HEAVY METAL STUDIES IN LAKHRA COAL

THESIS

SUBMITTED TO

THE NATIONAL CENTRE OF EXCELLENCE IN GEOLOGY
UNIVERSITY OF PESHAWAR

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF PHILOSOPHY

BY

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1999

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In the name of those Sawati coal miners
Who live in Heaven (Sawat)
But work in hell (underground coalmines).

Dedicated to my wife

Sheerin

CONTENTS

TOPICS **PAGE No.**

5. CHAPTER ONE INTRODUCTION

16. CHAPTER TWO GEOLOGY AND STRATIGRAPHY OF THE AREA

25. CHAPTER THREE METHODOLOGY

47. CHAPTER FOUR HEAVY METALS IN LAKHRA COAL

57. CHAPTER SIX HEAVY METALS IN GROUND WATER AT LAKHRA

67. CHAPTER SEVEN DISCUSSION AND RECOMMENDATIONS

LIST OF FIGURE

TOPICS **PAGE No.**

LIST OF TABLES

ABSTRACT

Pakistan is an energy deficient country. It, therefore, requires its fuel minerals, especially coal to be exploited in order to fulfil its energy requirements. However, the impact of coal exploitation on our environment is needed to be studied in order to protect ourselves from the environmental deterioration. Keeping this in mind, the Lakhra coal field, the oldest and second largest coal field of Pakistan, is selected for further studies. In this regard, heavy metal concentrations of Cr, Fe, Ni, Cu, Zn, Cd and Pb in the coal were determined by the instrumental techniques. It has been observed during this study that there is a greater variation in the heavy metals in all the samples collected from various coal mines.

The Lakhra coal is comparable with that of Canadian coal as for as the Cr, Ni, Zn, and Pb are concerned. However, Fe in Canadian coal and Cu in Lakhra coal have multifold high concentration. Comparison with Indian coal, it is noticed that the Lakhra coal has relatively low-concentration of almost all the heavy metals, except Cu.

The impact of Lakhra coal on surrounding air and ground water (dug wells) was also studied in regard to light and heavy metals. It shows that the concentration of metals in the air, both at nose and ground levels, suggest that the light metals especially Na, Mg, K and Ca are blown away as suspended load from the areas closer to the coal mines. The heavy metals also show high concentration at ground level as compared to that of nose level, especially in the areas away from the coal mines. The ground water chemistry of Lakhra

indicate that the ground water collected from dug wells has high TDS, SO_4*,* HCO_3*, Fe and Pb concentration as for as the maximum limit of US-EPA is concerned.*

These studies show that though usage and mining of Lakhra coal is not a environment friendly business but by taking some suggested precautions, it can be utilized as a cheaper domestic mineral wealth.

Acknowledgment

I am very much thank full to and highly obliged to my supervisor, Dr. Syed Hamidullah, Professor NCE in Geology and co-supervisor, Dr. M. Tahir Shah, Associate Professor, NCE in Geology, University of Peshawar, for their kind advises and intellectual supervision. Thanks are specially extended to Dr. M. Tahir Shah for his valuable assistance in the geochemical laboratory, NCE in Geology, University of Peshawar. Thanks are also extended to Mr. Shohab Danishwar, lecturer Department of Geology, University of Peshawar for assistance in analysis of water samples.

Mr. Nawaz Dahri mining engineer, Inus coal mine Limited and Mr. Akber mining engineer Habibullah coal mines are also acknowledged for helping in collecting coal, air and water samples from the area. In this regard author is also thankful to the lease owners of the coal mines for providing permission to carry out research in their area.

In the last but not the least author is also thankful to the local police authority for providing guards and other legal assistance in their jurisdiction.

CHAPTER ONE

INTRODUCTION

Development is the prime goal for any country. In mining sector, exploitation of mineral resources is the stepping stone for the development. However, mining is also an environmentally damaging activity causing large scale deforestation, destruction of wild life and other natural resources. Therefore, care must be taken to preserve man's natural habitat, the natural ecosystem to which he is at equilibrium.

Pollution is defined as the direct or indirect alteration of the physical, thermal, biological, or radio active properties of any part of the environment in such a way as to create a hazard or potential hazard to the health, safety or welfare of any living species (Gurdeep,1992). According to United Nation Development Program's report (1992), environmental pollution is mainly due to exploitation of energy resources (coal, oil, gas, nuclear) and industrial production.

Coal is the non-renewable resource. In Pakistan 82% of the mined coal is used in brick kiln industry, while 1.3% is being consumed for power generation Durrani,1993).

According to Khopkar (1995) 41% pollution is because of coal combustion i.e., coal burning, 16% due to petrol burning, 5% due to smelting, 7% due to refining products and 5% due to other resources.

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,1987).

Heavy metals are defined as highly electronegative with densities greater than 5g/cm^3 and having atomic number between 22 and 92 (Trivedy & Sinha, 1990). When a large amount of coal is burned these metals are released into the environment, causing toxicological hazards.

The eight most common heavy metal pollutants listed by the Environmental Protection Agency (EPA) are As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. Their toxicity varies with threshold limiting value (TLV=2 mg/m^3 to 500 mg/m^3) in air. From the environmental pollution point of view, these metals may be broadly classified into the following categories:

(1) Non-toxic but accessible

(2) Toxic but non accessible

(3) Toxic and accessible

It is the third category of potentially toxic and relatively accessible metals that have attracted more attention due to their potential as environmental pollutant and posing threat to the public health. These toxic metals occur in very small quantities in the earth's crust (<1000 ppm) and hence called 'trace metals' and those with densities above 5 g/cm^3 are designated as '**heavy metals**'. Thus metals like **Hg, Pb,** Cu, Cd, Zn, Ni etc. are generally known as **toxic heavy metals.**

Purpose and Scope

As discussed above coal also posses metals (heavy and trace) that are environmentally hazardous. Coal data from different parts of the world show these metals in different proportion (Table1.1).

The occurrence of Lakhra coal in Lakhra (Sindh) was first of all reported by Baluch wanderers as early as1853, while sinking a well at the depth of12.5 meters in Lialian stream bed. In 1867, W.T. Blanford of Geological Survey of India visited the Lialian area and gave a negative report on the occurrence of coal. Burma Oil Company (1948) and Pak Hunt International (1953) while drilling for the oil in the Lakhra area, reported the presence of coal in well cuttings of six drill holes at various depths (Shah et al., 1988). Among the Government and semi government agencies, Geological Survey of Pakistan was the first to carry out exploration and the geological evaluation of the Lakhra coal field during the period 1961 to 1966.

Table 1.1:TOXIC HEAVY METALS (in ppm) IN COAL OF VARIOUS COUNTRIES (Trivedy and Sinha, 1990).

Element	U S A	U K	Australia	India
Cd	2.52	0.4	2	8.5
Co	9.57	Not Available	4	3.5
Cr	13.75	33.6	6	50
Cu	15.16	Not Available	15	14.5
Hg	0.2	Not Available	0.1	Not Available
Mn	49.4	84.3	150	Not Available
Ni	21.07	27.9	15	38.5
Pb	34.78	38	10	118
Zn	272.29	Not Available	100	38

Afterwards, Pakistan Mineral Development Corporation and many other International agencies like Japan International Corporation Agencies (JICA) and United States Agency for International Development carried out detailed study of the area (Durrani,1993). Messieurs Habibullah Mines Limited had been the first mining company, that started commercial mining of the coal in Lakhra in 1959. At present more than 42 private companies are engaged in the extraction of Lialian coal in the area. The room and pillar method is practiced in the coal mines of this area.

Lakhra coal field is the second largest coal field of Pakistan, comprising an area of about 680 square kilometers and this coal field is surrounded by a number of villages like Kander, Sher Wala, Yari wala, Issa wala, Murid, Bund Virah, Bahram, Bandi wala, and labour colony at Lakhra. The Lakhra coal is exploited mainly for use in the first Coal Fired Power Plant at Khanota a major town on main Indus high way. The current study is, therefore, carried out to determine the quantities of heavy metals in various parts of this coal field in order to foresee the potential hazard to public health in the area.

Location of the area

The Lakhra coal field is located 225 km North East of Karachi in Dadu district of Sindh province, covering an area of 680 Km^2. It lies between latitudes 25° 30' and 25°45' N and longitudes 68° 0' and 68° 15' E (Fig. 1.1). It is also covered by survey of Pakistan topographic sheet Nos. 40 C/1 and 40C/2. Khanot is the nearest railway station, connected with Lakhra by a 19 km long metlled road upto Indus Coal mines.

The area has a network of fair weather jeapable tracts. Mining is active in the southern side of the coal field, and the method of mining is under ground long wall retreating system.

Coal samples were collected from the coal mines situated between latitude 25° 35' and 25° 45' N and longitude 68° 5' to 68° 15' E (Topographic sheet No. 40 C/2; Fig. 4.1).

Topography and relief

Flat topped hills, which slope down gently towards Indus plain stand out in the eastern, northern, and southern parts of the area. The broad Lakhra valley

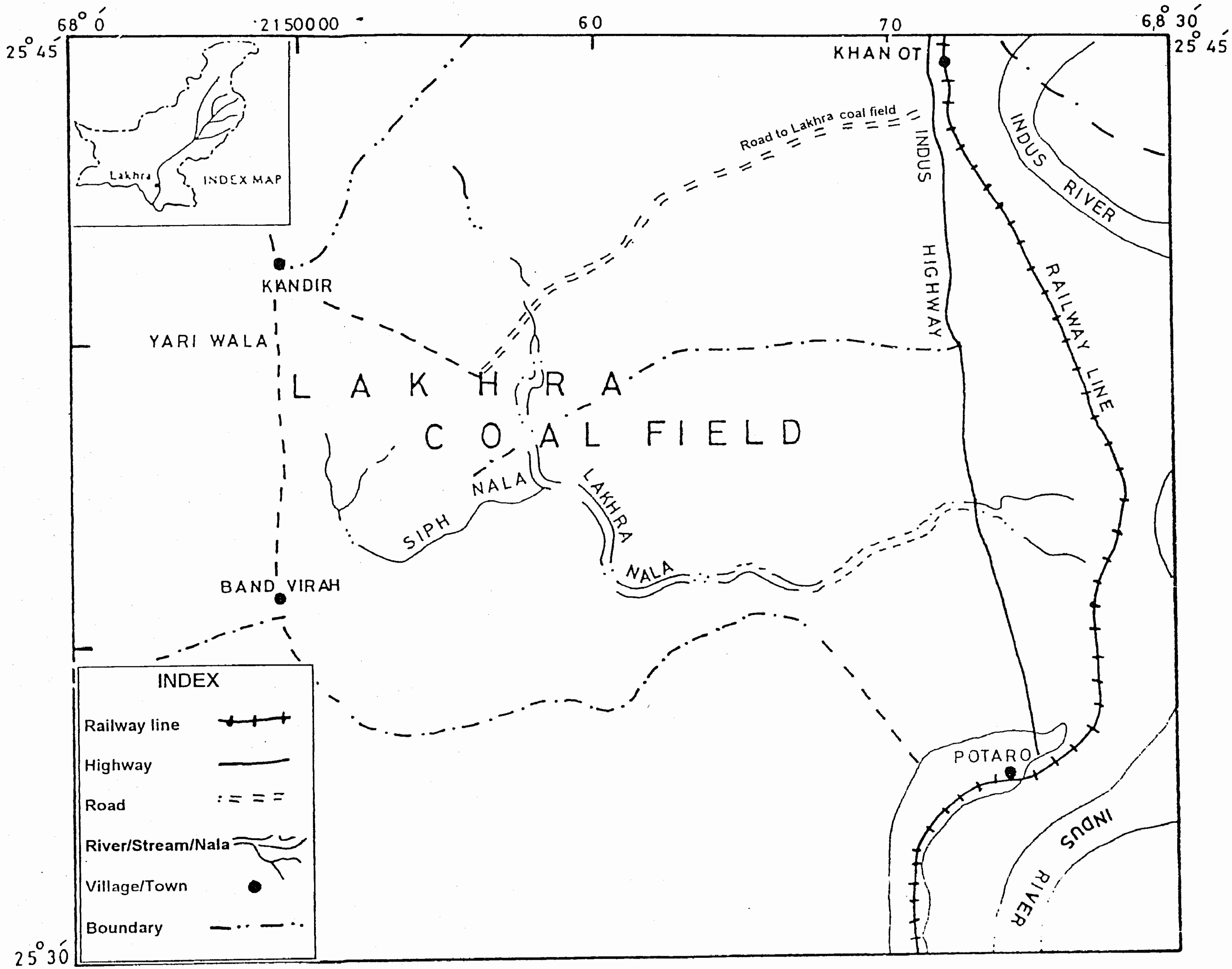


Fig. 1.1 Location map of Lakhra coal field.

crosses the central part of the area and is joined by a number of tributaries. Highest point 209 meters above sea level is near Lalian colliery, where as the lowest point in Siph Nala and Lakhra Nala (rainy streams) is about 72 meters above sea level.

General geology of the area

The Lakhra coal field area is underlain by sedimentary rocks. 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 conformably underlain by Lakhra Formation of Middle to Late Paleocene age and 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. 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).

Quality of Lakhra Coal

According to ASTM Standards(1986), Lakhra coal is ranked from lignite A to sub butiminous C and has high volatile matter, high sulfur and high ash. Following is the analysis of Lakhra coal (Ahmed et al., 1988)

Moisture (As received basis)	12.9-37.3%
Moisture (As air dried basis)	9.2%-23.3%
Ash (As air dried basis)	24.1%-43.3%
Total Sulphur (As air dried basis)	5.51%-5.99%
Heating Value/Gross Calorific Value	4, 930 k cal/kg - 970 k cal/kg

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 (Ahmed et al., 1986).

Climate

The climate of the area is semi arid and here the average annual rain fall is about 20 to 30 cm.

Drainage and water supply

Siph Nala is the main tributary which flows in monsoon season across the crest of the Lakhra anticline. Lakhra Nala (a rainy stream) flows from north-east to south-west. The drinking water is supplied to coal miners' colony at Lakhra coal field by water tankers from the river Indus at a distance of about 20 km. There are some shallow dug wells in near by villages i.e., Lillian Khoh (dug well), Kander jo Khoh (Kander's dug well), and Yaro-a- jo Khoh (Yaro's dug well).

Vegetation

The area is barren, the hills are bald, cultivation is limited to patches in comparatively low lying areas where rain water can accumulate. However, cultivated areas can be seen in the western parts around village Kander, Band Virah, and near by villages. Peoples of the area generally have nomadic life.

Settlements

The main villages in the area are Lakhra labour colony which is inhabiting more than 20,000 persons. The other villages in the area are Kander, Sher Wala, Yari wala, Issa Wala, Goth Murid, Bund Virah, Goth Bahram, and Goth Bandi wala with a population not more than five thousands.

CHAPTER TWO

GEOLOGY AND STRATIGRAPHY OF THE AREA

The rocks exposed in the study area belong to the Ranikot Group which is mainly composed of Bara Formation (Early Paleocene), Lakhra Formation (Late Paleocene), Sonhari member (Early Eocene), Laki Lime stone member (Early Eocene) and Manchar Formation (Pliocene) (Table 2.1). 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 conformably overlain by the Lakhra Formation of middle to late Paleocene. This is unconformably overlain by Laki formation of early Eocene. The unconformity is marked by a 4.6-7.6 m thick laterite bed of Sonhari member. The rocks of the Middle Eocene to Miocene (intervening the Laki Limestone and the Manchar Formation) (Khan et al,. 1988) are absent in the area, hence the Manchar Formation of Pliocene age directly overlies the Laki formation. A very thin cover of alluvium rests over the Manchar Formation. (Table 2.1 shows the general stratigraphic sequence in the Lakhra area)

The stratigraphic units, and structures as described by Ghani and Harbour (1969), and modified by Khan et al. (1988) are as under:

BARA FORMATION

Bara Formation is exposed in an elliptical area covering 51sq.km. Here only the upper 18 m of the unit is exposed. It is composed predominantly of sandstone with subordinate claystone, shale, siltstone and coal seams of variable thickness.

The sandstone is light gray, gray, white and greenish gray, weathered to various shades of yellow, red and brown. It generally contains fine to coarse-

Group	Formation / Member	Age	Thickness	Lithological Description
RANIKOT	Alluvium	Recent	Thin	Silt and Sand
	Manchar Formation	Pliocene	18-28 m	Ferrugeneous pebble, conglomerate, soft and poorly sandstone and clay in the study area.
		unconformity		
	Laki limestone member	Early Eocene	20.7 m	Limestone, cream coloured, chalky fossiliferous, hard and resistant.
		unconformity		
	Sonhari member	Early Eocene	7.62 m	
		unconformity		
	Lakhra Formation	Late Paleocene	137.16 m	Fossiliferous, sandy limestone, sandstone, clay and shale
	Bara Formation	Early Paleocene	20.7 m exposed	Sandstone, shale, clay and COAL SEAMS.

Table 2.1 General stratigraphic sequence in the Lakhra area.

grained sub angular quartz grains. It is poorly sorted, cross bedded massive to friable and loosely cemented. Ferromagnesiun minerals are present in minor amount.

The claystone, shale and siltstone are light gray to gray, pyretic coaly films irregularly distributed; partly sandy (arenaceous), gypsiferous and poorly laminated. The minable coal seam, designated as Lailian coal seam occurs within this unit and is sandwiched within the claystone roof and floor material in most of the area. The coal is black to brownish black resinous, and pyretic. It crumbles into small chips on exposure to air and sun for few days. It is liable to spontaneous combustion and rank as high grade lignite.

The Bara Formation conformably overlies the Khadro Formation. The contact is not exposed in the area. It is also conformable with the overlying Lakhra Formation and the well exposed contact is marked by one foot fossiliferous bed at the bottom of the Lakhra Formation (Khan et al.,1988).

LAKHRA FORMATION

Lakhra Formation is exposed in north, south, east and west of the studied area (Lakhra-Khanot section). It is 137.16 meters thick at this section. This unit is of variable thickness because of the unconformity. It consists of sandstone, limestone, clay- stone, shale and siltstone. Limestone is the dominant component in the upper part with subordinate sandstone and claystone. Sandstone is the dominant lithological unit in the lower part. It is light gray, yellow, brown and red in color. It is fine to coarse with sub angular to rounded grains and is calcareous and fossilifeous at different intervals.

The Lakhra Formation conformably overlies the Bara formation but unconformably underlies the Laki limestone. At places it underlies the Laki limestone. Where ever the contact is exposed, the unconformity is marked by a band of Laterite. The laterite attains a maximum thickness of 7.62 meters (Khan et al., 1988).

LAKI FORMATION

The Laki Formation consists of four units as given below in ascending srtatigraphic orders:

Laki Limestone member
Meting Shale member
Meting Limestone member
Sonhari member

Sonhari Member

In the studied area, Sonhari and Laki Limestone members of the Laki Formation are maily exposed. The Sonhari Member, having a thickness of is 7.62 meters, consists of lateritic clay and ferruginous sandstone of yellow, red and brown colour. It is a ferrugineous- alluminous laterite and marks the unconformable contact between the Laki limestone and Lakhra formation (Khan et al., 1988).

LAKI LIMESTONE MEMBER

In the study area, the Lakhra anticline is flanked by the Laki limestone member on eastern, northern, and western sides. The Laki limestone is 10.6 meters thick at the Lakhra Khanote section, however, its thickness varies between 12.19 and 28.35 meters. It consists of limestone with very subordinate amount of claystone and marl.

The limestone is creamy, white and light gray with yellow to brown staining. It weathers to light gray alteration. It is massive, nodular hard, resistant and cliff-forming. All the beds are rich in forums. Mega fauna occurs mostly in the middle part. Claystone is light gray to gray with yellow stains. It is gypsiferous, fossiliferous, calcareous, soft, laminated and occurs in lenses and thin bands at the lower half.

The Laki limestone is overlain unconformably by the Manchar Formation in the northern and western part of the area. However, in western part of the study area around Khanote, alluvium rests over the Laki limestone (Khan et al., 1988).

Manchar Formation

The Manchar Formation (Fig. 2.1) occurs in patches east of Kander village but more or less continuously to the west of Bund virah, Kander and Golora villages where it attains a thickness of 24.38 meters. In the study area, the Manchar Formation rests unconformably over the Laki limestone of the Lakhra Formation. On the east and north east of Kander village it rests over the Lakhra Formation. The unconformity marks the long period of erosion and non deposition from middle Eocene to Miocene. In most localities it is overlain by recent to subrecent deposits.

Generally the Manchar Formation consists of conglomerate, sandstone, silt-stone and claystone. The conglomerate has pebbles of sand stone, yellowish claystone and limestone, embedded in sand and clay matrix. The sandstone is gray to light gray with various shades of yellow and red. It is fine to coarse grained loosely cemented and poorly sorted (Khan et al., 1988).

Manchar Formation in the east of Kander village is composed of laterite and pebbles mixed with the sand, silt and clay. The laterite is (ferrugeneous) dark brown, red and yellow in color. The pebbles are of ferrugenous laterite and ferrugenous and gritty sandstone. These are of dark brown, red and gray color and posses smooth

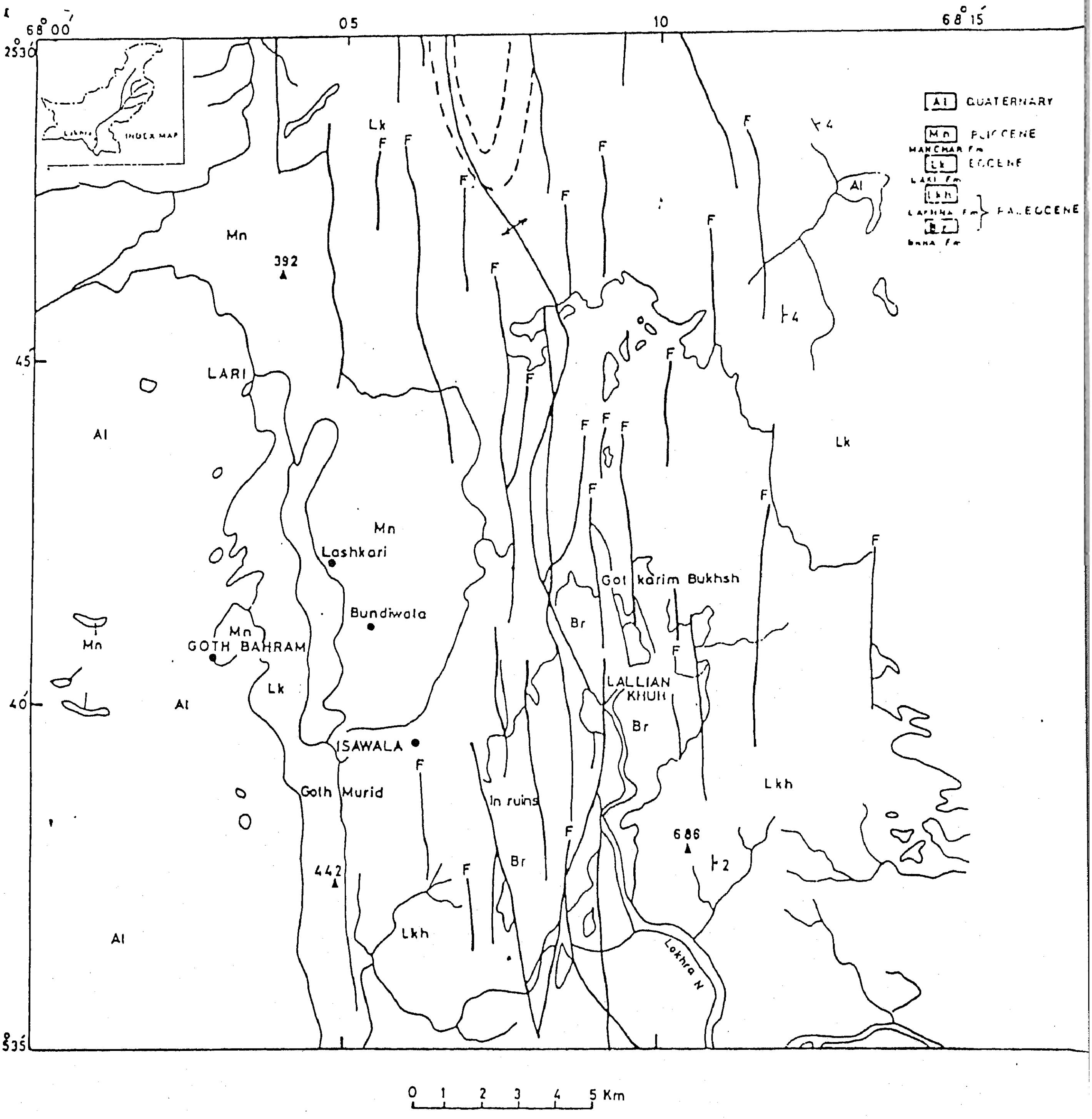


Fig. 2.1 Geological and structural map of Lakhra coal field.

surfaces with resinous luster.

