Geochemistry of Water and Soil from Dera Ismail Khan, N.W.F.P., Pakistan.

By

Anwar Hussain Khan Alizai

Requirement
for the Partial Fulfillment
of Thesis in
(Master of Philosophy)

Submitted to: National Center of Excellence in Geology
University of Peshawar

APPROVED BY

External Examiner
Dr. M.A.Q. Jahangir Durrani
Associate Professor
Deptt. of Civil Engineering
NWFP University of Engineering
& Technology, Peshawar.

Supervisor/Internal Examiner
Dr. M. Tahir Shah
Associate Professor/Supervisor
NCE in Geology
University of Peshawar.

Director
Prof. Dr. M. Qasim Jan (H.I., S.I.)
NCE in Geology
University of Peshawar.

Contents

Page

CHAPTER: I

CHAPTER: II

LIST OF FIGURES
Contents

LIST OF TABLES
Contents

LIST OF PLATES
Contents

ACKNOWLEDGEMENT

IN THE NAME OF ALLAH, THE COMPASSIONATE, THE MARCIFUL.

DURING WRITING THIS THESIS, I HAVE RECEIVED ENCOURAGEMENT, SUPPORT AND PRACTICAL HELP FROM SEVERAL TEACHERS AND FRIENDS. IT IS A PLEASURE TO ACKNOWLEDGE THIS HELP. FIRST AND THE MOST THANKS TO MY SUPERVISOR, ASSOCIATE PROF. DR. TAHIR SHAH, FOR HIS GUIDANCE AND KIND SUPERVISION THROUGHOUT MY WORK. THANKS TO MR. GHULAM KHAN AND MR. ANEES, LECTURERS, ENVIRONMENTAL DEPARTMENT, UNIVERSITY OF PESHAWAR, FOR PROVIDING LATEST INFORMATION AND REFERENCE BOOKS ON THE RELATED TOPICS.

SPECIAL THANKS TO MR. MUHAMMAD ATIQ, MY COLLEAGUE AND FRIEND, FOR HIS KIND SUPPORT IN THE COMPILATION OF MY THESIS.

Abstract

The aim and motive to start work on the waters and soils of D.I.Khan division was to establish a brief chemical and environmental report on the quality of water, because various types of diseases have been reported form the area. For this purpose water of the area was divided in to four categories i.e. deep water (tube-wells); shallow water (dug-wells, settling-ponds / nalas and hand-pumps);surface water (streams and rivers). A total of thirty-four water samples were selected for study of twenty-two parameters. In order to see any contribution made by soils and rocks to the water, twenty-two soils samples, adjacent to water samples and five rock samples were also analyzed for major and trace elements.

The results obtained for the water samples from different places of D.I.Khan division are compared with that US-EPA (1989) and WHO (1984) standards for safe drinking water. On the bases of these standards the water quality of many areas are found not suitable for drinking. For example water sample from Gomal Rivers suggest that it is not safe for drinking water, however, major portion of population of the D.I.Khan division use it for drinking. The chemical redicals exceeding the permissible limit of US-EPA (1989) and WHO (1984) are: Bicarbonate (225 mg/l), sulphate (400 mg/l), Iron (43.3 mg/l), Magnesium (47 mg/l), Maganese (0.21 mg/l), Na (102 mg/L) and copper (10 mg/l). In Poroa the follow constituent are out of permissible limit i.e. Sulphate (1600 mg/l); Bicarbonate (250 mg/l); Chloride (244 mg/l); Na (175 mg/l), Magnesium (73.7 mg/l). Apart from these two areas, the water quality of other areas, which is not safe for drinking purpose are Mullazai, Tank, Umer Ada, Potah, Chadhwan, Ramak, Kulachi and Gomal university. Sulphate is high in the middle and lower part of the D.I.Khan division. High sulphate concentration in water causes diarrhea and dehydration (Zunae, 1990). Nitrate is found high at shallow water (Dug well, hand pumps, settling ponds Nala). It is reported alarmingly high at Mullazai (17mg/l) and at Chudhwan spring (90 mg/l), as compared to the maximum limit (10mg/L) of WHO (1984) for safe drinking water. High nitrate cause infection to gastro-intestinal tract and large concentration of nitrate in water may result in the potential formation of carcinogenic nitro samines (Zunae, 1990). Chloride concentration is maximum i.e. 618 mg/l at Ramak area of D.I. Khan division, which considerably exceeds the permissible limit (200mg/L) of WHO (1984). It crosses the permissible limit at eight other places of D.I. Khan division. Except two samples, Iron is out of limit in all the water samples. Magnesium is also high at six places. Maganese is crossing the limit at sixteen places. Potassium is high at five places. In trace elements copper is considerably out of range in the water of Gomal River. Pb is high (0.3 mg/L)

in the water sample taken from Gomal University tube well where by the safe limit of lead in the drinking water is 0.05 mg/l. Fluoride is also high at six places. The generalized trend for many constituents increase from north to south. The results show the concentration of many elements are high towards south.

Collection of soil and rock samples was made from the same areas where water samples were collected. The objective of this detail geo-chemical results of the rock and soil samples were to see the influence of these rock and soil samples on the water samples of the same area. The results are discussed in the concerned chapter.

For the treatment or removal of these constituents can be done by the methods established by US–EPA, (1988). Filtration, ion exchange and lime softening can remove copper and iron. Nitrate can be removed by biological dentrification, sulphate by ion exchange and fluoride by reverse osmosis. All these methods are effective but practically non-economical.

CHPATER: 1
INTRODUCTION

1.1. GENERAL DISCUSSION: Water is an essence of life. It is needed for the survival of every organism or life on earth. It is, therefore, necessary that it should be clean to a required standard in order to reduce the health-related hazards. Water is a good solvent and it dissolves many elements (both organic and inorganic). A large numbers of organic micro-pollutants have been identified in surface and ground water. The contaminates reach drinking water supplies from various sources including municipal and industrial discharge and urban and rural runoff. Apart from this treatment of drinking water can contribute contaminants as well. Since its introduction in 1908, the chlorination of drinking water has been successful in preventing the transmission of infection water-borne diseases but the reaction of free chlorine with selected precursors in water has recently been found to produce organic micropollutants. Recent research showed that there is a risk of cancer of the bladder, stomach, large intestine and rectum by the contamination of chlorinated water (Agnem:1988).

All over the populated part of the earth, the quality of natural fresh water is being disturbed by human activities. This is basically the consequence of human reliance on rivers to carry away their waste by water, but soluble matter from the catchment including sulfur, fertilizer from crop fields, also reaches the rivers in large amount. The complex composition of natural water further complicates it. "The term water quality refers to the suitability of water for its desire use." The overall extent of pollution is yet unknown due to delayed response and detection difficulties.

In region of highly permeable soil and intensively fertilized land with large concentration of cattle or extensive human activities, the ground water may already have reached high nitrate levels, making it unfit for human, without an extra technical device in or around the individual well.

The excess of some of these elements, especially in drinking water may cause serious diseases. *According to the official figure, more than 55 million people in Pakistan live without the facility of safe drinking water. Over one hundred million people are deprived of any sanitation facility. According to Daily Frontier Post (1994), recent investigation carried out by the environmental protection agency (EPA) and the Public Health Engineering Department reveals that about 70-80 percent of the total population uses polluted water.*

Deforestation in the central Asian mountain ranges reduces the rate of evapotranspiration and subsequently the precipitation runoff from the land to the river system is much increased. One of the consequences of this increased runoff is a rise in the rate of soil erosion and an increase in the particulate content of river water. The deposition of this eroded material in the low reaches of the rivers. This has resulted in contamination of drinking water supplies and degradation of effluent treatment system. There is generally an increase rate of occurrence of water-born diseases.

Pakistan is not an industrial country, so we don't have environmental problem as severe that western countries are coped with. The environmental problems here are either natural or due to lack of vegetation. Taking the example of the longest river of Pakistan "the Indus" while traveling towards Gilgit, this river almost 500 kilometers, accompanies you. One can see its muddy water. This is due to soil erosion because of deforestation.

Dera Isamil Khan (D.I.Khan) district has been selected for the investigation of geo-chemistry in both surface and under-ground water during this study. It is situated in the southern-most region of the NWFP between latitude 31° 15′ and 32° 30′ N and longitude 70° 00′ and 71° 00′ E (Fig.1.1).

Physiography: The D.I.Khan area contains two main physiographic units, the alluvial lowlands, which include the structurally undisturbed Indus plains, and the folded belt, which includes the Khisor, Murwat, Bhittanni, and Sulaiman Ranges. These ranges and highlands form a nearly continuous mountain system between Salt Range- Potwar Plateau region to the northeast and Baluchistan to the southwest.

Climate: The climate is of the sub-arid subtropical continental lowland type. The average annual precipitation rages from 290 mm in the hills in the North to not more than 200 mm in Ramak in the South. The annual potential evapotranspiration is approximately 2200 mm.

Population and domestic water supply: According to census report (1987), the total population was estimated to be 7,78,000 of whom 6,35,000 were living in rural areas. These people obtain their domestic water from dug-wells and shallow drilled wells equipped with hand-pumps, ponds, the store runoff of the Indus River, and irrigation ditches or perennial streams. The public Health Engineering Department (PHED) has drilled tube-wells for the supply of major towns and large villages.

Drainage: Indus river forms the eastern boundary of the D.I.Khan District. There are three other rivers (Luni, Gomal, and Khor River) which are active in the area. These all flows from west to east. Beside these there are major intermittent streams, such as Largi Nala, Khud Hauz, Takwara and Maldan Khud. These streams also flow from west to east.

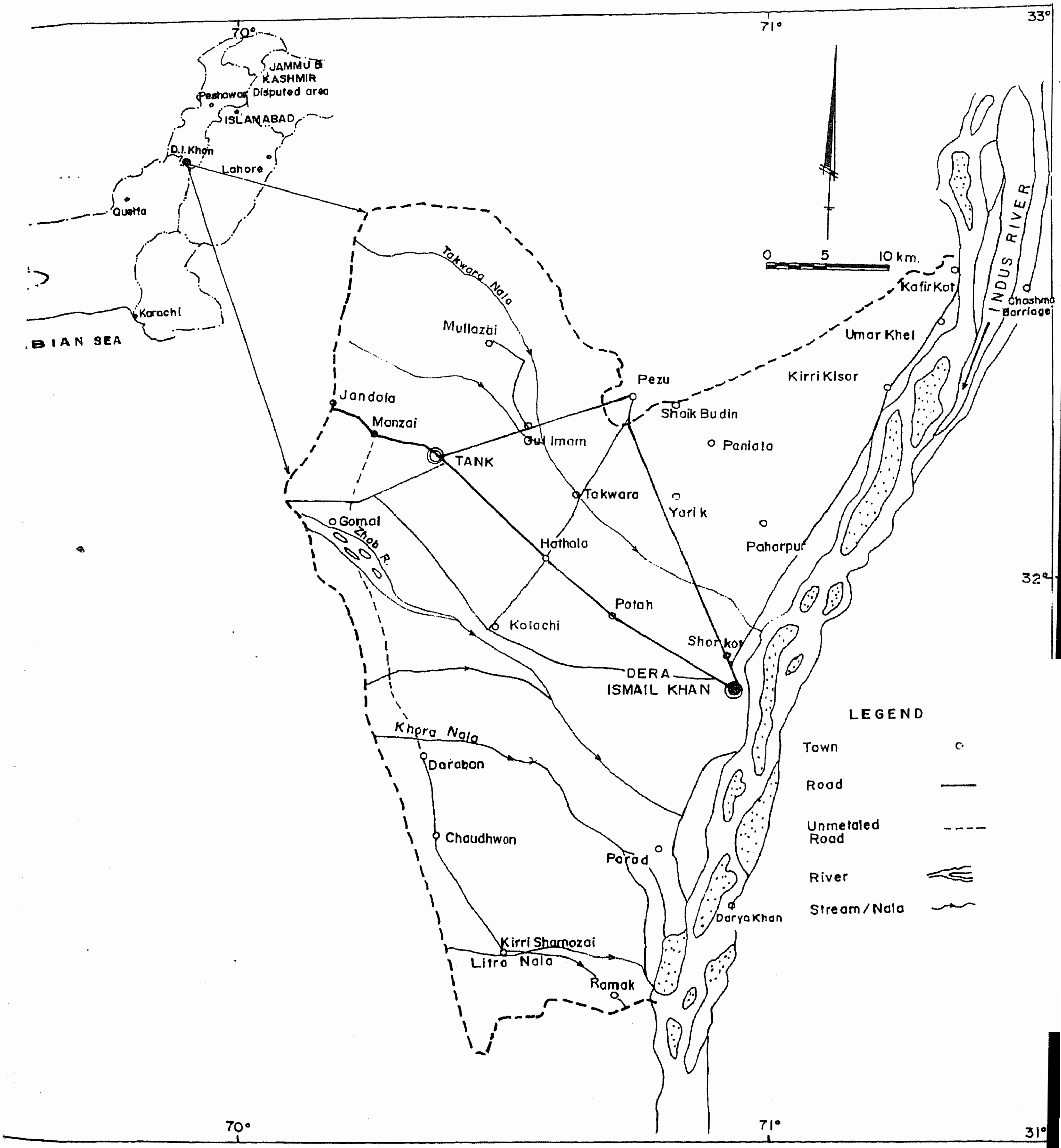


Fig. 1.1 Location map of Dera Ismail Khan Division (N.W.F.P.)

Vegetation and Forestation: The land gives the impression of a semi-desert land (Plate 1.1 & 1.2). The total surface cover of vegetation rarely exceeds ten percent as compare to the whole land. The Most common species are capparis aphylla (karir). Acacia Jacquemontii (Jandi). Saueda frutiscosa (Lana) and Salvadora Deoides (Wan). To the southern most part of D.I.Khan. the land support a moderate growth of Farash, Jandi, wan and Mesquite.

1.2.Previous Work:

Previous work showed that the D. I. Khan area has water problem both quantitatively as well as qualitatively. For he sake of sweat water exploration. the detailed work has been done by the hydro-geology Directorate of WAPADA. N.W.F.P. In this regard the ground water survey was conducted in collaboration with DGV institute of applied geo-science. Netherlands. under the Pakistan Dutch program for ground water investigation in N.W.F.P. during 1981 to 1985. The main objective was to obtain hydro-geologic information with respect to the alluvial fill and pore-water to help in planning ground water development in the D.I.Khan area.

Water And Soil Investigation Division (WASID) made the first comprehensive ground water investigation during 1961 to 1964 (Hood et al., 1970). Most of the work done was on the exploration of sweat water. But no work has been done to determine the quality of water.

In geological investigation of D.I.Khan area. the following geo-scientists made their investigations in the conorological order as under:-

Costello (1864). an army surgeon recognized brachiopods and mollusks at Shaikh Budin and in the Khisor range, and collected mammalian bones and teeth in the Marwat range. Verchere (1867) a physician, gave a report includes cross-sections of the Shaikh Budin -Paniala area. He correctly identified the ages of some of the rock units.

The most comprehensive and reliable of the early reports is that of Wynne (1880). the first professional geologist to visit the area. He described in detail many rocks that are recognized as mappable units at Shaikh Budin and in the Khisor, Murwat. and Bhittanni Ranges. His reports also include cross-sections and measured sections, a summary of the mineral resources. and geological maps.

Grieshbach (1884) was the first geologist to visit the northern Sulaiman Ranges. His reports include some excellent panoramic sketches made from the highest peaks of the ranges.

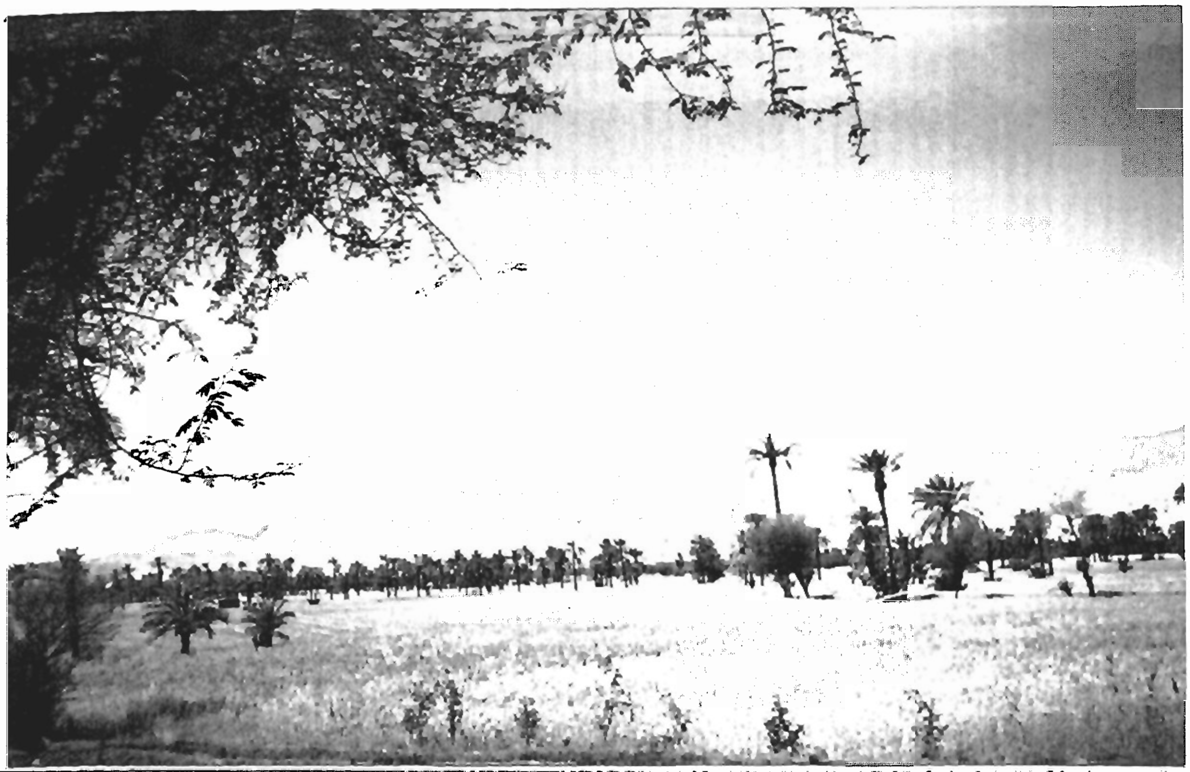


Plate # 1.1 Vegetation at Panaiala, northern part of D.I.Khan division.

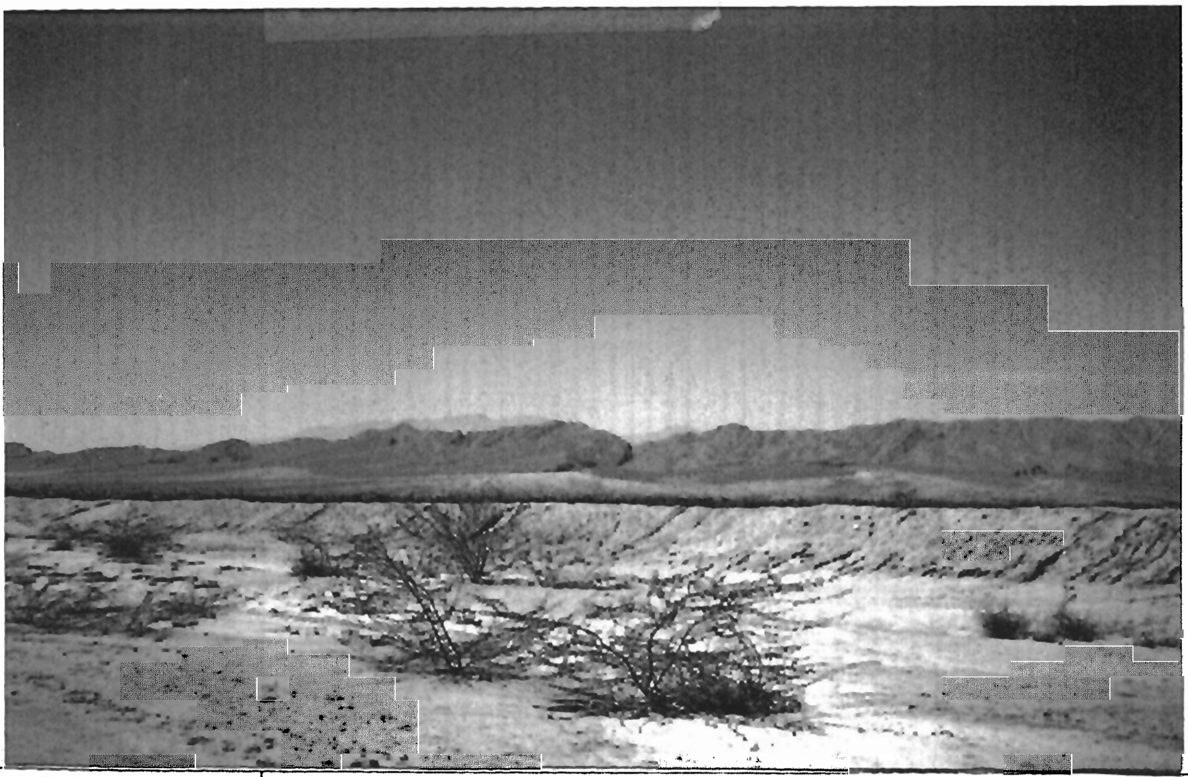


Plate # 1.2 Vegetation at southern most part of D.I.Khan division.

Morris (1938) mapped and described in some detail rocks of the Siwalik Group in the Khisor. Marwat and Bhittanni ranges and demonstrated the marked similarity of the heavy mineral assemblages of these rocks with litho-stratigraphic equivalents in the Potwar Plateau.

Williams (1959 & 1960) made comprehensive reconnaissance geology and stratigraphic studies with other worker from Geological Survey of Pakistan.

1.3.Purpose and Scope: Various types of diseases have been reported in the Dera Ismail Khan region. These diseases to certain extent could be due to the use of contaminated drinking water. Contamination in drinking water can be of two types.

a. Bacteriological
b. Chemical.

The bacteriological contamination can cure the short-duration problems (e.g. gastroenteritis, typhoid. liver abscess etc.), but the impact of chemically contaminated water on human health is very serious. This may cause long term diseases such as carcinoma. florosis etc.

This study is planned to carry out the chemical composition of waters (both surface. subsurface & river Indus), soils and rocks of D.I.Khan area. In order to see that if there is any link. the influence of geology on the general health of the inhabitants of the area, if yes then to identify the possible source of this contamination, as well as the remedial measured will also be suggested if possible.

1.4. GEOLOGY: D.I.Khan basin is geologically lies between western salt range and northeastern Baluchistan. It is an alluvial plain of 7,000 km^{2} and its catchment extends into Sulaiman, Bhittanni. Murwat and Khisor mountain ranges (Fig. 1.2, Plate # 1.3 & 1.4). The eastern boundary is the Indus river and in the south the plain continues into the into Dera Ghazi Khan District of the Punjab.

The mountains bordering the alluvial plain are mostly composed of rocks of late Tertiary age Hood at al. (1970) assumed that these rocks extend as basement rock of Siwalik Group. A consolidated or semi consolidated sandstone with thick clay or shale (Plate # 1.5 & 1.6) at relatively shallow depth below the alluvial fills. During the upper Pleistocene and Holocene the basin has been filled with silty clay, sand and gravel which occur either as:

a) Piedmont deposit in the west and the center of the basin.

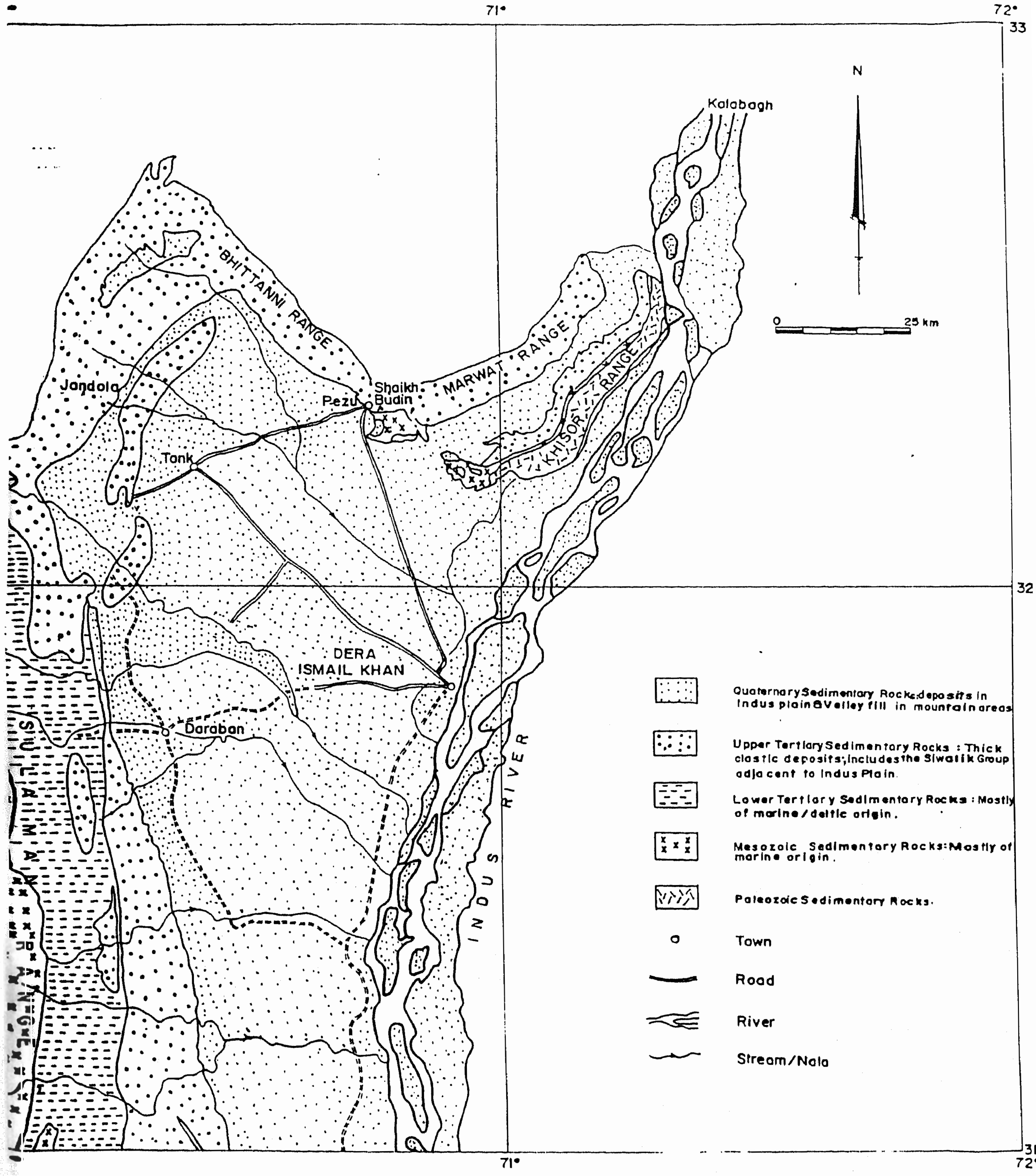


Fig. 1.2. Geological Map of D.I.Khan division.

(modified map of Professional Paper 716-B, Plate:5, Geological Survey of Pakistan)

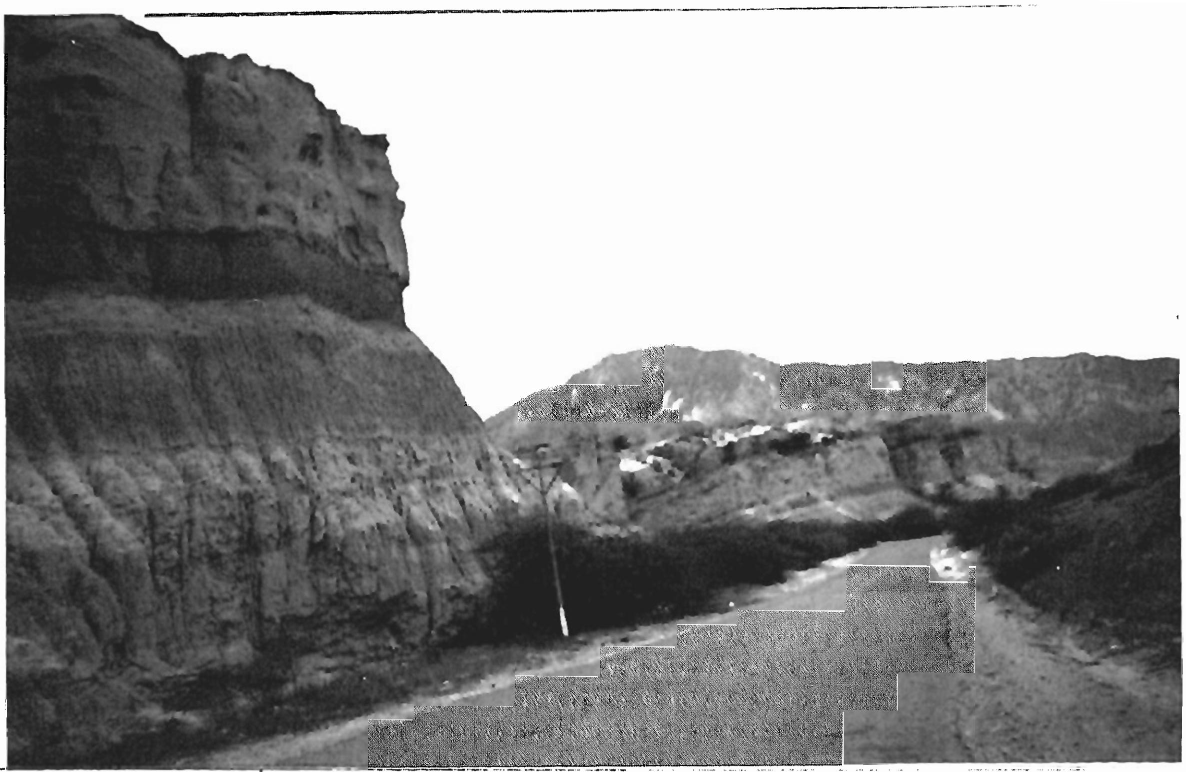


Plate # 1.3	**Road side section near Pezu.**

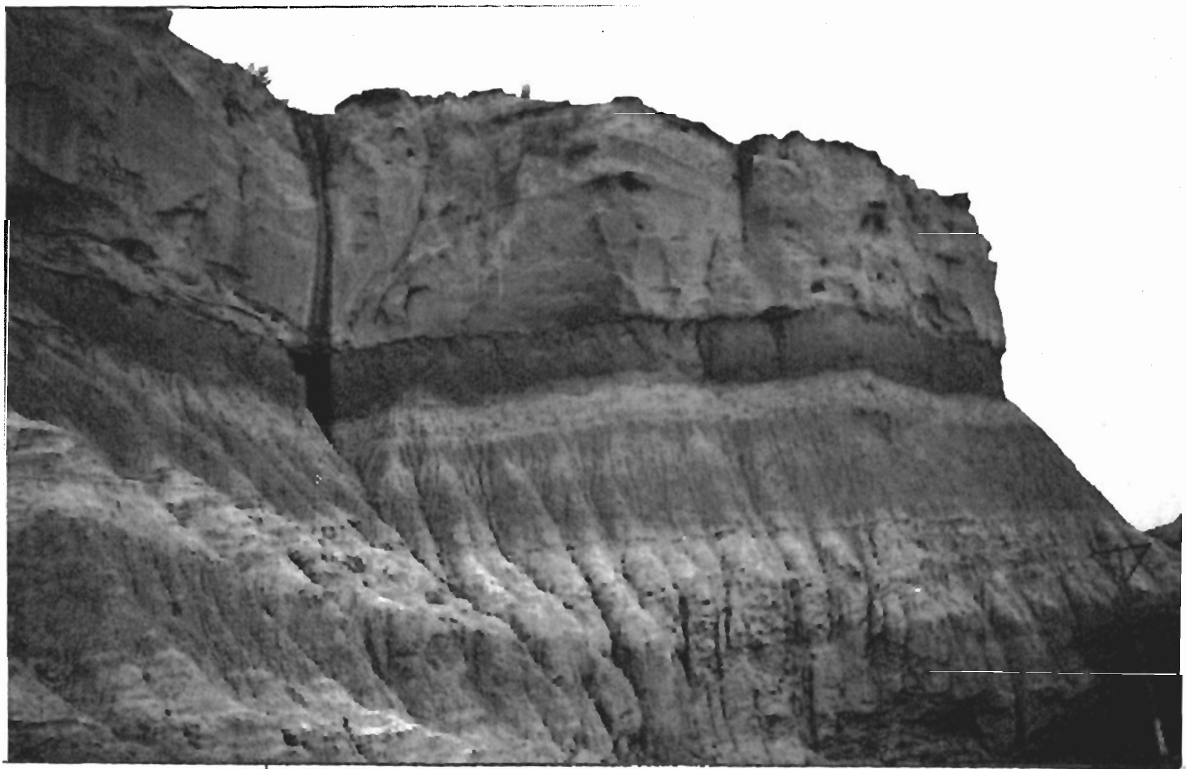


Plate # 1.4	**Section showing Kingriali dolomite at the top and carbonaceous shale of Datta formation at bottom.**

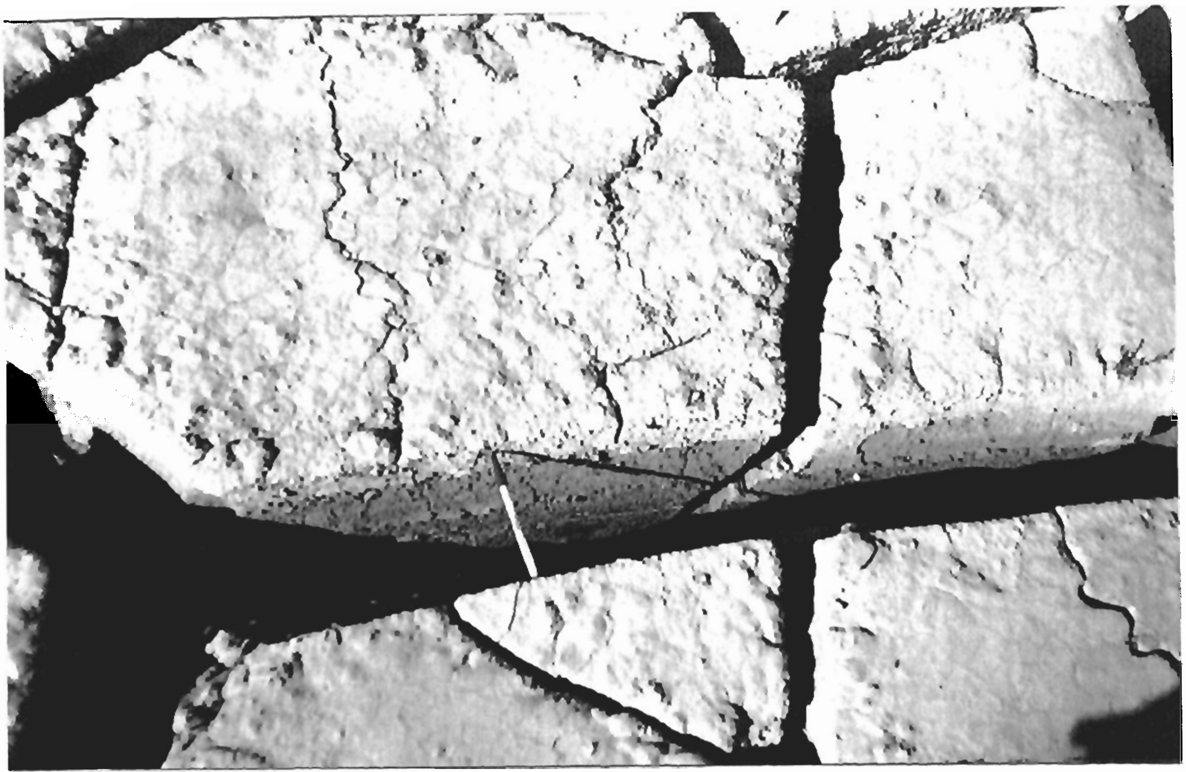


Plate # 1.5	Mud cracks in the soil of D.I.Khan.

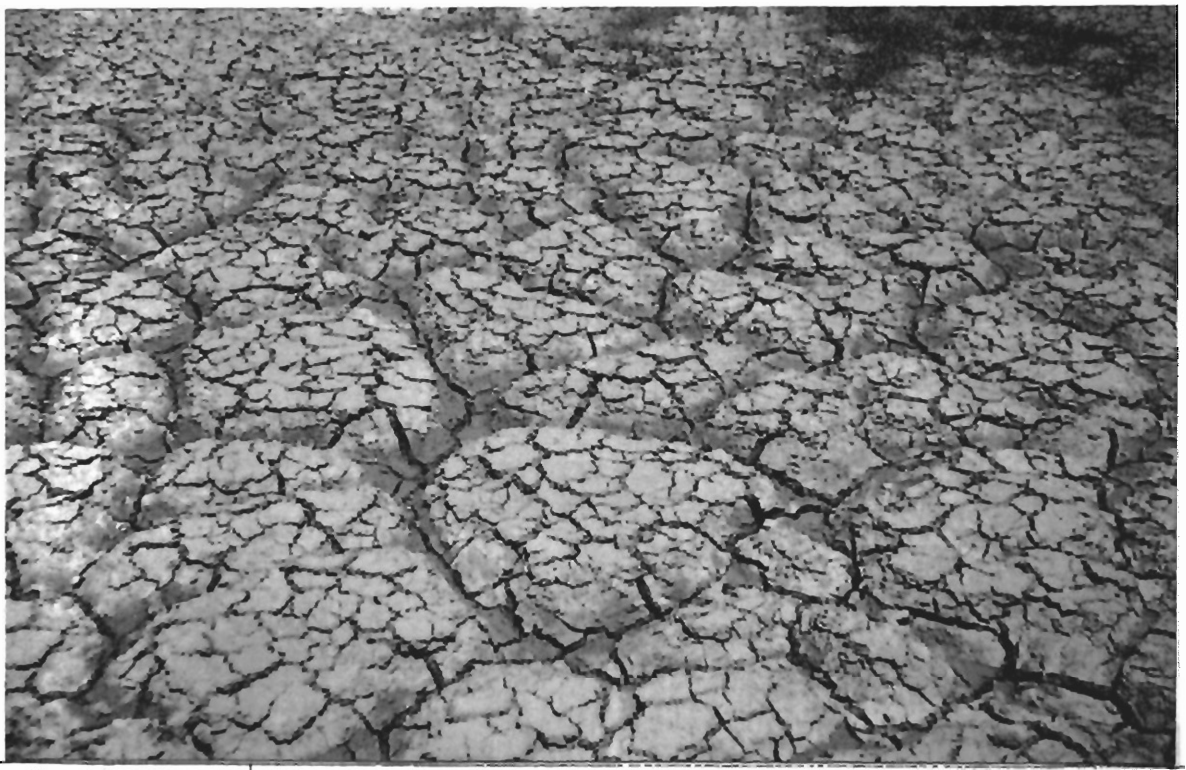


Plate # 1.6	Another view of mud-cracks in the soil of D.I.Khan.

b) Flood plain deposit of the Indus river that is found in the east. They interfinger in a transition zone.

