CHAPTER 1

INTRODUCTION

The earth is a small living unit of the whole universe, but it is so complicated that its own dimension cannot be clearly defined. The earth's living unit, biosphere also called ecosphere is consisting of the lithosphere; lower part of the atmosphere and hydrosphere. These three spheres influence the biosphere by their chemical and physical interactions (Kabata-Pendias and Pendias, 1992).

Generally the biosphere comprised of the three main ecosystems; land environment, fresh water and marine ecosystem, while environment is the sum of the all the features and conditions surrounding an organism that may influence it. The physical environment encompasses rocks, soils, air and water (Montgomery, 2008). Beside natural environment, humans inhabit the built environment so, the technological, cultural and social world are also the components of the environment (Cunningham et al., 2007).

Environment could be either a resource or a hazard. As a resource it provides water, soil, industrial raw and building material, energy, minerals and disposable sites for wastes but on the other hand environment constraint our development and infrastructure. Environment also generates some potent hazards in the form of the earthquake, volcanoes and floods (Bennett et al., 1997).

Environmental geology is one of important aspect of the Environmental Earth Sciences, which deals with the study of the human interaction with geological environment. The geological environment not only means the physical constituents of the earth, but also the earth surface, its landforms and all the process those could bring changes in these landforms through time (Bennett et al., 1997).

Water and soil are the two important components of the nature in terms of both hazard and resource. Water is the most abundantly available substance in the nature, forming about 75 % of the matter of the Earth's crust and is essential ingredient of all living biota of the earth, (Srivastava, 2002). Chemically water is found in all three states of the matter (solid, liquid and vapor), all of equal importance (Trividi and Raj, 1992).

Soil is a storage place for the solar energy. Solar energy reaching the soil is incorporated in the biomass of plants and is ultimately transferred to the other living beings and humans. The soil provides time and space to the dead organics and microorganisms to oxidise and release nutrients trapped in the organic matter (Davis and Masten, 2003).

In return of getting hundreds of benefits the water is the mostly suffered media from all the natural and anthropogenic activities (mining, agrichemicals, industries, domestic sewage etc), releasing heavy, trace and toxic metals, pesticides, sediments and organic compounds to the surface water had badly effected the quality and quantity of the fresh water as well as associated soil and atmospheric system (Montgomery, 2006). All their components are altered in their quality by various kinds of pollutions.

Environmental contamination by trace and toxic heavy metals is receiving great attention worldwide, as serious issues regarding health and environment are arising due to these metals. The presence of heavy metals in aquatic environment is of much concern due to their influence on plants, animals and human's lives. Elevated levels of heavy and trace metals may be mainly of anthropogenic influence rather than geogenic (Karenn and Baired. 2001). Heavy metals in soils are greatly associated with biological and geochemical processes. Although, heavy metals in soils are of geogenic origin, but humans activities such as agriculture, transport, industrial activities and waste disposal have resulted in manifold increase (Lund, 1990). Heavy metals in soils pose threats through their mobility by transport to water and bioavailability to plants (Adriano, 2002). Although, heavy metals are present in the Earth's crust, but they tend to accumulate in agriculture soils because of application of commercial fertilizers, insecticides and sewage sludge containing heavy metals (Peris et al., 2007; Wong et al., 2002). For example application of phosphate fertilizers has resulted in the accumulation of cadmium, a non essential element to plants along other heavy metals (Mordvet and Osborn, 1982). Heavy metals are important in toxicological studies. It has been reported that cadmium poses carcinogenic, embryotoxic, teratogenic and mutagenic properties (Sanders, 1986). Similarly, having a known record in toxicological history, mercury has no significant biological role, its compounds like mercuric chloride and organomercurial are highly toxic (Gutkentcht, 1981).

Besides the impacts of other heavy, trace and toxic metals, arsenic contamination has become a challenge for scientists worldwide. Presence of arsenic has long been determined in tube wells and drinking water supplies in south east Asia, India, Bangladesh and Pakistan (Smedley and Kinniburgh, 2002; Bhattacharya et al., 2003) and it is estimated that about 100 million peoples are at risk due to consumption of contaminated water in these countries (Nordstrom, 2002; Sun et al., 2004). Its chronic effects in human beings commonly include skin diseases (e.g., pigmentation, dermal hyperkeratosis, skin cancer), and many cardiovascular, neurological, hematological, renal and respiratory disorders which may effect lungs, bladder, liver, and kidney (Morton and Dunette, 1994; Smith et al., 1999).

Sources of drinking water in Pakistan include rivers, ground water, lakes and reservoirs. In present days disposal of agriculture, industrial and domestic effluents into natural bodies has greatly deteriorated water sources. One of such example is Manchar Lake which is a source of drinking water and food for the local inhabitants has been anthropologically contaminated with arsenic by main Nara Valley Drain (Arian et al., 2008). Due to reporting of arsenic problems in neighboring countries, Government of Pakistan has been taken initiatives regarding this problem since 1999 with assistance of UNICEF. In first step preliminary investigations were made from November 1999 to January 2001 by PCSIR and PCRWR with technical and financial support from UNICEF. In this study water samples from six Districts of Punjab province were collectd: result showed 14% of samples having arsenic above 10µg/l. Further similar studies were also conducted on water of 34 Districts in all four provinces of Pakistan (Ahmad et al., 2004).