STRUCTURE

Folds: Lakhra coal field is located on a prominent and large geological structure called **Lakhra anticline**. It is a doubly plunging fold, with its axis running more or less in north- south direction for about 65 kms and it covers a maximum of 25 kms area east to west. The Bara Formation is exposed along the axial part of the Lakhra anticline and younger rocks lie on the flanks. Unconformable Manchar Formation conceals the structure partly along the western flank and totally to the north of Ochha stream area (Memon et al., 1976). Southwards a few other small folds are present. These folds are probably due to the buckling of upper strata e.g., limestone of Laki Formation (Khan et al., 1988).

Faults: A number of closely spaced faults have been reported by various workers of the Geological Survey of Pakistan (Khan et al,.1988. Shah, et al.1988) and Pakistan Mineral Development Corporation (Memon et al., 1976). The general trend of fault lies is north-south i.e., parallel to fold axis and dip towards east in the eastern flank, while on the western flank they dip towards west (Khan et al., 1988).

CHAPTER THREE

METHODOLOGY

The fresh bed coal samples were collected from thirty leased coal mines at different depths, operating in the southern part of Lakhra coal field (south of toposheet 40 C/2). These were numbered accordingly and packed in the polythene bags. The collected coal samples were transported to the National Center of Excellence in Geology, University of Peshawar for the heavy and trace metal analysis.

Determination of heavy metals in coal:

Preparation of solution: Each coal sample was grinded separately in the ball mill (mortar) to 60 # (250 μm size) sieve. 1gram of powdered coal sample was taken in the Teflon beaker, in which about 10 ml HF and 4 ml of HCl was added, and heated at 120°C until a paste was obtained (avoided drying up of the sample). Subsequently 8 to10 ml of HNO_3 was also added, that evaporated until a paste was obtained. This was followed by the addition of 20 ml of 2N HCl and heated at low temperature for a while. Afterwards the solution was filtered through a very fine filter paper (whatman No.42), and filtrate of each sample was diluted to 100 ml with deionized water. This solution was stored in polythene bottles for the determination of Zn, Cu, Cd, Cr, Ni, Pb, and Fe by using Atomic Absorption Spectrophotometer.

Instrumentation

Absorption mode of model SP191 PYE UNICAM Atomic Absorption Spectrophotometer along with the detailed method for preparation of working standard conditions for different elements are described as follow:

Mode	Absorption
Silt width	0.4 nm
Fuel flow	1.2 l/min
Air flow	5 l/min
Burner height	10 mn

The instrument was set at wave lengths 213.9 nm for Zn, 357.9 nm for Cr, 240.7 nm for Co, 232 nm for Ni, 217nm for Pb and 248.3nm for Fe.

Standard stock solution of 1000ppm: One gram of required metal foil was dissolved in 50 ml of 5 HNO_3 and was diluted to 1000 ml with deionized water in volumetric flask. This standard stock solution contained 1000 ppm of a metal.

Standard stock solution 100 ppm

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

Working standards

Working standards of 2, 4, and 8 ppm were prepared by taking 2 ml, 4 ml, and 8 ml of the 100 ppm standard solutions in 100 ml volumetric flasks and the volumes were made upto the mark. These standard solutions were used for the calibrating the instrument.

Procedure

The atomic absorption spectrometer was turned on and warmed up for about thirty minutes. The cathode lamp of required element to be analyzed was inserted in it and turned on. After warming up of the cathode lamp, the air acetylene was ignited. The instrument was calibrated and standardized with working standards of 2, 4, and 8 ppm. A required wave length was selected by obtaining absorption.

The atomic absorption spectrometer was set at the selected wave length, and set as zero with blank. After confirming that the instrument has been properly calibrated and the results of the standards were with in the confidence limit, the concentration of each prepared solution of the sample was noted, and the Cu, Zn, Co, Ni, Pb and Fe contents were calculated, according to the following formula:

metal concentration in ppm = Atomic Absorption Spectrometer reading* volume/wt of sample

Method of air sampling

Air sampling was carried out in two different ways. Samples/suspended particles were collected in clean plastic pans (30cm diameter), half filled with distilled water. One group of samples was collected from the ground level position, while the other group was collected by hanging the pan with some support at man's nose height (about five feet above ground level). For each group five different location were selected (Fig. 5.1).

The samples collected in distilled water, were filtered through what man No.42 filter paper, and the residue were collected and dried in the oven at above 800°C over night. The residue was then weighed in order to calculate the rate of dust fall during the placing time i.e. 48 hours (Table 5.1 and 5.2). Each dried sample was kept in a glass bottle for the determination of heavy and trace metals.

Preparation of solution

A known weight (about 0.2 g) of each collected particulate matter was taken in the Teflon beaker, in which 5 to 10 ml of HF was added and heated at low temperature i.e. 75°C, for half an hour, subsequently 10 ml of HNO_3 was also added, that evaporated at 100°C, until the paste was obtained. This was followed by the addition of 20 ml of 2N HCl and heated at very low temperature for a few minutes. Afterwards the solution was filtered through a very fine (Whatman No.42) filter paper in a 25ml volumetric flask.

This solution was stored in polyethene bottles for the determination of trace and heavy metals(Sodium, Magnesium, Potassium, Calcium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Lead and Cadmium) by same method of Atomic Absorption Spectrophotometery. The results are given table 5.1 and 5.2.

Method for the geochemical analysis of water

Water analysis are most commonly pledged with samples in which the total amount of dissolved solids constitute only a small fraction of one percent of the total weight of the sample. The analyses, therefore, expressed more conveniently in parts per million (ppm) or milligram per litter (mg/l). One part per million means one part by weight of dissolved matter in a million parts by weight of solution. In other words, milligram per liter (mg/l) is a liter of pure water containing one million milligram at 3.89°C.

Collection of water samples

The collection of water samples from subsurface need precautions as the chemistry of water may change after collection. For this an enumerated geochemical investigation was carried out on six samples of water, collected from the dug wells in and around the study area (Lakhra coal field). It is now generally understood that the dug well water is never pure, it contain at least small amount of dissolved gasses and solids. The method of drawing up the samples, from the well makes variation in the chemistry of water. Collection and the chemical analysis of water samples from dug wells form an integral part of environmental study of water. Therefore, water samples were collected with great care to avoid any possibility of contamination. The bottles used for storing collected water samples were washed/treated with 5% HCl or HNO_3 and then rinsed with deionised water. During field, two water samples were collected in the already clean polythene bottles at the site. One sample was analyzed for the determination of alkalinity, temperature, pH, electrical conductivity, TDS and sulphates at the site. The other was acidified with drops of nitric acid (HNO_3) to a pH bellow 5.0 for minimizing precipitation and absorption on walls of the bottles. These polythene bottles of containing dug well water were capped tightly for heavy metal analysi`s.

Determination of Electrical Conductivity

Conductivity is a measure of the ease with which an electrical current can pass through a solution. Pure water is very good conductor, however, ions in solution will carry an electrical current. Therefore, the more are the charged ions present in water the more will be its conductivity. In the International System of Units (SI) the term conductivity is represented by millisiemens per centimeter "mS/cm". Freshly distilled water has a conductivity of 0.5 to 2 mS/m. The conductivity of potable water ranges generally from 50 to 1500 mS/m. COLE-PAMER'S(Model 148-55) conductivity meter was used for the determination of electrical conductivity of water samples.

The instrument was first calibrated with a standard KCl solution, having conductivity value of 1.45 mS/cm at 25°C. As the temperature coefficient of most of waters is only approximately the same as that of standard KCl solution. Therefore, the electrical conductivity of water samples was determined relative to KCl solution.

Determination of alkalinity

Alkalinity of water is its acid neutralizing capacity. Alkalinity of surface and ground water is a function of carbonate, bicarbonate and hydroxide contents. To determine alkalinity of water samples a special device of Hach Digital Titrator was used which is fitted with concentrated titrants in compact containers called cartridges. Each cartridge replaces about one quarter of standard titrant. A main drive screw in the digital Titrator controls a plunger that forces the titrating solution from titration cartridge in a regulated flow. The titrator body is constructed of precision-molded, heavy duty chemical impact resistant acetyl plastic. Accuracy is rated at +1% or better. Titration solutions are packed in disposable polythene plastic containers with Teflon covered neoprene seals and polythene resoluble closures to cover the cartridge tips.

Each cartridge contains approximately 13 ml of titrating solution. Most solutions are controlled to +0.5N by comparing with normality and tolerance listed on the label provided. Solution concentrations are designed for titration of 10-40 turns (100-400 digits) of the delivery knobs. To start the procedure, a known sample volume and sulfuric acid (H_2SO_4) Titration cartridge corresponding to the expected alkalinity concentration as mg/L calcium carbonate was selected from the Table 3.1.

Table 3.1. Titration Cartridges and their Digit Multipliers.

Range (mg/l) as $CaCO_3$	Sample Volume	Titration Cartridge N	Catalog Number	Digit Multiplier
10 -40	100	0.1600	14388 - 01	0.1
40 - 160	25	0.1600	14388 - 01	0.4
100-400	100	1.600	14389 - 01	1.0
200-800	50	1.600	14389 - 01	2.0
500-2000	20	1.600	14389 - 01	5.0
1000-4000	10	1.600	14389 - 01	10.0

A clean delivery tube was then inserted into the titration cartridge. The delivery knob was turned slowly and gradually to eject a few drops of titrant, the counter was then rested at zero. Selected sample volume was measured with the help of graduated cylinder and was transferred into 250 ml. Erlenmeyer flask and sometimes diluted to about 100ml with deionized water. The phenolphthalein Indicator Powder pillow was added to the sample and swirled to mix. The sample solution titrated to a colorless end until the colour turned pink. By immersing the delivery tube tip into the solution it was then titrated with sulfuric acid to get colorless end. The digital reading was recorded as P-Alkalinity. In case of not obtaining pink color with the addition of phenolphthalein, then bromocresol green methyl red indicator powder pillow was added to the solution. The titration was continued with the sulfuric acid to a light greenish blue-gray end. The number of digits recorded and T-Alkalinity was calculated as:

Total ml Required X Digits Multiplier = mg /l as $CaCO_3$ Total (T or M) alkalinity

Determination of Sulfate in water

Sulfate (SO_4), was determined by Hach DR/2000 spectrometer in the field. The purpose of determining the sulfate on the site immediately or with in 24 hours after collecting samples, was that in the presence of organic matter certain bacteria may reduce SO_4 to S^{2-}. The Spectrometer is a microprocessor-controlled single beam instrument suitable for use in the laboratory or in the field. It is precalibrated for 120 different spectrophotometeric measurements.

Test results can be displayed in percentage transmittance, absorbance or concentration of appropriate units of the measurement. The LCD dot matrix digital display offers automatic ranging in the pre-programmed parameters. This instrument is provided with procedure's manual in which step by step illustrated instructions for measuring 100 parameters constituents are presented. In this manual all procedures given are approved by the United States Environmental Protection Agency (US-EPA).

To perform analyses using DR/200 spectrophotometer, one has to enter the stored programmed number for parameter to be determined, and the wave length dial rotated to the required number.

Sulfate concentration was determined by "turbidimetric method" (Rossum & Villarruz, 1961). Sulfate was precipitated in an acetic acid medium with barium chloride so as to perform barium sulfate crystals of uniform size. Light absorbance of the barium sulfate was measured by photometer and the sulfate concentration was measured by comparison of the reading with a standard curve.

Atomic Absorption Spectrophotometer Technique

Pye Unicam Flame Atomic Absorption and Electrothermal (graphite furnace) Atomic absorption technique were used for the detection of trace elements in water samples. The flame atomic absorption technique was used for the determination of Fe in the water samples and electrothermal atomic absorption (Perkin Elmer 3300 model) equipped with HG-600 graphite furnace and As-60 Auto sampler was used for the determination of Cu , Pb , Ni , Fe and Cd in water samples.

The concentration of these elements was measured in µg/l (ppb). Graphite furnace has the advantages of simplicity, rapidity and freedom for water samples. The auto sampler permit automatic dispensing of up to 40 samples. During an operating cycle the capillary tip is flushed with 1.4 ml of deionized water. Before dilution the sampling arm raised and simultaneously a 25µl bubble of air drawn into the capillary tip to separate the diligent from the solution to be diluted. The capillary tip entered the sample introduction hole in the graphite tube. A computerized program of windows Benchtop software loaded to obtain the result of water samples, in which all system components are displayed on the Benchtop screen. Required lamp was installed and aligned for the geochemistry of water samples.

Determination of metals in water

The detail geochemical study of each element in dug well water determined by Electrothermal Atomic Absorption is given bellow :

1. Lead (Pb)

Lead is a serious cumulative body poison. Lead contamination in the water of coal field can be attributed to the presence of lead in coal. A 1000 ppm of Pb standard solution was prepared by taking 0.1599 gram lead nitrate, [Pb $(NO_3)_2$] dissolved in approximately 200 ml of de ionized water. Ten millimeters of concentrated HNO_3 was added and was diluted to 1000 ml with de ionized water in volumetric flask. This solution contained 1000 ppm of lead. From this solution 10 ppm standard solution was prepared and other working standard of 25, 50, 75 and 100 ppb were prepared. The graphite furnace was calibrated with these standards. The hollow cathode lamp for lead was used. A wave length 283.3 nm, silt opening 0.7, and a lamp current at Matrix Modifier of 0.2 mg phosphate, pyrolyses temperature of 700°C and atomization temperature of 1800°C were used during Pb determination.

2. Copper (Cu)

To determine the concentration of copper in water samples the standard solution of copper was prepared. A weight quality of 1.00 g of polished electrolytic gently copper wire was dissolved in 5 ml of concentrated HNO_3 ; until complete dissolution of the copper took place. Dilution to 1000 ml with deionized water in volumetric flask was followed. This standard stock solution contained 1000 ppm of copper. From this solution 10 ppm standard solution was prepared and then from this standard the working solutions of 25, 50, 100, 200 ppb were prepared by diluting them with de ionized water into 100 ml volumetric flask. To run the water samples by Atomic Absorption Spectrometer, the instrument was adjusted as following.

Hallow cathode lamp of Wave length 324.8, Silt of 0.7, Pyrolyses temperature of 1000°C and atomization temperature of 2300°C.

3. Cadmium (Cd)

Cadmium in water was determined by Atomic Absorption Spectrometer and for this purpose standard stock solution of cadmium was prepared by dissolving 1.000 g cadmium metal in a minimum volume of (1+1) HCl. It was then transferred to volumetric flask of 1000 ml with deionized water. From this solution, the working standard solutions of 25, 50 and 100 ppb were prepared. Hollow cathode lamp of cadmium is used with a wave length of 228.8, silt width of 0.7, matrix modifier of 0.2 mg and temperature of 1600°C.

4. Nickel (Ni)

To prepare the standard stock solution for Ni, 1.273 g of Nickel oxide was dissolved in a minimum volume of 10% v/v HCl. The solution was diluted with deionized water in volumetric flask up to the mark of 1000 ml. This standard solution contained 1000 ppm of nickel and was stored into polyethylene bottles to avoid contamination and absorption on the wall of container.

Working standard solutions of 50, 100 and 200 ppb were prepared from this standard solution. Three cells were filled with these solutions of different concentrations and one cell was filled with deionized water (blank). After the calibration of instrument with these standard, the remaining cells of sample tray were filled with samples of collected water to determine the concentration of nickel in µg/l. The instrument was standardized at the wave length of 232.0, Silt of 0.2, Pyrolysis temperature of 1400°C and atomization temperature of 2500°C.

5. Iron (Fe)

To prepare standard solution of iron, 3.115 g Mohar salt {$Fe(NH_4)_2.H_2O$} was dissolved in deionized water and diluted into a volumetric flask upto the mark of 1000 ml. This standard stock solution contained 1000ppm of Fe. The standard solution was stored in a polyethylene bottle for further appliance. From this solution, 10 ppm standard solution was prepared and then the working standards of 25, 50, 75 and 100 ppb were prepared by diluting it with deionized water into volumetric flask of 100 ml. The instrument was set at a wave length of 248.3, silt of 0.2. Matrix Modifier of 0.05 mg $Mg(NO_3)_2$, Pyrolysis temperature of 1400°C and atomization temperature of 2400°C.

CHAPTER FOUR

HEAVY METALS IN LAAKHRA COAL

After Thar coal field, Lakhra coal field is the second largest coal field of Pakistan discovered in 1853 by Britishers. But due to its lignitic quality and presence of high sulphur its utilization is quite limited. Since 1990 WAPDA started the usage of Lakhra coal in their coal fired thermal power station at Khanote, thus making it necessary to study its environmental effects, particular to those of heavy metals.

PECH (1980) has grouped the heavy metals into following six categories:

a) Elements of great concern; e.g., As, B, Cd, Hg, Mo, Pb and Se.

b) Elements of moderate concern; e. g., Cr, Cu, F, Ni, V and Zn.

c) Elements of minor concern; e. g., Ba, Br, Cl, Co, Ge, Li, Mn, Sr.

d) Radioactive elements, generally considered to be of minor concern, but adequate information is lacking for a proper assessment; e.g., Po, Ra, Rn, Th and U.

e) Elements of concern but with negligible concentrations in coal and coal residues; e. g. Ag., Be, Sn, Tl and

f) Elements of no immediate concern.

Swaine (1982) has grouped these elements into two following categories:

(i) Elements of prime environmental interest; e.g., As, Cd, Cr, F, Hg, Ni, Pb, Se, B, Be, Cl, Co, Cu, Mn, Mo and

(ii) Elements that could be of environmental interest; e.g. Sb, Sn, Th, Tl,U,V and Zn.

Considering our analytical constraints we analyzed a limited number of heavy metals including Cr, Fe, Ni, Cu, Zn, Pb and Cd in thirty samples collected from various coal mines at Lakhra during the present study. The location of the coal mines along with sample number is shown in Figure 4.1 and the data displayed in Table 4.1.

Following is the general description of the elements analyzed:

Chromium (Cr)

A micronutrient, which is essential for carbohydrate metabolism in animals; pollution of soils occur as a result of the dumping of chromate wastes, such as those from tanneries or electroplating and from sewage sludge disposal on land. However, unlike other heavy metals, chromium can exist in a trivalent (chromite) and a hexavalent form (chromate) and the Cr (VI) form is more phytotoxic than the Cr(III) form. Chromium is carcinogenic, causing cancer of respiratory organs in chromate workers chronically exposed to Cr-containing dusts (Langard, 1980).

Chromium in coal is listed as of " moderate concern " by P E C (1980), that means some problem could occur with high concentration of Cr in coal (Swaine,1990).

Chromium in coal was first reported by Mingaye (1907) who found 80 ppm in Japanese coal (Swaine, 1990).

Iron (Fe)

The excessive dose of iron causes diseases like hemosideroses, liver damage, diabetes etc. The WHO, (1970) and US Environmental Protection Agency, (1978) set a value of 0.3 mg/l as a maximum contamination limit (MCL) in water.

The presence of iron compounds in water upto this specific limit discloses an unpleasant taste and few tenth's ppm of iron in water make it unfit for some uses. Small amount of iron is beneficial to human being, while deficiency of iron in human body causes anemia.

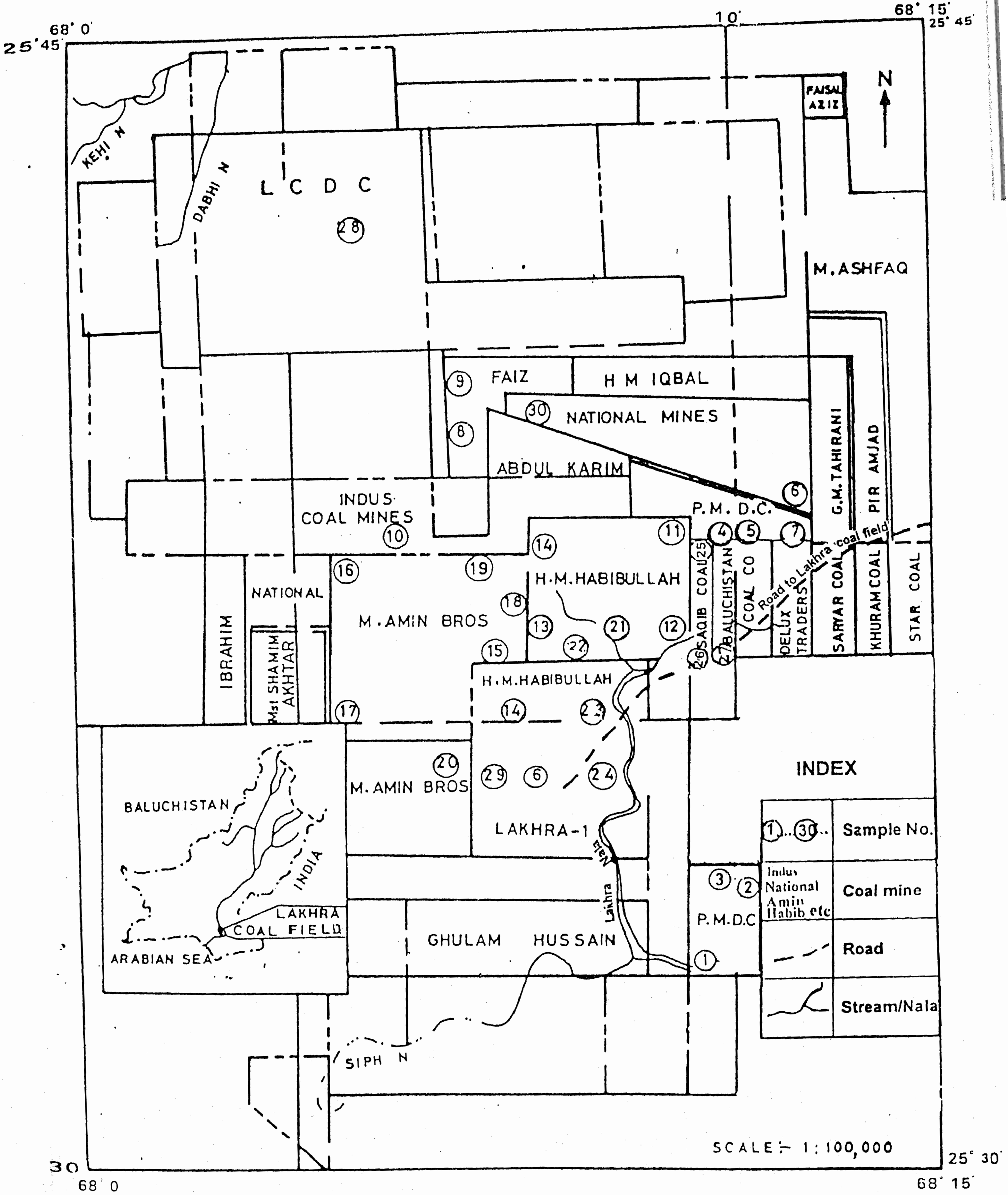


Fig. 4.1 Map showing location of mines / leased areas from coal samples were taken.

Nickel (Ni)

Nickel is silvery white, malleable and ductile. It is classified as border line element between hard and soft acid acceptors in chemical interaction towards donor atoms.

In nature, Nickel is added in atmosphere from volcanoes (Calle et all., 1973) and wind blown dust. Coal combustion also constitutes about 1.5% Ni in atmosphere. Nickel powder and its compounds cause a variety of cancers in rodents and are listed as possible causative agent for environmental cancer in man.

Elemental Ni is highly surface active and thus adheres to the breathable air-borne particles. Ni compounds induce nasal, laryngeal and lung cancers (Pedersen et al., 1978). Coal combustion constitute about 1.5 % of the global emission of nickel to the atmosphere (Bennett, 1982).

Copper (Cu)

Cu belongs to the third transition metal series, it is widely distributed in nature in the free state and in sulfides, arsenides, chlorides and carbonates. A micronutrient which can be deficient in some soils causing severe loss of yield in several crops, especially cereals. Toxicity problems can occur in crops in polluted soils and live stock grazing herbage growing on polluted soils. Copper pollution can arise from Cu mining and smelting, brass manufacture, electroplating and excessive use of Cu-based agrochemical (e.g. Bordeaux Mixture). Copper has been listed as of "moderate concern" (P E C H,1980), that means "some problems could occur with high concentration of copper in coal" (Swaine, 1990). It is supposed that during the peat stage of coalification, Cu was fixed, probably in humic acid (Swaine,1990). Cu in most coals occur as a sulfide and chalcopyrite associated with organic matter.