Close to the mountain, the piedmont deposit consists of gravel and boulders with intercalation of clay that forms alluvial fans. With increasing distance from the mountains the grain size decreases rapidly to stratified, silty clay and generally become the predominate material in the central plain. Fine to medium-grained sands, are some time intercalated. The flood plain deposit cover an area of about 1200 km^2 of the Indus river low lands and consists of sand with only a little intercalated clay. The sequence is generally 250-350 meters thick.

The Ranges and high lands form a nearly continuous mountain system between the Salt range-Potwar Plateau region to the northeast and Baluchistan to the southwest. Total stratigraphic thickness exceeds 14,000 feet in the Khisor and Marwat ranges. Sedimentary rocks varies in age from Cambrian (?) Permian, Triassic, Jurassic, Cretaceous, middle and late Tertiary and Quaternary (William & Hemphill, 1964). Lower Tertiary rocks are however, absent. Stratigraphic terminology for rocks in Khisor and Marwat Ranges is the same as that used in Salt range and Potwar Plateau region to the northeast. Total stratigraphic thickness exceeds 38,000 feet in the Sulaiman Ranges-Waziristan area. Sedimentary rocks of Jurassic, Cretaceous, Tertiary and Quaternary age is present. Rocks of Paleocene and Eocene age are well developed in this region, in places exceeding 13,000 feet. Stratigraphic terminology for units of Mesozoic age is the same as that used in Baluchistan to the southeast. New names are proposed and type sections are designated for seven units in the eastern foothills of the Sulaiman Range (William & Hemphill, 1964).

STRATIGRAPHY

Jhelum Group: The oldest unit exposed in the area is the Jhelum group of Cambrian age. Rocks of the Jhelum group, crops out along the southern flank of the Khisor Range. These are believed to be of Cambrian age because in the lithology and stratigraphic position they closely resemble rocks believed to be of Cambrian age by Gee (1934) in the Salt range. They are poorly exposed in the area and are devoid of index fossil (Hussain, 1960). Type locality of Jhelum group is in the Salt range. In the study area Jhelum group is limited to the southern Khisor range.

Abundant evaporites associated with the Jhelum group both in the Salt range and Khisor range suggest that at least part of the group was deposited under arid conditions. The Jhelum group is overlain unconformably by the rocks of Nilawahan and Zaluch group of Permian age (Table 1.1).

Nilawahan Group: The rocks of the Nilawahan group in the study area are limited to the Khisor range. The Nilwahan group of Permian age, includes that part of the stratigraphic sequence which was previously referred to by the following informal descriptive terms Lavender clay, speckled sandstone,

Age	Kishor - Bhittanni - Marwat Ranges & Shaikh Budin		Waziristan - Sulaiman Range	
Middle & Late Tertiary	Siwalik Group	Malagan Formation	Siwalik Group	Chaudhwan Formation
		Dhok Pathan Formation		Litra Formation
		Nagri Formation		Vihowa Formation
		Chinji Formation	Chitarwala Formation	
Early Tertiary	Rock unit not exposed		Kirthar Formation	Drazinda Shale Member
				Pir Koh Limestone Member
				Drazinda Shale Member
				Domanda Shale Member
				Habib Rahi Limestone Member
			Baska Shale	
			Ghazij Shale	
			Dunghan Formation	
Cretaceous	Lumshiwal Sandstone (?)		Pab Sandstone	
	Chichali Formation		Mughal Kot Formation	
			Parh Limestone	
			Sember Formation	
Jurassic	Samana Suk Limestone		Sulaiman Limestone Group (Undivided)	
	Datta Formation			
Triassic	Kingriali Dolomite		Rock unit not exposed	
	Tredian Formation	Khatkiara Sandstone Member		
		Landa Member		
	Mianwali Formation	Narmia Member		
		Mittiwali Member		
		Kathwai Member		
Permian	Zaluch Group	Chhidru Formation	Rock unit not exposed	
		Wargal Limestone		
		Amb formation		
	Nilawahan Group	Undivided		
Cambrian (?)	Jhelum Group	Undivided	Rock unit not exposed	

Table 1.1. **Geological Sequence and the age of the rock formations in the D.I.Khan Area.**

olive series or conularia beds and Talchir boulder beds. Because the units have not yet been given formal names and are thicker and better exposed in their type localities in the salt range. They are. therefore. discussed collectively as the Nilawahan group.

In the study area. the upper part of Nilawahan group. southeast of paniala consists of dark-brown to black claystone and a few thin beds of green and gray siltstone. The claystone is fissile. carbonaceous. micaceous and calcareous. According to Hussain (1960). one calcareous zone about 100 feet below the top contains abundant bryozoans and brachiopods (athyrid. productids and spiriferids). Various colored sandstone in the middle part is medium to coarse grained. massive. cross-bedded. soft. friable micaceous. and partly calcareous. The sandstone contains thin beds of purple micaceous siltstone. The lower part is a conglomerate. which commonly grades laterally into green. and gray siltstone and fine to coarse grained sandstone. The conglomerate contains boulders. cobbles and pebbles of quartzite. granite. granite gneisses and mafic rocks. The boulders are ellipsoidal. striated. and as much as 3 feet in diameter.

None marine lamellibranchs and flora Gangamopteris collected from the lower part of Nilawahan group in the Salt range indicate an Early Permian age (Reed. 1939). The upper part of the Nalawahan group is marine because sediments overlying this unit in the salt range contains conularia and other marine fauna. The upper contact of Nalwahan group with Zaluch group is conformable and sharp.

Zaluch Group: Zaluch group of Permian age is exposed both in the Southern Khisor range and along the southern flank of Saikh Budin . In the area. rocks of the Zaluch group are restricted to the southern flank of Shaikh Budin and to the area south and southeast of Paniala where they form steep. commonly impassable ridges and cliffs. The Zaluch group is richly fossiliferous and contains a particularly abundant brachiopod fauna (Teichert, 1966).

Mianwali formation: The Mianwali formation of Triassic age disconformably overlies the Zaluch group at Shaikh Budin and in the southern part of Khisor range. In the area Mianwali formation is restricted to the southern flank of Shaikh Budin and to the area south and southeast of Paniala (Hussain. 1960).

Tredian formation: In the study area the outcrops of Tredian formation are restricted to the southern flank of shaikh Budin and to the area south and southeast of Paniala village.

Kingriali dolomite: The Kingriali dolomite consist of hard brown and gray dolomite that weathers tan and is fine grained, crystalline, and thin bedded. thick bedded or massive. Thin beds of soft-green calcareous dolomite shale alternate with argillaceous dolomite in the upper part of the formation. The dolomite in the lower part contains Pelecypods, gastopods and cridnoids stems (Danilchik & Shah. 1973). The Kingriali dolomite forms ridges and cliffs. The Kingriali dolomite is about 465 feet thick in Paniala area (Ahmed, 1960). The upper contact with Datta formation is disconformable in Saikh Budin.

Datta formation: The rocks of Jurassic system are exposed in southern flank of Shaikh Budin and in the Khisor ranges. The Datta formation consists mostly of varicolored sandstone, with very subordinate amounts of varicolored siltstone and claystone.

The sandstone is fine to coarse grained, thick or thin bedded, soft, friable and micaceous in places Calcareous shale is present near the top of the formation, carbonaceous shale in the middle part, and gypsoferous shale near the base. Pure white sand is distinctive feature of the basal part of the sandstone near paniala.

The Datta formation is 1,470 feet thick south east of shaikh Budin, 624 feet south of Paniala, and 263 feet south-southwest of Budh Banda, where the formation is disconformably overlain by Nagri formation. (Ahmad, 1960). The Datta formation is considered to be as old as early Jurassic on the basis of ammonite fauna identified by Spath (1937) from what is presumably a bed in Datta formation, about one mile south-southeast of Paniala. The lower and middle part of Datta formation represent alternating shallow-marine and fresh water conditions.

Samanasuk limestone: In Shaikh Budin area, the Samana Suk limestone is brown and gray crystalline and fine-grained thin and thick-bedded limestone which is argillaceous at places. Oolites near the top are commonly coated with pyrite . Subordinate amounts of calcareous claystone alternate with the limestone beds. Purple and gray sandstone in the upper part is fine and medium-grained and thick and thin-bedded. Limestone near the base is gray and brown and thin bedded. The lower contact with Datta formation is transitional (Danilchick & Shah, 1973).

The Samana Suk Limestone is fossiliferous and contains abundant ammonites, particularly in the upper part, as well as foraminifera, corals, lamellibranchs and gastropods. The Samana suk limestone forms ridges and steep impassable cliffs. It is 1,030 feet thick east of Shaikh Budin, but it is absent in the Khisor range south of Budh Banda (Ahmed, 1960). The Samana Suk limestone appears to be as young as late Jurassic on the basis of a cephalopod fauna described by Spath (1939).

Lumshiwal sandstone: The formation in the Shaikh Budin area is not well established. East of shaikh Budin, sandstone in the upper part is brown and gray, soft and friable. Subordinate blue-gray shale is thin bedded and silty.

Dark gray siltstone in the lower part is glauconitic and calcareous (Coulson and Shani. 1939) reported yellow-green glauconitic sandstone containing ammonites. belemnites and brachiopods in the upper part and poorly preserved belemnites in the lower part on the western flank southeast of Pezu.

The combine thickness of the Lumshiwal sandstone and the Chichali formation is 288 feet east of Saikh Budin. The outcrop is restricted to Shaikh Budin area.

The Chichali formation is of early Cretaceous age as determined from the extensive collection of ammonites and belemnites from the Surghar range (Spath. 1939). While the age of the Lumsiwal sandstone is uncertain.

SIWALIK GROUP

In the Khisor, Bhittanni. and Marwat rages. the Siwalik group is divided into the Chinji. Nagri. Dhok Pathan and Malgan formations (see table 1.1).

Chanji formation: In Bhittanni range, the Chinji formation consists of brown red clay 1000-4000 feet thick. It is hard and silty at places and contains abundant burrows. Sandstone ranges from few inches to 35 feet thick and is hard, gray in color. The "Chanji formation" has been extended from the Potwar Plateau into the Khisor and Bhittanni ranges. The lower contact is not exposed but the formation rests disconformably on the rocks of Cretaceous age along the northwest flank of Shaikh Budin.

Morris (1938) reported a complete section of about 1.100 feet at the northwest corner of Shaikh Budin. The Chanji formation does not crop out in the Marwat range and is absent south-southeast of Paniala in the Khisor range.

Nagri formation: The Nagri formation has been extended from the Potwar Pleatu into the Marwat and Bhittanni ranges. In the Bain pass, the Nagri formation consists of gray sandstone crops out in zones of 20-60 feet thick. Beds are massive and thick. Commonly contains scatter pebbles. Most of the sand grains are medium, sub-angular and sub-rounded. Subordinate amounts of brown silty claystone alternate with fine-grained, thin-bedded sandstone and brown siltstone. Claystone and siltstone zone generally ranges from 30-80 feet in thickness and are as much as 425 feet thick near the top of the formation.

The Nagri formation is generally fossiliferous and contains mammalian bones and teeth. A nearly complete mammalian jawbone with teeth was reported. east of Budh Banda in the Khisor range.

Abundant fresh-water lamellibranchs have also been reported. 300 feet below the horizon marking extension of the Bain boulder bed (Morris. 1938).

The Nagri formation is 5,353 feet thick at the northeastern limb of the Marwat Kundi anticline near Bain Pass. A thickness of 5,000 feet is also reported east of Paniala (Morris. 1938).

The contact with Chinji formation is conformable and fairly sharp along the axis of the Marwat Kundi anticline, the Nagri formation, however, disconformably overlies rocks of Jurassic age southeast of Paniala.

Dhokpathan formation: Pilgrim (1913) gives the name "Dhok Pathan" to the faunal zone in the middle part of Siwalik. Lewis (1937) designated the type locality. The term Dhok Pathan formation has been extended from the Potwar Pleatu in to the Marwat and Bhittanni ranges.

Near Bain pass, the Dhok Pathan formation consists of brown claystone and subordinate amount of brown sandstone. The sandstone crops out in both thin and thick beds and cross bedding is common. Conglomerate stringers are reported near the top of the formation along the northeast limb of the Marwat Kundi anticline. Abundant pebbles and cobbles were also noted in scree that probably was derived from the middle part. Cross bedding in the lower part suggests an east or northeast direction of sediment transport (Moris, 1938). The formation forms low ridges and slopes along the flanks of the Bhittanni, Marwat and Khisor ranges.

The Dhok Pathan formation is 1,326 feet thick in the northeast limb of the Marwat Kundi anticline near Bain Pass (Moris, 1938). The formation has conformable and sharp contact with the underlying Nagri formation.

Malagan formation: Morris (1938) gave the name "Malagan formation" after the village Malagan on the southeast flank of Bhittanni range. Near Bain pass, the formation consists of brown medium to coarse-grained sandstone in thick, irregular and massive beds. Scattered pebbles, and conglomerate stringers, and burrows are common. Southeast of Bain pass on the northern flank of the Marwat Kundi anticline the formation becomes thinner, less conglomerate and more difficult to distinguish from the underlying Dhok Pathan formation. The formation is about 402 feet thick near Bain pass. Morris (1938) measured about 2,200 feet thickness on the southern limb. The contact with the overlying surficial deposits of the Indus plain is indistinct and unconformable.

WAZIRISTAN-SULAIMAN RANGES

Sedimentary rocks in the Sulaiman range and eastern Waziristan are Jurassic to Quaternary in age and total thickness is 38,000 feet. Lithology and stratigraphic nomenclature in this part of the area are similar to those of stratigraphic systems established in the lower Indus basin in Quetta division. Particularly for rocks of Jurassic and Cretaceous age.

Sulaiman limestone group: The name "Sulaiman limestone" is given by Pinford (1939) to the rocks of Jurassic age. The type section, in the gorge between Mughal Kot and Dhanasar. At the type section the Sulaiman limestone group is mostly dark-gray to blue limestone that is thin to thick bedded or massive, hard and in part oolitic. It contains some secondary calcite and chert nodules. Weathered surface is commonly light gray to brownish gray. Blue-black calcareous claystone intercalations are common in the lower part of the section. About 100 feet of ferruginous micaceous ripple-marked sandstone and calcareous sandstone crops out about 1200 feet above the base of the exposed section. A strong odour of notable petroleum is noticeable in the limestone bed near the base. Belemnites are found near the top. The formation also contains algae, orbitoids, corals, bryozoans, brachiopods, lamellibranchs, gastropods, crinoids and burrows. The Sulaiman limestone forms the highest peaks in the Sulaiman ranges. Its exposed thickness in the gorge west of Mughal Kot is 4,656 feet, but the total thickness is not known.

The Sulaiman limestone group forms a continuous out crop for more than 70 miles northward along the crest of the Sulaiman anticline. At the Gomal River the limestone plunges under the overlying younger rocks to the nose of the anticline. The Sulaiman limestone group is of Jurassic age, and the environment of deposition is marine.

Sember formation: The Sember formation is present throughout the Sulaiman range region. In the area west of Mughal Kot, the formation consists of soft black claystone, locally some what silty and sandy, with minor thin beds and concretions of dark-gray to black limestone. Ferruginous and calcareous sandstone crops out near the base. A basal conglomerate 4 feet thick is composed of belemnitic limestone pebbles and cobbles derived from the underlain Sulaiman limestone group. The Sember formation forms slopes and valleys. The formation is 931 feet thick in the gorge west of Mughal Kot, but no reliable measurement of its thickness could be made because of extensive folding and faulting (William, 1959).

In the gorge west of Mughal Kot, the Sember formation is believed to be of early Cretaceous age although foraminifera, belemnites, and other fossils are badly preserved (Stuart, 1922). The lower contact with Sulaiman limestone group is disconformable and sharp.

Parh limestone: In Dera Ismail Khan quadrangle, the Parh limestone is light gray, hard, procelaneous, thick and thin bedded. Limestone in the upper part contains abundant foraminifera (Ahmad, 1960). In the gorge west of Mughal Kot, clastic material is absent in the upper most 155 feet, but subsidiary dark-gray calcareous claystone beds, containing abundant foraminifer and belemnite, become increasingly abundant toward the middle part. Argillaceous limestone and calcareous claystone crop out in the lower part. A basal limestone bed contains nodules of marcasite (FeS_2).

The Parh limestone is 1,147 feet thick in the gorge west of Mughal Kot. The contact with the underlying Sember formation is transitional. Williams (1959) studied the Parh limestone in several localities in the lower Indus basin and reported that the formation is invariably of Late Cretaceous age.

Mughal Kot formation: Williams (1959) designated the type section of the Mughal Kot formation after the Mughal Kot post. In the type section, the top of the Mughal Kot formation consists of light-gray calcareous sandstone, about 160 feet thick. The sandstone is very calcareous, argillaceous, hard, and thick bedded to massive. It alternates with thin-bedded sandy calcareous gray claystone commonly sulfurous in beds as much as 5 feet thick oil seeps are found along the joints and bedding planes.

Calcareous claystone, sandy limestone and calcareous sandstone underlie the calcareous claystone sandstone at the top. The claystone is dark gray and silty in places. The limestone is gray and argillaceous. The sandstone is thin bedded, hard, commonly ferruginous. A conglomerate at the base contains sub-angular pebbles derived from the underlying Parh limestone.

West of Mughal Kot the formation is 3,722 feet thick. The Mughal Kot formation is believed to be late Cretaceous in age. The lower contact with Parh limestone is disconformable.

Pab sandstone: The Pab sandstone may be recognized throughout both the eastern and western flanks of the Sulaiman range. In the Mughal Kot area, the Pab sandstone is a quartzite gray and blue sandstone that is fine to coarse grained, sub-angular to rounded thin and thick bedded to massive, commonly crossbedded, an conglomerate near the base. It weathers light to dark brownish gray. Some beds contain burrows and plant roots. Crossbeding suggests a westerly direction of sediment transport. Subordinate silty claystone beds are blue and dark gray and commonly less than one foot thick but as much as 15 feet locally. These claystones are carbonaceous and sulfurous in places. According to Keizer (1959), it contains abundant plant fragments. In Mughal Kot gorge, oil seeps are found along bedding planes and fractures about 125 feet below the top of the unit. West of Mughal Kot, the Pab sandstone is 776 feet thick. The Pab sandstone is of Late Cretaceous (Keizer, 1959).

Dughan formation: The Dunghan formation may be recognized along the western flank of the Sulaiman range south of Waziristan. Near Mughal Kot, the Dunghan formation is a gray to dark-gray hard finely crystalline and very thick-bedded limestone. According to Keizer (1959), it contains algae foraminifer, corals and gastropods. The upper part becomes sandy downward. Very sandy bluish-gray limestone in the middle part becomes argillaceous downward. Two beds in the middle part are, each about 15 feet thick and are composed of brown fine to medium-grained calcareous sandstone. The lower part of the formation is composed of dark-blue micaceous silty claystone that according to Keizer (1959) contains gastropods.

The Dunghan formation is 625 feet thick west of Mughal Kot. Foraminifera collected from the part of the formation in the gorge west of Mughal Kot indicate a Paleocene age (Keizer, 1959), however, the lower part may be as old as late Cretaceous. The Dunghan formation forms a sharp ridge along the east flank of the Sulaiman range. The contact with the overlying Ghazij shale is distinct and conformable at Mughal Kot.

Ghazij shale: In the Mughal Kot area, the upper half of the Ghzij shale consists mostly of soft fissile claystone that is brown and brownish red and commonly weathers to red or maroon. Coarse-grained sandstone and conglomerate crops out near the top.

Near Mughal Kot the lower half of the Ghazij shale consist of green, dark-gray and brown claystone, weathering gray or drab. The claystone is carbonaceous at places. Locally, subordinate amount of gray siltstone contains, abundant larger foraminifera. Also present are ripple-marked cross-bedded sandstone and quartzitic sandstone that are calcareous at places. Plant fragments are present about 1,500 feet above the base. The lower 1,400 feet is entirely dark-gray to black fissile claystone.

The Ghazij shale forms valleys and low ridges, it is estimated to be 9,000 feet thick in the Mughal Kot area. Fritz (1963) suspected an early Eocene age for the Ghazij shale on the basis of foraminifer collected from the formation.

Baska shale: The type locality is one and a half miles east-northeast of Baska village. In the Sulaiman foothills, the Baska shale consists mostly of green and greenish-gray claystone, containing alabaster in nodules and veins. The claystone alternates with bedded alabaster, gysiferous limestone, and marl containing larger forminifera and lamellibrachs. Alabaster beds ranges in thickness from a few inches to more than 30 feet. Claystone is bright red and purple towards the base. The Baska shale forms slopes. The Baska shale is 620 feet near the Baska village.

The lower contact is fairly sharp in the northern part of D.I.Khan quadrangle where sandstone of underlying Ghazij forms low cliffs. Lower contact with Ghazij shale is transitional. Both Eames (1952) and Keizer (1959) believed that the Baska shale is of early Eocene age.

Kirthar formation: In the eastern foothills of the Sulaiman range, the Kirthar formation is divided into four members. From bottom to top, there are Habib Rahi limestone member, Domanda shale member, Pirkoh limestone member, and Drazinda shale member.

a) *Habib Rahi limestone member:* The upper part of the Habib Rahi limestone member is a grayish-brown hard limestone that weathers white. It is fine grained, thin bedded, contains large frominifera and in the Mughal Kot area, nodules and the discontinuous beds of chert are present. These hard beds alternate with subordinate beds of soft brown shaly limestone and calcareous siltstone. A weak odour of petroleum is notified in the limestone in places near the top (Keizer, 1959). The thickness of the unit is 100 feet northeast of Mughal Kot. The contact with the Ghazij shale in the North Waziristan is transitional.

b) *Domanda shale member:* The Domenda shale member consists mostly of dark-brown and greenish-gray claystone and contains foraminfera. Northeast of Nili Kach, near the top, Sandstone beds is as much as 18 feet thick and contains gastropods as much as 10 inches long. Near Nili kach the lower 30 feet contains hard grayish-brown limestone and gray siltstone. The limestone weathers light brown while siltstone is thin bedded in both hard and soft shale layers. Thickness is 739 feet northeast of Nili Kach and the contact with Habib Rahi limestone member is transitional (Keizer, 1959).

c) *Pirkoh limestone member:* The Pirkoh limestone member is light-gray and brown, fine grained, mostly thin and regularly bedded, argillaceous, and contains abundant large forminifera, it weathers white. This member commonly contains subordinate beds of soft shaly limestone and dark-gray calcareous claystone. Thickness of the member is 40 feet north east of Nili Kach. The lower contact with Domanda shale member is transitional (Keizer, 1959).

d) *Drazinda shale member:* The Drazinda shale member consists of dark-brown to gray claystone and subordinate fossiliferous marl beds that decrease in abundance near the base. The upper part is gypsiferous and particularly fossiliferous, containing abundance large foraminifera and lamellibrancls, as well as bryozoans and echinoids. A sandstone marked bed in the middle pat is greenish-gray fine grained, calcareous thick bedded to massive and weakly crossbedded. It is about 30 feet thick in the Gomal pass area, where it forms a sharp ridge. Thickness is 1,837 feet northeast of Nili Kach and less than 40 feet thick north of Jandola. The lower contact with Pirkoh member is conformable and sharp.

Environment of deposition and age: On the basis of marine fish fauna, collected from Habib Rahi limestone member and Domanda shale member, middle Eocene age is given by Rahman and Dunkle (1966).

Chitarwata formation: The Chitarwata formation crops out throughout the Sulaiman foothills of the Dera Ismail Khan quardrangle but it is most readily identified in the southern part of the area. The Chitarwata formation consists of red gray and green claystone and subordinate amount of siltstone and sandstone. The siltstone is variegated, friable, and feruginous, the sandstone is white brownish yellow, sub-angular to sub-rounded, fine grained, friable, calcareous in places, and commonly ferruginous. The Chitarwata formation is 1,260 feet thick south west of Domanda post. The thickness is estimated to be about 500 feet at Chitarwata post.

The formation is of late Oligocene to late Miocene age on the basis of occurrence of flora croftiella escheri rantzien and also of vertebrate fauna (Pilgrim, 1908) from these rocks in the range of hills south of Dera Bugti. The lower contact with Drazinda shale member of Kirthar formation is disconformable.

SIWALIK GROUP OF SULAIMAN RANGES

In the Sulaiman ranges, the Siwalik group is divided into the Vihowa, Litra and Chadhwan formations (see table 1.1).

1) *Vihowa formation:* The formation crops out throughout the Sulaiman foothills region of D.I. Khan quadrangle.

In Chaudhwan Zam, the Vihowa formation consists of gray and brown sandstone and subordinate amounts of red and brownish-red sandy siltstone. The sandstone is generally sub-angular, medium to coarse-grained and is massive, thick bedded and cross-bedded.

In Chaudhwan Zam, the Sandstone contains abundant scattered pebbles in the upper part, clay material and feromegnesian mineral grains in the middle part and abundant secondary calcite in the middle and lower parts. Very coarse-grained sandstone and pebbly conglomerate near the base contains abundant derived fossil fragments, mostly of foraminifera. Mammalian bones fragments were found near Baddha village. Parwara and Landai villages near the base of Siwaliks. The Vihowa formation is 1,410 feet thick at Chaudhwan Zam and is estimated to be about 2,300 feet thick in Vihowa Rud and Litra nala.

There is an unconformity between rocks of Siwalik group and the Chitarwata formation. the contact of Vihowa formation with Chitarwata formation is thought to be a disconformable contact.

2) ***Litra formation:*** The Litra formation crops out through out the Sulaiman foothill region. The Litra formation consists of friable light-gray and brown sandstone that is fine to medium grained. thick bedded. massive, silty and clayey in places. The grains are angular to sub-rounded. Some beds are coarsely micaeous and garnetiferous. Other beds contains abundant well-preserved burrows. some as long as 25 inches. Abundant mammalian bone fragments were noted in the vicinity of Nilohar Nala. In Chaudhwan Zam, conglomerate consisting of rounded pebbles and cobbles in a coarse-grained sandstone matrix are present in the upper 1,600 feet and become increasing common towards the top. Scattered pebbles and cobbles in the lower part on Chaudhwan zam consist of chert. sandstone. quartzite and limestone commonly containing forminifera.

The Litra formation is 5,560 feet thick in Chaudhwan zam and 5,408 feet thick in Gomal pass. and 5,600 feet is the estimated thickness in Litra Nala. The contact between Litra and the Vihowa formation is transitional (Morris. 1938).

3) ***Chaudhwan formation***: The Chaudhwan formation consists mostly of hard massive conglomerate composed of boulders, cobbles and pebbles of limestone. quartzite and sandstone in a medium and coarse-grained sandstone matrix. Subordinate amounts of brown and gray sandstone siltstone and claystone crops out in the middle part of the unit in Chudhwan Zam.

The formation contains a greater proportion of sandstone. siltstone and claystone in the southern part of Dera Ismail Khan quadrangle than in the Chaudhwan zam and Gomal river areas. where massive conglomerate in the predominant rock types. Throughout most of its out crops area, the Chaudhwan formation forms steep cliffs.

Boulders and cobbles conglomerate are generally thick and coarse in those regions adjacent to the high lands of Waziristan and the northern Sulaiman range where major faulting occurred during the Pleistocene. These deposits become fine grained away from the highlands.

The Chaudhwan formation is 49,000 feet thick in Chaudhwan Zam and 5,940 feet thick in Gomal pass. The thickness is estimated to be 5,000 feet in Litra Nala. The contact with the overlying surficial deposits of the Indus plains is commonly indistinct.

Environment of deposition and age: Late Pliocene is the age given to Litra formation on the basis of a horse tooth (Hipparion cf. H. antelopinum) collected from the formation near Raki Munh village. The age of underlying Viowa formation and overlying Chaudhwan formation are assumed to be Pliocene. According to Pilgrim (1908) his collection of vertebrate fauna from " Lower Siwalik near Dera Bugti is indicate of early to late Miocene age.

The correlation of the stratigraphy of Dera Ismail Khan region by the columnar sections is given in Fig.1.3.

INDUS PLAIN SURFICAL DEPOSITS (QUATERNARY SYSTEM)

Surfical deposits of Quaternary age include alluvium and sand dunes of the Indus plains, alluvial fans along the hill fronts, and unconsolidated detritus along the slopes and in the valleys of mountain ranges and foothills. These deposits are of Holocene age. Older terrace deposits cover extensive area underlain by rocks of early Tertiary age in the foothills of Sulaiman ranges. These terrace deposits are strongly cemented and in places attain a thickness of more than 250 feet. They may be as young as later Pleistocene.

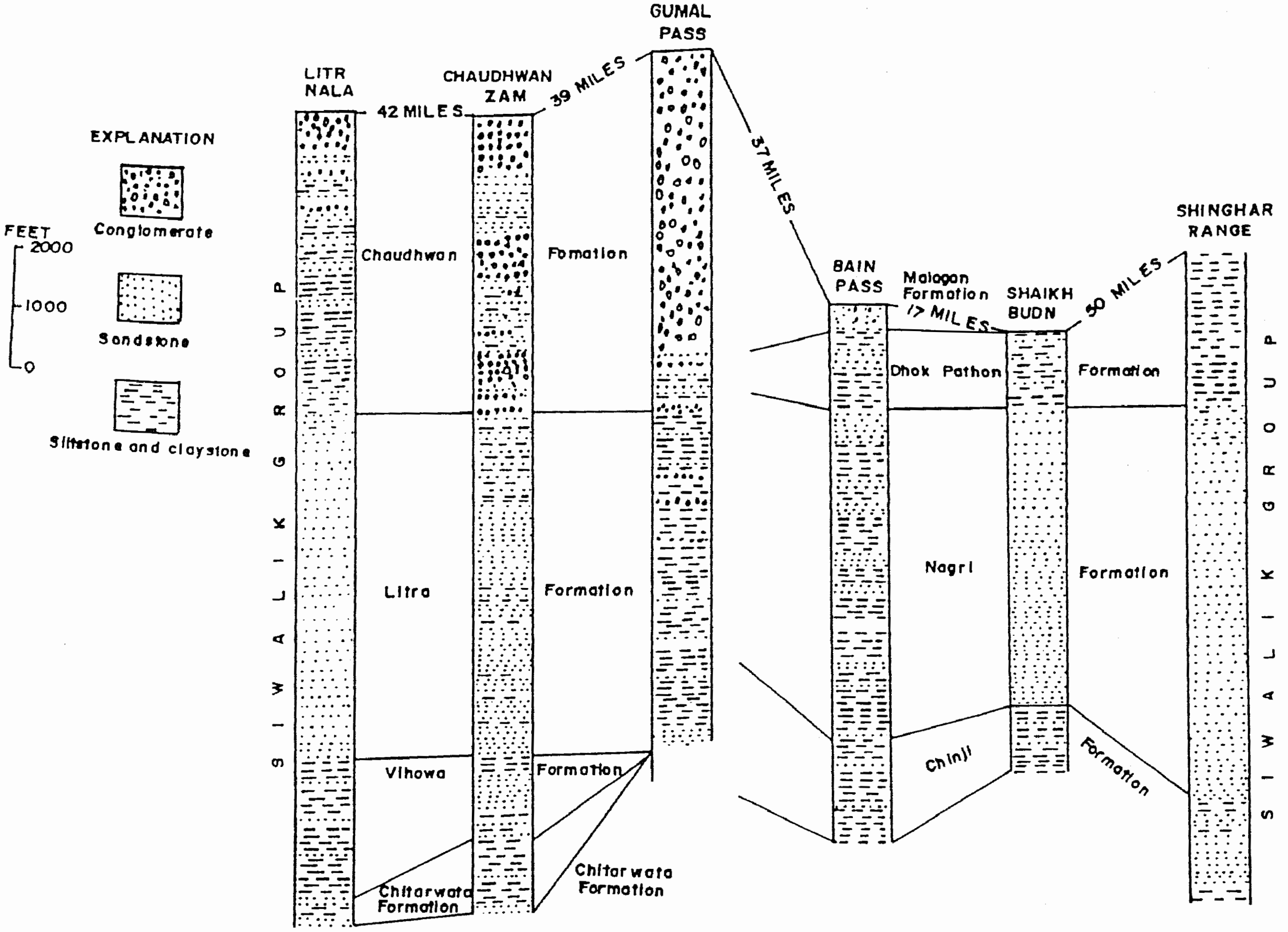


Fig. 1.3. Correlation of the different stratigraphic Columns in the D.I.Khan division.
(modified after Danilchik and Shah 1973.)

Chapter: II
Instrumentation, Adoption Techniques & Experiments

2.1. Water:

COLLECTION OF SAMPLES: The water samples were taken from every possible different source like, tube well, lakes, dug well, springs, streams and Indus (Plate # 2.1) and Gomal rivers (Plate # 2.2 & 2.3) within the study area.

Water samples representing different area were collected in polyethylene bottle. To avoid the slightest possible contamination the bottles were thoroughly washed with 5% HCl and 5% HNO_3, at the end rinsed with distilled water. The clean bottles were dried and properly capped.

From each collection point two bottle were filled to brink such that no bubble entrapped. One of the two samples from each point was acidified with nitric acid to a pH below 2.0 in order to minimize precipitation of various constituents. The other un-acidified sample was immediately used for the determination of temperature, pH, electrical conductivity, and other anions at the site. All the acidified samples collected in the field were stored at low temperature (4 °C) in refrigerator for laboratory analyses.

ANALYSIS DURING FIELD: Hach Digital Titrator was used for the accurate determination of alkalinity. DR/200 spectrophotometer was used for the determination of sulfate, nitrate, ammonia, phosphate, silica etc, soon after collection of water samples at the site. The methods for determination of various parameters are discussed below.

Temperature and pH: Instrument used for the analysis was provided with "Hach one combination pH electrodes" system. The portable Hach One combination pH electrodes (Model 44200), with a built-in temperature sensor. This sensor was compatible with the pH meter and gave very accurate temperature. To obtain reading for pH determination, the pH meter was first standardized with buffer solutions of pH 4.00, 7.00 and 8.00.

Plate # 2.1	A view of collection of water sampling at Chashma Barrage.

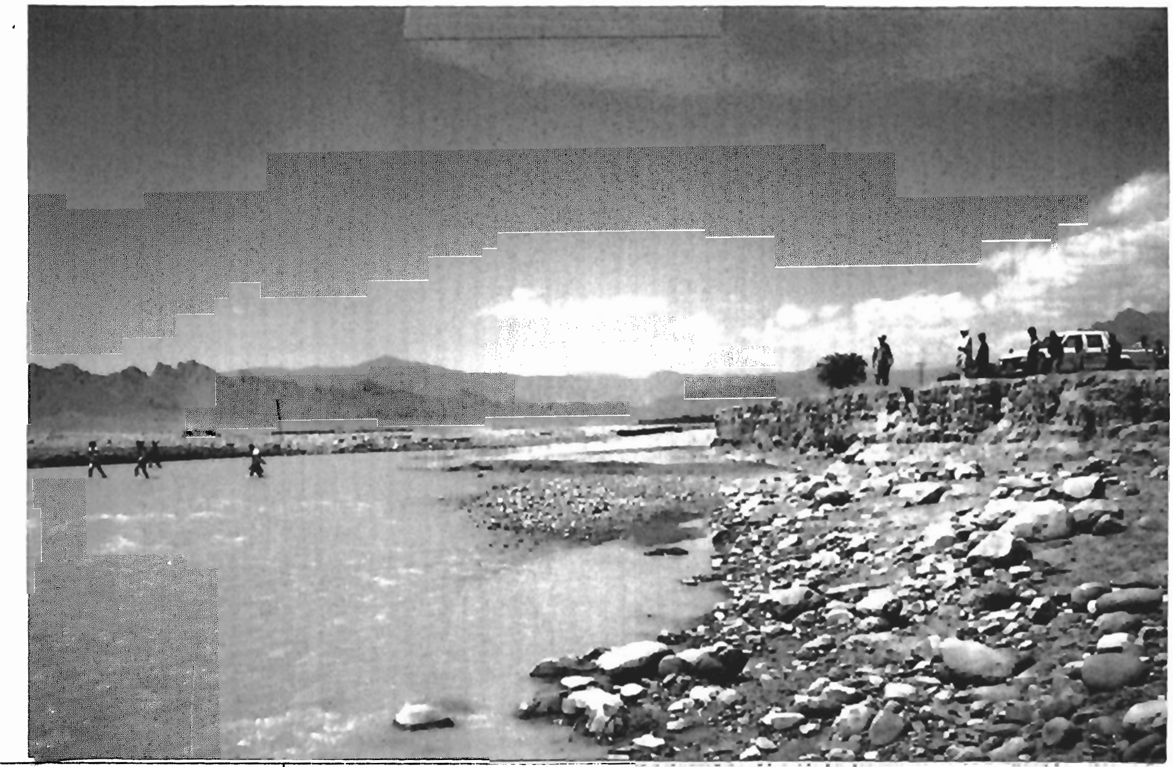


Plate # 2.2	**View of Gomal river near Kullachi from where the water sample was collected.**

Plate # 2.3	**Another view of Gomal river.**

The electrode bulbs of pH meter were immersed into the samples and the readings were directly noted from the meter. In order to avoid contamination, each reading was followed by carefully cleaning the bulb of the electrode. Standardization of pH meter was checked every time before the measurement for a new sample.