Similarly arsenic contamination has been reported in drinking water of three Districts (i.e., Mardan, D.I Khan and Chitral) of Khyber Pakhtun Khwa by PCRWR during National Water Quality Monitoring Programme (PCRWR Report, 2006)

Study Area Profile

General information regarding Mardan District has been taken from District Census Report (DCR) of Mardan (1998). General information about study area is;

Location, boundary and area

Mardan District is the part of Peshawar valley. Until 1937 Mardan District was a part of Peshawar District but it was set up as independent District in 1937. Mardan District lies between latitude 34° 05′ to 34° 32′ North and longitude 71° 48′ to 72° 25′ East. It is bounded on the north-east by Buner District, on the north and north-west by Malakand protected area, on the south-east by Swabi District, on the south by Nowshera District and on the west by Charsadda District. Total area of the District is 1632 square kilometers (DCR, 1998).

Physical features/ Topography

Mardan District can be divided into two parts, northern hilly area and south western plain area. The northern side is completely bounded by the hills. The two highest hills are Pajja or Sacra, 2056 meters high and Garo or Pato, 1816 meters high. The southern part is comprised of fertile plain which is accepted to be once the bed of the lake which was gradually filled up by the load of river (DCR, 1998).

Drainage

Most of the streams drain into the Kabul River. Kalpani is an important river which originates from the Baizai, flowing southwards and joins Kabul River at Nowshehra District. The other important streams which join Kalpani are Baghiari Khawar and Muqam Khawar, coming from Sudham valley and Naranji Khawar from the Naranji hills (DCR, 1998).

Climate

Summer season is hot and high temperature has been observed from May to July. The temperature reaches to its maximum (i.e., 40-48°C) in the month of June. The coldest months are December and January in which the temperature falls to the average 2.09 °C. Most of the rainfall occurs in the month of July, August, December and January. The maximum rainfall recorded for the month of August is 125.85 mm. The relative humidity is quiet high throughout the year with maximum (i.e., 73.33 %) humidity recorded in December.

Flora and Fauna

The flora in the irrigated areas is exotic. The common trees are mesquite, ber, species of acecia and jund. The most common shrubs are Tarmariax, Articulate, Spandsa. Akk, small red poppy, Spera, Pueghambrigual, Drab grass, Eamelthorl and Pohli chaulai etc. Variety of fauna is found in the District Mardan. The common animals are leopard, leopard cat, black Bear, brown Monkey, Jackal, wild Goat and Pheasant etc. (DCR, 1998).

Agriculture

Mardan District is best known for its agriculture. It’s land is well suited for the tobacco and sugar cane cultivation. The major crops grown in the District are wheat, sugar cane, tobacco, maize, rice, rape seed and mustered etc. (DCR, 1998).

Irrigation

The main source of irrigational water is the canals. The upper Swat canal irrigates most part of the District and lower Swat canal irrigates south-western part of the District. The other sources are tube wells and lift irrigation (DCR, 1998).

Horticulture and Forestry

The area is famous for orchards. The important fruit grown in the District are orange, plum, peach, apricot, pear, lechi, rare mango and apple. In Mardan District forestry is based on the canal and road sides and private land plantation (DCR, 1998).

Industry and Trade

In Mardan District, a small industrial state with 66 factories was established. In which only 33 factories are now operating. Mardan is rich in the production of the tobacco and sugarcane. In 1997-98, Mardan District had 77 working industrial units including tobacco, match, furniture, marble, flour mills, steel industries, aluminum goods and handy crafts (DCR, 1998).

Mining

In Mardan District commercial deposits of marble, limestone, dolomite and granite are present. Veins of good quality pink topaz have also been found in the hillocks of Shaheed Ghundai and Shamozai Katlang, Mardan. Deposits of the non sticky clay have also been prospected near the Indus river bank of Jehangira Swabi road. The mining activities of minor minerals (ordinary sand, bajri and gravel) are dealt with according to the N.W.F.P mining Concession Rules, 1971 (DCR, 1998).

Geology of the Study Area

Mardan District consists mainly of a north-eastern hilly part and south-western plain area. The plain area of Mardan is comprised of alluvial cover of hundreds of meters thickness while the mountainous area consists of the rocks of Shewa Shahbazgarhi. According to Ahmad (1986) Shahbazgarhi complex can be divided in to Acidic and basic rocks. Acidic rocks are microporphyry, porphyritic granite, aegirine riececkite porphyry, riececkite gneiss. The acidic rocks are intruded by basic rocks such as metagabbro, metadolorite and local quartz monozonite. Minerals in the basic rocks include hastingsite, clinopyroxene, orthopyroxene, biotite and epidote while the acidic rocks have orthoclase, plagioclase and ferromagnesian minerals. Along with acidic and basic rocks, the three types of microstructure observed in the area are i) deformation structure ii) recovery structure and iii) recrystallization structure. It can be estimated from the structure and texture that the rocks had undergone intense cataclization/and or mylonization in the past.

Jehan (1985) concluded that the origin of Shewa Shehbazgarhi is of igneous nature. It was suggested that catacalsite and metagabbro can be dated to Precambrian times and subduction phenomena. However, the origination of gneisses microgranite could be related with intrusion of basic magma, or either to tectonic activity. She has classified the rocks of small outcrop south of Shahbazgarhi into acidic dykes, gneissose microgranite, metagabbro, lamprophyric dykes and cataclastic types. In the east of Mardan, Salkala Formation, Tanowal Formation and Ambela Granitic Complex are present towards Swabi District. Salkala Formation has sulfide mineral seems while Ambela Granite Complex is a batholithic mass comprising of granites, alkali granite, quartz syenites and basic dykes (Rafiq and Jan, 1989).