Zinc (Zn)

Zinc is a member of the periodic classification of the elements along with Cd and Hg. A micro nutrient which is the most serious deficiency problem in crops in the world as a whole, especially in tropical regions and where the soils have developed on sandstones and sandy drift. In context of pollution, Zn is mainly a cause of phytotoxicity and has a relatively low toxicity to animals and humans. Zinc pollution is often associated with mining and smelting and Cd is always present as a guest element in the Zn S ore. Mining causes pollution of air, water, and soil with fine tailings particles which ultimately undergo oxidation to release Zn^{2+}. Zinc sulphide (sphalerite) ore often occurs together with PbS (galena), the main ore of Pb, and so Zn pollution is often associated with Pb and also Cu, in some cases, as well as traces of Cd. The geochemical association with Cd implies that impure Zn compounds may contain Cd, but also that Zn- Cd antagonism may mitigate some of the effects of Cd contamination.

Lead (Pb)

Lead is a member of group IV element (C, Si, Ge, Sn and Pb) of the periodic classification. In atmosphere other than several sources about 6% of lead in coal may reach the atmosphere from coal burning (Lovering,1976). A non-essential element; it is a neurotoxin and a good example of multimedia pollutant. The main sources of Pb pollution in the environment are petrol (air pollutant, but can also be water or soil pollutant from spillage), particulate in exhaust fumes from the petrol combustion (air pollutants, inhaled by humans), particulate from petrol, fossil fuel combustion in soil (soil pollutant-taken up by plants and also ingested with plant food crops), paint flakes from old paints containing a percentage of Pb, Pb in some traditional ethnic cosmetics (e.g., Surma - skin absorption), constituents of solders and varnishes used on interiors of food cans (food contaminant), Pb pipes for potable water (water pollutant), pesticide (historic use of Pb and As containing pesticide sprays in orchids), lead shot used for game and clay pigeon shooting (soil pollutant, but also a food contaminant if inadvertently consumed with game flesh) and Pb pollution from mining and smelting of the ore (usually Pb S) - this includes acid mine drainage with soluble Pb (water pollutant), tailings from ore dressing (particulate water pollutants and soil pollutant), weather to release soluble Pb, and smelter fumes - Pb aerosols (air and soil pollutants).

Lead is generally more ubiquitous in the environment and is a cumulative toxin in the mammalian body, so toxic concentrations can accumulate in the bone marrow, where red blood corpuscle formation (haematopoiesis) occurs. At least five stages in the formation of the hemoglobin are affected by Pb but two enzymes most affected are δ-amino laevulinic dehydrates (ALAD) and ferrochelatase (Waldron, 1980).

This inhibition of haem synthesis results in anaemia. Kidney damage also occurs as a result of exposure to Pb. Lead, like Hg, is a powerful neurotoxin and a range of pathological conditions are associated with acute Pb poisoning, most characteristic of which is cerebral oedema.

Cadmium (Cd)

The stable state of Cd in the natural environment is Cd^{2+}. Cadmium is silvery white and ductile with a faint blue tinge(Moore, 1984). It is listed as of an element of prime environment concern by P E C (1980). It is a highly toxic non-essential metal which accumulates in the kidneys of mammals and can cause kidney failure.

In humans, kidney damage diagnosed by the presence of micro globulin proteins is the main toxic effect resulting from chronic exposure to the metal. High concentrations of inhaled Cd aerosols can cause emphysema and related acute lung conditions. Cadmium becomes very volatile above 400°C and hence is likely to be dispersed as an aerosol when mixtures of metals containing Cd are heated or cast.

Cadmium tends to be less strongly absorbed than many other divalent metals and is, therefore, more mobile in soils and sediments. There is more danger from this metal moving through the human food chain from contaminated soils than most other metals. Coal combustion constitute about one-tenth of the amount emitted by volcanoes (Nriagu,1979).

By comparing the results of the studied coal samples in table 4.1 it is noticed that Cr is highest (i.e., 28 ppm) in Habib coal min IV (Sample No. 24) and lowest (i.e. 1 ppm) in PMDC coal mine No. 21 and Amin coal mine No. 27, while in Habib coal mine-a (sample No. 11) and b (sample No. 12) concentration of Cr is nil or 00 ppm. Iron is highest in National coal mine No.26 (sample No. 6) and Habib coal mine-a (sample No. 11). It is lowest in PMDC coal mine No. 26. In Habib coal mine No. IV, nickel is found in highest concentration while its lowest concentration is found in Amin coal mine No. 27 (sample No. 17). The highest concentration of Cu is found/analyzed in National coal mine No. 26 (sample No. 6) while in Amin coal mine No. 27 (sample No. 17) it is present in lowest amount (i.e. 10 ppm). Zinc pollutant, that is often associated with mining is found in highest concentration in Saquib coal mine No. II (sample No. 26) and its lowest concentration is found in Amin coal mine No. 27

Table 4.1 Heavy Metal Pollutants in Lakhra coal (values in ppm).

Sample No.	Location	Cr	Fe	Ni	Cu	Zn	Pb	Cd
1.	PMDC coal mine No.24	03	18	12	43	05	03	19
2.	PMDC coal mine No.21	01	24	06	52	38	29	11
3.	PMDC coal mine No.2	10	16	20	87	11	03	19
4.	PMDC coal mine No.18	14	19	17	60	14	13	08
5.	PMDC coal mine No.26	09	4	06	91	14	13	02
6.	National coal mine No.26	12	44	08	119	04	17	05
7.	PMDC coal mine No.8	16	7	16	108	10	24	13
8.	Faiz Coal mine No2	10	14	10	57	10	07	07
9.	Faiz Coal mine No.4	15	38	10	63	30	20	13
10.	Indus Coal mine No.4	10	15	13	60	07	26	12
11.	Habib Coal mine-a	00	44	06	40	09	17	09
12.	Habib Coal mine-b	00	18	03	86	14	20	08
13.	Habib Coal mine-c	11	17	10	84	20	20	11
14.	Habib Coal mine-d	09	23	09	52	85	00	39
15.	Amin Coal mine No.29	04	14	06	58	03	44	08
16.	Amin Coal mine No.35	04	18	04	49	08	18	06
17.	Amin Coal mine No.27	01	7	01	10	02	15	07
18.	Amin Coal mine No.28	03	17	02	33	04	30	21
19.	Amin Coal mine No.30	07	28	03	34	02	15	<1
20.	Amin /Imdad Coal mine	10	18	07	42	23	00	03
21.	Habib Coal mine No. I	08	7	10	28	10	16	<1
22.	Habib Coal mine No. II	10	16	26	112	14	21	<1
23.	Habib Coal mine No. III	06	28	09	54	05	19	08
24.	Habib Coal mine No. IV	28	36	103	43	86	45	44
25.	Saquib Coal mine No. I	04	10	04	36	06	19	<1
26.	Saquib Coal mine No. II	13	21	27	60	131	34	04
27.	Baluchistan Coal mine	15	18	18	45	14	07	07
28.	Lakhra Coal Dev. Corporation Mine	16	15	18	72	72	12	14
29.	Habib Coal Mine No.3	16	17	29	53	38	18	21
30.	National Coal mine No.3	27	15	18	92	41	08	15
Average or Mean		10	19	14	61	24	18	11

(sample No. 17) and 30 (sample No. 19). A highly toxic pollutant; Cadmium is found in its highest concentration in Habib coal mine No. IV(sample No. 24) and its lowest concentration is found in Habib coal mine No. I (sample No. 21), II (sample No. 22) and Saquib coal mine No. I (sample No. 25). Lead is found in highest concentration in Habib coal mine No. IV (i, e. 45 ppm in sample No. 24) and its lowest concentration is in PMDC coal mine 24 and 2 (3 ppm in each sample), while sample collected from Habib coal mine C and Amin/Imdad coal mine posses no (i. e. 00 ppm) lead.

Individual elements were plotted against each other in Fig. 4.2 (a-z &a_1-a_4) to find out if any correlation exists among these metals which could reflect light on the process of deposition or source of coal. In general most of the samples show similar pattern with low Chromium (0-28 ppm; 9.730 or 10 ppm mean), high iron (44.36 ppm, mean 19 ppm). Most of the heavy metals are positively correlated but with high scatter except Cr, Ni, Zn and Cd (having R^2 above 0.2), which could be considered as relatively better correlation.

Fig. 4.2 a' & b' shows comparison of. the Lakhra coal with Canadian and Indian lignite coal on the basis of mean heavy metals content, It is clear from this figure that the Lakhra coal in comparison to Canadian coal, have high Cr, Ni, Cu and Pb concentration and Lakhra coal is comparably high Cu concentration against Indian coal. According to Swaine (1990) Chromium in coal was first reported by Mingaye (1907) in Japanese coal. It is comparable to Canadian coal but is much lesser than that of Indian coal (Fig. 4.2 a' & b'). Figure 4.3 shows the concentration of Cr in various coal samples collected from coal mines at Lakhra. It is clear from this figure that the Habib coal mine No. IV and National coal mine No. 3 are relatively enriched in chromium.

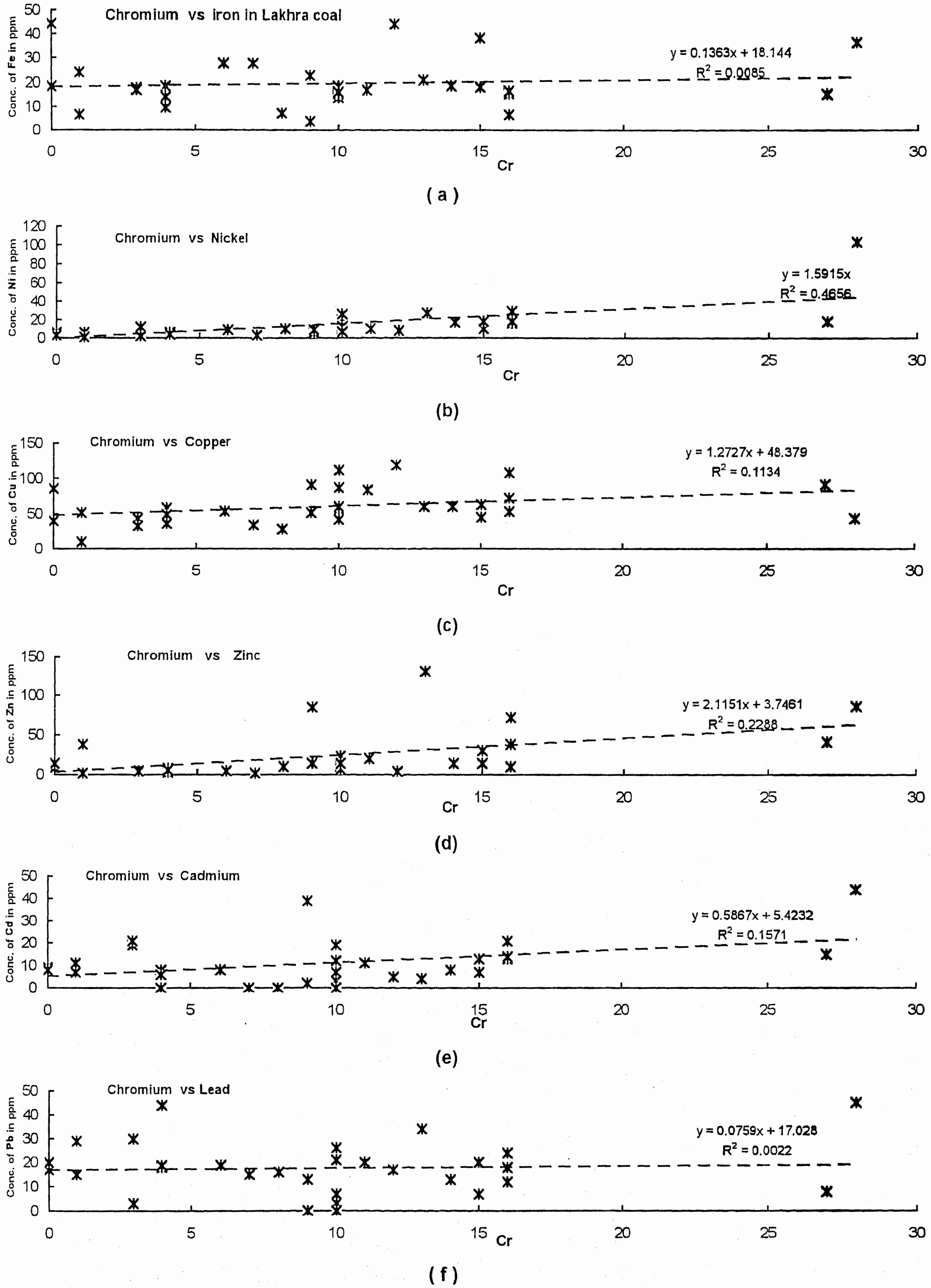
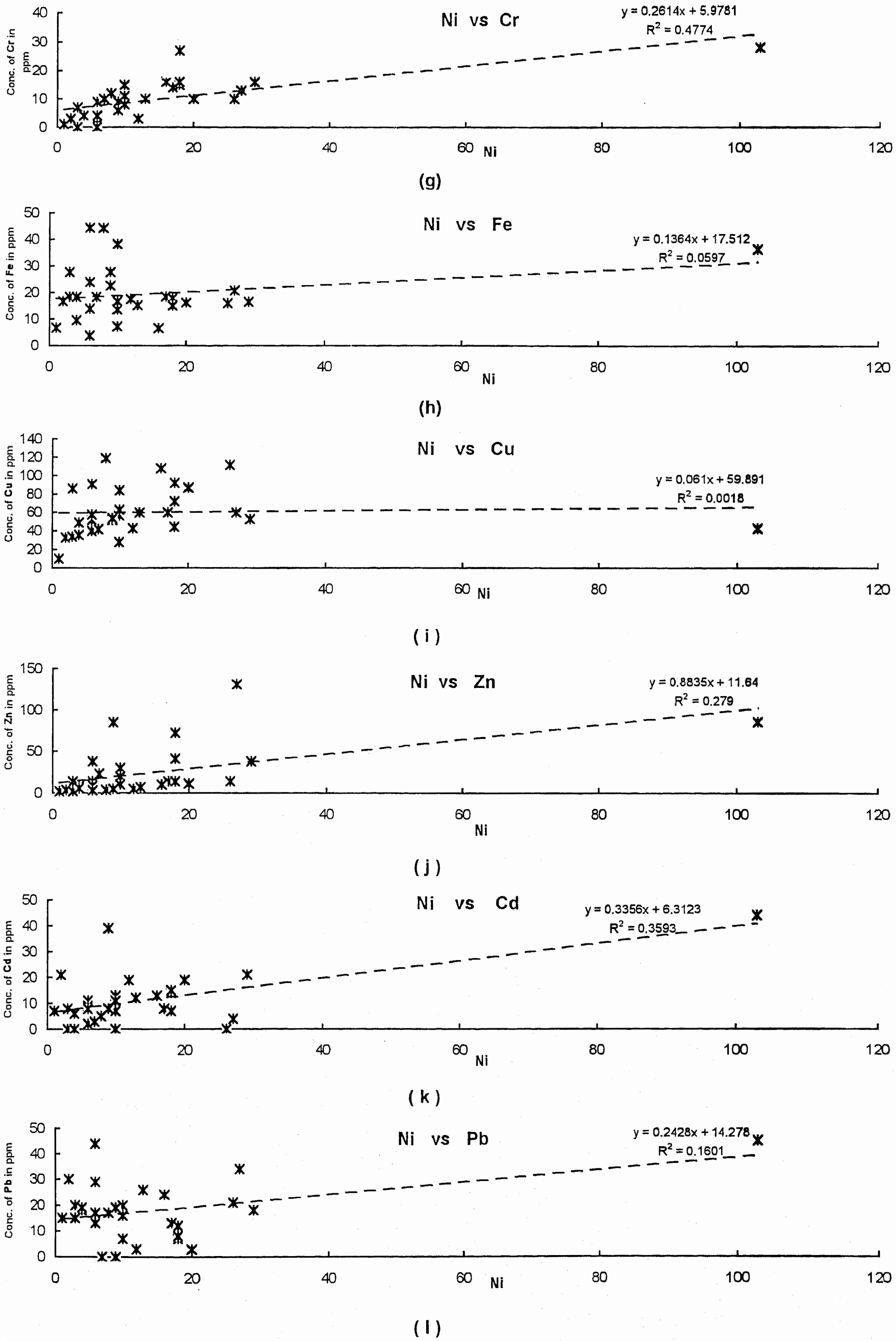


Fig.4.2(a-f) Comparison of chromium vs heavy metals in coal samples collected from Lakhra coalfield.



(g)

(h)

(i)

(j)

(k)

(l)

Fig.4.2(g-l) Comparison of nickel vs heavy metals in coal samples collected from Lakhra coalfield.

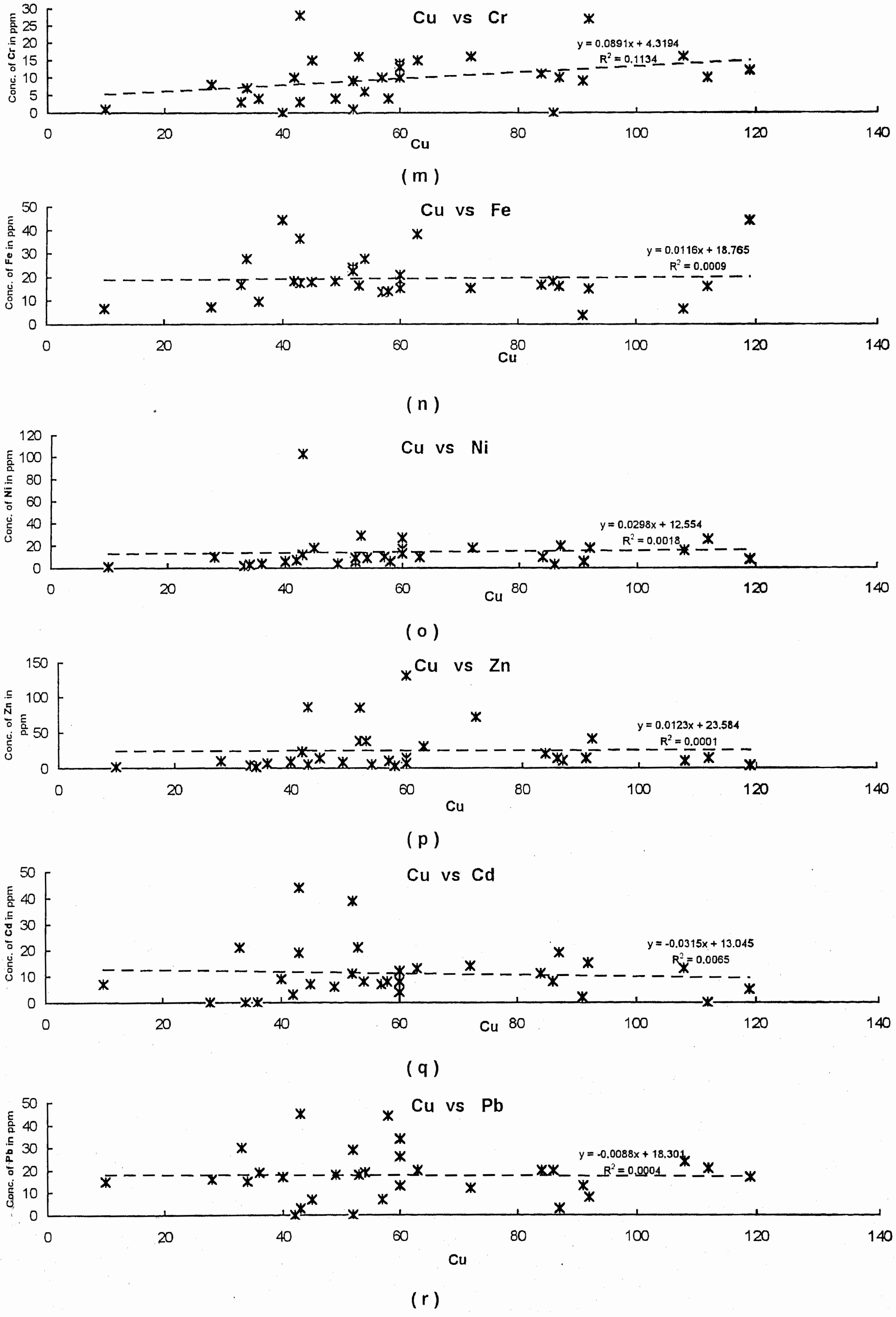


Fig.4.2(m-r) Comparison of copper vs heavy metals in coal samples collected from Lakhra coalfield.

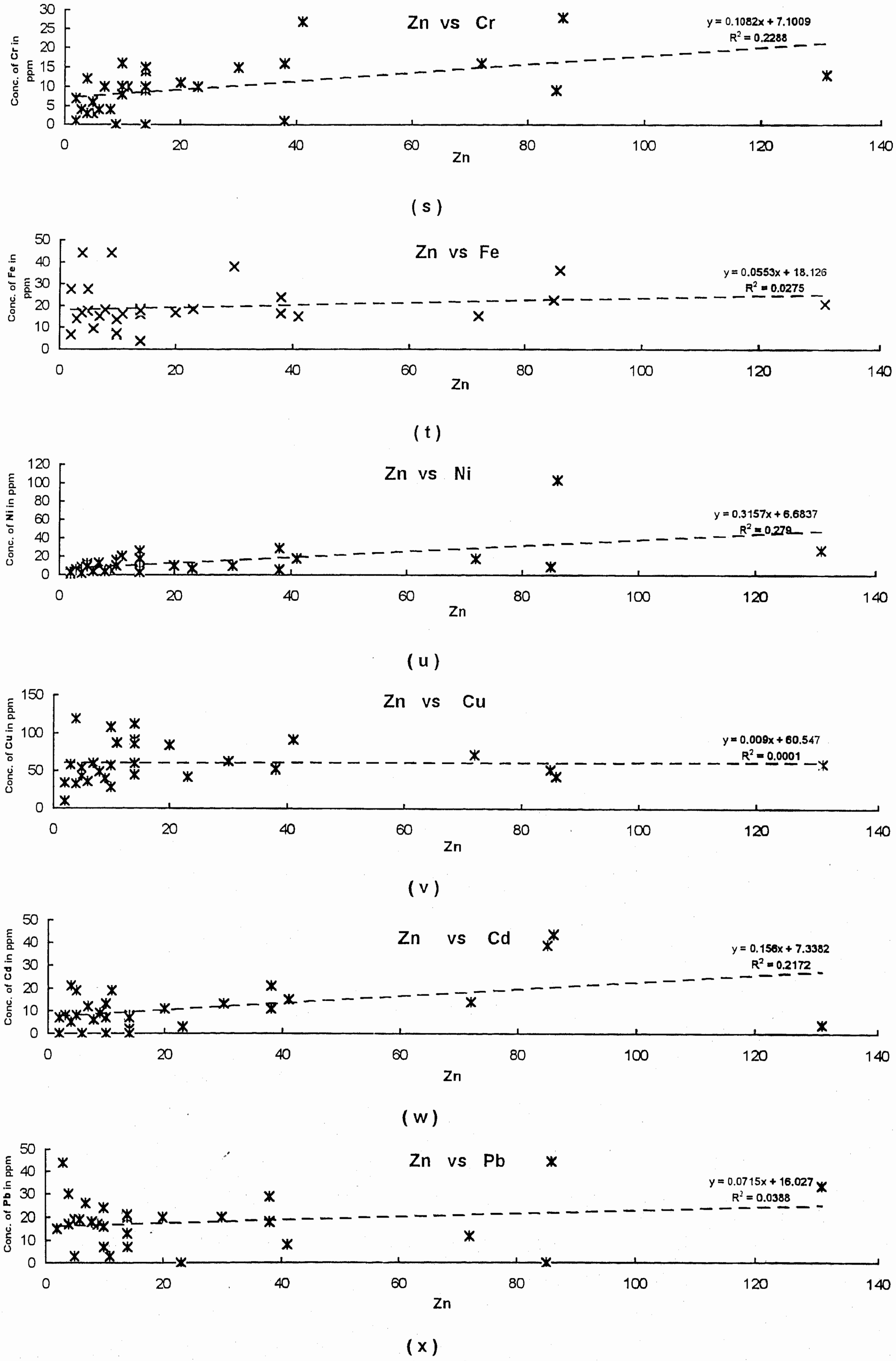
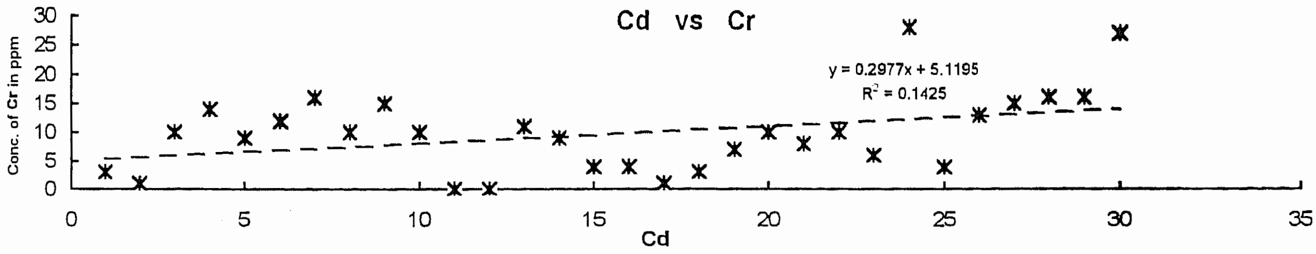
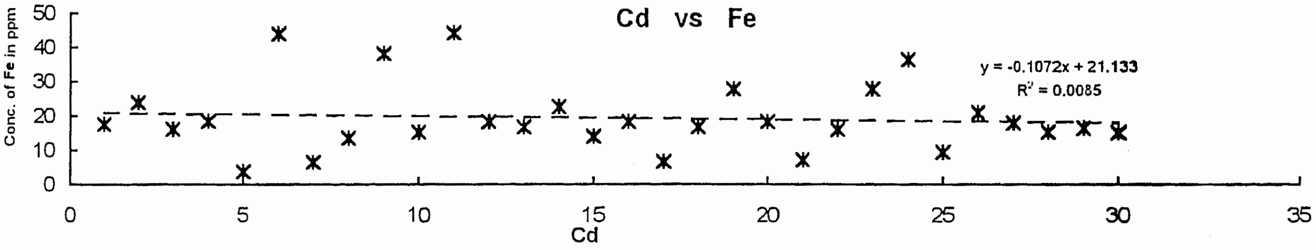


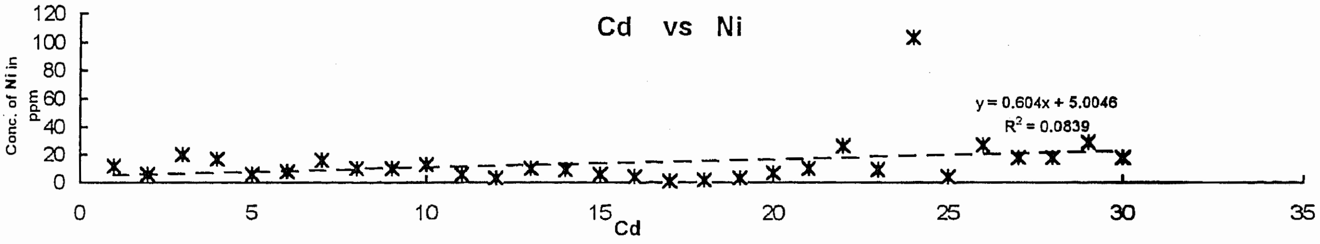
Fig.4.2(s-x) Comparison of zinc vs heavy metals in coal samples collected from Lakhra coalfield.