Electric Conductivity: A portable conductivity meter (cole-parmers 1481.55) was used for on sight conductivity determination. The instrument was first calibrated with a standard KCl solution, which has a conductivity value of 1.417 ms/cm at 25 C°, and then was used for measurement of conductivity of each water sample.

Alkalinity: Special type of Hack Digital Titrator was used for the determination of alkalinity. Hach digital titrator is a precision-dispensing device 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 titratior controls a plunger, which forces the titrating solution from a titration cartridge in a carefully regulated flow. The titrator body is constructed of precision-molded, heavy-duty chemical and impact- resistant acetyl plastic. Accuracy is rated at +1% or better. Titration solutions are packaged in disposable polyethylene with cap to cover the cartridge tips. Each cartridge contains approximately 13 ml of titranting solution. Most solutions are controlled to +0.5 N 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 knob.

First of all sample volume and sulfuric acid titration cartridge, corresponding to the expected alkalinity concentration, was selected from the table given in the instruction manual. A clean delivery tube was then inserted into the titration cartridge and the cartridge was attached to the titrator body. The delivery knob was turned to eject a few drops of titrant; the counter was then reset to zero. Selected sample volume was measured with the help of graduated cylinder and was poured into 250-ml titration flask. The Phenolphthalein Indicator Powder Pillow, provided with the instrument, was added to the sample and was swirled to mix. If the sample solution attained pink color, it was then titrated with sulfuric acid to get colorless end point and the reading was noted as P-alkalinity. In case of not obtaining pink color with the addition of Phenolphthalein, the Bromocresol Green- Methyl Red Indicator Powder Pillow was added to the solution. The titration was continued with sulfuric acid to a light greenish blue-gray end point. The number of digits were recorded and T-alkalinity was calculated as:

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

Chloride: Chloride was determined by Mercuric Nitrate method using digital titrator. A sample volume and Mercuric Nitrate cartridge was selected for chloride concentration, from the table given in the instruction manual. A clean delivery tube was inserted into the titration cartridge and the cartridge was attached to the titrator body. A known volume of sample was transferred to 250-ml flask, and was diluted to 100ml with de-ionized water. Contents of one Diphenylcarbazone powder pillow, provided with instrument, was added to the flask. The tip of delivery tube was dipped into the solution and the flask was swirled while titrating with mercuric nitrate. The titration was continued until pale yellow color was changed to light pink color (the end point). The reading was recorded and the results were calculated as follows.

Digits Required * Digit Multiplier = mg/l Chloride.

Hach DR/2000 Spectrophotometer: Hach DR/2000 spectrophotometer was used for on site determination of sulfate, nitrate, phosphate and silica. This spectrophotometer is a microprocessor-controlled single beam instrument (Fig. 2.1). It is handy to use in laboratory as well as in field. It can be pre-calibrated for 120 different spectrophotometric measurements. Test results can be displayed in percent transmittance, absorbance or concentration of the appropriate units of measurements. The LCD dot-matrix digital display offers automatic ranging in the pre-programmed parameters. This instrument is provided with procedures manual in which step by step illustrated instructions for measuring 100 different parameters or constituents are presented. In this manual the United States Environmental Protection Agency approves all procedures given.

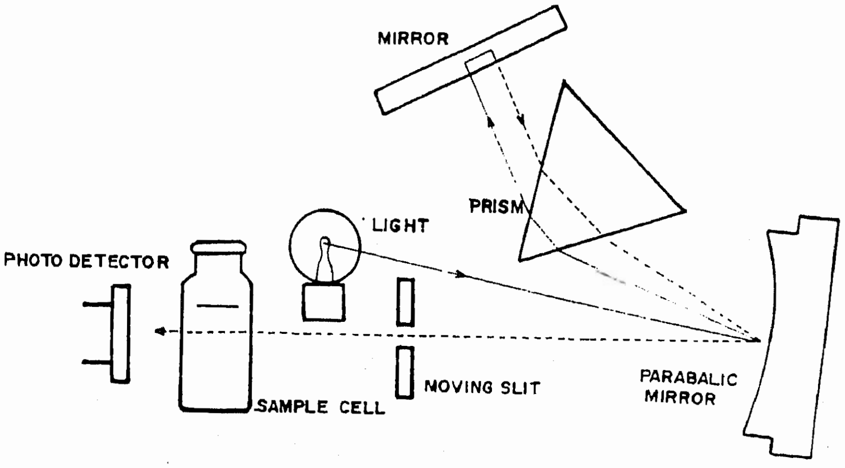


Fig. 2.1. Scheme Diagram for Hach DR/2000 spectrophotometer

Working Conditions: To perform analyses on DR/2000 spectrophotometer, one has to enter the stored program number for parameter to be determined, then the wavelength dial is to be rotated to the specific wavelength used for that parameter or constituent. Out of the two sample cells, provided with this photometer, one is filled with 25ml of sample and another with 25ml of deionized water as blank. Various constituents are determined by the intensity of color produced by the addition of specific coloring reagents. These coloring reagents are packed in small plastic pillows and are added to the sample cell according to the given procedure. After the addition of coloring reagent, a reaction starts the reaction time varies from one constituent to another. The reaction period is noted by pressing the timer button on spectrophotometer. As soon as the reaction is completed, the timer beeps and this is the time to place the blank sample in cell holder and zero is pressed. With this the zeroing process of the machine is completed and the machine is ready for measuring the concentration of unknown water samples (containing coloring reagents) already placed in the cell holder.

Various parameters (i.e. sulfate, nitrate, phosphate, silica and fluoride) in the water samples are determined by Hach DR/2000 Spectrophotometer as follows:

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

Nitrate: "Cadmium Reduction Method" of Connors and Beland (1976) was used for the determination of nitrate concentration. The nitrate ion reacts in an acidic medium with sulfanilamide to form an intermediate diazomium salt which couples to gentisic acid to form an amber-colored Product that was measured by spectrometer. A correction may be made for any nitrate present in the sample. A plastic pillow provided with the instrument for nitrate, which has appropriate content of cadmium metal and gentisic acid, was added to the 25 ml of sample and after five minutes reaction period the sample was analyzed for nitrate.

Phosphate: "Ascorbic Acid Method" of USEPA (1979) was used for the determination of phosphate. Actually orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense blue color, suitable for photometric measurements. A reagent powder pillow containing ammonium molybdate and ascorbic acid was added and phosphate was analyzed after 2 minutes reaction period.

Silica: "Hetropoly Blue Method" of Strickland (1952) was used for silica determination. In this method silica and phosphate in the sample reacts with molybdate ion under acidic conditions to form silicomolybdic acid and phosphomolybdic acid complexes. Addition of citric acid destroys the phosphate complex. An amino acid is then added to reduce the yellow silicomolybdte to an intense blue color, the optical density of which is then proportional to silica concentration. Ammonium molybdate solution (0.5 ml) was added to 25ml of water sample. After 4 minutes at 25 C° citric acid was added from a powder pillow provided with the instrument. One minute after reaction time, amino acid Reagent powder pillow was added and the sample was then analyzed for silica after one minute.

Alumina: Alumina was determined by erichrome cyanine R method as devised by Shull and Guthan (1967). According to this method, 5 mL of water sample was taken in 50 mL of volumetric flask, then 1 ml of ascorbic acid. 10 mL of buffer reagent (136gms. of sodium acetate dissolved in deionized water mixed with 40 mL 1N acetic acid and diluted to 1000 mL) and 5 mL of working dye reagent (300 mg erichrome cyanine R dissolved in 50 mL deionized water) were added in it. The flask was made to the mark and was allowed for 5-8 minutes for complete reaction. After this alumina concentration was determined by Hach DR / 2000 spectrophotometer.

Sample preparation for determination of Fluoride: "SPADNS Method" was used for the determined of Fluoride content of water sample. It is approved by UNEPA and is adopted from standard methods for the examination of water and wastewater (Arnold et al., 1985). This method required a) Preliminary distillation of the water sample and then b) fluoride determination by spectrophotometer.

Distillation of Fluoride: Fluoride can be separated from other non-volatile constituents in water by conversion to hydrofluoric or hydrosilicic acid and subsequent distillation. The conversion is accomplished by using strong high boiling acid. The distillation will separate fluoride from most water samples. Chloride is the only commonly volatile constituent likely to cause interference with calorimetric analysis of the distillate. When chloride is high enough to interfere, silver sulfate is added to the distilling solution, which minimizes volatilization of hydrogen chloride.

Apparatus: Distillation apparatus consisting of a 500 mL long neck borosilicate glass boiling flask, a connecting tube, a thermometer adopter and a thermometer reading upto 200 °C.

- Heating mantle for full voltage operation.
- Soft glass beads.

Reagents:

- Sulfuric acid (H2So4) reagent grade
- Silver sulfate (AgSO4) crystals reagents grade.

Procedure: 200 ml of distilled water was taken in the distilling flask, and 100mL-concentrated sulfuric acid was carefully added to it. A few glass beads were added and the whole assembly of the distillation apparatus was fixed. Heating was started at this stage and was continued until flask contents attained a temperature of 180 °C. When the temperature reached 178 °C, the heating was discontinued because of the heat retention by the mantle. The distillate was discarded. This process removed fluoride contamination and adjusted the acid-water ratio for subsequent distillation. This acid mixture was cooled to 120 °C or below and then 150 mL of water sample was added to it and heating was again started. Heating was stopped at 178 °C in order to prevent sulfate carryover. The distillate was collected for fluoride determination. In samples of high chloride concentration (where chances of interference were high) silver sulfate was added to the distilling flask at the rate of 5mL/L Cl.

Spectrophotometer determination of Fluoride: As mentioned earlier SPADNS method was used for fluoride determination. This method involves reaction of fluoride with a red zirconium dye solution. The fluoride combines with part of the zirconium to form a colorless complex, thus bleaching the red color in an amount proportional to the fluoride concentration. A stored program number (190) was entered in the DR/2000 photometer. The wavelength dial was set to 580ηm. 25mL of sample was taken in one cell and 25-mL of deionized water in another cell. 5.00mL of SPADNS reagent were added to each cell with the help of pipette. After one minute of reaction period the blank sample was placed in the cell holder and zero was pressed. When the instrument displayed "0.00 mg/L F" the water samples, already treated, was placed in the cell holder and reading of fluoride concentration was noted.

LABORATORY ANALYSES

All the laboratory tests were performed in Geochemistry Laboratory of the National Center of Excellence (NCE) Geology, University of Peshawar. For obtaining precise result, sophisticated instrument such as Atomic Absorption Spectrophotometer and UV/visible spectrophotometer were used. The methodology for the determination of copper, zinc, lead, nickel, chromium and cadmium by using Perkin-Elmer 3300 Atomic Absorption equipped with graphite furnace (HG – 600) and As – 60 auto-sampler sodium, potassium, calcium, magnesium, iron and manganese by using SP – 190, Atomic Absorption (flame version) is discussed here in detail.

Atomic Absorption Spectrophotometer: This instrument work on the principle "If the light of just the right wavelength impinges on a free ground state atom, the atom may absorb the light as it enters an excited state in a process known as atomic absorption" (Fig.2.2). Our interest in atomic absorption measurement is the amount of light at the resonant wavelength, which absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increase, the amount of light absorbed a quantitative determination of the amount of analyze element present can be made. The use of specula light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others. Supplying enough thermal energy to the sample to dissociate the chemical compounds into free atoms produces the atomic cloud required for atomic absorption measurements. As pirating a solution of the sample into a flame aligned in the light beam serves this purpose. Under the proper flame conditions, most of the atoms will remain in the ground state form and a source lamp. The precise and accurate determinations that of this technique have made atomic absorption one of the most popular methods for the determination of metals.

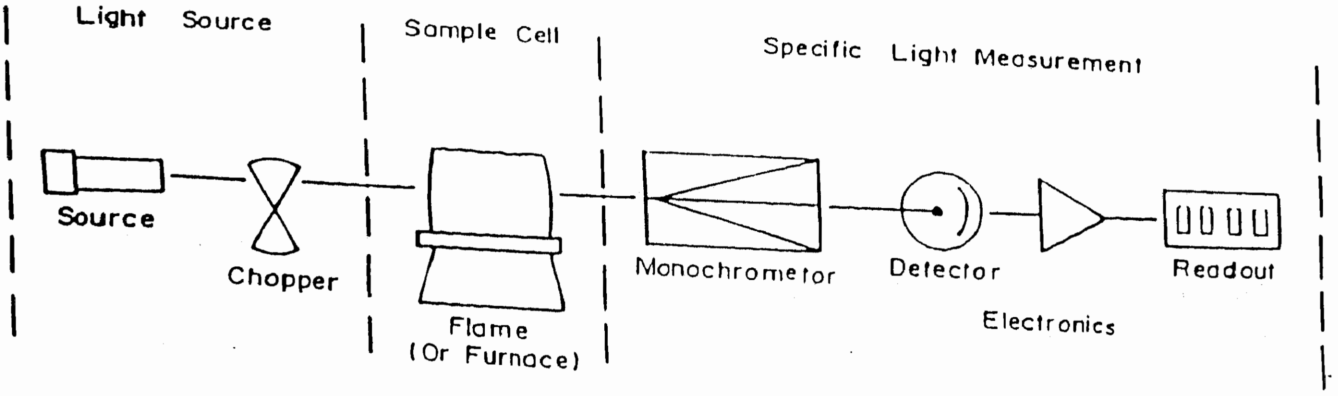


Fig.2.2. Scheme Diagram for Atomic Absorption Spectrophotometer.

Analyses by (Graphite Furnace): Graphite furnace is an advance instrument, capable of rapid and accurate processing of samples, provided with an auto sampler that permits automatic processing of up to 40 samples in a single run. The mechanical arm attached with capillary tube takes the sample from the sample tray and to the graphite furnace. A computerized program of windows Benchtop software loaded to regulate and obtain the results of the samples. In which all system components are displayed on the Benchtop screen. Required lamp was installed and aligned for the geochemistry of samples. The atomic absorption lab Benchtop software includes three linear calibration methods, zero intercept, calculated intercept, and bracketing standards. The first two are applied when the sample concentrations are within the linear range of the instrument. The bracketing standard technique is applicable over a restricted concentration range at higher concentration.

Instrumental condition was maintained for the following determination various trace elements in water samples.

Copper

Preparation of Working Standards: One gram of copper metal was dissolved in 5-mL of concentrated HNO_3 solution. The mixture was warmed until the complete dissolution of copper metal. Then it was diluted to 1000 mg/L. From this solution 10 mg/L standard solution was prepared and then from this standard solutions of 25, 50, 75 and 100 μg/L were prepared with double deionized water. These standards were used for the calibration of copper.

Detection Conditions: Hallow cathode lamp for copper was installed in Atomic Absorption Spectrophotometer. Wavelength was adjusted to 324.8ηm with slit of 0.7 and pyrolysis temperature of 1000 C°. The copper atomization temperature of 2300 C° was used during the determination of copper.

Lead

Preparation of Working Standards: 1.599 grams of lead nitrate was dissolved in 200 mL of deionized water, containing 1.5 mL of concentrated nitric acid was diluted to 1000 mL in volumetric flask. From this 10 mg/L standard solution was prepared. The standard solutions of 25, 50, 75 and 100 μg/L were prepared. These standards were used for the calibration of lead.

Detection Conditions: The hallow cathode lamp for lead was used. The instrument was set at a wavelength of 283.3 ηm. and silt opening at 0.7. Matrix Modifier of 0.2 mg PO_4 was used. Pyrolysis temperature of 700C° and atomization temperature of 1800 C was used during lead determination.

Chromium

Preparation of Working Standards: To prepare standard solution of Chromium, 2.828 grams of anhydrous potassium dichromate, ($K_2Cr_2O_7$) was dissolved in 200 mL of double deionized water, added 1.5 mL of conc. HNO_3 and diluted the solution with deionized water in a volumetric flask up to 1000 mL. This standard stock solution contained 1000 mg/L of chromium. The ready-made solution was transferred into the bottle for further treatment. From this solution, 10-mg/L standard solution was prepared and then from this standard the working solution of 25, 50, 75 and 100 µg/l were prepared for the calibration of instrument for chromium.

Nickel

Preparation of Working Standards: Nickel standard solution of 1000 µg/L was prepared by dissolving 1.273 mg Nickel oxide in minimum value of 10% v/v HCl and then diluted to 1000 mL of deionized water. From this 1000 mg/L standard solution 10 µg/L standard was prepared and then the working standards of 50, 100 and 200 µg/L were prepared for the calibration of instrument for nickel.

Detection Conditions: After the calibration of instrument with these standard solutions, the remaining cells of samples tray were filled with samples of water to determine the concentration of Nickel in µg/L. The wavelength and silt were set on 232.0 ηm and 0.2 respectively for the determination of nickel. Pyrolysis temperature of 1400°C and atomization temperature of 2500°C was used.

Zinc

Preparation of Working Standards: One gram zinc metal was dissolved in 20 mL (1.1) HCl and diluted to 1000 mL with double deionized water. From this 10 mg/L standard was prepared. This standard was used for the double preparation of working srtandards of 25, 75 and 100 µg/L.

Detection Conditions: These standard solutions were used in the calibration process provided by the Graphite Furnace. To analyze the water samples by Atomic Absorption Spectrometer 3000 the following parameters were adjusted. Hallow cathode lamp for zinc was installed. Wave length of 213.9 ηm and slit of 0.7 Matrix Modifier of 0.006 mg of $Mg(NO_3)_2$ was used. Pyrolysis temperature of 700 C° and atomization temperature of 1800 C° was used for the determination of Zinc.

Cadmium

Preparation of Working Standards: (1+1) HCl Cadmium was prepared by dissolving 1.000 gram of cadmium metal in a minimum volume. It was transferred to volumetric flask of 1000 mL and diluted to 1000 mL with double deionized water. From this solution, the working standard solution of 25, 50, 75 and 100 µg/L were prepared for calibrating the instrument for Cadmium.

Detection Conditions: Hallow cathode lamp of cadmium was used. The wavelength of 228.8 ηm and Slit of 0.7 was adjusted. Matrix Modifier of 0.2 mg of PO_4 was used. Pyrolysis temperature of 700 C and atomization temperature of 1600 °C was used for the determination of cadmium.

ANALYSES BY FLAME ATOMIC ABSORPTION

Details of the determination of various elements (i.e., Ca, Mg, Na, K, Fe & Mn) by using atomic absorption spectrophotometer (Pye Unican SP 191; flame version) is given below.

Calcium and Magnesium

Preparation of standards: 2.497 grams of calcium carbonate and 4.952 grams of magnesium sulphate were dissolved in 50 mL of deionized water, containing 10 mL of HCl. The solution obtained was further diluted to 500 mL. The solution thus obtained contains 1000 mg/L of calcium and magnesium. From this solution this working standard solutions of 0,1,2,4 and 8 mg/L were prepared.

Detection Conditions: After preliminary adjustment of the instrument, the working standard solutions were run for the calibration of the instrument. Then the concentration of Ca and Mg was determined.

Sodium and Potassium

Perpetration of standards: 1.91grams of potassium chloride and 2.542 grams of sodium chloride were dissolved in 1000 mL of deionized water. From the 1000 mg/L of K and Na solutions, working standard solutions of 1,2,4 and 8 mg/L for both Na and K were prepared.

Detection Conditions: The Na and K were determined by using emission mode of the instrument by maintaining the following conditions. Settings wavelength of 589.00 ηm for Na and 766.49 ηm properly adjusted the instrument for K.

Iron

Perpetration of standards: In case of iron, 3.115 grams of Mohr salt was dissolved in 1000 mL of deionized water. From this standard solution of 0, 2, 4 and 8 mg/L were prepared.

Detection Conditions: The instrument was set at a wavelength of 248.3 ηm, slit of 0.2 and air/acetylene flow of matrix .

Maganese

Perpetration of standards: 4.419 grams of maganese sulphate was dissolved in 200 mL of deionized water containing 1.5 mL of nitric acid. It was diluted to 1000 ml with deionized water. This standard stock solution contains 1000 mg/L of magnaese was used for the preparation of working standard of solution 1,2,4 and 8 mg/L.

Detection Conditions: This instrument was set at a wavelength of 248.3 ηm and bandwidth of 0.2 and air / acetylene flow of matrix.

2.2. *Soil and Rock:*

Collection of Samples: The soil of the area has been divided into three zones (A, B & C) in order to establish their chemical characteristics. Therefore, the soil samples have been collected from these three zones separately by auguring into the soil. Generally the samples have been collected at each site where from the water sample has been collected.

Beside soil and water samples, the rock samples, if exposed in the vicinity of each site, were also collected.

Laboratory Analyses: All the analyses of soils and rocks were also performed at the geochemistry laboratory of the National Center of Excellence in Geology, University of Peshawar by using Pye-UNICAM 191, atomic absorption (flame version) and SP-400 UV/Visible Spectrophotometer. The detail methodology is discussed here.

After the collection of the soil and rock samples, they were properly labeled and transferred into polythene bags. The color, texture and loose fragments of these samples were noted with naked eye and noted in the field notebook at each site.

Preparation of Solution: The soil samples were dried in air. Both soil and rock samples were pulverized to 200-mesh size in a Tungsten Carbide Ring Mill. The mill was properly cleaned before the treatment of each sample in order to avoid any possible contamination. The powder of each sample was dried over night at 110 °C in oven.

1. ***HF & $HClO_4$ Method for Sample (Solution A)***: 0.50 grams of soil sample was taken in a platinum crucible and moisten with few drops of demonized water to avoid the powder blowing away in draughts and effervescence. The Crucible was then kept in the fume cupboard. 10 ml Hydrofluoric acid (HF) was added by Polly measure cylinder and after 20 minutes. 4.0 mL of perchloric acid (60%) was added. The crucible was then placed on sand bath. After one hour. 2.0 mL of perchloric acid was further added and continued heating on sand bath until a paste was obtained. The crucible was allowed to cool for a while. Then some deionized water and 4 mL of perchloric acid were again added to it. The content of crucible was thoroughly washed with deionized water into a beaker. The beaker was warmed and when a clear solution was obtained, it was transferred to a 250-mL volumetric flask and diluted with deionized water up to the mark. In case of turbidity in the solution further treatment was given with HCl until clear solution was obtained. 5 to 10 mL of HCl was added to the beaker having the prepared solution and then it was heated to complete removal of chlorine (fumes). After this precipitate was dissolved and a clear solution was obtained. This solution was then diluted with deionized water in a volumetric flask and marked up to 250 mL. The solution then stored into the clean polythene bottle. The samples prepared from this method were used for the determination of CaO. MgO. Fe_2O_3. Na_2O. K_2O and P_2O_5

2. ***HF & HNO_3 method for the sample digestion (solution B)***: 0.5 grams of soil or rock sample was taken in Teflon beaker and 5mL of hydrofluoric acid was added to it. After 15 minutes. 15 mL of HNO_3 was added to it. It was again heated on hot plate at a temperature of about 70 °C till the sample was completely dried. 50 mL 2N HCl was added to the beaker. The beaker was heated on low flame for a short time until the residue was almost dissolved. The solution was stored in the clean polythene bottles for detection of trace elements. Solution prepared by this method was used for the determination of trace elements e.g. Cu. Pb. Zn. Ni. Cr. & Co. for both soil and rock samples.

3. ***Water Dissolved Soil Solution (solution C)***: 5.0 grams of each soil sample taken in a series of volumetric flasks of 100 mL. Approximately 50 to 60 mL of deionized water was added to it.

Then these volumetric flasks were shaken on automatic flask shaker, for one hour. If some sample is not properly mixed then these were shaken for longer period. After that it is filtered through Whatman – 42 filter paper in 100-mL flask. Filtered solution was then diluted with deionized water up to the mark in a volumetric flask of 100 mL. Using atomic absorption spectrophotometer used these solutions for the determination of water-soluble constituents in soil samples.

Defusion method (Solution D): This solution was prepared only for the determination of Si and Al. A solution of NaOH was prepared by dissolving 30 grams of sodium hydroxide in deionized water and diluted to 100 mL in volumetric flask. This solution was stored in polythene bottle. 5 mL of NaOH solution was taken in a series of eight clean nickel crucibles. These crucibles were evaporated to dryness on hot plate. Accurately weighed 0.5 grams of samples was taken in each crucible. Each crucible was covered with lid and was heated on low flame for few minutes. The crucible was then heated to dull redness for exactly 5 minutes on the Maker burner. After five minutes heating, the crucible was removed from burner and was swirled while hot and was allowed to cool. The content of each crucible was washed in separated 1000-mL plastic beakers. Both crucibles and lids were washed in respective beaker. The solution of each beaker was diluted to 500 mL and then 10 mL of conc. HCl was added to every beaker. The solution was stirred for a while and kept for half an hour until complete dissolution occurred. Each solution was then transferred to 1000-mL volumetric flask and was made to volume with deionized water. The certified rock standard (G_2, AGV_1 & W_2) was also treated by the same method. The solutions were kept in polythene bottles for the determination of Silica and Aluminum.

Calorimetric method: UV/ Visible Spectrophotometer (Pye-Unicam 400) was used for the determination of silica, Alumina and phosphorous in the soil and rock samples.

Silica: Silica was determined by ammonium molybdate method of Shapiro and Brannock (1962). In this method molybdate reacts with silica to form yellow silicomolybdate. Phospho-molybdate, however, may also give yellow color but it can be able to be decomposed by adding tartaric acid solution. The yellow silico-molybdate can be reduced to molybdate blue by adding 1 amino 2-naphthol 4-sulphnic acid. So ammonium molybdate solution, tartaric acid solutions and reducing solution were prepared as reagents for silica determination. Then a measured quantity of 10 mL samples solution (prepared by NaOH Fusion Solution) was taken in 100 mL volumetric flask and was, diluted with 50 mL deionized water. 2 mL of the ammonium molybdate solution was added, swirled to mix and set aside for ten minutes. After this, 4 mL of tartaric acid solution was added followed by the addition of 1.00 mL of reducing solution that gives blue color to it. The volume was made up to the mark by deionized water. The instrument was set at a wavelength of 650 ηm and the concentration of unknown soil sample (solution D) was determined relative to that of certified rock standard (solution D).

Phosphorus: The concentration of phosphorus was determined by the spectrophotometer method. In this vanado-molybdate reagent solution and diluted nitric acid as a colouring reagent was used as suggested by Kitson and Mellon (1944). For the preparation of vanado-molybdate reagent solution dissolved 20grams of crushed ammonium molybdate in water and poured gradually into 140 mL of concentrated nitric acid. Added of 1 gram of ammonium vandate, stirred it well until solution is complete and then it was diluted with water up to the mark of 1,000 mL. In dilute orthophosphate solution, ammonium molybdate reacts under acid conditions to form a hetroploy acid and molybdophosphoric acid. In the presence of vanadium yellow color molybdovanadophosphoric acid is formed. The intensity of yellow color is proportional to the phosphorus concentration that was determined by spectrophotometer. Solution A was used for the determination of P_2O_5.

Alumina: Riley and Boltz (1958) method was used for the determination of alumina. In this method 5 mL of rock sample solution (obtained by fusion of NaOH) was taken in 100 mL of separating funnel. 5 mL deionized water and 10 mL of completing reagent solution obtained by dissolving 1.00 g of hydroxyklamine hydrochloride, 3.6 gms. of sodium acetate trihydrate and 0.4 gms. of beryllium sulfate in 50 mL of deionized water 0.04 gms. of 2.2 di-pyridyl dissolved in 20 ml of 0.2 N. HCl) both the solutions were then mixed and made to (100 mL) was added to it. 20 mL of 8-hydroxyquinoline reagent solution (obtained by dissolving 1.25 gms. of 8-hydroxyquinoline in 250 mL of chloroform) was also added to separating funnel.

Afterward the separating funnel was shaken for 5-8 minutes on automatic shaker. Organic layer was then collected in 25 mL of volumetric flask. Then the separating funnel was washed thrice with chloroform and these washing were also added to the flask and the volume was made with chloroform. The alumina was determined solution D by 400 UV/VIS spectrophotometer at a wavelength of 380 ηm.

2.3. Units of Measurement

Physical Quality: The physical quality of water includes color, odour, taste turbidity and temperature. Concentrations of dissolve salts or ions in water are commonly expressed by weight, weight and volume or by chemical equivalence.

Weight and Weight - Volume Method: The weighted method expresses the relative weights of the solute and the solution, usually in parts per million (ppm). Concentration of one part per million means that one part by weight of dissolve matter is present in one million part by weight of the solution. The value so expressed is nearly equal to the weight of dissolve matter in milligrams is one litre (mg/L) of water if the concentration of the dissolve solid is low. But due correction has to be applied for the change in the Specific gravity (Sp. G.) of water if the dissolved solids concentration is high.

Chemical Equivalence Method: The equivalent weight of an ion equals its atomic or molecular weight divided by its valency by dividing ionic concentration, reported in ppm, by the equivalent weight of that ion, the resulting value expresses the concentration in equivalents per million (epm), or more precisely, milligram equivalent per kilogram.

To calculate the conversion factor from ppm to emp of a known (cation or anion) e.g., Na.

Atomic weight Of Na = 22.99
Equivalent weight of Na= 22.99 / 1
Known weight Of Na (ppm) = X
Weight of Na (epm) = X / 22.99
Weight of Na (epm) = 1 / 22.99 (If X is equal to one)
= 0.04350 (is the conversion factor for "Na") * weight in ppm.

Conversion factors for different anion and cations from ppm to epm.

Cation	C.F.
Calcium	0.04990
Magnesium	0.08224
Potassium	0.02558
Sodium	0.04350

Anion	C.F.
Bicarbonate	0.01639
Carbonates	0.03333
Chloride	0.02820
Fluoride	0.05263
Nitrate	0.01613
Sulfate	0.2182

No. 42-c

Units of Measurement for Constituents (anion, cation and traces)

Volume: Length x width x height

(cm) x (cm) x (cm) = cm^3

The volume measurement in metric system is litres, cubic centimeter (cm^3) or cubic meter $(m)^3$.

Weight: The weight Measurement in metric system is in grams.

Milligram	(mg)	1/1000	(gms)	10^{-3}	Gms
Microgram	(μg)	1/1000000	(gms)	10^{-6}	Gms
Nanogram	(ηg)	1/1000000000	(gms)	10^{-9}	Gms

Ohm: The Unit of resistance is the ohm and is defined as the resistance of a conductor through which a current of one ampere is flowing when the potential difference of one volt is applied across its ends. It symbol is "Ω"

1 Ohm = Volt / 1 ampere

Solution: A solution is a single phase, a homogeneous mixture of two or more substances, the composition of which can be varied over a wide or narrow range.

Solute : The component of the solution present in smaller amount is conventionally called as the solute.

Solvent: The component of solution present in greater quantity is called as the solvent.

One Molal Solution: One mole of solution per 1000 grams of solvent is one molal solution. One mole is the formula weight of the compound in grams.

One Molar Solution: One mole of solute per liter of solvent is a one molar solution.

Chapter III

Results & Discussions

3.1.Water

GENERAL DISCUSSION: Water is essential for life, next to air. It is one of the principle needs, which directly effects economic, industrial and agricultural growth of mankind. All the ancient civilizations flourished mainly along the water resources.

Water resources are divided into two distinct categories: -

1. The surface water resources.
2. Ground water resources.

The **total quantity** of fresh water on the earth is estimated at about **$4.1*10^{16}$ m^3**. Which is distributed as follows: **74%** in polar ice and glaciers, **14%** in ground water between depth 800 to 4000 meters and **11%** at depths of less than 800 m, **0.3%** in lakes, **0.6%** as soil moisture, **0.035%** in atmosphere, and **0.03%** in rivers (Chow, 1964, Fig.3.1)

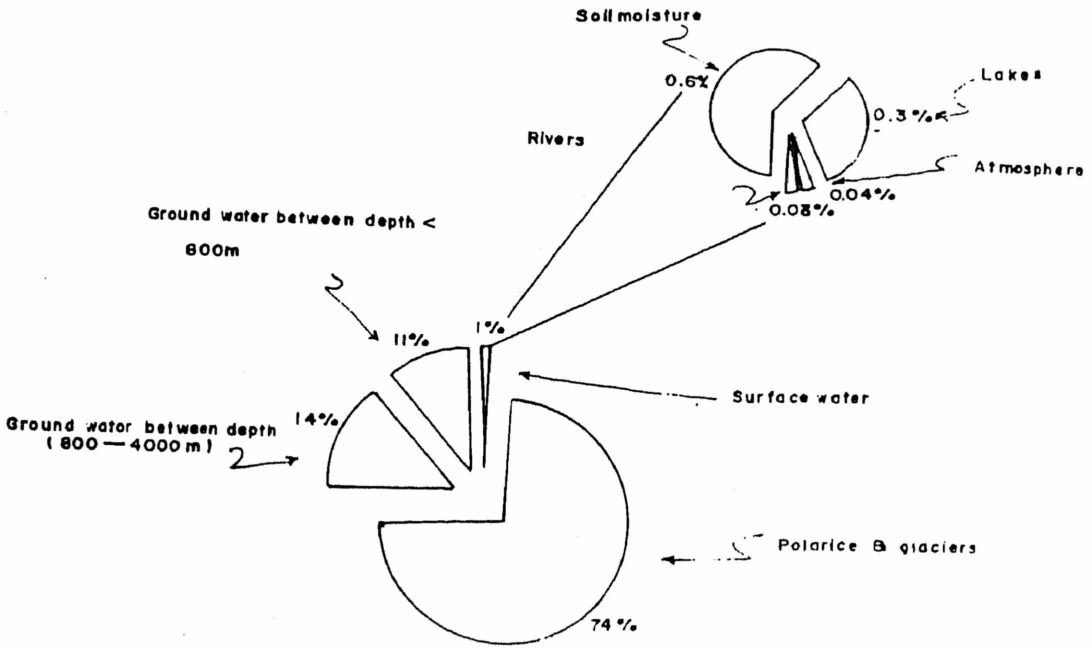


Fig. 3.1. Pie graph showing the fresh water distribution on earth surface.
(after Cow,1964)

The geological framework broadly governs the occurrence of water in the subsurface (Fig.3.2). Water as a best solvent, has the ability to dissolve, constituent of a rock formation from which it passes through. But ground water supplies are generally free from suspended and organic impurities due to natural filtration characteristics of subsurface material, unlike surface water, which is generally loaded with suspended solids and organic matter.

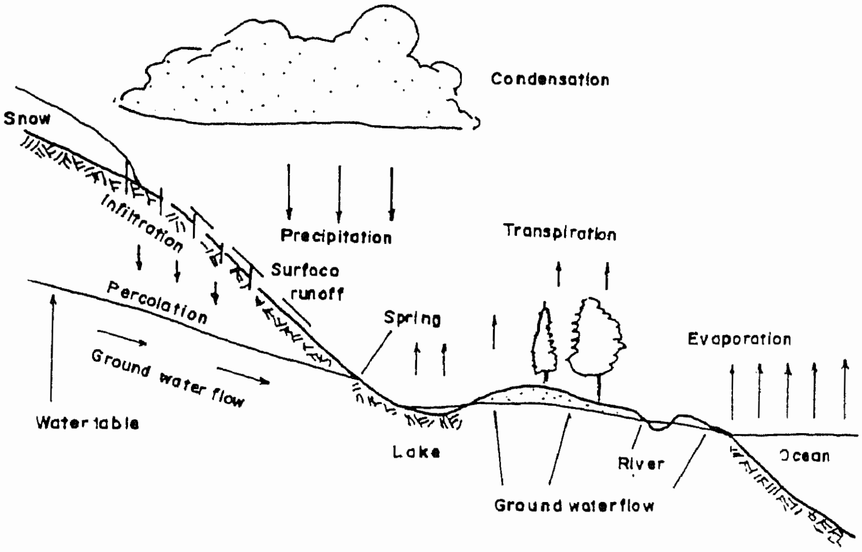


Fig. 3.2 The hydrological cycle by Todd.

Most of the human activities, some of the major adverse effects have arisen from construction of reservoirs, surface water irrigation, heavy ground water exploitation, deforestation and industrial and urban waste disposal. The emphasis is notable on the quality and quantity of ground water resources, the fertility of land and the stability of land mass (Todd, 1980; Karanth, 1987; Vohra, 1987.)

GEOCHEMISTRY OF WATER OF D.I.KHAN

Purpose: As mentioned earlier that D.I.Khan district has both quantitative as well as qualitative problems of water. This causes health hazards in various parts of D.I.Khan division. In order to understand the causes of these diseases, the geochemistry of water, soil and rocks of the area has been conducted. This study could help in determining the source of water contamination, if any. The study of the soils and rocks of the area would further clarify the input of the geology in regard to increase and decrease of various elements in the water of the D.I.Khan area.

In this chapter the result obtained were discussed in brief in the light of worldwide-recognized standards of US- Environmental Protection Agency (EPA) and World Health Organization (WHO). The samples collected from tube-wells, dug-wells, streams/nalas, settling-ponds and rivers have been analysed by the techniques used in chapter III and the results are discussed here for further interpretation.

Classification of waters for the area:

The water of the study area has been divided in to four different categories as follows.

i) Deep water (tube-wells)

ii) Shallow water (dug-wells, settling ponds, streams/nalas and hand-pumps)

iii) Streams

iv) Rivers

The results of various parameters of the waters of different areas of D.I.Khan are given in table 3.1. For comparison the world standards for drinking water are also presented in table 3.2. The tables, figures and graphs charts are made according to the above-mentioned classification of the D.I.Khan waters.

