropathy). Chronic (long-term) exposure to arsenic can cause stomach ailments, headaches, fatigue, neuropathy, dark splotches on the skin, and small "corns" or "warts" on the palms of the hands, soles of the feet, and torso. People exposed to inorganic arsenic can have more cancer of the lung, skin, bladder, liver, kidney, and prostate.

The concentration of As in the Thar coalfield varies from 0.9 ppm to 2.1 ppm (average 1.55 ppm) in Block – I, from 1 ppm to 2.7 ppm (average 1.59 ppm) in Block –II and 1.9 ppm to 4.2 ppm (average 2.91 ppm) in Block-III (Table 3.2; and Fig. 3.5h). It is clear from the Table 3.2 and Figure 3.5h that the Block-III of the Thar coalfield has relatively high As content.

Iron (Fe)

Iron is the fourth abundant element by weight in the earth's crust; placed in-group VIII of periodic table. It has a melting point of 1538°C and boiling point 2862. The concentration of iron varies from 3421ppm to 7632ppm in Block-I, from 331ppm to 8473ppm in Block-II and from 2845ppm to 8762ppm in Block-III (Table 3.2; and Fig. 3.5g). Block-I has relatively high average contents of Iron (i.e. 5882.54ppm).

Cobalt (Co)

Cobalt is silvery white metal and is resistant to corrosion and alkalies but soluble in acids. Cobalt occurs as a sulphide in rocks and ore bodies and commonly associated with sulphides of silver, nickel, lead, copper and iron. It is placed in-group VIII of periodic table. It has a boiling point 2928°C and melting point 1495°C.

The concentration of Co in the Thar coalfield varies from 2 ppm to 8 ppm (average 5 ppm) in Block – I, from 7ppm to 25ppm (average 14 ppm) in Block –II and 11 ppm to 25 ppm (average 16 ppm) in Block-III (Table 3.2; and Fig. 3.5h). It is clear from the Table 3.2 and Figure 3.5h that the Block-II of the Thar coalfield has relatively high Co content.

Manganese (Mn)

A silvery white metal, that occurs as pyrolusite and is used for many alloys. It is a member of the transition elements of the 3d series of the periodic table, falling between chromium and iron, having melting point 1245°C and boiling point 2150°C. Air born manganese sources are widespread and its distribution over large distances is favored by the fact that emitted manganese is predominantly associated with smaller dust particles.

Manganese in the Thar coalfield varies from 0.14ppm to 1.0ppm (average 0.61ppm) in Block-I, from 0.17 ppm to 1.84 ppm (average 0.75 ppm) in Block-II and from 0.13 ppm to 1.37 ppm (average 0.59 ppm) in Block-III (Table 3.2; Fig. 3.5i).

Antimony (Sb)

Antimony a silvery-white metal. Antimony oxide is used to produce fire retardants, paints, ceramics and fireworks. Antimony alloys are used in lead storage batteries, older, sheet and pipe metal, bearings, castings, type metal, ammunition and pewter. Antimony does not degrade and is not destroyed by combustion. It cycles between the soil, the atmosphere, surface waters and ground water. Breathing or ingesting high levels of antimony for a long time can cause heart and lung problems, joint or muscle pain, stomach pain, diarrhea, vomiting and stomach ulcers. Antimony usage and pollution should be reduced wherever possible. In 1999, Ohio's hazardous waste program-regulated facilities reported generating 1.4 million pounds of antimony and antimony compounds in waste (Kirk-Othmer, 2004).

Antimony concentration in U. S. lignite is 0.7 ppm, Average concentration of antimony in U. S. coal is 1.1ppm and worldwide concentration of antimony is 3.0ppm (Volkovi'c, 1983).

Antimony concentration in U. S. lignite is 0.7 ppm, Average concentration of antimony in U. S. coal is 1.1ppm and worldwide concentration of antimony is 3.0ppm (Volkovi'c, 1983).

Antimony is released to the environment from natural sources and from industry. Rivers, lakes, and streams contain low levels of antimony. Because antimony is found naturally in the environment, people are exposed to low levels of it every day, primarily in food, drinking water, and air. Workers in industries that process or use antimony ore can be exposed to higher levels.

Breathing high levels of antimony for a long time can irritate a person's eyes and lungs and can cause heart and lung problems, stomach pain, diarrhea, vomiting, and stomach ulcers. Ingesting large doses of antimony can cause vomiting. Concentrations of antimony in worldwide coal range from 0.5-5 ppm.

The concentration of Sb in the Thar coalfield varies from 1.3 ppm to 3.2 ppm (average 1.96 ppm) in Block – I, from 1.3 ppm to 3.7 ppm (average 2.29 ppm) in Block –II and 1.4 ppm to 4.3 ppm (average 3.08 ppm) in Block-III (Table 3.2; and Fig. 3.5h). It is clear from the Table 3.2 and Figure 3.5 k that the Block-III of the Thar coalfield has relatively high Sb content.

Uranium

Uranium is a naturally occurring radioactive element. It is a normal part of rocks, soil, air, and water. Natural uranium is a mixture of three types, or isotopes, called U-234 (^{234}U), U-235 (^{235}U), and U-238 (^{238}U).

All three types of uranium are the same chemical, but they have different radioactive properties. U-238 is by far the most common type of uranium on earth and is the least radioactive. U-234 is the most radioactive type of uranium. U-235 is used as a fuel in power plants and weapons. The amount of U-234 and U-235 in natural uranium is increased through a process called enrichment.

Uranium leached from the overlying tuffs and epigenetically emplaced in the underlying lignite beds (Denson and Gill, 1956). Uranium was transported to the coal beds by groundwater passing the overlying uniferous sandstone (Pipiringos, 1956).

Uraniferous deposits are generally confined to near-outcrop portions of the seams, Ultimate source of Uranium was overlying volcanic beds (White, 1958).

Mapel and Hail (1959) have studied have studied coal and support the hypothesis that the Uranium was leached from the volcanic ash and deposited in the lignite beds by groundwater.

Uranium entered the coal in aqueous solution as a complex alkali or alkaline earth UO_2 CO_3 and that UO_2^{++} ion was absorbed by the coal and reduced to UO_2. Autoradiographic studies revealed that UO_2 is dispersed throughout the coal.

Three hypothesis advanced to explain the occurrence of uranium in some coals were describe by Denson (1959) as follows:

1. Syngenetic: The uranium was deposited from surface waters by living plants or in dead organic matter in Swamps prior to coalification.
2. Diagenetic: Uranium was introduced into the coal during coalification by water bearing the Uranium from areas marginal to the coal deposits or from the consolidating enclosing sediments.
3. Epigenetic: Uranium was introduced in the coal after coalfication and after consolidation of the enclosing sediments by groundwater deriving uranium from hydrothermal sources or from unconformably overlying volcanic rocks.

The accumulation of uranium in coal may vary markedly from place to place, and the occurrence of uranium in each deposit should be interpreted in relation to the geological history of the region.

Secondary concentration of Uranium in coal may occur when solution of small quantities of uranium by groundwater from ovelying volcanic rocks is followed by downward percolation of these waters through previous strata until the uranium is taken up and retained by the highest underlying lignite beds.

In general, the Uranium bearing coal in each of these areas formed the topmost coal bed of a sequence overlain unconformably by layers of silicic volcanic materials or other strata from which uranium may have leached by groundwaters. The uranium content of succeeding lower coal beds decreases to the vanishing point. The enrichment of uranium in coals, which lie near the erosion zone of granite, is noted in Thar coal.

Human activities, wind, and streams can move uranium through the environment and change the amount of uranium people are exposed to. Uranium exists in dust in the air that can settles onto surface water, soil, and plants. People can be exposed to uranium by breathing air, drinking water, or eating food-containing uranium.

Large amounts of uranium can react with the tissues in the body and damage the kidneys. This damage results from the chemical properties of uranium, not from its radioactive properties. As with other radioactive elements the more radioactive the element, the higher the chance of getting cancer. For uranium, the chance of getting cancer is greater for people who are exposed to enriched uranium. No cancer of any type has ever been seen in humans as a result of exposure to natural (nonenriched) uranium. Even though studies have reported lung and other cancers in uranium miners, some of the miners also smoked and were exposed to other substances that cause cancer, such as automobile exhaust fumes and silica dust.

The concentration of U in the Thar coalfield varies from 1.0 ppm to 2.1 ppm (average 1.54 ppm) in Block – I, from 0.9 ppm to 1.8 ppm (average 1.43 ppm) in Block – II and 1.8 ppm to 4.3 ppm (average 3.1 ppm) in Block-III (Table 3.2; and Fig. 3.5h). It is clear from the Table 3.2 and Figure 3.5l that the Block-III of the Thar coalfield has relatively high U content.

LIGHT ELEMENTS IN THAR COAL

Magnesium (Mg)

A light, silvery-white metal, which tarnishes in air and burns with an intense white flame to magnesium oxide (MgO). It belongs to group I B of the periodic table and has a boiling point 2472°C and melting point of 1289°C. The concentration of magnesium in the Thar coalfield is shown in Table 3.2 and graphically presented in Figure 3.7a. The Block-I has relatively low (45 ppm to 75 ppm). magnesium as compared to Block-II (Mg= 28 ppm to 171 ppm) and Block-III (Mg= 51 ppm to 115 ppm). The average concentration of Mg in block I, II and III is 62, 81, and 78 respectively (Table 3.2 and fig. 3.6a).

Calcium (Ca)

Calcium is a soft metal and is an essential nutrient for plants and animals. It belongs to group II A and has a boiling point 1494°C and melting point 842°C. It is clear from Table 3.2 and Figure 3.7b that the calcium varies from 81 ppm to 418 ppm (average 230 ppm) in Block-I, from 81 ppm to 470 ppm (average 254 ppm) in Block-II and in Block-III it is ranging from 151 ppm to 364 ppm (average 258 ppm) (Table 3.2; Figure and 3.6b). All the three blocks have similar contents of Ca on average basis.

Sodium (Na)

A soft, silvery-white metal, it is very reactive, tarnishes rapidly in air, and reacts violently within water to produce sodium hydroxide and hydrogen gas. It is placed in group IA of periodic table. Over all, it is most important member of the alkali metals. Sodium represents about 26g/kg of the earth's crust. It has a boiling point 883°C and melting point 97.8°C.

The concentration of sodium in the Thar coalfield varies considerably in three blocks. It ranges from 465 ppm to 670 ppm (average 564 ppm) in Block-I, from 470 ppm to 925 ppm (average 680 ppm) in Block-II and from 290 ppm to 318 ppm (average 304 ppm) in Block-III (Table 3.2; Figure 3.6c). The average concentration of sodium in all three blocks of Thar coalfield suggests that the Block-II has relatively high Na contents.

Potassium (K)

A silvery-white metal, can be readily molded, oxidizes instantly on exposure to air, and reacts violently with water. It is one of the alkali-metal group, placed in group IA of periodic table. It has a boiling point 759°C and melting point 63.71°C.

The concentration of potassium varies from 165 ppm to 412 ppm (average 223 ppm) in Block-I, from 158 ppm to 290 ppm (average 229 ppm) in Block-II and from 110 ppm to 180 ppm (average 147 ppm) in Block-III (Table 3.2; Fig. 3.6d). It is clear from the Table 3.2 and Figure 3.14 that the Block-I and II of the Thar coalfield are relatively enriched in Potassium.

It is clear from the data of the various blocks of the Thar coalfield that the average concentration of all the analyzed heavy metals (i.e., Pb, Zn, Cu, Ni, Cr, Cd, Fe, Co and Mn) and light elements (i.e., Ca, Mg, Na and K) have variable concentration in all the three blocks as shown in Figure 3.7a and b respectively. These heavy and trace elements have smooth decreasing trend from Fe to Cd (i.e., Fe>Ni>Zn>Pb>Cr>Cu>Co>Cd) and the concentration of these elements gradually increase from block-I to block-III (Fig. 3.7a). The block-I is, however, relatively enriched in Fe. Among the light elements the decreasing trend is from Na to Mg (i.e., Na>Ca>K>Mg). However, the concentration of these elements is relatively high in block-1 and II as compare to block-III (Fig. 7b).

PROXIMATE ANALYSIS OF THAR COAL

The proximate analyses of the Sindh coalfield were performed by following the method of Harker (1981)

Fixed carbon

The fixed carbon content of coal is that carbon found in the residue remaining after the volatile matter has been liberated. Fixed carbon contents of the Thar coal have been given in Table 3.3. It is ranging from 33.56 to 48.21% in the block-I, from 34.78 to 48.34% in block-II and 34.56 to 48.45% in the block-III with an average amount of 38.61%, 41.06% and 40.76% respectively. No significant difference on average in the fixed carbon between three blocks is noticed.

Ash

The ash of a coal is an inorganic residue that remains after combustion. It represent the bulk of the mineral matters in the coal after losing the volatile components. The ash contents of the Thar coalfield are given in Table 3.3. Ash is ranging from 9.00 to 13.46% in block-I, from 9.52 to 12.90% in block-II and from 9.12 to 12.46% in block-III with an average amount of 10.88%, 11.57% and 10.72% respectively. No significant difference on average ash contents of the three coal filed is noticed.

ULTIMATE ANALYSIS OF THAR COAL

Carbon(C)

Carbon is liberated as CO_2 when the coal is burned. It also includes he CO_2 liberated by the carbonate minerals present. The carbon contents of the Thar coalfield are given in Table 3.3. It is clear from this table that the Thar coalfield has carbon in the range of 52.70 to 70.53% (average = 60.24%) in block-I, 54.26 to 67.41% (average = 63.00%) in block-II and 53.91 to 66.23% (average = 61.84%) in block-III. No significant difference on average is observed in the carbon contents of the three blocks of the Thar coalfield.

Hydrogen (H)

Hydrogen is liberated as H_2O when the coal burned. It can be derived from clay minerals and inherent moisture in the air-dried coal or both. The hydrogen contents of the Thar coal are given in Table 3.3. It is clear from this table that the Thar coalfields have hydrogen in the range of 5.34 to 8.28% (average = 6.68%) in the block-I, 5.85 to 8.76% (average = 7.12%) in block-II and 5.61 to 7.66% (average = 6.59%) in block-III. No significant difference on average in the hydrogen contents of three blocks of Thar coal is observed.

Nitrogen (N)

Nitrogen helps to form oxides, which may be released as flue gases when the coal is burned. Nitrogen contents in the Thar coal are given in Table 3.3. It is clear from this table that nitrogen varies from 0.27 to 0.41% (average = 0.34%) in block-I, from 0.29 to 0.44% (average = 0.36) in block-II and from 0.28 to 0.39% (average = 0.33%) in block-III. The Thar coals have very low contents of nitrogen with no significant difference in the three blocks.

Sulfur (S)

Sulfur is also released as flue gas when the coal is burned. Sulfur can be present in the form of organic sulfur, pyretic sulfur and as sulfate minerals. The sulfur contents of Thar coalfield are given in Table 3.3. It is clear from this table that the sulfur contents in the Thar coal are ranging from 0.98 to 4.00% in block-I, from 0.45 to 2.56% in block-II and from 0.44 to 2.32% in block-III with an average amount of 1.55%, 1.11% ad 0.99% respectively. There is no significant difference on average in the sulfur contents of three blocks of the Thar coalfield. However, the block-I is having relatively high amount of sulfur.

COMBUSTION PROPERTIES OF THAR COAL

The determination of the effects of combustion on coal generally influences the selection of coals for particular uses. This can be done by carrying out tests to determine the coal's performance in furnace (i.e., calorific value).

Calorific value (CV)

Calorific value of a coal in the amount of heat per unit mass of coal when combusted. It is also referred to as the specific energy (SE). The calorific values of the Thar coalfield are given in Table 3.3. It is clear from this table that the CV varies from 8445 to 11303 btu/lb in the block-I, from 8695 to11335 btu/lb in block-II and from 8640 to 12113 btu/lb in block-III with the average values of 9653 btu/lb, 10265 btu/lb and 10190 btu/lb respectively. There is no significant difference e on average in the calorific values of the three blocks of the Thar coalfield.

3.1. The generalized stratigraphic sequence of the Thar coalfield (Jaleel et al., 2002)

Formation	*Age*	*Thickness*	*Lithology*
Dune Sand	Recent	14m to 93m	Sand, Silt and Clay
…………………………		Unconformity	………………………………
Alluvial Deposits	Sub Recent	11m to 209m (variable)	Sandstone, Siltstone, Clay stone, mottled
………………………………		Unconformity	………………………………
Bara Formation	Paleocene to Early Eocene	+52m (variable)	Clay stone, shale, sandstone, coal, carbonaceous claystone
……………………………		Unconformity	………………………………
Basement Complex	Pre-Cambrian	----	Granite and quartz diorite

Table 3.2. Heavy, trace and light elements (in ppm) in the Thar coalfield.

Sample No.	Pb	Zn	Cu	Ni	Cr	Co	Cd	As	Fe	Mn	Sb	U	Ca	Mg	Na	K
BLOCK-I (SINHAR VIKIAN VARVAI)																
SV-1	26	16	8	26	10	3	0.3	1.7	6754	0.14	1.3	1.2	220	70	570	213
SV-2	24	25	10	28	11	4	0.3	1.8	5281	0.19	1.5	1.4	95	72	650	225
SV-3	20	31	14	30	20	7	0.3	1.4	5423	01	2.3	2.1	81	60	578	315
SV-4	36	18	12	15	8	6	0.3	0.9	7453	00	2.7	1.7	315	65	560	170
SV-5	9	21	11	9	13	3	0.4	1.2	7215	0.71	1.5	1.3	418	64	615	218
SV-6	8	27	13	11	16	3	0.4	1.5	7314	0.57	1.9	1.7	370	56	591	170
SV-7	30	25	17	27	16	2	0.3	2.1	7632	0.85	3.2	1.2	212	56	580	212
SV-8	27	18	12	15	8	4	0.4	1.6	6854	0.46	1.8	1.6	280	62	590	216
SV-9	8	21	8	16	15	6	0.3	1.9	4873	01	1.9	2.1	317	67	478	165
SV-10	7	22	13	25	20	8	0.5	2.1	4321	0.65	2.4	1	95	75	488	202
SV-11	25	36	15	31	21	8	o.4	1.3	4622	0.64	1.6	1.7	88	61	670	412
SV-12	27	18	9	27	16	3	0.3	1	5310	0.62	1.5	1.8	370	58	491	185
SV-13	11	10	12	32	17	4	0.3	1.6	3421	0.53	1.9	1.2	130	45	465	190
Average	**20**	**22**	**12**	**22**	**15**	**5**	**0.34**	**1.55**	**5883**	**0.61**	**1.96**	**1.54**	**230**	**62**	**564**	**223**
BLOCK-II (SINGHARO BHITRO)																
SB-1	27	71	28	21	29	14	0.4	1.5	7521	0.93	2.4	1.5	215	65	850	217
SB-2	30	42	18	25	20	8	0.4	1.2	4314	0.67	3.2	1.7	418	61	715	250
SB-3	36	40	17	32	22	7	0.4	1.3	4587	1.05	2.8	1.3	214	59	711	265
SB-4	37	36	25	59	35	10	0.4	2.2	3477	1.10	1.8	1.2	81	58	690	212
SB-5	29	31	24	28	10	10	0.3	1.9	5287	0.75	1.9	1.1	430	61	698	290
SB-6	20	28	15	22	24	12	0.4	1.7	8473	0.68	1.7	1.4	150	57	670	158
SB-7	25	32	12	13	26	11	0.4	1.3	5421	1.12	2.2	1.3	165	58	665	232
SB-8	7	26	18	32	18	13	0.2	2.1	785	0.43	2.5	1.7	368	71	680	256
SB-9	56	41	10	35	14	13	0.3	1.4	4672	1.16	3.7	1.5	304	78	645	212
SB-10	34	08	14	46	11	14	0.3	1.7	6132	1.40	1.8	0.9	325	65	615	280
SB-11	10	26	13	42	13	12	0.3	1.8	4312	1.46	1.9	1.2	145	57	714	245
SB-12	12	24	18	41	20	12	0.3	1.5	5743	1	3.2	1.4	170	52	615	190
SB-13	12	18	16	31	17	9	0.3	1.2	874	1.10	2.8	1.6	298	57	605	235
SB-14	29	38	10	45	24	10	0.3	1.6	685	0.36	1.9	1.8	250	121	770	212

Table3.2 continued

Sample No.	Pb	Zn	Cu	Ni	Cr	Co	Cd	As	Fe	Mn	Sb	U	Ca	Mg	Na	K
SB-15	26	65	18	48	16	12	0.3	1.5	5371	0.83	3.4	1.3	350	91	910	168
SB-16	28	68	15	45	14	13	0.3	2.3	5462	0.57	1.3	1.8	180	75	870	265
SB-17	29	30	17	46	13	13	0.3	1.9	5501	1.84	1.7	1.2	202	28	715	270
SB-18	37	42	25	43	21	15	0.2	1.5	4892	0.57	1.9	1.1	340	70	720	266
SB-19	45	45	29	51	35	17	0.3	1.5	5321	0.74	2.6	1.4	195	161	698	198
SB-20	40	18	18	49	18	18	0.3	1.2	1872	0.35	1.8	1.3	215	99	731	175
SB-21	42	52	21	48	14	14	0.3	2.7	6210	0.51	3.2	1.5	315	97	685	175
SB-22	42	55	22	47	22	16	0.3	1.8	5302	0.58	1.8	1.3	232	91	698	191
SB-23	53	66	31	62	27	21	0.4	2.3	6214	0.36	2.8	1.1	118	89	925	214
SB-24	42	43	38	62	08	15	0.3	1.1	3201	0.28	1.9	1.8	202	90	615	265
SB-25	40	62	32	61	9	17	0.3	1.2	4021	0.34	1.8	1.4	230	84	621	260
SB-26	42	45	36	65	11	17	0.1	1.4	822	0.31	3.4	1.3	140	88	617	281
SB-27	40	18	20	51	17	25	0.4	1.8	340	0.17	2.1	1.9	165	95	518	245
SB-28	45	32	21	48	10	25	0.1	1	4210	0.39	1.9	1.6	351	81	531	231
SB-29	30	37	31	14	17	8	0.3	0.8	331	0.73	1.8	1.2	470	171	532	240
SB-30	32	33	20	25	18	10	0.4	1.2	585	0..54	1.6	1.7	305	91	590	212
SB-31	31	17	28	38	14	11	0.3	1.8	6724	0.57	2.1	1.8	340	99	470	198
Average	**33**	**38**	**21**	**41**	**18**	**14**	**0.31**	**1.59**	**4150**	**0.75**	**2.29**	**1.43**	**254**	**81**	**680**	**229**
Block-III (SALEH JO TAR)																
Sample No.	**Pb**	**Zn**	**Cu**	**Ni**	**Cr**	**Co**	**Cd**	**As**	**Fe**	**Mn**	**Sb**	**U**	**Ca**	**Mg**	**Na**	**K**
ST-1	56	25	14	31	32	25	0.2	2.4	3241	0.22	2.4	1.8	360	51	318	150
ST-2	36	81	12	58	25	17	0.3	2.8	6745	1.01	4.3	3.1	364	55	312	170
ST-3	32	83	18	59	27	14	0.2	1.9	3824	1.05	2.8	2.7	270	53	311	134
ST-4	46	89	13	61	47	15	0.3	3.4	6452	0.63	3.7	1.9	215	115	298	125
ST-5	48	112	25	62	22	15	0.3	2.2	8762	1.37	1.4	3.8	212	75	318	135
ST-6	49	95	21	75	25	14	0.3	2.6	4210	0.81	3.1	4.1	205	91	302	110
ST-7	35	97	23	65	18	15	0.3	3.8	4428	0.17	2.7	2.7	218	71	301	175
ST-8	51	83	20	60	19	11	0.4	4.1	4652	0.53	1.9	2.6	315	84	290	140
ST-9	52	84	27	58	35	13	0.3	2.4	3459	0.42	4.3	2.8	290	99	295	180
ST-10	65	45	31	61	12	18	0.3	3.2	4768	0.13	3.4	4.3	151	92	296	112
ST-11	56	116	21	62	32	16	0.3	4.2	6524	0.23	4.1	2.9	226	95	311	165
ST-12	57	113	28	65	13	15	0.3	1.9	2845	0.52	2.8	3.1	275	59	298	170
Average	*49*	*85*	*21*	*60*	*26*	*16*	*0.29*	*2.91*	*4993*	*0.59*	*3.08*	*3.1*	*258*	*78*	*304*	*147*

Table 3.3. Mean values of various proximate and ultimate analysis (in percent) and calorific values (btu/lb) of the Thar coalfield.

S. No.	Fixed Carbon	Ash	Hydrogen	Carbon	Nitrogen	Sulfur	Calorific value
Block-I							
SV-1	36.20	4.50	5.34	56.47	0.27	4.00	9050
SV-2	35.76	4.70	5.78	55.79	0.29	1.17	8940
SV-3	34.67	5.12	6.30	54.09	0.32	2.23	8668
SV-4	33.78	6.70	8.24	52.70	0.41	1.11	8445
SV-5	38.56	5.30	6.52	60.15	0.33	1.81	9640
SV-6	36.23	4.89	6.01	56.52	0.30	0.92	9058
SV-7	38.34	5.43	6.68	59.81	0.34	1.08	9585
SV-8	39.45	4.89	6.01	61.54	0.30	1.89	9863
SV-9	42.45	6.12	7.53	66.22	0.38	1.80	10613
SV-10	41.32	5.34	6.57	64.46	0.33	1.08	10330
SV-11	39.89	5.67	6.97	62.23	0.35	1.00	9973
SV-12	40.12	5.34	6.57	62.59	0.33	0.98	10030
SV-13	45.21	6.73	8.28	70.53	0.42	1.05	11303
Average	38.61	5.44	6.68	60.24	0.34	1.55	9653
Block-II							
SB-1	43.12	6.12	7.53	67.27	0.38	2.56	10780
SB-2	39.01	5.12	6.30	60.86	0.32	0.80	9753
SB-3	38.56	5.34	6.57	60.15	0.33	0.98	9640
SB-4	38.56	6.32	7.77	60.15	0.39	1.60	9640
SB-5	39.45	6.34	7.80	61.54	0.39	0.77	9863
SB-6	41.21	5.78	7.11	64.29	0.36	1.26	10303
SB-7	40.12	6.12	7.53	62.59	0.38	1.45	10030
SB-8	41.12	4.98	6.13	64.15	0.31	1.08	10280
SB-9	41.32	6.31	7.76	64.46	0.39	0.76	10330
SB-10	45.34	5.87	7.22	64.23	0.36	1.05	11335
SB-11	37.23	6.23	7.66	58.08	0.39	1.30	9308
SB-12	45.21	5.78	7.11	66.32	0.36	0.64	11303
SB-13	43.12	5.98	7.36	67.27	0.37	0.83	10780
SB-14	45.21	6.45	7.93	65.78	0.40	1.14	11303

Table3.3 continued:

S. No.	Fixed Carbon	Ash	Hydrogen	Carbon	Nitrogen	Sulfur	Calorific value
SB-15	38.45	7.12	8.76	59.98	0.44	1.86	9613
SB-16	39.01	5.34	6.57	60.86	0.33	0.97	9753
SB-17	40.32	5.87	7.22	62.90	0.36	1.52	10080
SB-18	41.34	5.12	6.30	64.49	0.32	0.90	10335
SB-19	45.12	6.13	7.54	64.35	0.38	0.98	11280
SB-20	41.23	6.02	7.40	64.32	0.37	0.93	10308
SB-21	39.23	5.67	6.97	61.20	0.35	0.73	9808
SB-22	41.12	4.89	6.01	64.15	0.30	0.45	10280
SB-23	42.12	4.76	5.85	65.71	0.29	0.61	10530
SB-24	34.78	5.65	6.95	54.26	0.35	0.88	8695
SB-25	37.45	5.12	6.30	58.42	0.32	1.01	9363
SB-26	39.13	6.34	7.80	61.04	0.39	0.83	9783
SB-27	40.12	6.12	7.53	62.59	0.38	1.81	10030
SB-28	43.23	5.56	6.84	67.44	0.34	0.86	10808
SB-29	41.06	5.82	7.16	64.05	0.36	0.88	10265
SB-30	48.34	6.34	7.80	64.23	0.39	0.64	12085
SB-31	42.17	4.76	5.85	65.79	0.29	2.23	10543
Average	41.06	5.79	7.12	63.00	0.36	1.11	10265
Block-III							
ST-1	40.34	4.89	6.01	62.93	0.30	1.21	10085
ST-2	38.24	5.23	6.43	59.65	0.32	0.62	9560
ST-3	39.02	6.23	7.66	60.87	0.39	0.46	9755
ST-4	35.46	5.23	6.43	55.32	0.32	2.32	8865
ST-5	39.67	6.23	7.66	61.89	0.39	0.93	9918
ST-6	40.45	4.78	5.88	63.10	0.30	0.67	10113
ST-7	45.67	5.67	6.97	63.45	0.35	0.44	11418
ST-8	48.45	6.23	7.66	65.76	0.39	0.94	12113
ST-9	41.23	4.56	5.61	64.32	0.28	0.86	10308
ST-10	40.03	5.56	6.84	62.45	0.34	0.83	10008
ST-11	41.78	5.67	6.97	65.18	0.35	0.95	10445
ST-12	39.56	4.78	5.88	61.71	0.30	1.61	9890
ST-13	34.56	5.12	6.30	53.91	0.32	0.87	8640
ST-14	39.02	4.89	6.01	60.87	0.30	1.10	9755
ST-15	47.89	5.34	6.57	66.23	0.33	0.97	11973
Average	40.76	5.36	6.59	61.84	0.33	0.99	10190
'otal average Thar coa	**40.44**	**5.16**	**6.89**	**62.10**	**0.35**	**1.17**	**10111**

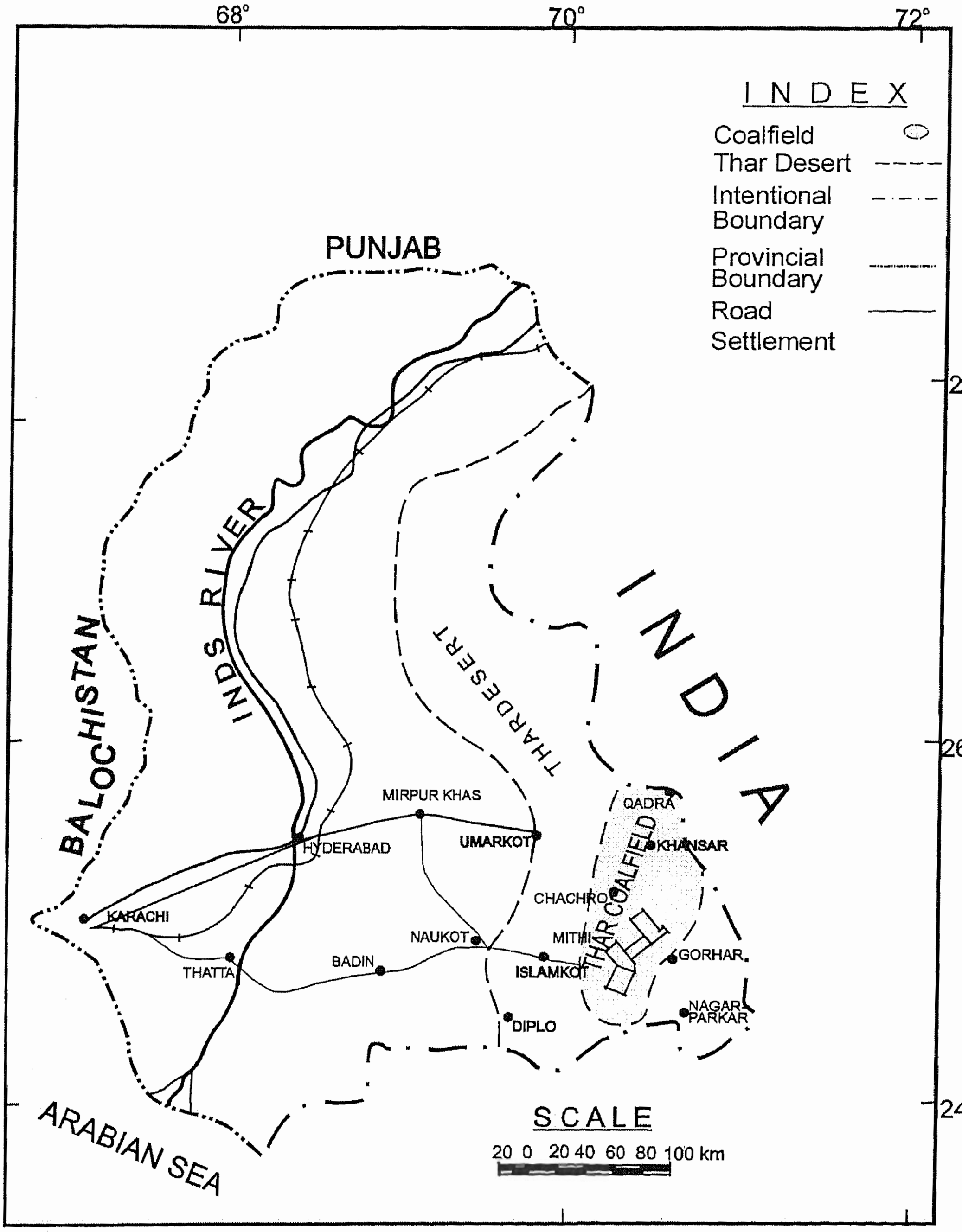
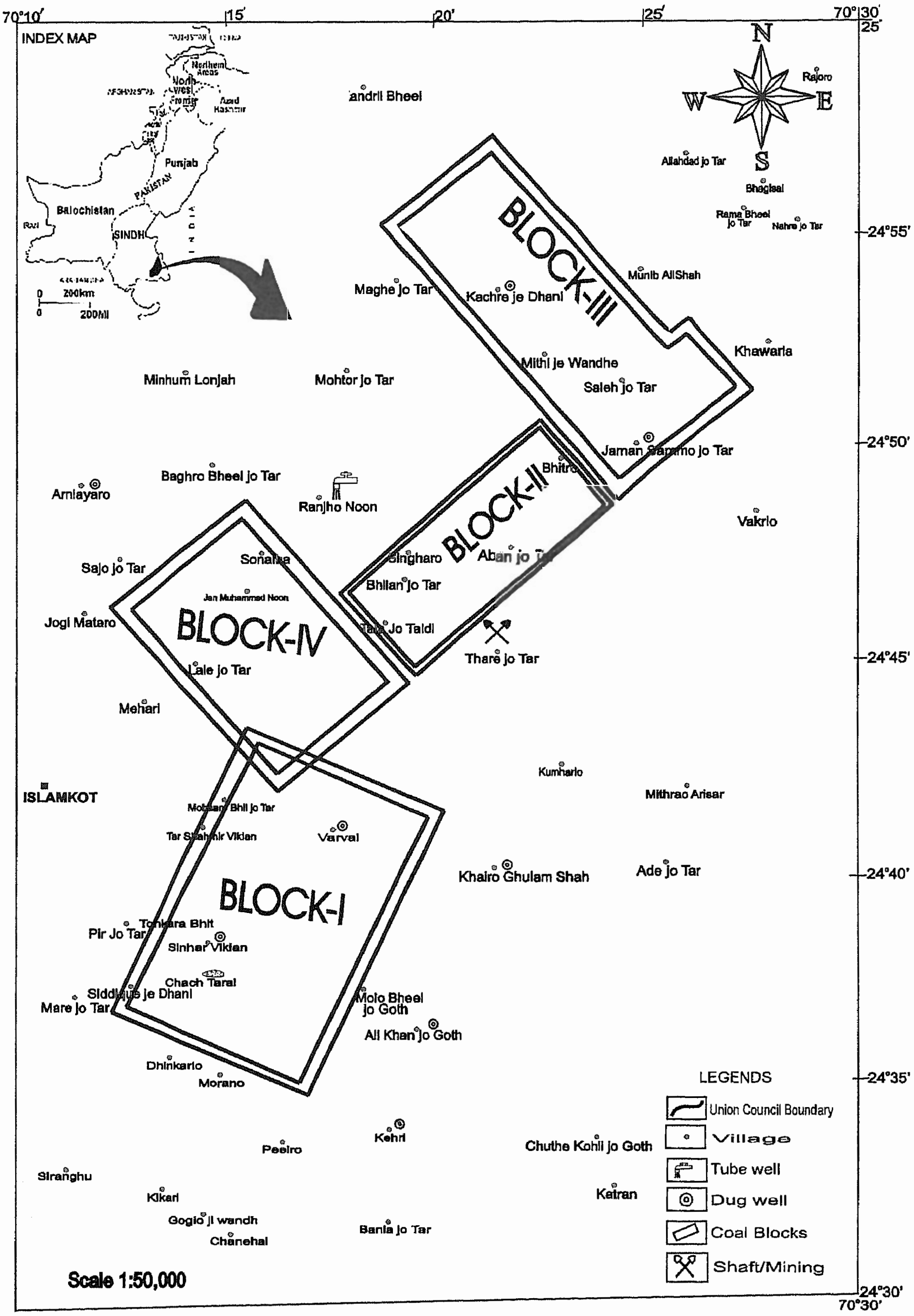


Fig. 3.1 Figure showing location map of Thar coalfield, Sindh, Pakistan.



ure 3.2 Map showing coal Blocks in Thar Coalfield (Redrawn and modified from Jaleel et al., 199).