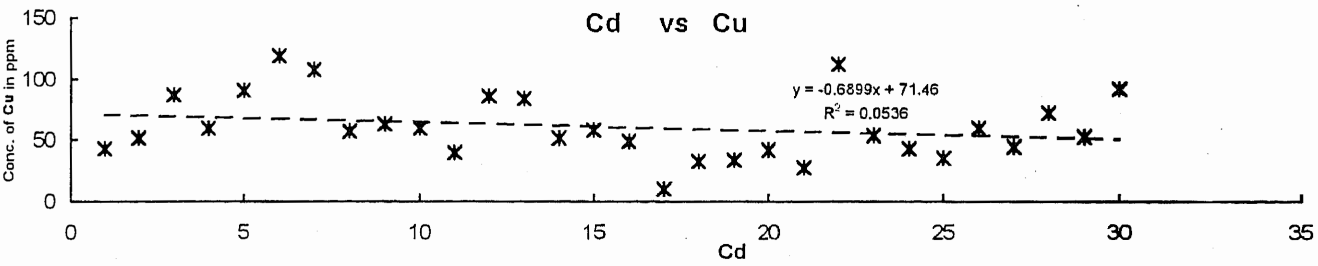
(y)



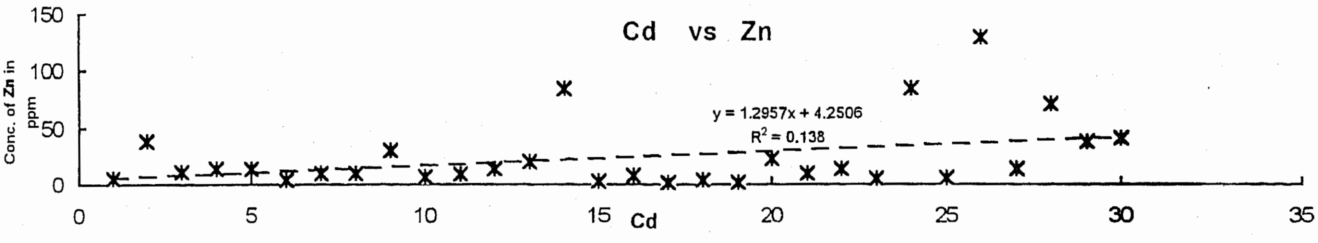
(z)



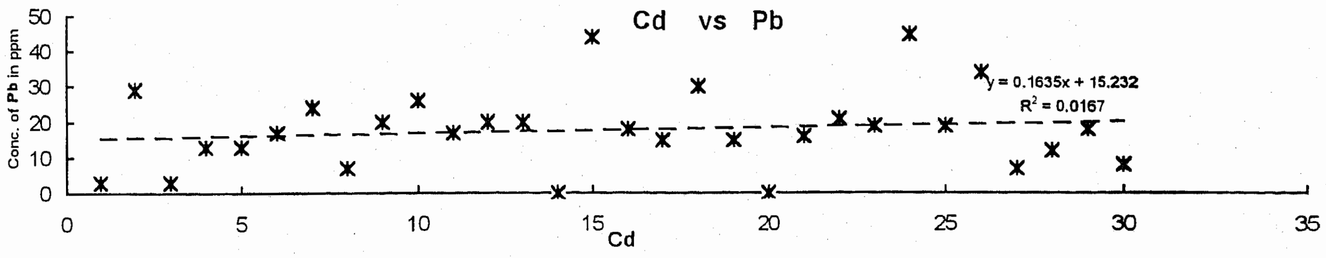
(a-1)



(a-2)



(a-3)



(a-4)

Fig.4.2(y-z&a1-a4)Comparison of copper vs heavy metals in coal samples collected from Lakhra coalfield.

Table 4.2 Comparison of heavy metals of Lakhra coal with Canadian coal(Ripley et al., 1996) and Indian lignite coal (Trivedy and Sinha, 1990). All values in parts per million.

Metals	Lakhra coal	Canadian coal	Indian coal
Cr	9.73	9.23	50
Fe	19.47	3537	Not Reported
Ni	14.36	10.1	38.5
Cu	60.76	11.76	14.5
Zn	24.33	51.04	38
Cd	11.13	Not Reported	8.5
Pb	17.76	9.21	118

Iron data is not available for the Indian coal but the Canadian coal show higher concentration of 3537 ppm iron as compared to that of Lakhra coal (19.47 ppm). The presence of iron in various coal sample of Lakhra coal field is shown by bar diagram in Fig. 4. 4. This figure shows that the National coal mine No. 26 and Habib coal mine-a are relatively enriched in iron.

Nickel in the coal seams was first of all detected by Descloizeaux (1880). Indian coal is having about 4 fold high amount 38.5 ppm as compare to that of Canadian coal (10.1 ppm) and Lakhra coal (14.36 ppm) (Table 4.2 & Fig 4.2 a' & b'). In Fig 4.5 the nickel content in coal samples collected from various coal mines at Lakhra are shown. It is evident from this diagram that the Habib coal mine No. IV has relatively multifold high concentration.

Copper in coal was first reported by Platz (1887), who found copper in coal ash from Germany. It is highest in Lakhra coal (60.76 ppm), while that of Canadian coal (11.76 ppm) are having lesser amount (Table 4.2 & Fig. 4.2). The distribution of Cu content in Lakhra coal samples is shown in Fig. 4.6. This diagram shows that several of the samples of Lakhra coal are having Cu > 60 ppm.

Zinc in coal was first reported by Jensch in 1887 in German coal ashes. It is highest in Canadian coal (51.04 ppm) as compared to that of Lakhra (24.33 ppm)

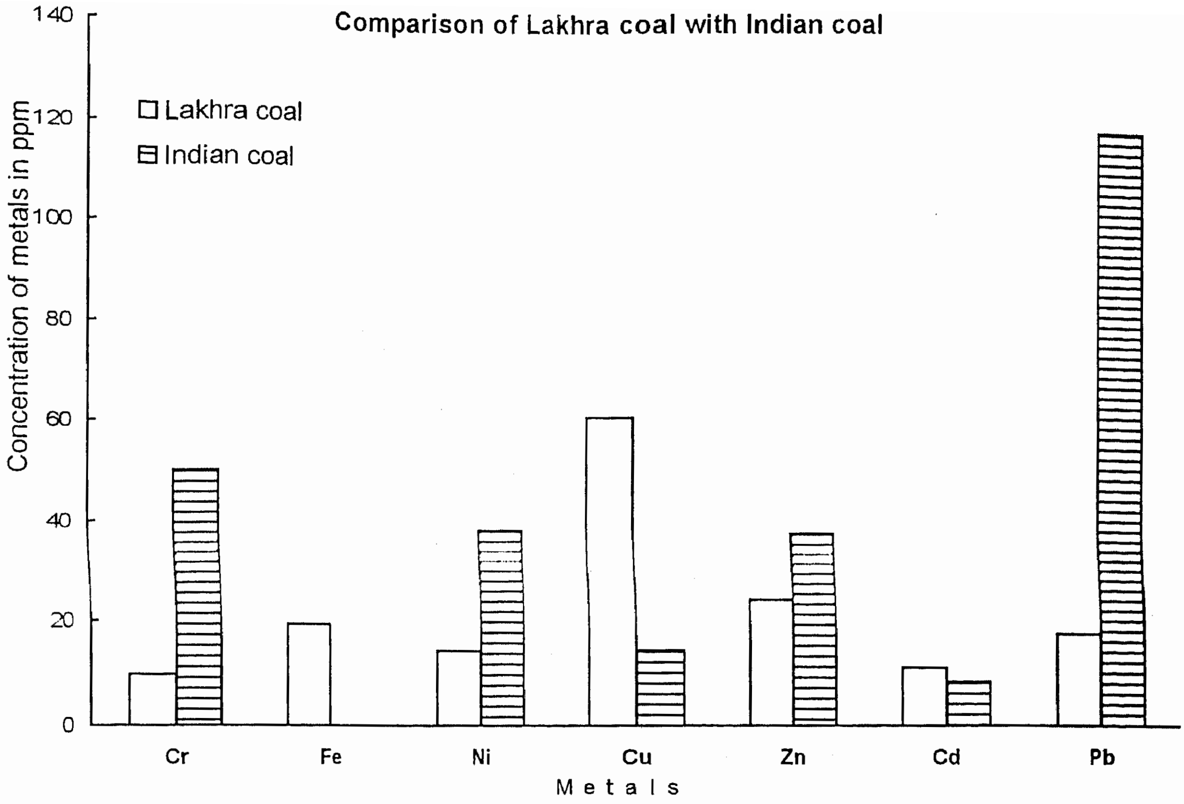


Fig. 4.2 a'. Comparison of Lakhra coal with Indian coal

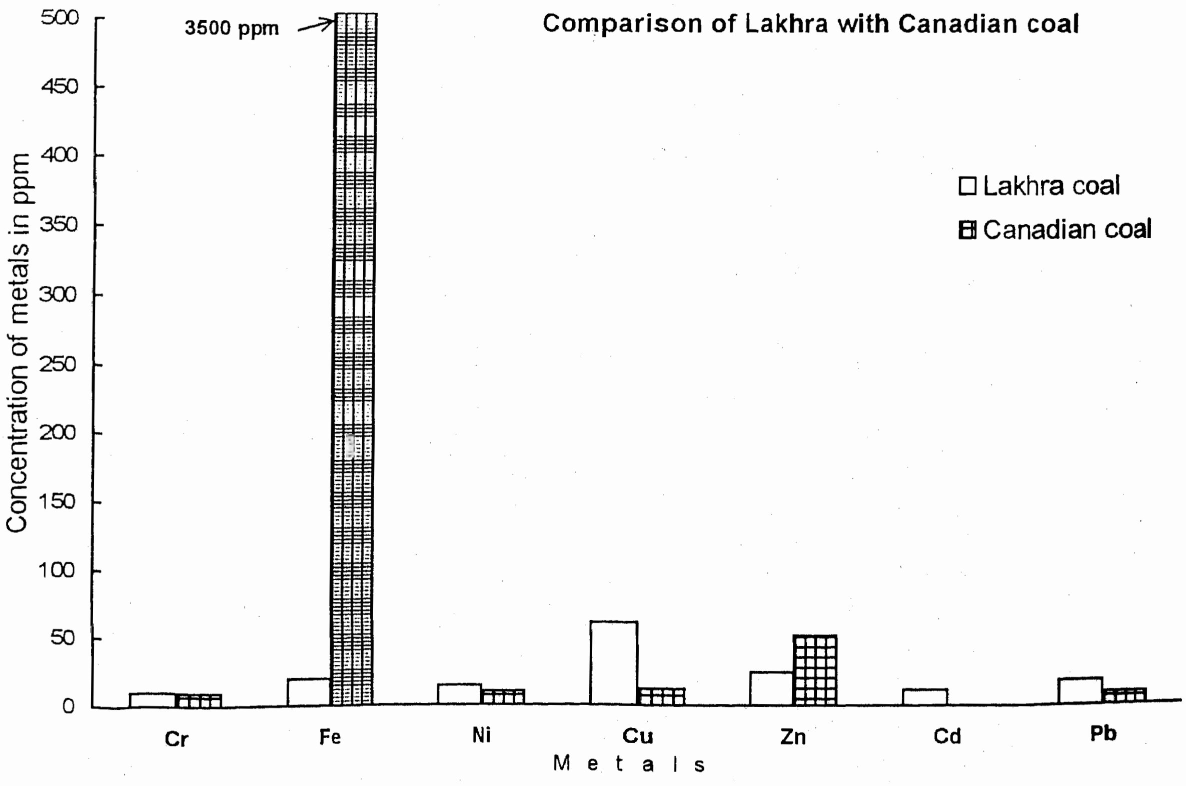


Fig. 4.2 b'. Comparison of Heavy metals of Lakhra with Canadian coal

and Indian (38 ppm) coal (Table 4.2 & Fig. 4.2). Fig. 4.7 shows the concentration of Zn in Habib coal mine-d and IV and Saqib coal mine No. II and Lakhra coal development corporation mine area having > 60 ppm Zinc (Table 4.2 & Fig. 4.7). Cadmium in coal was first reported by German scientist Jensch(1887). In Canadian coal Cd is not reported, however, Lakhra coal is having relatively high (11.13 ppm) Cd as compare to that of Indian (8.5 ppm) coal (Table 4.2 & Fig. 4.2). Lead was first reported in coal by Goldschmidth & Peters in 1933. It is highest in Indian coal (118 ppm) with second highest in Lakhra coal (17.76 ppm) and Canadian coal show the lowest value (9.21 ppm). Fig. 4.8 shows the distribution of Pb concentration in coal samples, collected from various mines at Lakhra coal field. This diagram shows that the coal samples collected from Habib coal mine No. IV and Amin coal mine No. 29 are enriched in Pb (i.e. 45 ppm and 44 ppm (Fig. 4.8). In Fig. 4.9, Cd concentration in various coal samples of Lakhra coal field is shown. This diagram two samples of Habib coal mine-d and IV are having relatively high (>38 ppm) concentration of cadmium (Fig. 4.9).

This comparison indicates that except for relatively high Cu and Cd content, the Lakhra coal is not enriched in heavy metals as compare to the other coals of the world from combustion point of view. However, from environmental point of view the data shows that this coal can be a source of contamination for air and water in the surrounding areas.

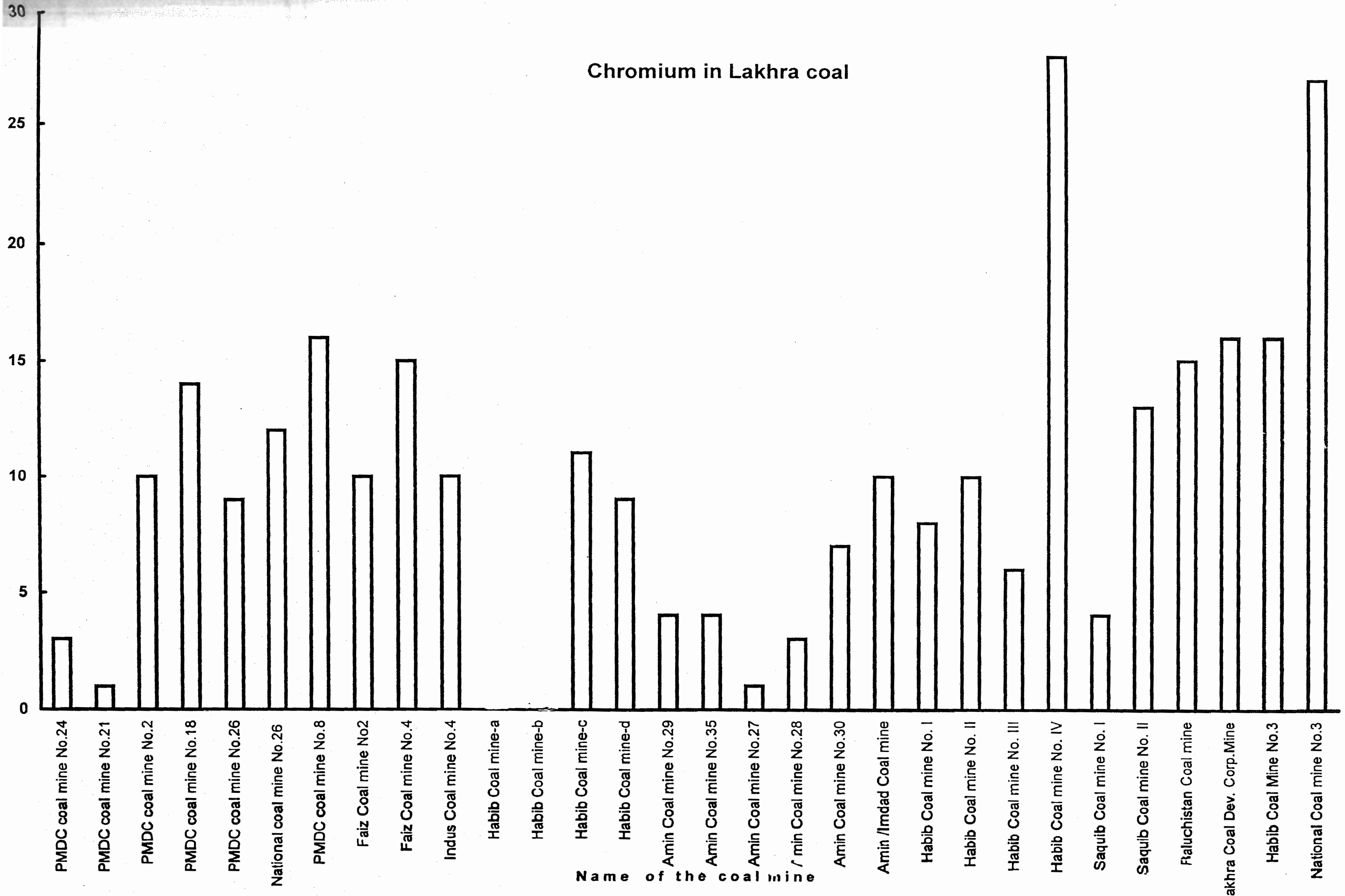


Figure 4.3 Chromium in coal samples collected from various coal mines of Lalkhra coal field.

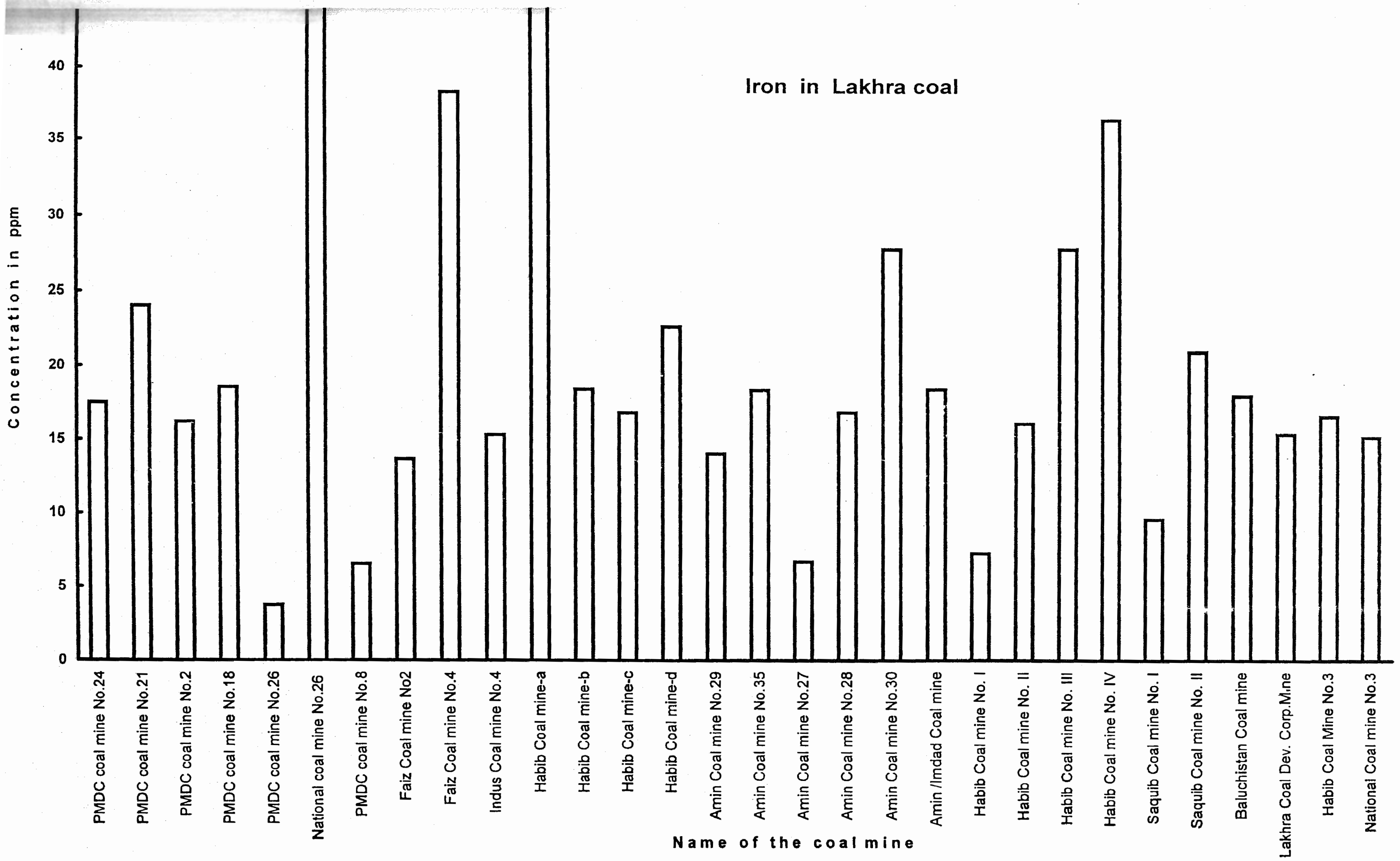


Figure 4.4 Iron in coal samples collected from various coal mines of Lalkhra coal field.