The chemical data presented in the tables 3.8 to 3.14 have been plotted in the Piper diagram (Fig. 3.21 to 3.24) which show the classification scheme of water (Piper, 1944). According to this scheme the majority of water samples from tube-wells in the D.I.Khan division are plotting within the field of sodium-potassium, chloride-sulphate type (normally called as alkaline earth fresh water); calcium-magnesium, bicarbonate type (named as alkaline fresh water) and chloride-sulphate type (Fig. 3.21). The surface water also has the range of sodium-potassium, chloride-sulphate type and calcium-magnesium, bicarbonate type (Fig. 3.22), similar to the composition of stream waters of the D.I.Khan area (Fig. 3.23). The water samples from various

Table 3.1 Geochemistry of Water from Dera Ismail Khan Division

Location	Sample No.	Depth W.T.	Temp.	EC	TDS	pH	ANIONS					CATIONS							TRACES					
							HCO_3	NO_3	SO_4	PO_4	Cl	Si	Fe	Mg	Mn	Na	K	Ca	Cu	Pb	Cr	Cd	Ni	Zn
		meters	C	mmhos/cm	mg/L		mg/L					mg/L							ug/L					
Pezu	A1	7	22.8	460	322	8.17	125	2	100	0.08	40.01	31.73	0.6	18.2	0.01	27.1	7.9	35.5	8	1	0	12	0	50
Mullazai	A2	185	26	930	651	7.87	210	3.2	200	0.06	241.2	37.05	0.5	27.3	0.02	157.5	2.45	28	15	0	0	0	0	10
Mullazai	A3	52	27.5	1600	1120	7.51	305	17	375	0.1	333	33.4	0.8	49.2	0.11	214	2.03	49.4	14	12	3	0	0	180
Gul Imam	A4	-	22.8	790	553	9.07	250	0.2	125	0.13	241	36.7	0.8	9	0.03	152.5	1.65	6.4	6	6	0	1	0	150
Indus at Chashma	A5	-	19.5	310	217	8.26	180	0.8	15	0.06	24.4	27.425	8.4	11.8	0.05	15.2	3.74	29.3	39	30	4	16	32	10
Umer Khel	A6	10	23.2	620	434	7.66	143	0.2	65	0.11	57.2	34.08	2.2	15.5	0.27	40.9	8.3	47	11	3	0	1	0	10
Kirri Khisor	A7	16	22.4	580	406	7.79	230	0.2	50	0.13	45	30.6	1.5	15.5	0.06	30.3	8.6	47.7	2	0	0	0	0	0
Pahar Pur	A8	25	26	840	588	7.47	307.6	3	80	0.29	69.8	33.5	2.1	31.3	0.02	43.7	11.4	68.1	26	13	0	1	0	370
Pahar Pur	A9	-	27	320	224	7.79	137.5	0.9	50	0.13	31.2	27.75	7.5	12.8	0.05	20.1	3.73	28.4	18	12	2	1	0	10
Panayala	A10	36	33.4	500	350	8.18	136	0.6	75	0.13	145.3	17.38	0.8	7	0.03	93.5	33.9	7.7	14	16	2	0	0	0
Panayala	A11	-	33.2	1090	763	8.35	362.5	0.4	220	0.14	269.1	24.125	1	19.1	0.05	179.5	9.5	36.4	33	0	1	1	0	20
Yarak	A12	450	27.9	1200	840	8.25	142.6	6	55	0.1	312	31.73	1.4	20.3	0.06	188.5	6.6	19.5	11	2	16	0	0	10
Yarak	A13	-	27.9	890	6.23	8.41	110	1.3	20	0.06	190.28	14.025	11.8	16.1	0.8	120	5.9	33.2	87	20	9	1	0	0
Pushapull	A14	-	22	320	224	7.85	97.5	1.1	40	0.17	26.3	19.225	7.9	12.6	0.05	16.8	3.7	32.1	25	12	3	0	60	20
Shor Kot	A15	-	26.7	1110	777	7.66	275	0.1	250	0.14	145.3	25.95	5.8	49	0.08	92.5	7.4	46.5	7	4	1	1	0	20
Tank	A16	72	23	1450	1050	7.43	410	1.4	450	0.03	168	36.75	0.7	71	0.03	107	2.92	68.7	0	0	0	0	0	10
Tank Zam	A17	-	21.8	690	483	8.19	140	2.6	300	0.07	89.1	18.425	1.5	29.4	0.1	49.1	3.44	42.4	7	4	0	1	0	10
Umer Ada	A18	90	26.8	830	581	7.62	265	2	450	0.08	89	37.25	0.7	39.5	0.04	52.5	3.22	42.1	6	1	4	1	4	20
Gomal River	A19	-	27.2	1130	791	8.45	225	1.4	400	0.09	158.5	272	43.3	47	0.21	102	5.6	51.7	10000	4	19	2	3	0
Kullachi	A20	300	26.5	1410	987	7.71	205	0	700	0.03	293	29.78	0.1	0.51	0.51	21.9	2.97	40.4	31	0	0	0	0	10
Hathala	A21	-	24.2	1900	1330	7.83	166	0.5	775	0.04	333	23.25	7.6	60.7	0.08	215	11.3	54.9	69	0	1	1	51	10
Potah	A22	395	24	2280	1596	7.18	215	2.2	900	0.11	314	35.05	2.4	89.3	0.14	204.5	11.1	85.5	14	2	0	1	0	20
D.I.Khan	A23	15	23.3	1140	987	6.91	345	0	275	0.02	152.5	35.93	0.9	47.1	0.11	98.5	12.6	43.2	9	5	0	1	0	30
D.I.Khan	A24	-	22	570	399	7.8	130	0	75	0.02	63	17.88	1.3	17.2	0.15	41.2	8.4	37.5	8	0	1	1	0	50
D.I.Khan	A25	-	21.3	560	392	7.54	125	0	200	0.02	72	19.4	2.8	17.9	0.09	43.3	5.4	40.6	109	30	4	2	0	20
Indus at D.I.Khan	A26	-	21.5	380	266	7.87	175	0.7	75	0.04	45	19.85	7.6	14.1	0.08	28.7	3.9	34.8	15	30	0	1	0	0
D.I.Khan	A27	405	21	1110	777	7.34	220	0	400	0.03	N.D	20.05	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Daraban	A28	400	26.7	1390	973	7.2	176	0.1	450	0.04	149	22.58	12.7	48.7	0.38	107	3.94	85.3	24	0	3	0	0	30
Chadhwan	A29	400	22	1200	840	7.39	460	0.4	450	0.02	130	13.68	1.7	51.7	0.05	88	3.62	60.8	83	2	6	1	0	30
Chadhwan Spring	A30	-	23.2	830	581	7.88	145	90	425	0.1	73	21.25	4.1	36.6	0.04	51.5	3.83	51.9	7	1	0	7	0	40
Poroa	A31	26	26	1880	1316	7.46	250	0	1600	0.02	244	35.55	0.3	73.7	0.02	175	9.4	83.9	5	0	0	0	0	30
Ramak	A32	25	27.9	3000	2100	7.63	155	0	675	0.08	618	38.65	5.3	72.3	0.16	402.5	11.1	84.3	34	0	0	1	0	20
Gomal Univ.	A33	100	33	940	658	7.43	215	0.6	225	0.1	148	18.8	3.5	35.9	0.11	96.5	7	44	287	2	3	1	11	50
Indus at Darya Khan	A34	-	22	380	266	8.08	75	0.8	100	0.19	46	N.D.	1.3	13.3	0.05	28.8	3.92	22.5	44	287	2	3	1	11

•W.T. = Water Table • E.c. = Electric Conductivity • TDS = Total Dissolve Solids • Temp. = Temperature • N.D. = Not Determined

Table 3.2 **World Standards for Safe Drinking Water (US-EPA, 1989), (Europan Community, 1980) and (WHO Guide Line, 1984)**

Element	US-EPA (1989)	European Community (1980)	WHO Guide Line (1984)
	mg/l		
Cd	0.005	0.005	0.005
Cu	1	0.1	1
Pb	0.02	0.05	0.05
Cr	0.1	0.05	0.05
Ni	0.15	0.05	Set no standards
Al	0.05	0.2	0.2
Zn	5	0.1	5
K		10	
F		1.5	1.5
Ca		100	75
Cl		250	250
Na	20	20	200
Fe		0.05	0.3
Mg		30	50
Mn		0.02	0.05
Nitrate	10	0.1	10
Sulphate	250		400
Phosphate		0.4	

Table 3.3 Detailed Geochemistry of deep water from Tube-wells.

							ANIONS					CATIONS							TRACES					
Location	Sample No.	Depth W.T.	Temp.	EC	TDS	pH	HCO_3	NO_3	SO_4	PO_4	Cl	Si	Fe	Mg	Mn	Na	K	Ca	Cu	Pb	Cr	Cd	Ni	Zn
		meters	C	mmhos/cm	mg/L		mg/L					mg/L							ug/L					
Mullazai	A2	185	26	930	651	7.87	210	3.2	200	0.06	241.2	37.05	0.5	27.3	0.02	157.5	2.45	28	15	0	0	0	0	10
Umer Khel	A6	10	23.2	620	434	7.66	143	0.2	65	0.11	57.2	34.08	2.2	15.5	0.27	40.9	8.3	47	11	3	0	1	0	10
Kirri Khisor	A7	16	22.4	580	406	7.79	230	0.2	50	0.13	45	30.6	1.5	15.5	0.06	30.3	8.6	47.7	2	0	0	0	0	0
Panayala	A10	36	33.4	500	350	8.18	136	0.6	75	0.13	145.3	17.38	0.8	7	0.03	93.5	33.9	7.7	14	16	2	0	0	0
Tank	A16	72	23	1450	1050	7.43	410	1.4	450	0.03	168	36.75	0.7	71	0.03	107	2.92	68.7	0	0	0	0	0	10
Umer Ada	A18	90	26.8	830	581	7.62	265	2	450	0.08	89	37.25	0.7	39.5	0.04	52.5	3.22	42.1	6	1	4	1	4	20
Kullachi	A20	300	26.5	1410	987	7.71	205	0	700	0.03	293	29.78	0.1	0.51	0.51	21.9	2.97	40.4	31	0	0	0	0	10
Hathala	A21	-	24.2	1900	1330	7.83	166	0.5	775	0.04	333	23.25	7.6	60.7	0.08	215	11.3	54.9	69	0	1	1	51	10
Potah	A22	395	24	2280	1596	7.18	215	2.2	900	0.11	314	35.05	2.4	89.3	0.14	204.5	11.1	85.5	14	2	0	1	0	20
D.I.Khan	A23	15	23.3	1140	987	6.91	345	0	275	0.02	152.5	35.93	0.9	47.1	0.11	98.5	12.6	43.2	9	5	0	1	0	30
D.I.Khan	A24	-	22	570	399	7.8	130	0	75	0.02	63	17.88	1.3	17.2	0.15	41.2	8.4	37.5	8	0	1	1	0	50
D.I.Khan	A25	-	21.3	560	392	7.54	125	0	200	0.02	72	19.4	2.8	17.9	0.09	43.3	5.4	40.6	109	30	4	2	0	20
D.I.Khan	A27	405	21	1110	777	7.34	220	0	400	0.03	N.D	20.05	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Daraban	A28	400	26.7	1390	973	7.2	176	0.1	450	0.04	149	22.58	12.7	48.7	0.38	107	3.94	85.3	24	0	3	0	0	30
Chadhwan	A29	400	22	1200	840	7.39	460	0.4	450	0.02	130	13.68	1.7	51.7	0.05	88	3.62	60.8	83	2	6	1	0	30
Poroa	A31	26	26	1880	1316	7.46	250	0	1600	0.02	244	35.55	0.3	73.7	0.02	175	9.4	83.9	5	0	0	0	0	30
Ramak	A32	25	27.9	3000	2100	7.63	155	0	675	0.08	618	38.65	5.3	72.3	0.16	402.5	11.1	84.3	34	0	0	1	0	20
Gomal Univ.	A33	100	33	940	658	7.43	215	0.6	225	0.1	148	18.8	3.5	35.9	0.11	96.5	7	44	287	2	3	1	11	50

•W.T. = Water Table • E.c. = Electric Conductivity • TDS = Total Dissolve Solids • Temp. = Temperature • N.D. = Not Determined

Table 3.4 Detailed Geochemistry of shallow water from Dug-well / Hand-pump /Settling ponds.

						ANIONS					CATIONS							TRACES					
Location	Sampl No.	Temp.	EC	TDS	pH	HCO_3	NO_3	SO_4	PO_4	Cl	Si	Fe	Mg	Mn	Na	K	Ca	Cu	Pb	Cr	Cd	Ni	Zn
		C	mmhos/cm	mg/L		mg/L					mg/L							ug/L					
Pezu	A1	22.8	460	322	8.17	125	2	100	0.08	40.01	31.725	0.6	18.2	0.01	27.1	7.9	35.5	8	1	0	12	0	50
Mullazai	A3	27.5	1600	1120	7.51	305	17	375	0.1	333	33.4	0.8	49.2	0.11	214	2.03	49.4	14	12	3	0	0	180
Gul Imam	A4	22.8	790	553	9.07	250	0.2	125	0.13	241	36.7	0.8	9	0.03	152.5	1.65	6.4	6	6	0	1	0	150
Paharpur	A8	26	840	588	7.47	307.5	3	80	0.29	69.8	33.5	2.1	31.3	0.02	43.7	11.4	68.1	26	13	0	1	0	370
Yarik	A12	27.9	1200	840	8.25	142.5	6	55	0.1	312	31.725	1.4	20.3	0.06	188.5	6.6	19.5	11	2	16	0	0	10
Shorkot	A15	26.7	1110	777	7.66	275	0.1	250	0.14	143.3	25.95	5.8	49	0.08	92.5	7.4	46.5	7	4	1	1	0	20

•W.T. = Water Table • E.c. = Electric Conductivity • TDS = Total Dissolve Solids • Temp. = Temperature

Table 3.5 Detail Geochemistry of water for Streams / Nalas

						ANIONS					CATIONS							TRACES					
Location	Sample No.	Temp.	EC	TDS	pH	HCO_3	NO_3	SO_4	PO_4	Cl	Si	Fe	Mg	Mn	Na	K	Ca	Cu	Pb	Cr	Cd	Ni	Zn
		C	mmhos/cm	mg/L		mg/L					mg/L							ug/L					
Paharpur	A9	27	320	224	7.79	137.5	0.9	50	0.13	31.2	27.75	7.5	12.8	0.05	20.1	3.73	28.4	18	12	2	1	0	10
Panaiala	A11	33.2	1090	763	8.35	362.5	0.4	220	0.14	269.1	24.125	1	19.1	0.05	179.5	9.5	36.4	33	0	1	1	0	20
Yarik	A13	27.9	890	623	8.41	110	1.3	20	0.06	190.28	14.025	11.8	16.1	0.8	120	5.9	33.2	87	20	9	1	0	0
Pushapull	A14	22	320	224	7.85	97.5	1.1	40	0.17	26.3	19.225	7.9	12.6	0.05	16.8	3.7	32.1	25	12	3	0	60	20
Tank Zam.	A17	21.8	690	483	8.19	140	2.6	300	0.07	89.1	18.425	1.5	29.4	0.1	49.1	3.44	42.4	7	4	0	1	0	10
Chudhwan spring	A30	23.2	830	581	7.88	145	90	425	0.1	73	21.25	4.1	36.6	0.04	51.5	3.83	51.9	7	1	0	7	0	40

•W.T. = Water Table • E.c. = Electric Conductivity • TDS = Total Dissolve Solids • Temp. = Temperature

Table 3.6 Detailed Geochemistry of water for Rivers.

						ANIONS					CATIONS							TRACES					
Location	Sample No.	Temp.	EC	TDS	pH	HCO_3	NO_3	SO_4	PO_4	Cl	Si	Fe	Mg	Mn	Na	K	Ca	Cu	Pb	Cr	Cd	Ni	Zn
		C	mmhos/cm	ppm		mg/l					mg/l							ug/l					
Indus at Chashma	A5	19.5	310	217	8.26	180	0.8	15	0.06	24.2	27.425	8.4	11.8	0.05	15.2	3.74	29.3	39	30	4	16	32	10
Indus at D.I.Khan	A26	21.5	380	266	7.87	175	0.7	75	0.04	45	19.85	7.6	14.1	0.08	28.7	3.9	34.8	15	30	0	1	0	0
Indus at Darya Khan	A34	22	380	266	8.08	75	0.8	100	0.19	46	N.D.	1.3	13.3	0.05	28.8	3.92	22.5	16	0	2	1	0	10
Gomal River	A19	27.2	1130	791	8.45	225	1.4	400	0.09	158.5	272	43.3	47	0.21	102	5.6	51.7	10000	4	19	2	3	0

•W.T. = Water Table • E.c. = Electric Conductivity • TDS = Total Dissolve Solids • Temp. = Temperature

rivers of the D.I.Khan division are plotted in the field of sodium-potassium, chloride-sulphate type and calcium-magnesium, bicarbonate type (Fig. 3.24).

This classification scheme suggests that the water from various sources in the D.I.Khan division is generally alkaline water.

Electrical Conductivity (EC): The term Electrical Conductance denotes the characteristics of a medium to the passage of electricity. In water quality determination, conductivity, defined as the conduct of a cube of a substance one-centimeter on a side is reported in mhos/cm. When reported in mhos/cm the conductivity of most natural waters is much less than unity. For convenience conductivity is, therefore, expressed in micromhos/cm, which is equal to one million times the value given in mhos/cm.

The conductivity changes significantly with temperature, it is, therefore, necessary to refer them to a standard temperature, normally taken as 25°C. A correction factor has to be applied for conversion of conductivity to the standard temperature. The conductance increase approximately 2% for each increase in temperature 1°C (Hem, 970).

Results from the Study area: The electrical conductivity is in the range of 500-3000, 460-1600, 320-1090 and 310-1130 in deep water, shallow water, streams and rivers of D.I.Khan respectively (Table 3.3 to 3.6). It is extremely high in the water of tube well from Ramak area (Table 3.3). The surface water generally has low electrical conductivity (Table 3.5 & 3.6).

Total Dissolved Solids (TDS): Surface and ground water in never pure. It contains both dissolved and undissolved substances. The undissolved substances are usually referred as suspended matter or suspended solids.

Water is called mineralized water because it always contains fraction of dissolved solids and gases. To some extent these are beneficial for human health, on the other hand, excess of these create problems. Later on this was denoted as TDS, stands for "Total Dissolved Solids" As the term refers, these are the dissolved solids in water, which consists mainly of inorganic salts, small amount of organic matter, and dissolved gasses

Different type of water categorized on TDS basis.

Name	TDS, ppm
Fresh water	< 1000
Brackish water	1000 - 10,000
Salty water	10000 - 100,000
Brine	> 100,000

This is due to best solubility of water, consider as the best solvent. This is also controlled by the pH of water. Water is corrosive in acidic medium while it shows non-corrosive behavior in alkaline medium. TDS present in drinking water are divided into two categories, major and trace elements. Major elements are further divided into anion and cations. From where these solids come and how they occupy the free space, depends upon the geologic formation through which water percolates.

Results from the Study area: By looking at the generalized trend of TDS in figure 3.3, it increases from north to south. In Pezu, northern most town of D.I.Khan, it is 322 mg/L and to the southern most extreme at Ramak, it is 2100 mg/L. The generalized contour map of TDS in figure 3.3 is made in the SUFFER (a computerized program for contouring).

Alkalinity: The alkalinity of water is a measure of its capacity to neutralize acids. The alkalinity of natural water is due primarily to the salts of weak acids, although weak or strong bases may also contribute. Bicarbonates represent the major form of alkalinity. Since they are formed in considerable amounts from the action of carbon dioxide upon basic materials in the soil. Other salts of weak acids, such as borate and phosphate may be present in small amounts.

Organic acids such as humic acid also contribute alkalinity to natural water. In other contributor weak acids such as acetic, propionic, hydrosulfuric are present. In other cases, hydroxides may make a contribution to the total alkalinity of water (Sawyer & Mc Carty, 1967).

Under certain conditions natural waters may contain appreciable amounts of carbonate and hydroxide alkalinity. This condition is particularly true in surface waters where algae are flourishing. The algae release more carbon dioxide, free and combined with the water, to such an extent that the pH value of 9 to 10 is often obtained.

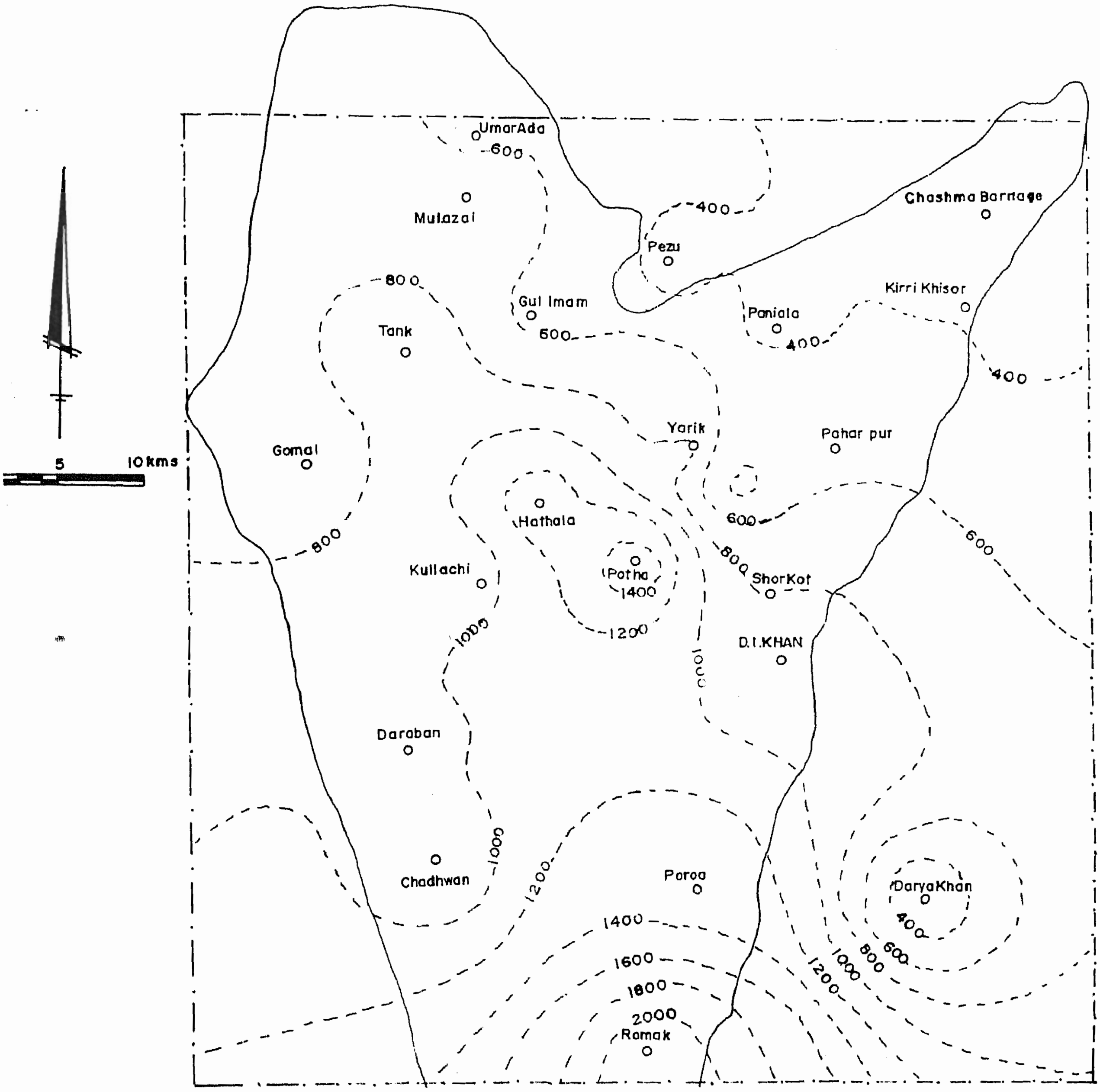


Fig. 3.3 **Contour map showing TDS concentration in D.I.Khan division.**

Although many material may contribute to the alkalinity of water. But the major portion of the alkalinity in natural water is caused by three major classes of materials. Which may be ranked in order of their association with high pH values as follows 1) Hydroxide, 2) Carbonates and 3) bicarbonates for most practical purposes. Alkalinity due to other material in natural water is insignificant and may be ignored. Thus alkalinity of waters is due principally to the salts of weak acids or strong basis.

Most of the area in D.I.Khan division has the pH value ranging around 7.00 in general. But areas where the pH is above 8.00 are concentrating in the northern part of the study area. It is 9.07 at Gul Imam that is the highest value in the area and the lowest value of pH is obtained from D.I.Khan colony, which is 6.91. Samples containing bicarbonate alkalinity have a pH value of 8.3 or less, usually less (Sawyer & Mc Carty, 1967).

PH: pH is term used to express the intensity of the acid or alkaline condition of a solution. It is a very effective way of expressing hydrogenation concentration, or more precisely, the hydrogen ion activity.

Results from the Study area: pH in the waters of D.I.Khan area is more basic (> 7.5) in nature (Table 3.1). The pH of deep water (Table 3.3) is relatively lower than shallow water (Table 3.4), stream water (Table 3.5) and river water (Table 3.6).

CLASSIFICATION OF D.I.KHAN WATERS

(Anion Elements Concentration)

NITRATE

Natural Existence: Nitrate is a salt of ester of nitric acid (HNO_3) or an end product of the aerobic stabilization of organic nitrogen. Also, a product of conversion of nitrogenous material. Combined nitrogen should be considered a potential source of nitrate. Sources of nitrates include mineral deposit (sodium and potassium nitrate), soils, seawater and atmosphere.

Uses: Nitrate is used as a fertilizer, as a food preservative and as an oxidizing agent in the chemical industry.

Environmental impact: Nitrates are particularly detectable in soil and water. High concentrations are also expected where fertilizers are used, in decayed animal and vegetable matters, in leaches from sludge and refuse disposal and in industrial discharge. Lakes and reservoirs usually have less than 2 mg/L of nitrate measured as nitrogen. Higher levels of nitrates are found in ground water ranging up to 20 mg/L but much higher values are detected in shallow aquifers, polluted by housing (sewage) and or excessive use of fertilizers (Zunae, 1990).

The utilization of nitrates by plants and the synthetic action convert nitrates into organic nitrogen which tend to reduce substantially the concentration of nitrates in surface water thus, leaving the problem to ground water (Zunae, 1990).

Health effect: Partial reduction of nitrates to nitrites in humans takes place in saliva for all ages and in the gastrointestinal tract in infants during the first three months of life. Therefore, babies up to 3 months of age are more susceptible. Nitrite acts in the blood to oxidize the hemoglobin to methemogloblin, which is not an oxygen carrier to the tissues with consequent anoxia (methemoglobinemia). Large concentrations of nitrite in water may result in the potential formation of carcinogenic nitro-samines (Zunae, 1990).

Results from the Study area: The concentration of nitrate (NO_3) in D.I.Khan area is ranging from 0-90 mg/L (Table 3.1). Almost all the samples of water of D.I.Khan area, accept two places, are having NO_3 within the permissible limit of less than 10 mg/L (Table 3.1 & Fig. 3.4). The shallow water at Mullazai and spring water at Chudhwan are

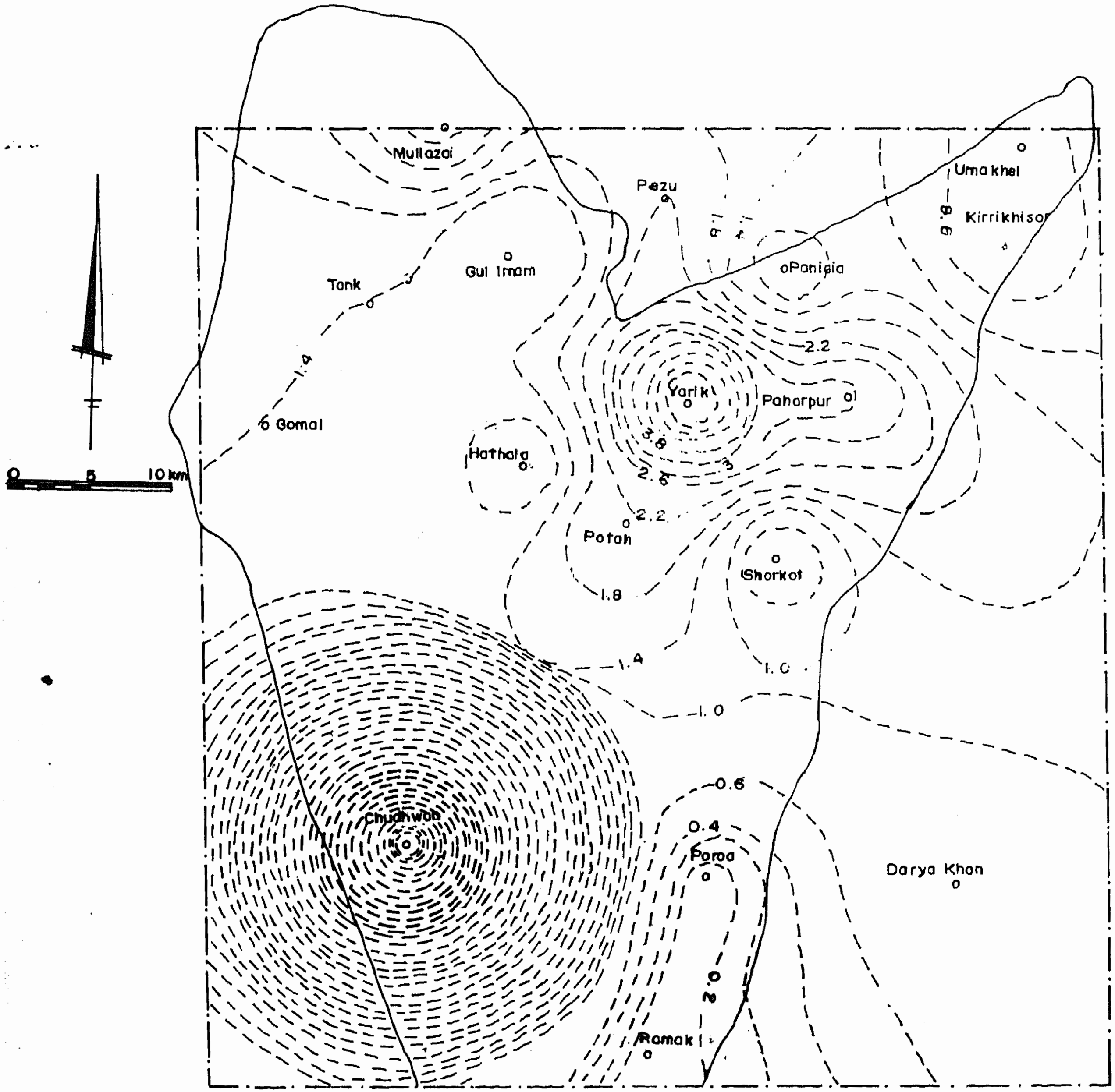


Fig. 3.4 **Contour map showing nitrate (NO_3) concentration in D.I. Khan division.**

Fig. 3.5 Nitrate (NO3) in the deep waters (tube-wells) for different locations of D.I.Khan division.

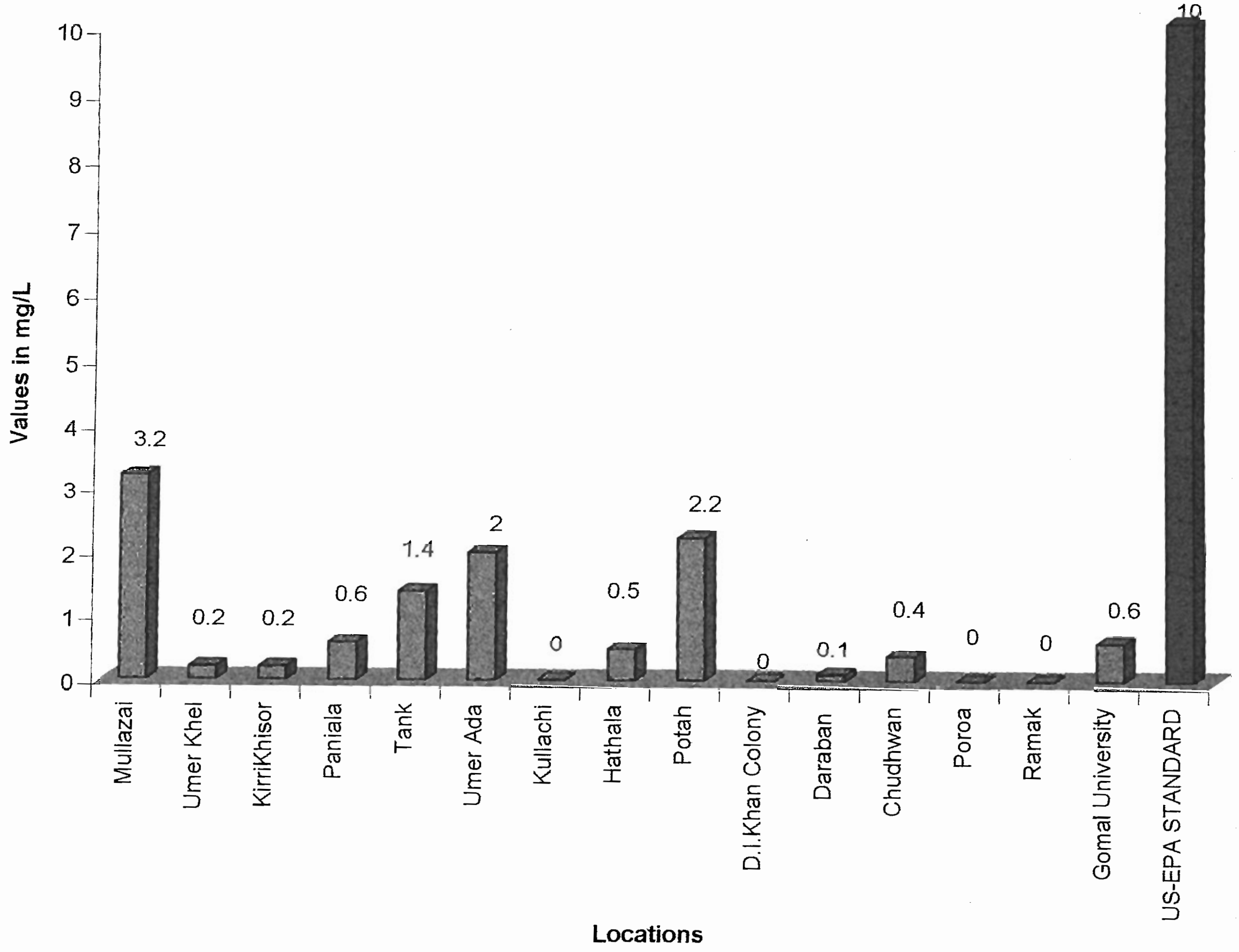
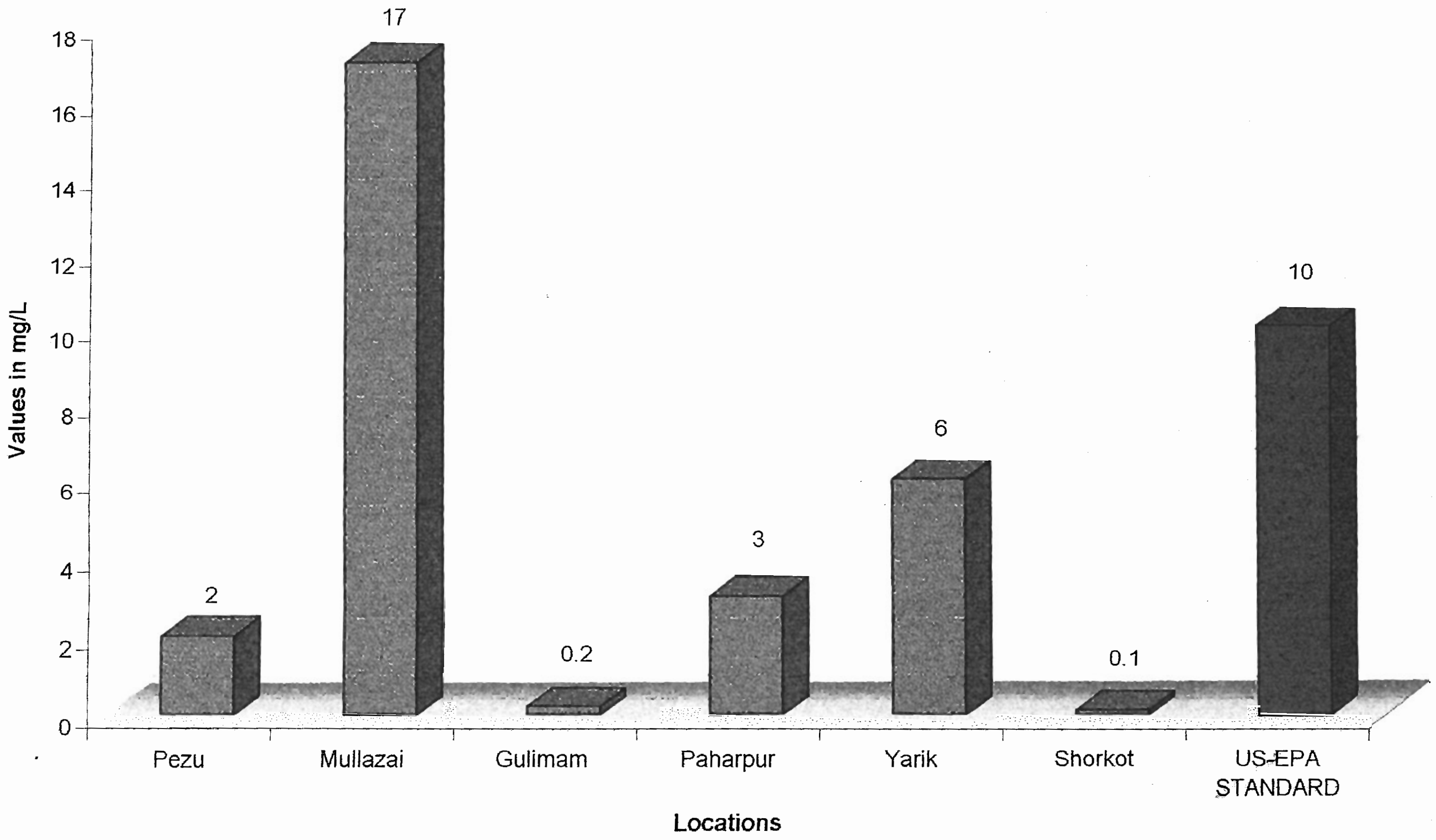


Fig. 3.6 Nitrate (NO3) in the shallow waters (dug-wells/hand-pumps/settling-ponds) from different locations at D.I.Khan division.