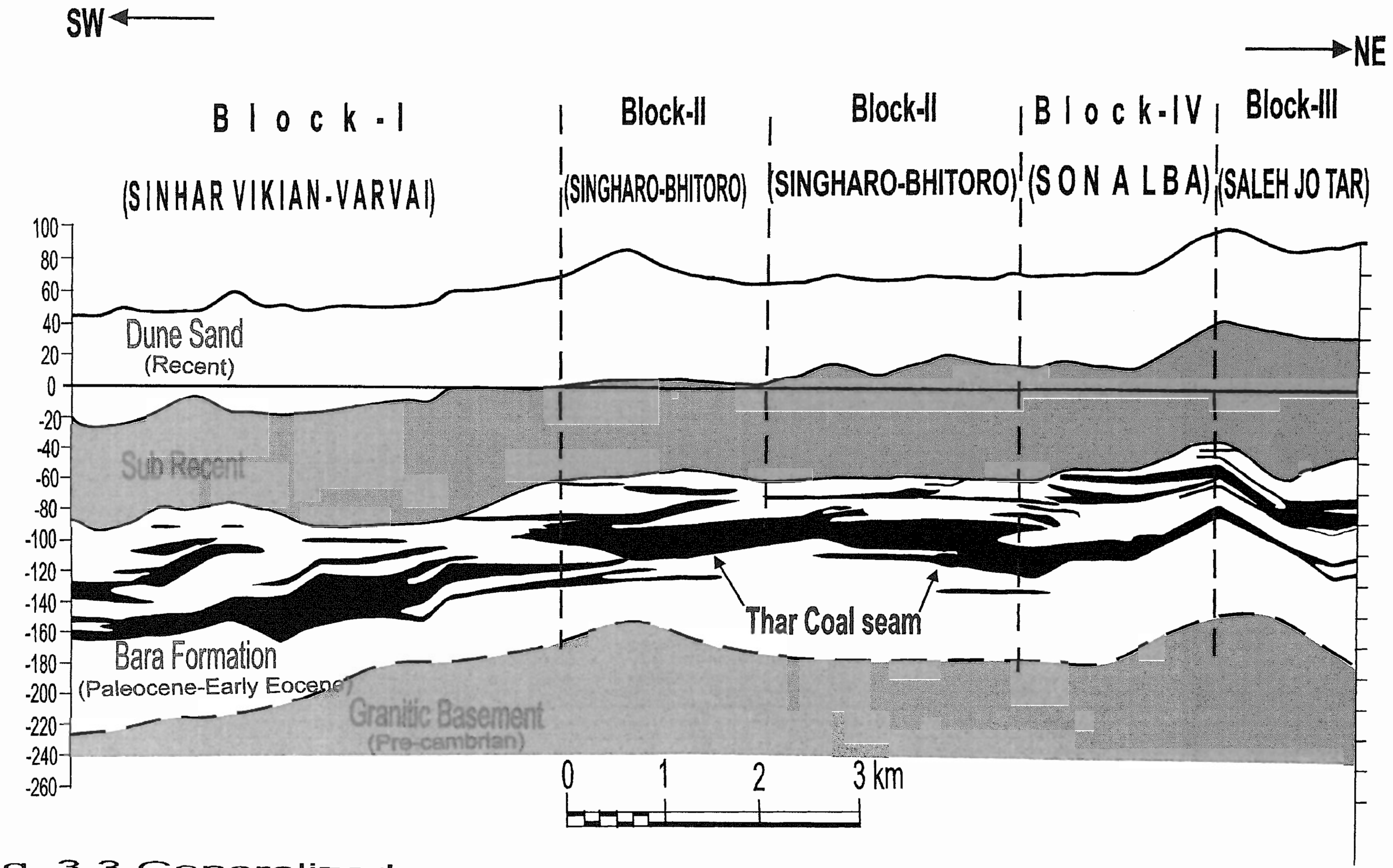


Fig. 3.3 Generalized cross-section of Thar (Jaleel et al., 1999).

(Block-1, IV, II and III)

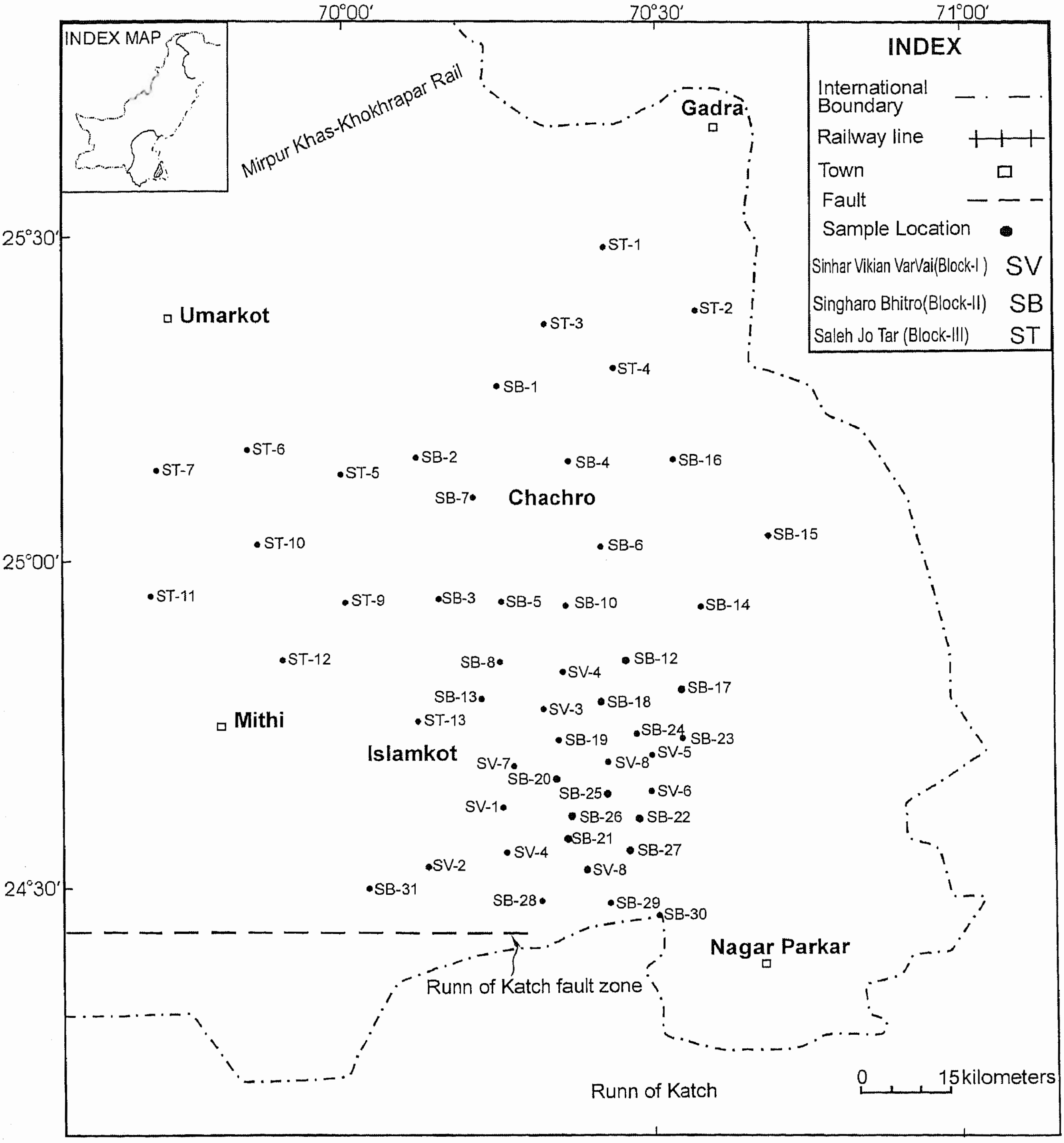


Figure 3.4 Map showing sample locations and names collected from Thar coalfield, Sindh, Pakistan

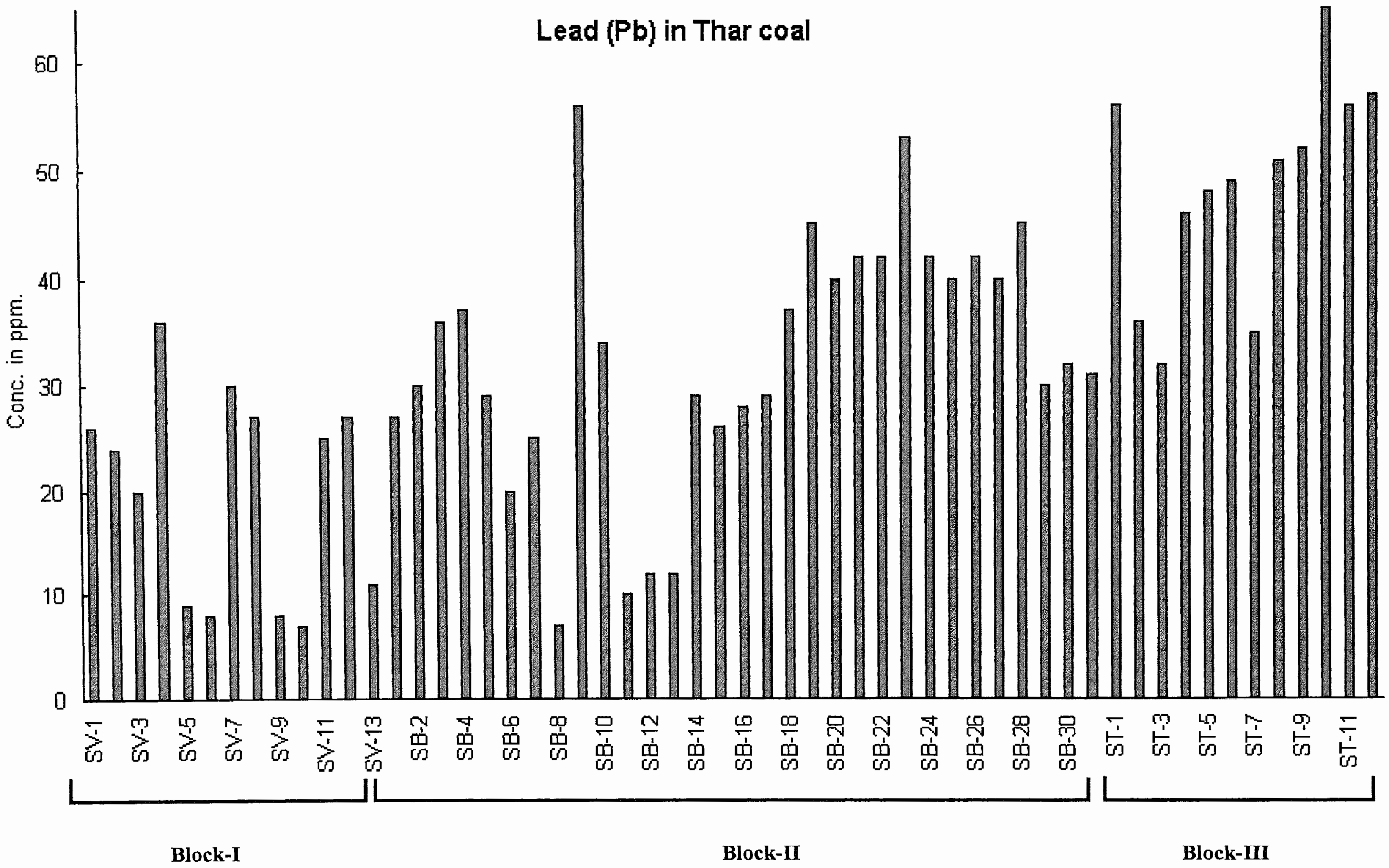


Fig. 3.5a. Bar plot of Lead contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Pb is given in parts per million (ppm).

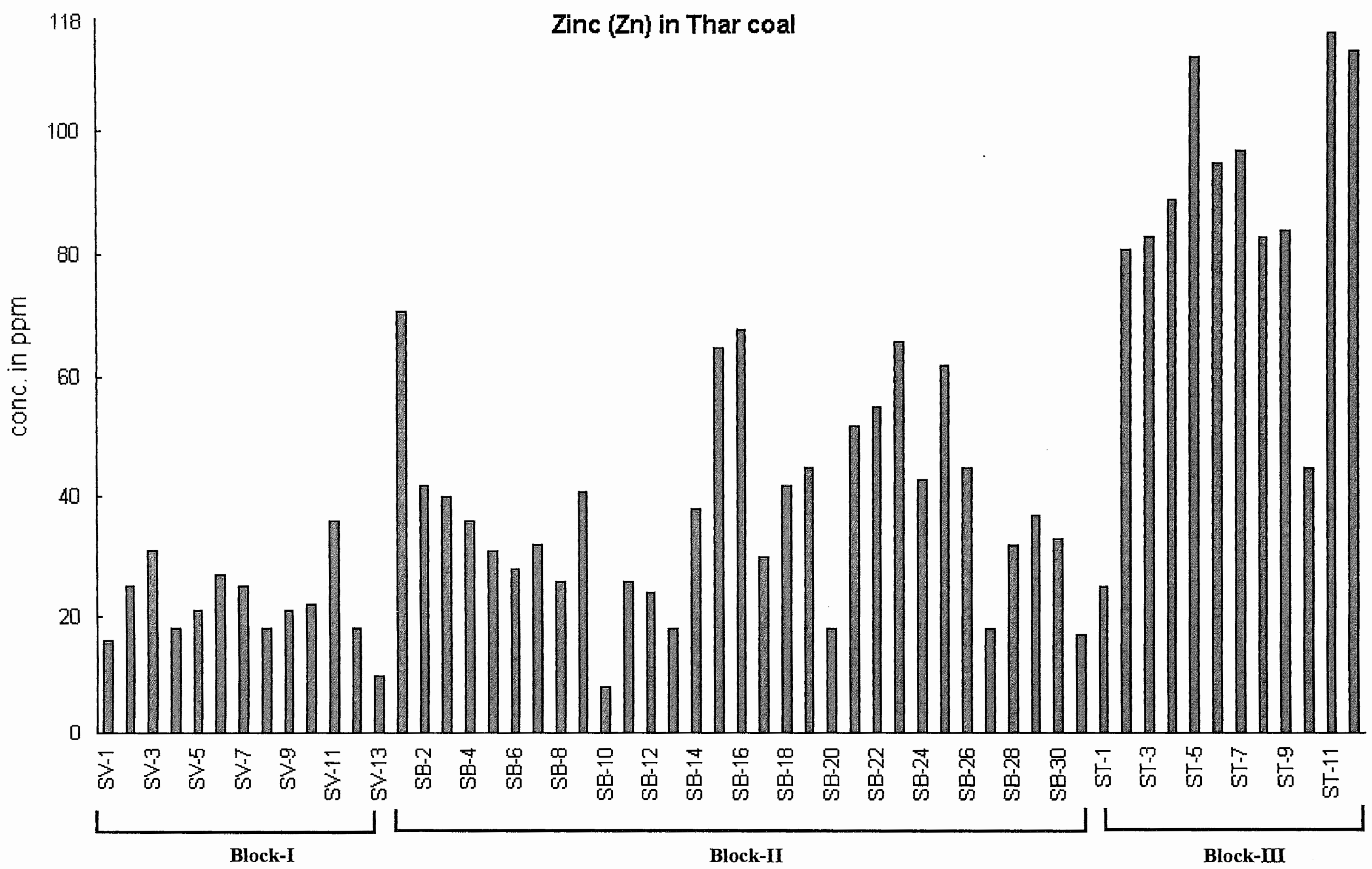


Fig. 3.5b. Bar plot of Zinc contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Zn is given in parts per million (ppm).

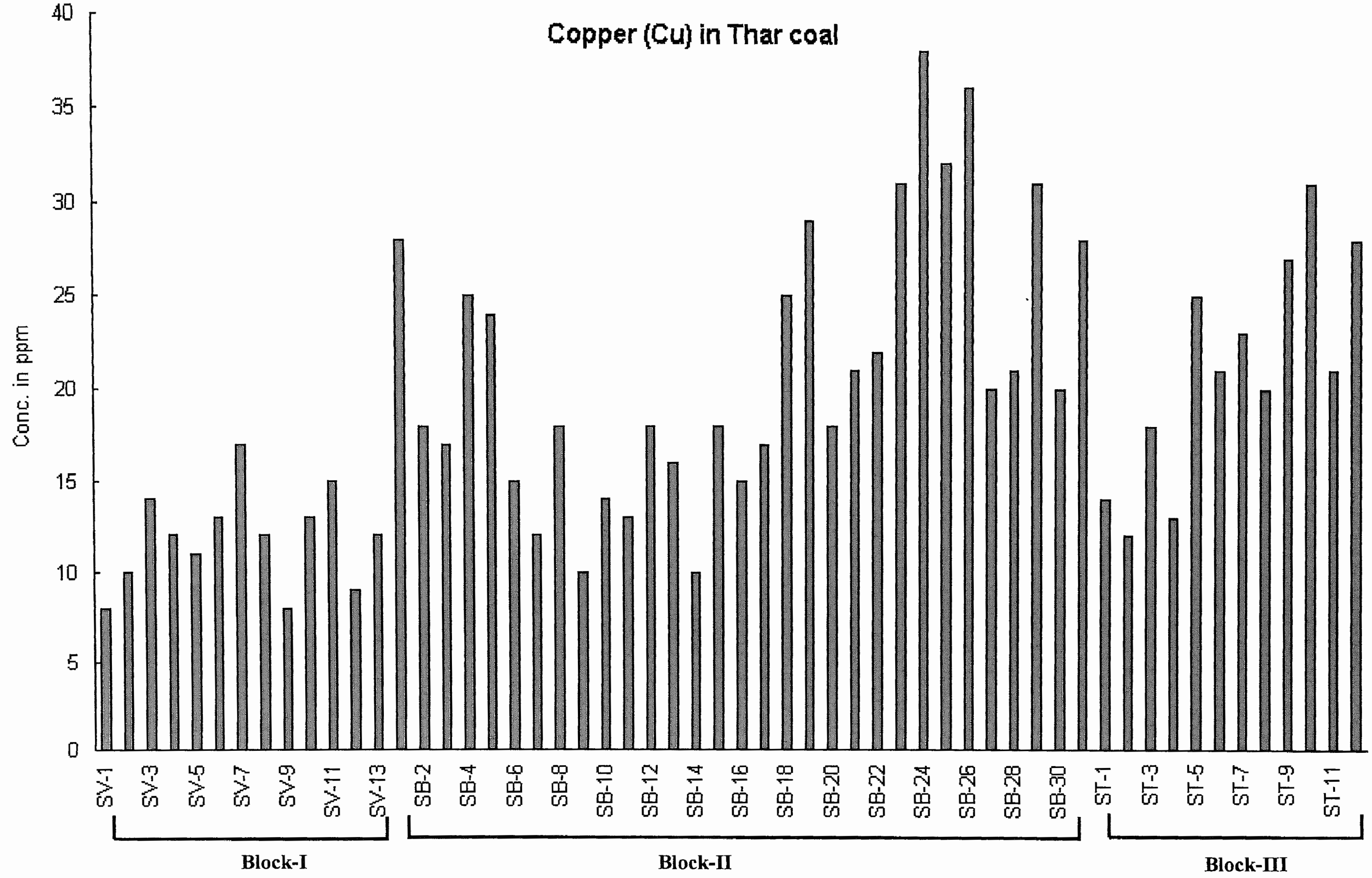


Fig. 3.5c. Bar plot of Copper contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Cu is given in parts per million (ppm).

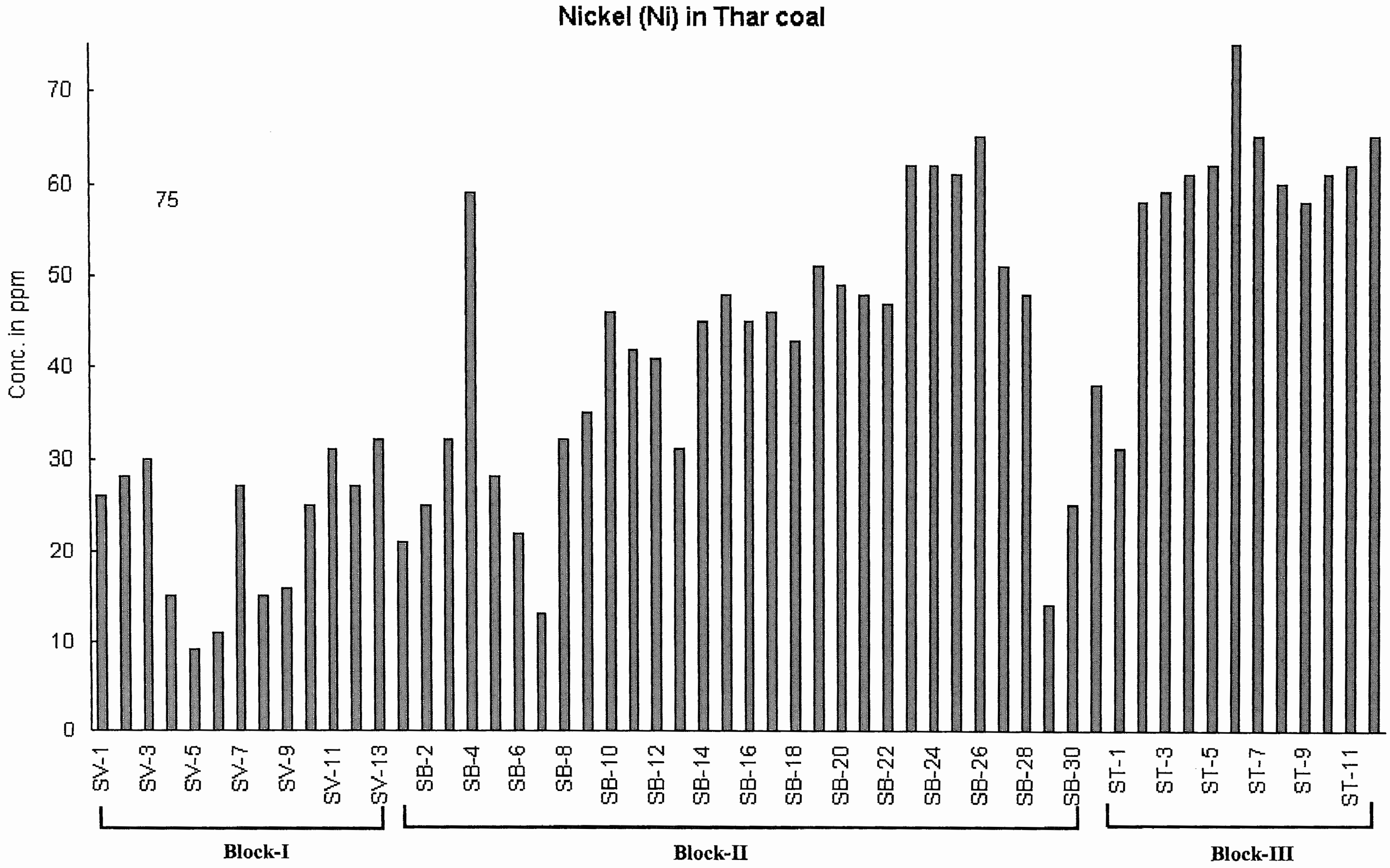


Fig. 3.5d. Bar plot of Nickel contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Ni is given in parts per million (ppm).

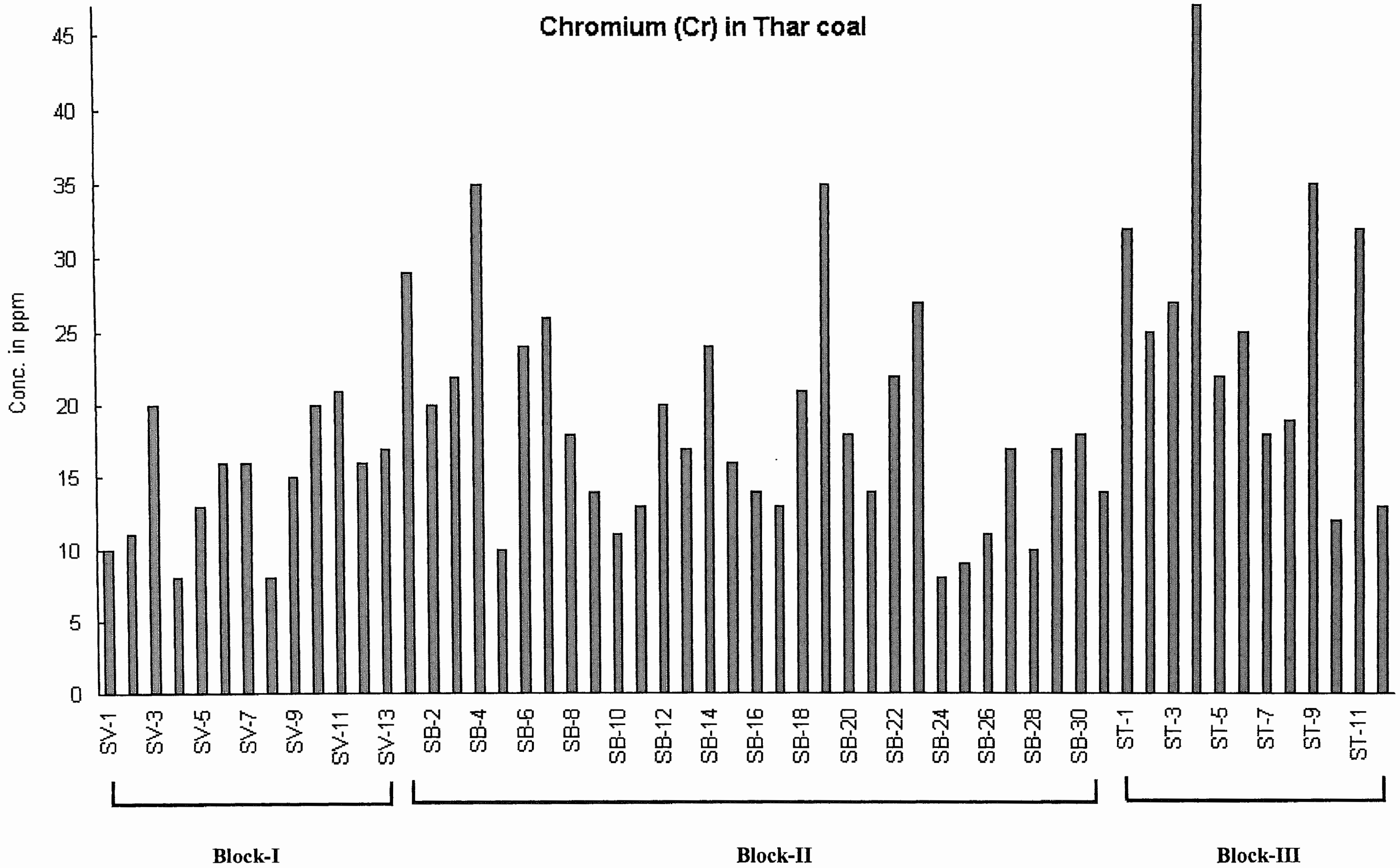


Fig. 3.5e. Bar plot of Chromium contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Cr is given in parts per million (ppm).

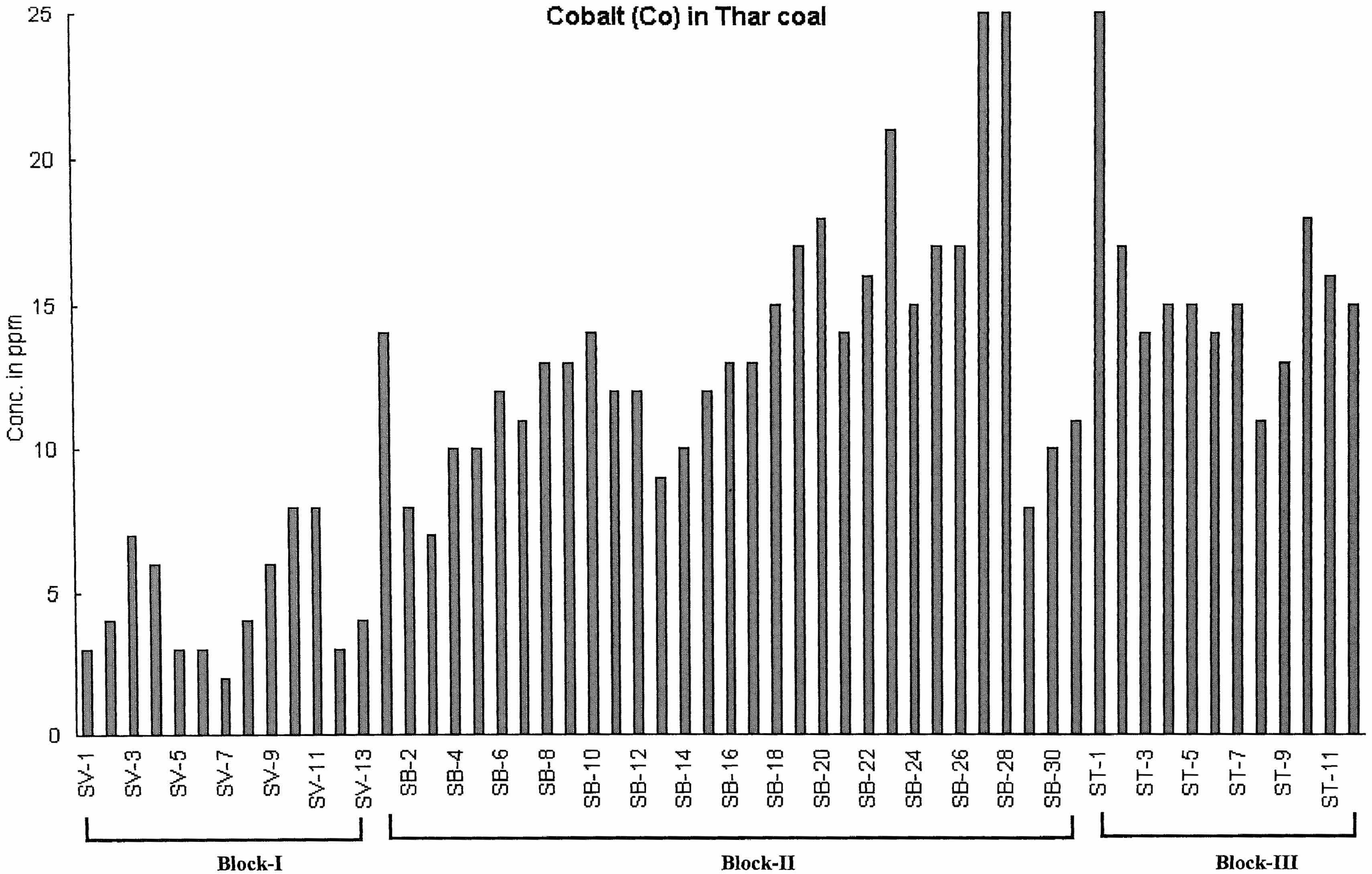


Fig. 3.5f. Bar plot of Cobalt contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Co is given in parts per million (ppm).