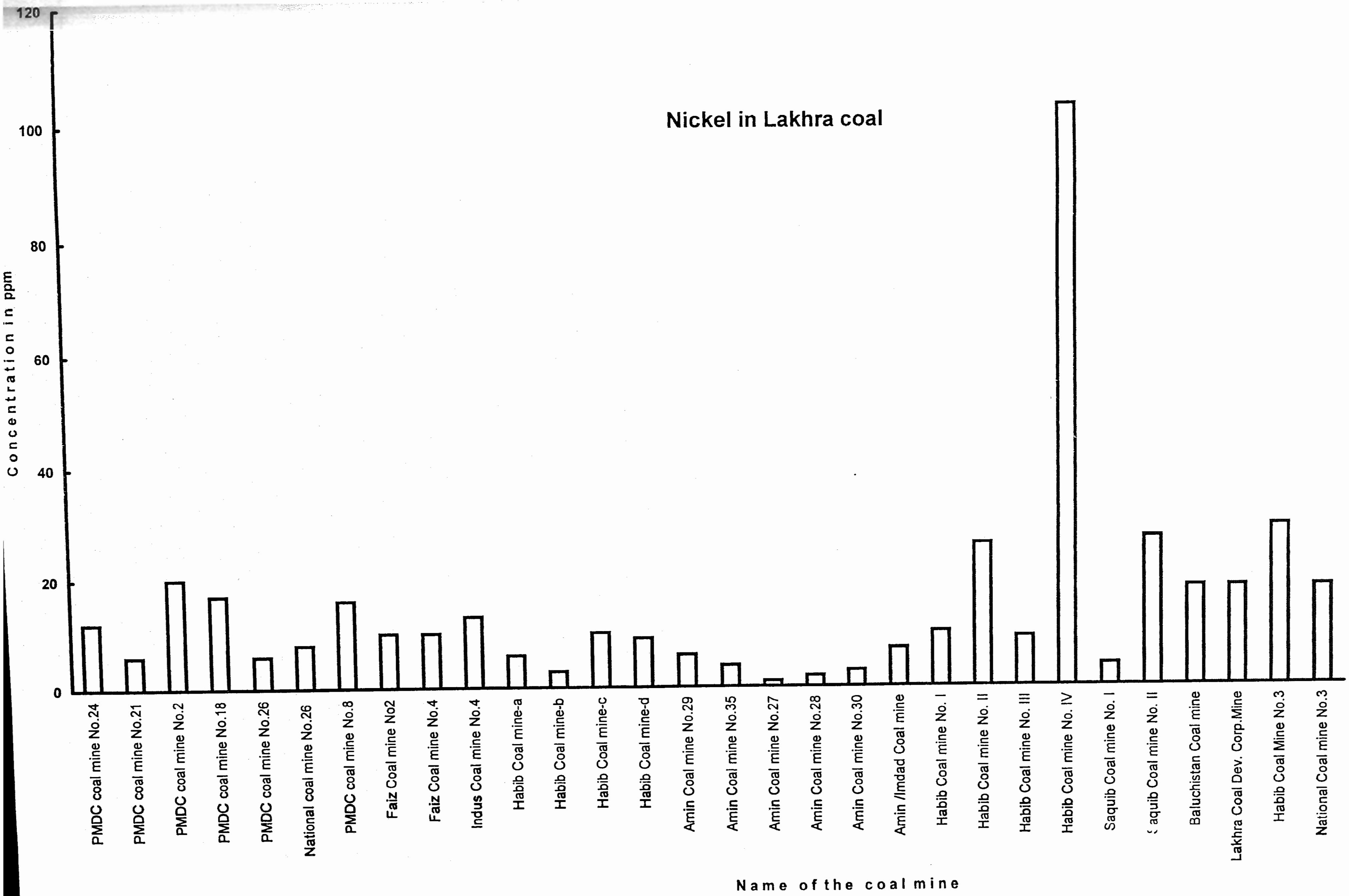


Figure 4.5 Nickel in coal samples collected from various coal mines of Lalkhra coal field.

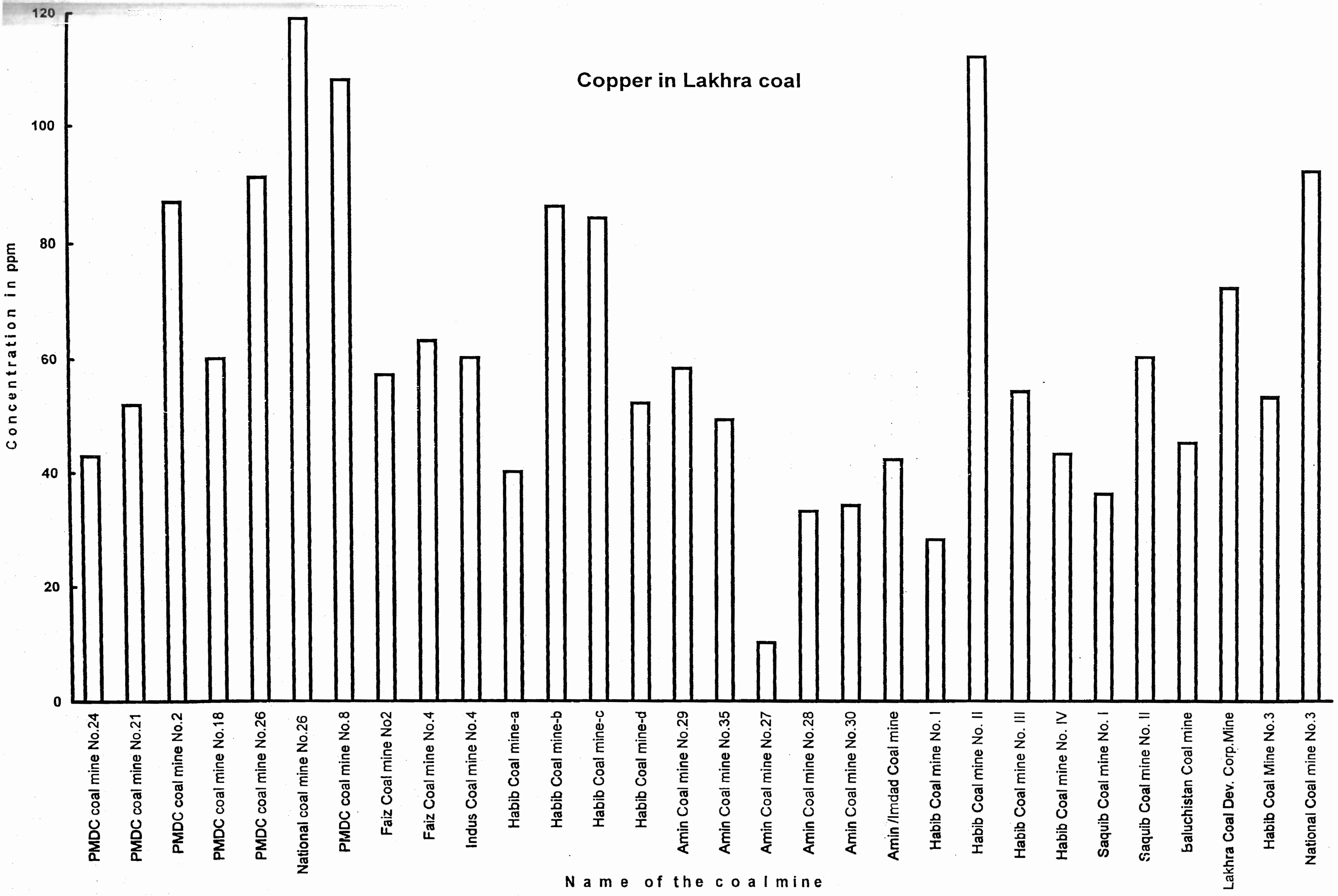


Figure 4.6 Copper in coal samples collected from various coal mines of Lalkhra coal field.

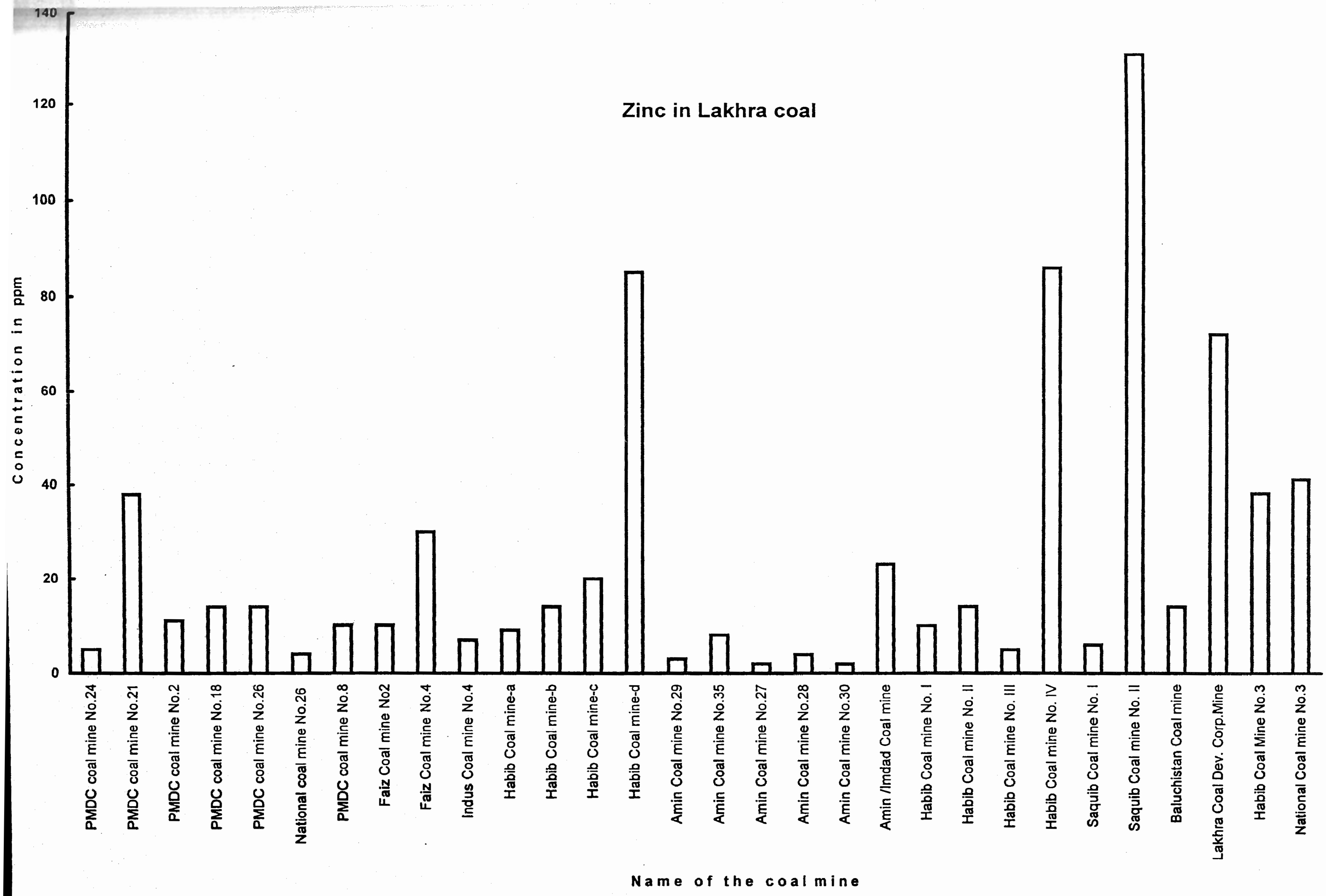


Figure 4.7 Zinc in coal samples collected from various coal mines of Lalkhra coal field.

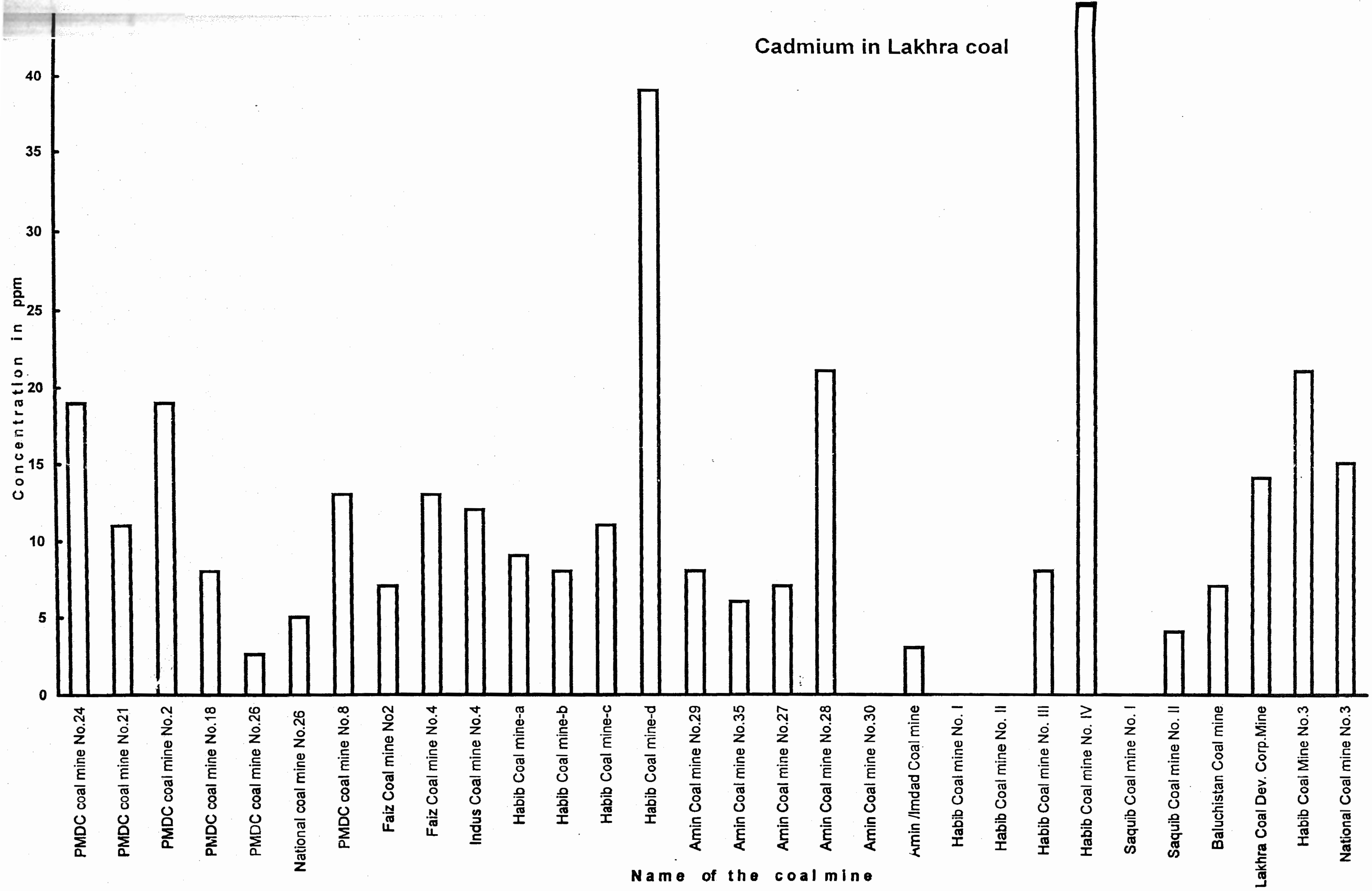


Figure 4.8 Cadmium in coal samples collected from various coal mines of Lalkhra coal field.

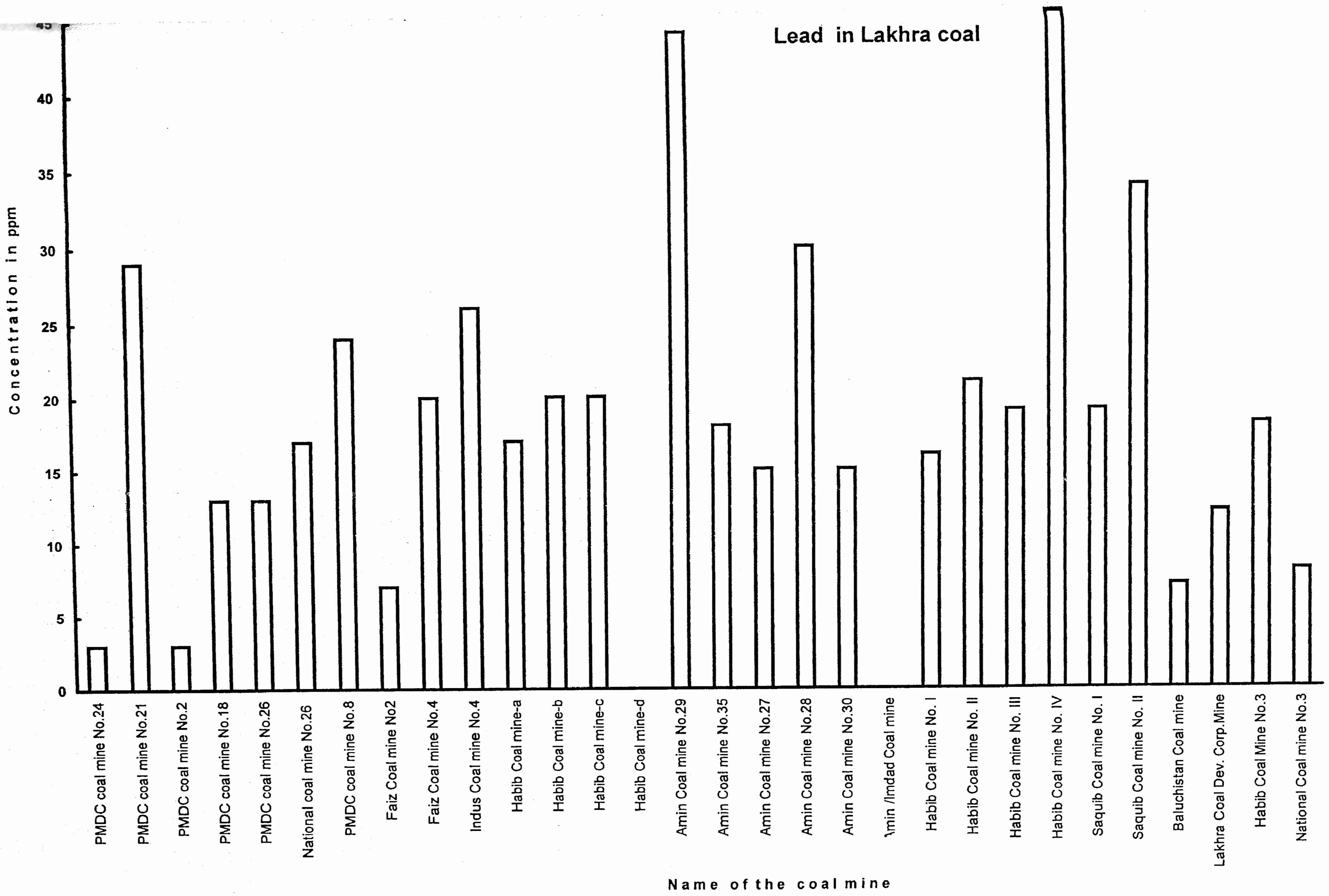


Figure 4.9 Lead in coal samples collected from various coal mines of Lalkhra coal field.

CHAPTER FIVE

AIR POLLUTION

Air pollution is defined as any atmospheric condition in which certain substances are present in such concentration that they can produce undesirable effects on man and his environment (Rao,1994). These substances include gases like sulfur dioxide, nitrogen oxide, carbon monoxide, hydrocarbon, smoke, fumes, aerosols, radio active material, particulate matter (dust etc). Most of these are naturally present in the atmosphere in the low concentrations and considered as harmless. However, when their concentrations exceeds their threshold limits, they are classified as harmful. Coal mining activity like exploitation/excavation, stock pilling, loading or transportation of coal from one place to the other, disperse the coal dust in the form of particulate matter as pollutants in the air. A large amount of particulate matter of coal dust that disperses in the atmosphere reach back to the earth's surface as fallout or wash out. These particulate matters are the major cause of silicosis and pneumoconiosis disease among the peoples working and living/residing in the area as they breath that polluted air.

The Lakhra coal samples analyzed during current study have shown various proportions of heavy metals (Chapter 3). Mining activity is in progress in Lakhra coal field for last few years. By considering the dispersion and accumulation characteristics of heavy metals in air as controlled by their availability, gravity and wind intensity and direction, it is expected that these pollutants must be forming part of the particulate matter of the air. During the present study, 5 samples of particulate matter both at hanging/nose level and ground position were collected from the Lakhra coal field, and analyzed for heavy metals. Among these samples 3

Samples were collected near the mines of PMDC leased area, Habib coal mines and National coal mines, while the remaining two samples were collected away from these mines at Indus chowk and coal chungi area (Fig. 5.1). The location of the samples collected during 48 hours in open buckets of 30 cm diameter filled with distilled water both in hanging and ground position are shown in Figure 5.1. The weight of suspended particulate matter and the metal concentration in hanging position (nose height or in air) as well as at ground level position are given in Tables 5.1 and 5.2. The weight of particulate matter collected in 48 hours at hanging position varies from minimum of 0.113 grams collected at coal Habib coal field up to a maximum of 1.512 grams collected at National coal field area.

Variations in the concentrations of both light and heavy metals are also noticed at various localities at hanging position. It is clear from Table 5.1 & 5.2 that Na is highest (904.86 ppm) at coal chungi and lowest (1.512 ppm) at National Coal field area, Mg is highest (491.25 ppm) at PMDC coal field area and lowest (303.75 ppm) at Indus chowk, K is highest (1875 ppm) at National coal field area and lowest (141.25 ppm) at Indus chowk, Ca is highest (655.38 ppm) at coal chungi and lowest (426.25 ppm) at National coal field area, Cr is highest (42.5 ppm) at National coal field area and lowest (11.25 ppm) at Indus chowk.

Table 5.1 Weight of suspended particulate matter along with the concentration of metals (in ppm) collected from various locations at hanging position.

Location	Weight in hanging position (in gms)	Na	Mg	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd
PMDC coal field	0.928	751.25	491.25	1062.5	467.50	38.75	132.50	16.22	13.75	38.75	36.25	50.00	7.50	0.02
Coal Chungi	0.140	904.86	421.42	335.71	655.38	14.10	187.18	13.20	10.25	16.66	56.41	28.20	2.56	0.011
Habib coal field site	0.113	694.87	400.44	378.31	639.38	13.75	132.50	9.725	12.50	20.00	31.25	25.00	0.00	0.023
Indus chowk	0.382	520.87	303.75	141.25	518.75	11.25	257.50	36.25	12.50	12.50	138.75	37.50	38.75	0.028
National coal field	1.512	231.25	455	1875	426.25	42.5	125.00	25.27	13.75	30.00	35.00	48.75	17.50	0.048

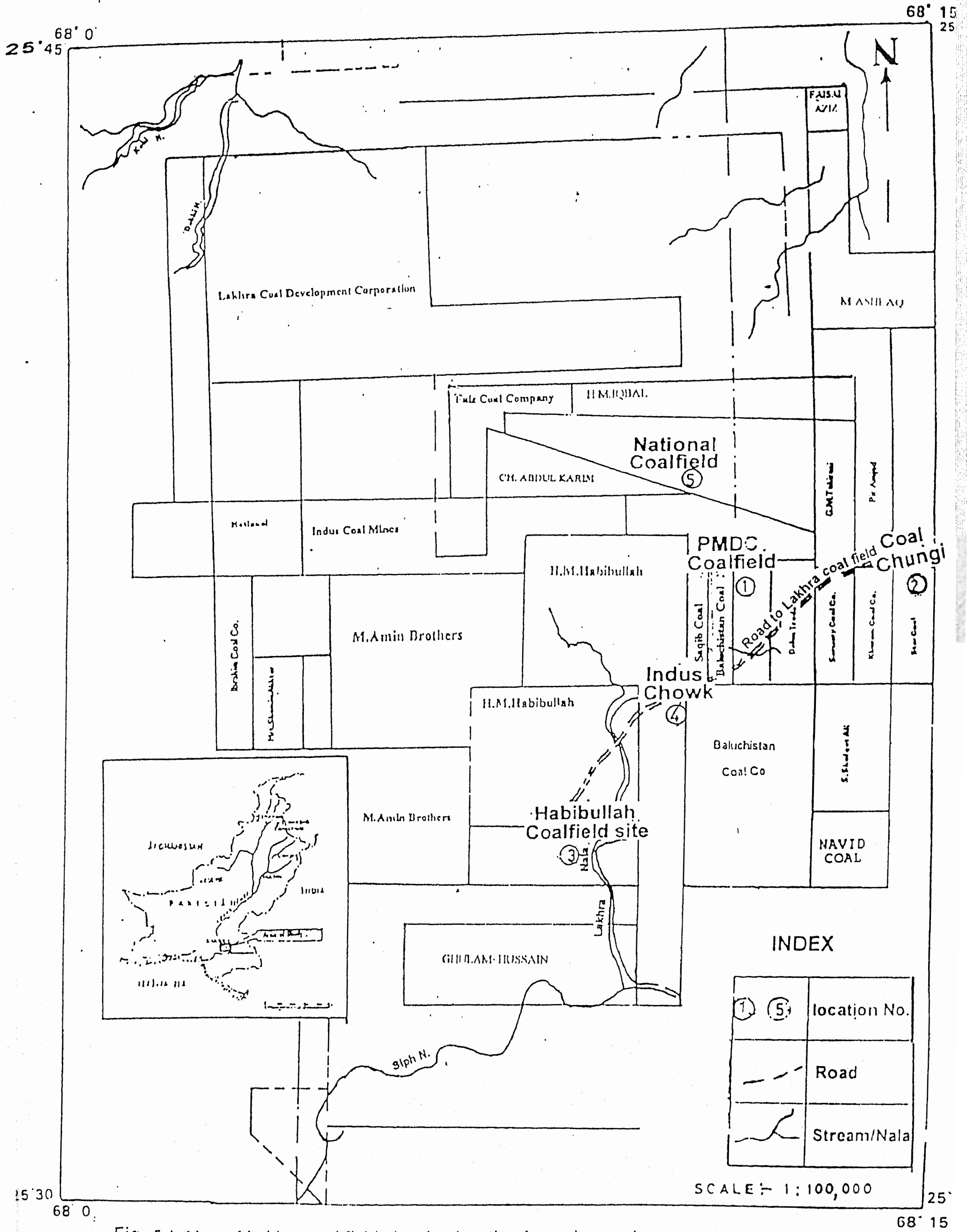


Fig. 5.1. Map of Lakhra coal field showing location from air samples were collected.