AIMS AND OBJECTIVES

Following are the aims and objectives of the present study:

- Identification and chemical characterization of the waters and soils of the Mardan District.
- Determination of Physico-chemical parameters and their environmental impacts on the inhabitants of the area.
- Investigation and verification of the already reported enhanced values of arsenic and if the arsenic enhancement is noticed then to identify possible ways and means for reducing the level of contamination.
- Preparation of geochemical zonation maps of the District to delineate areas of environmental concern using GIS.

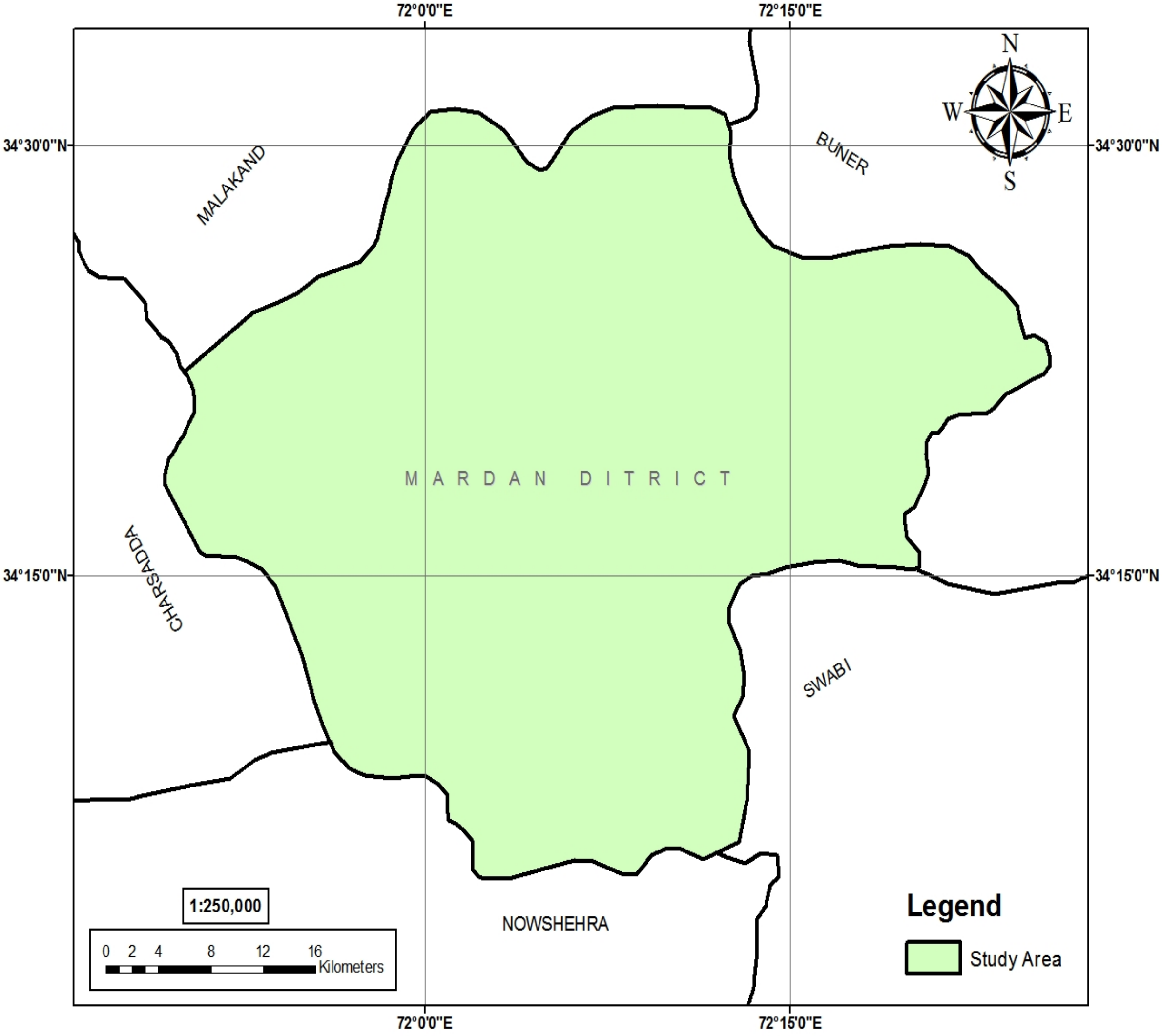

Fig. 1.1 Location Map of Mardan District

CHAPTER 2

LITERATURE REVIEW

Literature review on water and sediments contamination

Arienzo et al. (2009) carried out an extensive review on Potassium (K) from wastewater and its impacts on the soil, irrigated with such water. The main sources of K are effluent discharge from cheese and dairy processing; winery, oil mills and potatoes processing at several hundred to several thousand mg/l, besides effluents, solid waste dumping from such sources also elevate the K level. Potassium from these sources is more exchangeable than that of fertilizers. The irrigation with effluent increases soil organic, soil respiration, enzymatic activities and mineral content. Addition of K to soil with sufficient clay may hold K while with less clay soil K may leach to ground water. Despite of some positive effects, K in alkaline effluent may elevate K level and hinders the hydraulic conductivity of soil. Therefor the study suggested that some legume plants and grasses can be used to remove excess K from soil.