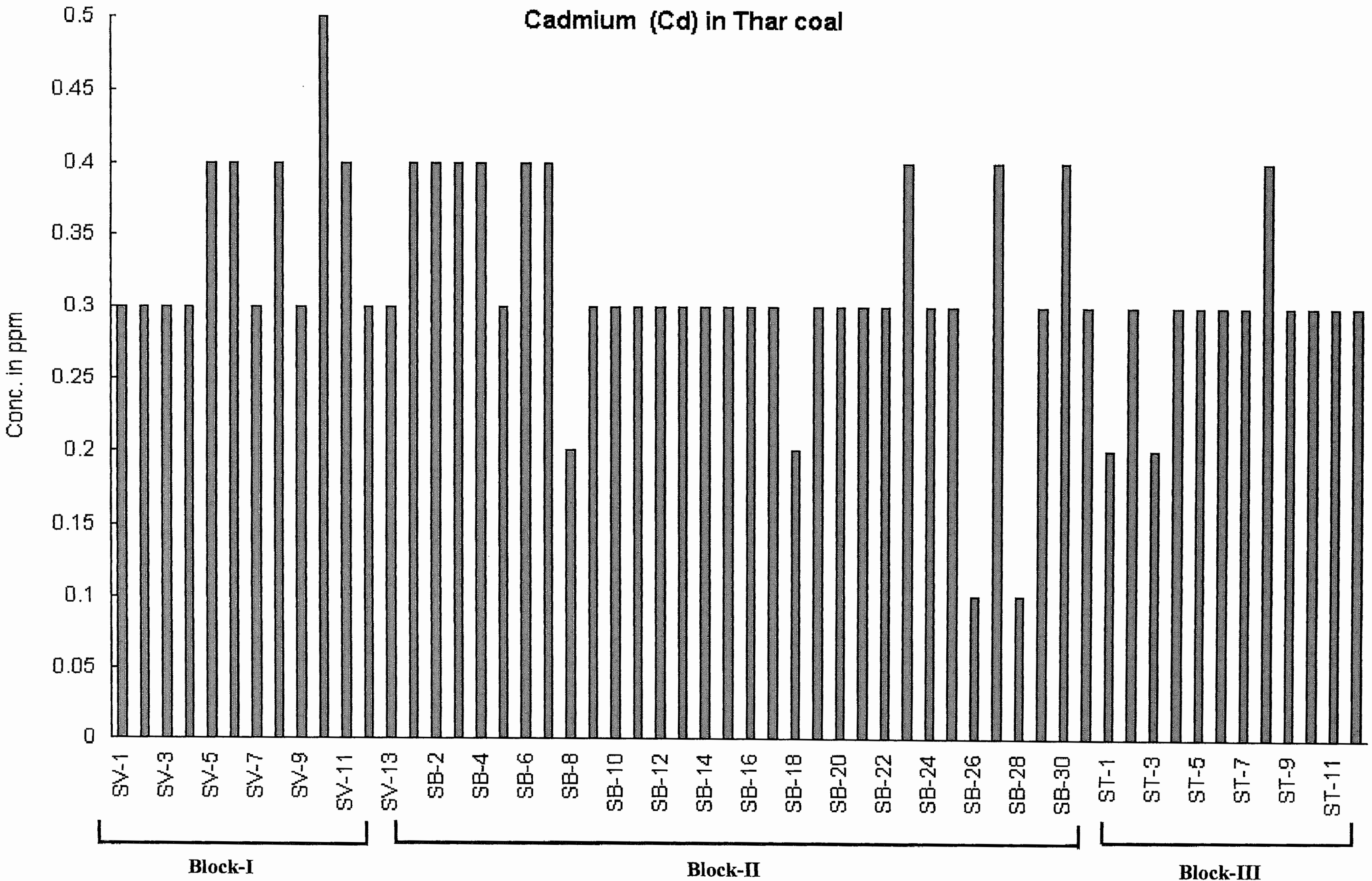


Fig. 3.5g. Bar plot of Cadmium contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Cd is given in parts per million (ppm). the concentrations of Cd is given in parts per million (ppm).

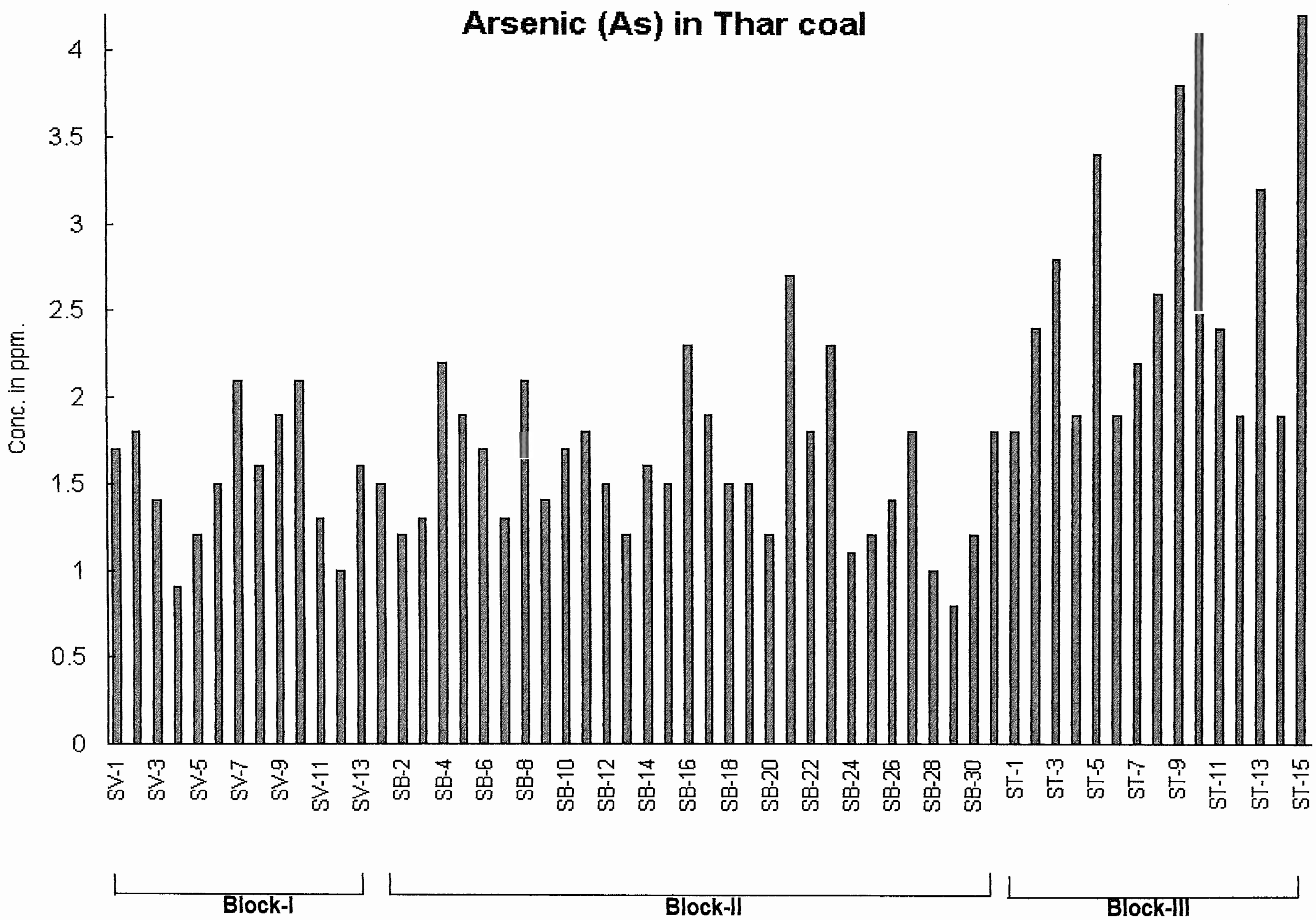


Fig. 3.5h. Bar plot of Arsenic (As) contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of As is given in parts per million (ppm).

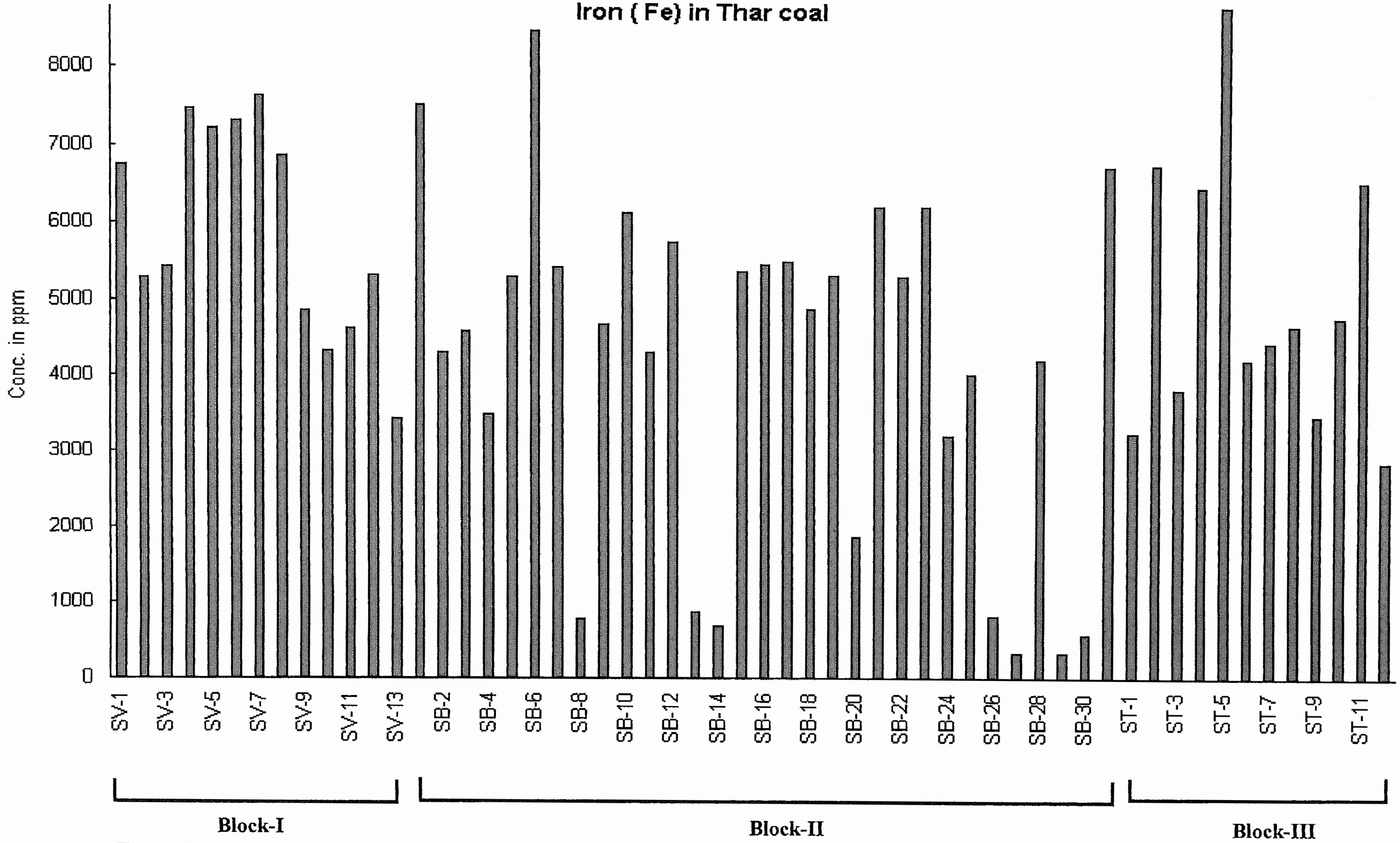


Fig. 3.5i. Bar plot of Iron contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Fe is given in parts per million (ppm).

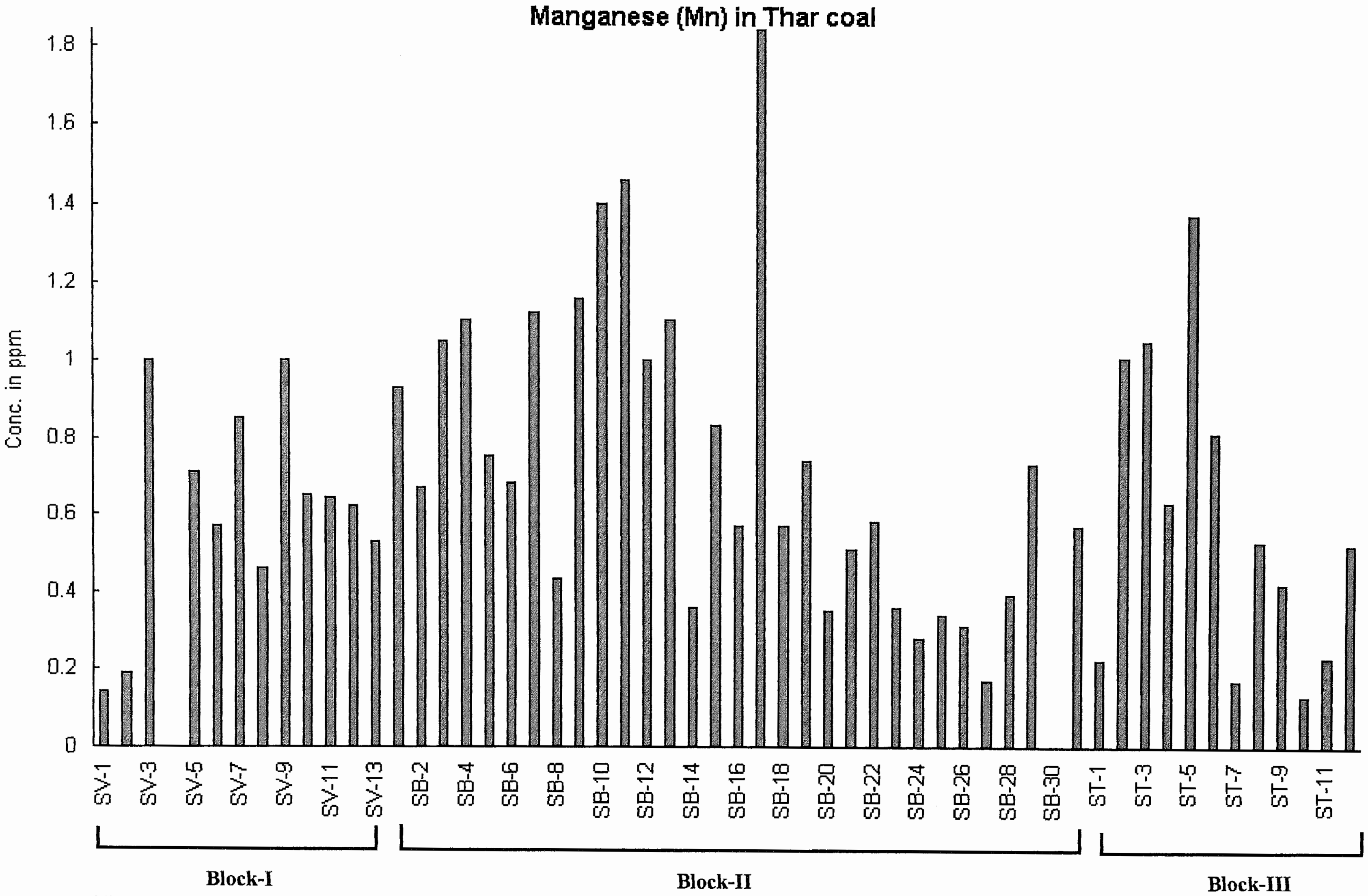


Fig. 3.5j. Bar plot of Maganese contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Mn is given in parts per million (ppm).

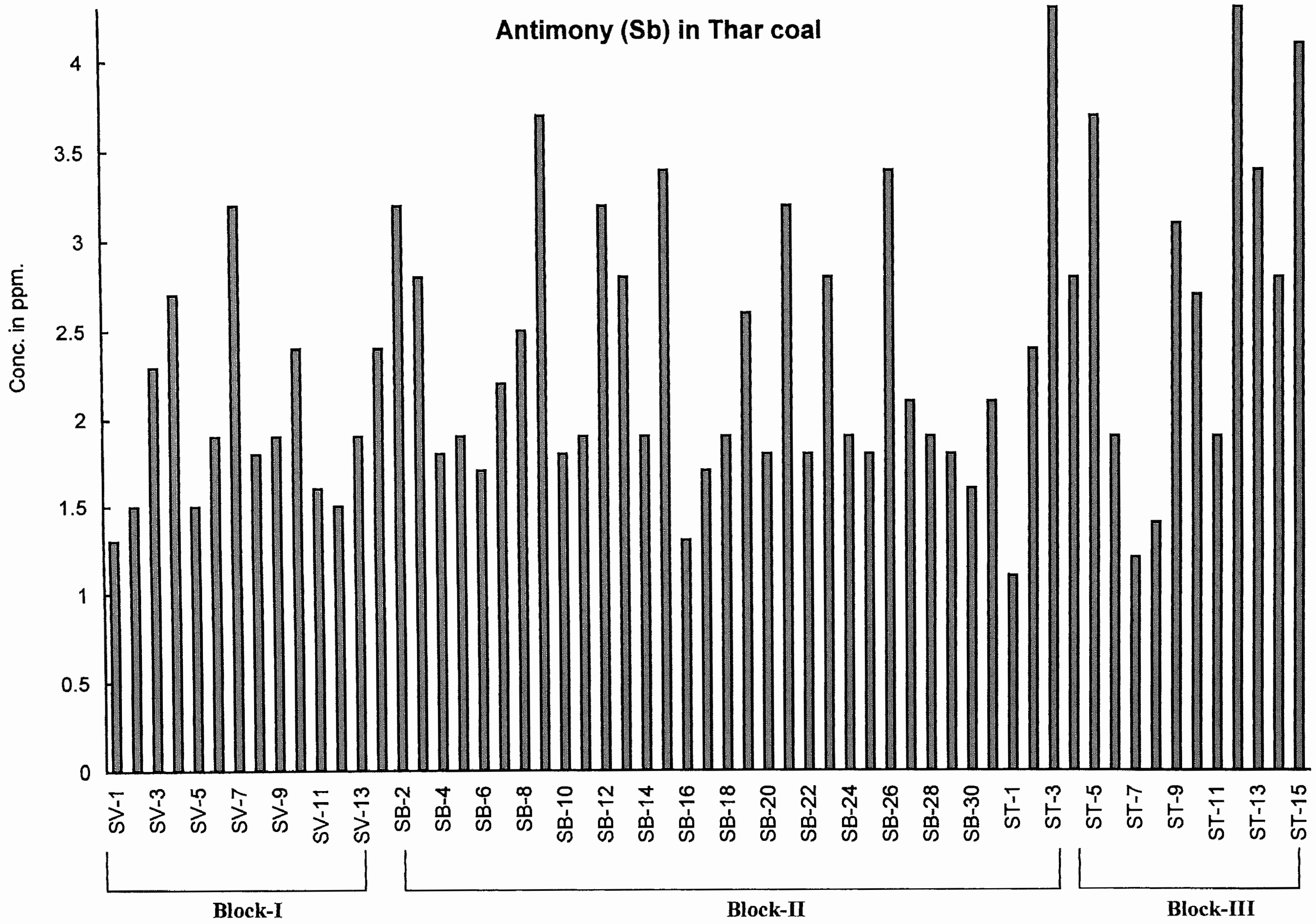


Fig. 3.5k. Bar plots of Antimony content in various Blocks (Block-I, II and III) of Thar coalfield, Sindh province, Pakistan The Concentration of (Sb) in parts per million (nppm).

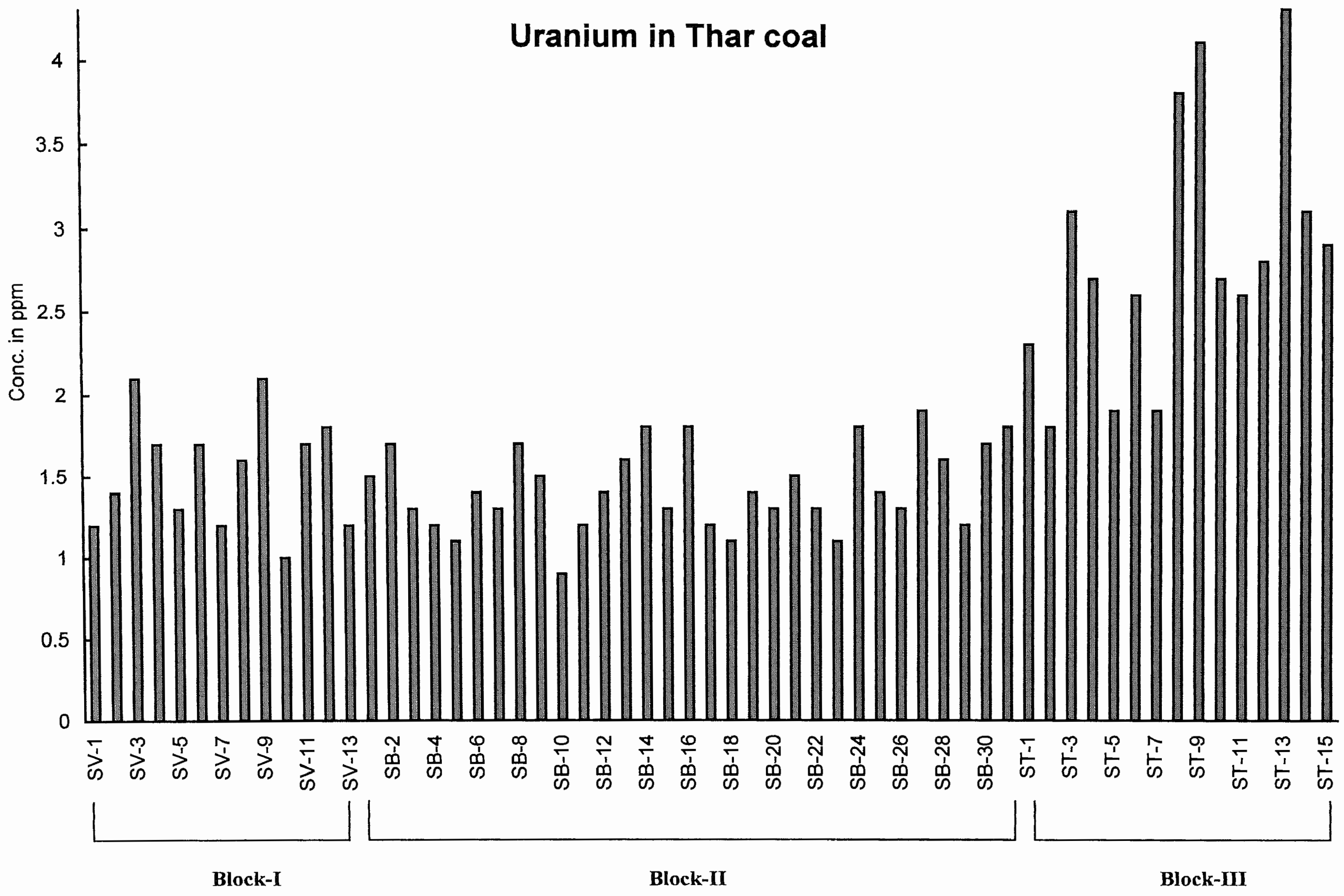


Fig. 3.5*l*. Bar plots of Uranium content in various Blocks (Block-I, II and III) of Thar coalfield, Sindh province, Pakistan
The Concentration of (U) in parts per million (ppm).

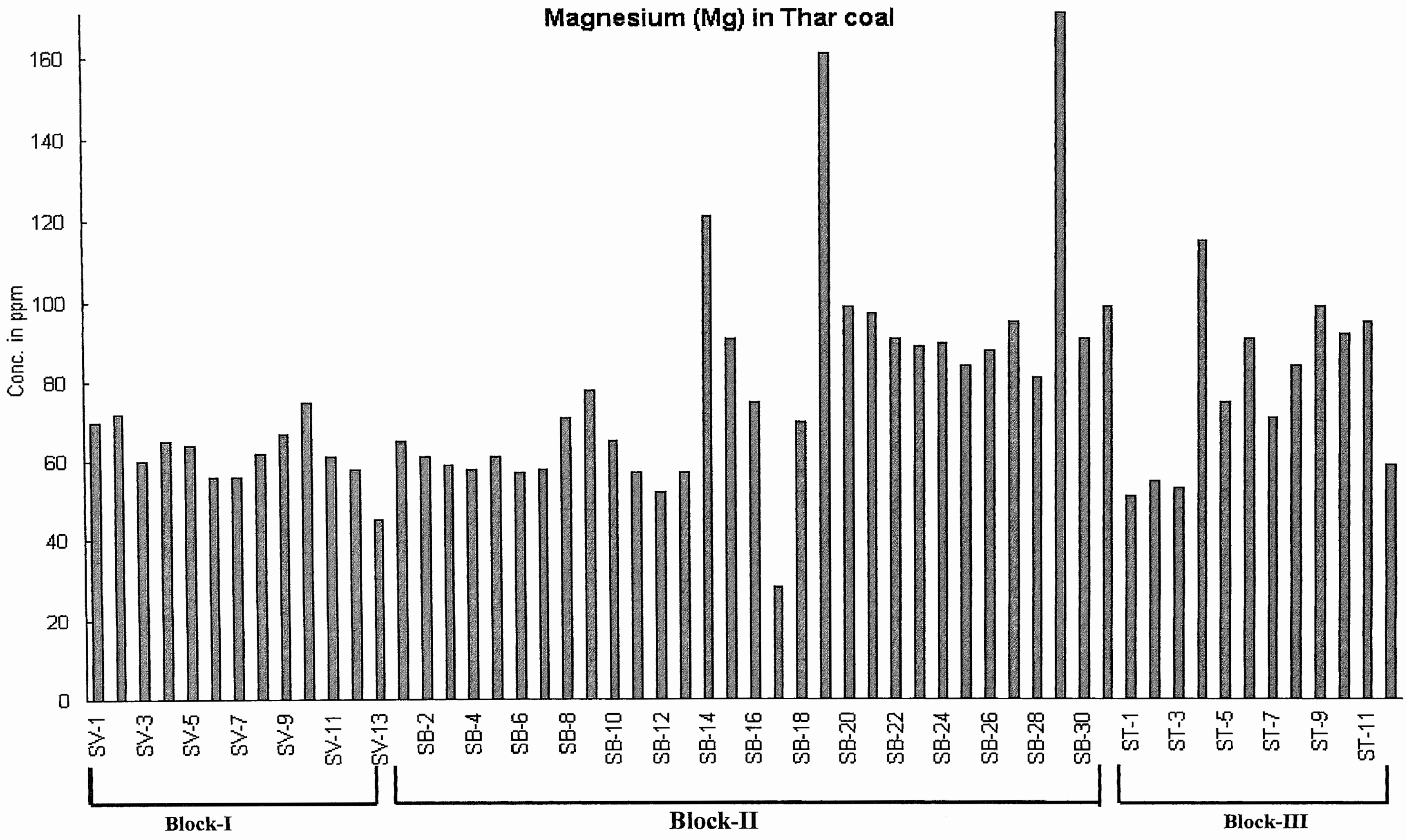


Fig. 3.5m. Bar plot of Magnesium contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Mg is given in parts per million (ppm).

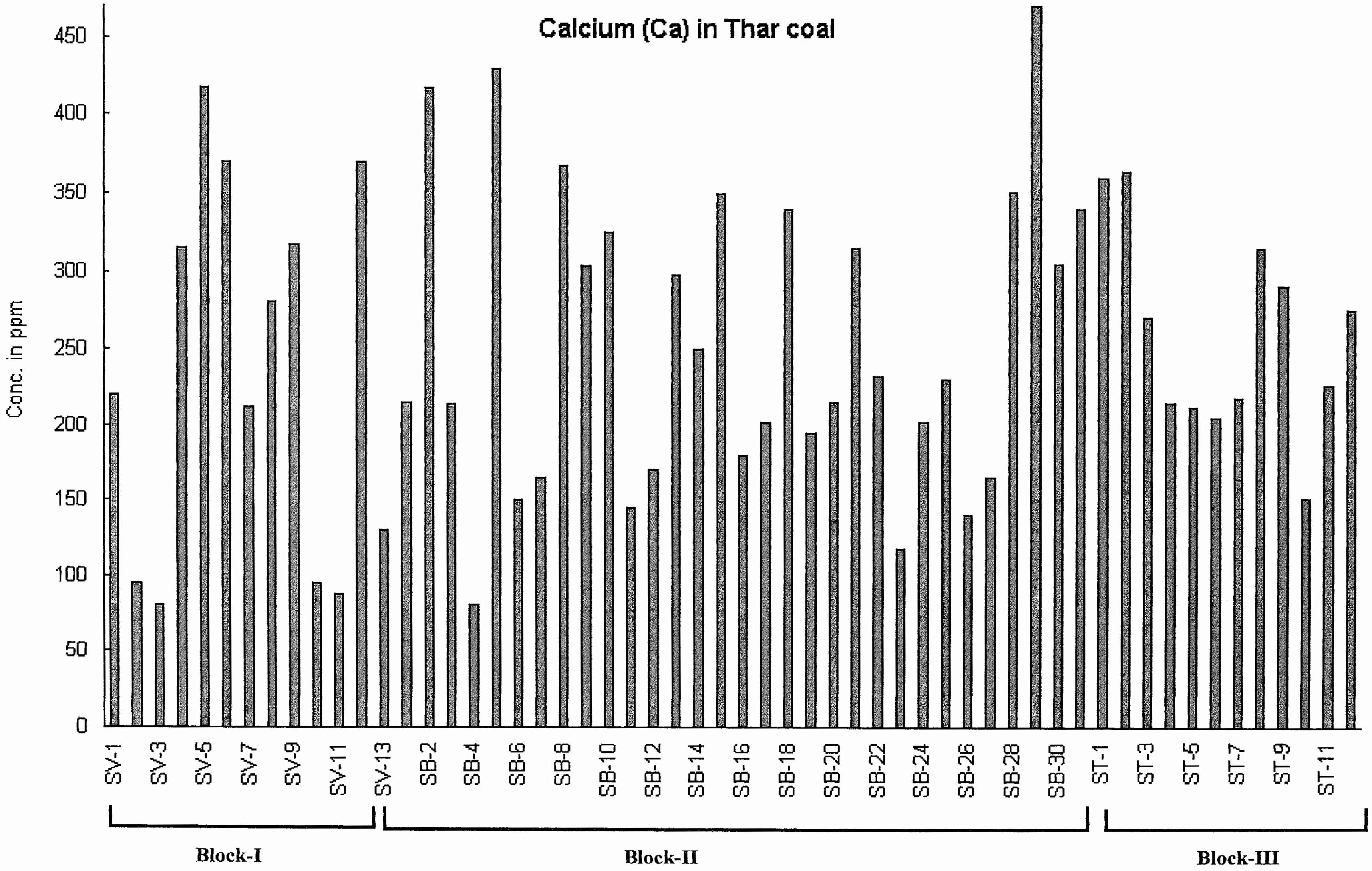


Fig. 3.5n. Bar plot of Calcium contents in vaious blocks (Block- I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan the concentrations of Ca is given in parts per million (ppm).