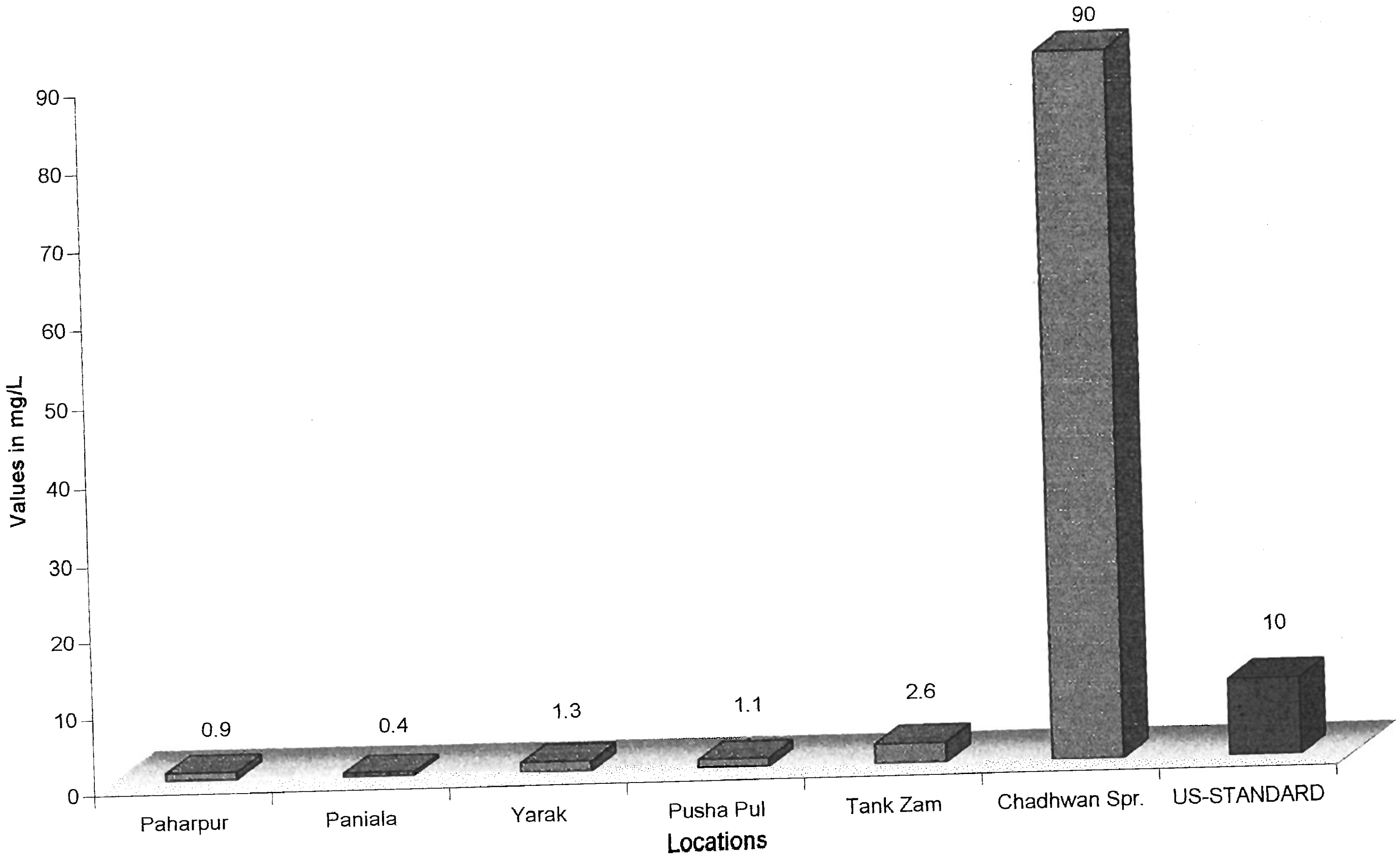
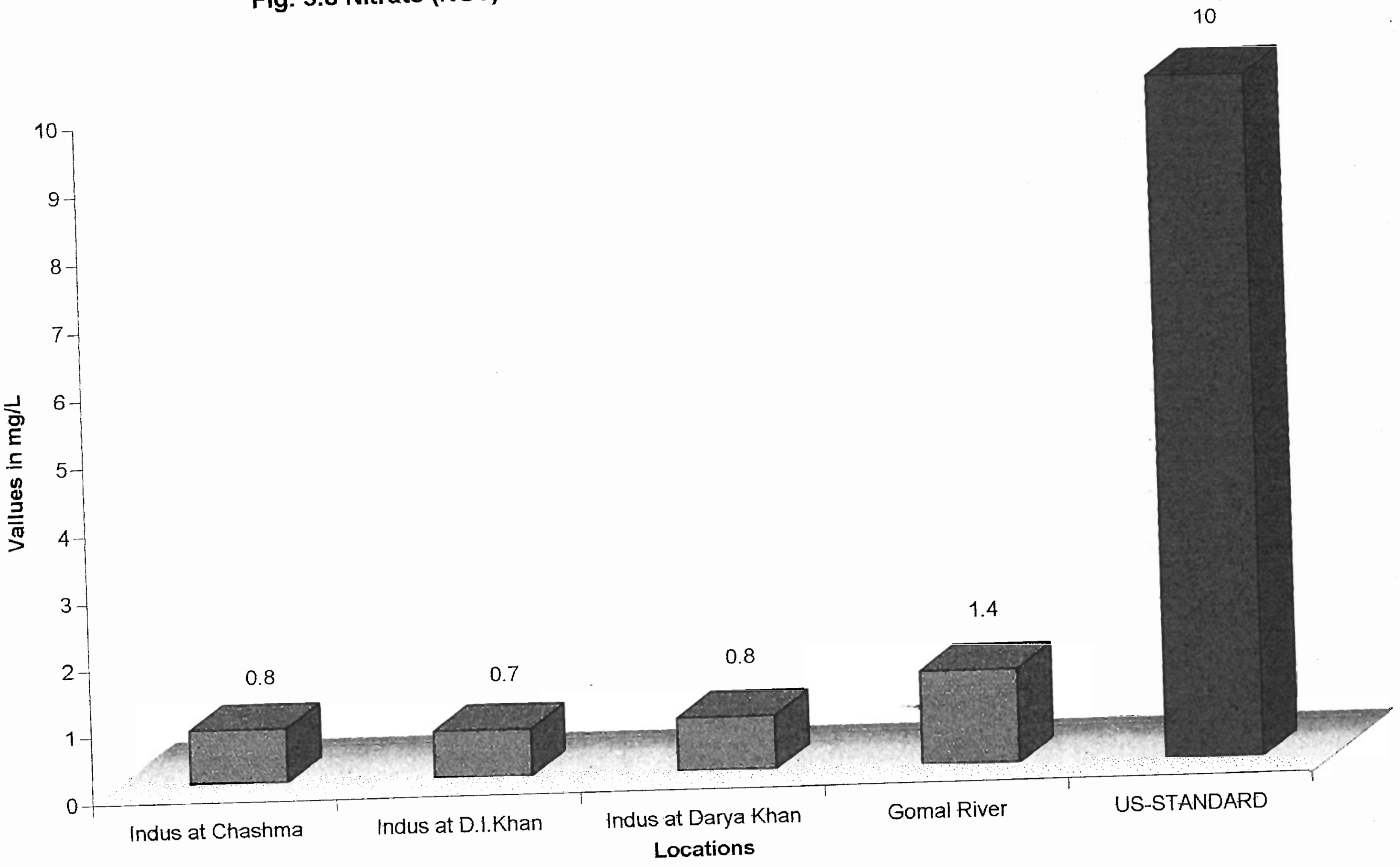


Fig. 3.7 Nitrate (NO3) in streams from different locatons at D.I.Khan division.

Fig. 3.8 Nitrate (NO3) in rivers in different locations at D.I.Khan division.



having 17 mg/L and 90 mg/L of NO_3 respectively (Tables 3.4, 3.5 & Fig.3.6, 3.7). The waters of these two areas are, therefore, unsafe for health as for as the NO_3 is concerned.

SULFATE (SO_4)

Physical Appearance: Sulphate is salt or ester of sulfuric acid.

Chemistry:

Symbol	At. Wt.	At. No	Valance
S	32.06	16	2,4 & 6

It is a pale yellow odorless brittle non-metallic solid, insoluble in water. It is indicated as So_4^-.

Occurrence : Sulfates are found in natural waters in the final oxidized stage of sulfides, sulfites and thio-sulfates or in the oxidized state of organic matter in the sulfur cycle in all cases as a product of pollution sources related to mining and industrial wastes. Sodium, potassium and ammonium sulfate are highly soluble in water. The SO_2 anion also occurs frequently in rainfall in or near metropolitan areas where sulfate is produced as fossil fuel combustion by product. Industrial pollutants from tanneries, steel mills, sulfate pulp mills and textile plants may contaminate water (Zunae, 1990).

Environmental impact: Metropolitan area rainfall may show concentrations sometimes greater than 10 mg/L (Zunae, 1990).

Health effect: High levels of sulfate cause diarrhea and dehydration. No adverse health effect noted (Zunae, 1990).

Results from the Study area: The sulphate contents in D.I.Khan area range from 15-1600 mg/L in samples taken from different areas of D.I.Khan district (Table 3.1). According to US-EPA, maximum contamination level for sulphate is 250 mg/L. Hence areas where the concentration of sulphate in hazardous are, mostly in the middle and lower part of D.I.Khan district (Fig. 3.9). The highest concentration (1600 mg/L) is noticed in the deep water at Poroa area (Fig. 3.9 & Table 3.3). SO_4 concentration in the waters of all the four categories in generally high and at many places it exceeds the permissible limit (Table 3.3 to 3.6). The tube-wells water at Tank, Umer Ada, Kullachi, Hathala, Potah, D.I.Khan city, Daraban, Chadhwan, Poroa and Ramak; shallow water at

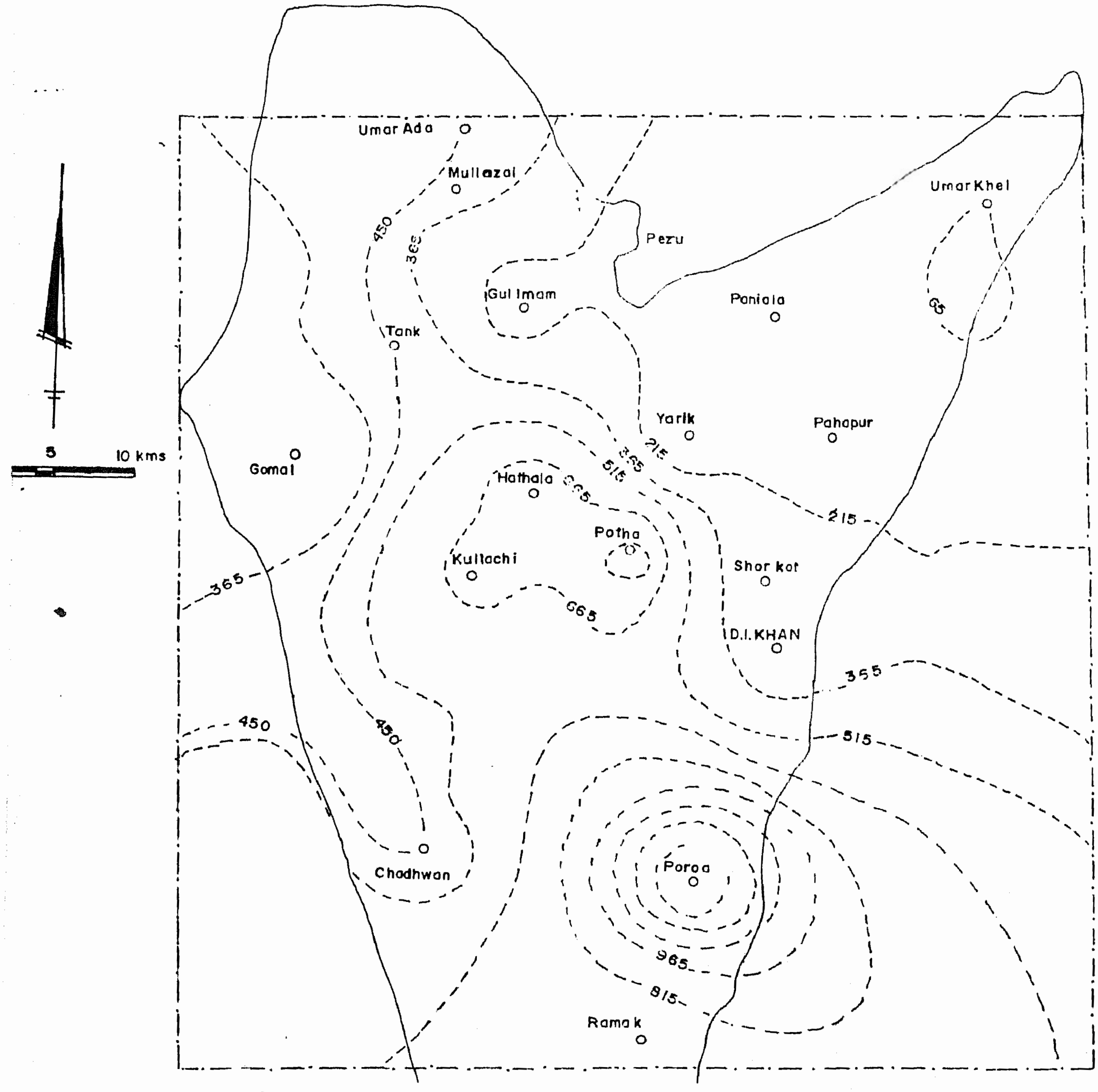


Fig. 3.9 **Contour map showing sulphate (SO_4) concentration in D.I. Khan division.**

Fig. 3.10 Sulphate (SO4) in deep waters (Tube-wells) from different locations at D.I.Khan division.

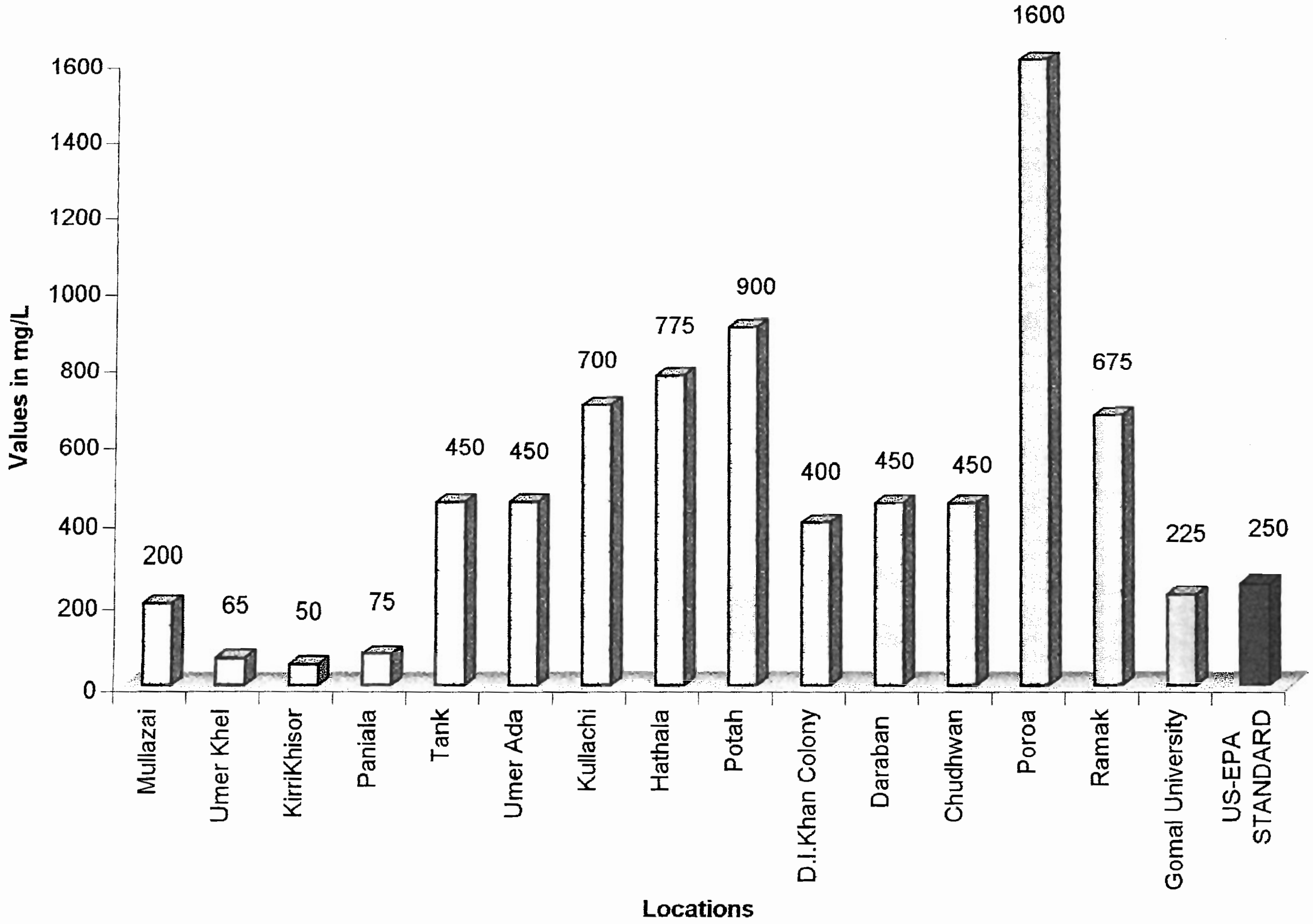
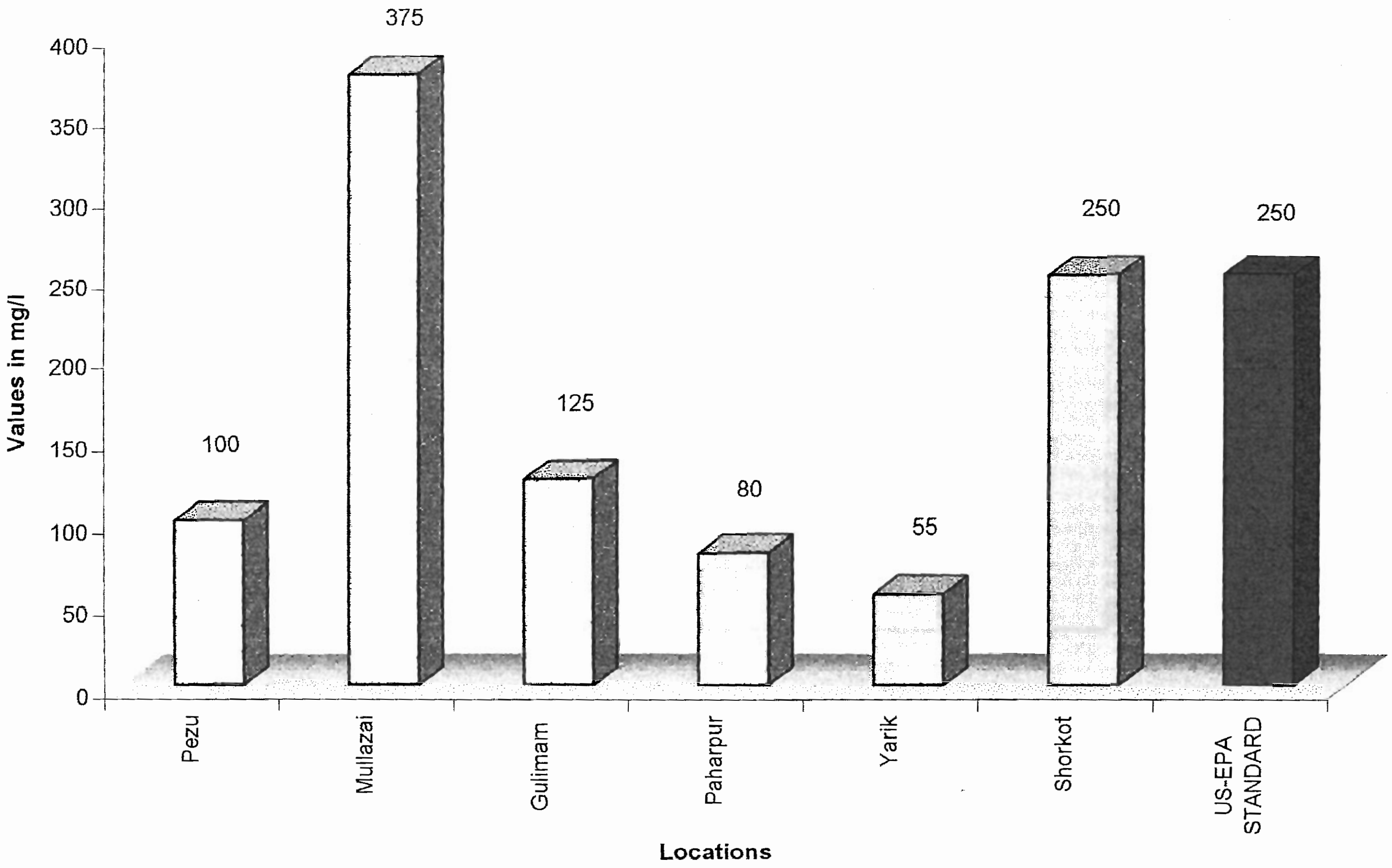


Fig. 3.11 Sulphate (SO4) in shallow waters (dug-wells/hand-pumps/settling-ponds) from different locations at D.I.Khan division.



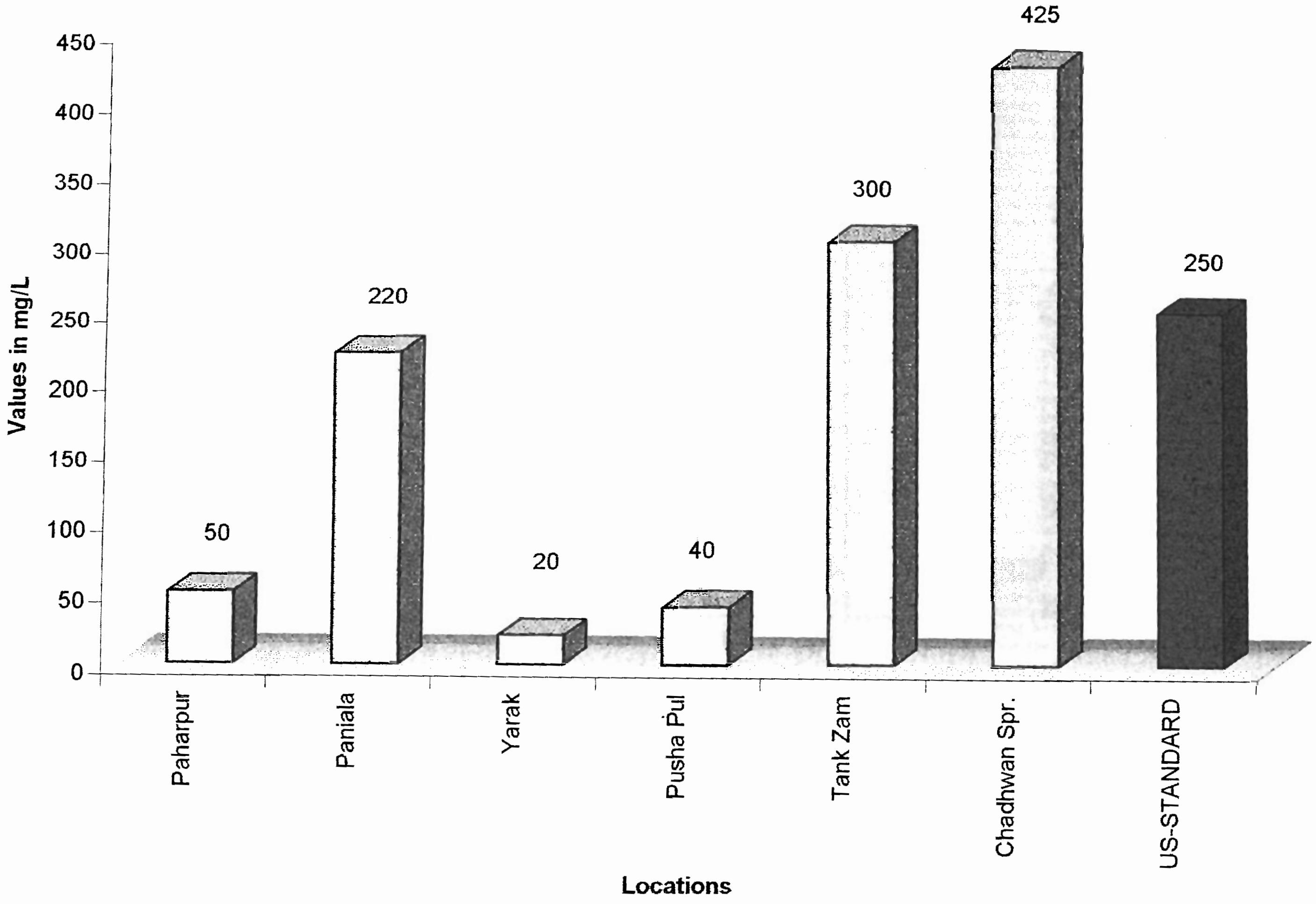
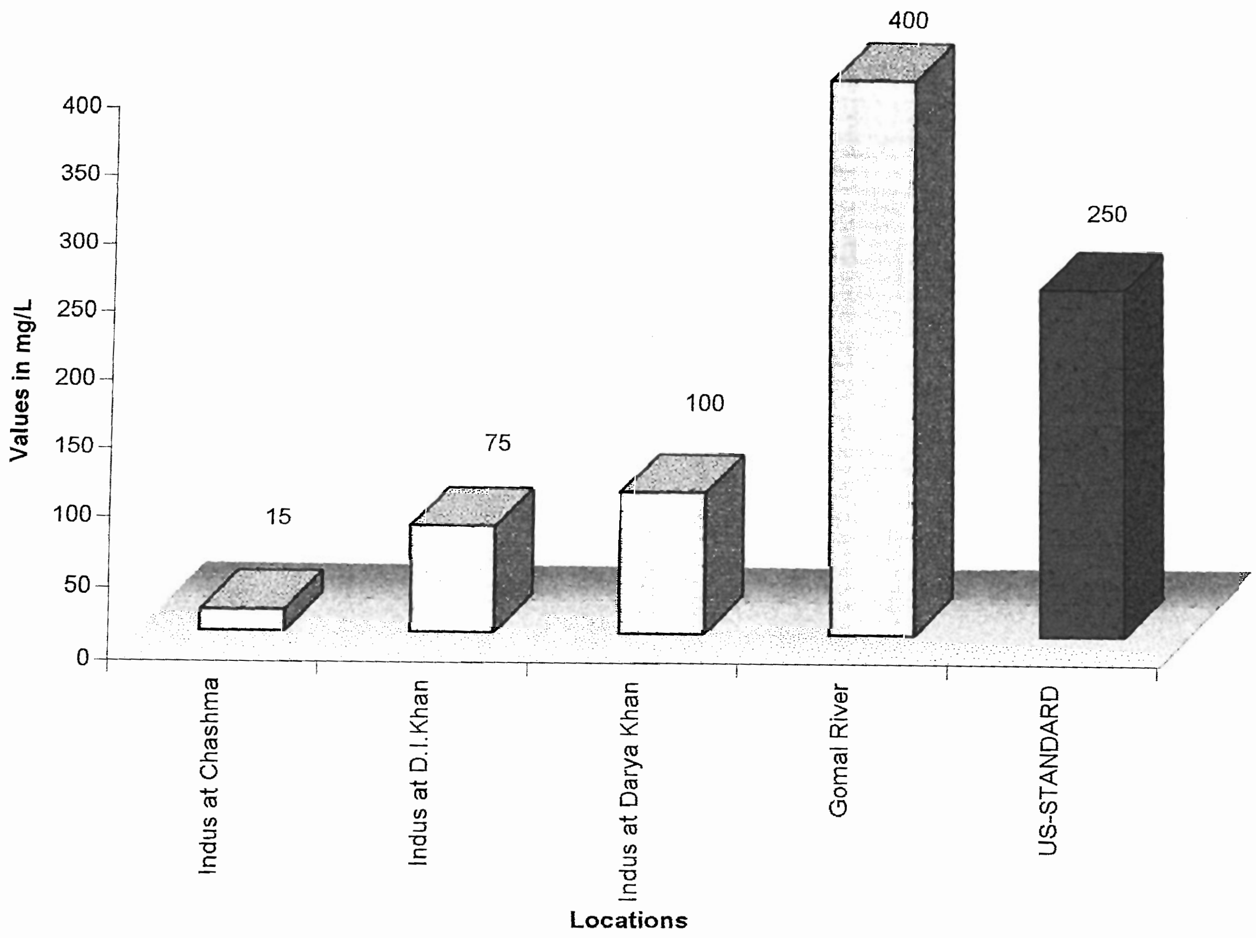


Fig. 3.12 Sulphate (SO4) in streams from different locations at D.I.Khan division.

Fig. 3.13 Sulphate (SO4) in rivers from different locations at D.I.Khan division.



Mullazai; stream water at Tank zam and Chudhwan spring and water of Gomal river are not safe for health as for as the SO_4 contents are concerned (Tables 3.3 to 3.6 & Figs. 3.10 to 3.13).

As well as the SO_4^- ion concentration in the study area is concerned, we can't relate it to industries and not to population. Because D.I.Khan division is not thickly populated and lacks industrial setup, so third option left is probably the geology of the area.

PHOSPHATE (PO_4)

Natural Existence: Phosphate is mainly a salt of phosphoric acid.

Occurrence: Phosphate in nature is found in phosphate rock, in the mineral known as aptite. It is important source of phosphorous. It is the in organic compound of bones and teeth.

Uses: It has greater use in the chemical fertilizer. It is used for production of special glasses, chinaware, backing power and detergents.

Environmental impact: Water supplies may contain phosphate derived from natural contact with Phosphate bearing minerals or through the fertilizers, sewage and industrial waste. Ground waters, therefore, are more likely to have higher phosphate concentration.

Health effect: The human daily requirement of phosphorous is equal to that of calcium. Dietary deficiency is not expected because of the abundance of phosphorous in the diet. No adverse health effect reported.

Results from the Study area: Phosphate generally varies from 0.02 to 0.29 mg/L in the waters of D.I.Khan area (Table 3.1). The concentration of PO_4 in the shallow water of Paharpur is reaching to maximum (0.29 μg/L) (Table 3.4 & Fig. 3.16). All the waters of D.I.Khan are, however, safe as far as the PO_4 concentration is concerned. The contouring pattern for PO_4 in D.I.Khan division is shown in Fig. 3.14.

CHLORIDE (Cl)

Chloride is a compound of chlorine. It remains soluble in water, unaffected by biological processes. Therefore, it is reducible by dilution. Seawater intrusion in well water may be a major source of contamination. In the past sodium chloride has been used as a tracer in water flow since it is not toxic, not visible and is not changed by the biological processes.

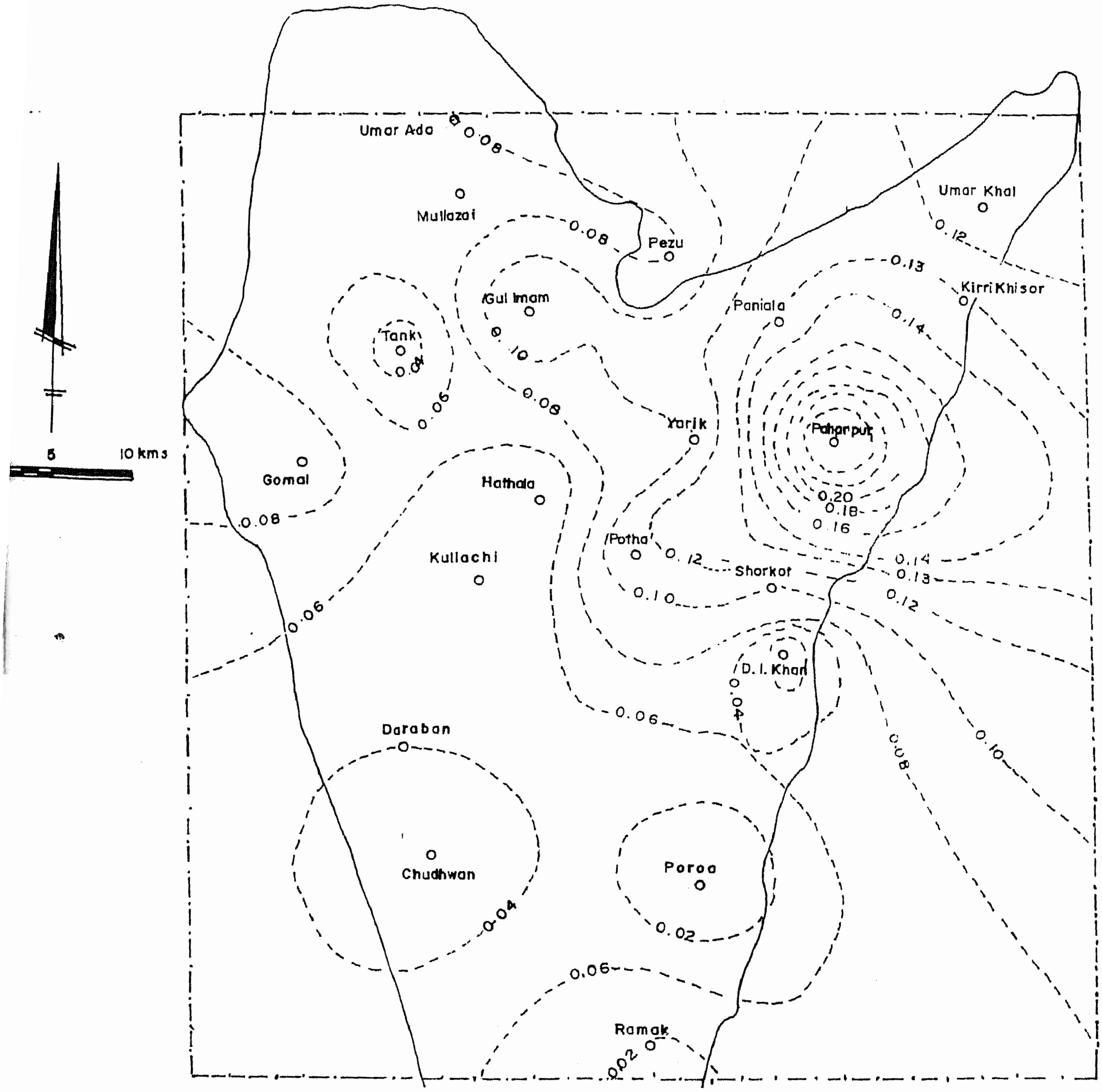


Fig. 3.14 **Contour map showing phosphate (PO_4) concentration in D.I. Khan division.**

Fig. 3.15 Phosphate (PO4) in deep waters (tube-wells) from different locations at D.I.Khan division.

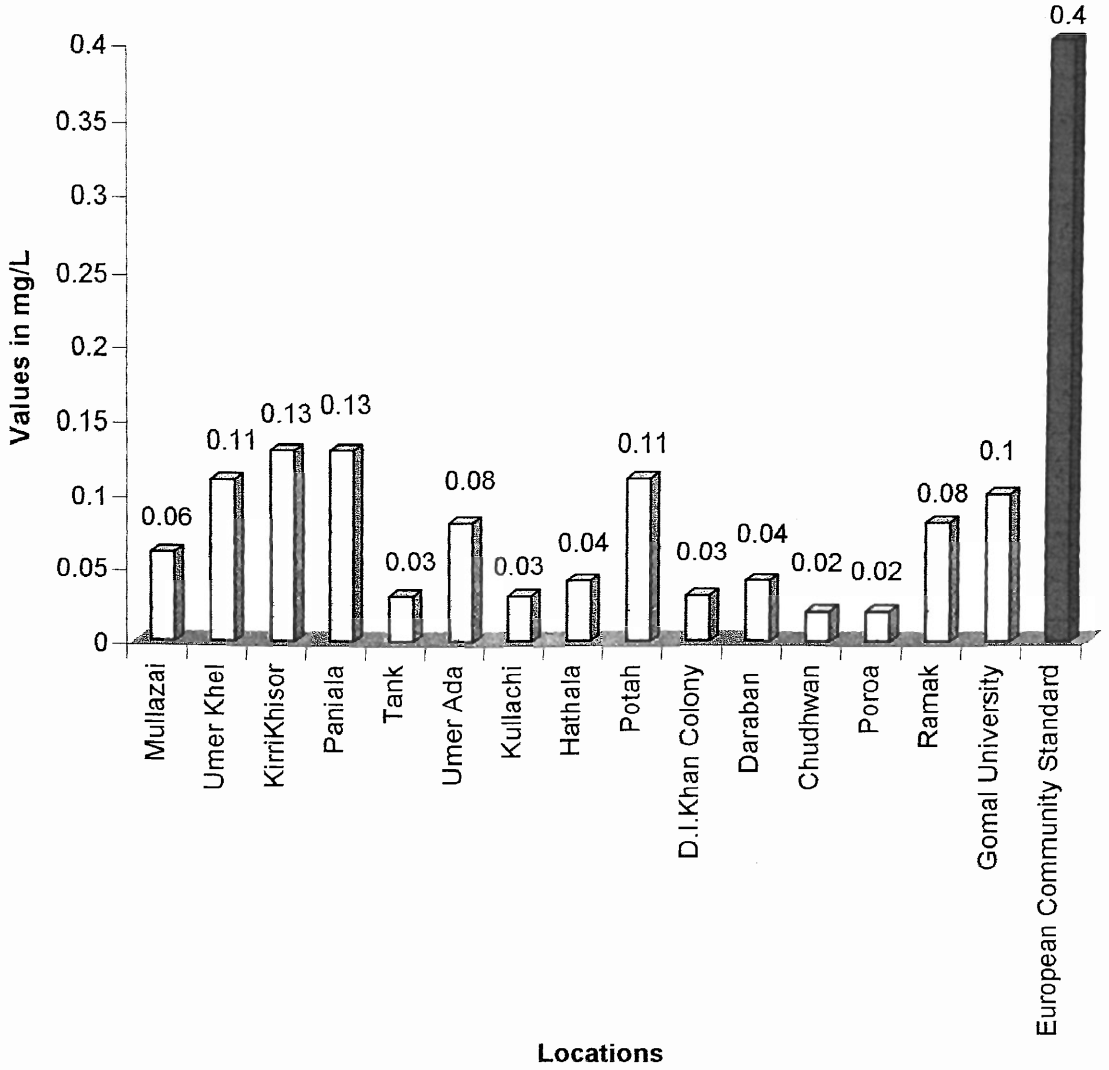


Fig. 3.16 Phosphate (PO4) in shallow waters (dug-wells/handpumps/settling-ponds) from different locations at d.I.Khan division.