Emmaneul et al. (2009) conducted physiochemical-biological study regarding Health Risk Assessment (HRA) of wastewater from hospital in Haiti. Water samples from the septic tanks were compared with ground water. The ground water had showed high concentration of Cd, Pb, Cr and Ni due to leaching of effluent.

Kazi et al. (2009) have studied the level of arsenic contamination in Manchar Lake, Sindh, Pakistan. They studied the impacts of contamination by analyzing scalp hairs and blood of the residents. The range of arsenic concentrations in lake surface water was 35.2–158 µg/l, which are 3–15 folds higher than WHO limits. On the other hand good correlation was found between As in surface water and skin diseases in the area.

Latif et al. (2009) analyzed level of arsenic, chromium and iron in the water, foodstuff and sediments from different areas of Bangladesh. They found that arsenic of geogenic nature is positively correlated with iron in many samples; also chromium was found in excessive amount in the sediments from the tannery area of Bangladesh.

Bibi et al. (2008) conducted geochemical study on Meghna river delta. Water samples from different tube wells were collected. High As and Fe were recorded in the water samples from shallow tube wells. It was concluded from the leaching test that As release was significant under both acidic and alkaline conditions. However, Fe release was maximum under acidic conditions. It was concluded that the As release might be governed either by the dissolution of iron hydroxide fraction or organic matter in the sediments.

Giang Luu et al. (2008) conducted research on trace elements contamination in the ground water of Kandal province of Cambodia. For this purpose 15 water samples were collected from three villages and were analyzed for heavy metals contamination. About 86% of the samples were notified with high As concentration with average value of 552 µg/l; with dominant form of hazardous AsIII. Among other trace elements Ba, Mn and Pb were also in high concentrations.

Sthiannopkao et al. (2008) studied As and Mn contamination in the tube wells water of Prey Veng and Kandal provinces of Cambodia. Water samples were collected at different depths from tube wells. Arsenic was found in high concentration in about 54% samples. The remaining 46% tube wells water showed upto 400µg/l of Mn with low As. Arsenic concentration in the water of tube wells could be related to reducing conditions.

Farooqi et al. (2007) worked on arsenic, fluoride and sulfate concentration in the ground waters of Lahore and Kasure Districts. During their study 5 samples of rain water and 24 samples of ground water (shallow and deep ground) samples were collected and analyzed to measure health impacts on the residents. High fluoride and arsenic contants were observed in the shallow ground water samples. Samples from the local rain water contained all the three (F^-, As and SO_4^{-2}), which could be due to the brick factories in premises of Lahore and Kasure Districts.

Rapant and Krcmova (2007) investigated different metals in ground water. Through conducting screening Health Risk Assessment they found that 11 % of the Slovakia territory has about 1 % Arsenic chronic risk level.

Begum (2007) conducted physico-chemical analysis of different parameters in water, soil and plants samples collected from Kabal-Mingora area. Among light and heavy elements Mg, Cr and Ni were high in water samples near mélange zone. In the soil samples all the light element oxides and Cu, Pb, Zn, Ni, Cr, Co and Cd were in high contents. Similarly some plant samples also had elevated levels of these elements. The concentration of these elements was also correlated with the mafic and ultramafic rocks within mélange zone of swat.

Nasreen (2006) conducted study on the waters and soils of Peshawar basin. It was concluded that the waters from the shallow ground water sources were having high contents of cations, anions and trace and heavy metals as compared to deep ground waters. Similarly soils of Peshawar basin were also enriched in these elements. This enrichment of different elements with the passage of time could be attributed to fluctuation of water table, changes in sediments lithology and anthropogenic interferences.

Nickson et al. (2005) analyzed the ground water samples of Muzaffargarh District of south western Punjab. The samples were analyzed for various elements with more emphasize on As. The results showed that 58 % of the samples were recorded with high As content. It was further concluded that the samples collected from the rural areas had low As as compared to urban areas. This high As in the urban waters could be due to the reduction of Ferric hydroxide and release of Arsenic through anthropogenic activities.

Tamasi and Cini (2004) worked on water quality regarding heavy metals. Water samples from springs and public aqueducts in Mount Amiata region, Italy. This region has been active regarding volcanic activities. In samples many heavy metals were found at maximum allowable concentrations, except As which was found higher than maximum limit.

Rahman and Miah (2002) conducted a case study in rural areas of Chandpur District, Bangladesh. They found that 98.5 % of tube wells in the area were affected by arsenic contamination. The inhabitants severely affected by various As borne diseases due to consumption of As contaminated water.

Mandal and Suzuki (2002) have extensively reviewed different studies about the sources, fate, distribution and impacts of As throughout the world. They categorized the distribution of As into different rock types and sediments. They point out the ground water contamination with As is a major threat to human health. Fruit, fish and vegetables contain mainly organic As while, milk, dairy products, beef and cereals poses inorganic form. Major human diseases associated with As contamination are dermal problems, respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological, developmental, reproductive, immunologic, genotoxic, mutagenetic, and carcinogenic effects.