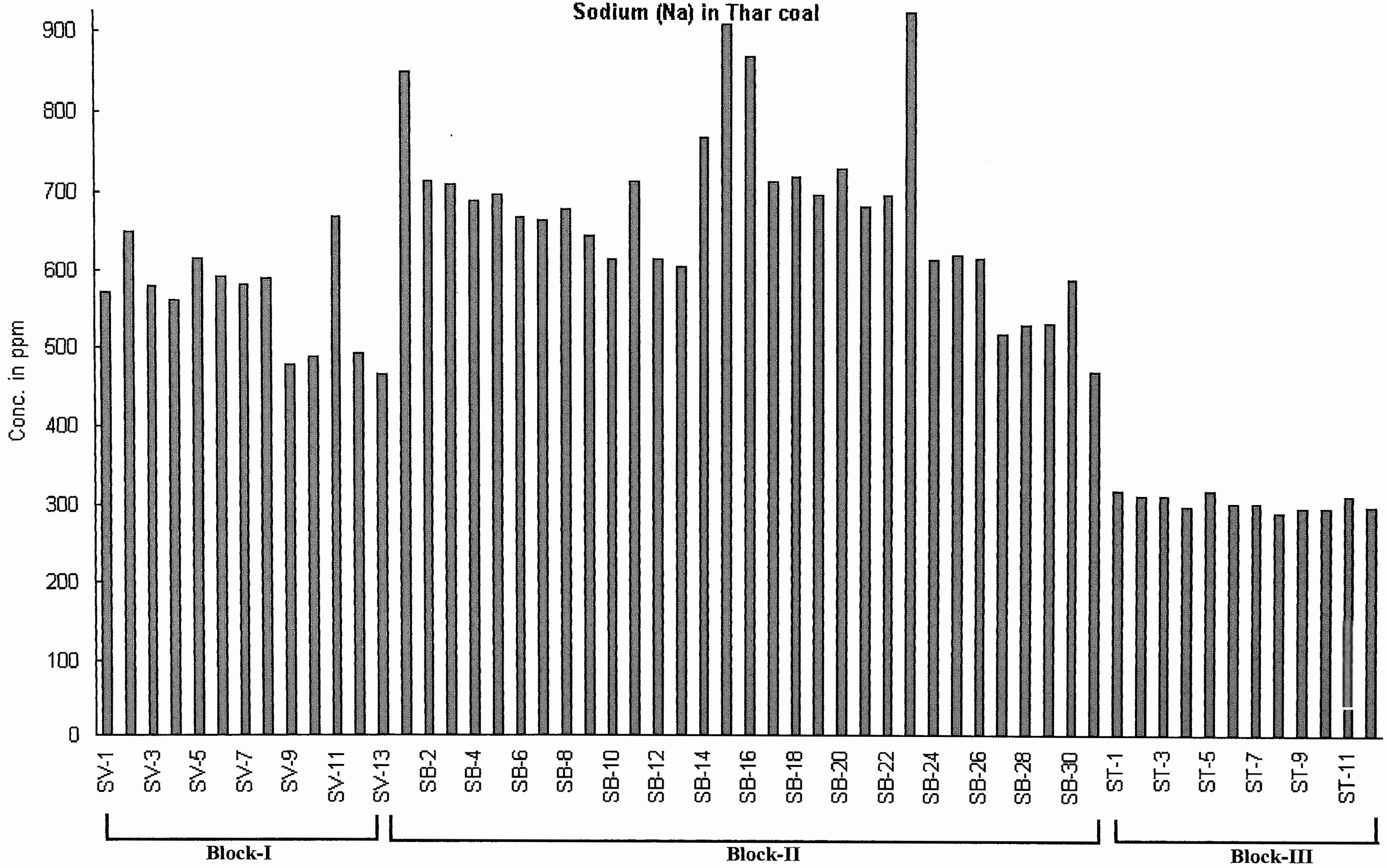


Fig. 3.5o. Bar plot of Sodium contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of Na is given in parts per million (ppm).

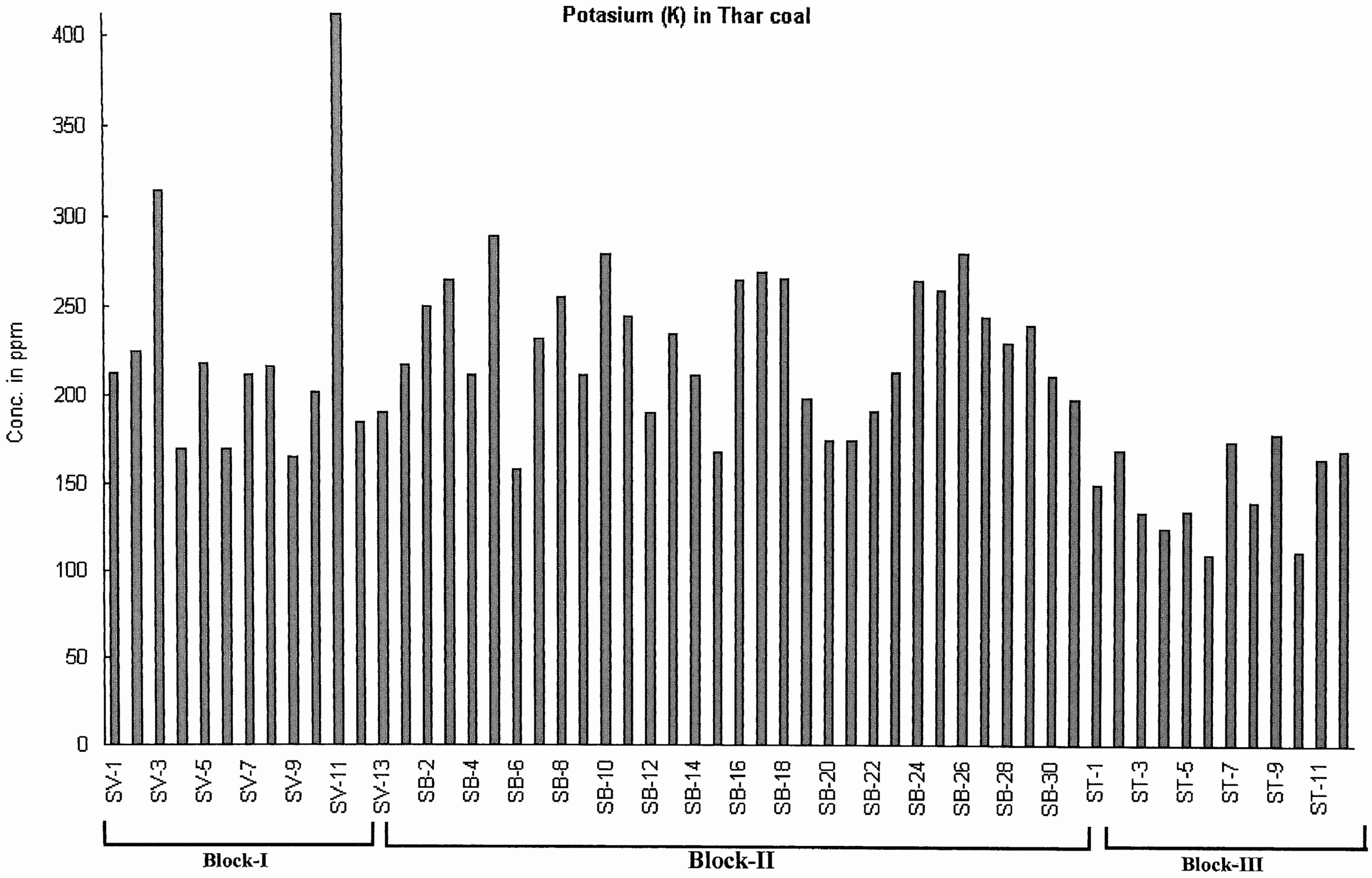


Fig. 3.5p. Bar plot of Potasium contents in vaious blocks (Block-I, Block-II and Block-III) of Thar coalfield, Sindh province, Pakistan; the concentrations of K is given in parts per million (ppm).

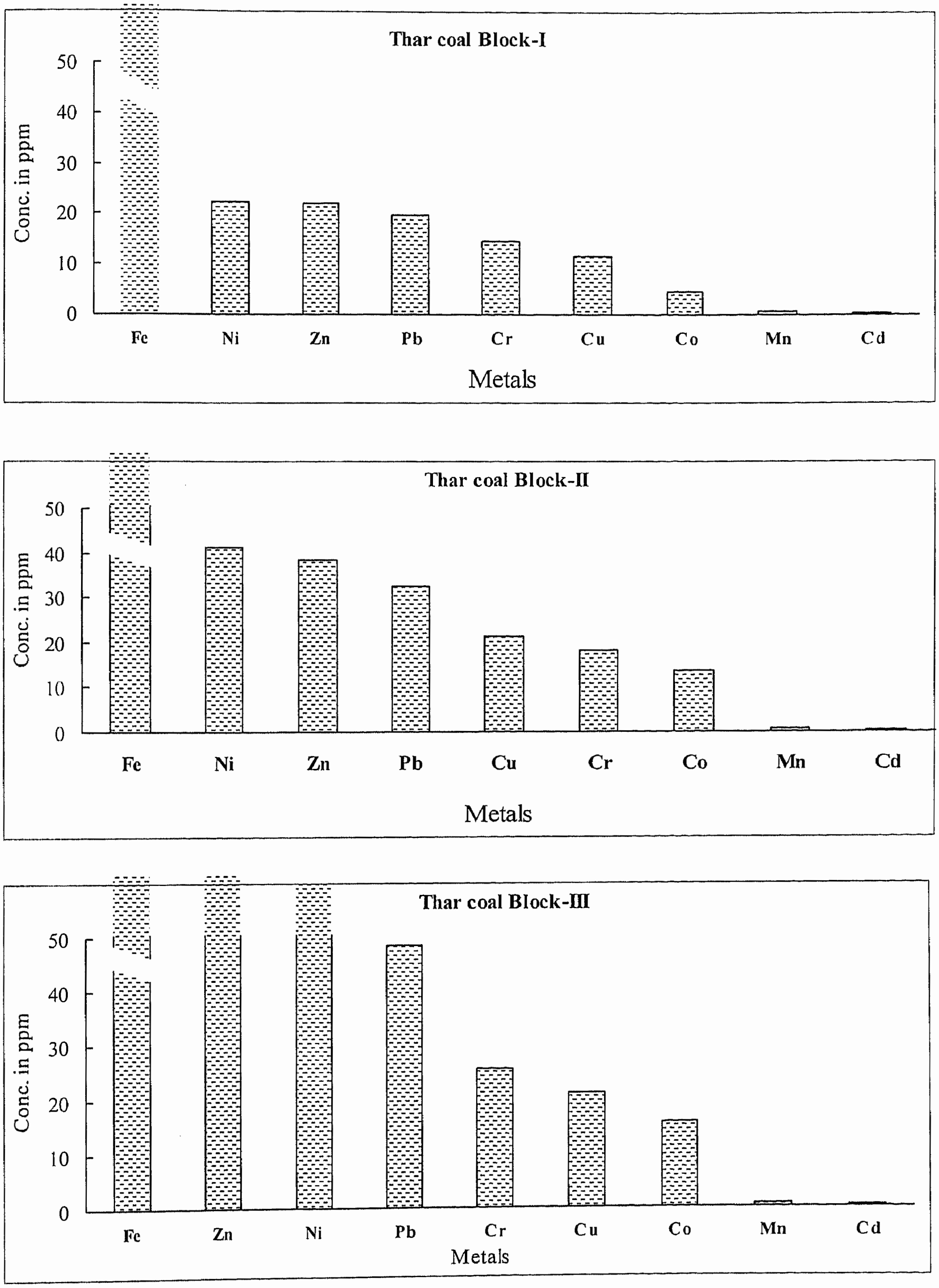


Fig. 3.6a. Inter-elemental comparison of heavy and trace elements in the coals of Thar coalfield.

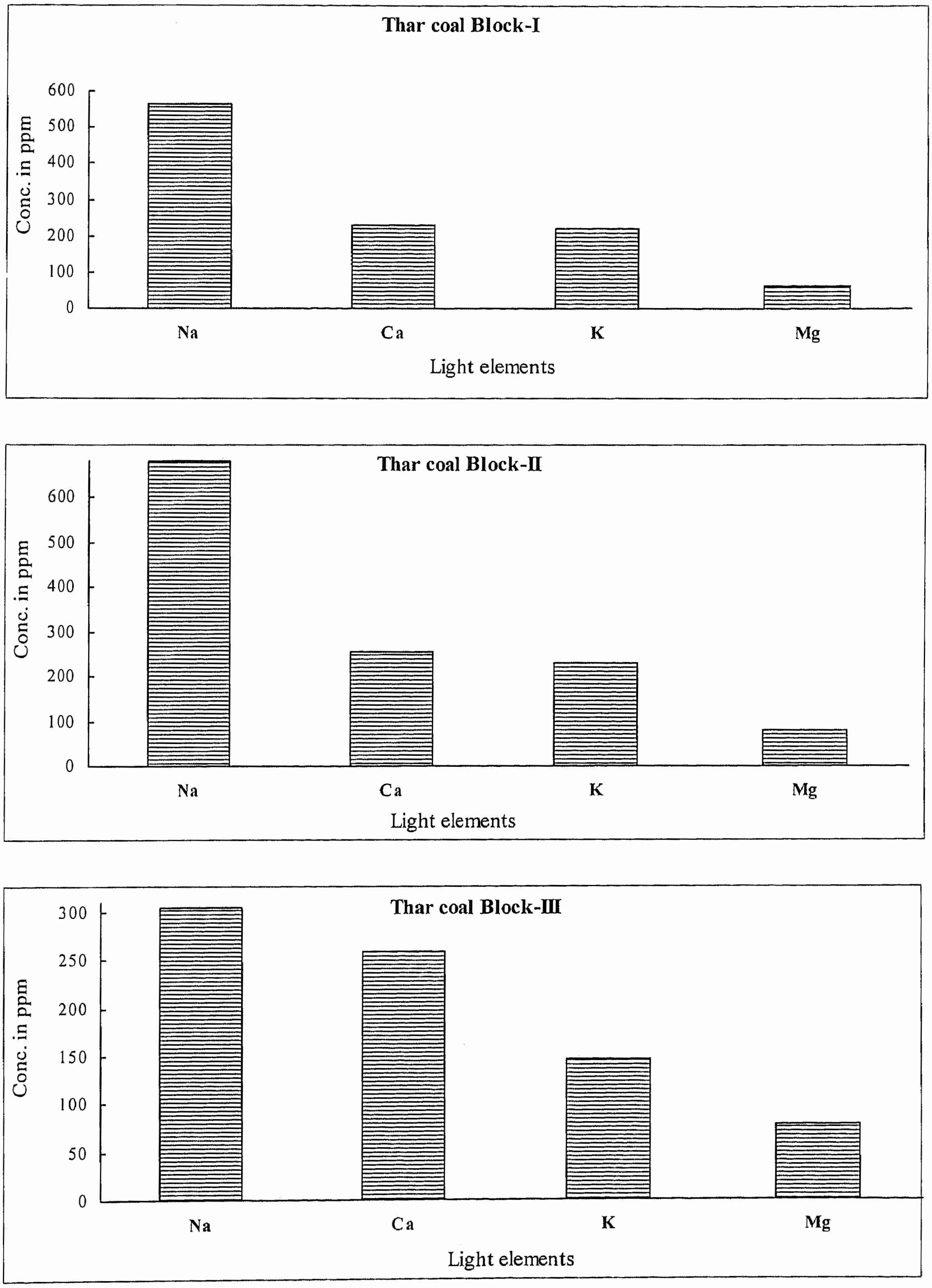


Fig. 3.6b. Inter-elemental comparison of light elements in the coals of Thar coalfield.

CHAPTER FOUR

SONDA COALFIELD

INTRODUCTION

Sonda coalfield was discovered in 1981 by Geological Survey of Pakistan, in a small village Sonda, located in the deltaic area of lower Indus, on the National Highway 40 kms from Thatta and 130 kms from Karachi towards Hyderabad. The region includes plains, mostly overlain by old and new alluvium. The relief is generally low with southwesterly landforms controlled by active fluviatile processes. This coalfield lies in the east and northeast of Keejhar Lake in District Thatta and falls in toposheet No. 40 D/1 and 40 C/4. It extends from Jherruck to Thatta in northeast and southeast direction and Jhimpir to Sujawal in north-south direction covering an area of 1500 sq. Km (Fig. 4.1). More than 29 coal seams of varying thickness and continuity occur at different horizons in Sonda coalfield, the maximum thickness of one coal seam is 6.2 meters. The total reserves have been estimated as over 295 million tones (Waheeduddin et al., 1992).

The area is part of tropical coastland dominated by sea breezes. The mean annual temperature is generally over 90^{O}F, humidity exceeds 50% through out the year. The average annual rainfall is between 7 to 15 inches. Natural vegetation comprises forests, shrubs, herbs, and grasses. Tidal forests of mangrove occur in the eastern part of the area (Khan, 2003).

GENERAL GEOLOGY

The general stratigraphic units in and around Sonda range in age from Paleocene/Cenozoic to Recent/Holocene. The oldest unit of the Cenozoic age is the upper part of the Bara Formation, Lakhra Formation, and Laki Formation, while the youngest units include the surficial parts of Holocene alluvium of the Indus river flood plain. Coal seams occur in two major formations, i.e. Bara Formation of Paleocene and Laki Formation of Eocene age. The generalized stratigraphic sequence exposed in the area is described below.

Bara Formation

The unit is composed predominantly of sandstone and subordinate amounts of claystone or shale, siltstone and coal. The unweathered sandstone is light grey, grey, white and greenish grey, but weathers into various shades of yellow red and brown. It is coarse to fine-grained, mostly subangular and poorly sorted, cross-bedded, massive, friable, loosely cemented. The claystone or shale and sandstone are light-grey to grey, pyritic, sandy and gypsiferous, associated with irregularly distributed coalyphile and range from non-laminated to poorly laminated. Its upper contact with the Lakhra Formation is conformable (Fig. 4.2).The generalized stratigraphy of the rocks exposed in Sonda-Thatta-Jharruck area is given in Table 4.1. An Early to Middle Paleocene age (Domian to Montian) may be assigned to Bara Formation (Thomas et al., 1993).

The strata are exposed along a very narrow strip of right bank of River Indus at Dhaduri ridge, at Sonda, where it directly underlies the alluvium cover. The subsurface contact of Bara Formation and overlying Lakhra Formation is exposed along the River Indus at many places (Waheeduddin et al., 1988).

Lakhra Formation

This name has been proposed by Ahmed and Ghani (1967) after the village Lakhra (a type locality) in Dadu District for the Upper part of the Rani Kot Formation of Vredenburg (1906). Lakhra Formation consists of sandstone, limestone, claystone or shale and siltstone. Sandstone is dominant in the basal beds whereas limestone is dominant in the upper part and alternates with sandstone and claystone. The sandstone is thin to thick-bedded, light-grey, dark-brown/chocolate, yellow - brown and red in colour. It is fine to coarse grained in texture with subangular to subrounded grain, fossiliferous in certain layers and calcareous, at places grades into sandy limestone. It is hard and resistant when calcareous and fossiliferous (Thomas and Khan., 1989) .

The limestone is light grey, weathered to yellow and brown, sandy, fossiliferous and in places grades with coquina. It is typically thick bedded to massive and resistant. The shale or claystone and siltstone are light grey, stained yellow and brown, soft and slope forming. This Formation conformably overlies the Bara Formation but unconformably underlies the Laki Formation. At places the Laki Formation is missing and Manchar Formation overlies the Lakhra Formation. The unit is of variable thickness because of post Lakhra erosion (Thomas et al., 1993).

The thickness of this formation increases from northeast to southwest and the total thickness recorded in a section is about 113 meters. The age assigned to this formation is Middle to Late Paleocene. The base of Lakhra Formation is exposed only along a narrow strip below Dadhuri ridge near Sonda. The rocks of Lakhra Formation crops out along the right bank of river Indus, on both sides of the National Highway. In Lakhra Formation, four prominent, continuous, limestone beds are noted which alternate with sandstone, shale and marl (SanFillipo et al., 1990).

Laki Formation

Laki Formation is the term used for the "Laki Group" of Hunting Survey Corporation (1960) which was earlier "Laki Series" of Noetling (1903). The name Laki is derived from the Laki Hill range and village in the western part of Hyderabad Division. The formation consists of finely crystalline limestone, lateritic claystone, siltstone and shale. This formation is best developed in the southern part of Kirthar Province. It attains a thickness of 55 meters near Thatta. The lower contact of the formation is unconformable with Lakhra Formation and is marked by Sonhari member. This is divided into members namely Sonhari bed member, Meting limestone and shale member and Laki limestone member (Schweinfurth & Hussain, 1988).

Sonhari bed Member

The Sonhari Member comprises of lateritic clays, sandstone and gypsiferous shales. Clays are of various colors ranging from violet to reddish-brown, yellowish-brown, bluish-grey, off white, grey-brown, and buff and are silty, sandy and highly ferruginous with local patches of fire clay and lenticular lignite beds ranging in thickness from 0.30 to 0.75meters. Sandstones are yellowish-brown to light-brown and dark-gray in color, fine to coarse-grained and even gritty at places with rounded and subrounded grains and are ferruginous and calcareous. Friable silica sand bands occur in sandstone with variable thickness which gradually passes into buff, reddish, ferruginous sand (Wnuk et al., 1991).

Shales are found in various colors, like blackish-grey and dirty-brown, containing carbonaceous shale with poorly developed lignitic material and pyrite crystals. Small bands of laterite occur on the middle part of the beds. Sonhari member varies in thickness from 10 to 30 meters (Thomas and Khan., 1990).

Meting Limestone and shale Member

It consists mainly of creamy white nodular limestone with subordinate sandstone in the upper part. The shale is grey, greenish-yellow, weathering dark rusty brown, ferruginous and gypsiferous. The limestone is thin bedded and arenaceous where as the sandstone is commonly ferruginous. The Meting Member is about 70 meters thick at the type locality (Waheeduddin et al., 1988).

Laki limestone member

The limestone is light yellowish grey, white and light-grey, stained yellow to brown and weathers to light grey. It is nodular, hard, resistant and massive and forms cliff containing foraminfera in abundance and mega fauna mostly in upper part. It is characterized by steep scarps.

Coal beds and zones

Sonda coal beds are commonly lenticular, partly as a result of original lenticular deposition and partly as result of post deposition erosion, folding and faulting during which coal beds are squeezed and broken into complex, distorted, discrete lenses and isolated patches. The thickness of the coal bed ranges from a couple of centimeters to 2.45 meters in various places. Pinching and swelling of lensoid coal beds are pronounced which makes the correlation of seams difficult. The coal beds are almost horizontal; slightly dipping towards west. In general the number of coal seams are classified in three different coal zones including upper, middle and lower on the basis of their position in geologic/stratigraphic columns. The main middle coal seam is termed "Sonda Seam" which is considered to have reasonable consistency in its extension, although it could be discontinuous and may change to carbonaceous shale. The coal seam in the upper zone and above Sonda seam in the geologic column are termed as "Dadhuri Seam" where as the name "Jherruck" is assigned to the coal seams falling in the lower coal zone below the Sonda Seam. Three other coal seams encountered only above the Sonda Coal Seam and falling in middle coal zone are named as "Enayatabad Seams". Waheeduddin et al. (1988) have divided Sonda coalfield into the following coal zones:

Dadhuri Coal Zone or Zone–I: It is the top coal zone lying between stratigraphic interval from the top of Bara Formation to the base of the lowermost fossiliferous limestone bed ('A' Bed) of Lakhra Formation. It contains two to three coal beds in stratigraphic column varying in thickness from 0.10 to 0.75 meters associated with highly carbonaceous clays on top and bottom which vary in thickness from 0.10 to 0.6 0 meters. The roof of this zone is sandy claystone with sandstone at places, while the floor rocks are claystone and carbonaceous claystone (Waheeduddin et al., 1988).

Generally coal is brownish-black to greyish-brown, dull laminated, brittle, conchoidal to uneven fracture with silty and clayey inclusions. This zone consists of claystone with interbedded sandstone carrying, clayey laminae, that posses calcitic, pyritic and sideritic nodules.

Sonda coal zone or zone-II: This is the main and middle coal zone which lies in a stratigraphic interval varying from a depth of 150 meters from top of Bara formation. It contains four to five coal beds in statigraphic column alternating with claystone and carbonaceous shale but at places these coal beds lie very close to each other, where they range in thickness from 0.30 to 2.50 meters and are associated with highly carbonaceous shale (0.20 to 1.50 meters) on top and bottom. The coal is brownish black to black, dull to sub-vitreous, laminated, brittle and unevenly to conchoidaly fracture. The zone consists of claystone, siltstone with interbedded sandstone and carbonaceous shale carrying pyritic and calcareous siderite nodules (Thomas et al., 1990).

The coal bed throughout in its extent consists of claystone and carbonaceous claystone as roof and floor. This claystone is olive grey, dark grey and light bluish-grey to greenish grey. It is hard, compact, non-calcareous and silty at places. The carbonaceous shale is dark grey to brownish black, brittle, compact, pyritic and non calcareous (Thomas et al., 1990).

Jherruk Zone or Zone-III: The lower most coal zone lies between stratigraphic intervals 170 to 220 meters from the top of Bara formation or from the base of lowest limestone bed (Bed ‘A’) of Lakhra formation and contains two to three coal beds in stratigraphic column. These coal beds vary in thickness from 0.30 to 0.80 meters and are associated with grey carbonaceous clays on top and bottom (Thomas et al., 1988).

Coal is generally brownish black to black, brittle, pyritic, dull, laminated with uneven to conchoidal fractures. This zone consists of sandstone (Silica 85%), siltstone, sandy claystone and interbedded claystone. Generally roof rock is siltstone of dark grey to olive grey, hard, compact, sandy, with clayey laminations and pyritic. While the floor rocks are underclays that are light bluish grey, compact, fissile at places and interbedded with brownish black, laminated carbonaceous claystone (San Filipo et al., 1990).

HEAVY, TRACE AND LIGHT ELEMENTS IN SONDA COAL

Eleven representative samples were collected from various localities at Sonda coalfield, and these samples have been analyzed for Pb, Zn, Cu, Ni, Cr, Co Cd, As, Fe, Mn, Sb, U, Ca, Mg, Na, and K by using atomic absorption technique (see Appendix-I). The data have been given in Table 4.2 and graphically presented in Figures 4.3 and 4.4.

It is clear from the Table 4.2 and Figures 4.3a&b that among the heavy and trace metals of the Sonda coals Copper is ranging from 6 ppm to 32 ppm (average

= 14 ppm), Lead from 8 ppm to 28 ppm (average= 17 ppm), Zinc from 9 ppm to 75 ppm (average= 44 ppm), Nickel from 14 ppm to 46 ppm (average= 34 ppm), Chromium from 7 ppm to 18ppm (average= 11 ppm), Cadmium from 0.10 ppm to 0.4 ppm (average= 0.19 ppm), Iron from 891 ppm to 8421 ppm (average= 5867 ppm), cobalt from 2ppm to 4ppm (average= 2.91 ppm) and Manganese from 0.14 ppm to 0.42 ppm (average= 0.27 ppm).

Among the light elements in Sonda coal, Magnesium varies from 28ppm to 68ppm (average= 43 ppm), Calcium from 85 ppm to 512 ppm (average= 203 ppm), Sodium from 370 ppm to 438 ppm and Potassium from 218 ppm to 340 ppm (average= 289 ppm).

By comparing the heavy and trace elements concentration in the Sonda coals (Fig. 4.4a), it is clear that the iron has the highest concentration with gradual decreasing trend towards Cd (i.e., Fe>Ni>Cu>Pb>Cr>Co>Mn> Cd). While among the light elements in the Sonda coals, sodium has the highest concentration with gradual decreasing trend towards magnesium (i.e., Na>K>Ca> Mg) (Fig. 4.3b) (Fig. 4.4b).

PROXIMATE ANALYSIS OF SONDA COAL

Among the proximate constituents of the Sond coalfield, fixed carbon and ash contents were determined and the results are given in Table 4.3. It is clear from this table that the fixed carbon varies from 39.34 to 44.78% with an average amount of 41.20% whereas the ash contents varies from 9.5 to 12.68% with an average amount of 11.55%.

ULTIMATE ANALYSIS OF SONDA COAL

Among the ultimate constituents of Sonda coalfield, hydrogen, carbon, nitrogen and sulfur contents have been determined and the results are presented in Table 4.3. It is clear from this table that hydrogen is ranging from 5.88 to 7.3% (average = 6.90%), carbon is ranging from 54.78 to 67.45% (average = 61.43%), nitrogen is ranging from 0.23 to 0.40% (average = 0.31%) and sulfur is ranging from 2.00 to 7.00% (average = 4.33%) in the Sonda coals. The Sonda coals are having three times higher amount of sulfur as compare to Thar coals.

COMBUSTION PROPERTIES OF SOND COAL

The calorific values (CV) of the Sonda coals were determined and the results are given in Table 4.3. It is clear from this table that the calorific values of Sonda coals are ranging from 9835 to 11195 btu/lb with an average value of 10301 btu/lb.

Table.4.1 Stratigraphic sequence of exposed rocks in Sonda area (after Thomas et al., 1993).

Age	Unit	Thickness	Lithology
Recent	Alluvium	---- ? ----	Unconsolidated strata, alluvial and Aeolian Deposits of sandstone, siltstone and claystone with limestone and sandstone and pebbles beds
		---- unconformity ----	
Eocene	Laki Formation (Laki limestone, Meting shale, Meting limestone, sonhari beds).	125 meters	Limestone, Clays, Sandstone, Marl, Lateritic clays and Lenticular coal in the Basal part.
		---- unconformity ----	
Paleocene	Lakhra Formation (Upper part of the Ranikot Formation)	100 meters	
Paleocene	Mountain to Landimian	125 meters	Fossiliferous, Limestone, Sandstone, Clay Stone or Shale.
	Bara Formation (lower part of Rani kot Formation)	100 meters	
Domain to Mountain	?	5 meters	Sandstone, shale or Claystone, Coal, devoid of mega fauna.

Table 4.2 Heavy, trace and light elements (in ppm) in Sonda coalfield.

Sample No.	Pb	Zn	Cu	Ni	Cr	Co	Cd	As	Fe	Mn	Sb	U	Ca	Mg	Na	K
SND-1	28	18	32	26	10	3	0.40	1.2	7845	0.23	0.8	2.8	315	68	412	218
SND-2	21	28	31	14	18	2	0.40	1.7	7321	0.14	1.2	3.4	238	60	418	240
SND-3	25	70	9	34	8	2	0.10	1.3	4385	0.24	1.7	3.9	145	30	438	295
SND-4	19	9	18	28	9	4	0.20	1.9	5786	0.31	1.8	2.8	512	38	430	315
SND-5	12	75	12	35	12	3	0.10	1.3	5423	0.41	0.9	2.9	195	41	421	325
SND-6	11	71	8	38	16	3	0.10	0.9	4976	0.22	0.8	4.1	191	43	419	305
SND-7	17	72	6	36	9	3	0.10	0.7	5314	0.31	1.4	3.8	175	39	418	340
SND-8	14	51	9	40	7	3	0.10	1.4	7856	0.25	1.8	2.8	185	31	398	298
SND-9	8	37	8	46	15	4	0.30	2.3	8421	0.42	2.1	3.2	90	62	432	275
SND-10	12	40	12	42	8	2	0.10	1.4	6314	0.18	0.9	4.1	102	28	370	242
SND-11	24	10	11	35	7	3	0.20	1.9	891	0.21	1.7	3.2	85	38	395	330
Average	**17**	**44**	**14**	**34**	**11**	**3**	**0.19**	**1.45**	**5867**	**0.27**	**1.37**	**3.36**	**203**	**43**	**414**	**289**

Table 4.3. Mean values of various proximate and ultimate analysis (in percent) and calorific values (btu/lb) of the Sonda coalfield.

S.No.	Fixed Carbon	Ash	Hydrogen	Carbon	Nitrogen	Sulfur	Calorific value
SND-1	40.32	5.76	7.22	63.23	0.36	4.00	10102
SND-2	41.34	5.23	6.34	64.12	0.32	3.80	10335
SND-3	39.34	6.34	7.02	56.78	0.23	7.00	9835
SND-4	44.78	5.98	7.45	67.45	0.40	4.20	11195
SND-5	39.45	6.34	6.98	61.54	0.28	3.00	9863
SND-6	40.98	5.78	7.11	58.23	0.36	6.40	10245
SND-7	40.12	5.78	7.23	62.59	0.27	2.00	10030
SND-8	39.56	5.12	6.13	54.78	0.31	2.30	9890
SND-9	41.32	6.31	7.23	64.46	0.30	3.00	10330
SND-10	43.78	6.12	7.34	64.23	0.29	5.40	10945
SND-11	42.17	4.76	5.85	58.34	0.29	6.50	10543
Average	**41.20**	**5.77**	**6.90**	**61.43**	**0.31**	**4.33**	**10301**

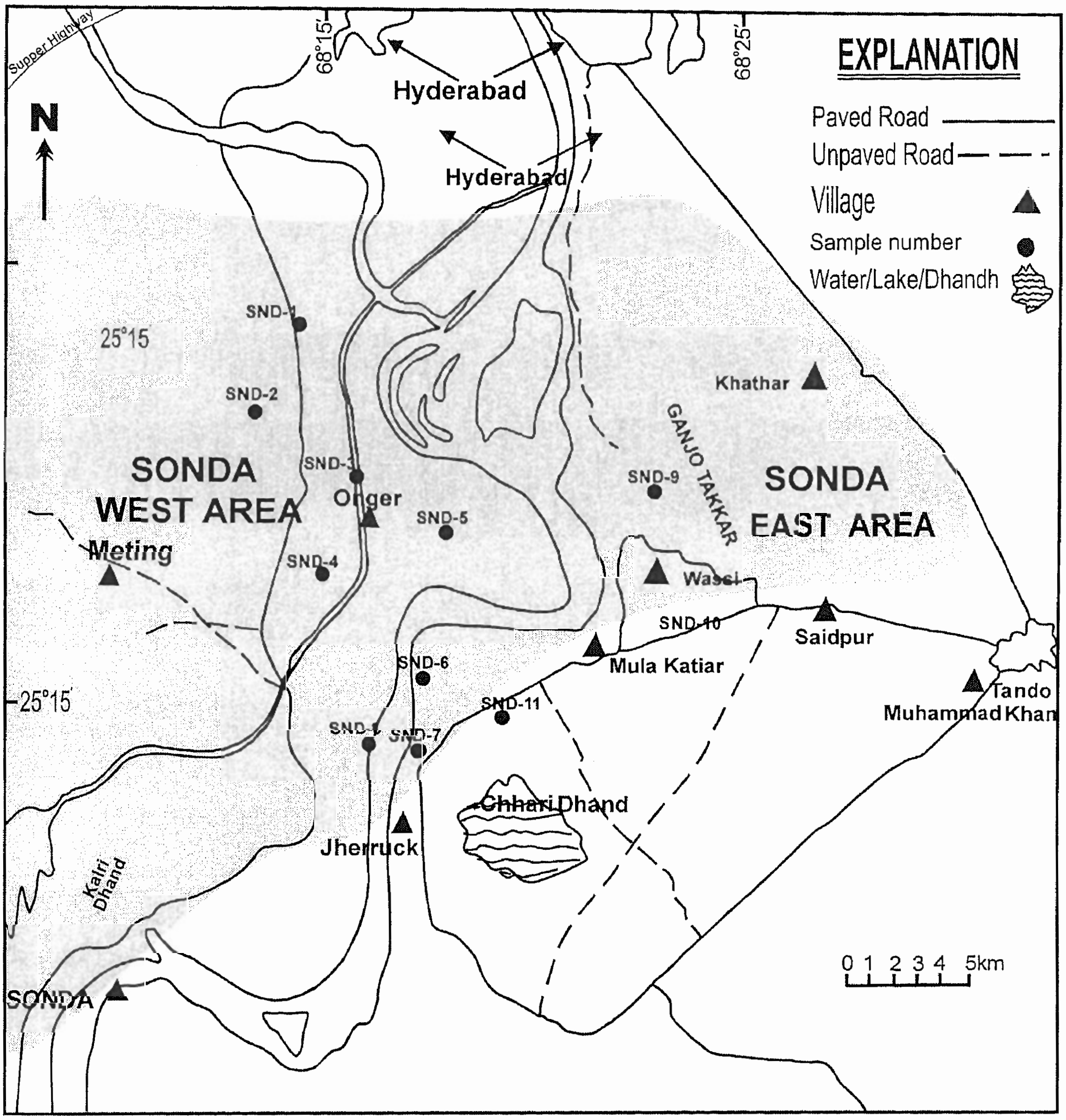


Figure 4.1 Map showing location of Sonda coalfield and the sampling location (Thomas and Khan., 1992).