Table 5.2 Concentration of heavy metals (in ppm) in air sample's collected from various locations at ground level position.

Location	Weight at ground level (in gms)	Na	Mg	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd
PMDC coal field	1.476	738.75	446.25	2125	451.25	41.25	111.25	2.647	15.00	33.75	37.50	66.25	47.50	0.034
Coal chungi	0.195	806.25	321.82	325.41	529.48	28.76	336.28	25.70	17.69	33.18	117.25	99.55	24.33	0.041
Habib coal field	1.281	707.50	462.50	2281.25	456.25	38.75	121.25	26.175	12.50	33.75	785.00	62.50	6.25	2.40
Indus chowk	0.580	506.25	176.25	131.25	433.75	14.28	326.78	23.57	10.71	21.42	164.28	53.57	21.42	0.016
National coal field	2.930	220.12	446.25	2125	372.5	41.25	122.50	26.02	13.75	33.75	42.50	42.5	38.75	0.012

Mn is highest (257.5 ppm) at Indus chowk and lowest (125 ppm) at National coal field area, Fe is also highest (36.25 ppm) at Indus and lowest (9.725 ppm) at Habib coal field area, Co is highest (13.75 ppm & 13.75 ppm) at PMDC coal field area as well as National coal field area and lowest (10.25 ppm) at coal chungi, the concentration of Ni is highest (38.75 ppm) at PMDC area and lowest (12.50 ppm) at Indus chowk, Cu is extremely high (138.75 ppm) at Indus chowk and lowest (31.25 ppm) at Habib coal field area, Zn is highest (50 ppm) at PMDC area and lowest (25 ppm) at Habib coal field area. Pb is highest (38.75 ppm) at Indus chowk and lowest (2.56 ppm) at coal chungi while at Habib coal field area it is not found (00 ppm). . The concentration of Cd in hanging position is highest (0.048 ppm) at National coal field area and lowest (0.011 ppm) at coal chungi

At ground position similar variations in concentration of particulate matter and metals are noticed. The weight of particulate matter collected at ground level varies from a minimum of 0.195 grams at coal chungi up to 2.93 grams at National coal field area.

The concentration of light and heavy metals at ground level exhibits similar variation as noticed at hanging or nose level. Na is highest (806.25 ppm) at coal ***chungi and lowest (220.12 ppm) at National coal field area, Mg is highest (462.50*** ppm) at Habib coal field area and lowest (176.25 ppm) at Indus chowk, K is extremely high (2281.25 ppm) at Habib coal field area and lowest (131.25 ppm) at Indus chowk, Ca is highest (529.48 ppm) coal chungi at lowest (372.50 ppm) at National coal field area.

Among heavy metals it is noticed that Cr is highest (41.25 ppm) at PMDC coal field area as well as National coal field area (41.25 ppm) and lowest (14.28 ppm) at Indus chowk, Mn is highest (336.28 ppm) at coal chungi and lowest (111.25 ppm) at PMDC coal field area, Fe is highest (26.175 ppm) at Habib coal field area and lowest (2.647 ppm) at PMDC coal field area, Co is highest (17.69 ppm) at coal chungi and lowest (10.71 ppm) at Indus chowk, Nickel is highest (33.75 ppm) at PMDC coal field area and National coal field area (33.75 ppm), and its lowest concentration (21.42 ppm) is noticed at Indus chowk, Cu is highest (785.00 ppm) at Habib coal field area and lowest (37.50 ppm) at PMDC coal field area, Zn is highest (99.55 ppm) at coal chungi and lowest (42.50 ppm) at National coal field area, Pb is highest (47.50 ppm) at PMDC coal field area and lowest (6.25 ppm) at Habib coal field area. Similarly the concentration of Cd is highest (2.40 ppm) at Habib coal field area and lowest (0.012 ppm) at National coal field area.

These samples are plotted on spidograms from left to right according to their increasing atomic masses (Figs. 5.2 a-e and 5.3 a-e). At the PMDC leased area except for K showing light metal concentration at ground level are compared to nose level, the rest of the light metals, i.e., Na, Mg, and Cr have more or less similar concentrations at both positions (Fig. 5.2 a).

At Habib coal mine area the light metals show similar behavior as noticed at PMDC leased area (Fig. 5.2 b).

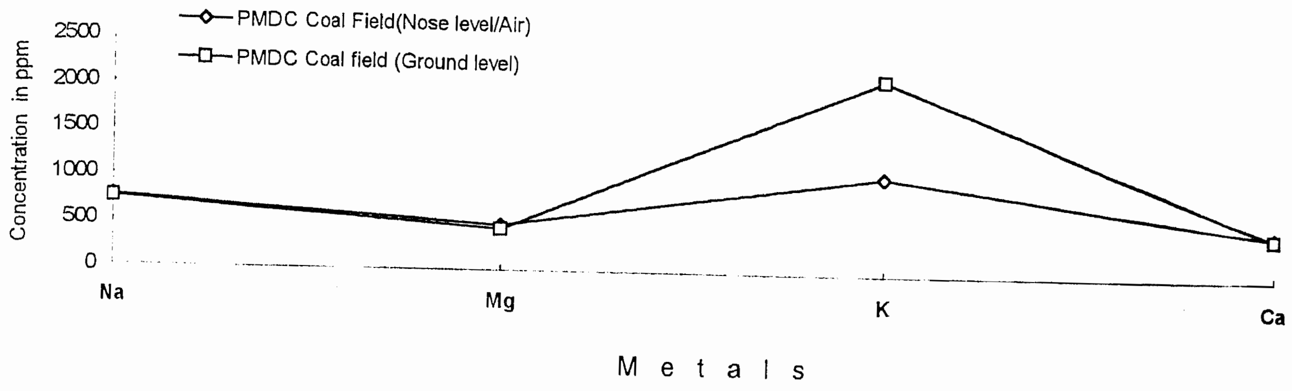


Figure 5.2-a. Light metals at PMDC coalfield(leased) area.

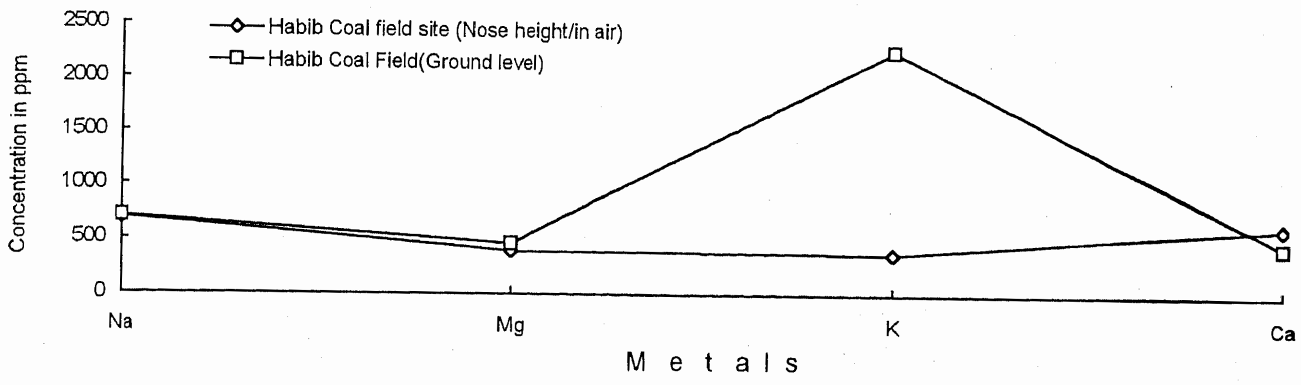


Figure 5.2-b. Light metals at Habib coalfield(leased) area.

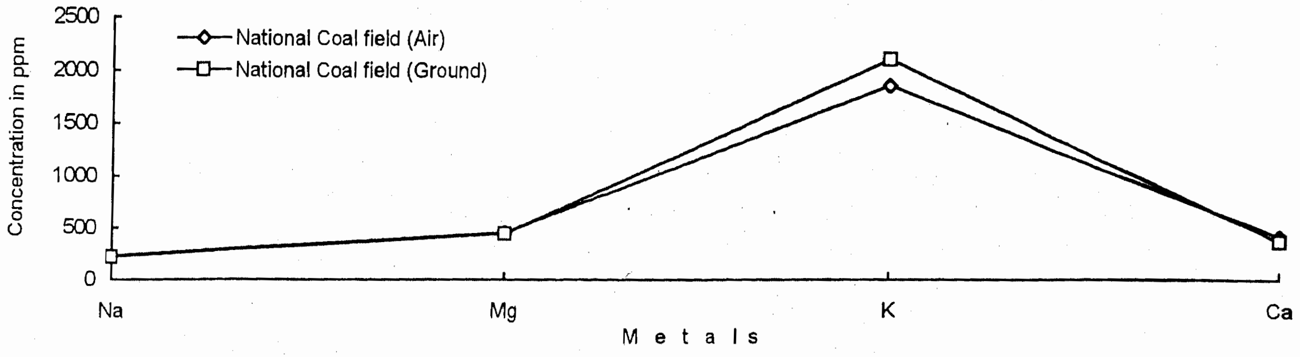


Figure 5.2-c. Light metals at National coalfield(leased) area.

At National coal mining area the concentration of all light metals analyzed is more or less the same (Fig. 5.2 c). These data indicate that the light metal concentration both at ground and in air (at nose level) have similar pattern in the samples collected closer to the mines, the pattern for light metals in the samples collected away from the coal mining areas i. e., coal chungi and Indus chowk, area vary similar in both air/nose level and at ground levels (Fig. 5.2 d & e). However, these patterns are different from those areas which are closer to the coal mines. It is clear from diagrams that the air/wind blowing or swirling has played a role in transfering of these light metals, especially Na, Mg and Ca in the form of suspended load from the areas closer to the coal mines and the areas away from the coal mines. However, Potassium (K) in this case escaped this transfer by any reason.

Under calm and quite conditions of the air and equal availability of all metals, it is expected that the conditions of the metals, particularly heavy metals, may vary systematically according to their atomic masses, when collected as free fall of the dust in open buckets filled with distilled water. Also the heavy metals concentration in samples collected at ground level will be higher than in those collected at nose level (Hamidullah et al., 1994).

The heavy metal concentration patterns of the analyzed samples are shown in Figure 5.3a-e. With few exceptions, the heavy metals concentration at ground levels are generally higher than that at nose level or in air in all the samples, especially in areas away from the coal mines such as coal chungi, and Indus chowk (Fig 5.3 a-b). The systematic increase according to atomic radii is, however, not noticed in these patterns. Mn and Cu are showing anomaly in variable strength in

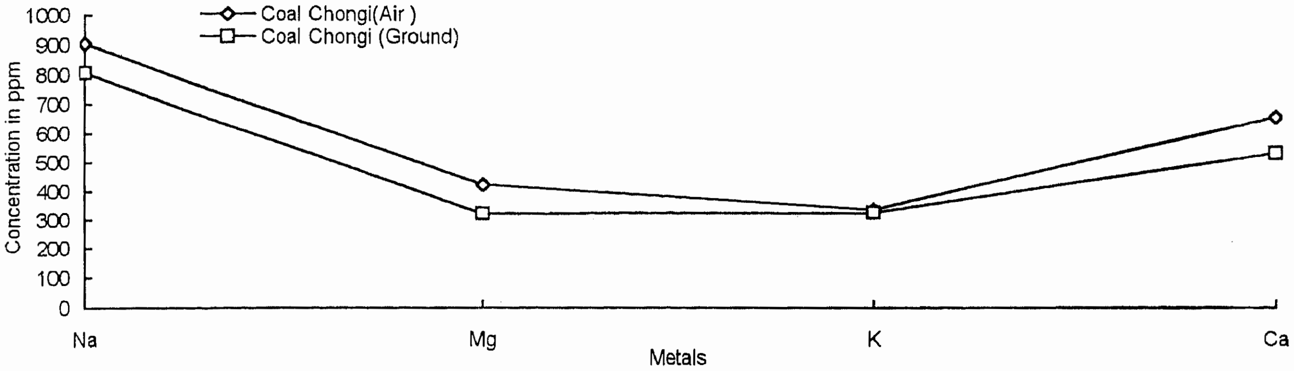


Figure 5.2-d. Light metals at coal chungi area.

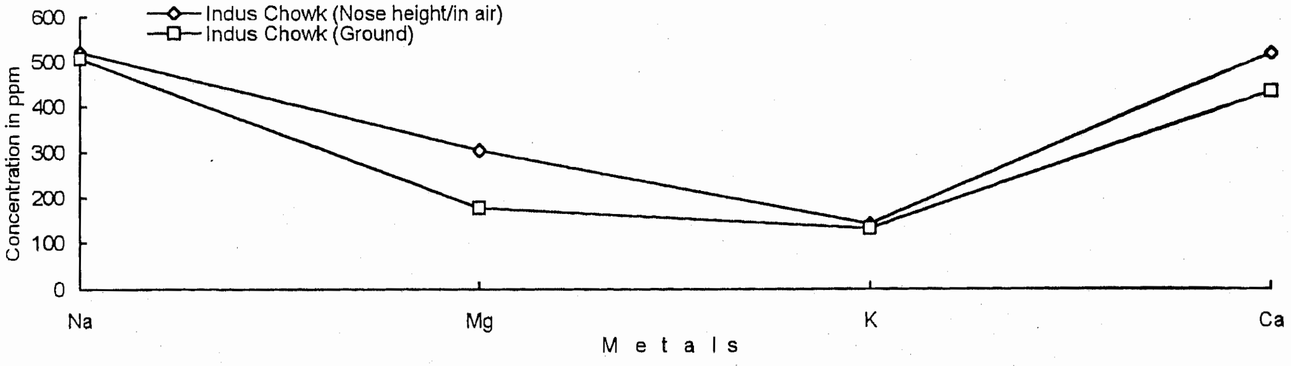


Figure 5.2-e. Light metals at Indus chowk area.

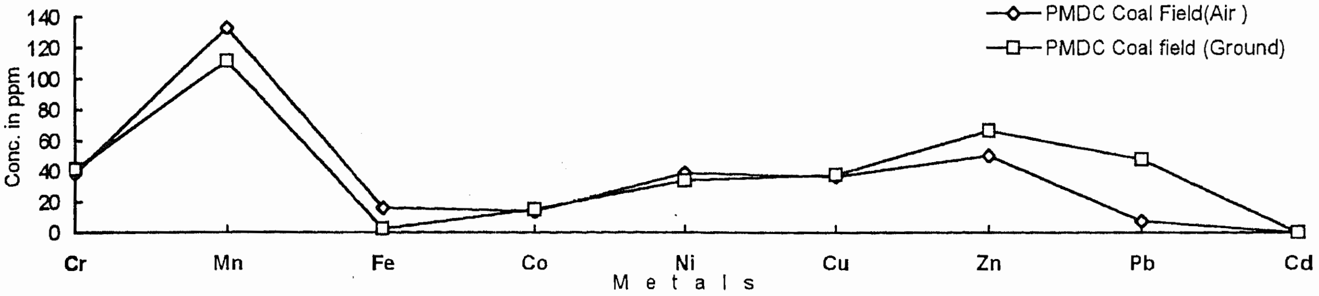


Fig. 5.3-a. Heavy metals collected in hanging (in air) and ground level position at PMDC coalfield (leased) area.

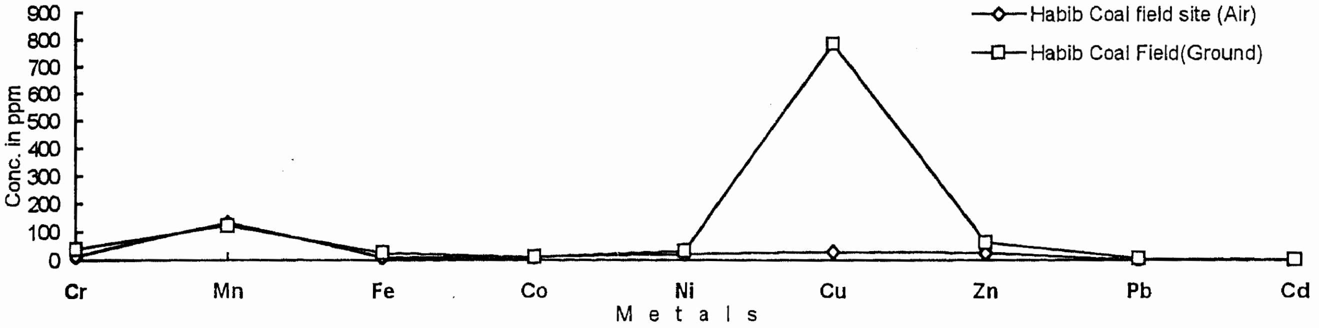


Fig. 5.3-b. Heavy metals collected in hanging (in air) and ground level position at Habib coalfield (leased) area.

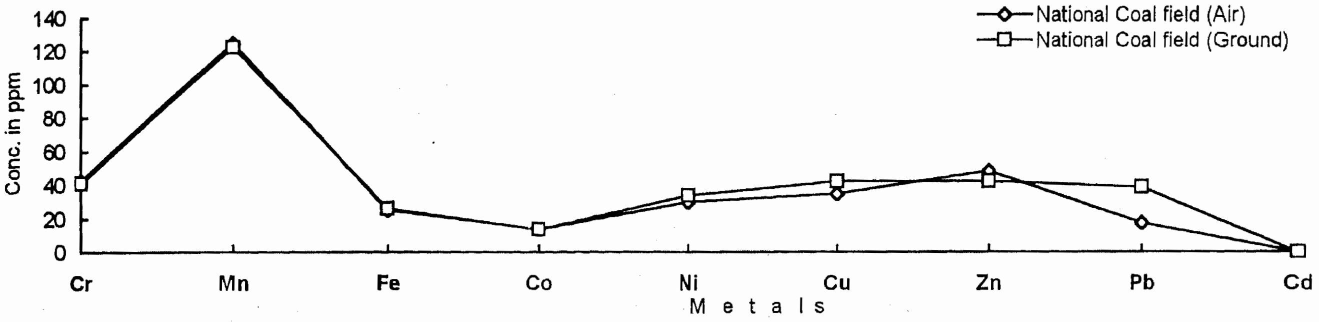


Fig. 5.3-c. Heavy metals collected in hanging (air) and ground level position at National coalfield (leased) area.

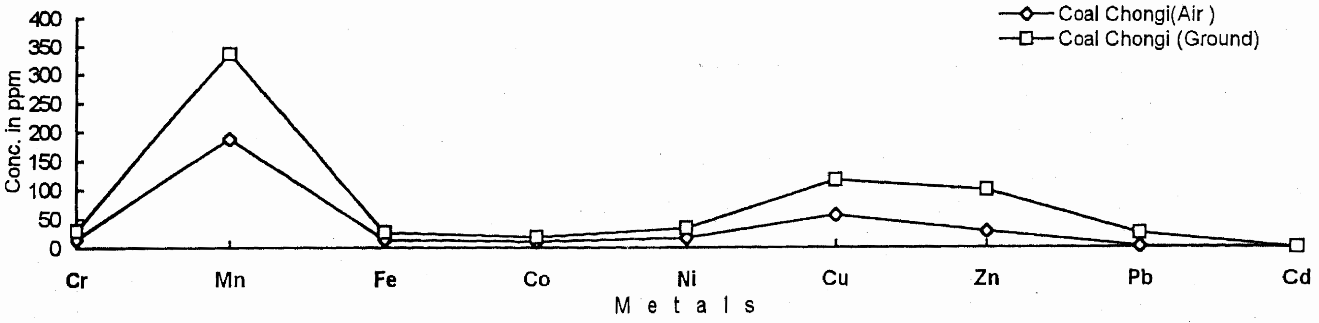


Fig. 5.3-d. Heavy metals collected in hanging (air) and ground level position at Coal chungi area.

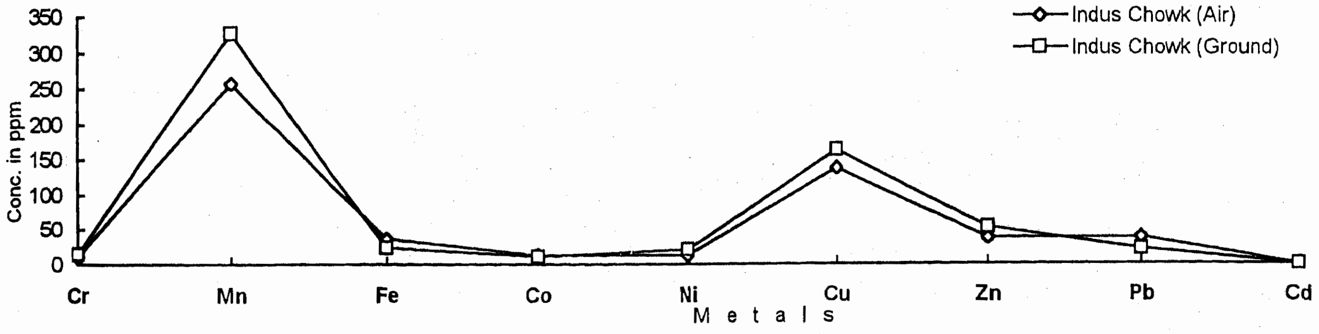


Fig. 5.3-e. Heavy metals collected in hanging (air) and ground level position at Indus Chowk area.

almost all the samples. Cu is, however, negligible in the air/nose level in sample taken at Habib coal field area. Zn and Pb are high at ground level while the concentrations of Fe, Co, Ni, and Cd are more or less similar in both the levels.

It is clear from the study of patterns formed by heavy metals both at air/nose level and at ground level that the distribution of heavy metals in the Lakhra coal field is not solely controlled by gravity but other factors like their availability and constant remixing by the blowing air also play a major role.

The data of metals collected at various localities in Lakhra coal field both at hanging and ground level position indicate that both heavy and light metals persist in air and pose a tremendous threat to human and ecological life. On the basis of the presence of these metals in the coal samples collected from these mines (Chapter 4, Table 4.1) and the spatial affiliation of the air sample with coal field indicate that the source of these metals is the coal of the study area.