Berg et al. (2001) studied arsenic in drinking water and sediments of red river area, Hanoi at different seasonal interval. In the 68 water samples, 78 % were having Arsenic above Vietnam’s standards of 50µg/l. Holding capacity of arsenic in sediments was in order brown black clay > gray clay > brown gray sand.

Cooper and Gillespie (2001) carried out research on As, Hg in water and sediments in relation with these metals accumulation in fish tissues. Their study area was a 10.1 km^2 oxbow lake of Mississippi River called Moon Lake. With passage of time most of the surrounding areas are brought under cultivation and wetlands are drained. resulting in lake contamination and degradation. For analysis samples of water, sediments, fishes and surrounding soil were taken. Mercury in water was detected by cold vapor atomic absorption spectrometry with a detection limit of 0.2 mg/l while As concentrations in sediments and water were determined by stabilized temperature graphite furnace AA spectrometry. In the results of water samples both As and Hg were within permissible limits, average concentration of 5.12 mg/l and 2.16 mg/l respectively. Arsenic in soil, lake sediments, wetland sediments and fishes were in average concentration of 5727.88, 5614.41 mg/kg, and 6746.47 mg/kg, and 36.99 mg/kg respectively. Average Hg concentrations in soils, lake sediments, and fishes were, 55.1 mg/kg, 14.5 mg/kg and 125 mg/kg respectively. It was clear from results that the main source of contamination is run off from surrounding soils, as they have more metals than other mediums.

Khan et al. (2000) have done work on the quality of potable water of Mardan city and surrounding areas. In 31 water samples most showed high BOD and COD where some deep well water showed higher concentration of nitrates and magnesium values.

Literature review on soil

Javied et al. (2009) studied and compared the values of phosphate rocks collected from different localities of Abbotabad with national and international values, in order to assess environmental impact of phosphate fertilizers. Different light (K, Mg, Mn and Na) and heavy (Cd, Cu, Cr, Ni, Pb and Zn) elements were analyzed in the phosphate rocks to measure their threats to soil, water and air. On comparison with samples from international values, the average concentrations of elements were relatively lower than those in foreign samples. However, the uncontrolled use of fertilizer in agricultural soils may results in soil, water and air pollution.

Kanai et al. (2009) have identified impact of Fe deficiency on Zn uptake, accumulation and plant growth in *Zea mays.* In their study seedlings were treated with four different nutrient solutions separately in such combination: a complete nutrient solution (+Fe+Zn), a nutrient solution without EDA-Fe (−Fe+Zn), a nutrient solution without $ZnSO_4$ (+Fe−Zn), and a solution without either EDA-Fe or $ZnSO_4$ (−Fe−Zn). The amount of taken and accumulated nutrients was determined from dried maize shoots digested with HNO_3: $HClO_4$ (4:1) at 100–180 °C for 4 hours. Results showed that in Fe-deficient conditions, the uptake of Zn was 15-fold higher and Zn accumulation was 16-fold higher than that under normal nutrient conditions. Plant growth under conditions of both Fe and Zn deficiency was significantly higher than that under only Fe-deficient condition, because during Fe deficiency high uptake of Zn hinders plant growth.

Yang et al. (2009) studied the accumulation of cadmium in plants, grown on contaminated soil. They grew six different plants in the pot treated with cadmium and as a result linear relationship was found between level of contamination and accumulation. However level of accumulation differed in different plants.

Dinakar et al. (2008) did research on the Cd phytotoxicity on *Arachis hypogaea* L. They studied the impacts of Cd on chlorophyll, protein, proline, nitrate and nitrite reductase, antioxidant enzyme activity in leaves and roots. The seedlings were grown in the pots and provided with $CdCl_2$ in 25, 50, and 100 µmol/l concentrations for 10, 15, 20 and 25 days. Different extracts were made from leaves and roots according to enzyme type to be studied. The results showed direct relationship between the damage, to concentration and exposure time. The higher concentration of cadmium (100 µmol/l) resulted (leaves and roots) total chlorophyll 91.01%, protein 79.51%, 83.61%, nitrate reductase 79.39%, 80.72% and nitrite reductase 77.07%, 75.88% activity decreased with increase in cadmium concentrations and exposure periods.

Nwajei et al. (2007) worked on contaminated soil. In their study, they collected samples from the waste disposal sites in Onitsha metropolis, Nigeria. These samples were analyzed for seven (As, Ba, Cd, Cr, Mn, Pb and Li) metals and these elements were found in elevated concentration as compared to normal soils of the area.

Ganne et al. (2006) studied soils of Angleur, Belgium which is an industrial and zinc metallurgical waste dumping site. Four elements (As, Cu, Pb and Zn) were found at high concentration, however, leaching behavior of these metals was very low in relation with pH of that soil, posing low risk.

Sarkar et al. (2005) studied the speciation and bioavailability of As in two different soils: acidic sandy soil with low As retention and sandy loam with high concentration of amorphous Fe/Al-oxides. Both soils were spiked with dimethylarsenic acid (DMA), a low toxic herbicide at three rates: 45, 225, and 450 mg/kg. Arsenic speciation and bioavailability tests were done at the beginning and after four months of incubation. They concluded that soil with amorphous Fe/Al-oxides retain more As hence poses low bioavailability. Although As from such soil was less bioavailable but under acidic conditions of human gastrointestinal system As may become available.