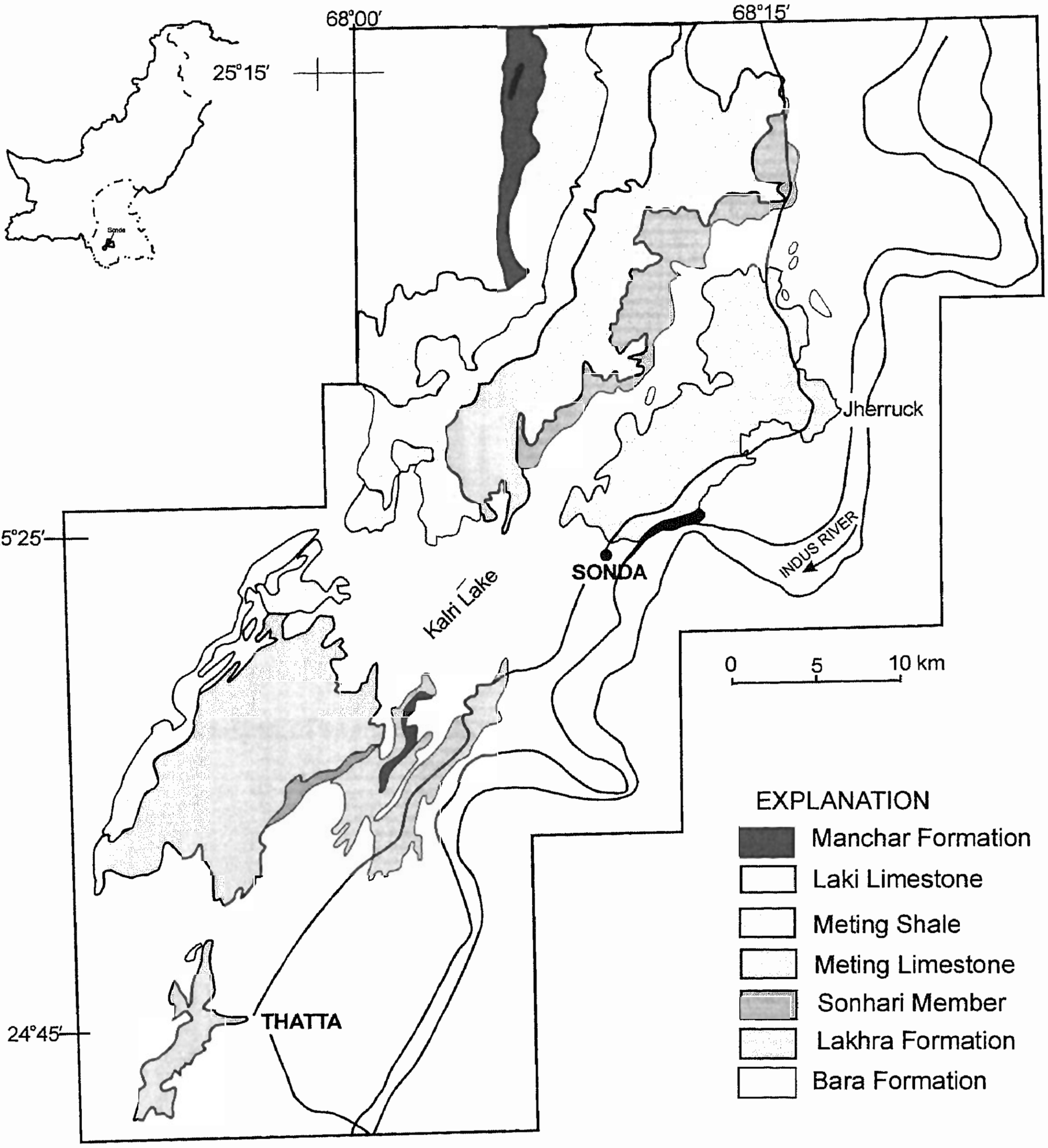


Fig. 4.2 Geological Map of Sonda coalfield (Ahmed et al., 1986).

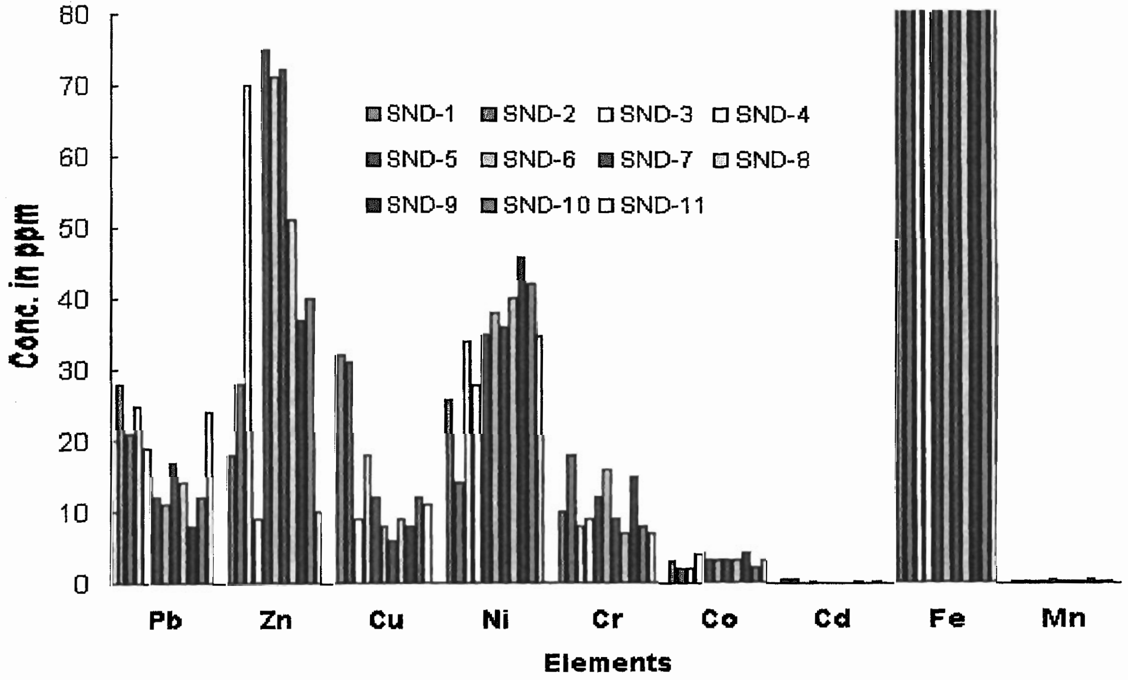


Fig. 4.3a Variation of various heavy and trace elements in the Sonda Coals.

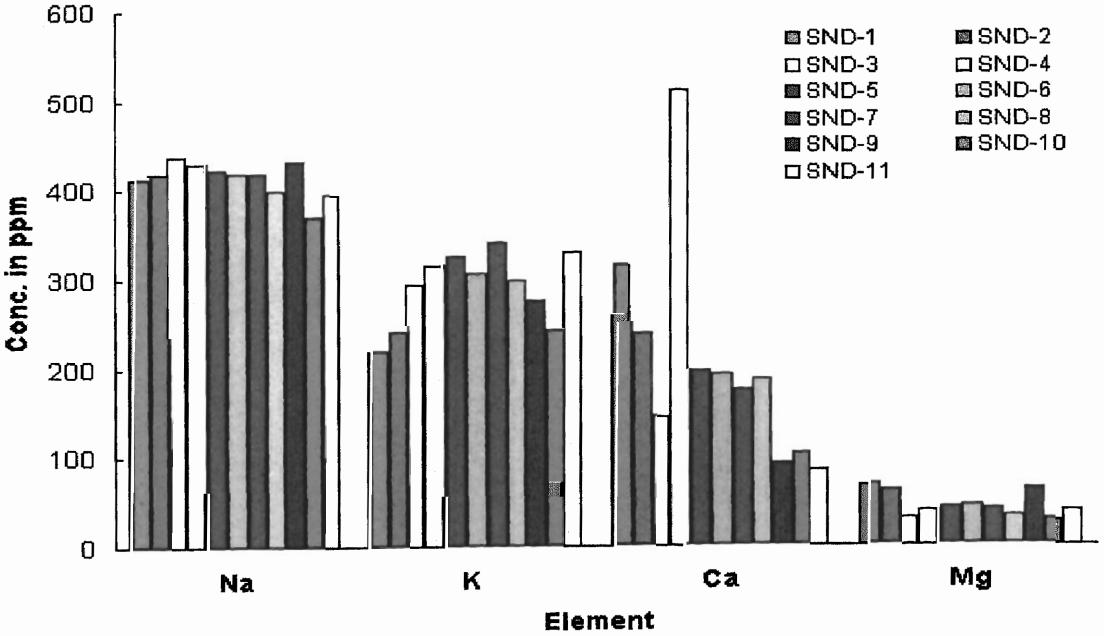


Fig. 4.3b. Variation of various light elements in the Sonda Coals.

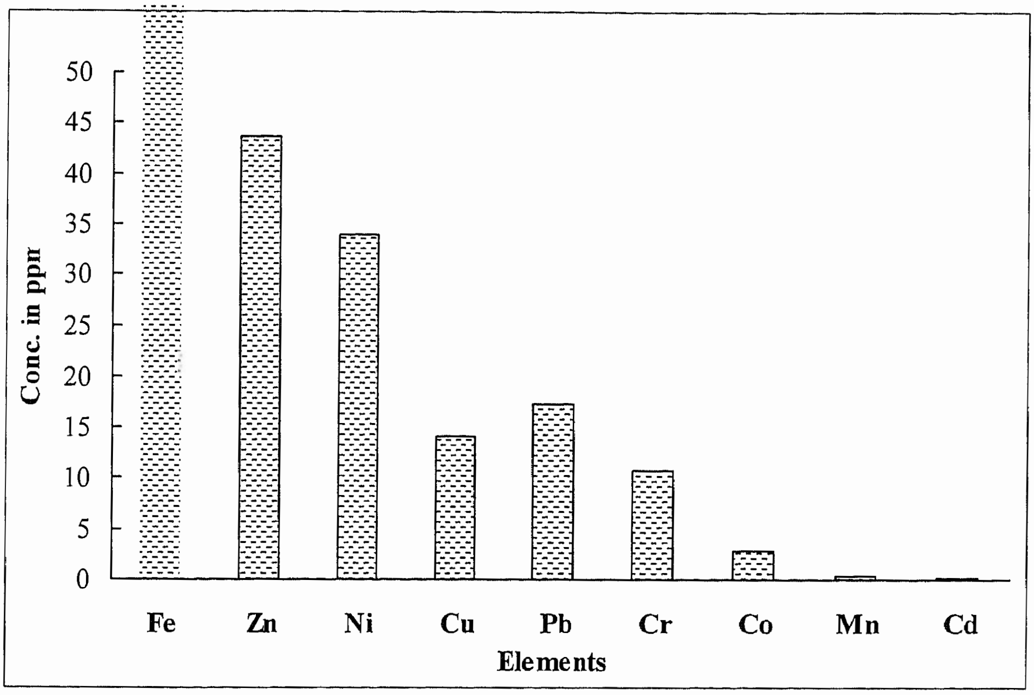


Fig. 4.4a. Inter-elemental comparison of heavy and trace elements in the Sonda caol.

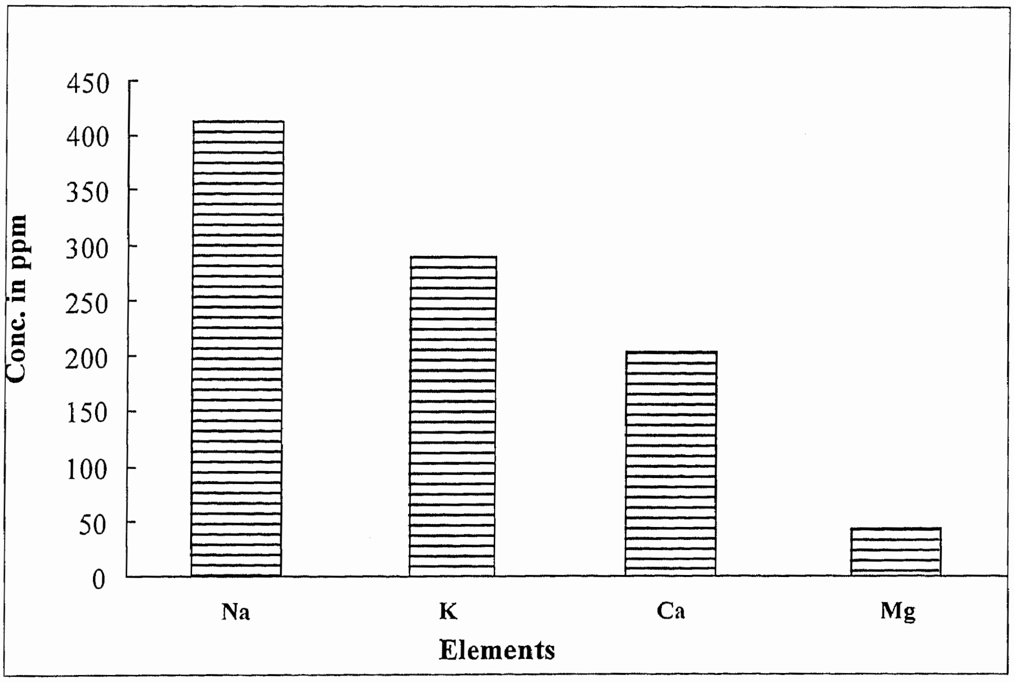


Fig. 4.4b. Inter-elemental comparison of light and trace elements in the Sonda caol.

CHAPTER FIVE

METING - JHIMPIR COALFIELD

INTRODUCTION

The Meting-Jhimpir coalfield lies approximately 125km east of Karachi in the vicinity of Meting-Jhimpir railway stations on the main railway line extending from Karachi to Peshawar. This coalfield covers an area of about 218km in Thatta district. Only one seam with thickness ranging from 0.3 to 1.0 metre is being commercially mined in the area. The total reserves of coal have been estimated as 161 million metric tones. The coal of Meting-Jhimpir is classified as highly volatile bituminous 'C' to high volatile bituminous 'B'

Meting-Jhimpir coalfield is the second oldest coalfield of Sindh, after Lakhra coalfield lying between latitudes 25° 03'- 25° 07' 30'' N and longitudes 68° 02'-68° 08'E and falls in toposheet No. 40 D/1 and 40 C/4. (Fig. 5.1). The railway line between Jhimpir and Meting runs along the western limit of the coalfield whereas the old Karachi-Hyderabad National Highway runs close to the eastern limit of the coalfield. The area is part of tropical coastland dominated by sea breezes, with humid climate. Natural vegetation comprises shrubs, herbs, and grasses (Khan, 2003).

GENERAL GEOLOGY

Meting-Jhimpir coal basin has been developed as small coal basin in between Sonda and Lakhra coalfield. The field covers an area of about 218 km with small lenticular bodies or seams ranging in thickness of 0.2 to 1 meter at the depth of 50 meters in depth.

In Meting-Jhimpir areas, coal is associated with basal part of laterite where a sequence of lateritic clay and shale with beds of arenaceous sandstone of Laki Formation, named as Sonhari Member of Early Eocene age is found. However, the latter sequence of Laki Formation is mainly composed of nodular limestone with shale and sandstone. The Sonhari coal is of poor quality lignite with high Sulfur (Shah, 1987).

The generalized stratigraphic sequence is as follows:

Laki Formation

The formation consists of finely crystalline limestone, lateritic claystone, siltstone and shale. This formation is best developed in the southern part of Kirthar Province. It attains a thickness of 55 meters near Thatta (Fig. 5.2). The lower contact of the formation is unconformable with Lakhra Formation and is marked by Sonhari member. This is divided into members namely Sonhari bed member, Meting limestone and Shale member and Laki limestone member (Schweinfurth and Hussain, 1988).

Sonhari bed Member

The Sonhari Member, comprises of lateritic clays, sandstone and gypsiferous shales. Clays are of various colors ranging from violet to reddish brown, yellowish brown, bluesh grey, off white, grey brown, and buff and are silty, sandy, and highly ferruginous with local patches of fire clay and lenticular lignite beds.

Sandstones are yellowish brown to light brown and dark grey in color, fine to coarse grained and even gritty at places with rounded and subrounded grains and geological map are ferruginous and calcareous. Friable silica sand bands occur in sandstone with variable thickness which gradually passes into buff, reddish, ferruginous sand (Fig. 5.2). Shales are of variegated colours like blackish grey and dirty brown, containing carbonaceous shale with poorly developed lignitic material and pyrite crystals. Small bands of laterite occur on the middle part of the beds. Sonhari member varies in thickness from 10 to 30 meters.

Meting Limestone and Shale Member

It consists mainly of creamy white nodular limestone with subordinate sandstone in the upper part. The shale is grey, greenish yellow, weathering dark rusty brown, ferruginous and gypsiferous. The limestone is thin bedded and arenaceous where as the sandstone is commonly ferruginous (Fig. 5.2). The

Meting Member is about 70 meters thick at the type locality (Waheeduddin et al., 1988).

Laki limestone member

The limestone is light yellowish-grey, white and light-grey, stained yellow to brown and at places it is light grey. It is nodular, hard, resistant and massive and forms cliff containing foraminfera in upper part. It is characterized by steep scarps (Kazmi et al., 1990).

HEAVY, TRACE AND LIGHT ELEMENTS IN METING-JHIMPIR COAL

Thirteen representative samples (one from each coal mine) from Meting-Jhimpir coalfield have been analyzed for the heavy, trace and light elements such as Pb, Zn, Cu, Ni, Cr, Co, Cd, As, Fe, Mn, Sb, U, Mg, Ca, Na and K (see Appendix-I). The results have been shown in Table 5.1 and graphically presented in the Figures 5.3 and 5.4.

It is clear from the table 5.1 and Figure 5.3a that among the heavy and trace elements, the Pb is ranging from 7ppm to 39 ppm (average = 23 ppm), Zn from 12 ppm to 75 ppm (average = 40 ppm), Cu from 6 ppm to 49 ppm (average = 22 ppm), Ni from 8 ppm to 41ppm (average = 23 ppm), Cr from 8 ppm to 41 ppm (average = 12 ppm), Co from 0.05 ppm to 0.55 ppm (average = 0.25 ppm), Cd from 0.1 ppm to 0.4 ppm (average=0.24 ppm), Fe from 724 ppm to 6834 ppm (average = 4500 ppm) and Mn from 0.02 ppm to 0.49 ppm (average = 0.09 ppm).

Among the light elements Mg varies from 40 ppm to 72 ppm (average= 60 ppm), Ca from 145 ppm to 390 ppm (average = 241ppm), Na from 321 ppm to 681 ppm (average = 515 ppm) and K from 104 ppm to 440 ppm (average = 252 ppm) (Table 5.1 & Fig. 5.3b).

By comparing the average concentration of heavy and trace elements in the Meting-Jhimpir coal (Figure 5.4a), the iron has the highest concentration with gradually decreasing trend towards manganese (i.e., Fe>Zn>Pb>Ni>Cu> Cr>Co>Cd>Mn) whereas among the light elements the sodium has highest concentration in average with gradually decreasing trend towards magnesium (Na>K>Ca>Mg) (Fig. 5.4b).

PROXIMATE ANALYSIS OF METING-JHIMPIR COALS

Among the proximate analyses, the fixed carbon and the ash contents in the Meting-Jhimpir coals have been determined and the results are presented in Table 5.2. It is clear from this table that the fixed carbon is ranging from 38.43 to 45.67% with an average amount of 41.11% and the ash contents are ranging from 9.52 to 12.42% with an average amount of 11.05% in the Meting-Jhimpir coalfield.

ULTIMATE ANALYSIS OF METING-JHIMPIR COALS

Among the ultimate constituents of coal, carbon, hydrogen, nitrogen and sulfur contents in the Meting-Jhimpir coals have been determined and the results are given in Table 5.2. It is clear from this table that the carbon varies from 54.78 to 66.23% (average = 60.20%), hydrogen varies from 5.34 to 7.34% (average = 6.82%), nitrogen varies from 0.29 to 0.40% (average = 0.32%) and sulfur varies from 2.00 to 5.20% (average = 3.65%) in the Meting-Jhimpir coalfield. The sulfur contents in the Meting-Jhimpir coalfield are less than the Sonda coalfield but much higher than the Thar coalfield.

COMBUSTION PROPERTIES OF METING-JHIMPIR COALS

Among the combustion properties of coal, the calorific values for the Meting Jhimpir coals have been determined and the results are shown in Table 5.2. It is clear from this table that the calorific values are ranging from 9640 to 11418 btu/lb with an average value of 10143 btu/lb in the Meting-Jhimpir coalfield.

Table 5.1 Heavy, Trace and light elements (in ppm) in the Meting-Jhimpir coalfield.

Sample No.	Location	Pb	Zn	Cu	Ni	Cr	Co	Cd	As	Fe	Mn	Sb	U	Mg	Ca	Na	K
MJ-1	Hidayatullah Coalmines-1	8	75	10	8	22	0.23	0.2	2.3	724	0.34	2.3	0.9	58	170	545	170
MJ-2	Hidayatullah Coalmines-2	29	70	38	9	16	0.09	0.4	3.4	4678	0.04	3.5	0.8	70	220	432	104
MJ-3	Hidayatullah Coalmines-3	32	35	40	22	12	0.05	0.3	1.8	5421	0.49	3.5	1.2	72	161	341	220
MJ-4	Amin coalmine-I	31	26	49	21	8	0.07	0.3	2.9	4301	0.06	5.2	1.8	68	170	574	110
MJ-5	Amin coalmine-II	27	28	51	28	13	0.26	0.4	1.9	4454	0.07	4.8	1.1	60	156	321	290
MJ-6	Amin coalmine-III	25	45	36	31	9	0.37	0.4	3.4	6834	0.07	6.1	1.6	63	230	681	415
MJ-a	Lucky coalmine-I	28	12	6	36	15	0.13	0.4	3.1	4201	BDL	4.3	0.9	59	270	576	302
MJ-D	Lucky coalmine-II	21	32	6	21	9	0.42	0.3	2.8	4451	BDL	3.8	1.2	68	365	601	232
MJ-F	Lucky coalmine-III	7	70	12	12	14	0.17	0.1	3.1	4761	BDL	4.1	1.4	65	315	515	315
MJ-G	Umaid Ali-I	9	13	11	15	16	0.16	0.1	1.9	3485	0.04	2.9	1.1	46	335	525	212
MJ-b	Umaid Ali-II	21	42	13	41	8	0.43	0.1	2.1	4901	BDL	2.7	1.5	42	145	469	201
MJ-c	Umaid Ali-IIII	39	57	9	37	8	0.31	0.1	---	5412	BDL	--	---	40	201	611	270
MJ-E	Umaid Ali-IV	22	12	8	21	9	0.55	00	--	4875	BDL	---	---	72	390	507	440
Average		**23**	**40**	**22**	**23**	**12**	**0.25**	**0.24**	**2.61**	**4500**	**0.09**	**3.93**	**1.23**	**60**	**241**	**515**	**252**

Table 5.2. Mean values of various proximate and ultimate analysis (in percent) and calorific values (btu/lb) of the Meting-Jhimpir coalfield.

S.No.	Fixed Carbon	Ash	Hydrogen	Carbon	Nitrogen	Sulfur	Calorific value
MJ-1	39.34	11.56	6.89	62.78	0.36	2.96	9835
MJ-2	41.34	10.23	6.34	64.12	0.34	2.90	10335
MJ-3	40.23	11.23	7.12	56.78	0.24	3.12	10058
MJ-4	45.67	10.34	7.20	66.23	0.39	2.00	11418
MJ-5	38.90	9.52	7.34	59.89	0.28	5.20	9725
MJ-6	41.46	9.67	7.11	58.23	0.35	4.50	10365
MJ-a	42.34	10.56	6.98	61.67	0.27	4.85	10585
MJ-D	38.56	12.42	6.56	54.78	0.32	2.80	9640
SND-F	42.17	9.87	5.85	57.34	0.29	4.55	10543
MJ-G	38.43	10.68	5.34	62.12	0.32	3.65	9608
MJ-b	40.12	12.13	6.57	59.56	0.35	5.00	10030
SND-c	38.56	11.49	6.34	60.15	0.40	3.52	9640
SND-E	40.34	10.34	5.89	62.34	0.39	4.00	10085
Average	**41.11**	**10.77**	**6.82**	**60.20**	**0.32**	**3.65**	**10143**

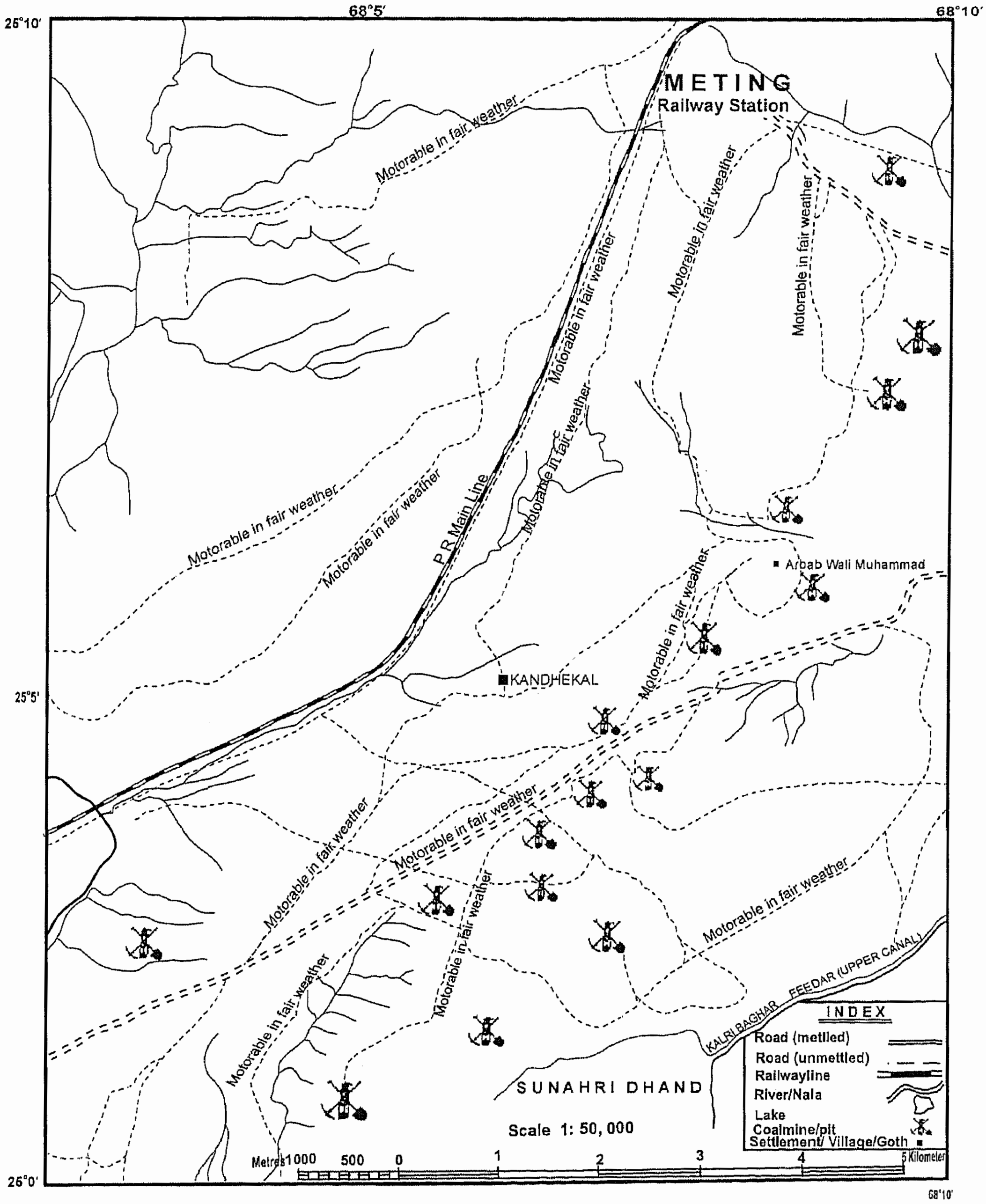


Fig. 5.1 Map of Meting-Jhimpir coalfield showing location and sampling site.

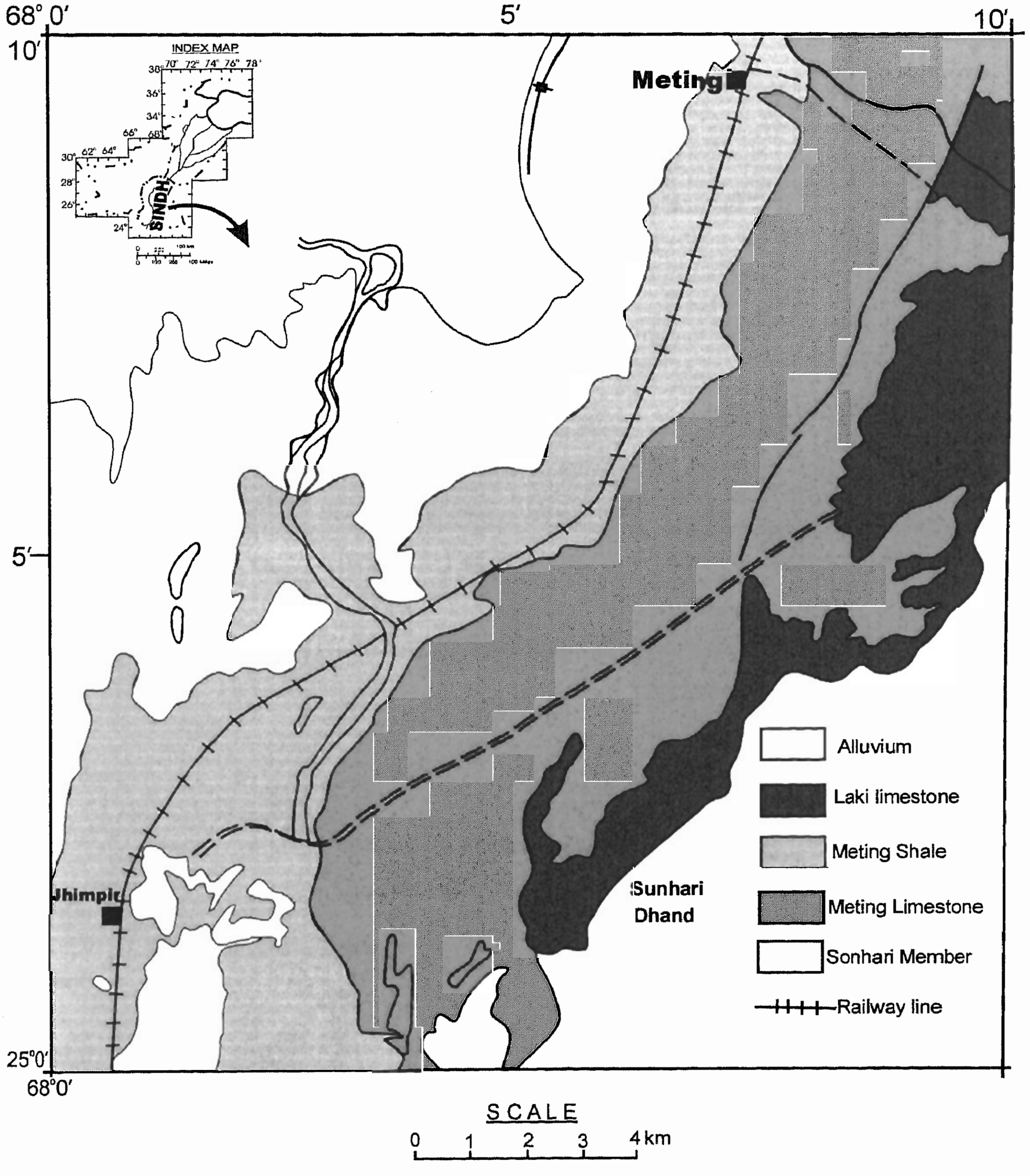


Fig. 5.2 Geological map of Meting-Jhimpir coalfield (Ahmed et al., 1986).