CHAPTER SIX

HEAVY METALS IN GROUND WATER AT LAKHRA

Water is essential for the survival of any form of life. On an average, a human being consumes about three litters of water per day. Water accounts for seventy percent of the weight of the a human body. About eighty percent of the earth's surface (i.e. 80% of the total 50,000 million hectares in area) is covered by water. Out of estimated 1,011 million km^3 of the total water present on the earth, only 33,400 m^3 of water is available for drinking, agriculture, domestic, and industrial consumption (Keller, 1992). The rest of water is locked up in oceans as salt water, polar ice caps, glaciers, and underground. This limited quantity of water available for our uses is being polluted mainly by three processes in which the chemical composition of groundwater may change drastically. The first is due to the natural processes. Mineralization resulting from leaching and evaporation can concentrate salts in the water. Chlorine, sulphates, nitrates, florid and Fe commonly occur in localized deposits and their concentration in groundwater may therefore exceed the limits set by The United States Environmental Protection Agency's (US-EPA) standards (Mathess,1982). The second process of contamination is due to man's waste disposal practice and its effect on groundwater US-EPA (1977) has provided estimates of the sources and extent of groundwater contamination. Contaminant sources from waste disposal practice include individual sewage disposal system, solid waste disposal sites, collection and treatment of municipal waste water, industrial and other waste impoundment, land spreading of sludge and brine disposal associated with the petroleum industries. All of the potential sources of contamination have direct effects resulting in natural and synthetic substances processes is also related to the direct result of human activities but is unrelated to waste disposal practices. It includes accidental spills and leaks, agricultural activity, mining, atmospheric contaminant and acid rains, improperly planned groundwater development leading to salt water intrusion and improper well construction and maintenance.

At Lakhra coal field there is scarcity of natural water. A few shallow dug wells exist i. e., two historical Lillian wells near Habib's rest house at Habibullah coal mining area, two dug wells in Kander village and two in Yaro-a-jo khuh villages (in Sindhi language term khuh is used for a dug well) (Fig. 6.1). Water from these dug wells is used for domestic and agriculture proposes. For mining and mining personal drinking water is transported by water tankers from river Indus at a distance of 20 kms. The geochemical analyses of the water of shallow dug wells performed during the current investigation are given in Table 6.1 Generally the quality of the dug well water or ground water depends upon the local geology and agricultural activity i. e., use of synthetic fertilizers that sweeps or percolate beneath the sub surface and contaminate the ground water. Following is the description of data obtained.

Table 6.1 Water Quality of well water at Lakhra

Sample No.	Location/Name of the dug well	E C µS/cm	T D S mg/l	HCO_3 mg/l	SO_4 mg/l	Fe µg/l	Ni µg/l	Cu µg/l	Pb µg/l	Cd µg/l
	US-EPA	300	500	500	250	300	1000	1000	50	10
W1	Lialian-I	910	637	305	52.5	6	0	10	4	1.9
W2	Lialian-II	860	595	115	300	223	7	70	47	2.4
W3	Kandeer-I	830	581	70	40	53	4	68	20	0
W4	Kandeer-II	800	560	202	42.5	45	5	11	0	1.3
W5	Yaro's well-I	1010	707	85	352	844	5	89	24	0.1
W6	Yaro's well-II	1210	847	360	125	0.28	5	79	38	0

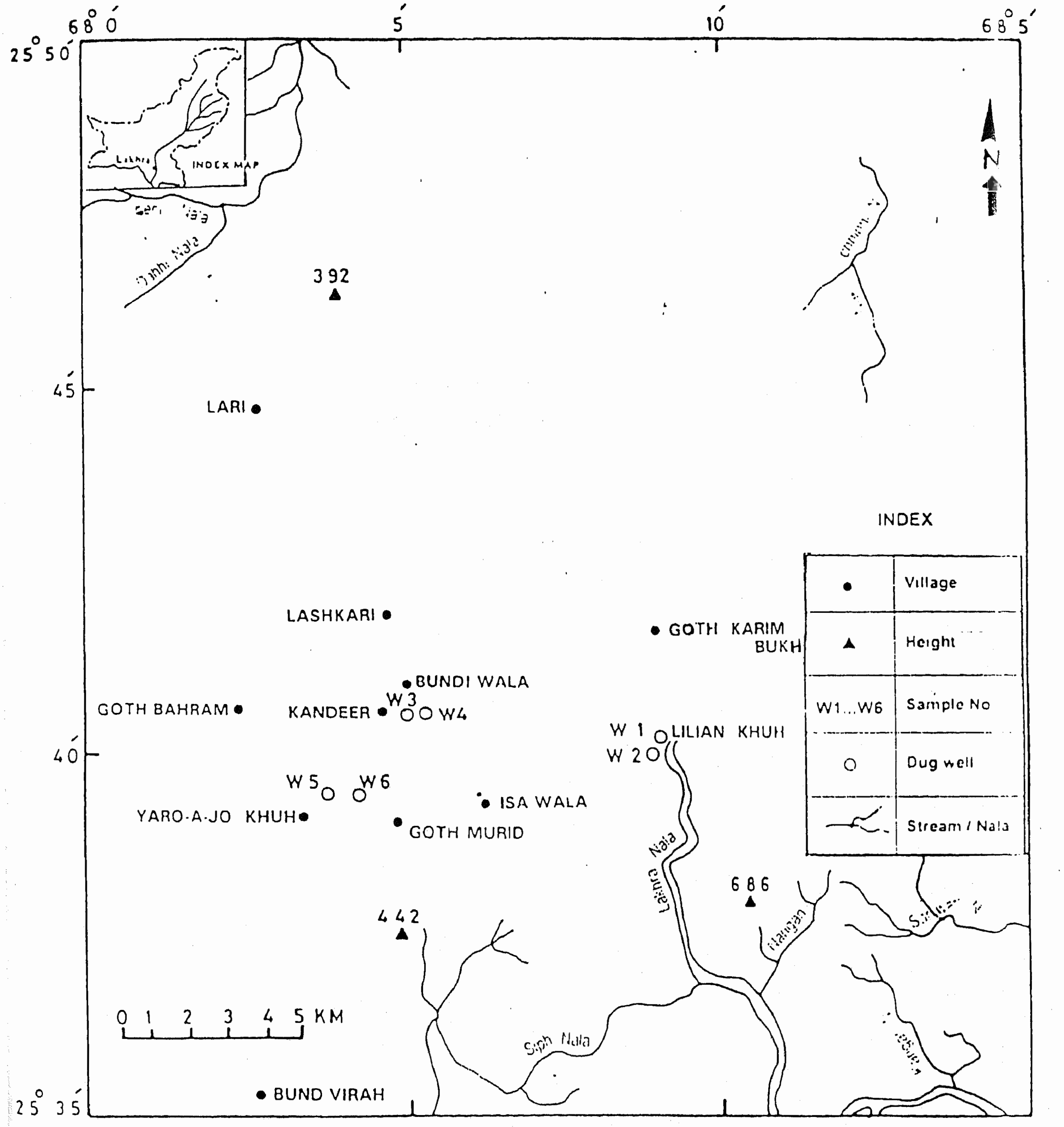


Fig. 6.1 Map of Lakhra coal field showing location of dug wells from water samples were collected.

The electrical conductivity or specific conductance is a measure of the ability of water to conduct an electric current. It is expressed as microsiemens per centimeter (μS/cm) and for a given water body it is related to the concentration of total dissolve solids and major ions. Conductivity is a non specific parameter which can be measured to establish pollution zone (Chapman, 1992).

At Lakhra among the six shallow dug wells, it is seen that the measured values of conductivity of the water of these wells range from 800 to 1210 μS/cm. The Lialian-I, Lialian-II, Kandeer-I, Kandeer-II, Yaro´s well -I and Yaro´s well-II are the dug wells whose water samples have the conductivity values of 910, 860, 830, 800, 1010 and 1210 μS/cm respectively which is multifold higher than the permissible limit of 300 given by US-EPA (1979) (Fig. 6.2). Such high values indicate higher content of dissolved solids.

The Total Dissolved Solids of water is the most widely used criterion of knowing the quality of water. Because, water is solvent that can hold in solution of various solids and gases found in nature. Most of the dissolved solids in natural water consists of the same kind of solutes, whether, in sea, in river and lakes or in the ground. According to the U. S. Public Health Service, drinking water can be classified on the basis of total dissolved solids (U. S. Geological Survey, 1985).

Table 6.2 Classification of water on the basis of TDS.

Total Dissolved Solids (ppm)	
Less than 1,000	Fresh
1,000 - 3,000	Slightly saline
3,000 - 10,000	Moderately saline
10,000 - 35,000	Very saline
More than 35,000	Brine

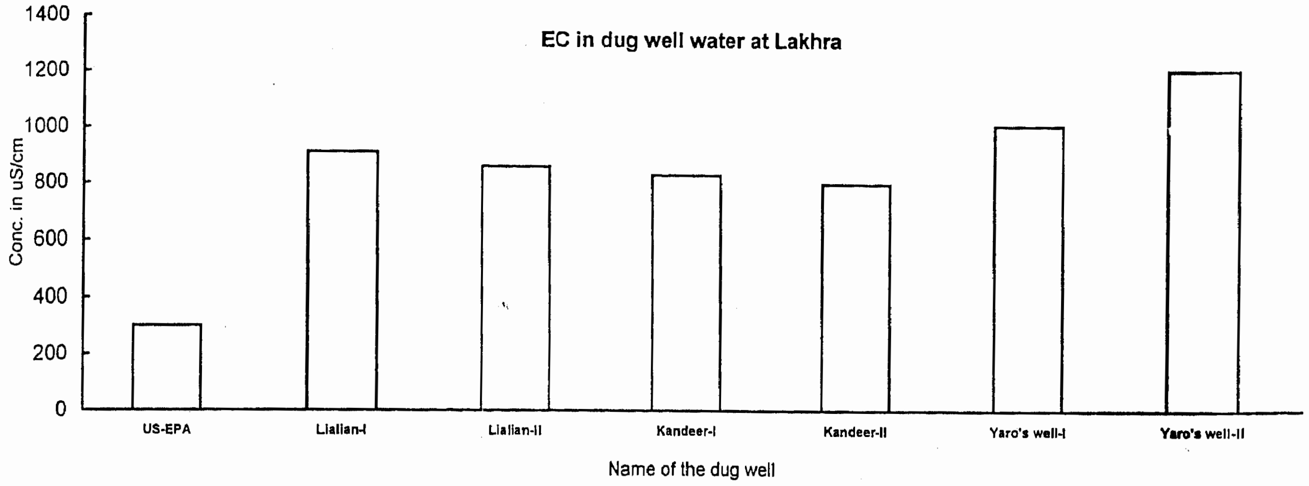


Fig. 6.2 Electric Conductivity of dug well waters at Lakhra

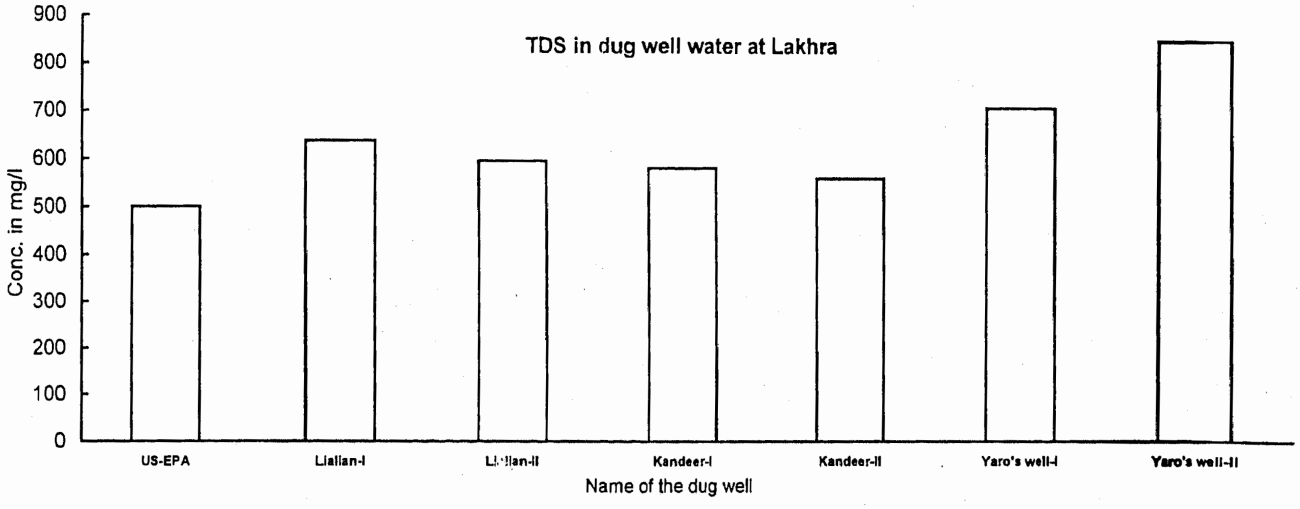


Fig.6.3 Total Dissolved Solids in dug well water at Lakhra

these dug wells though can be classified as having fresh water according to the USGS (1985) classification, however, the recommended upper limit of TDS by US-EPA (1979) is 500 mg/l. Considering this safety limit, the Lakhra dug well water can not be recommended at least for drinking purpose with the currently obtained values of TDS (Fig. 6.3).

The TDS values of Lakhra ground water were compared with HCO_3, SO_4, and heavy metals. All the plots are showing scattering of the data. However, the data in these plots suggest that the HCO_3 and SO_4 show positive correlation with TDS. Among the heavy metals the Ni, Cu and Pb show positive correlation with the TDS. This suggest that the anions (i. e., HCO_3 & SO_4) and other cation bearing phases (except those of Fe and Cd) have been dissolved in water as TDS (Fig. 6.4a-g).

Bicarbonate (HCO_3)

It is the quality or property through which the water may become temporarily hard, called as Bicarbonate hardness. Bicarbonate hardness is caused by the presence of soluble calcium or magnesium bicarbonates in water which can be removed or softened by boiling or adding hydroxide.

The bicarbonate data of the water of dug wells from Lakhra shown in Fig. 6.5 indicate that sample collected from Yaro's well-II has the highest concentration (360 mg/l) while that collected from Kandeer well-I has the lowest (70 mg/l). These observed values are within the permisible limit of 500 mg/l set by US-EPA(1979).

Sulfate (SO_4)

Sulfates are found in natural water either in the oxidized state of sulfide, sulfate and thiosulfates or in oxidized state of organic matter in sulfur cycle. In all

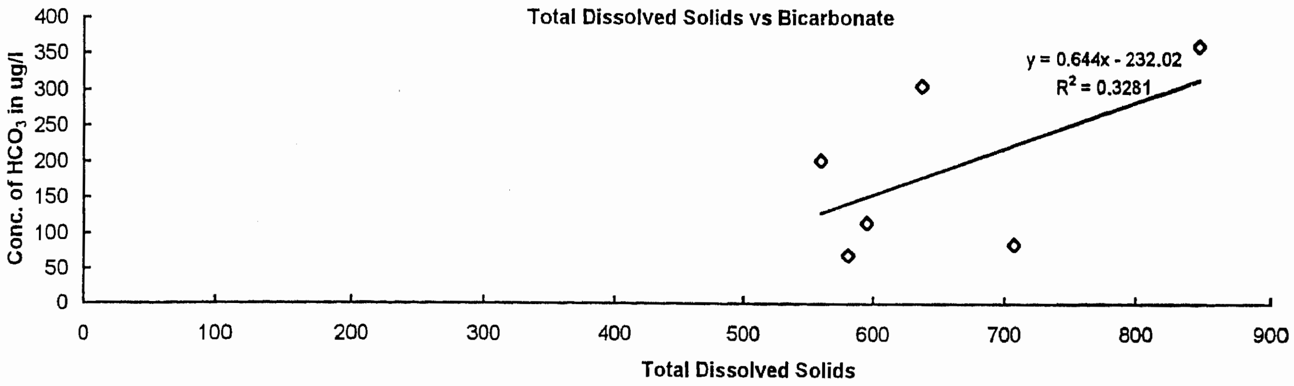


Fig. 6.4-a Total Dissolved Solids vs Bicarbonate

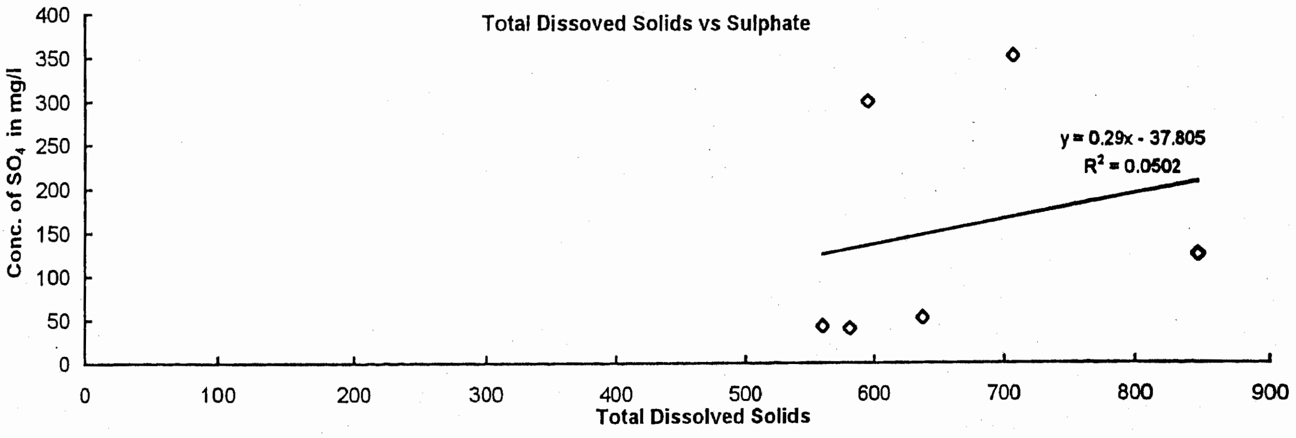


Fig. 6.4-b Total Dissoved Solids vs Sulphate

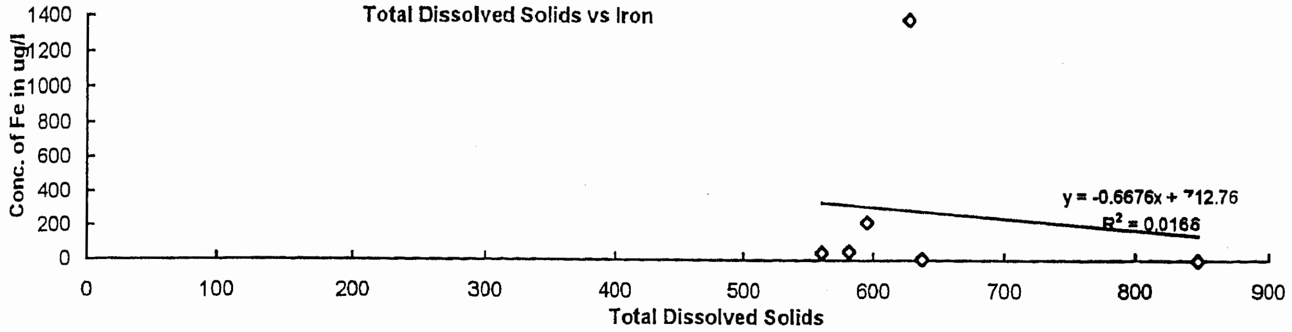


Fig. 6.4-c Total Dissolved Solids vs Iron

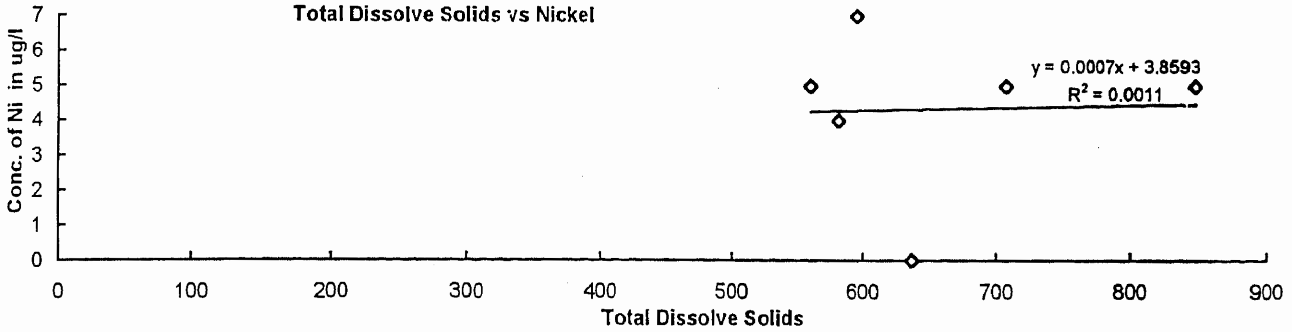


Fig. 6.4-d Total Dissolve Solids vs Nickel

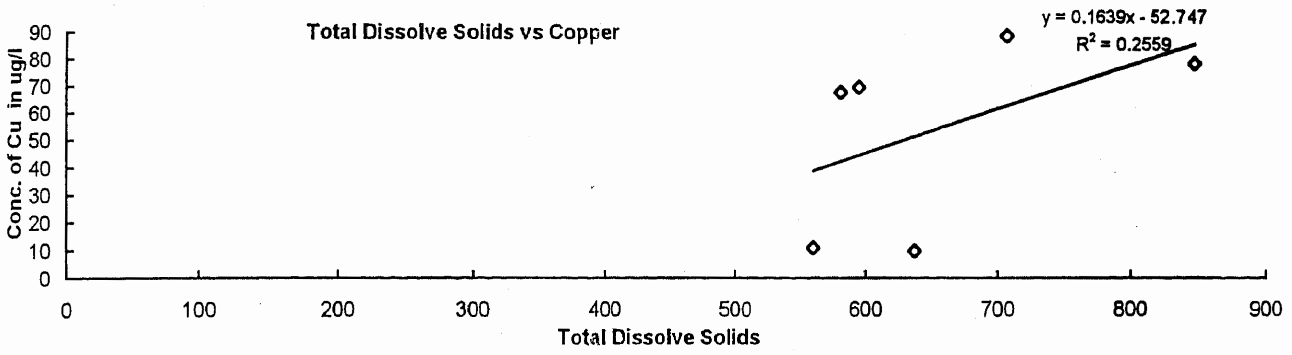


Fig. 6.4-e Total Dissolve Solids vs Copper

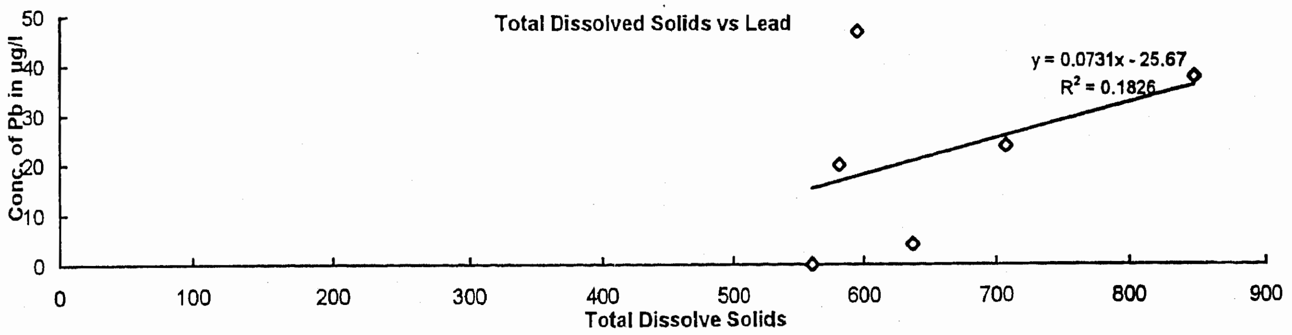


Fig. 6.4-f Total Dissolved Solids vs Lead

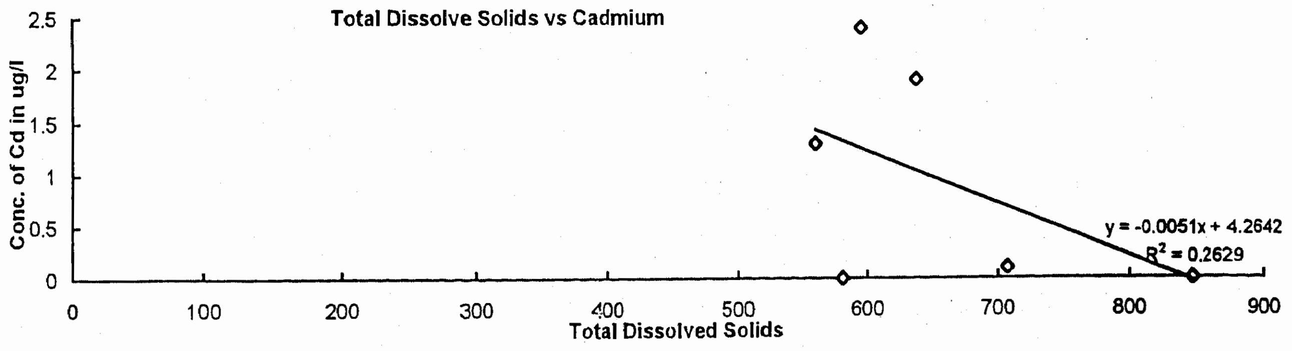


Fig. 6.4-g Total Dissolve Solids vs Cadmium

gastrointestinal diseases (Block et all., 1986). Because of the toxicity of sulfate, the US-EPA (1979) recommended the concentration of 250 mg/l as a maximum contaminant level of sulfate in drinking water. Result of Lakhra dug wells water show that with the exception of two wells i.e., Yaro's well-I (352 mg/l) and Lilian well-II (300 mg/l) the rest of the water samples are bellow the Standard limit set by US-EPA (1979) (Table 6.1; Fig. 6.6).