Smeets et al. (2005) studied the Cd phytotoxicity and antioxidative reaction in bean (*Phaseolus vulgaris* L.). The seedlings were exposed to minimum Cd level. Major biochemical and physiological changes were observed within 24 hours. Some important enzymes were reduce in functioning, similarly ascorbate peroxidase and glutathione reductase increased to cope the oxidative stress generated in leaves. After 72 hours of exposure visual effect like chlorosis was visible, showing high oxidative stress due to Cd.

Tamura et al. (2005) worked on Phyto accumulation of Pb, on buckwheat. Soil was sieved upto 2mm size, CEC and pH were also determined. One soil type was kept as control while the 2nd type was made contaminated through Pb pellets. The soils were than provided with urea, calcium superphosphate, potassium chloride and magnesium lime. Three seedlings were grown in each pot provided with 60% humidity and light for 12 hours of day for 8 weeks. Before one week of harvesting Pb contaminated wheat were treated with chelators, citrate (trisodium citrate), ethylenediaminetetraacetic acid disodium salt (EDTA) or methylglycinediacetic acid trisodium salt (MGDA) at concentration of 0, 1, 5, 10, and 20 mmol/kg. Results showed that more Pb was accumulated in plants grown on Pb contaminated soil than those of control soil. Among plant tissues leaves ((8,000 mg/kg DW), had higher accumulation than shoot (2,000 mg/kg DW), and roots (3,300 mg/kg DW). Also among chelators, MGDA which is biodegradable enhanced the uptake of Pb from the soil. From this experiment the author concluded that Pb at level of 1000mg/kg DW can be accumulated in shoots of buckwheat without significant effects.

Ali et al. (2004) worked on the phytotoxicity of Cd and Cr in control and forest soils by using barley (*Hordeum vulgare L.*). Soils were spiked with $K_2Cr_2O_7$ and $CuSO_4$ on dry (DW) weight bases. Soil concentrations ranged from 0.30 to 305mg Cu/g and from 0.3 to 101mg Cr/g DW in silica; and from 17.2 to 322mg Cu/g and from 12.4 to 318mg Cr/g DW. Plants were taken after 14 days of exposure. Results were studied from various aspects like effect of concentration; subtract type and exposure, to plant emergence, growth and tissue accumulation. In all forms plants in forest soil were less affected than those in artificial soil due to low bioavailability.

Kosobrukhov et al. (2003) worked on Pb phytotoxicity in *Plantago major* plants which are generally grown on Pb contaminated soils. Phytotoxicity was checked through parameters of plant growth, photosynthesis, and chlorophyll content and leaf anatomy. Analysis was carried out in two parts: on plants grown in laboratory having no Pb and 2nd on plants collected from their habitats with Pb content in soil determined in 0.1 N HCl soil extract was 486 ± 20mg. On each category of plants separate experiments were made for comparison. Various parameters like photosynthetic photon flux density (PPFD), CO_2

gas Exchange, stomata per unit Leaf area in adaxial and abaxial epidermis etc. The results showed decreased in plant growth and photosynthesis due to reduction in leaf area, decrease in chlorophyll content and change in the leaf structure with increase of Pb from 500 and 2000 mg/ kg.

Jonesa et al. (2000) worked on the roadside Hg deposition and its consequences on plants. Methylcyclopentadienyl manganese tricarbonyl (MMT: $C_9H_7MnO_3$), that is used as anti knocking agent; its combustion releases oxides of manganese which are deposited along roadside. To measure their effects on plants they selected Radish (*Raphanus sativus*) for experiment. Seedlings of Radish were sprouted in manganous chloride (0, 0.25, 0.5, 1.0, 5.0, 10.0, 50.0, 100.0, 500.0, 750.0, and 1000.0 mg/l Mn). After five days the optimum temperature for Mn effectiveness was determined at 5°C intervals from 5°C-45°C, with the help of Calorimeter. Respiratory rate was determined by heat produced from the reaction between CO_2 from tissues and NaOH. Concentration of Mn in seedling and tissues were also determined. Mn in solution and in 5 days seedlings were in good linear relation. Similarly the plant metabolism got increased with temperature but beyond 100mg/l, oxidative stress due to Mn was observed. Growth rate was good at higher temperature and low Mn, while at higher amount growth decreased.

Carbonellu et al. (1998) studied the phytotoxic effects of different As compounds on marsh grass called *Spartina alterniflor*. Soil was treated with four chemical forms of As, AsO_2, $AsO_{3,}$ Monomethylacetamide (MMAA) and Dimethylacetamide (DMAA) and four As concentrations 0, 0.2, 0.8 and 2.0. The entire chemicals were in the forms sodium salts. Uniform seedlings were grown in the controlled environment and were harvested after 30 days. Plants treated with organic forms (MMAA and DMAA) showed significant growth reduction while those with As (V) had highest matter production due to more uptake of P by plants. Increased concentration of Na in roots and Ca in leaf was observed in plants treated with organic form.

Das et al. (1997) reviewed many studies on the phytotoxic impacts of Cd. Cadmium being a non essential element gets concentrated in the soil through various anthropogenic activities like automobiles exhaust, mining and industrial sources. The common symptoms of Cd phytotoxicity are chlorosis and stunning. Chlorosis is due to deficiency of iron and other essential nutrients. High Cd content lowers the P and Mn uptake. It also destroys enzymes, mitochondria and reduces concentration of Adinotriphosphate (ATP) and chlorophyll.