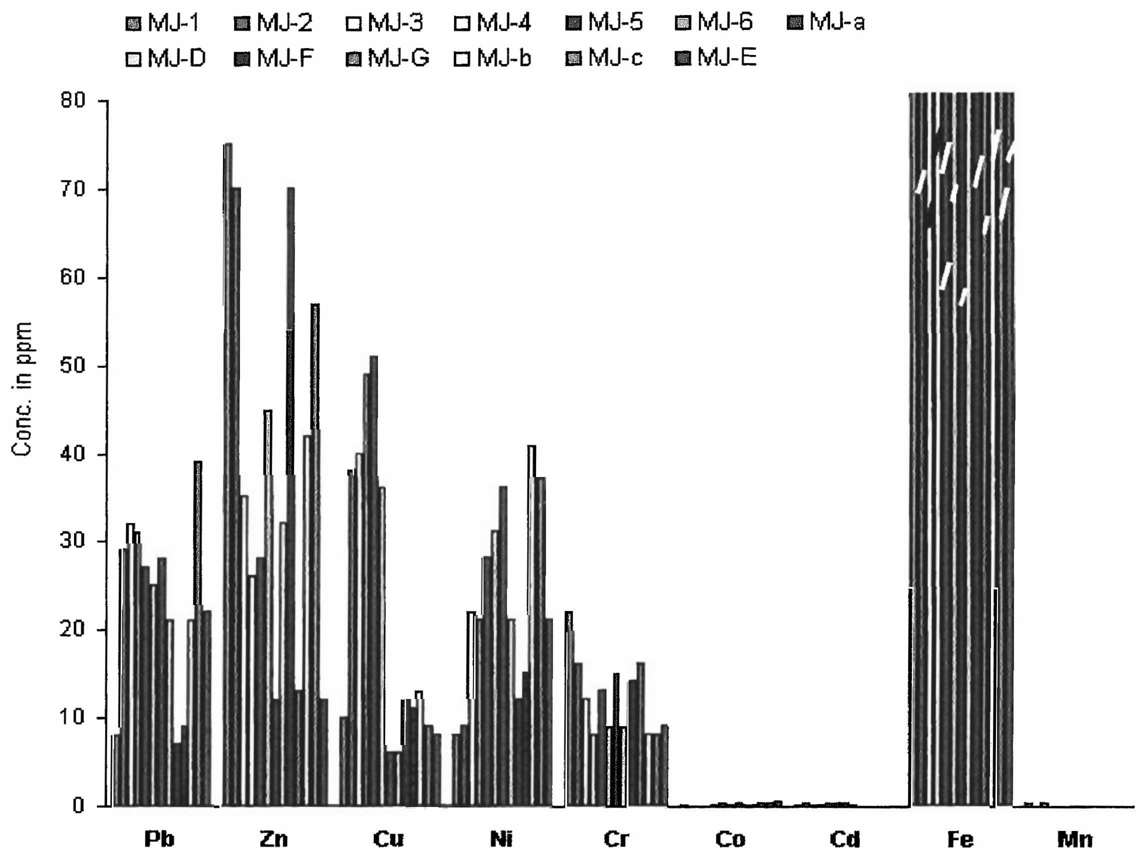


Fig. 5.3a. Variation of various heavy and trace elements in the Meting-Jhimpir coalfield.

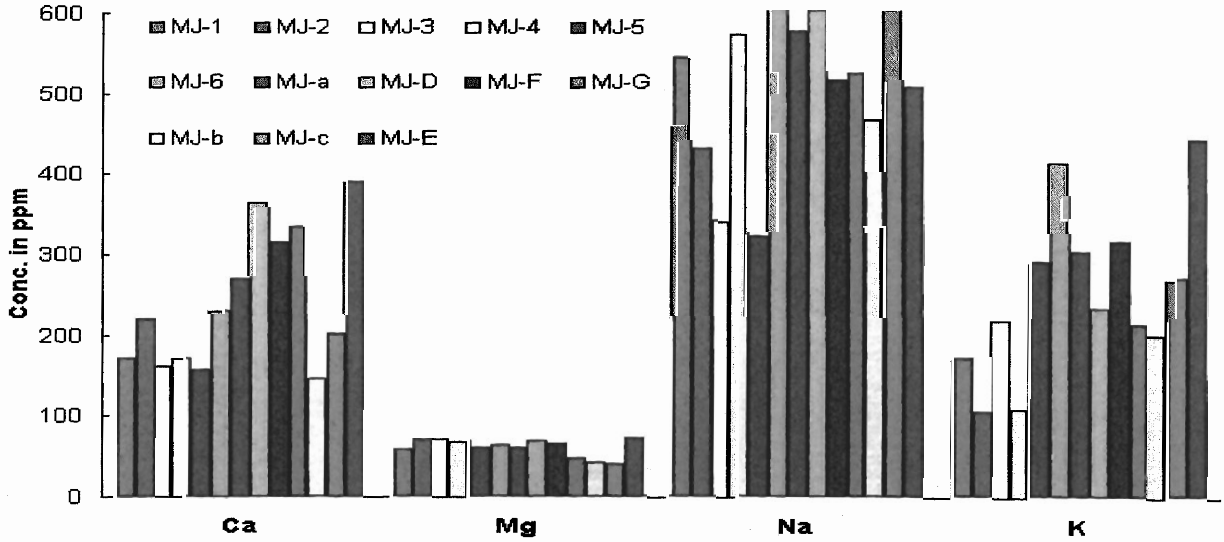


Fig. 5.3b. Variation of various light elements in the Meting-Jhimpir coalfield.

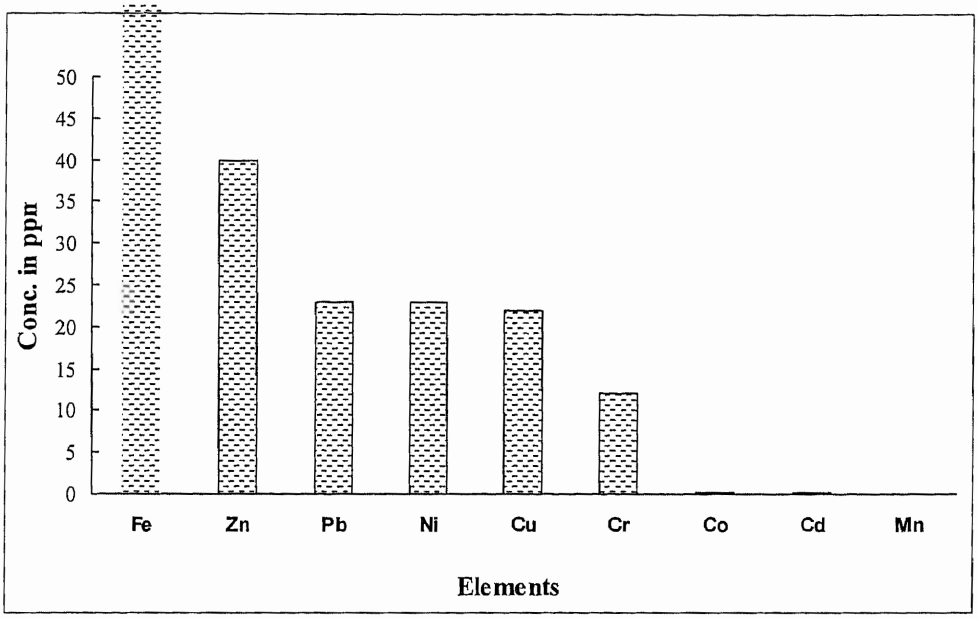


Fig. 5.4a. Inter-elemental comparison of heavy and trace elements in the Meting-Jhimpir coalfield.

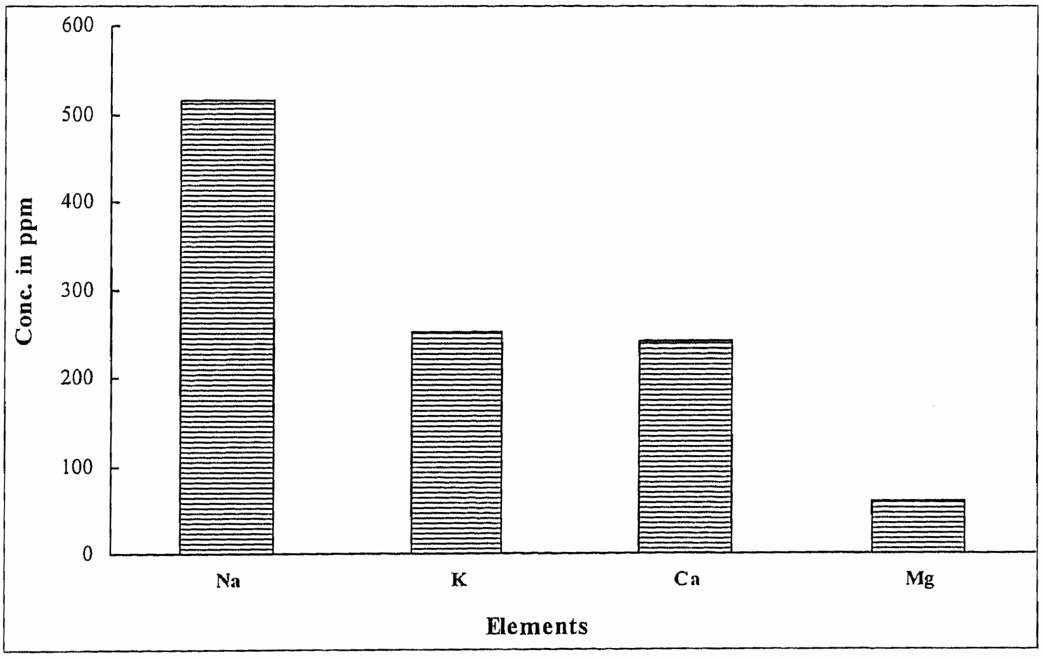


Fig. 5.4b. Inter-elemental comparison of light elements in the Meting-Jhimpir coalfield.

CHAPTER SIX

DISCUSSION AND RECOMMENDATIONS

Coal is geologically formed in three stages, i.e., microbial, biochemical, and geochemical. The microbial stage involves the initial formation of peat and require wet and acidic conditions. It also requires proximity to an area such as rising sea or subsiding land to cover the decomposition of plant material quickly. The biochemical stage begins when sediments suddenly cover the peat. Finally, the start of the geochemical stage occurs as the plant structure becomes compacted and plant material begins to alter. At any point during these three processes of coal formation, the coal bed could have become impregnated with heavy and trace elements (Swaine, 1990).

Heavy, trace and light elements have very diverse origins in coal seams. Swaine (1990) identifies several possible mechanisms by which metals may become included in the coal matrix. For example, the original vegetation that makes the coal matrix could have taken up metals via biological and/or chemical processes. Restricted drainage in peat swamps could also have enhanced the uptake of several heavy and trace metals into the peat during early stages of coal formation. Depending on the chemical characteristics of the elements and the rank of the coal, the individual element is associate with the inorganic and organic constituents of the coal (Raasak, 1985). Elements associated with the inorganic fraction in coal may be present either within the structures or adsorbed onto the surface of the mineral. The organically associated metals/elements are present as chelated ions or ion exchange positions (Rimmer, 1991).

Coal is likely to remain an important part of the world energy supply, largely because it is the most abundant, domestically available fossil fuel. However, it has special problems associated with different parts of the mining, cleaning, transportation, utilization and waste disposal cycle. These problems are reported by a panel of the National Research Council (1980). This report classified the hazardous elements in six categories in coal resource development. These are: (1) elements of greatest concern, (2) elements of moderate concern, (3) elements of minor concern, (4) radioactive elements, (5) elements of less concern but with negligible concentration in coal and coal residue and (6) elements potentially released to the environment. The environment and health risks associated with an intensified use of coal has been discussed in detail by Braunstein et al. (1981). One of the major concern related to the use of coal for electricity production is the release of elements during combustion and the resulting coal combustion product (CCP$_S$), fly ash and bottom ash to the environment. The most threatening health hazard relating to the coal combustion in these coal-fired plants is the air pollution. It includes dust, SO_x, No_x, total suspended particulates (TSP) O_3, CO_2, Hg, Se, F, S, B, As, Pb, Zn, Ni, Cr, Cd, Mo, V, radionuclides and polynuclear aromatics (PNA). These are causing the pulmonary irritation and other sever toxic effects in the human body (Kagey, 1983).

The present study involving geological and geochemical characterization of the Sindh coal fields on the basis of proximate and ultimate analysis and heavy, trace and light elements analysis in the feed coal for the electric generation can, therefore, be used to predict the properties of the fly ash produced and hence the environmental impact of the studied coal can be evaluated.

Coal is a complex combustible rock made up of organic and inorganic minerals components, each containing many elements. Many factors contribute to, and control, how coal and coal combustion products will affect the environment and the aqueous solution that they contact. During combustion, elements present in the organic and mineral components of the coal are redistributed, as a result of high temperatures, into gaseous and solid phase reactions products such as coal combustible products (CCPs). In these products, the elements may be uniformly distributed throughout a fly ash grain, enriched in certain grains or areas of grains, or present as coatings or absorbed onto fly ash grain surfaces. Particle size, coal rank, amount of ash, coal mineralogy and heavy and trace element contents are important variables controlling the combustion and mobility of elements in coal. For fly ash, the distribution and mobility of elements are in flounced by the original composition of the feed coal, the combustion conditions, the size of the fly ash particles and the fly ash mineralogy (Brownfield et al., 2005).

The whole-coal samples of the various coalfields of Sindh have been analyzed for the heavy, trace and light elements and the results are given in Tables 3.2, 4.2 and 5.1 and are discussed in Chapters 3, 4 and 5. The average contents of the heavy and trace elements of the studied coals are compared with the other coalfields of Pakistan and elsewhere in the world. The concentration of Pb, determined in the Sindh coalfields, is the highest in Thar coal (34 ppm) with its decreasing trend in Meting-Jhimpir coal (23 ppm), Lakhra coal (18 ppm) and Sonda coal (17 ppm) (Table 6.1; Fig. 6.1). The average Pb contents of the Sindh coals are compared with other coalfields of Pakistan located in Makarwal, Degari, Shahrigh and Sor-range (Table 6.1; Fig. 6.2). It has been noticed that the Sindh coals are relatively enriched in Pb as compare to the other coals of Pakistan. The average Pb contents of the Sindh coal are also compared with the coals from India, Turkey, China, Canada, U.S. and the average worldwide coal (Table 6.2; Fig. 6.3). Lead in Indian coals has been reported as 118 ppm (Trivedy & Sinha, 1990), in Turkish coals as 6.8 ppm (Palmer et al., 2004), in Chinese coals as 4.4 ppm (Zhang et al., 2004), in Canadian coals as 9.21 ppm (Ripley et al., 1996), in U. S. coals as 65 ppm and average worldwide coal as 25 ppm (Valkovic, 1983). It is clear from this comparison that Sindh coals on average have high concentration of Pb relative to the coals of other countries, except Indian and US coals, which are multifold higher than the Sindh coal.

In the studied Sindh coals, Zn on average in the Thar coal (48 ppm), in Sonda coal (44 ppm) and in Meting-Jhimpir coal (40 ppm) is more or less the same, however, the Lakhra coal has relatively lower amount (24 ppm) of coal (Table 6.1; Fig. 6.1). The average Zn contents of the Sindh coalfields are compared with the other coalfields of Pakistan such as Degari, Shahrigh and Sor-Range of axial belt, Baluchistan and Makarwal of upper Indus Basin, Punjab in Table 6.1 and Figure 6.2. It is noticed that the average concentration of Zn in Thar, Sonda and Meting-Jhimpir is higher than the average concentration of Zn in Sor-Range (20 ppm), Shahrigh (29 ppm), and Degari (16 ppm) whereas the Makarwal coal has higher (104) Zn contents as compare to Sindh coals (Ahmed et al., 2004). The average concentration of Zinc in Sindh coal is also compared with the coals from elsewhere in the world in Table 6.2 and Figure 6.3. It is noted that on average the Chinese coal contains 120 ppm (Zhang et al., 2004), the Canadian coal contains 51.04 ppm (Ripley et al., 1996), the Indian coal contains 38 ppm (Trivedy &

Sinha, 1990), the Turkish coal contains 32 ppm (Palmer et al., 2004) and the U.S. and the average worldwide coals contain 50 ppm of Zn (Valkovic, 1983). In this regard the studied Sindh coals are relatively low in Zn as compare to that of Chinese, Canadian, U.S. and average worldwide coals and are relatively high as compare to that of Indian and Turkish coals (Table 6.2; Fig. 6.3).

Average Cu contents in the Sindh coalfields is high in Lakhra coal (61 ppm) while rest of the coals from Thar, Sonda and Meting-Jhimpir contain 18 ppm, 14 ppm, and 22 ppm of Cu respectively (Table 6.1; Fig. 6.1). By comparing the average concentration of Cu in Sindh coal with other coalfields of Punjab and Baluchistan, it is observed that the coals of Makarwal in Punjab, Degari, Shahrigh and Sor-range in Baluchistan are having lower amount of Cu (Ahmed et al, 2004) as compare to that of the studied coals (Table 6.1; Fig. 6.2). Comparing the average concentration of Cu of Sindh coal with the various countries of the world in Table 6.2 and Figure 6.3, it is noticed that the Chinese coal has 25.5 ppm of Cu (Zhang et al., 2004), the U.S. and average worldwide coals have 15 ppm of Cu (Valkovic, 1983), the Indian coal has 14.5 ppm of Cu (Trivedy & Sinha, 1990), the Turkish coal has 14 ppm of Cu (Palmer et al., 2004) and the Canadian coal has the Cu content of 11.76 ppm (Ripley et al., 1996).

The average concentrations of Ni of various coals in the Sindh coal fields have been compared among each other in Table 6.1 and Figure 6.1 and with the coals of the various countries of the world in Table 6.2 and Figure 6.3. As the Ni contents of the other coalfields of Pakistan are not available, therefore, the comparison is not made. The data indicate that the coals from Turkey have the highest Ni contents (i.e., 64 ppm) (Palmer et al., 2004) while the coals from other countries such as India, China, U.S. have 38.5 ppm, 19.6 ppm and 15 ppm of Ni respectively (Trivedy & Sinha, 1990; Zhang et al., 2004;Valkovic, 1983). However, the coals from Canada have the lowest (10.1 ppm) Ni contents. The Ni contents of the studied coals as a whole are higher than that of Chinese, Canadian, US and average worldwide coals (Table 6.2; Fig. 6.3).

The Sindh coalfields have on average 10 ppm of Cr in Lakhra coal, 20 ppm in Thar coal, 12 ppm in Meting-Jhimpir coal and 11 ppm in Sonda coal (Table 6.1; Fig. 6.1). The Cr contents of the other coalfields of Pakistan are not available, therefore, the comparison is not possible. However, the average Cr contents of the Sindh coals have been compared with that of the various countries of the world in Table 6.2 and Figure 6.3. This shows that the Indian coals have the highest Cr contents (i.e., 50 ppm), Turkish coals have 45 ppm, Chinese coals have 19.8 ppm, U.S. and the average worldwide coals have 10 ppm of Cr while the Canadian coals have the lowest concentration (i.e., 9.32 ppm) of Cr. This suggests that the Sindh coalfields have relatively lower amount of Cr as compare to that of the other countries of the world.

The average concentration of Cd in Sindh coal ranges from 0.24 to 11 ppm (Table 6.1; Fig. 6.1). The Cd contents of the other coalfields of Pakistan are not available therefore, the comparison with the other Pakistani coalfields is not possible. However, its comparison with various coalfields of the world in the Table 6.2 and Figure 6.3 shows that average content of Cd in the Indian coal is 8.5 ppm (Trivedy & Sinha, 1990), in

Chinese coal is 0.1 ppm (Zhang et al., 2004) and in U.S. coal is 1.3 ppm (Valkovic, 1983). It is indicated that the Lakhra coal has relatively high amount of Cd as compare to the colas from other countries of the world.

The average concentrations of Fe in the Thar, Sonda, Meting-Jhimpir and Lakhra coalfields of Sindh are 5008 ppm, 5867 ppm, 4500 ppm and 3192 ppm respectively (Table 6.1; Fig. 6.1). Comparing the Fe concentration of the Sindh coalfields with the other coalfield of Pakistan in Table 6.1 and Figure 6.2, it is noticed that the Sindh coals are comparable with the coals of Degari and Shahrigh but have high Fe contents as compare to that of Makarwal and Sor-range. The Fe concentration of Sindh coal is also compared with the other coals elsewhere in the world in Table 6.2 and Figure 6.3. The Sindh coal is also enriched in iron as compare to the other coals of the world .

The average Co contents of the Sindh coals have been compared among each other and with the other coals elsewhere in the world in Table 6.2 and Figure 6.1 and Table 6.2 and Figure 6.3 respectively. As the Co contents of the other coalfields of Pakistan are not available, therefore, the comparison could not be possible. It is clear from the available data that the Thar coal has relatively high concentration (12 ppm) of Co as compare to the other coals of Sindh and also of the other countries of the world.

By comparing the average Mn contents of the Sindh coals with the other coals of Pakistan (Table 6.1; Fig. 6.2) and elsewhere in the world (Table 6.2; Fig. 6.3), it is clear that the Sindh coals have negligible amount (<1 ppm) of Mn as compare to the coals from the other countries of the world whereas the U.S. coals have the highest amount (120 ppm) of Mn.

The average light elements (i.e., Ca, Mg, Na, K) in the Sindh coals are compared with the other coalfields of the country in Table 6.1 and Figure 6.2. It is clear from the data that the Sindh coals are having relatively lower amount of the light elements.

The coal samples of various Sindh coalfields (i.e., Thar, Sonda and Meting-Jhimpir) have been analyzed for proximate (fixed carbon and ash contents) and ultimate (hydrogen, carbon, nitrogen and sulfur) components of coal along with calorific values (Tables 3.3, 4.3 and 5.2). According to Thomas (2002), the total sulfur contents in the steam coal used for electricity generation should not exceed (0.8-1.0%), for cement industry a total sulfur content up to 2.0% is acceptable and a maximum of 0.8% total sulfur content is required for the coking coal, because higher values affect the quality of steel. The studied coals of the Sindh coalfields have high amount of total sulfur (Table 3.3, 4.3 & 5.2). The total sulfur contents in the Thar coal are ranging from 0.44 to 4.00% (average = 1.17%), in the Sonda coal it is varying from 2.00 to 7.00% (average = 4.33%) and in the Meting-Jhimpir coal it is ranging from 2.00 to 5.20% (average = 3.65%). In this regard the Thar coal is having relatively low amount of total sulfur on average and therefore, can be used for industrials purposes. But the coals of Sonda and Meting-Jhimpir are having total sulfur contents higher than 2%. The coals from these coalfields may have higher SO_2 emission as flue gases to the environment and may also cause corrosion and fouling of boiler tubes.

In order to estimate the amount of SO_2 produced daily from the power station, it is necessary to know calorific value, hydrogen and moisture contents of the coal and the station heat rate (Thomas, 2002). According to World Bank Group (1998), a 500 Mwe plant using coal with 2.5% sulfur, 16% ash, and a calorific value of 12898 btu/lb will emit each day: 200t SO_2, 70t NO_2, 500t fly ash, 500t solid waste and 17 (GWh) of thermal discharge. As the Sindh coal on average is having more than 2.5% sulfur, therefore, the SO_2 release will be more than 200t per day if 500t Mwe of Sindh coals are used everyday in the power generation plant. This suggest that there would be the higher amount of SO_2 release to the atmosphere during combustion of the studied coals. The Sindh coals, especially from Sonda and Meting-Jhimpir coalfields, therefore, need to be desulfurized before their use in power generation plants and also in the other industries of the region.

Nitrogen content of coal is significant particularly in relation to atmospheric pollution. Upon combustion of the coal, nitrogen helps to form oxides (NO_X) which may be released as flue gases and thereby pollute the environment. Among the NO_X emissions from the power plants is nitrous oxide (N_2O); this gas has a significant effect on the atmosphere, it is a stronger absorber of infrared radiation and is considered as major contributor (20%) to ozone depletion. The coal should not have nitrogen content more than 2% because of these NO_X emissions (Thomas 2002). The nitrogen contents of the Sindh coal from all the coalfields (i.e. Thar, Sonda and Meting-Jhimpir) are within the permissible limits (Table 3.3, 4.3 and 5.2) and, therefore, have no environmental impact as far as the combustion of Sindh coal and NO_X emission is concerned.

The recommended maximum ash contents for the steam coals are up 20% and for coking coals a maximum of 10-20% is recommended (Thomas, 2002). The Sindh coals are having <11% of ash in all the three coalfields (Table 3.3, 4.3 and 5.2). This coal, therefore, may not have any drastic effects on efficiency of the blast furnace.

Mineralogy of the selected whole-coal samples of Thar, Sonda and Meting-Jhimpir coalfields was determined by X-ray Diffraction method (See appendix-1). XRD patterns (Fig. 6.4) of the majority of the Thar coal shows quartz (SiO_2), kaolinite ($Al_2Si_2O_5(OH_4)$) as the dominant mineral phases while calcite ($CaCO_3$), dolomite ($CaMgCO_3$), muscovite [$KAl_2(OH)_2(AlSi_3O_{10})$], illite [$KAl_2(OH)_2AlSi_3(O,OH)_{10}$] and pyrite ($FeS_2$) are also present in lesser amount. The XRD patterns of the Sonda coals (Fig. 6.5) and the Meting-Jhimpir coals (Fig. 6.6) suggest that the Quartz and kaolinite are the dominant while calcite, dolomite and pyrite are the subordinate mineral phases in both type of coals. The mineralogy of the Sindh coalfields suggests that there seems to be two mineral suites in the Sindh coals: a primary detrital suite and an authigenic suite. The primary detrital suite consisted of quartz and muscovite while authigenic mineral suite consisted of kaolinite, calcite, dolomite, illite and pyrite. The detrital minerals (i.e., quartz and muscovite) may have been derived from the basement rocks that have very high quartz and muscovite contents. There could also be some input from the plant derived silica in the marine environment or the quartz overgrowth on the beta-form of quartz grains. Kaolinite may have been present as plant-cell fillings. The carbonates (calcite and dolomite) occur within coal mercerals and are usually associated with clay minerals and appears to be as diagenetic (syngenetic) minerals. Pyrite may be present as secondary phase probably formed as a result of sulfur reduction of marine environment.

Sequential leaching techniques are used to develop models to predict the behavior of elements during combustion of coal and the potential leaching of coal combustion products (CCPs). This requires quantitative data on the modes of occurrence of those elements in the feed coal. Such data can also be beneficial for evaluation of the environmental impacts, technological impacts and economic byproduct potential of coal and CCPs. Sequential leaching experiments provide data that determine modes of occurrences of trace elements in feed coal, fly ash and bottom ash (Brownfield, 2005). The sequential leaching analysis were performed on the Sindh coal and the chemical data were processed to obtain the percentage for each elements leached by four solvents and the results are shown in Table 6.3 and Table 6.4. In this experiment sequence of solvent was selected (see appendix-1), so that (1) exchangeable cations, water soluble compounds and some carbonates would be removed by $NH_4C_2H_3O_2$; (2) cations associated with carbonates, mono-sulfides, iron oxides and chelated organic compounds would be removed by HCl; (3) elements associated with silicates would be removed by HF and (4) elements associates with disulfides, especially pyrite and marcasite, would be removed by using HNO_3 (Brownfield, 2005). The sample residue present following the sequential leaching procedure contains the insoluble elements associated with the organic matter and the insoluble or shield minerals (Brownfield, 2005). It is clear from the Tables 6.3 and 6.4 that 40 percent or more of the elements Pb, Zn, Cu, Cd, Co and Mn are associated with HCl-soluble compounds (Table 6.3) such as carbonates, mono-sulfides, oxides, phosphate and sulfates where as more than 30 percent of the elements Zn, Ni, Cr, Cd and Co are associated with insoluble phases or organic shielded matter. 60 percent of Fe is associated with HNO_3 soluble compounds while some portions (5-15%) of all the elements are associated with HF and HNO_3 soluble compounds including clays and other silicates and pyrite and other disulfides. This suggests that Pb, Zn, Cd and Cu in these coals mainly occur in mono-sulfides or oxides and carbonates whereas Co and Mn generally occur as oxides. Fe is mainly occurring in the form of disulfides (i.e., pyrite and marcasite). Ni and Cr generally occur as insoluble organically shielded matters, while Zn, Co, and Fe also occur as insoluble organically shielded matters.

One of the most serious effects of the underground coal mining has been the escape of polluted water from the coal mine workings. These acid and alkaline waters pollute waterways and surrounding land, rendering the area unusable and sterile. The acid mine drainage is the principal cause of contaminated water arising from coal mining. It result from the exposure of sulfide minerals, particularly pyrite, to water and oxygen during and after mining or in piles of mine waste. The presence of pyrite and marcasite (both FeS_2) as expected in the studied Sindh coalfields can cause sever problems during the mining of these coals due to their reaction with atmospheric oxygen. These may produce the oxidation products such as ferrous and ferric sulfates, sulfuric acid and hydrated ferric oxide. With the exception of ferric oxide, these products are soluble in water and in turn may react with clays and carbonate minerals to form aluminum, calcium, magnesium and other sulfates. This ferruginous water that flow in the presence of air in mine workings may cause the precipitation of ferric oxide which could result in the extensive red / orrange staining of walls and equipments in the underground working and may also cause the contamination of the aquifers of the area. There are also chances that acid drain water in coal mining in the Sindh coalfields may excavange various water soluble toxic organic compounds of the heavy and trace metals and hence contaminate the underground water when the underground mining of these coal deposits will start in full swing in future. The contaminated water may cause various type of diseases in the inhabitants, especially those working in the underground mines and living around the Sindh coalfields. A diseases known as Balkan endemic nephropathy, a kidney diseases that leads to death, has already been reported in the villages situated on alluvial deposits overlaying the lignite coal elsewhere in the world (Finkelman et. al., 1991).

The concentration of trace elements in ash is dependent upon particle size. Increasing concentrations of trace elements are correlated with the decreasing particle size (Thomas, 2002). The trace elements of the feed coal is variably distributed among the bottom ash, fly ash and flue gas in the power generation plant (Valkovic, 1983). The fly ash has relatively high concentration of trace and heavy elements, however, chlorine, chromium, mercury, nickel, selenium and sulfur are in high percentage in the flue gas fraction (Valkovic, 1983; Thomas, 2002). By considering the ultimate, proximate and heavy and trace elements, with the exception of sulfur, the Sindh coal, especially the Thar coal fields, can be considered as of good quality as far as its use in the power generation plants or in other industries is concerned. However, relatively high concentration of sulfur and certain heavy metals such as Pb, Zn, and Ni may have environmental problems during mining and combustion processes. There are sever health effects associated with

S, Pb, Zn, and Ni in coal mining and combustion. Sulfur dioxide produced during combustion has been used as one of the major indices of air pollution. The major physiological response to SO_2 is one of increased airway resistance and causing lower reparatory tract infection, impairment and irritation of eyes, throat and lungs (Goldstein, 1979; Waldbott, 1978). Pb, Zn and Ni are the elements of greatest and moderate concern during coal mining to combustion process and should be dealt with seriously (National Research Council, 1980). These may predominate in small particles emitted from high temperature combustion sources (Braustein et al., 1981). The environmental problems related with these particulates in Sindh colas can be overcome if the particulates emission level of the power generation plants, which will be running on these coals in future, should be substantially reduced. In this regard necessary measure should be taken by following the guide-lines proposed by World Bank Group (1998).

Table 6.1. Comparison of the various heavy, trace and light elements of Sindh coals with the available data of other coals of Pakistan.

Metals	Thar coal	Sonda coal	Meting-Jhimpir Coal	Lakhra coal	Makarwal coal	Degari coal	Shahrigh coal	Sor-range coal
Pb	34	17	23	18	9	9	11	7
Zn	48	44	40	24	104	16	29	20
Cu	18	14	22	61	10	8	18	8
Ni	41	34	23	14	NR	NR	NR	NR
Cr	20	11	12	10	NR	NR	NR	NR
Cd	0.31	0.27	0.24	11	NR	NR	NR	NR
Co	12	3	0.25	NR	NR	NR	NR	NR
Fe	5008	5867	4500	3192	2170	5580	6479	1750
Mn	0.67	0.27	0.09	NR	13	53	204	22
Ca	250	203	241	NR	3420	12420	NR	8765
Mg	76	43	60	NR	440	178	NR	345
Na	573	414	515	NR	360	1871	324	198
K	210	289	252	NR	56	140	170	64

NR = Not reported.

The data of Makarwal, Degari, Shahrigh and Sor-range coalfields is from Ahmad et al. (2004).

Table 6.2. Comparison of various heavy and trace elements (in ppm) of Sindh coalfields with the coals of various countries of the world.

Coalfiled/country	**Pb**	**Zn**	**Cu**	**Ni**	**Cr**	**Cd**	**Co**	**Fe**	**Mn**
Thar coal	34	48	18	41	20	0.31	12	5005	0.67
Sonda coal	17	44	14	34	11	0.19	3	5864	0.27
Meting-Jhimpir coal	23	40	22	23	12	0.24	0.25	4500	0.09
Lakhra coal	18	24	61	14	10	11	NR	3192	NR
Indian coal[1]	118	38	14.5	38.5	50	8.5	3.5	NR	NR
Turkish coal[2]	6.8	32	14	64	45	0	7	2000	81
Chinese coal[3]	4.4	120	25.5	19.6	19.8	0.1	6.4	1100	62
Canadian coal[4]	9.21	51.04	11.76	10.1	9.23	NR	3.5	3537	47.81
US coal[5]	65	50	15	15	10	1.3	7	1600	120
Average worldwide coal[3]	25	50	15	15	10	NR	5	1000	50

NR = Not reported.