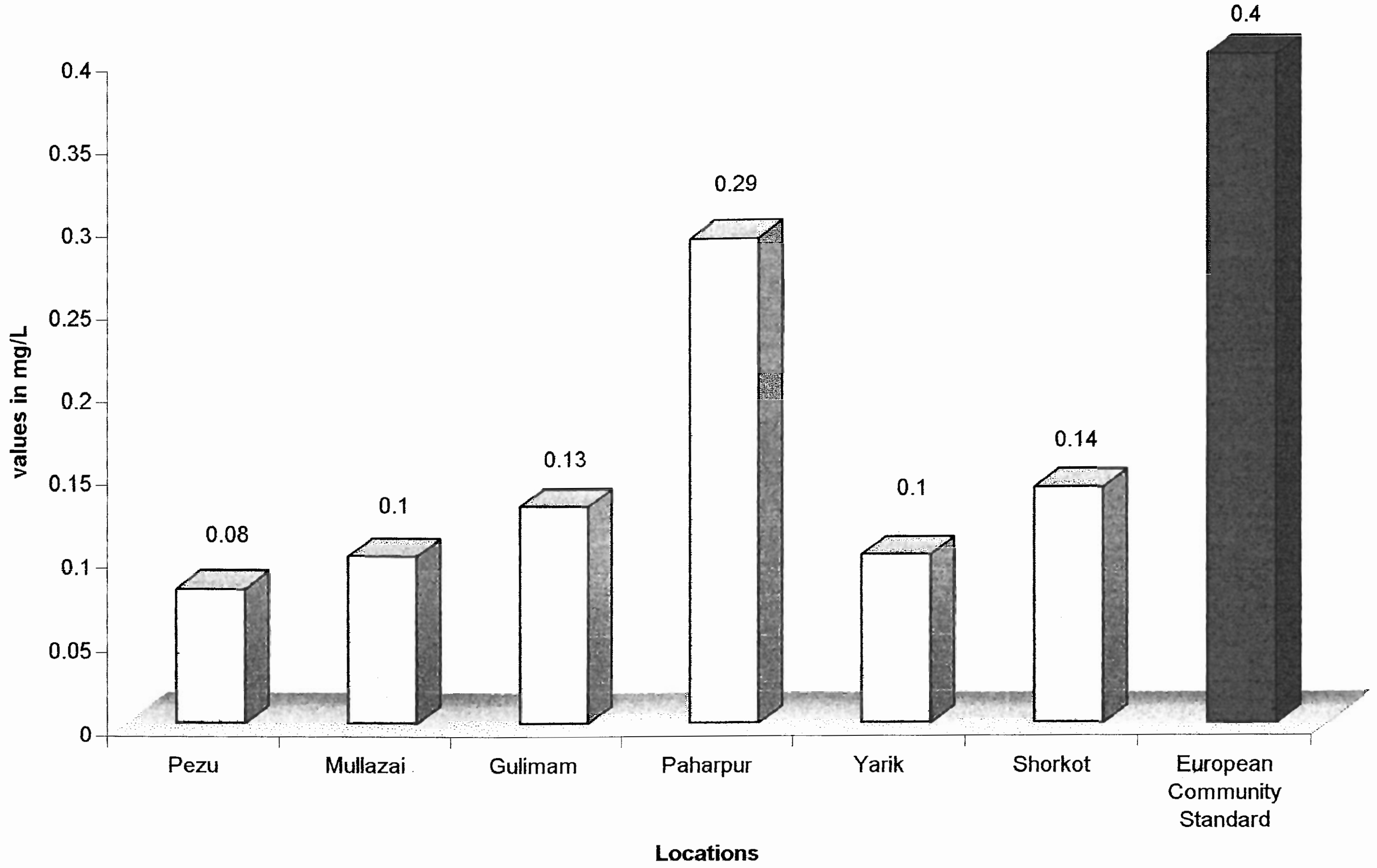


Fig. 3.17 Phosphate (PO4) in streams from different location at D.I.Khan division.

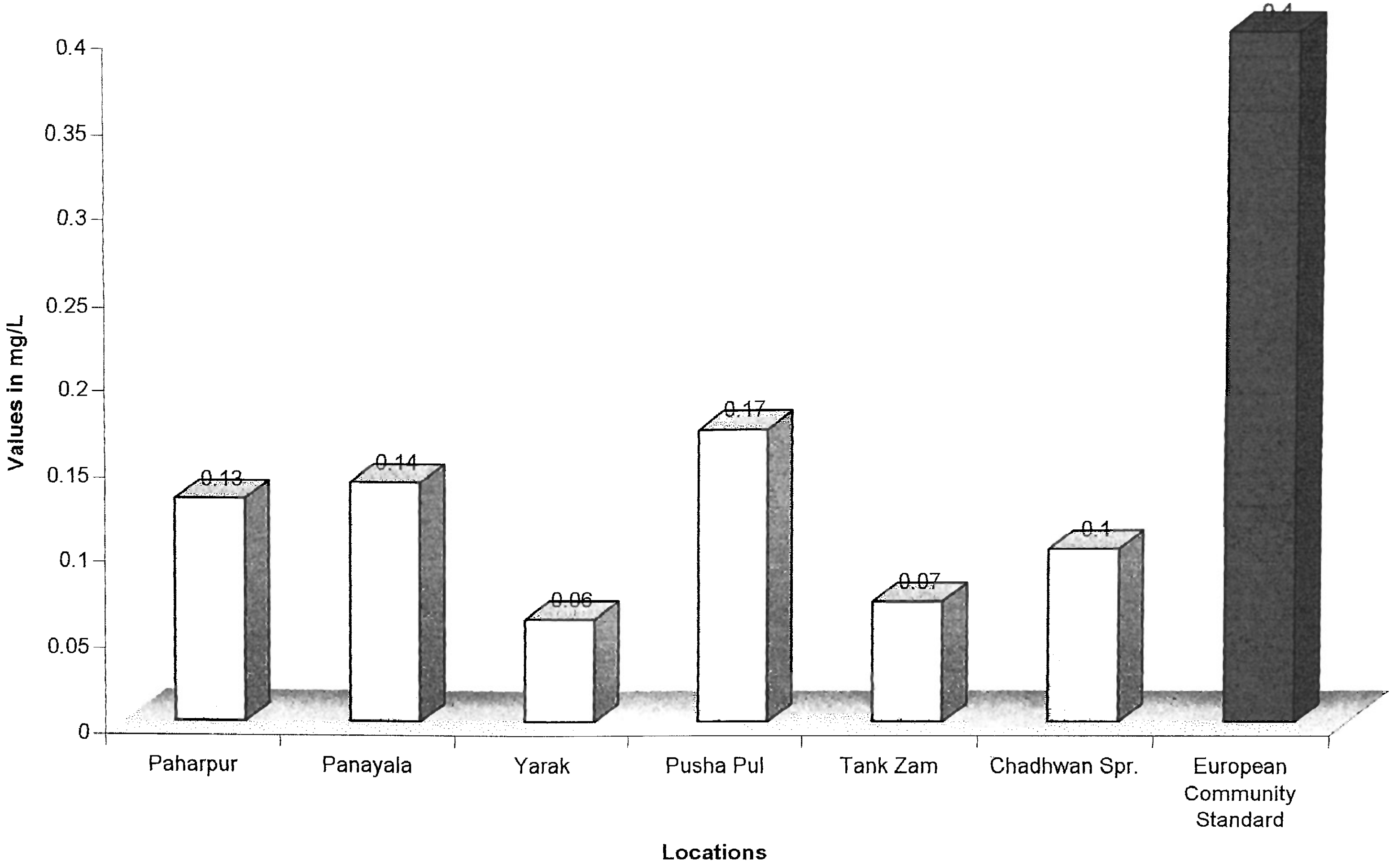
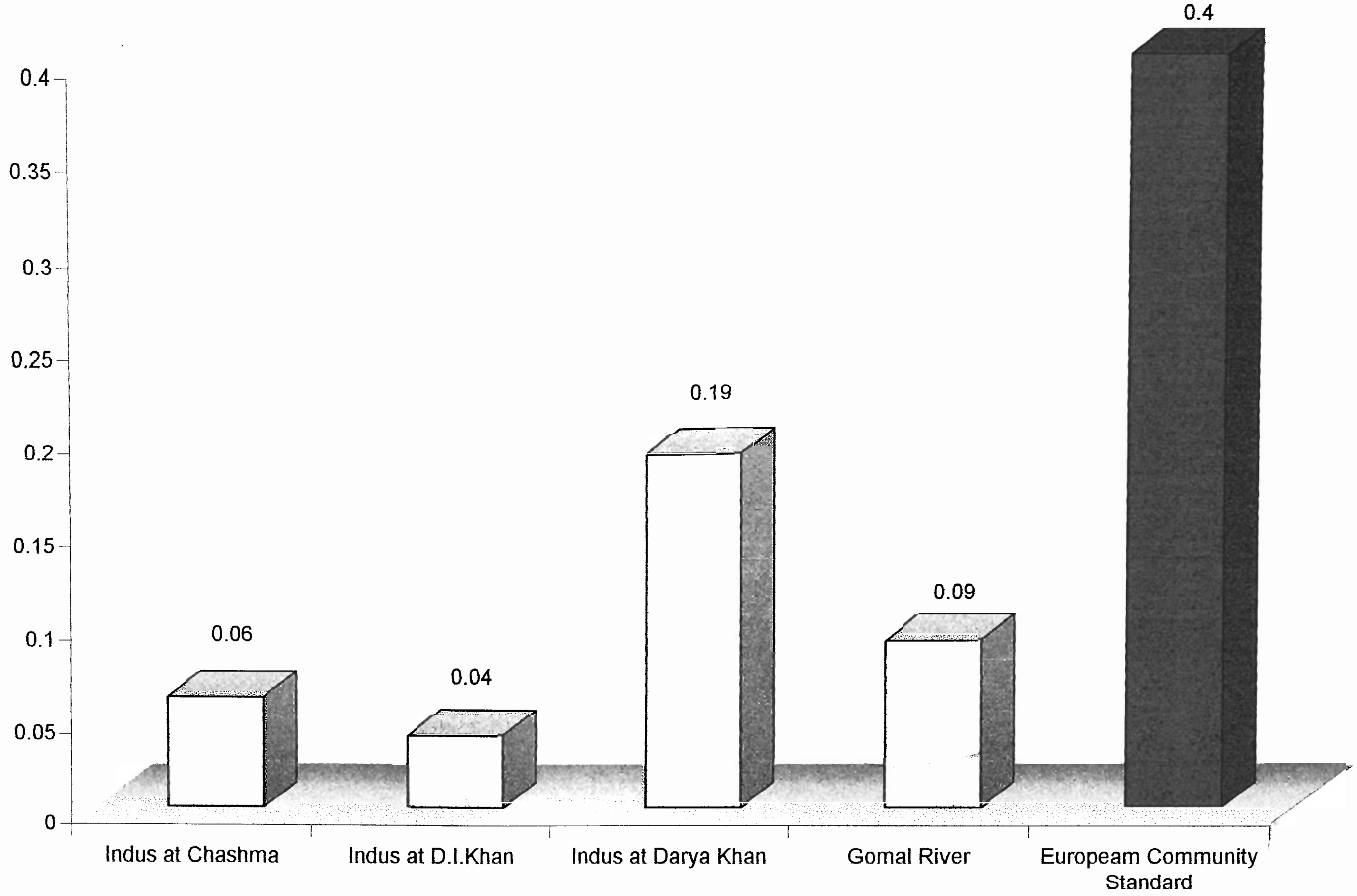


Fig. 3.18 Phosphate (PO4) in rivers form different locations at D.I.Khan division.



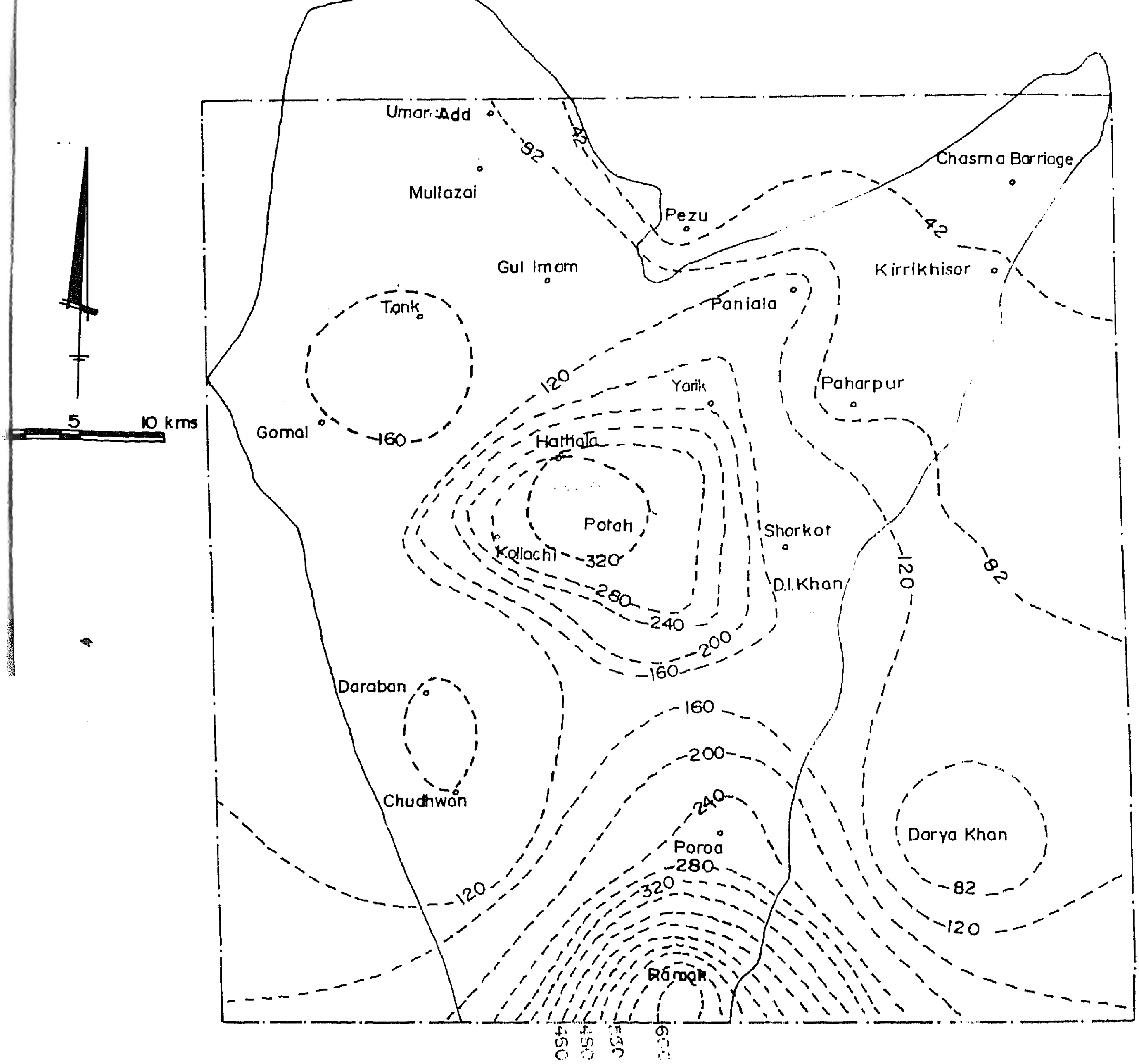


Fig. 3.19 Contour showing chloride concentration in D. I. Khan division.

It is not absorbed by soil and easily measured. No adverse health effect of chloride on human has been noted.

Results from the Study area: The Concentration of chloride (Cl) is ranging from 24 mg/L to 618 mg/L in the waters of D.I.Khan area (Table 3.1 & Fig. 3.19). The deep water at Kullachi (293 mg/L) and Ramak (618 mg/L). shallow water at Mullazai (333 mg/L) and Yarik (312 mg/L), stream water at paniala (269 mg/L) have exceeding the permissible limit of 250 mg/L (Table 3.3 3.4 & 3.5). The river waters. however. have low chloride (Table 3.6).

BICARBONATE (HCO_3)

These show the alkalinity of water. The concentration of bicarbonate in D.I.Khan division ranges from 75 to 460 mg/L. The highest concentration of bicarbonate obtained at chudhwan (i.e. 460 mg/L). It is lowest at Darya Khan of river Indus (75 mg/L). In other places where bicarbonate exceeds considerably the permissible limit of WHO guide line (1984), standards for safe drinking water are Mullazai (210 & 305 mg/L): Gullmam (250 mg/L): Kirrikhisor (230 mg/L): Pharpur (307.6 mg/L): Panaiala (362.5 mg/L): Shorkot (275 mg/L): Tank (410 mg/L): Umer Ada (265 mg/L): Gomal river (225 mg/L): Kullachi (205 mg/L):Potah (215 mg/l): D.I.Khan colony (345 mg/L): Chudhwan (460 mg/l) and Poroa (250 mg/l). Contour pattern for bicarbonate in the study area is shown in Fig. 3.20. For brief consult Table 3.1.

FLUORIDE: (F)

Physical Appearance: Fluorine is a halogen. defined as corrosive. pale greenish-yellow gaseous chemical element. The most reactive non-metallic element known. forming fluorides with almost all the known elements both organic and inorganic.

Chemistry:

Symbol	At. Wt.	At. No.	Density	Valance
F	18.998	9	1.696	1^-

Occurrence: Fluorine is found in fluorspar (Ca F_2) and cryolite (Na_2Al F6).

Uses: Fluorine and its compounds are used in producing uranium and over 100 commercial fluoro-chemicals including high temperature plastics. used in tooth pastes as well.

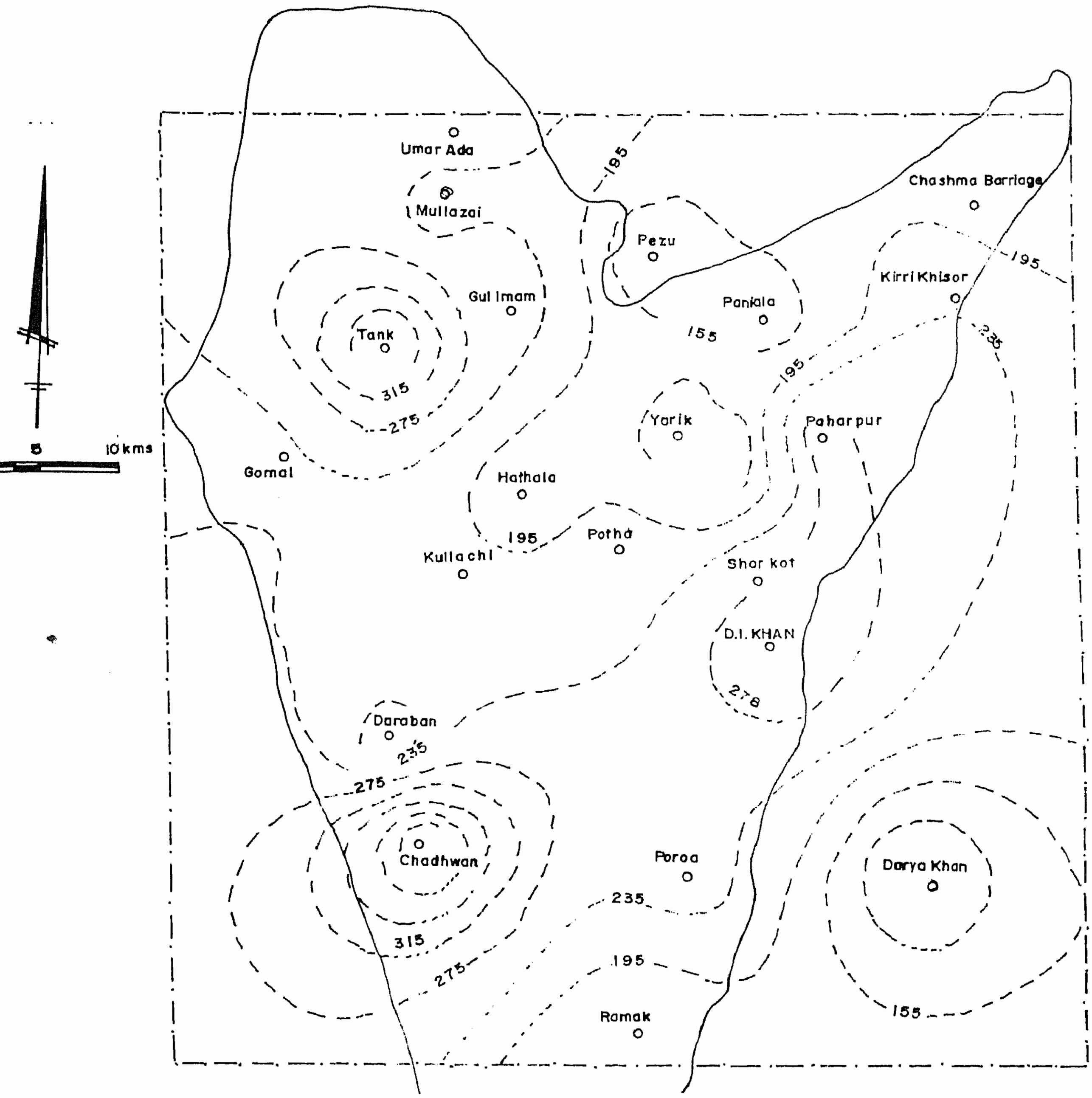


Fig. 3.20 Contour showing Bicarbonate (HCO_3) concentration in D. I. Khan division.

Characteristics: The free laments have a characteristic pungent odor. detectable at concentration below 20 ppb. Which is below the safe working level. The recommended maximum allowable concentration for an 8 hours time weighted exposure is 0.1 ppm.

Environmental impact: In surface water from rivers. average concentration has been recorded at 0.2 mg/L. In ground water an average of 0.3 - 0.4 mg/ L for limestone and dolomites. shales and clays as high as 8.7 mg/L average for alkali rocks. as low as 0.1 mg/L average for basaltic rocks. and 9.2. all in mg/L in granite rocks.

Health effect: Dental fluoresces appears in a very small percentage when fluoride in drinking water is in the range of 1 - 2 mg/L. Long term intake of fluoride in concentrations higher than 4 mg/L may cause asymptotic osteosclerosis in small percentage of persons. Crippling fluoresces has been detected in individuals exposed to fluoride levels from 10 - 40 mg/L. Sharply reduced dental caries formation has been determined when the fluoride level is at least 0.8 mg/L. reaching maximum benefits around 3 mg/L (Zaunae. 1990).

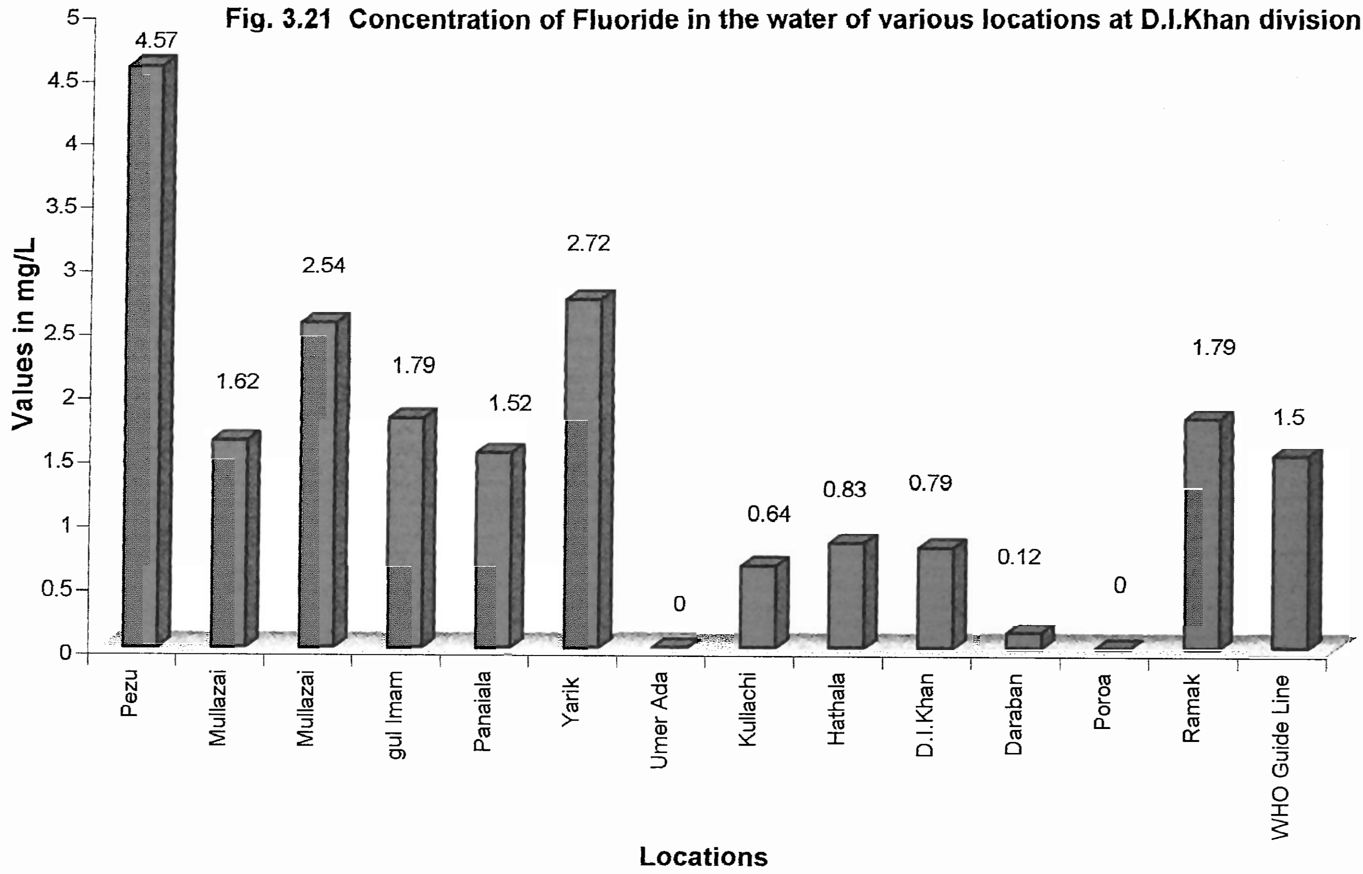
No Carcinogenicity or other adverse effects have been detected. As for as toxic reactions at high concentrations is concerned. fluoride with doses from 250 - 450 mg gives severe symptoms and causing death when reaching 4.0 g (Zaunae. 1990).

Results from the Study area: Fluoride contents in the drinking water of D.I.Khan division have been determined and the results given in Table 3.7 and graphically presented in figure 3.20. The fluoride concentration at many places exceeds the permissible limit is 1.5 mg/L (WHO. 1984) (Table 3.7. Fig. 3.20). These includes Pezu (4.57 mg/L); Mullazai (1.62 mg/L): Yarik (2.72 mg/L): Gulimam (1.79 mg/L): Paniala (1.52 mg/L) and Ramak (1.79 mg/L). Rest of the places have fluoride below permissible limit.

Table 3.7 FLORIDE ANALYSIS OF THE SELECTED SAMPLES

LOCATION	Sample NO.	FLORIDE (mg/l)	World standards for safe drinking water		
PEZU	A1	4.57	US-EPA (1988)	European Community	WHO guideline
MULLAZAI	A2	1.62			
MULLAZAI	A3	2.54	mg/l		
GUL IMAM	A4	1.79			
PANAYALA	A10	1.52	No carcinogenity	0.7 - 1.5	1.5
YARAK	A12	2.72			
UMER ADA	A18	0.00			
KULACHI	A20	0.64			
HATHALA	A21	0.83			
D.I.KHAN	A24	0.79			
DARABAN	A28	0.12			
POROA	A31	0.00			
RAMAK	A32	1.79			

Fig. 3.21 Concentration of Fluoride in the water of various locations at D.I.Khan division.



CLASSIFICATION OF D.I.KHAN WATERS

(Cation Elements Concentration)

IRON (Fe)

Physical Appearance: Iron is a white malleable, ductile, metallic chemical element, vital to animal and plant life.

Chemistry:

Symbol	At. Wt.	At. No	M. Pt.	B. Pt.	Sp. G.	Valance
Fe	55.85	26	1535°C	2750°C	7.87	2,3,4 &

Occurrence: It is the fourth most abundant element by weight in the earth's crust. Common ores are Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Limonite ($Fe_2O_3 . 3H_2O$), Sidrite ($FeCO_3$), and Pyrite (FeS_2) or chemically as oxides, carbonates, silicates, chlorides, sulfates and sulfides.

Environmental impact: In water supplies, the presence of iron is almost exclusively due to corrosion of pipes and storage tanks. In ground water it can be due to the effect of the elevated iron level in the earth strata related to feeding aquifer. Leaching of iron salts (acid mine drainage) and iron product industrial waste may be the source of iron pollution in water.

Salt of ferric and ferrous compounds (such as chlorides) is highly soluble in water. Ferric iron may become soluble under anaerobic conditions and reduces it to ferrous iron (Zaunae, 1990).

Health effect: It is a known fact that iron in trace amounts is essential for nutrition. In cases of iron deficiency anemia, larger doses are taken for therapeutic reasons. However, concentration of 1.0 mg/L would no significant effect in the daily diet (Zaunae, 1990).

Results from the Study area: Iron ranges from 0.5 to 43.3 mg/L, shows lowest in concentration at Mullazai and highest at Gomal river. Iron is critical as well as it presence in water is concerned. In D.I.Khan division iron concentration is high to very high in all most all the localities. The limit for safe drinking water is 0.3 (WHO guide line, 1984).

MAGNESIUM (Mg)

Physical appearance: Magnesium is a light silver-white malleable and ductile, metallic chemical element.

Chemistry:

Symbol	At. Wt.	At. No	M. Pt.	B. Pt.	Sp. G.	Valance
Mg	24.3	12	648°C	1090°C	1.74	2

Occurrence: It is eighth most abundant element in the earth's crust. It is never found as a free element. It is an important constituent of magnesite and common rock forming dolomite [$CaMg(CO_3)_2$].

Uses: It is used in flashlight photography, alloy, pyrotechnics and incendiary bombs.

Environmental impact: It is a nutritional element in animal and plant life. Most of the magnesium salts are very soluble in water.

Health effect: Magnesium has been considered as non-toxic to human life up to maximum acceptable level of 50mg/L (Zaunae, 1990). Chemical softening, reverse osmosis, electrodialysis and ion exchange can reduce high magnesium concentration (Zaunae, 1990).

Results form the Study area: Magnesium concentration ranges from 7.00 to 89.3 mg/L in the study area (Table 3.1). Lowest value obtained at Paniala and highest at Potah. The place where it exceeds the limit given by WHO guideline (Table 3.2) are Hathala (60.7 mg/L): Ramak (72.3 mg/L) and Poroa (73.7 mg/L).

MAGANESE (Mn)

Physical appearance: Maganese is a very brittle grayish-white metallic chemical element resembling iron but harder.

Chemistry:

Symbol	At. Wt.	At. No.	M. Pt.	B. Pt.	Sp. G.	Valance
Mn	54.94	25	1244°C	1962°C	7.3	1,2,3,4,6 & 7

Occurrence: Oxides, silicates and carbonates are most common maganese minerals such as Pyrolusite (MnO_2) and rhodochrosite ($MnCO_3$).

Uses: It is very important contributor to alloy and wildly used in chemical industry.

Environmental impact: The concentration higher than 1.0 mg/L is found where manganese-bearing minerals are contacted by water under reduced conditions or where bacteria are active. In water Mn concentration is suspected between 0.001 - 0.60 mg/L (Zaunae. 1990).

Health effect: Maganese is essential trace nutrient for plant and animals life. Nutritional deficiency in man has not been evaluated as a health hazard. Minimum requirements for nutrition have not yet been established (Zaunae. 1990).

World Health Organization (WHO) estimates an average daily requirement for normal physiological functions of 3–5mgs. Manganese poisoning for work-related exposure is rare. High concentration of manganese dust or fumes and prolong inhaling are necessary to cause chronic maganese poisoning (effect similar to Parkinson`s disease) Zaunae. 1990).

Results from the Study area: Maganese values obtain are lowest at Pezu (0.01 mg/L) and highest at Kullachi (0.51 mg/L). Apart from Kullachi it exceeds the permissible limit (WHO. 1984) are Mullazai (0.1 mg/L); Umerkhel (0.27 mg/L); Kirrikhisor (0.06 mg/L); Yarik (0.06 mg/L); Shorkot (0.08 mg/L); Tankzam (0.10 mg/L); Gomal river (0.21 mg/L); Hathala (0.08 mg/L); Potah (0.10 mg/L); D.I.Khan colony (0.11,0.15,0.09 mg/L); Indus at Chashma (0.08 mg/L); Daraban (0.38 mg/L); Ramak (0.16 mg/L) and Gomal University (0.16 mg/L) (Table3.1 & 3.2).

SODIUM (Na)

Physical Appearance: Sodium is a soft silver - white. extremely active alkaline element, found in nature only in combined form. It is the sixth most abundant element on earth.

Chemistry:

Symbol	At. Wt.	At. No.	M. Pt.	Sp. G.	Valance
Na	22.99	11	97.81°C	0.97	1^{-}

Uses: Sodium compounds are used in paper, glass. soap. textile and petroleum chemical and metal industries.

Occurrence: It commonly occurs as rock salt NaCl. Soda ash ($Na_2 CO_3$). baking soda ($NaH CO_3$) and caustic soda (NaOH), sodium phosphates. sodium thio-sulfate and borax ($Na B_4 O_7$) 10 H_2O).

Environmental impact: Sodium is a natural constituent of water, but its concentration is increased by contamination from rock salt treatment of road. It also concentrates in ground water by the rocks of the area.

Health effect: Sodium is considered harmful in drinking water at higher concentrations to persons suffering from Cardiac, renal and circulatory diseases (Zaunae, 1990). High blood pressure is reported in communities using high level of sodium (Zaunae, 1990).

Results form the Study area: It dominates in the entire cation domain. It has lowest value in the waters at Chashma of Indus river (i.e. 15.2 mg/L) and as rich in concentration as 402.5 mg/L at Ramak towards south. Hence the trend remains the same as previous. Concentration increase from north to south (Table 3.1 & 3.2).

POTASSIUM (K)

Natural Existence: A soft light silver-white, wax like, metallic, common chemical element of alkali group, similar to sodium that oxidized rapidly when exposed to air. Potassium is seventh most abundant element of the earth's crust. It is never found free in nature. Most potassium minerals are insoluble. It decomposes in water, generating hydrogen and catching fire spontaneously. Chemically many potassium salts are very important such as hydroxide, nitrate, carbonate, chloride, chlorate, bromide, iodide, cyanide, sulfate and chromate.

Uses: It is extensively used in fertilizers in glass and in a limited way in the chemical industry.

Environmental impact: Potassium is definitely an essential nutritional element for human animal and plants. It is non-toxic but act as a cathartic in excessive concentration (Zaunae, 1990).

Health effect: The effect of potassium in drinking water is negligible either to reach minimum requirements or to cause any health problem (Zaunae, 1990).

Results from the Study area: The concentration of K in the waters of D.I.Khan division is generally ranging from 1.65 mg/L to 33.9 mg/L (Table 3.1). It is < 12 mg/L in all types of deep, shallow and surface waters (Table 3.3- 3.6). However, one sample collected from tube-well at Paniala has the highest (33 mg/L) concentration of K (Table 3.3).

CALCIUM (Ca)

Physical Appearance: Calcium is a silver-white, chemically active metallic chemical element, found always in combination with other elements in Limestone, marbles, and chalk. It is one of the alkaline earth element and is fifth in abundance in the earth crust (3%). It is an essential constituent of bones and teeth.

Chemistry:

Symbol	At. Wt.	At. No.	M. Pt.	B. Pt.	Sp. G.	Valance
Ca	40.08	20	839°C	1484°C	1.55	2

Occurrence: It occurs in most common compounds such as limestone ($CaCO_3$), gypsum ($CaSO_4$, $2H_2O$), fluorite (CaF_2), calcium carbide (CaC_2), chloride ($CaCl_2$), Cyanamide ($Ca\ CN_2$), hypochlorite $|Ca(ClO)_2|$, Nitrate $|Ca(NO_3)_2|$ and sulfide (CaS).

Uses: calcium is used as calcium oxide, quick lime (CaO), produced by heating limestone. Then turn into slaked lime $|Ca(OH)_2|$ by slow addition of water, for a more stabilized condition. Also used in construction and chemical industries.

Controlled heating of limestone produces the base material of portland cement widely used in construction. It is also used as a reducing agent in preparation of other metals and in treatment of ferrous and non-ferrous alloys. It is also used in the preparation of calcium hydroxide and bleaching powder.

Environmental impact: Because of no toxicity in regard to health hazards, there is no wide range survey for determination of calcium in its elemental form.

Health effect: No adverse health effect has been sorted but kidney or bladder stones may be suspected (Zaunae, 1990). However, high content of calcium and magnesium in drinking water should be avoided.