Heavy metals

As mentioned earlier (Chapter 1), heavy metals are defined as having densities five times greater than water (Goyer, 1986). The Lakhra dug wells' waters were analyzed for heavy metals including Fe, Ni, Cu, Pb and Cd. There behavior in general and in Lakhra dug wells are discussed as under:

Iron (Fe)

Iron is an essential element for biological life. It is an important element of drinking water. Iron in surface-water is generally present in the feric ($Fe3+$) state. The presence of higher amount of iron in natural waters can be attributed to the dissolution of rocks and minerals, acid mine drainage, landfill leachates, sewage or iron-related industries.

The iron concentration in water collected from dug wells of studied area is highly variable and is ranging from 0.28 to 844μg/l (Table 6.1). A sample collected from Yar's well # I possesses highest concentration of iron (844 mg/l) that exceeds the Maximum Contaminant Level of 300 mg/l set by US-EPA (1979). Rest of the samples in the studied area show values below this limit (Figure 6.7). It is, therefore,

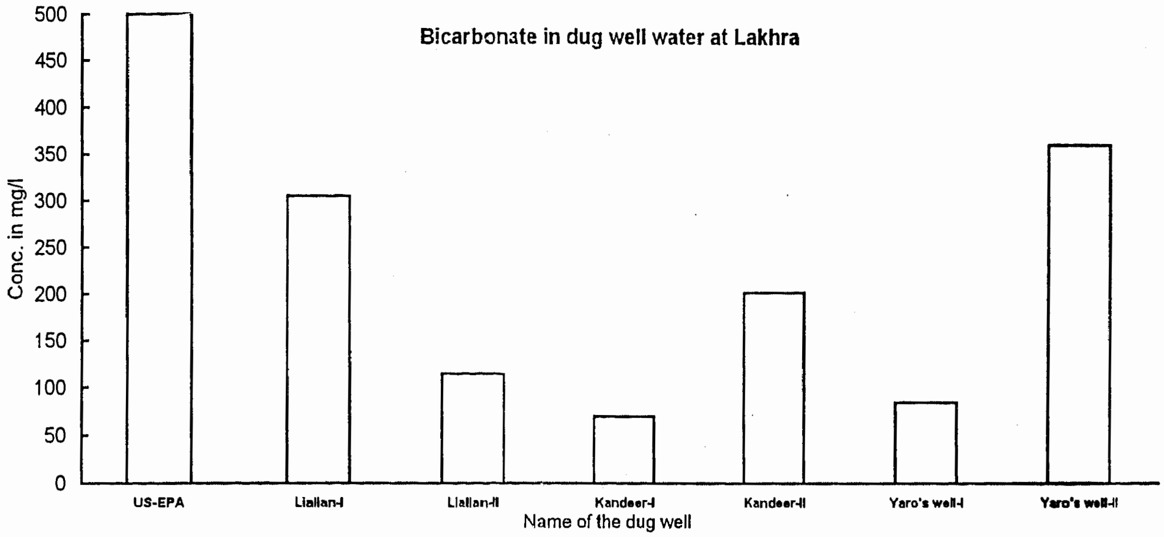


Fig.6.5 Bicarbonate in dug well water at Lakhra

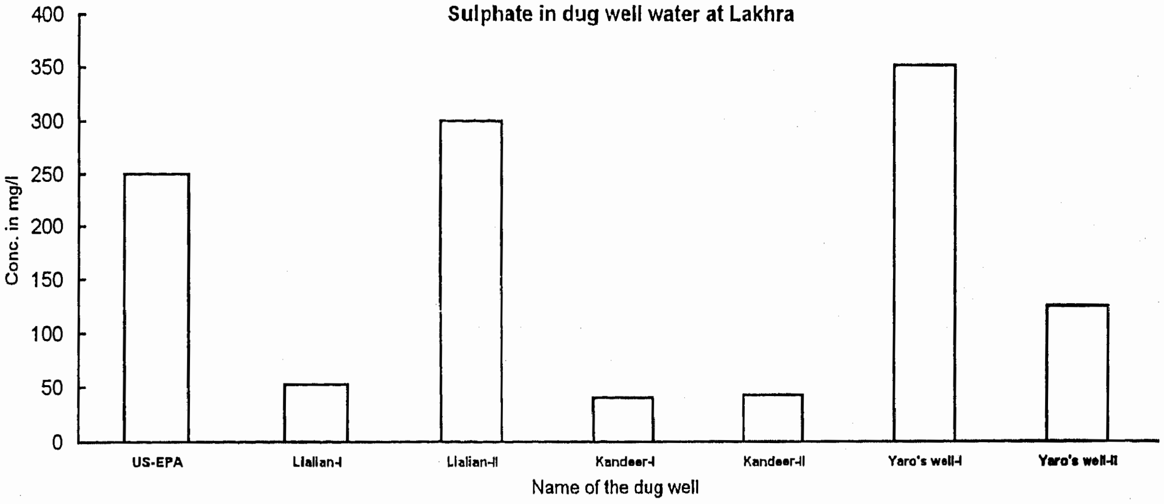


Fig.6.6 Sulphate in dug well water at Lakhra

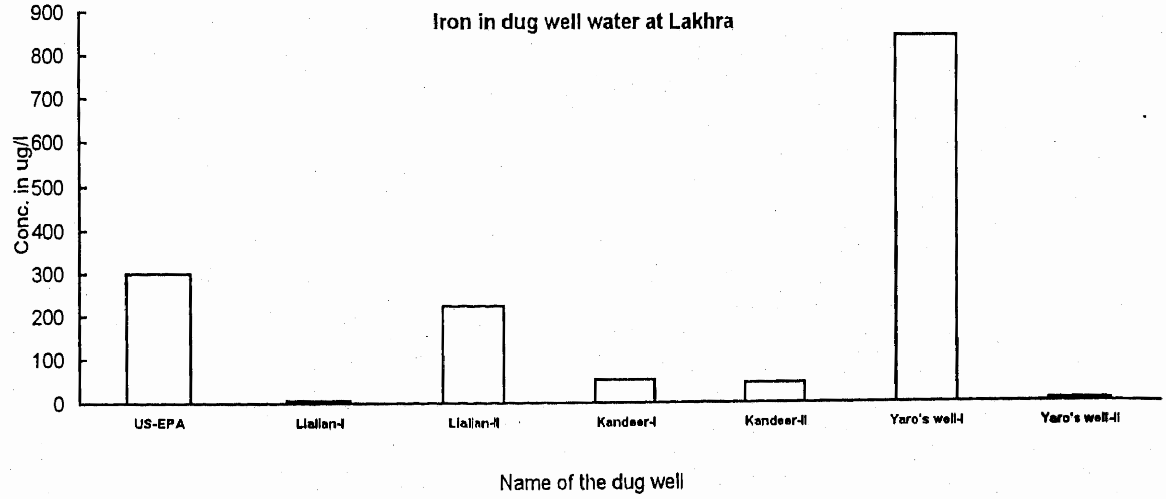


Fig.6.7 concentration of Iron in dug well water at Lakhra

The water samples of this well is also having high SO_4 content. The high concentration of Fe and SO_4 in this well could due to the high amount of pyrite within the host rocks.

Nickel (Ni)

Concentration of Ni in water collected from dug wells at Lakhra area varies from 4 to 7 μg/l (Table 6.1). Fig. 6.8 indicates that the studied samples lie below the recommended value of 1000 μg/l set by US-EPA (1979). Therefore, there is no possible negative impact related to this element in dug wells' water of Lakhra.

Copper (Cu)

Copper is gastro intestinal-tract irritant, and irritates the nerve endings in the stomach (Pathy, 1962).Copper concentration in well waters of the studied area varies between 10 and 89 μg/l (Table 6.1). All the studied samples from Lakhra indicate Cu concentration far below the highest recommended value of 1000 μg/l (US-EPA, 1979; Fig. 6.9).

Lead (Pb)

Though Lead (Pb) is one of the carcinogenic element in the environment, it is considered as a general protoplasmic poison which is cumulative, slow-acting and subtle. Fortunately all the well water samples collected from the studied area shows that Pb values are below the permissible limit proposed by US-EPA (1979). Water sample collected from Lilian-II dug well has the highest value of 38 μg/l (Fig. 6.10). In General no drastic effect in relation to Pb contamination is expected from the drinking of well water in the studied area.

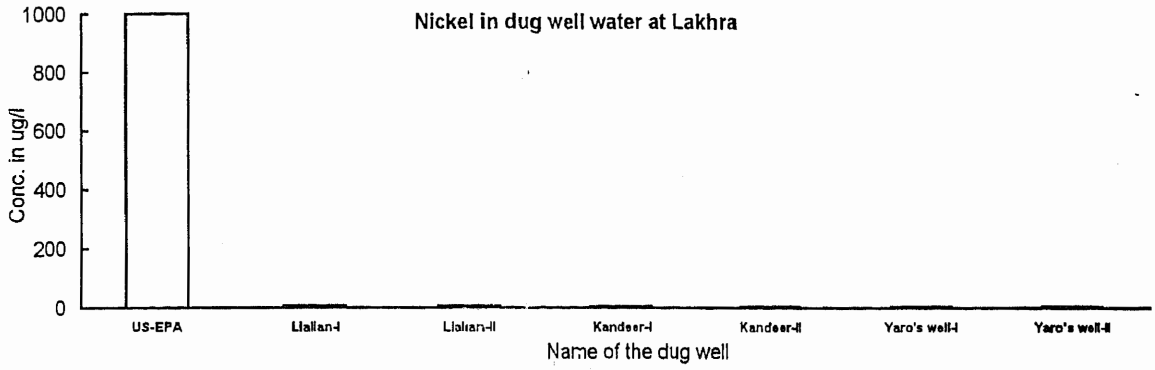


Fig.6.8 concentration of Nickel in dug well water at Lakhra

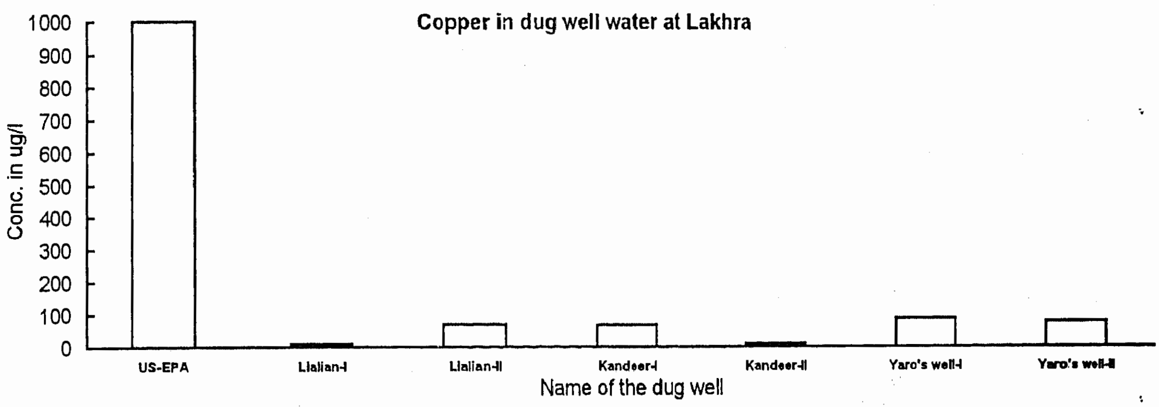


Fig.6.9. concentration of Copper in dug well water at Lakhra

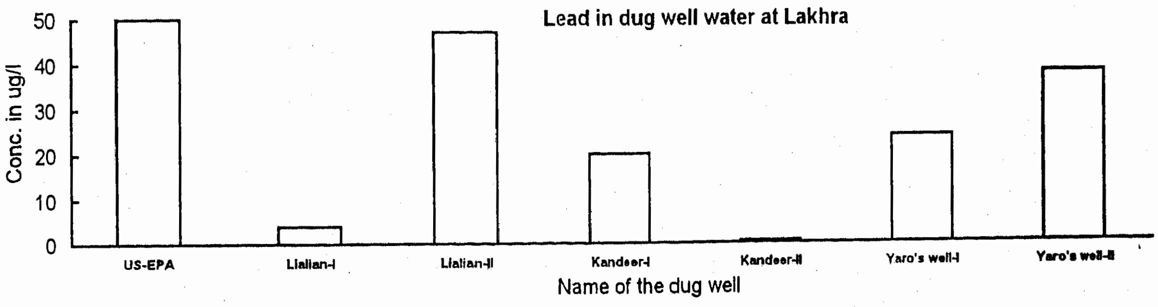


Fig.6.10. concentration of Lead in dug well water at Lakhra

Cadmium (Cd) is a toxic heavy metal, occurring in various minerals in association with Zn. The solubility of Cd in water is influenced by the nature of the source of the cadmium and the acidity of water. The estimated daily exposure to Cd through water, based on water consumption of 2 liters per day, is substantially less than 1 μg to 10 μg per day (Sharma,1994). The maximum contaminant level for cadmium in drinking water recommended by US-EPA (1979) is 10μg/ l. All the water samples collected from the dug wells at Lakhra show Cd concentration bellow this permissible limit (Fig. 6.11) and, therefore, no drastic impact of Cd contamination can be expected from these waters.

The data from dug well water of Lakhra coal field indicate that electrical conductivity is considerably high in relation to the recommended value of US-EPA. These high values are related to high TDS, particularly in Yaro's well No. II. This interpretation is supported by the high SO_4 and HCO_3 in certain dug wells of the area. Except the Yaro's well-I dug well indicating high Fe (iron) relative to the recommended value, rest of the wells indicate heavy metals, which are within the permissible limits as recommended by US-EPA(1979). The data interpretation, therefore, indicate the following:

1. The heavy metals from Lakhra coal mines so far noticed in air samples of the area, have not reached to the underground water system.
2. High electrical conductivity (EC) or total dissolved solids (TDS) and high SO_4 and Fe in certain well water have probably their source in surrounding rocks, including limestone and shale.

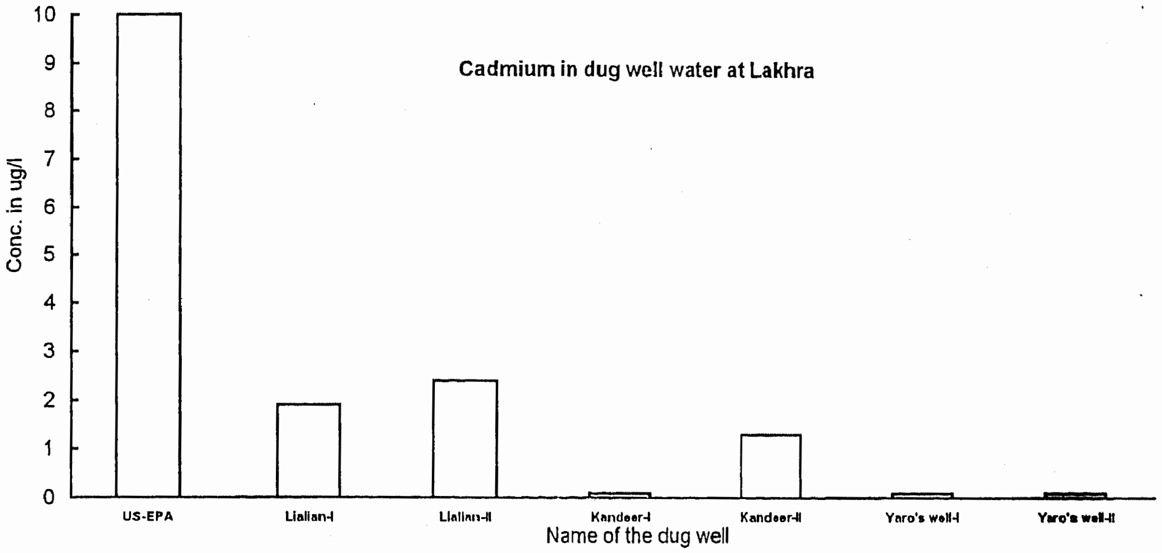


Fig.6.11. concentration of Cadmium in dug well water at Lakhra

It may be however, born in mind that these wells are at shallow depth and therefore, may could be effected by contamination from coal. However, the occurrence of coal seams at greater depth bellow the limestone, sandstone and shale certainly add heavy metals, sulfur and other contaminants in the deep wells. This fact is supported by the high Pb contents of Lilian-I well which indicate a value (47µg/l) close to the recommended value of US-EPA (50 µg/l).

A comparison of all the wells with each other on the basis of data obtained indicate that the Yaro's well-I reflects highest iron and SO_4, where as the Yaro's well-II indicate highest EC, TDS, HCO_3, Pb and Cu. Their waters may be classified as of the lowest quality in the area.

CHAPTER SEVEN

DISCUSSION AND RECOMMENDATIONS

Previous studies and the one carried out during the present investigation indicate that the coal seams of Lakhra coal mines occur in the Bara Formation of Early Eocene age. This coal is of high lignite grade and is liable to spontaneous combustion (Chapter 1). Because of high sulphur content it can be classified as a low quality coal in comparison with other coals (Ahmed et al., 1986, Malik, 1989, Shah, 1977).

The current studies indicate the presence of heavy metals including Cr, Fe, Ni, Cu, Zn, Cd and Pb in variable proportion. On Comparison with coals from different parts of the world especially Canadian and Indian lignitic coal (Table 4.2), the data show that in Lakhra coal Cr, Ni, Cu, Cd and Pb are higher than the Canadian coal while Indian coal contain higher Cr, Ni, Zn and Pb than the Lakhra coal.

The present studies also show that the coal mining activities certainly contribute heavy metals into air in the form of coal dust/suspended particulate matter. The study of coal dust in the form of particulate matter as pollutants in the air at Lakhra coal field carried out under current investigation has shown considerable quantities of light and heavy metals including Na, Mg, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd both at hanging and ground positions (Table 5.1 and 5.2). The data also show that the proportions of light metals at different locations are overlapping between hanging ang ground positions, indicating the role of blowing air/wind in the area. On the other hand the heavy metals indicate relatively higher digree of distribution, with ground position generally containing higher proportion of heavy metals than at hanging position (Figs. 5.2a-e and 5.3a-e). Such data indicate that coal mining activities are rendering metals into the air of Lakhra coal field area. The type of differentiation indicating increase of heavy metals in dust according to increase in atomic weight observed by Saifullah (1997), Sultan (1996) and Hamidullah et al., (1997a, 1997b) at Peshawar metropolis is not followed completely by these workers, the type of differentiation and systematic of heavy metals in air is controlled by several factors including availability of source release fashion, dispersion agent (air) and its intensity etc. It can be stated in the context of Lakhra coal field that blowing wind (natural) and the round the clock movement of vehicles (trucks) did not let the heavy metals to settle orderly and generate trend similar to those observed at certain localities either in hanging position or ground position or both types of samples (e.g., PMDC and National coal field area; Figs 5.2 a & c). Exceptionally high Cu is observed at ground position in Habib coal field area and both at ground and hanging position at Indus coal field area (Figs 5.3b, e).

As mentioned in Chapter 6, In orde to determine the effect of coal mining activity on the water resources of the area, Electrical Conductivity, Total Dissove Solids, Carbonate, Sulphate and heavy metals studies were carried out for six dug wells in coal field area (Figure 6.2 & 6.3, 6.4 a-g, Table 6.1 and 6.2). Comparison with International Standards (US-EPA) it is interesting to note that except iron (Fe) in Yaro's well-I all heavy metals are bellow the US-EPA maximum contaminating limit (MCL), in all dug wells (Figure 6.7 to 6.11). Lead and Cadmium are though bellow the US-EPA limit but sufficiently high in Lilian-II and Yaro's-I. These observations indicate that the underground water in these wells have received contamination either directly through air transportation or underground seepage.

The lower level of metals in certain wells may be related to the fact that these metals settle down easily and may not be collected during sampling. On the other hand samples showing relatively higher values of heavy metals (e.g., Pb in Lilian-II and Yaro's-II weell (Figure 6.10) were probably collected in turbulent conditions.

The higher values of iron (Fe) in Yaro's-I dug well (Figure 6.7) is most probably related to the occurrence of this well in the vicinity of coal field and higher leaching capability of iron from the pyrite bearing host rocks.

The higher values of Electric Conductivity, Total Dissolve Solids, bicarbonate, sulfates and heavy metals in some of the wells (Figures 6.2, 6.3, 6.6 & 6.7 and Table 6.1) indicate that these waters are not suitable for drinking and agriculture purposes. As mentioned earlier (Chapter 6). The following diseases are expected to effect the general population of the area:

Unpalatable mineral tastes and higher costs because of corrosion or the necessity for additional treatment is caused due to the excess of Total Dissolve Solids in water (Anon, 1976). High concentration of TDS may reduce solubility of gases (like oxygen) and utility of water for drinking, irrigational and industrial purposes, as many salts are found dissolved in natural water. The common ones have been carbonate, bicarbonate, chloride, sulphates and nitrates of calcium, magnesium, sodium, potassium, and iron etc (Chatwal et al., 1989).

Pollution zone can be establish by measuring the Electric Conductivity, though conductivity is a non specific parameter but it is related to the concentration of total dissolve solids and major ions (Kumar De, 1986).

Excessive bicarbonate may cause eyes irritation problem, as this alters pH of lacrimal fluid around the eyes (Anon, 1976).

Elementary sulphur may slightly irritate but the noxious effects associated with sulphur are usually due to its oxide or hydride. Sulphuric acid attacks the enamel of the teeth, while sulphate is poorly absorbed from the human intestine; it slowly penetrates the cellular membrane of mammals and is rapidly eliminated through kidneys (Rosum, 1961).

The high values of iron in water may causes diseases like hemosideroses, liver damage, diabetes etc (Rosum, 1961).

Cancer may occur due to the excess dose of nickel and its compounds, these also induce nasal, laryngeal and lung cancers (Pedersen et al., 1978).

Intestinal trac may irritate by copper, specially it irritates nerve endings in the stomach and cause nausea, vomiting, gastric pain, hemorrhagic gastritis, diarrhea, cramps in the calves. It constant exposure to the liver, kidneys and spleen may be injured and anemia may develop in human body (Patty, 1962).

Severe gastrointestinal disturbances and anemia, neuromuscular dysfunction and encephalopathy are the diseases caused by prolonged absorption of lead. Lead in water may also cause weakness, weight loss, hypertension, lassitude and insomnia (Kehoe, 1972, NIOSH, 1972,).

High blood pressure and heart diseases are caused due to cadmium in human body. It may also cause kidney diseases. Cadmium in water is causing Itai-Itai or Ouch-ouch diseases in Japan by drinking contaminated river water, it causes pain in back /backache, pain in joints and renal failure (Emerson, 1970).

RECOMMENDATIONS

On the basis of the study performed and the above discussion the following mitigation procedures are recommended for coal mining activity and for the safe drinking and agricultural water supply:

1. It has been observed that Lakhra coal posses higher concentration of heavy metals, therefore, it is suggested that before utilizing this coal in Power Plants or in other industries it should be treated chemically, so that environmental hazardous metals could be removed.
2. As dust can cause irritation, particularly to the eyes mucous membrane, so strict measure should be adopted to combat it, i.e., miners should be provided air masks and dust suppression and extraction system should be provided at each mining site.
3. About 7000 tons of coal per day is transported to the various parts of the country from Lakhra, it is assumed that about 0.05-1% of coal is lost from coal handling and transportation, that also pollute the air. It is therefore recommended that Water or suitable chemicals should be sprayed on the top of Trucks carrying coal. In this respect NLC type sealed containers may also be used for coal transportation.
4. To reduce dispersion of Suspended Particulate Matter in air hoods should be constructed at the transfer or storage points.
5. Dense belt of trees should be planted on road sides. These trees would serve as dust arresters As it has been estimated that trees planted on one hectare can catch (arrest) about 40 tones of dust.

For controlling dust or Suspended Particulate Matter on dumping site fast growing grass or herbs should be planted.

6. Wells around Lakhra coalfield be covered to prevent falling of fine coal dust in the form of suspended particulate matter.
7. Walls of wells should be cased in order to avoid incoming pollutants from the surrounding coal mines.

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