[1] Trivedy and Sinha (1990);

[2] Palmer et al. (2004);

[3] Zhang et al. (2004);

[4] Ripley et al. (1996);

[5] Valkovic (1983)

Table 6. 3. Elemental concentration data for selected elements from sequential leaching experiments from Sindh coalfield samples.

Elements	Pb	Zn	Cu	Ni	Cr	Cd	Co	Fe	Mn
Original concentration (ppm)									
Sindh coal feed	29	41	19	37	13	0.22	3	4895	0.45
Percent leached by CH_3COONH_4									
Sindh coal feed	0	1	0	5	1	0	1	0	10
Percent leached by HCl									
Sindh coal feed	80	40	80	20	10	80	40	10	80
Percent leached by HF									
Sindh coal feed	10	10	10	5	10	10	5	10	5
Percent leached by HNO_3									
Sindh coal feed	10	15	10	5	10	10	5	60	5
Percent unleached									
Sindh coal feed	0	34	0	65	69	0	49	20	0

Note: Original concentration (in ppm) are presented on a whole-coal basis; solvent data presented in percent leached by each solvent.

Table 6.4. Modes of occurrence data for selected elements for feed coal samples from Sindh coalfileds.

Elements	Exchageable cations, water soluble compounds	Pyrite and other disulfides	Silicates	Carbonates, arsenenates, iron oxides, monosulfides, phospahtes and sulfates	Organic association or insoluble and shielded minerals
Pb	0	10	10	80	0
Zn	1	15	10	40	34
Cu	0	10	10	80	0
Ni	5	5	5	20	65
Cr	1	10	10	10	69
Cd	0	10	10	40	40
Co	1	5	5	40	49
Fe	0	60	10	10	20
Mn	10	5	5	90	0

Note: Mode of occurrence data presented in percent leached by each solvent's compounds and (or) mineral association. NH4 = water soluble compounds, some carbonates, and elements bonded onto exchangeable sites; HCl = carbonates, iron oxides, monosulfides, phosphates, and chelated organic compounds; HF = silicates; HNO3 = disulfides, especially pyrite.

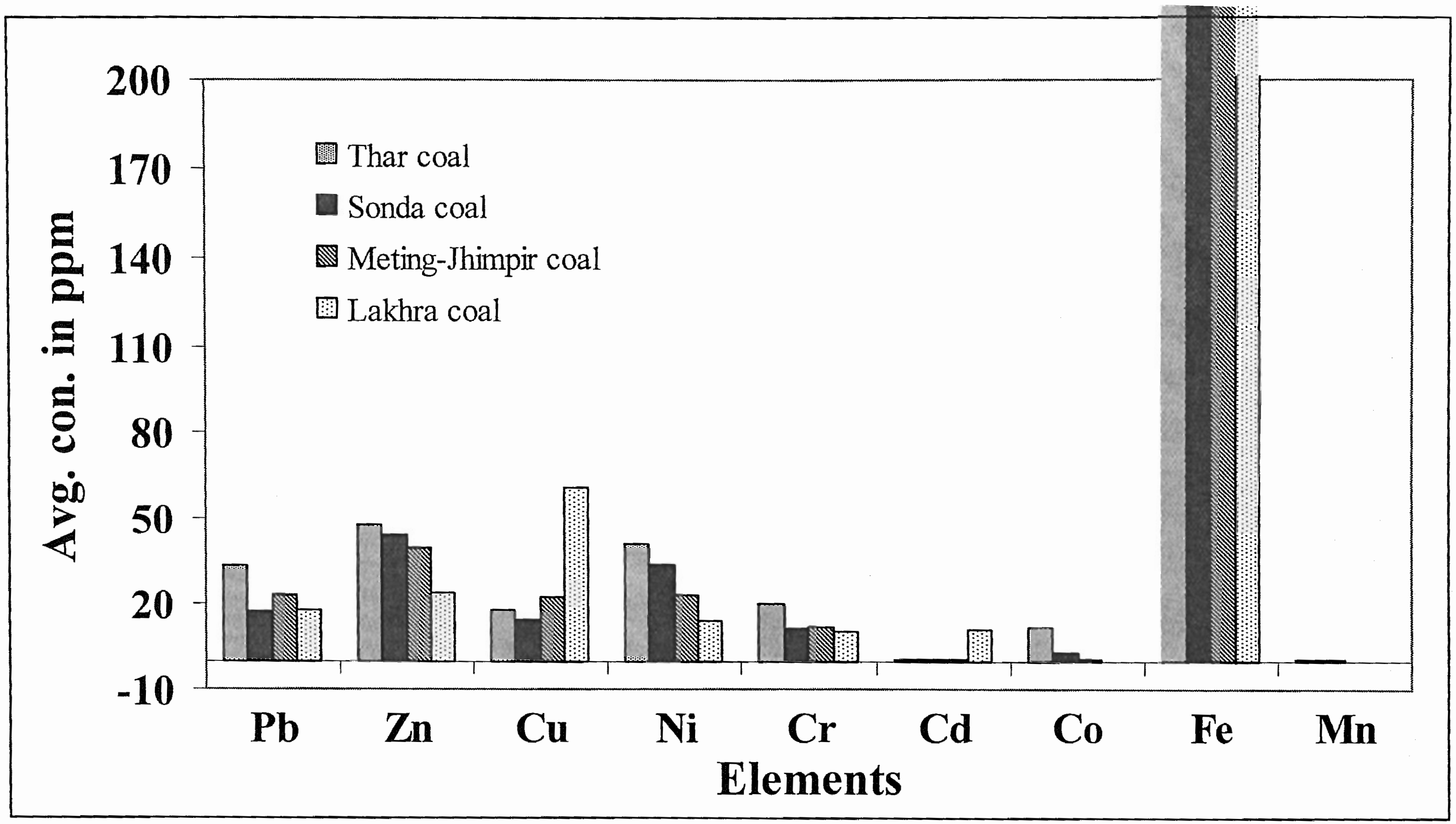


Fig. 6.1. Comparison of the heavy and trace elements of various coalfields of Sindh.

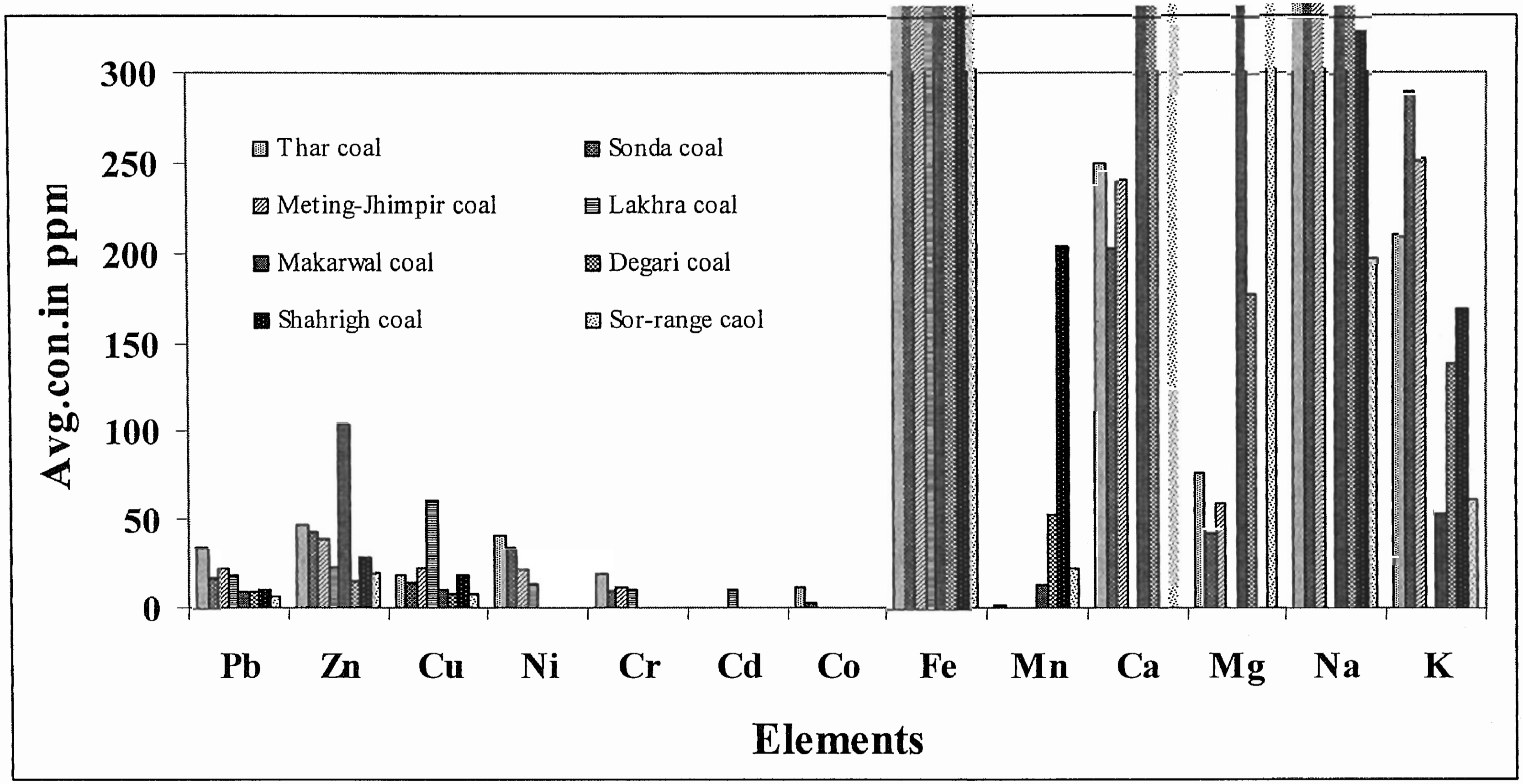


Fig. 6.2. Comparison of the various heavy, trace and light elements of Sindh coals with the available data of other coals of Pakistan.

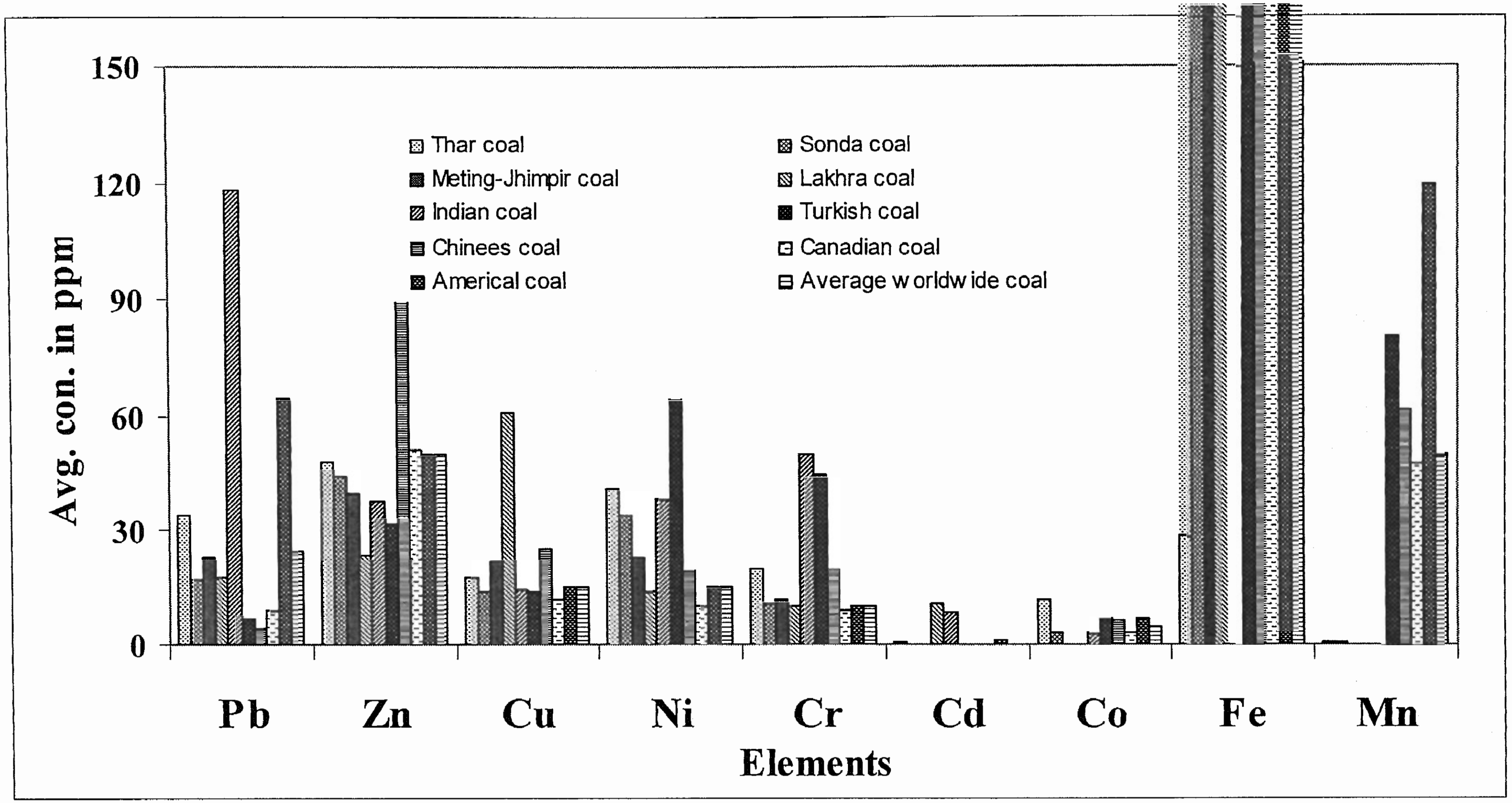


Fig. 6.3. Comparison of heavy and trace elements of Sindh coal with the coal from other countries of the world.

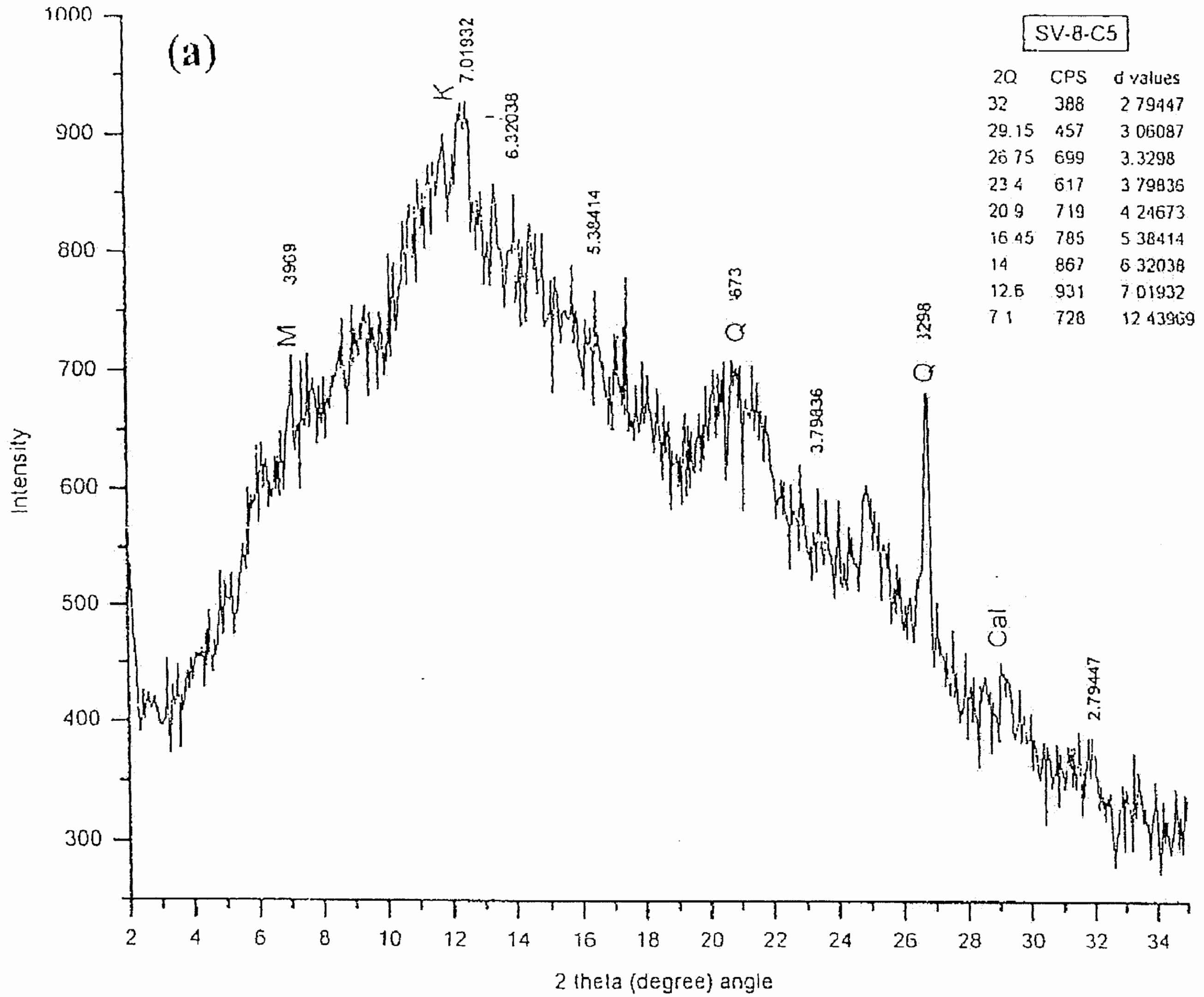
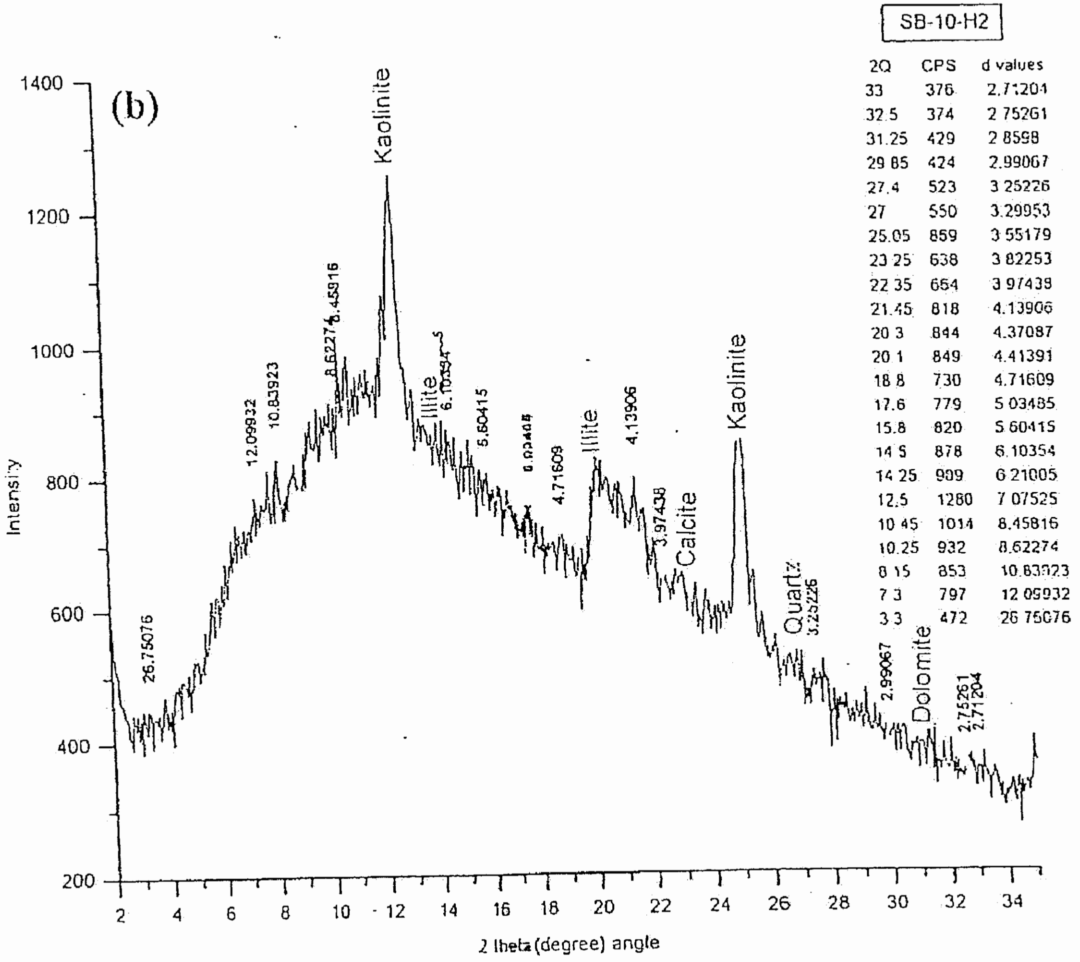
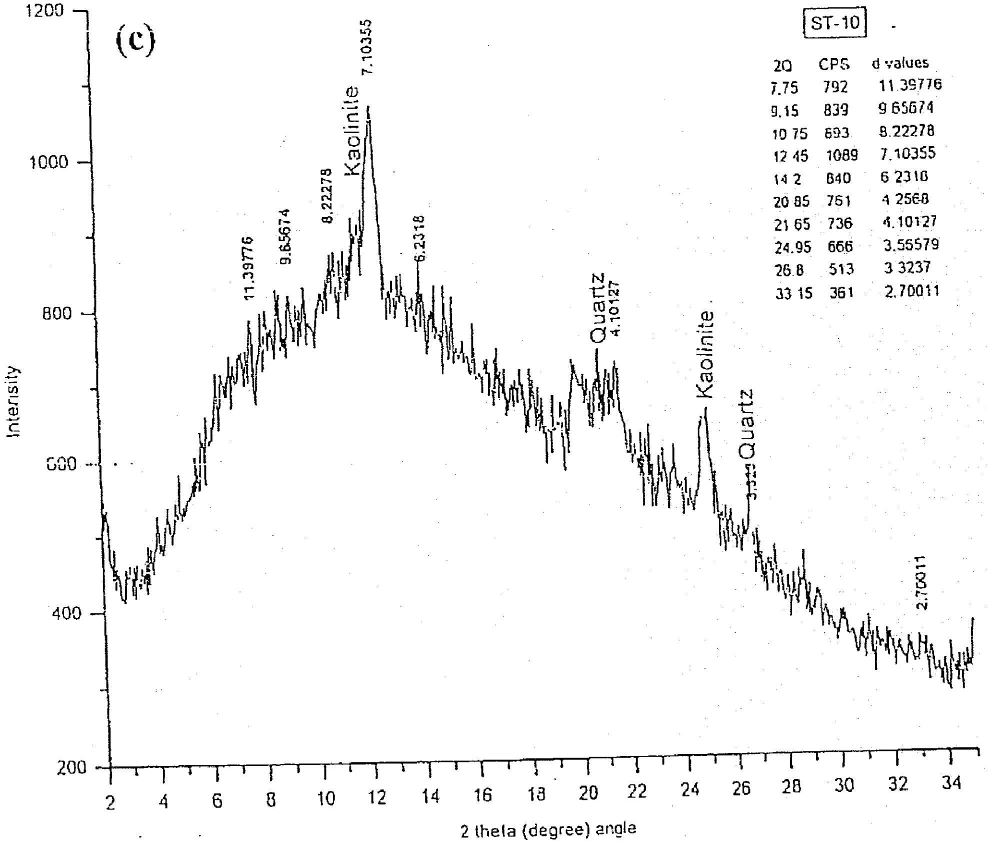


Fig. 6.4 (a-d) X-ray diffrectogram of the coal samples collected from Thar coalfield.



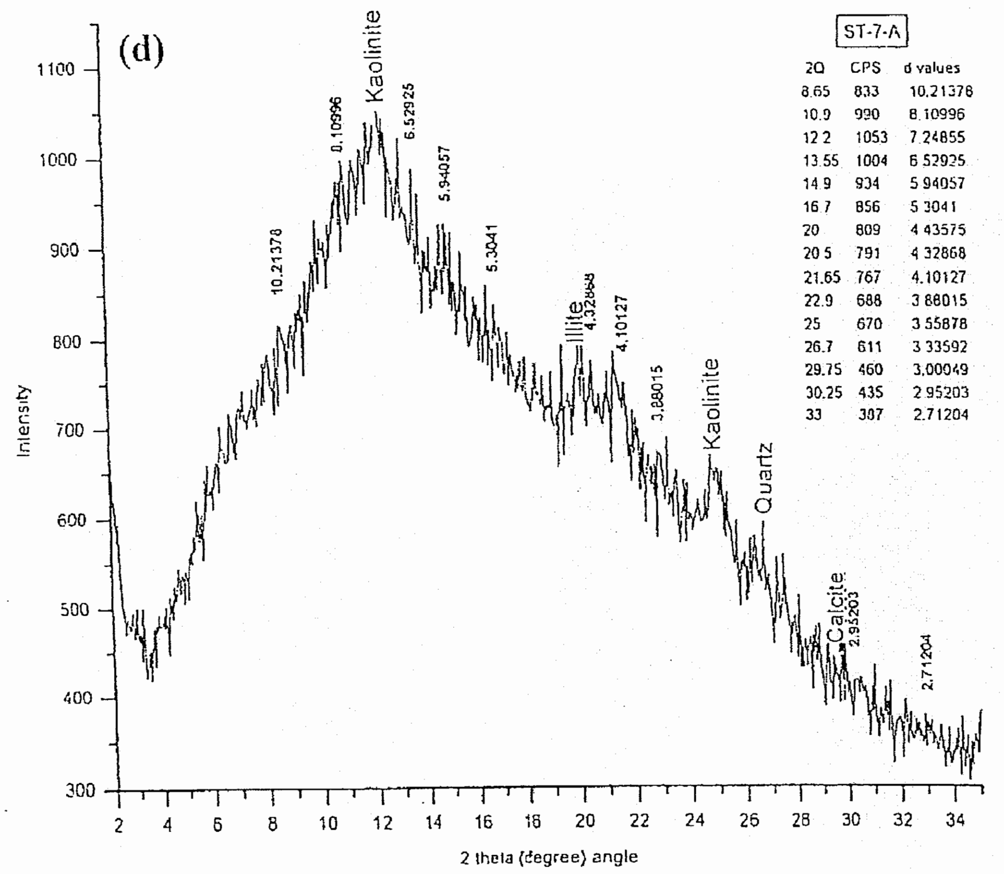
2Q	CPS	d values
33	376	2.71204
32.5	374	2.75261
31.25	429	2.8598
29.85	424	2.99067
27.4	523	3.25226
27	550	3.29953
25.05	859	3.55179
23.25	638	3.82253
22.35	654	3.97439
21.45	818	4.13906
20.3	844	4.37087
20.1	849	4.41391
18.8	730	4.71609
17.6	779	5.03485
15.8	820	5.60415
14.5	878	6.10354
14.25	909	6.21005
12.5	1280	7.07525
10.45	1014	8.45816
10.25	932	8.62274
8.15	853	10.83923
7.3	797	12.09932
3.3	472	26.75076

Fig. 6.4 (b) X-ray diffrectogram of the coal samples collected from Thar coalfield.



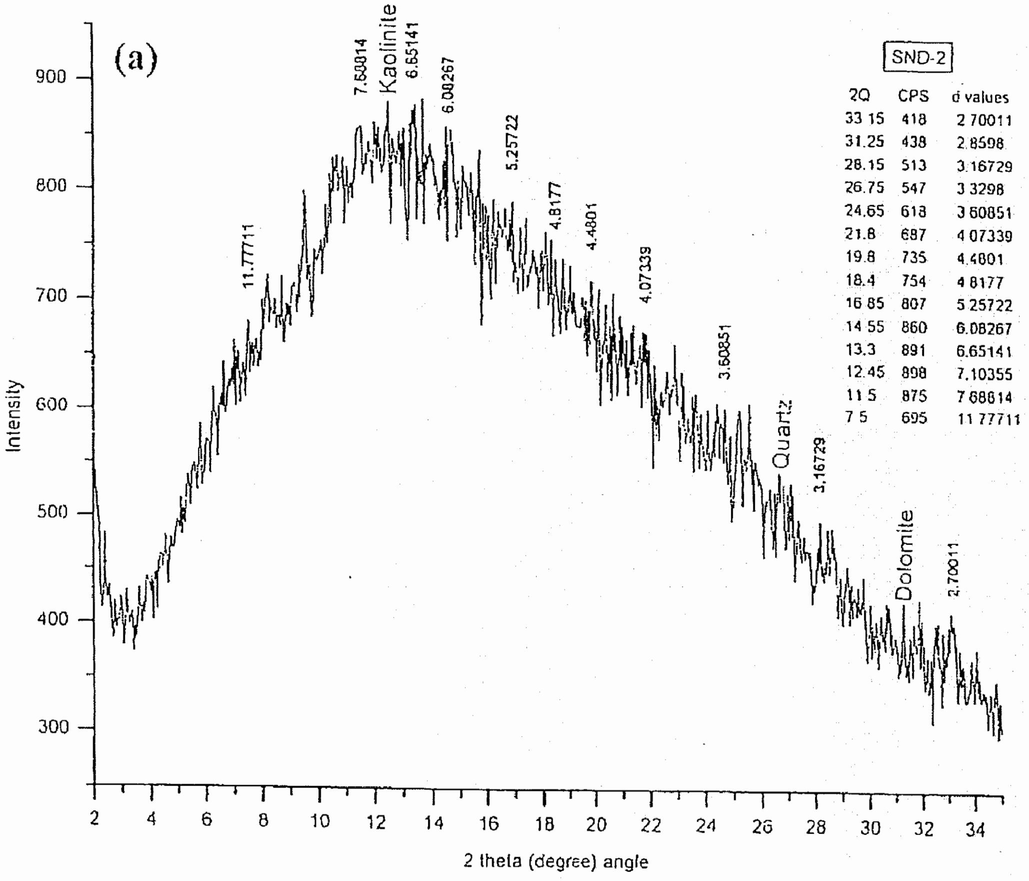
2Q	CPS	d values
7.75	792	11.39776
9.15	839	9 65674
10 75	693	8.22278
12 45	1089	7.10355
14 2	840	6 2310
20 85	761	4 2568
21 65	736	4.10127
24.95	666	3.55579
26.8	513	3 3237
33 15	361	2.70011

Fig. 6.4 (c) X-ray diffrectogram of the coal samples collected from Thar coalfield.



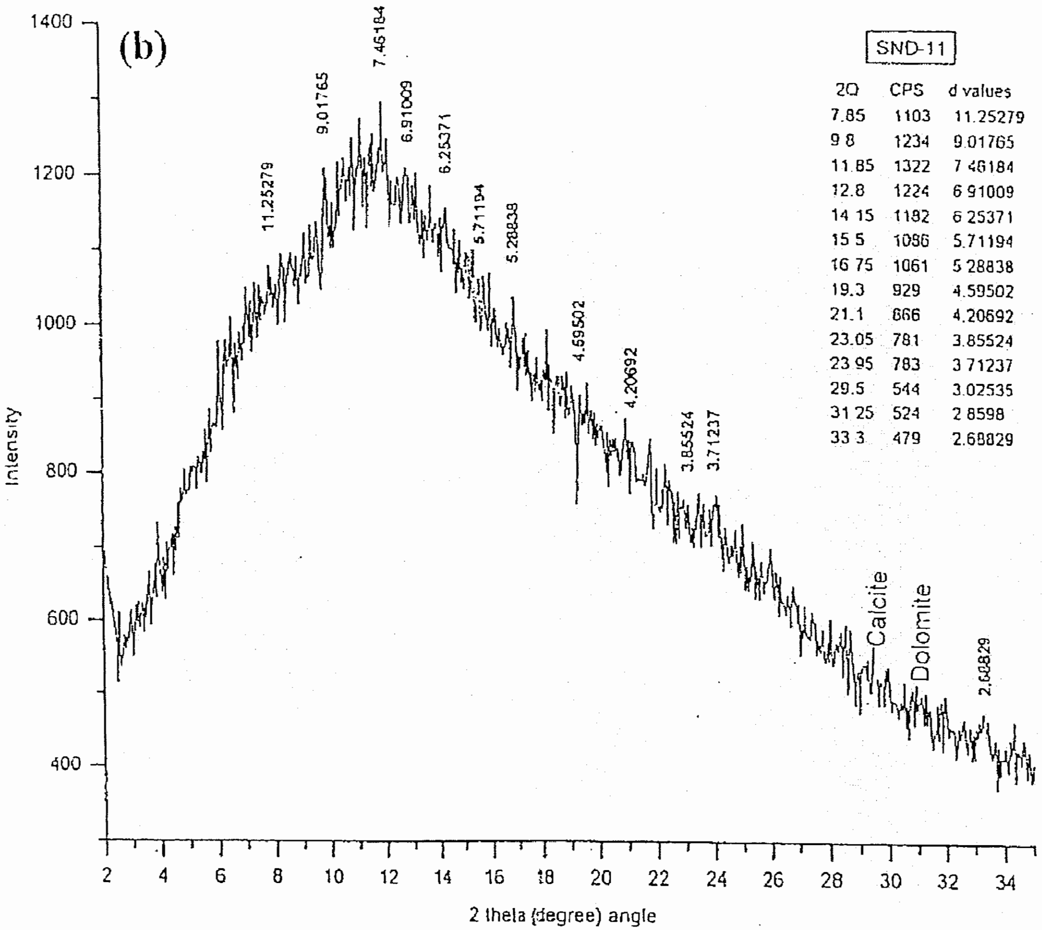
2Q	CPS	d values
8.65	833	10.21378
10.9	990	8.10996
12 2	1053	7.24855
13.55	1004	6 52925
14 9	934	5 94057
16.7	856	5 3041
20	809	4 43575
20 5	791	4 32868
21.65	767	4.10127
22.9	688	3 88015
25	670	3 55878
26.7	611	3 33592
29.75	460	3.00049
30.25	435	2 95203
33	307	2.71204

Fig. 6.4 (d) X-ray diffrectogram of the coal samples collected from Thar coalfield.