CHAPTER 3

METHODOLOGY

Research methodology of present study is divided into two folds: Field and Laboratory work.

Field Work

Water Sampling

To conduct hydro-geochemical study of Mardan District, representative water samples from all the fresh water resources including dug wells and hand pumps (<10m deep), tube wells and bore holes (>30m deep), seasonal streams, springs and irrigational canals were collected. The samples locations were taken by the GPS. Before collecting the water samples the polyethylene bottles were washed with double deionized water. From the field each representative sample was stored in two bottles one un-acidified for the identification of physical parameters while, another was acidified with 5% HNO_3 for elemental analysis. Temperature, electric conductivity and pH were recorded on the spot in the field. Color, depth and flow of water were also observed in the field. Water samples were further taken for analysis in the Geochemistry Laboratory of National Centre of Excellence, University of Peshawar.

Soil Sampling

In order to determine the Pedo-chemistry of Mardan District, the soil samples were collected from different agricultural fields of the area. Each samples of about 1kg was taken upto a depth of 30 cm by an uger and stored in the polyethylene bags. These soil samples were labeled in the field; GPS position for each sample was recorded. The samples were taken further for analysis to Geochemistry laboratory.

Determination of Physical Parameters of Water

The physical properties temperature (T), pH and electric conductivity (EC), were measured in the field with the help of portable instruments.

Determination of Temperature

Temperature of water is greatly dependant upon the source, depth and season, chemical and biological activities. Ground water is less affected by surface temperature and processes while, temperature and other phenomena of surface water vary with atmospheric temperature. The living biota of water ecosystems is adapted to a narrow range of temperature. In the field the temperature of water sample was determined with simple thermometer.

Determination of pH

Hydrogen ion concentration is an important parameter regarding the quality of any substance. Chemically pure water dissociates in to 10^{-14}g molecules per liter of water into H^+ and OH^- in equal proportion at 25ºC. pH of drinking water below seven indicates acidic while above seven for alkaline, it may be little alkaline due to presence of carbonates. pH may be measured either by colorimetric method or by electric method. pH of the samples was again determined in the laboratory with Consort Electrochemical

Analyzer. The pH meter was calibrated with buffer solutions of 4 and 7 pH. pH meter was immersed in samples and pH was noted. For accurate results pH meter was calibrated with buffer solutions after few samples.

Determination of Electric Conductivity (EC) and Total Dissolved Solids (TDS)

Electric conductivity is the ability of solution to pass the amount of electric current. It is directly related to the amount of dissolved substances. Pure water is supposed to have low electric conductivity. Electric conductivity and TDS in the water samples were determined with the help of Consort Electrochemical Analyzer C931. Conductivity meter was first calibrated with 0.01M KCl solution and results recorded in µS/cm. To get accurate results after few samples again meter was calibrated with KCl solution.

Determination of Turbidity

Turbidity is the optical property of water in which scattering of light occurs due to suspended particles. In water turbidity arises from silt, clay particles, mineral dissociation and organic particles. In the laboratory turbidity was measured by using JENWAY 6035 Turbidity meter. Before analyizing the water samples instrument was first calibrated with blank, 2 and 5NTU standards.

Determination of Anions in water samples

The following anions (SO_4^{-2}, NO_3^-, Cl^- , CO_3^{-2} and HCO_3^-) were determined in the samples:

Determination of Sulfate (SO_4^{-2})

Sulfate concentrations in the water samples were determined by HACH DR 2800 photometer. From the stored programs method 680 was selected for measuring sulfate in range of 2-70g. One square cell was filled with 10 ml of sample and to it powder content of SulfaVer 4 reagent was added. Content of the cell was thoroughly mixed by swirling and left for 5 minutes. In second cell same sample was taken as blank sample. After five minutes the blank containing cell was inserted and pressed zero. Similarly the cell having sample with reagent was inserted and reading for sulfate was recorded in mg/l.

Determination of Nitrates (NO_3^-)

Nitrate concentrations in the water samples were determined by HACH DR 2800 photometer. Method for nitrate was selected. Two cells were filled with 10 ml of same sample. In one cell reagent was added from powder pillow. A time of one minute was set during which cell's contents were shaked vigorously. Reaction cell was left for 5 minutes. Blank was wiped, inserted in the cell holder and reading was set to zero mg/l. Then sample's cell was inserted into the cell holder and concentration of nitrate was recorded in mg/l.

Determination of Chlorides (Cl^-)

Chloride in water was also determined by HACH DR2800 photometer. From stored program 70 chloride was selected. One square sample cell was filled with 10 ml of deionized water and reserved as blank. In second cell 10 ml of sample was taken; in both cells 0.8ml of Mercuric Thiocyanate solution was added. After mixing well, 0.4 ml of ferric ion solution was added in each cell, on mixing an orange color developed in cells. Both cells were kept for two minutes for reaction, after reaction time first blank than sample's cell was inserted into cell holder and the results were noted in mg/l.