Results from the Study area: Calcium is useful for human health. It plays an important role in the growth of bones and teeth. The lowest value of calcium is obtained at

Table 3.8 Deep water (Tube-wells) Data for Piper Diagram (Cations)

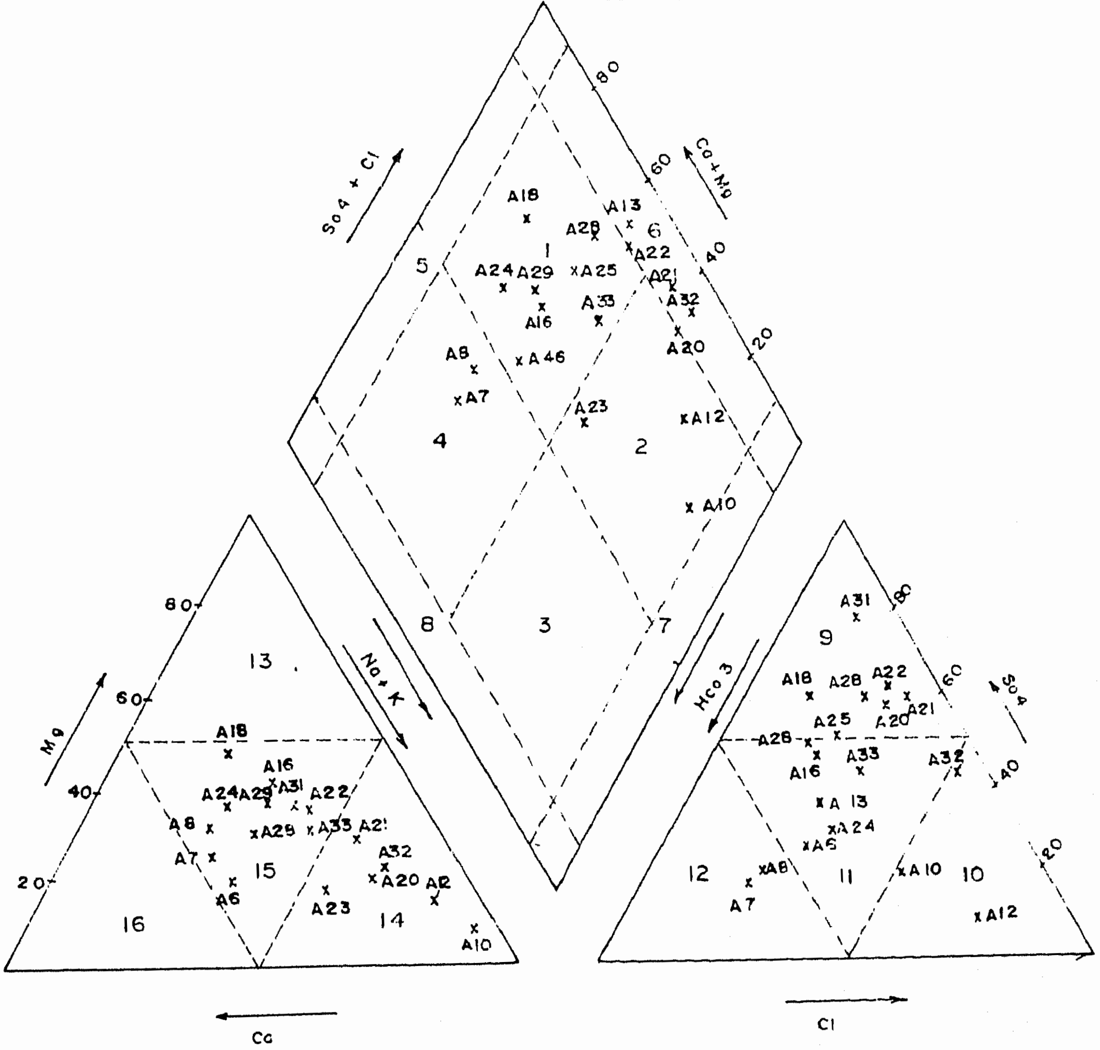
Locality	S.No.	Cations (ppm)				Cations (epm)					SUM [Mg+Ca(Na+K)]	Cations (epm)		
		Mg	Ca	Na	K	Mg	Ca	Na	K	Na+K		Mg %	Ca %	(Na+K) %
Mullazai	A2	27.30	28.00	157.50	2.45	2.24	1.40	6.85	0.06	6.91	10.55	21.23	13.27	65.50
Umer Khel	A6	15.50	47.00	40.90	8.30	1.27	2.34	1.78	0.21	1.99	5.60	22.68	41.79	35.54
Kirrikhisor	A7	15.50	47.70	30.30	8.60	1.27	2.38	1.32	0.22	1.54	5.19	24.47	45.86	29.67
Panayala	A10	7.00	7.70	93.50	33.90	0.57	0.38	4.07	0.87	4.94	5.89	9.68	6.45	83.87
Tank	A16	71.00	68.70	107.00	2.92	5.84	3.43	4.65	0.07	4.72	13.99	41.74	24.52	33.74
Umar Ada	A18	39.50	42.10	32.50	3.22	3.25	2.10	1.41	0.08	1.49	6.84	47.51	30.70	21.78
Kulachi	A20	33.40	40.40	190.00	2.97	2.75	2.02	8.26	0.07	8.33	13.10	20.99	15.42	63.59
Hathala	A21	60.70	54.90	215.00	11.30	4.99	2.74	9.35	0.29	9.64	17.37	28.73	15.77	55.50
Potah	A22	89.30	85.50	204.50	11.10	7.34	4.27	8.90	0.28	9.18	20.79	35.31	20.54	44.16
D.I.Khan	A23	17.90	43.20	98.50	12.60	1.47	2.15	4.28	0.32	4.60	8.22	17.88	26.16	55.96
D.I.Khan	A24	17.20	37.50	41.20	8.40	1.41	1.87	1.79	0.21	2.00	5.28	26.70	35.42	37.88
D.I.Khan	A25	17.90	40.60	43.30	5.40	1.47	2.03	1.88	0.13	2.01	5.51	26.68	36.84	36.48
Daraban	A28	48.70	85.30	107.00	3.94	4.00	4.30	4.65	0.10	4.75	13.05	30.65	32.95	36.40
Chaudhwan	A29	51.70	60.80	88.00	3.62	4.25	3.03	3.82	0.09	3.91	11.19	37.98	27.08	34.94
Poroa	A31	73.70	83.90	175.00	9.40	6.06	4.19	7.61	0.24	7.85	18.10	33.48	23.15	43.37
Ramak	A32	72.30	84.30	402.50	11.10	5.95	4.21	17.51	0.28	17.79	27.95	21.29	15.06	63.65
Gomal University	A33	35.90	44.00	96.50	70.00	2.95	2.20	4.20	0.18	4.38	9.53	30.95	23.08	45.96

Table 3.9 **Deep water (Tube-wells) Data for Piper Diagram (Anions)**

Locality	S.No.	Cations (ppm)			Cations (epm)			SUM (HCO_3+Ci+SO_4)	Cations (epm)		
		HCO_3	Ci	SO_4	HCO_3	Ci	SO_4		HCO_3 %	Ci %	SO_4 %
Mullazai	A2	210.00	241.00	200.00	3.44	6.80	4.16	14.40	23.89	47.22	28.89
Umer Khel	A6	148.00	57.20	65.00	2.43	1.61	1.35	5.39	45.08	29.87	25.05
Kirrikhisor	A7	230.00	45.00	50.00	3.77	1.30	1.04	6.11	61.70	21:28	17.02
Panayala	A10	135.00	145.30	75.00	2.21	4.10	1.56	7.87	28.08	52.10	19.82
Tank	A16	410.00	168.00	450.00	6.72	4.74	9.37	20.83	32.26	22.76	44.98
Umar Ada	A18	265.00	89.00	450.00	4.34	2.51	9.37	16.22	26.76	15.47	57.77
Kulachi	A20	205.00	293.00	700.00	3.36	8.26	14.57	26.19	12.83	31.54	55.63
Hathala	A21	165.00	333.00	775.00	2.70	9.39	16.14	28.23	9.56	33.26	57.17
Potah	A22	215.00	314.00	900.00	3.52	8.85	18.74	31.11	11.31	28.45	60.24
D.I.Khan	A23	345.00	152.50	275.00	5.65	4.30	5.73	15.68	36.03	27.42	36.54
D.I.Khan	A24	130.00	63.00	75.00	2.13	1.78	1.56	5.47	38.94	32.54	28.52
D.I.Khan	A25	125.00	72.00	200.00	2.05	2.03	4.16	8.24	24.88	24.64	50.49
Daraban	A28	175.00	149.00	450.00	2.86	4.20	9.37	16.43	17.41	25.56	57.03
Chaudhwan	A29	410.00	130.00	450.00	6.72	3.67	9.37	19.76	34.01	18.57	47.42
Poroa	A31	250.00	244.00	1600.00	4.10	6.88	33.31	44.29	9.26	15.53	75.21
Ramak	A32	155.00	618.00	675.00	2.54	17.43	14.05	34.02	7.47	51.23	41.30
Gomal University	A33	215.00	148.00	225.00	3.52	4.17	4.68	12.37	28.46	33.71	37.83

TYPES OF FIELD

1	Na – K, Cl – SO_4	Type
2	HCO_3, Ca – Mg	Type
3	Cl – SO_4, Na – K	Type
4	Ca – Mg HCO_3	Type
5	Ca – Mg	Type
6	Cl – SO_4	Type
7	Na – K	Type
8	HCO_3 – CO_3	Type
9	SO_4 -	Type
10	CR	Type
11	No dominant	Type
12	HCO_3	Type
13	Mg	Type
14	Na / K	Type
15	No dominant	Type
16	Ca	Type



ig. 3.22 **Piper's diagram showing water chemistry of deep water (tube-wells) in D.I.Khan divisio**

Table 3.10 **Shallow water (Dug-wells / Hand-pumps / Settling ponds) Data for Piper Diagram (Cations)**

Locality	S.No.	Cation (ppm)				Cations (epm)				(Na+K)	SUM [Mg+Ca+(Na+K)]	Cations (epm)		
		Mg	Ca	Na	K	Mg	Ca	Na	K			Mg %	Ca %	(Na+K) %
Pezu	A1	18.20	35.50	27.10	7.90	1.50	1.77	1.18	0.20	1.38	4.65	32.26	38.06	29.68
Mullazai	A3	49.20	49.40	214.00	2.03	4.04	2.46	9.31	0.05	9.36	15.86	25.47	15.51	59.02
Gul Imam	A4	9.00	6.40	252.50	1.65	0.74	0.32	6.61	0.04	6.65	7.71	9.60	4.15	86.25
Paharpur	A8	31.30	68.10	43.47	11.40	2.57	3.40	1.90	0.29	2.19	8.16	31.50	41.67	26.84
Shorkot	A15	49.00	46.50	92.50	7.40	4.02	2.32	4.00	0.19	4.19	10.53	38.18	22.03	39.79

Table 3.11 **Shallow water (Dug-wells / Hand-pumps / Settling ponds) Data for Piper Diagram (Anions)**

Locality	S.No.	Anions (ppm)			Anions (epm)			SUM (HCO_3 +Ci+SO_4)	Anions (epm)		
		HCO_3	Ci	SO_4	HCO_3	Ci	SO_4		HCO_3 %	Ci %	SO_4 %
Pezu	A1	125.0	40.01	100	2.05	1.13	2.08	5.26	38.97	21.48	39.54
Mullazai	A3	305.0	333.00	375	5.00	9.39	7.81	22.20	22.52	42.30	35.18
Gul Imam	A4	250.0	241.00	125	4.10	6.80	2.60	13.50	30.37	50.37	19.26
Paharpur	A8	307.5	69.80	80	5.04	1.97	1.67	8.68	58.06	22.70	19.24
Shorkot	A15	275.0	145.00	250	4.51	4.09	5.21	13.81	32.66	29.62	37.73

TYPES OF FIELD

1	Na – K, Cl – SO_4	Type
2	HCO_3, Ca – Mg	Type
3	Cl – SO_4, Na – K	Type
4	Ca – Mg HCO_3	Type
5	Ca – Mg	Type
6	Cl – SO_4	Type
7	Na – K	Type
8	HCO_3 – CO_3	Type
9	SO_4 -	Type
10	CR	Type
11	No dominant	Type
12	HCO_3	Type
13	Mg	Type
14	Na / K	Type
15	No dominant	Type
16	Ca	Type

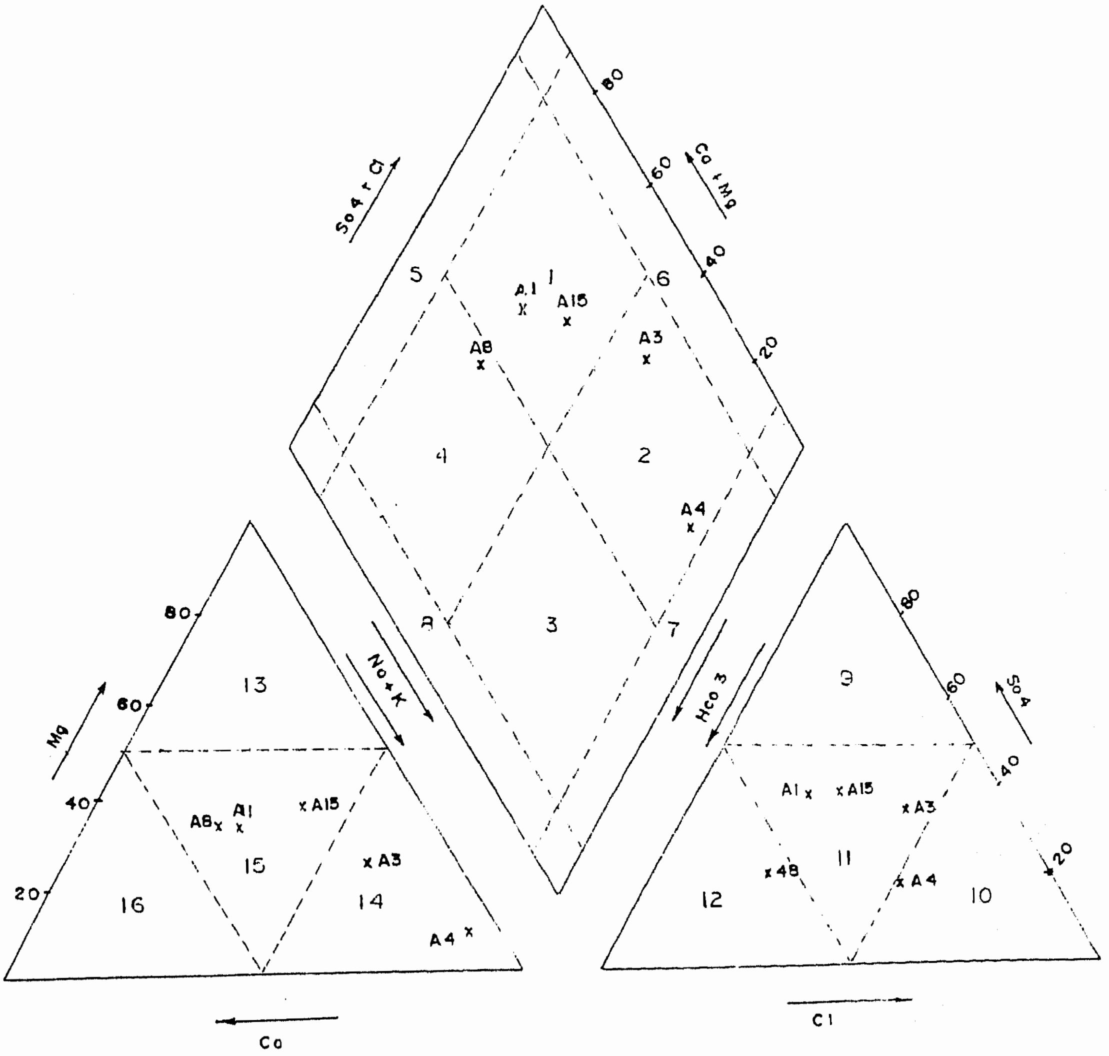


Fig. 3.23 Piper's diagram showing water chemistry of Shallow water (dug-wells/hand-pumps/settling-ponds) in D.I.Khan division.

Table 3.12 Streams / Nalas Data for Piper Diagram (Cations)

Locality	S.No.	Cation (ppm)				Cations (epm)				SUM [Mg+Ca+(Na+K)]	Cations (epm)		
		Mg	Ca	Na	K	Mg	Ca	Na	K		Mg %	Ca %	(Na+K) %
Paharpur stream	A9	12.80	28.40	20.10	3.73	1.05	1.42	0.87	0.10	3.44	30.52	41.28	28.20
Panayala stream	A11	19.10	36.40	179.50	9.50	1.57	1.82	7.81	0.24	11.44	13.72	15.91	70.37
Yarak stream	A13	16.10	33.20	120.00	2.90	1.32	1.66	5.22	0.15	8.35	15.81	19.88	64.31
Pusha Pul stream	A14	12.60	31.20	16.80	3.70	1.04	1.60	0.70	0.09	3.46	30.06	46.24	23.70
Tank Zam stream	A17	29.40	1.04	49.10	3.44	2.42	2.12	2.14	0.09	6.77	35.75	31.31	32.94
Chadhwan stream	A30	36.60	2.42	51.50	3.83	3.01	2.59	2.24	0.10	7.79	37.91	32.62	29.47

Table 3.13 Streams / Nalas Data for Piper Diagram (Anions)

Locality	S.No.	Anions (ppm)			Anions (epm)			SUM (HCO_3+Ci+SO_4)	Anions (epm)		
		HCO_3	Ci	SO_4	HCO_3	Ci	SO_4		HCO_3 %	Ci %	SO_4 %
Paharpur stream	A9	137.50	31.20	50.00	2.25	0.90	1.04	4.19	53.70	21.48	24.82
Panayala stream	A11	362.50	269.10	220.00	5.94	7.60	4.58	18.12	32.78	41.94	25.27
Yarak stream	A13	110.00	190.20	20.00	1.80	5.36	0.42	7.58	23.75	70.71	5.54
Pusha Pul stream	A14	97.50	26.30	40.00	1.60	0.74	0.83	3.17	50.47	23.34	26.18
Tank Zam stream	A17	140.00	89.10	300.00	2.30	2.51	6.25	11.06	20.80	22.69	56.51
Chadhwan stream	A30	145.00	73.00	425.00	2.38	2.06	8.85	13.29	17.90	15.50	66.59

TYPES OF FIELD

1	Na – K, Cl – SO_4	Type
2	HCO_3, Ca – Mg	Type
3	Cl – SO_4, Na – K	Type
4	Ca – Mg HCO_3	Type
5	Ca – Mg	Type
6	Cl – SO_4	Type
7	Na – K	Type
8	HCO_3 – CO_3	Type
9	SO_4 -	Type
10	CR	Type
11	No dominant	Type
12	HCO_3	Type
13	Mg	Type
14	Na / K	Type
15	No dominant	Type
16	Ca	Type

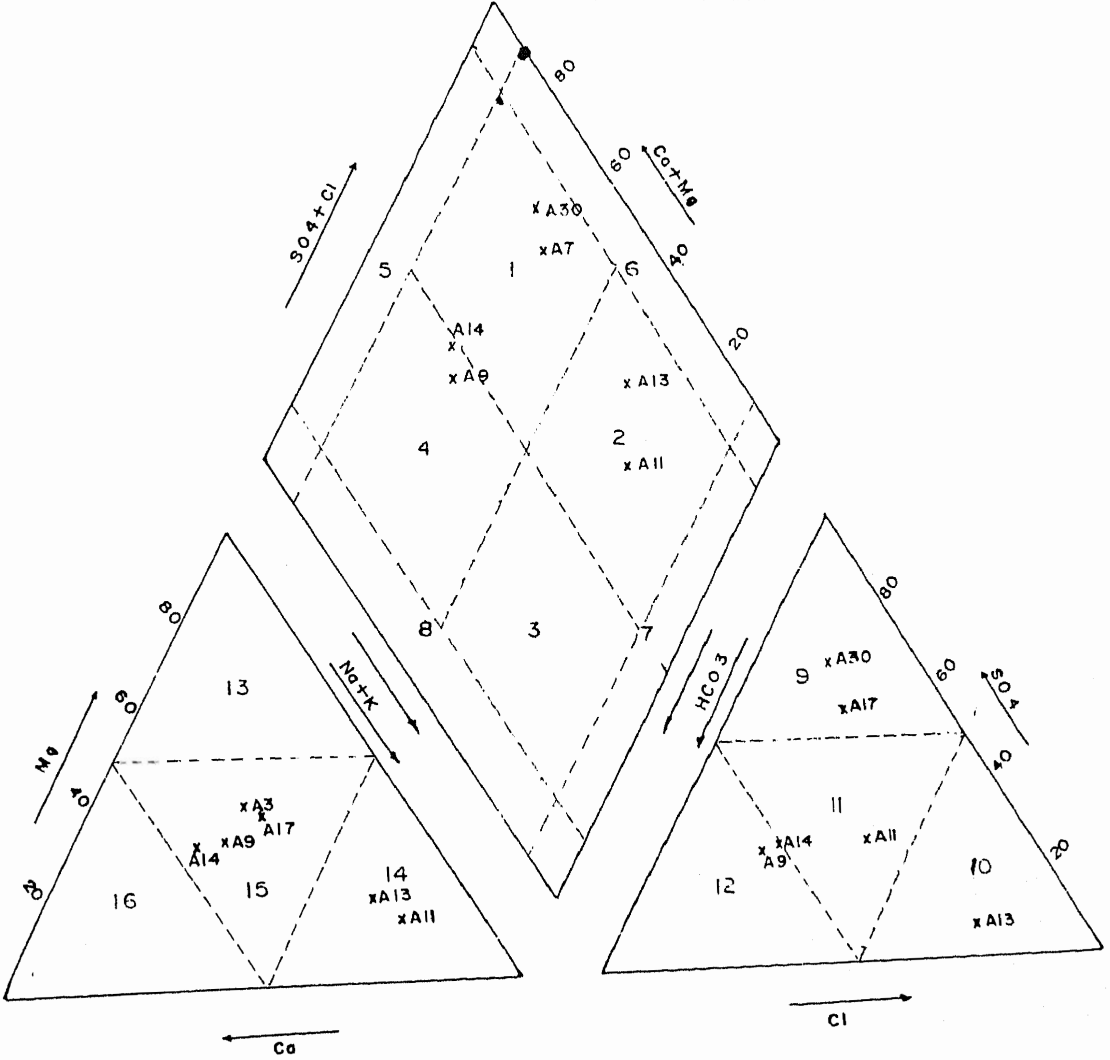


Fig. 3.24 **Piper's diagram showing water chemistry of streams in D.I.Khan division.**

Table 3.14 River Data for Piper Diagram (cations)

Locality	S.No.	Cation (ppm)				Cations (epm)				(Na+K)	SUM [Mg+Ca+(Na+K)]	Cations		(epm)
		Mg	Ca	Na	K	Mg	Ca	Na	K			Mg %	Ca %	(Na+K) %
Indus at Chashma	A5	11.80	29.30	15.20	3.74	0.97	1.46	0.66	0.10	0.76	3.19	30.41	45.77	23.82
Indus at D.I.Khan	A26	14.10	24.80	28.70	3.90	1.16	1.74	1.25	0.10	1.35	4.25	27.29	40.94	31.76
Indus at Dyria Khan	A34	13.30	22.50	28.80	3.92	1.49	1.12	1.25	0.10	1.35	3.96	37.63	28.28	34.09
Gomal River	A19	4.70	51.70	102.00	5.60	3.87	2.58	4.44	0.14	4.58	11.03	35.09	23.39	41.52

Table 3.15 River Data for Piper Diagram (Anions)

Locality	S.No.	Cations (ppm)			Cations (epm)			SUM (HCO_3 +Ci+SO_4)	Cations (epm)		
		HCO_3	Ci	SO_4	HCO_3	Ci	SO_4		HCO_3 %	Ci %	SO_4 %
Indus at Chashma	A5	180.0	24.20	15	2.95	0.68	0.31	3.94	74.87	17.26	7.87
Indus at D.I.Khan	A26	175.0	45.00	75	2.87	1.27	1.56	5.70	50.35	22.28	27.37
Indus at Dyria Khan	A34	75.0	46.00	100	1.23	1.30	2.08	4.61	26.68	28.20	45.12
Gomal River	A19	225.0	158.15	400	3.69	4.47	8.33	16.49	22.38	27.11	50.52

TYPES OF FIELD

1	Na – K, Cl – SO_4	Type
2	HCO_3, Ca – Mg	Type
3	Cl – SO_4, Na – K	Type
4	Ca – Mg HCO_3	Type
5	Ca – Mg	Type
6	Cl – SO_4	Type
7	Na – K	Type
8	HCO_3 – CO_3	Type
9	SO_4 -	Type
10	CR	Type
11	No dominant	Type
12	HCO_3	Type
13	Mg	Type
14	Na / K	Type
15	No dominant	Type
16	Ca	Type

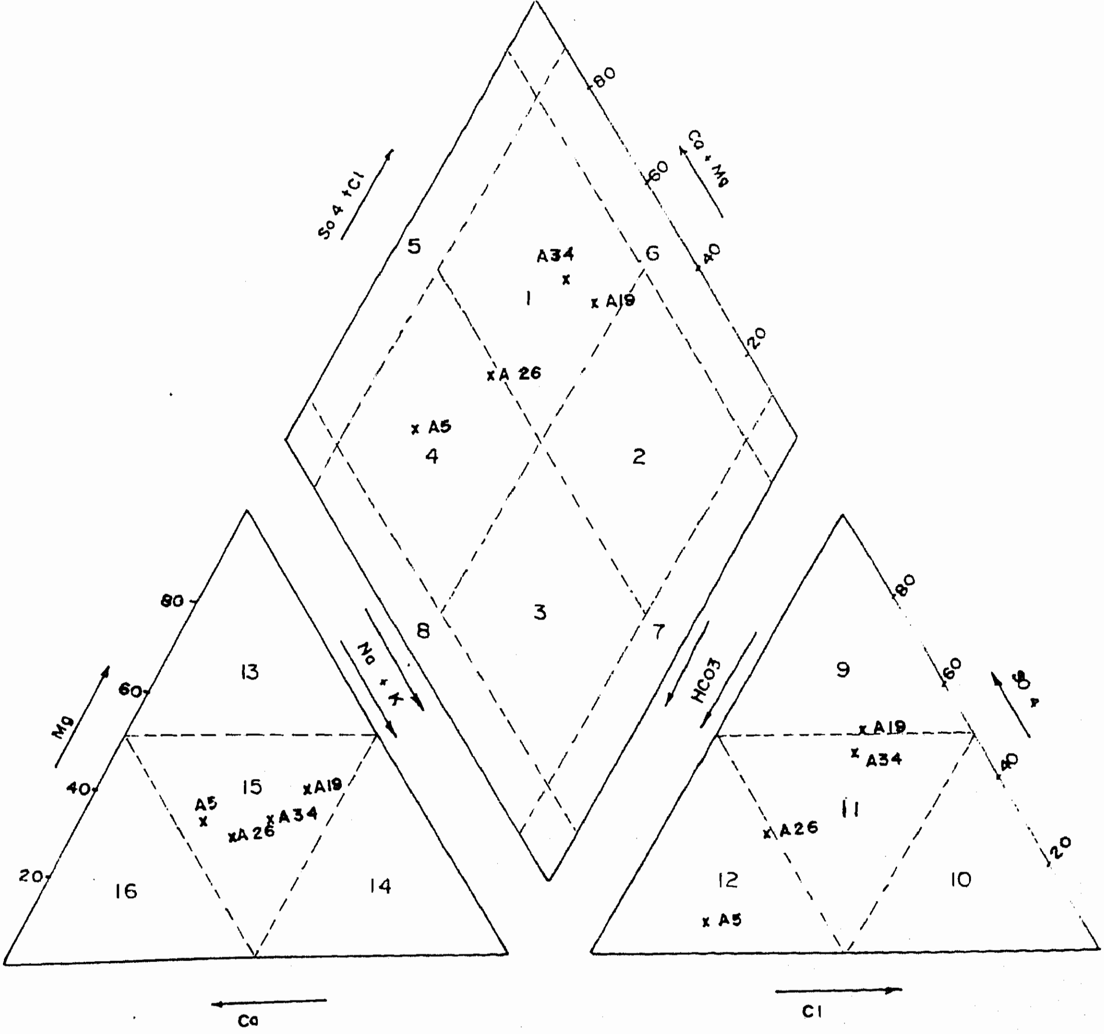


Fig. 3.25 **Piper's diagram showing water chemistry of rivers in D.I.Khan division.**

Gullmam (6.4 mg/L) and highest at Ramak (84.3 mg/L) (Table 3.1). The concentration trend increases from north to south.

SILICA (SILICON)

Natural Existence: Silica is a hard, glassy mineral found in a variety of forms, such as quartz sand and opal.

Chemistry: Its formula is SiO_2 (Silicon dioxide).

Occurrence: Silicate minerals and crystal are common in the earth crust. It occurs in all the rock forming silicate minerals for example amethyst, agate, flint, jasper, also granite, hornblends, asbestos, feldspar, clay and mica etc. Silicon makes up 25.7% of the earth crust by weight, being the second most abundant element.

Uses: It is used in concrete, refractory, as silicates in enamel, pottery and glass. In natural waters, silica may be detected as the result of disintegration of rocks containing silica. In water silica appears as suspended particles.

Results from the Study area: The silicon is generally ranging from 13.68 to 272.00 mg/L in the waters of D.I.Khan division. The deep water, shallow water, and surface water of streams and rivers have < 40 mg/L (Table 3.3 - 3.6). However the Gomal river has extremely high 272 mg/L of SiO_2 Table 3.6).

CLASSIFICATION OF D.I.KHAN WATERS

(Trace Elements Concentration)

CADMIUM (Cd)

Physical Appearance: Cadmium is a soft blue white metallic chemical element occurring as a sulfide or carbonate in Zinc ores.

Chemistry:

Symbol	At. Wt.	At. No	Sp. G.	Valance
Cd	112.41	48	8.65	2

Occurrence: As an element it is insoluble in water. In nature cadmium appears in zinc. copper and lead ores. Chloride. nitrates. and sulfate of cadmium are soluble in water (cadmium will precipitate at high pH since carbonate and hydroxide are insoluble).

Uses: It is used in electroplating in many types of solders. batteries. television sets. and as a yellow pigment. It is also used in ceramics. photography. and insecticides and as an alloy with copper. lead. silver aluminum and nickel.

Environmental impact: Since it is found in low concentration in rocks. coal and petroleum. it is found in ground water more than in surface water as a natural occurrence. therefore, it may either enter the water supply from mining. industrial operation and leachates from landfill. Also cadmium may enter the distribution system from corrosion of galvanized pipes. Raw water may contain normally less than 1 mg/L. (Zuane. 1990)

Health effect: Human beings reported nausea and vomiting at 15 mg/L. with no adverse effect at 0.25 mg/L. Severe toxic. but not fatal. symptoms are reported at concentrations of 10 - 326 mg (Nas. Vol.4. 1932). The death of a boy with 1.5 hours was reported after ingestion of 9 g of cadmium chloride. The kidneys are the critical target organs by ingestion (renal dysfunction, hypertension and anemia). (Zuane. 1990)

Results from the Study area: Cadmium is generally ranging from 0.00 to 16 µg/L in the water of D.I.Khan area (Table 3.1). Cadmium in the deep water is with in the permissible limit (5 µg/L) of EPA / WHO (1984). It exceeds the permissible limit at Pezu (12 µg/L) in shallow water (Table 3.4). in spring water at Chaudhwan are (7 µg/L: Table

3.5) and at Chashma (16 μg/L) in the water of Indus river (Table 3.6). Rest of the waters of the categories here Cd falls within permissible limit.

CHROMIUM

Physical Appearance: Chromium is a grayish white crystalline, very hard metallic chemical element with a high resistance to corrosion.

Chemistry:

Symbol	At. Wt.	At. No	Sp. G.	Valance
Cr	51.996	24	7.20	2,3, & 6

Occurrence: principal ore is chromite ($FeCr_2O_4$) The most important compounds are the chromate's of sodium and potassium ($K_2 CrO_4$), the dichromate's ($K_2 Cr_2 O_7$) and the potassium and ammonium chrome alums ($KCr (So_4)_2 \times 12 H_2O$) and lead chromate.

Uses: It is used in chromium electroplating, in alloy steel (stainless steel) and in alloys containing nickel, copper, manganese and other metals. Chromium is also used as a corrosion inhibitor in the textile, glass and photographic industries.

Environmental impact: Found in earth's crust from 10 - 20 ppm, chromium is a naturally occurring metal in drinking water. Chromite is a commercial chromium ore for the mining industry (run off and leaching is a potential source of contamination). Chrome plating and chrome metallurgical and chemical operations may contaminate the atmosphere with chromium, in addition to fossil fuel combustion, solid waste incineration, and cement plant emission. Other chromium salt usage is found in the leather industry, paints, dyes, explosives, ceramics, and papers, leading to industrial pollution. (Zuane, 1990)

Health effect: Trivalent chromium may nutritionally essential with a safe and relative innocuous level of 0.20 mg/day. Hexavalent chromium has deleterious effect on the liver, kidney, and respiratory organs with hemorrhagic effects, dermatitis, and ulceration of the skin for chronic and sub-chronic exposure. (Zuane, 1990)

Results from the Study area: Chromium is generally ranging from 0.00 to 19 μg/L (Table 3.1). Which is within the permissible limit of 50 μg/L (Table 3.2). Relatively high

Cr content, but within the permissible limit, are noticed in the Gomal river water (19 μg/L; Table 3.6) and shallow water at Yarik (16 μg/L; Table 3.5).

COPPER

Physical Appearance:Copper is a reddish brown malleable, ductile, metallic element, and is an excellent conductor of electricity and heat.

Chemistry:

Symbol	At. Wt.	At. No.	Sp. G.	Valance
Cu	63.546	29	8.96	1or 2

Occurrence: The most important copper ores are sulfides, oxides and carbonates. Very commonly found on the earth's crust as sulfides, oxides (cuprite, malachite, a-Zurite, chalcopyrite & bornite).

Uses: It is used in pipes, brass, domestic utensils, electrical industry, coins and Monel.

Environmental impact: It is found in surface water generally at concentration below 20 mg/L. It may be detected in higher values from the consumer's faucet as a corrosion product of brass and copper pipes. Industrial sources of contamination can be listed as smelting and refining industries, copper-wire mills, and coal burning industries, electroplating, tanning, engraving, photography, insecticide fungicides, and coal burning industries and iron and steel producing industries. In ground water it can be detected as an industrial pollutant. (Zuane, 1990)

Health effect: Copper is not a commutative systemic poison. Doses up to 100 mg taken by mouth cause symptoms of gastroenteritis with nausea. Values of less the 30 mgs. even for many days, has not caused poisoning. Copper in water is normally avoidable because taste threshold concentration of copper is at 1.0-2.0 mg/L. Levels at 5 - 8 mg/L make the water undrinkable, but poisoning occurs at higher concentrations. Copper is considered an essential element for human nutrition since it is required in many enzymatic reactions. The daily requirement has been estimated at 2 mg/L. (Zuane, 1990)

Results form the Study area: The copper concentration in the water of D.I.Khan is generally within the permissible limits of 100 μg/L (Tables 3.1 & 3.2). However, the Cu concentration in the water of Gomal river is extreemly high (10,000 μg/L; Table 3.6).

The deep water at Gomal University tube-well (287 µg/L; Table 3.3) exceeds the permissible limit of copper.

LEAD (Pb)

Physical Appearance: Lead is a heavy very soft, highly malleable, bluish gray metallic element. It is a poor conductor of electricity and resistant to corrosion.

Chemistry:

Symbol	At. Wt.	At. No.	Sp. G.	Valance
Pb	207.2	82	11.35	2 or 4

Uses: It is used primarily in storage batteries. Lead is used in cable covering plumbing ammunition and in the manufacture of lead tetra ethyl (used as an anti knocking compound in gasoline). It is also used as radiation shield from nuclear reactors to X-ray equipment in the glass industry and in paints (recently the lead content has been curtailed due to potential lead poisoning).

Occurrence: Native lead occurs rarely in nature. The most known compounds are galena (PbS) Anglesite ($PbSo_4$) Cerussite ($PbCo_3$) and Minim (Pb_3O_4).

Environmental Impact: Concentration of lead in natural waters has been reported as much as 0.4 - 0.8 mg/L. Pb in surface and ground waters range from traces to 0.04 mg/L with averaging about 0.01 mg/L. industrial and mining sources may contribute to some extent the localized pollution effects. Usually high values of lead are also detected in drinking waters due to lead service lines and house plumbing. (Zuane, 1990)

Health effect: blood lead levels measure Health effects of a toxicological nature. The effects are neurotic which include irreversible brain damage. Such a toxic level is reached when the blood level exceeds 100-120 mg/dl. Severe gastrointestinal symptoms are associated with the encephalopathic symptoms. These symptoms start to be observed in adult lead-workers at blood lead levels of 40-60 mg/dl. In nonfatal cases, permanent. severe mental retardation with other neurological symptoms is observed at levels as low as 40-60 mg/dl. In rats a high level of lead may have produced renal tumors. The health effect can be summarized as follows: 1) Lead is not considered an essential nutritional element. 2) Lead is a cumulative poison to humans. 3) Acute lead poisoning is extremely rare. (Zuane, 1990)

Typical symptoms of advanced lead poisoning are constipation. anemia. gastrointestinal disturbance. tenderness and gradual paralysis in the muscles specifically arms with possible cases of lethargy and moroseness. A total Intake of lead of 0.6 mg per day over an extended period may result in lifetime dangerous accumulation. There is no evidence to reach to conclusion that lead is carcinogenic or teratogenic in humans. As a piping material lead corrodes easily and accumulates in concentrations higher than the maximum allowable limit. particularly in still water. Its major effect in humans is impairment of hemoglobin and porphyrin synthesis upset metabolism connected with utilization of chemicals. (Zuane. 1990)

Results from the Study area: Lead concentration is generally ranging from 0.00 to 287 µg/L (Table 3.1). Almost all the samples. except one sample of deep water of tube well at Gomal University (287 µg/L: Table 3.3). have Pb concentration within the permissible limit of 50 µg/L (Table 3.2).

NICKEL

Physical Appearance: Nickel is a hard silver-white malleable. ductile metallic ductile metallic element. Fair conductor of electricity and heat.

Chemistry:

Symbol	At. Wt.	At. No.	M. Pt.	B. Pt.	Sp. G.	Valance
Ni	58.69	28	1453°C	2732°C	8.90	1.2. & 3

Uses: Nickel is extensively used in making stainless steel. Inver. Monel. Inconel and all corrosion resistant alloys. It is also used in ceramics. special batteries. electronics and space applications.

Occurrence: It is not commonly found in nature. as a pure metal. it occurs in sulfides. arsenides. antimonides, oxides and silicates. Nickel salts are soluble in water. as are many of its compounds.

Environmental Impact: No nickel concentration reported naturally. Most of the nickel in surface water and ground water originate from human activities. The water percolating through ultramafic rocks can also be contaminated with nickel.

Health effect: It has been demonstrated that nickel is an essential element for animals while nickel nutritional deficiency has not been recognized in humans (Zaunac. 1990).