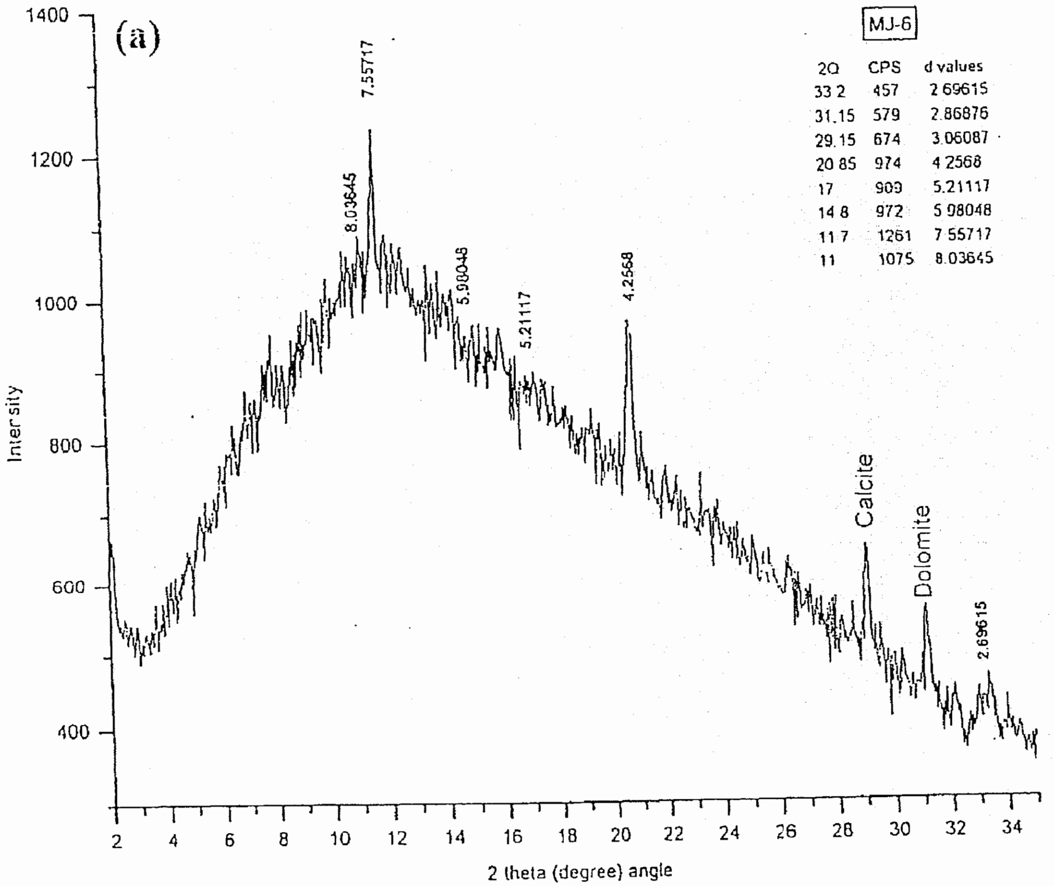
2Q	CPS	d values
33.15	418	2.70011
31.25	438	2.8598
28.15	513	3.16729
26.75	547	3.3298
24.65	618	3.60851
21.8	687	4.07339
19.8	735	4.4801
18.4	754	4.8177
16.85	807	5.25722
14.55	860	6.08267
13.3	891	6.65141
12.45	898	7.10355
11.5	875	7.68814
7.5	695	11.77711

Fig. 6.4 (a) X-ray diffrectogram of the coal samples collected from Sonda coalfield.



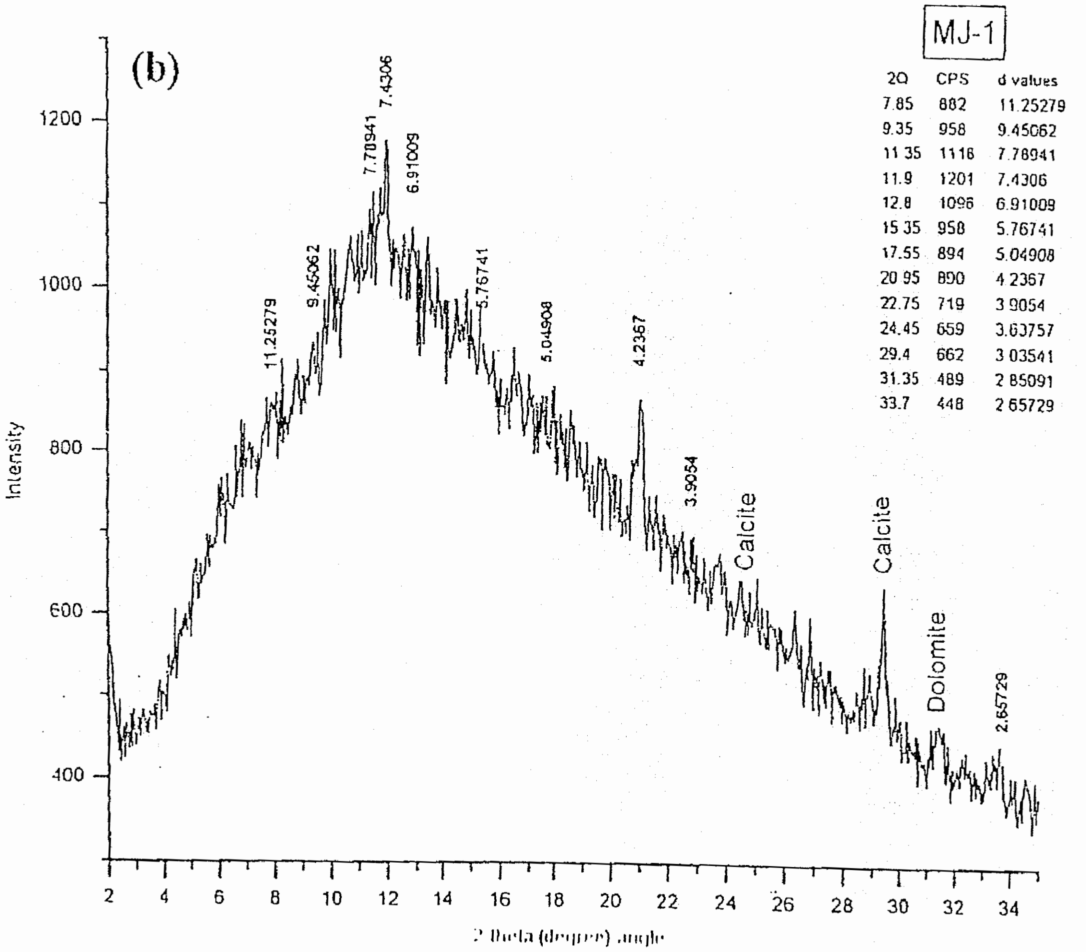
2Q	CPS	d values
7.85	1103	11.25279
9.8	1234	9.01765
11.85	1322	7.46184
12.8	1224	6.91009
14.15	1182	6.25371
15.5	1086	5.71194
16.75	1061	5.28838
19.3	929	4.59502
21.1	866	4.20692
23.05	781	3.85524
23.95	783	3.71237
29.5	544	3.02535
31.25	524	2.8598
33.3	479	2.68829

Fig. 6.4 (b) X-ray diffrectogram of the coal samples collected from Sonda coalfield.



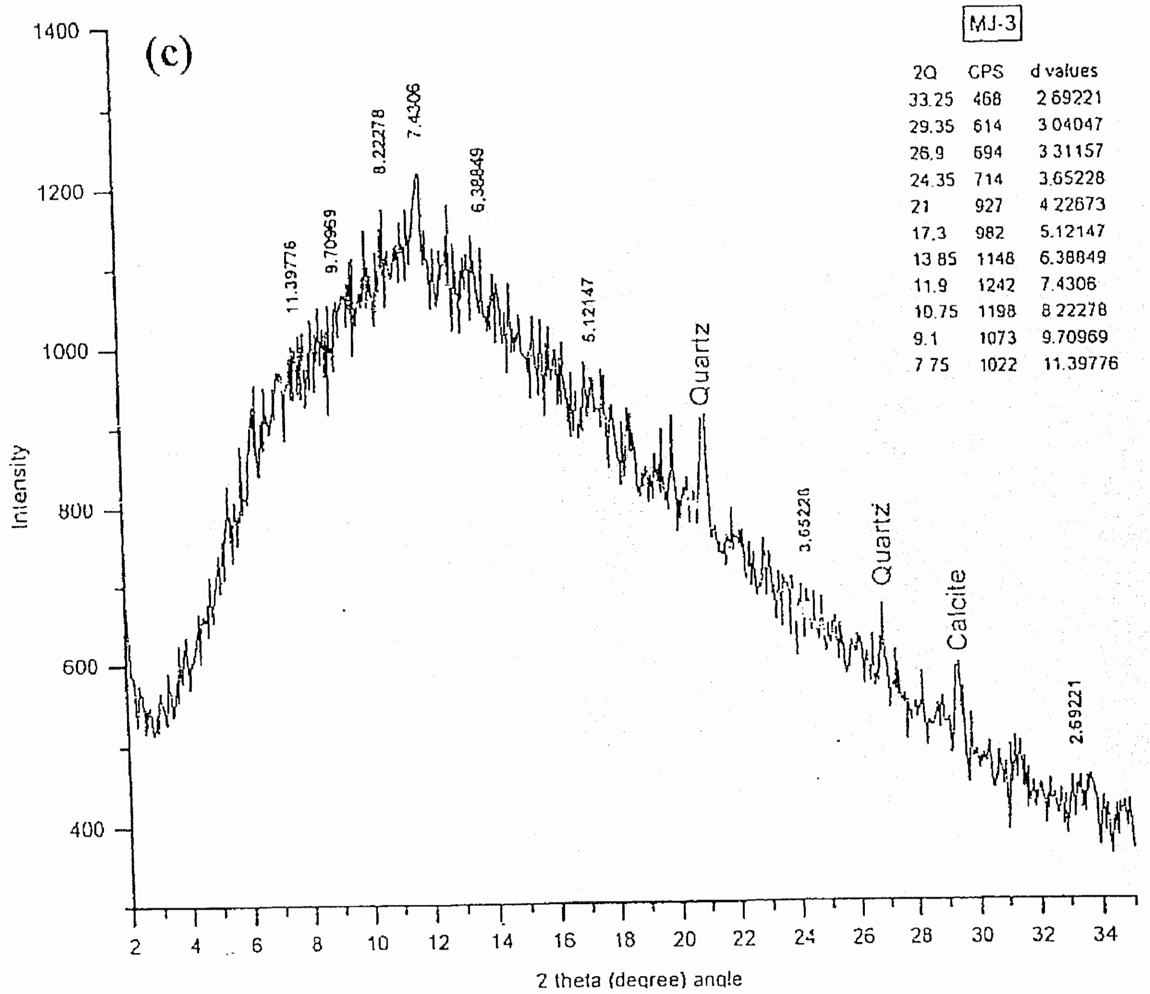
2Q	CPS	d values
33 2	457	2 69615
31.15	579	2.86876
29.15	674	3.06087
20 85	974	4 2568
17	909	5.21117
14 8	972	5 98048
11 7	1261	7 55717
11	1075	8.03645

Fig. 6.4 (a) X-ray diffrectogram of the coal samples collected from Meting-Jhimpir coalfield.



2Q	CPS	d values
7.85	882	11.25279
9.35	958	9.45062
11 35	1116	7.78941
11.9	1201	7.4306
12.8	1096	6.91009
15 35	958	5.76741
17.55	894	5.04908
20 95	890	4 2367
22.75	719	3 9054
24.45	659	3.63757
29.4	662	3 03541
31.35	489	2 85091
33.7	448	2 65729

Fig. 6.4 (b) X-ray diffrectogram of the coal samples collected from Meting-Jhimpir coalfield.



2Q	CPS	d values
33.25	468	2.69221
29.35	614	3.04047
26.9	694	3.31157
24.35	714	3.65228
21	927	4.22673
17.3	982	5.12147
13.85	1148	6.38849
11.9	1242	7.4306
10.75	1198	8.22278
9.1	1073	9.70969
7.75	1022	11.39776

Fig. 6.4 (c) X-ray diffrectogram of the coal samples collected from Meting-Jhimpir coalfield.

CHAPTER SEVEN

CONCLUSIONS

- Among the studied coal fields of Sindh (i.e., Thar, Sonda and Meting-Jhimpir), the Thar coal field occurs in the Bara Formation of the Paleocene-Eocene age, Sonda coal field occurs in both Bara Formation and Laki Formation (Eocene) while the Meting-Jhimpir coal field is found in the Sonhari Member of early Eocene age of the Laki Formation.

- The heavy and trace element chemistry of these coal fields indicate that these coals have variable concentration of heavy and trace elements with decreasing trend from Fe to Cd as Fe>Ni>Zn>Pb>Cr>Cu>Co>M>Cd in the Thar coals; as Fe>Zn>Ni>Cu>Pb>Cr>Co>Mn>Cd in Sonda coals and as Fe>Zn>Pb>Ni>Cu>Cr>Co>Mn>Cd in the Meting-Jhimpir coals.

- These coals, especially of Sonda and Meting-Jhimpir, have relatively high amount of total sulfur and hence may have higher SO_2 emission as flue gases to the environment. However, the studied coals have no environmental impact as far as the NO_x emission is concerned.

- The mineralogy of the Sindh coals suggests that these coals have quartz and kaolinite as the dominant phases with minor amount of calcite, dolomite, pyrite, illite and muscovite.

- The sequential leaching of the Sindh coals indicates that most of the heavy and trace elements (i.e., Pb, Zn, Cu, Cd and Mn) in these coals are present in the HCl-soluble compounds while some (i.e., Cr, Ni) occur as insoluble organically shielded matters. Fe is generally present as mono-sulfide (i.e., pyrite, marcasite) in the studied coals.

- The presence of pyrite and marcasite further suggest that the studied coals may cause sever problems in mining of these coals because of oxidation and formation of soluble toxic organic compounds of heavy and trace elements and hence contamination of underground water.

- The relative high concentration of sulfur and the various heavy and trace elements in the Sindh coal may have environmental problems during the coal combustion in the future power generation plants. Wherefrom there are chances of liberation of the toxic elements as fly ash particulates which may cause severe heath hazards in the region.

- To overcome this problem the special measures should be taken to reduce the particulate emission level by following the guide-lines proposed by the World Bank Group.

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APPENDIX-1

METHODOLOGY

A. FIELD METHODS

Collection of samples

Representative coal samples (≅ 2-4 kg) were hammered through the coal seam in the Meting-Jhimpir coalfield and for Thar and Sonda coalfield drill core samples were collected from the core library of Geological Survey of Pakistan's Sindh regional office located in Karachi. Both samples were collected in different sample bags, these samples were properly numbered in the field and brought to the Geochemistry Laboratory of the National Centre of Excellence in Geology, University of Peshawar for further experimentation.

B. LABORATORY METHODS

CRUSHING AND PULVERIZING OF COAL SAMPLES

Representative coal samples collected during field were air-dried and crushed by the jaw-crusher. The crushed coal samples were then pulverized in a tungsten carbide ball mill to - 75 micron (200 mesh size) with a quartz flush between the samples. A portion of individual sample was collected after proper quartering and coning. During this whole process greater care was practiced to avoid contamination. The powdered samples were stored in the airtight glass bottles. These bottles, after removing the lids, were kept in the oven at 110 °C for two hours in order to remove the moisture.

PREPARATION OF STOCK SOLUTION-A FOR COAL SAMPLES

For the decomposition of the coal samples, a method of Jeffery and Hutcheson (1986) was adopted as follows. About 1.0 g of finely powdered coal sample was taken in a 100 ml teflon beaker. 10ml of hydrofluoric acid (HF) was added to it and was kept on hot plate at low temperature. After half an hour, about 4 ml perchloric acid ($HClO_3$) was added and let the acid to evaporate until paste was obtained. Then 15 ml of concentrated HNO_3 was added and the heating was continued until complete dryness. Then 20 ml 3N HCl was added to the residue and was heated until the maximum dissolution of residue. The solution was filtered through a fine filter paper with thorough washing with de-ionized water. The final volume was made to 50 ml with 3N HCl and was stored in polythene bottle. This solution was then used for the determination of heavy, trace and light elements by using atomic absorption spectrophotometer (AA).

PREPARATION OF STOCK SOLUTION- B FOR CERTIFIED ROCK STANDARDS

The stock solution-b for the certified rock standards AGV-1 and W-2 was also prepared by the same method as described above and was used for the verification of the analysis accuracy.

ANALYSIS OF HEAVY AND TRACE ELEMENTS

Determination of Copper (Cu)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument conditions

Mode	Absorption
Wave length	325.8nm
Slit width	0.4nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

1. Standard stock solution of 1000 ppm: 1 g of copper metal was dissolved in 30 ml of (1:1) HNO_3 and was made to the volume of one liter with de-ionized water.

2. Standard stock solution of 100 ppm: 10 ml of 1000 ppm standard stock solution was taken in 100 ml volumetric flask and was made to the mark with de-ionized water.

3. Working standards: 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4, and 8 ml from 100 ppm standard stock solution into a series of 100 ml volumetric flasks and made to the volume with de-ionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Cu cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspired into the flame and the Cu concentration of each sample was noted. The Cu contents in ppm were calculated.

Determination of Lead (Pb)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument conditions

Mode	Absorption
Wavelength	217 nm
Slit width	0.4 nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

1. **Standard stock solution of 1000 ppm:** 1.598 g of lead nitrate $Pb(NO_3)_2$ was dissolved in 1% HNO_3 and was diluted to 1 liter with de-ionized water.

2. **Standard stock solution of 100 ppm:** 10 ml of 1000 ppm standard stock solution was taken in 100 ml volumetric flask and was made to the volume with de-ionized water.

3. **Working standard solutions:** 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4 and 8 ml of 100 ppm stock solution in a series of 100 ml volumetric flask and volume was made to the mark with de-ionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Pb cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspired into the flame and the Pb concentration of each sample was noted. The Pb contents in ppm were calculated.

Determination of Zinc (Zn)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument conditions

Mode	Absorption
Wavelength	213.9 nm
Slit width	0.7 nm

Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

1. **Standard stock solution of 1000 ppm:** 1g of zinc metal was dissolved in (1:1) HCl and was diluted to 1 liter with de-ionized water.

2. **Standard stock solution of 100 ppm:** 10 ml of 1000 ppm standard stock solution was taken in 100 ml volumetric flask and was made to the volume with de-ionized water.

3. **Working standard solutions:** 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4 and 8 ml of 100 ppm stock solution in a series of 100 ml volumetric flask and volume was made to the mark with de-ionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Zn cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspired into the flame and the Zn concentration of each sample was noted. The Zn contents in ppm were calculated.

Determination of Nickle (Ni)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument conditions:

Mode	Absorption
Wavelength	232nm
Slit width	0.2nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

1: Standard stock solution of 1000 ppm: 1g of Ni metal was dissolved in a minimum volume of(1:1) HNO_3 and was diluted to 1 liter with de-ionized water.

2. Standard stock solution of 100 ppm: 10ml from 1000 ppm stock standard solution was transferred into a 100 ml volumetric flask and was made to the mark with de-ionized water.

3: **Working standards:** 0.5, 1, 2, 4, 8 ppm standard solution were prepare by taking 0.5, 1, 2 and 4, 8 ml from 100 ppm standard solution into a series of 100 ml volumetric flask and was made to the mark with de-ionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Ni cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspired into the flame and the Ni concentration of each sample was noted. The Ni contents in ppm were calculated.

Determination of Chromium (Cr)

Atomic Absorption method

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument conditions

Mode	Absorption
Wave length	357.9nm
Slit width	0.2nm
Fuel flow	4.5 l/min
Air flow	5.0 l/min
Burner height	10 mm

1: Standard stock solution of 1000 ppm: 3.735g of K_2CrO_4 was dissolved in de-ionized water and diluted to one liter with de-ionized water.

2. Standard stock solution of 100 ppm: 10ml of 1000ppm standard stock solution was taken in 100 ml volumetric flask and was made to the mark with de-ionized water.

3. Working standards: 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4 and 8 ml from the standard stock solution of 100 ppm in a 100ml volumetric flask and was made to the mark with de-ionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Cr cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspired into the flame and the Cr concentration of each sample was noted. The Cr contents in ppm were calculated.

Determination of Cobalt (Co)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument conditions:

Mode	Absorption
Wave length	240.7 nm

Slit width	0.4 nm
Fuel flow	1.2 l/min
Air flow	5 l/min
Burner height	10 mm

1: Standard stock solution of 1000 ppm: 1.0 g of cobalt metal was dissolved in 30 ml of (1:1) HCl and was diluted to one liter with de-ionized water.

2. Standard stock solution of 100 ppm: 10ml of 1000 ppm stock solution was taken in 100 ml volumetric flask and was made to the mark with de-ionized water.

3. Working standards: 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4 and 8 ml from 100 ppm standard stock solution in a series of 100 ml volumetric flasks and made to the mark with de-ionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Co cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspired into the flame and the Co concentration of each sample was noted. The Co contents in ppm were calculated.

Determination of total iron (Fe)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrumental conditions

Mode	Absorption
Wavelength	248.3 nm
Slit width	0.2 nm
Air flow	5litre/minute
Fuel flow	1litre/minute
Burner height	10 mm

1. Stock solution of 1000 ppm for Fe: I gram of pure iron metal was dissolved in minimum amount of HCl and was made to the volume with de-ionized water in one litre volumetric flask.

2. Stock solution of 100 ppm: 10 ml from 1000 ppm stock solution was taken in 100 ml volumetric flask and made to the mark with de-ionized water.

3: Working standard solutions: 1, 2, 4 and 8 ppm working standard solutions were prepared by taking 1, 2, 4 and 8 ml from the 100 ppm stock standard solution in a 100 ml volumetric flask and made to the volume with de-ionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Fe cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspired into the flame and the Fe concentration of each sample was noted. The Fe contents in ppm were calculated.

Determination of Manganese (Mn)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument conditions:

Mode	Absorption
Wave length	279.5nm
Slit width	0.2nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10mm

1:Stock solution of 1000 ppm for Mn: 4.058g of $MnSO_4.4H_2O$ was dissolved in 20 ml of 1N H_2SO_4. It was then transferred to 1000 ml volumetric flask and was made up to the mark with de-ionized water.

2: Stock solution of 100 ppm: 10 ml of 1000 ppm stock solution was taken in 100ml volumetric flask and was made up to the volume with de-ionized water.

3: Working standards: 1, 2, 4 and 8 ppm working standards of Mn were prepared by taking 1 2, 4 and 8 ml of 100 ppm stock solution in a 100ml volumetric flask and was made to volume with de-ionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Mn cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspired into the flame and the Mn concentration of each sample was noted. The Mn contents in ppm were calculated.

Determination of Cadmium (Cd)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument conditions

Mode	Absorption
Wavelength	228.8 nm
Slit width	0.7 nm

Tube/site	Pyro/Platform
Matrix modifier	0.2 mg $NH_4H_2PO_4$
Pretreatment T °C	700
Atomization T °C	1600

1. **Standard stock solution of 1000 ppm:** 1 g of copper metal was dissolved in 30 ml of (1 :1) HCl and was made to the volume of one liter with de-ionized water.

2. **Stock solution of 1 ppm:** 0.1 ml from 1000 ppm stock solution was taken in 100 ml volumetric flask and made to the mark with de-ionized water.

3. **Working standard solutions:** 25, 50, 100 and 200 ppm working standard solutions were prepared by taking 2.5, 5, 10 and 20 from the 1 ppm stock standard solution in a 100 ml volumetric flask and made to the volume with de-ionized water.

Procedure: The graphite furnace was set according to the above-mentioned conditions. Cd cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp, the instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspired into graphite tube and the Cd concentration of each sample was noted. The Cd contents in ppm were calculated.

ANALYSIS OF LIGHT ELEMENTS

Determination of Calcium (Ca) and Magnesium (Mg)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument conditions:

Element	Ca	Mg
Mode	Absorption	Absorption
Wavelength	422 nm	285.2nm
slit width	0.4nm	0.4nm
Air flow	5l/min	5 l/min
Fuel flow	5 l/min	To best flame
Burner height	10mm	10mm

1. Stock solution of 1000 ppm for Ca & Mg: 2.497g $CaCO_3$ and 3.057g $MgCO_3$ were dissolved in 1N HCl and was diluted to one liter with de-ionized water in a 1000 ml volumetric flask.

2: Stock solution of 100 ppm for Ca & Mg: 10 ml of 1000 PPM stock solution was taken in 100 ml volumetric flask and was made up to the mark with de-ionized water.

3: Lanthanum 5% Solution: 58.64g of La_2O_3 was dissolved in 200 ml de-ionized water to which 150 ml 60 % $HClO_4$ was added. It was heated until complete dissolution. The solution was then filtered through ordinary filter paper into 1000 ml volumetric flask and the volume was made up to the mark with de-ionized water.

4. Working Standards: 1, 2, 4 and 8 ppm of working standards for Ca and Mg were prepared by taking 0.5, 1, 2 and 4 ml of 100 ppm stock solution in a series of 50 ml volumetric flasks. To these flasks 10 ml lanthanum solution was added and the volume was made up to the mark with de0ionized water.

5. Dilution of Samples: 5 ml (depending upon the expected concentration of Ca & Mg) of the stock solution-A and B the studied coal samples and the certified rock standards respectively were taken in a series of 50 ml volumetric flasks. 10 ml of lanthanum solution was added to each flask and the volume was made to the mark.

Procedure: Atomic absorption spectrophotometer was set according to the above-mentioned conditions for Ca and Mg separately. The cathode lamp for both Ca and Mg were turn ON to warm up for at least 10 minutes. The instrument was then calibrated and standardized with the working standards of 1 to 4 ppm. All the working standards were run as unknown and their actual concentration was verified. For further accuracy the certified rock standards were run as unknown and the results were compared. After making sure that the results of the certified standards were within the confidence limit, the diluted stock solution containing lanthanum oxide were run on the atomic absorption and the concentrations of Ca and Mg in ppm were noted for each sample.

Determination of Sodium (Na) and Potassium (K)

Instrument: Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

Instrument Conditions:

Element	Na	K
Mode	Emission	Emission
Wavelength	589 nm	766 nm

Slit width	0.2 nm	0.4 nm
Air flow	5 l/min	5 l/min
Fuel flow	1 l/min	1 l/min
Burner height	20 mm	20 mm

1. Stock solution of 1000 ppm for Na & K: 3.087 g moisture free Na_2SO_4 and 2.228g moisture free K_2SO_4 were dissolved in de-ionized water and the volume was made to 1000 ml in a volumetric flask. The solution was stored in a polythene bottle.

2. Stock solution of 100 ppm Na & K: 10 ml of 1000 ppm stock solution was taken in a 100 ml flask and diluted to mark with de-ionized water.

3. Working Standards: 1, 2, 4 and 8 ppm working standards were prepared by taking 1, 2, 4, and 8 ml from 100 ppm stock solution in 100 ml volumetric flasks and was diluted up to the mark with de-ionized water.

4. Diluted samples: All the samples as well as certified rock standards were diluted to 20 times.

Procedure: The atomic absorption spectrophotometer was set according to the above-mentioned instrumental conditions in order to get the maximum absorbance. The instrument was set on emission mode and a conical burner head was used. In this case no cathode lamp was required. The instrument was calibrated and standardized by working standards of 1 to 8 ppm and then the working standards were also run as unknown in order to verify the standardization of the instrument. The diluted certified rock standards were then run and the results were compared to know the accuracy of the method. The diluted solutions of coal samples were sprayed one by one through the flame and the concentration of Na and K was noted in ppm each sample.

PROXIMATE ANALYSIS OF COAL

The simultaneous determination of carbon, hydrogen, nitrogen and sulfur contents (in percent) in the samples of Sindh coalfields was made by the EurVector Elemental Analyzer in the Geochemistry Laboratory of the National Center of Excellence in Geology, University of Peshawar by the following procedure:

Sample preparation: The coal sample was ground to –60 mesh size and dried in the oven at 110°C for at least two hours. After cooling the sample in the desiccators, about 0.5-1.00 mg sample of coal was taken in the tin cap (provided with the machine) and wrap it in to a rounded capsule and then put it in the auto-sampler. This procedure was done for all the coal samples, a blank and a standard (L-Cystine) before running these samples on the machine.

Instrumental conditions: The instrument was turned ON and waited for the furnace to heat up to 1020°C. Then the required information of the samples and standards were entered through the software. The samples were run by the machine under the following standardizing conditions:

Carrier flow: 80 Kpa
Purge flow: 80 ml / min
Oxygen: 20 ml
PO_2: 35 Kpa
Oxidation time: 8.7 Sec
Sampling delay time: 10 Sec

Run time: 500 Sec

Furnace T: 1020°C

GC-Oven T: 115°C

The machine started analyzing the samples simultaneously by taking these samples one by one from the auto-sampler. At the end, the simultaneous results of carbon, hydrogen, nitrogen and sulfur were obtained for the blank, standard and samples. The standards results were within 95% confidence limit of the certified values.

ULTIMATE ANALYSIS OF COAL

The determination of Fixed carbon, Moisture, Volatile matter and Ash contents (in percent) in the samples of Sindh coalfields was made by the muffle furnace in the Geochemistry Laboratory of the National Center of Excellence in Geology, University of Peshawar by the following procedure:

A) Moisture: The coal sample was ground to –60 mesh size and a known weight (3g) of coal was taken in pre weighted crucible and placed in oven for one hour at 105°C. Moisture was calculated as follows:

Weight of moisture (X) = Wt. of crucible containing coal after heating – Wt. of crucible containing coal before heating .

X = Wt. of moisture

Y = Wt. of coal

3g coal contain moisture = x

100g $= \dfrac{100 \times X}{3}$

B) Volatile matter:

The coal sample was ground to –60 mesh size and a 1 g of coal was taken in pre weighted crucible and the crucible was covered tightly. Then crucible was placed in furnace at 750°C for 5-7 minutes. It was cooled in desiccator, the lid of crucible was removed and weighed and calculated as follows:

$$\textbf{Volatile matter:} \frac{\text{Wt. of crucible containing coal before heating} - \text{Wt. of crucible containing coal after heating.}}{\text{Weight of sample}}$$

% Volatile matter: 1gm coal contain = X Volatile matter

100gm contain = $\frac{100 \times X}{1\ \text{gm}}$

C) Ash

The coal sample was ground to –60 mesh size and a 1 g of pulverized coal was taken in pre weighted crucible and placed in furnace at 750°C for 24 hours until the carbon contents completely diminishes. The crucible was cooled in desiccator, and calculated as follows:

$$\textbf{Ash:} \frac{\text{Wt. of crucible containing coal before heating} - \text{Wt. of crucible containing coal after heating.}}{\text{Weight of sample}}$$

% Ash 1gm coal contain = X Ash

100gm contain = $\frac{100 \times X}{1\ \text{gm}}$

Fixed Carbon = 100 – (% of moisture + % of volatile matter + % of Ash

LEACHING OF COAL SAMPLES

The sequential leaching procedure as described by Finkelman et al. (1990) and Palmer et al. (2000) was used during this study. One representative coal sample of Sindh coal feed was prepared by mixing of 50 grams, pulverized – 60 mesh, each of the Thar coal, Soda coal and Meting –Jhimpir coal. Duplicate 100 gram samples of this coal were combined with different solutions and agitated for 18 hours separately. The solutions were then centrifuged and the leachates were separated by filtration. The samples were first leached with IN ammonium acetate ($NH_4C_2H_3O_2$). The procedure was repeated in subsequent leaching steps using 3N Hydrochloric acid (HCl), concentrated hydrofluoric acid (HF) and 2N nitric acid (HNO_3). These leachates were then used for the determination of heavy and trace elements by the Perkin Elmer Atomic Absorption Spectrometric technique under the standardizing conditions of each element as already discussed.

ANALYSIS ON X-RAY DIFRACTOMETER

The X-ray difrectometer (XRD) analyses of few coal samples from Thar, Sonda and Meting Jhimpir coalfields were carried out on the Rigaku XRD, calibrated with Cu (K-alpha) radiations generated at a tube voltage of 40Kv and tube current of 25mA. D spacing value was 2Q count per second. The X-ray Diffraction patterns of the 2θ verses intensity for an angular range of 2-37° 2θ were obtained The JCPDS Mineral Powder Diffraction File (1980) was used for interpreting the diffractograms by the Hanawalt methods of qualitative analysis.

ANALYSIS ON X-RAY FOURANCE RACTOMETER (XRF)

To determine As, Sb and U in the coal samples, the S4- PIONEER X-ray spectrometer was used. This is a PC-based unit and controlled through a computer program, known as S4 tools. This is a standardless software and analyzes almost all the elements of the periodic table except some light elements, inert gases and some rare earth elements. The collected representative samples of the coal was analyzed for As, Sb and Uranium.