Nickel has low toxicity comparable to zinc manganese and chromium. It does not accumulate in tissues. It is assumed that toxic symptoms in human could appear with a daily dose of 25 mg of soluble nickel (Zaunac. 1990).

Results from the Study area: Nickel concentration in the waters of D.I.Khan is generally negligible (Table 3.1). However deep water at Hathala and stream water at Pushapull has 51 µg/L and 60µg/L Ni respectively (Table 3.3 & 3.5) which exceeds the permissible limit of 50 µg/L (Table 3.2).

ZINC (Zn)

Physical Appearance: Zinc is a bluish - white metallic element. brittle at ordinary temperature but malleable at 100 °C - 150 °C. It is a fair conductor of electricity.

Chemistry:

Symbol	At. Wt.	At. No.	M. Pt.	B. Pt.	Sp. G.	Valance
Zn	65.38	30	419.6°C	907°C	7.13	2

Uses: Zinc is used as an alloy with brass. nickel. commercial bronze. soft solder and aluminum solder. It is used in galvanization to prevent corrosion. in preparation of paints, rubber products, cosmetics, pharmaceuticals. floor covering plastics, printing inks, soap, storage batteries, textiles, electrical equipment and other products. Low solubility in water reported for carbonates, oxides, and sulfides of zinc, contributing to low zinc concentration in natural waters (Zaunae, 1990).

Environmental impact: Many of the zinc salts are highly soluble in water other are not (carbonate, oxide, sulfide). It is likely that the presence of zinc can be detected only in traces in natural waters, but industrial pollution, particularly in zinc, mining areas, may contribute to a concentration as high as 50 mg/L. No adverse physiological effect upon human up to the concentration level of 20 mg/L (Zaunac. 1990).

Health effect: USEPA has not identified any adverse effects that are caused by zinc. Drinking water containing up to 20 mg/L of zinc has been consumed without any toxic effect. A higher concentration of zinc is objectionable in drinking water due to milky appearance and a greasy film in boiling (Zaunac, 1990).

Results from the Study area: Zinc concentration in the water of D I.Khan is generally ranging from 0.00 to 370 µg/L (Table 3.1). The Zn contents in the deep water, stream water and river water is found within the permissible limit of 50 µg/L (Table 3.2, 3.3, 3.5 & 3.6). However, the Zn concentration in the shallow water at Mullazai (180 µg/L; Table 3.4), Gullmam (150 µg/L; Table 3.4) and Paharpur (370 µg/L; Table 3.4) exceeds the permissible limit.

3.2.Soil and Rock

GENERAL DISCUSSION: Soil has a vital importance to all the living organisms because it provides the inorganic nutrients essential for the continued health and growth of the plants and animals.

Many factors play their role in the formation of soil. Soils are the result of the physical and chemical reactions conditioned by the variables involved in soil formation. Among these variable are parent rock material, climate, topography, the biosphere, and time.

Parental material, whether residual or transported, is the basis of all soils. Of the five variables involved in soil development, parental material, time and topography are passive in the process. One might suspect that parental material is the strongest factor in determining the ultimate soil that will be developed. However, this is true only of soils that have been recently developed from fresh rock material (i.e., young soil). In the development of soil, the time factor and the influence of climate and other factors are directly related to the length of time. Soil formed from rock material in which magnesium is either absent or only minimum will contain, of course, little or no magnesium. In many cases, lack of a trace element such as boron makes an entire area unfit for growing certain crops. This lack is a direct result of absent of boron in the basic chemistry of parental material. It is not always true that if the parent rock is rich in certain inorganic nutrients the resulting soil will also be rich in those nutrients. Time and climate may join to strip and deprive the area of these nutrients leaving a very poor, nutrient deficient soil.

Soil scientist feel that the development of acid soils, in regions having a forest cover and blanketed by sandy well-drained material may take no more than 100-200 years (Veslay, 1979). The estimates are very considerable, but an average of several thousands of years seems to be acceptable. Tropical soil once formed, are very resistant to change and may maintain stability for five million years or more (Veslay, 1979).

Topography, another passive factor, also exerts its influence in soil formation. In general, it is magnitude and orientation of slope, which are the prime variables of the topography. Magnitude of slope has a dual effect on the local soil picture. First the erosion problem, the steeper the slope, the greater the erosion and the thinner the soil profile, for soil is carried away as rapidly as it is formed. In absence of slope that is in poorly drained flatlands, not only soil horizon tends to get thicker, but the character of the soil will be totally different from that in areas of steeper slope of all the processes invaled in soil formation. Climate is of primary importance while the parent rock and plants contribute the materials from which soils are made.

In any given area, the soil climate may differ greatly from the atmospheric climate. Climate affects the soil directly, as well as indirectly. Climate is an important influence on chemical reactions. Many chemical reactions are much more active at high temperature than at low temperature. In areas of relatively high temperatures and heavy rainfall, leaching of soluble components from the upper parts of soil profile is both common and rapid. In these regions decay of organic material is considerably accelerated and releases substances into the groundwater system, which greatly enhance the water's power to dissolve. Often this rapid decay of organic material is the direct result of the presence of more abundant and varied animal life, which attack and devours the rotting organic matter. In cold climates chemical reactions are retarded, decomposition of organic matter is slow, and the fauna is neither as abundant nor as varied. It is very hard for any type of change to take place in frozen ground. However, leaching is often pronounced under these conditions, thereby giving the soils a distinct character.

One must keep in mind that for biological or chemical reactions to occur, water must be present. In very dry climate (hot or cold) leaching and decay are retarded, and normally soluble minerals (calcium carbonate, salts, and alkalies) become heavily concentrated in the soils.

Biological activities serve two purposes in soil development. Chemically, it changes the local soil conditions, and physically, it adds bulk to and churns the soils. Chemically, the decomposition of vegetation is more rapid because of the presence of living organisms. Grasses tends to maintain soil fertility by bringing calcium and magnesium up from some depth in the soil and transferring them into the stems of the grass. When the grass dies, these inorganic nutrients are deposited on the surface of the soil and thus help to maintain a circulation of inorganic nutrients.

Some bacteria have the function of taking nitrogen from the air, which can not be used by plants, and converting it to nitrate, which can be used by the plants. Thus, the presence or absence of these organisms changes the chemistry of the soil.

Biological activities also affect the physical conditions of soil formation. The stems leaves, and roots of plants help to keep soil loose while decay is taking place. Soil containing large amounts of vegetable matter doesn't become hard and crusty. Animals affect the soil largely through their physical actions like digging and burrowing disturbs, agitates, and generally reworks the soil. Generally, profile development is poorer in an area inhabited by numerous animals because of their reworking action. Ants, termites, gophers, moles, field mice, and other digging animal continually bring material from lower horizons to the surface, causing a constant recycling of soil. As burrows collapse, the surface is lowered and the material again slowly sinks to some depth. Earthworms create interconnected openings, which give good aeration to the soil, but perhaps even more important, they change the texture and chemistry of the soil as it is passed through their digestive tracts.

Soil Classification: The major features of classification system was first published in 1938, and modified to its present form in 1949. This system identifies several great soil groups, and it is these groups which are usually represented on world soil maps.

Cold Zone Soil: These are the soils of the Tundra, which is the summer commonly show a few inch of acidic, brown loamy soil, with permafrost underneath at a depth of about of one foot. Utilization of this soil is hampered severely by low temperatures.

Desert Soil: These soils are often quite coarse, since weathering is mostly restricted to physical weathering. Since there is little water for leaching, the soils are often limy or salty. In low swampy places these soils tend to accumulate salts. Often there is a concentration of clay in lower horizons. Lack of water presents a problem in any attempts to utilize these soils. Salt also complicates this problem, for even if there is not enough salt present to make the soil sterile, the amount is usually sufficient to upset the optimum balance of inorganic material for plant nutrition.

Grass Land Soil: These soils are represented by chernozem, chestnut, and prairie soils. The latter two being transitional between the chernozems and podzolic soils of water regions is typically black and high in both humus and ions of calcium and magnesium, and potassium. In terms of agriculture, these soils are the most useful to man.

Temperature Forest Soil: These are pldzol and podzolic soils, which show strong to moderate leaching, are composed of layers of clay or dense accumulations of colloids, and tend to be of limited agricultural value. However, with the application of lime and fertilizers, these soils can become almost as useful in agriculture as are the grass land soils.

***Latosols*:** These soils are found under conditions of high temperatures and heavy rainfall. These conditions cause significant chemical weathering of the parent rock and removal of most of the silica through leaching. This leaves high concentrations of the oxides and hydroxides of aluminum, manganese, and iron in the soil. The lack of humus and the excessive leaking make this soil almost useless for agriculture purposes. Although latosal soils support native rain forest vegetation, they become brick like when exposed to the atmosphere through the removal of this vegetation. In fact, in some areas of Southeast Asia these soils are used as a building material.

***Other Soil Types*:** The inter zonal soils are usually limited to peculiar local environments and are represented by the saline and alkaline soils of arid climates, the bog, marsh and meadow soils, and the calcimorphic soils in which the parent material (limestone) overcomes any conditions imposed by the climate. The zonal soils, often grouped together as "mountain" soils, consist of either transported soil or very coarse soil which are the result of primarily of the physical weathering of the parent material.

The Soils of Dera Ismail Khan Area: The Dera Ismail Khan and surrounding areas have been divided in to the following four basic physical units (Directorate Soil Survey of Pakistan).

i) Mountains
ii) Steep sloping alluvial fans
iii) Daman
iv) Flood plain basin of Indus River.

The Mountains and Steep Sloping Alluvial Fans: The mountains and the steep sloping units within and around D.I.Khan (Plate # 3.1 & 3.2) have no soil cover. The steep sloping alluvial fans mainly comprise of gravel and stones. These have no or little use for cultivation, with little value of grazing.

Daman: Daman and the imperceptibly sloping piedmonts, which cover three quarters of the are in D.I.Khan. The northern part of Daman is built up with detritus brought down from the adjacent Bhittanni, Marwat and Khisor ranges. In this undulating region almost all the soil are sandy. The sand grade from coarse nears the foot of the hills and along the major torrents to sandy loams.

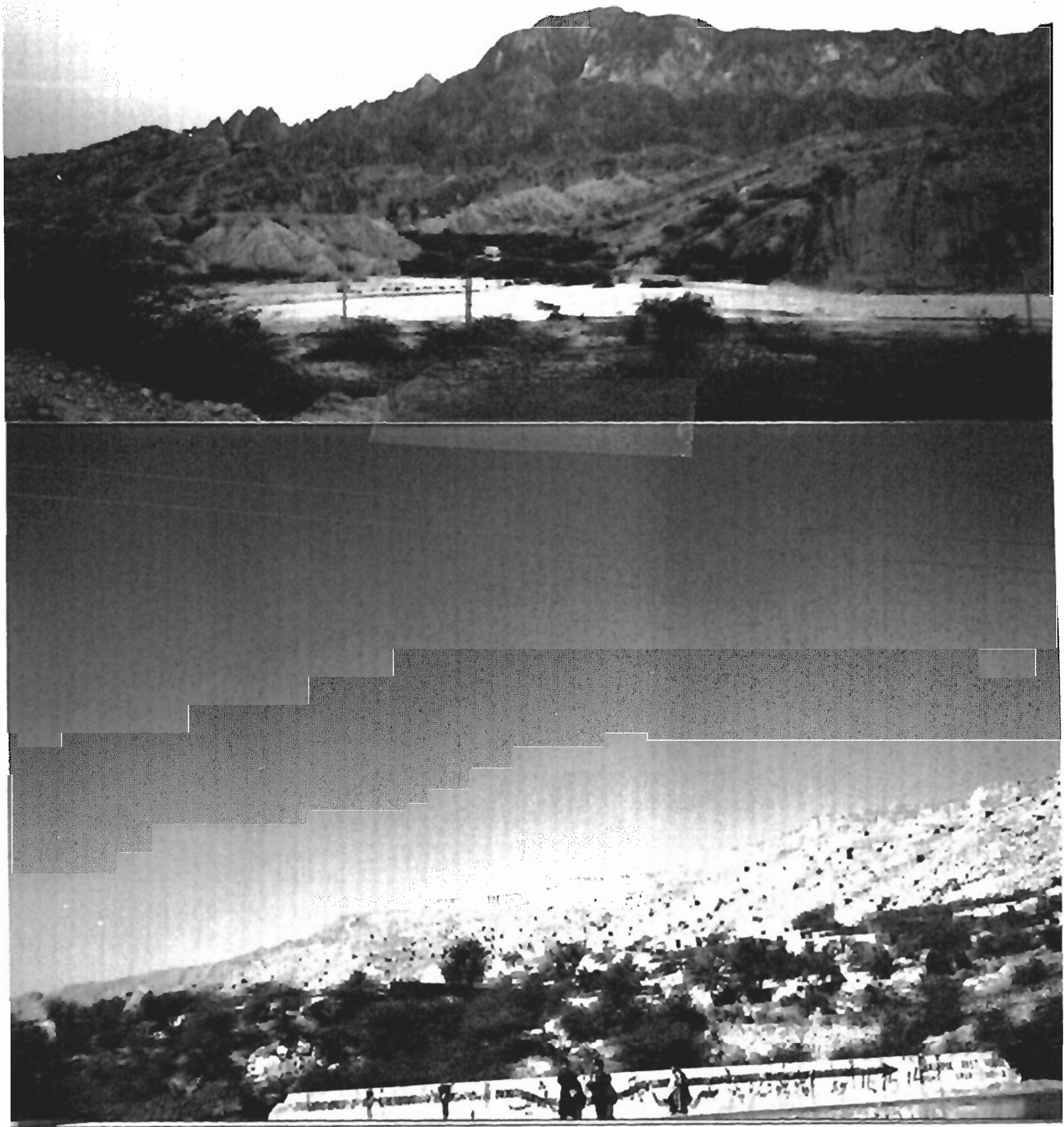


Plate # 3.1 Two distinct views of Sulaiman Range.

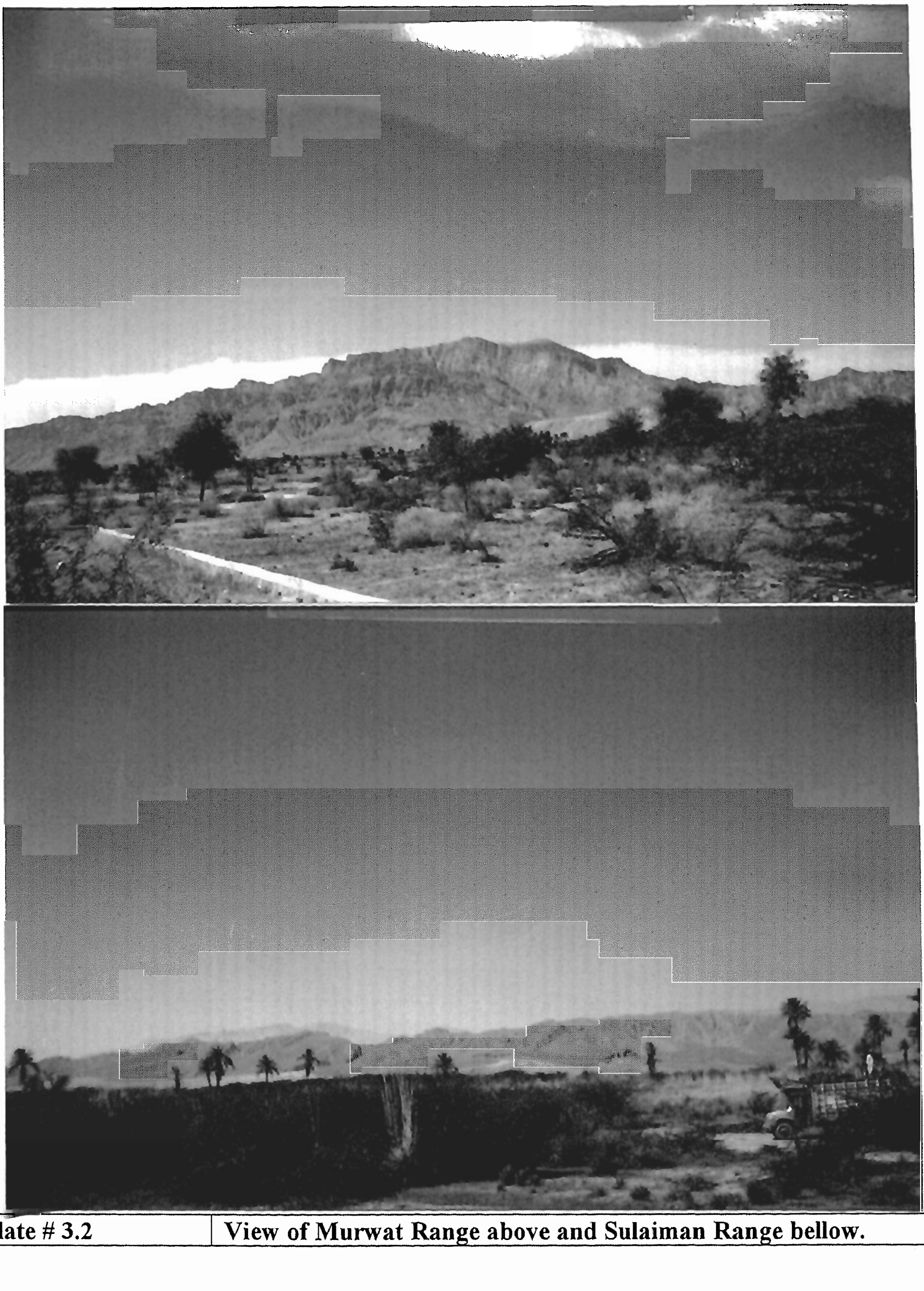


Plate # 3.2 **View of Murwat Range above and Sulaiman Range bellow.**

Stratified silt loam occurs in narrow low-lying strips of land. All the soils of this region are moderately to strongly calcareous. Towards the south the country changes to a vast fairly uniform plain where soil conditions improve somewhat. The soil here are subject to flash flooding, causing both sheet and gully erosion, but once the vegetation cover is maintained through persistent cropping, the suffer little loss through erosion. Except in the vicinity of outwash fans and local variations such as sandy levees, the soils of this area contain thick clay. All these soils are brown to dark brown, moderate to strongly calcareous, suggesting alkalic conditions.

Flood Plain: The flood plain soils are developed in Indus laid alluvium derived from a wide range of igneous, metamorphic and sedimentary rocks of Himalayas.

The soil has great local variation from coarse, moderately coarse, medium to fine texture. Soils are stratified. All the soils of this tract are dark grayish brown, moderately calcareous, and except Kasur non-alkalic.

The soils and rocks play a vital role in changing the chemistry of water, which is percolating through them. It dissolves the inorganic salts from the soil, sometime retains it and sometime transports it to another regions. Therefore, the study of soils of the area can help in understanding the geo-chemical behavior of both surface and under ground waters of the area. In order to attain this goal, the soils of the area has been divided in to three horizons (A, B & C) on the basis of depth.

***Horizon A*:-** This is the top most layer (0 – 15 cms deep), which is directly expose to weather conditions. This is also called as the zone of leaching, because water can readily dissolve and take away the soluble minerals constituents present in it. This layer is abundant in organic constituents. Microorganisms are also active in this part due to the availability of air.

***Horizon B*:** This Horizon is ranging from a depth of 15 – 30 cms. This is relatively low in organic matter as compare to the upper part. This zone retains the salts present in it. Organic activity is lesser than the horizon A.

***Horizon C*:-** This layer is ranging from a depth of 30 - 45 cms. It is less permeability, compact zone with no or fewer organism activity.

Results from the Study area: The Chemical composition (both major and trace elements) of composite soil samples (up to a depth of 30 cms.) collected from various places of the D.I.Khan division are given in table 3.16 and 3.17. Among the major oxides Fe_2O_3 varies from 1.86 to 3.21; Na_2O from 0.63 to 2.65; K_2O from 0.86 to 1.26; MgO from 2.72 to 4.11; CaO from 13.01 to 56.71; and MnO from 0.01 to 0.05; (Table 3.16). Among the trace elements Cu is ranging from 212 to 320; Pb from 76 to 198; Ni from 44 to 104; Cr from 32 to 176 and Zn from 50 to 494 (Table 3.17).

Major and trace elements data of some of the representative rocks of the D.I.Khan area are presented in table 3.18 & 3.19

These rocks have greater variation in their chemical composition because of variable mineralogy. Fe_2O_3 is in the range of 0.13 to 1.80; Na_2O is 0.05 to 1.67; K_2O is 0.03 to 3.25; MnO is 0.01 to 0.05; MgO 0.42 to 4.61; and CaO is 13.01 to 56.71 (Table 3.18). Cu is ranging from 72 to 96; Pb from 32 to 128; Ni from 32 to 66 (Table 3.19).

Table 3.16 Major Oxides in the Soil of Dera Ismail Khan Division

LOCATION	Samp.NO.	Fe_2O_3	Na_2O	K_2O	MgO	CaO	MnO
		%age					
Shorkot	Ans-1	2.90	1.00	0.96	3.27	9.88	0.11
D.I.Khan T&T colony	Ans-2	2.60	1.25	0.95	3.03	10.27	0.11
Pusha Pull Stream	Ans-3	2.43	1.46	0.86	2.88	10.73	0.11
Paniala	Ans-4	1.99	2.37	1.13	3.28	7.22	0.08
Paniala Stream fine Sediments	Ans-5	1.86	2.65	1.05	3.21	7.75	0.67
Paniala Stream Coarse Sediments	Ans-6	1.88	2.65	0.94	3.10	8.51	0.11
Gomal	Ans-7	2.43	1.21	0.88	3.18	9.72	0.10
Chadhwan	Ans-8	2.77	0.63	1.02	2.95	13.40	0.09
Tank Zam Stream Sediments	Ans-9	3.21	0.64	1.33	2.82	8.35	0.10
Kirri Khisor	Ans-10	2.15	2.25	1.07	3.50	9.93	0.08
Ramak	Ans-11	2.86	1.21	1.07	2.98	6.71	0.10
Gul Imam	Ans-12	2.98	0.79	0.95	2.72	9.79	0.12
Poroa	Ans-13	2.05	1.03	0.69	2.55	9.93	0.11
Tank Zam	Ans-14	3.03	0.78	1.14	2.80	8.53	0.10
Kulachi	Ans-15	2.40	1.00	0.91	2.98	8.87	0.10
Potah	Ans-16	2.93	1.32	1.12	3.60	8.64	0.12
Gomal University	Ans-17	3.14	1.02	1.26	4.11	7.50	0.11
Tank	Ans-18	2.75	0.85	1.13	3.23	8.97	0.11
Pahar Pur	Ans-19	2.21	2.27	1.16	3.07	7.11	0.11
Mullazai	Ans-20	2.63	1.03	0.96	2.95	10.37	0.12
Yarak	Ans-21	2.93	1.03	1.13	3.05	9.88	0.12
Daraban	Ans-22	2.48	1.12	1.06	3.36	21.47	0.08

Table 3.17 Trace Elements in the Soil of Dera Ismail Khan Division

LOCATION	Samp.NO.	Cu	Pb	Ni	Cr	Zn
		ppm				
Shorkot	Ans-1	256	138	96	106	110
D.I.Khan T&T colony	Ans-2	244	134	88	102	494
Pusha Pull Stream	Ans-3	212	104	78	88	92
Paniala	Ans-4	226	98	54	46	348
Paniala Stream fine Sediments	Ans-5	228	134	56	32	62
Paniala Stream Coarse Sediments	Ans-6	220	112	44	32	50
Gomal	Ans-7	222	128	92	98	182
Chadhwan	Ans-8	222	198	74	114	408
Tank Zam Stream Sediments	Ans-9	246	152	86	154	124
Kirri Khisor	Ans-10	240	136	68	100	88
Ramak	Ans-11	262	124	100	126	116
Gul Imam	Ans-12	284	154	90	140	314
Poroa	Ans-13	274	116	92	118	92
Tank Zam	Ans-14	296	122	88	148	94
Kulachi	Ans-15	238	112	100	136	84
Potah	Ans-16	248	100	112	174	126
Gomal University	Ans-17	264	76	126	204	198
Tank	Ans-18	284	126	96	152	180
Pahar Pur	Ans-19	290	92	68	126	106
Mullazai	Ans-20	316	142	102	160	126
Yarak	Ans-21	320	118	104	176	118
Daraban	Ans-22	274	92	86	166	166

Table 3.18 **Major Oxides in the Rocks of Dera Ismail Khan Division**

Location	Rock Description	Samp. No.	Fe2O3	Na2O	K2O	MnO	MgO	CaO
			ppm					
One km. Southwest of Chashma Barrage Rest House.	Reddish brown limestone (on fresh surface) and whitish yellow on weathered surface.	R1	0.29	0.05	0.03	0.02	0.42	46.17
3 kms. South-west of Chashma Barrage Rest House.	Compect gray color fossiliferous limestone	R2	0.3	0.06	0.06	0.01	1.93	52.49
3 kms. South-west of Chashma Barrage Rest House.	Greenish (fresh surface) calcareous sandstone and gray on weathered surface.	R3	1.8	1.67	2.25	0.05	0.62	25.74
4 kms. Southwest of Chashma Barrage Rest House.	Maroon color breciated rock (fragments of calcite, Qtz., sandstone, siltstone).	R4	0.8	5.2	3.25	N.D.	4.61	13.01
4 kms. southwest of Chashma Barrage Rest House.	Gray color fossiliferous limestone.	R5	0.13	0.07	0.03	0.02	0.71	56.71

Table 3.19 **Trace Elements in the Rocks of Dera Ismail Khan Division**

Location	Rock Description	Samp. No.	Cu	Pb	Ni	Cr	Zn
			ppm				
One km. Southwest of Chashma Barrage Rest House.	Reddish brown dolomitic limestone (on fresh surface) and whitish yellow on weathered surface.	R1	72	110	66	6	36
3 kms. South-west of Chashma Barrage Rest House.	Compect gray color fossiliferous limesone	R2	82	104	56	12	28
3 kms. South-west of Chashma Barrage Rest House.	Greenish (fresh surface) sandstone and gray on weathered surface. And also gluconatic.	R3	86	48	46	34	54
4 kms. Southwest of Chashma Barrage Rest House.	Maroon color breciated rock (fragments of calcite, Qtz., sandstone, siltstone.	R4	92	32	32	24	38
4 kms. southwest of Chashma Barrage Rest House.	Gray color fossiliferous limestone.	R5	96	128	60	12	38

CONCLUSIONS AND RECOMMENDATIONS

After the completion of detailed geochemistry of the water from Dera Isamil Khan division, some conclusions and recommendations are made in the light of these obtained results. If we give a quick glance to the results, we can see a generalized trend showing the increase in the constituents from north to south. The concentration of constituents in the water samples taken from extreme south are very high in comparison to those water samples taken from northern side of the study area. As it was mentioned earlier that the water of the D.I.Khan division is divided in to four categories. Now these results are discussed accordingly.

In deep water (tube-wells) "NaCl" ; sulphate; iron and maganese dominates the other entire constituents. As the most samples taken for analyses are from tube-wells. NaCl %age is high in these samples. If we give a quick glance to the results we obtained for "NaCl" %age dominant the other entire constituents. On the other hand we know that the geology of the area shows the Salt beds of the Salt Range under these rock sequences. Salt lenses can also be seen while passing through Shakar-Dara near Kala-Bagh, the same continuation of the Salt Range passes through D.I.Khan division and enters in to Baluchisthan. There is no other source rather than this, in sight, causing the enrichment of NaCl in water. Ground water dissolves NaCl from there. Hence it is assumed that the geology of the area is contributing to it.

Nitrate dominates in shallow waters (dug-wells, hand-pumps and settling-ponds) and streams/nalas. The results obtain plotted on contour map shows that it is a localized phenomenon. The concentration is restricted to single place or locality. At Chaudhawan nitrate is 90 mg/L which exceeds the limit (0.3 mg/L) established by WHO and US-EPA for safe drinking water. This clearly indicates that it is not at all recommendable for drinking purpose. Conversely the local population use it for drinking purpose. The results suggest that nitrate is high in open source of water and hence the human and cattle are responsible for this contamination . For this local population should be educated for the cleanliness of the water sources. Water sources used by human should be separated from the source used by cattle. Precautionary measures should be taken to keep the source clean, as much as possible if not then avoid the source for drinking purpose.

In case of rivers, the Indus bounds the eastern boundary of Dera Isamil Khan while Gomal river is flowing west to east. These two are the major rivers in the study area and the big sources of water used by local population. In Indus at Chashma, the concentration for trace elements are found to be high. But no detail study has been carried out. Therefore, it is difficult to interpret the actual cause of enrichment of *these trace elements in Indus river. In Gomal river the concentration of cations, is very high. In case of iron and copper, the situation is alarming. Because these two constituents are much higher than the permissible limit established by US-EPA ande WHO. Gomal river is also the other biggest source used for drinking water by the local population. Only one water sample was taken from Gomal river. Therefore it is not possible to say with certainty however, it is suggested that proper sampling of the Gomal river is mandatory. As it flows through Wiziristan ultramafic complex, the enrichment of constituent like, copper, iron, magnesium, chromium and nickel can be the expected. It is therefore suggested that the water of Gomal river should be avoided for drinking purpose.*

Sulphate concentration (i.e.,1600 mg/L) is the highest in Poroa, the southern town of the D.I.Khan division, and decreases away from this location. The other highest concentration for sulphate (i.e., 900 mg/L) is at Potah, situated in the center of D.I.Khan division. These two places show the points of highest concentration for sulphate in the whole study area. Iron and maganese concentration are found to be high at many localities. Out of total thirty-four water samples, iron crosses the permissible limit of US-EPA and WHO in thirty-one and maganese in eighteen water samples.

Fluoride is high at six localities out of twelve selected places. Highest concentration of fluoride is obtained at Pezu (4.57 mg/L). Other places where the concentration of fluoride crossing the limit for safe drinking water are Mullazai (1.62 & 2.54 mg/L), GulImam (1.79 mg/L), Yarik (2.72 mg/L), and Ramak (1.79 mg/L).

In trace elements copper is highest and alarmingly (i.e., 10,000 µg/L) in Gomal river. Lead concentration is highest in the water of Gomal University (i.e.,287µg /L; tube-well sample). Nickel is highest in Paharpur water (i.e.,60 µg /L) and Zinc at Paharpur (i.e.,370 µg /L) in D.I.Khan division.

In area-wise comparison, the general quality of water in Gomal river, the following constituents are high, sulphate (400 mg/L), iron (43.3 mg/L), magnesium (47 mg/L), maganese (0.2 mg/L) and copper (10 mg/l). The water of Gomal river is used by large proportion of population domestically, as well as for drinking purpose. While the results suggest that this water is not safe for drinking, according to the US-EPA and WHO guide line. Poroa is another area where quality of water is not safe for drinking purpose but frequently used for drinking. In Poroa following constituents are high, sulphate (1600 mg/l), chloride (244 mg/l) and magnesium (73.7 mg/L). The other areas where the quality of water is not permissible for drinking are Ramak, Chaudhwan,, Daraban, Potah, Hathala, Kullachi, Umer Ada, Tank, Shorkot and Panaiala.

As for as the study area is concerned there is neither much population and nor the industrial setup that can be a major threat to the water contamination and the enrichment of the constituents. The problem assumed as purely geological. Apart from it is necessary to see the bacteriological aspect for the waters of the Dera Ismail Khan division.

In brief general recommendations and conclusions are as under:-

1. *Geology of the area is playing major role in the enrichment of the chemical constituents in the water of D.I.Khan division.*
2. *In general the concentration trend is from north to south.*
3. *"NaCl" is contributed to water by the presence of Salt beds of Salt Range under the rock sequences of the D.I.Khan.*
4. *Origin for major and trace element concentration in water can be related to Wiziristan ultramafic complex.*
5. *Iron, Magnesium and Fluoride are crossing the permissible limit for safe drinking water in many places.*
6. *Gomal river water is not at all permissible for drinking purpose.*

For the treatment of the water for drinking purpose the following methods, established by the US-EPA (1989) and WHO (1984), can be used.

Treatment for the Removal of the different Constituents from water

Here are the treatments for the removal of the constituents that are high in the studied area. No single economic method is available for the removal of these constituents. In this regard, first the elimination of the source of pollution is necessary. It must be attempted not only because it is economical but mainly to trace the paths of pollution.

For Copper: *US-EPA (1988) specified the. filtration, ion exchange, lime softening and reverse osmosis for treatment of high copper for drinking pruposes.*

For Iron: *Iron can be removed by using aeration, sedimentation/filtration, pH adjustment, chlorine treatment, chemical precipitation/filtration, ion exchange (softening) and lime softening.*

For Nitrate: *Nitrate can be removed by ion exchange, biological dentrification and reverse osmosis. These are effective methods but are practically non-economical.*

For Sulphate: *Ion exchange can be used for sulphate removal from municipal water supplies. As compare to other methods used for sulplhate removal, this is the most economical.*

For Fluoride: *Activated alumina adsorption, reverse osmosis and modified lime softening are proven methods for fluoride concentration reduction.*

REFERENCES

Adriano, D.C. 1986. *Trace elements in the terrestrial environment*. Spring – Verlag. New York.

Adriano, D.C., Doner H.E. 1982. *Methods of Soil analyses*. Part-12. 449-483. Amer.Soc.Agron Inc., Madison, W.I.

.Agnem A.F., Ruedisilic Lon C and Speidel D.H. 1988. *Perspectives on Water Uses and Abuses*. New York Oxford University Press.

America Public Health Association, 1985. *Standard methods for the examination of water and wastewater*. 6th ed. Washington D.C.

Baetyer, M., Damron, C. W., Clark, J.H., Budacz, V. & Arch. A. M. A., 1955. Ind. Heath 12, 258.

Baranowska, I., 1993. *Heavy metals in human bones, civilizations poison*. Pol. J. Env. Std., 2, 5-9.

Berlin, M., ed. 1986. *Hand book on the toxicology of metals. Specific methods*. 2nd.ed. vol. II. Elsevier. Amsterdam, 387-445.

Brown., H. Konoplejantrue., A.A., Insen., J. and Kovalchsky V.S., (UNESCO). Groundwater studies.

Bundeschuh, J. 1992. *Hydrochemical and hydrogeological studies of ground water in Peshawar Valiey Pakistan*. Geol.Bull.Univ.Peshawar, Vo.25, pp.23-37.

Chow, V.T. 1964. *Hand book of applied hydrogeology*. New York. Mc. Graw – Hill Book Comp.

Fetter C.W., 1988. *Applied hydrogeology*. Merrill publishing company U.S.A.

Cargo, N.D. & Mallory B.F., 1974. *Man and his geological environment*. Addision Wesley publishing Company Inc.

Craun, G.F., 1984. *Health aspects of ground water pollution. Microbiology*, ads, Bitton, G., and Gebra C.P., New York Willey P.135-179.

Danishwar, S. and Shah. M.T. *Geochemistry of ground water and the source of contamination of fluoride in the drinking water of the Naraji area, district Swabi N.W.F.P., Pakistan*. Pak. J. Sci. Ind. Res., Vol.40, nos 5-12, May – December, 1997.

Directorate of Soil Survey 1967. *Reconnaissance soil Survey of D.I. Khan*.

Domenico P.A., and Schwartz, F.W., 1991. *Physical and Chemical Hydrogeology*. John willey and Sms. Inc.

Duka S.,Pitrowska. M., Chlopecka, A. and Witek, T., 1995. *Trace metal contamination of soil and crop plants by mining and smelting industry in Upper Silesia, south Poland.* Jour. Geoch. Explor., 52. 237-238.

Elkins H. B., ed. 1951. *The chemistry of industrial toxicology.* John willey and sons., Newyork.

Fairbridge, R.W. *The Encyclopedia of Geochemistry an Environment science.*

Ghosh, T.K., Ktargale, J. P. & Krishna Moorthi, K.P., 1980. *Toxicity of selected metals to fresh water algae.* Env. End. 8,356 – 360.

Gornel, H. A., 1958. *Classification formation waters based on NaCl content.* A. Asssoc.Petrol.Geol.Bull.42,pp.2513.

Hem, J.D., 1985. *Study and interpretation of the chemical characteristics of Natural water.* U.S. Geol. Surv. Water Supply Paper.

Health, R.C., and Trainer, F.W., 1968. *Introduction to ground water hydrology.* John Wiley and Sons Inc.

Karanth, K. R. 1993. *Hydrogeology.* Tata Mc. Graw – Hill publishing company limited. Delhi, India.

Keller, E.a., ed., 1992. *Environmental Geology.* Macmillan publishing company, USA.

Kruseman, G.P., & Naqvi, S.A. HJ. 1988. *Hydrogeology and Groundwater Resources of the N.W.F.P.*, Institute of Applied Geoscience Netherland.

Manning J.C., ed 1987. *Applied principle of hydrogeology.* 2nd ed. New York Merrill publishing company.

Montgomery, C.W. ed 1992. *Environmental Geology.* 3rd ed Wm.C. Brown Publishers.

Raveendran, E., and Madany, I. M. 1991. *The quality of ground water in Bahrain. The science of the total environment.* 103 pp.177 – 183. Elsevier Science Publishers B. V., Amsterdam

Rosum, J.R. and Villarruz P., 1961. *Suggested methods for tubidimetric determination of sulphate in water.* J. Amer. Water works Assoc. 55. P-853.

Sawyer, C.N., 1967. *Chemistry for sanitary Engineers.* Mc Graw Hill Inc.

Soofi, M. A., *Effects of fluoride in water on dental health.* Quarterly "SPECIALIST", vol-6, No.3, April – June, 1990.

Surgeon, D.J., Hopkins, S.P. and Jones D.T., 1984. *Effects of Dc. Cu, Pb, and Zn on growth, reproduction and survival of earthworm.* Env.Poll, 84,123-130.

US-Environmental Protection Agency, 1991. *Hand book of Ground water, methodology.* vol-II, Washington D.C.

US-Environmental Protection Agency, 1978, Federal Register No.266.

US-Environmental Protection Agency, 1979. *Method for Chemical Analyses of Water and Water.* EPA-600/4-79-020, National Environmental Research Center, Cincinnati Ohio.

Wesley. I., 1979. *Soil.* II ed. Mc. Graw- Hill Inc.

Zuane, J.D., 1990. *Hand book of drinking water quality standards and controls.* Van Nostra and Reinhold New York.