Determination of Carbonates (CO_3^{-2}) and Bicarbonates (HCO_3^-)

Carbonates and bicarbonates were measured by titration method using 0.1N hydrochloric acid. Phenolphtalene and methyl orange were used as indicators. The 25 ml of water sample was taken in flask and few drops of Phenolphtalene were added but no color developed as all samples were having pH below 8.3. In the same volume 2-3 drops of methyl orange were added. Light orange color developed in samples which were titrated with 0.1N HCl until color disappeared. The volume of acid used was noted and results were recorded in mg/l in terms of $CaCO_3$ using following formula (Srivastava, 2004);

$$\text{mg/l of } CaCO_3 = \frac{(\text{Volume} \times \text{N of acid used}) \times 50{,}000}{\text{Volume of sample}}$$

Determination of Light, Trace and Heavy Elements by Atomic Absorption Technique

Major portion of the analysis was done with the help of atomic absorption using flame, electrothermal (graphite furnace) and Mercury Hydride System (MHS). Flame technique was used for the analysis of Calcium (Ca), Magnesium (Mg), Sodium (Na), Potassium (K), Iron (Fe) and Manganese (Mn) for both soil and water samples. The remaining elements such as Copper (Cu), Lead (Pb), Zinc (Zn), Nickel (Ni), Chromium (Cr) and Cadmium (Cd) were also determined by flame technique in the soils and concentrations were recorded in mg/kg. While these elements were determined by graphite furnace and the results were noted in µg/l. Mercury Hydride System was used for measuring Arsenic in both soil and water samples in µg/l.

Water Analysis

Determination of Major Elements in water with Flame Technique

Determination of Calcium and Magnesium (Ca + Mg)

Instrumental conditions:

Element	**Ca**	**Mg**
Mode	**Absorption**	**Absorption**
Wavelength	**422nm**	**285.2nm**
Energy	**57**	**58**
Current	**10**	**1.6**
Slit width	**0.7nm**	**0.4nm**

Air flow	**17 L/m**	**17L/min**
Fuel flow	**2L/min**	**2L/min**

Standard stock solutions of 1000 mg/l of Ca and Mg were prepared by dissolving 2.479g of $CaCO_3$ and 4.952g of $MgCO_3$ in 50ml of double deionized water and adding drop wise 10ml of HCl, and then diluted to one liter with double deionized water for calcium and magnesium respectively. From these stock solutions working standards of 2.5, 5 and 10 mg/l were prepared. Before running samples, 3ml of lanthanum oxide was added to the working standards and samples. Instrument was calibrated according to above mentioned conditions and standardization was done by the working standards solutions.

Determination of Sodium and Potassium (Na + K)

Instrumental conditions:

Element	**Na**	**K**
Mode	**Absorption**	**Absorption**
Wavelength	**589nm**	**766.5nm**
Energy	**57**	**89**
Current	**8**	**12**
Slit width	**0.2nm**	**0.4nm**
Air flow	**17 L/mi**	**17L/min**
Fuel flow	**2L/min**	**2L/min**

Standard stock solutions of 1000mg/l of Na and K were prepared by dissolving 2.542g of NaCl and 1.907g of KCl in deionized water and diluted to one liter with double deionized water in a volumetric flask. Standard working solutions of different concentration i.e., 2.5, 5 and 10mg/l were prepared from 1000mg/l stock solutions. The samples were diluted with double deionized water where required. The instrument was calibrated with the above mentioned conditions and standardized with working standards solutions.

Determination of Manganese (Mn)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**279.5nm**
Energy	**38**
Current	**20**
Slit width	**0.2nm**
Air flow	**17L/min**
Fuel flow	**2L/min**

1000mg/l standard was prepared by dissolving 4.418g of $MnSO_4.4H_2O$ in double deionized water in 1000ml volumetric flask and made to the mark. This stock solution was used for preparation of working standards of 2.5, 5, 10 mg/l. When proper conditions were attained; instrument was calibrated with working standards. Samples were run on atomic absorption and concentration was noted in mg/l.

Determination of trace and heavy elements in Water Samples on Graphite Furnace

Determination of iron (Fe)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**248.3nm**
Pretreatment temp	**1400˚C**
Atomization temp	**2400˚C**
Energy	**40**
Current	**30mA**
Tube/site	**pyro/platform**
Slit width	**0.2nm**

Stock solution of 1000mg/l was prepared by dissolving 3.115g Mohr salt [Fe $(NH_4)_2$. $(SO_4)_2$ H_2O] in double deionized water and further diluted in volumetric flask to one liter. Working standards of different concentrations i.e., 50, 100 and 200µg/l were prepared from the stock solution. Atomic absorption was calibrated with working standards and concentration of iron was measured in µg/l.

Determination of Copper (Cu)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**324.8nm**

Pretreatment temp	**1200˚C**
Atomization temp	**2300˚C**
Energy	**23**
Current	**15mA**
Tube/site	**pyro/platform**
Slit width	**0.7nm**

1000mg/l stock solution was prepared by dissolving 1g copper metal in (1:1) HNO_3 and further diluted to one liter with deionized water in a volumetric flask. From the stock solution, working standards of 2.5, 5 and 10mg/l were prepared. Instrument was set according to the above mentioned conditions; calibrated with working standards and concentration in samples was noted in µg/l.

Determination of Lead (Pb)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**283.3nm**
Pretreatment temp	**850˚C**
Atomization temp	**1800˚C**
Energy	**35**
Current	**10mA**
Tube/site	**pyro/platform**
Slit width	**0.7nm**

1000mg/l stock solution was prepared by dissolving 1.598g of $Pb (NO_3)_2$ in 1% of HNO_3 and diluted to one liter with double deionized water. Working standard solutions of 50, 100 and 200µg/l were prepared from this 1000mg/l stock solution. Instrument was calibrated according to above mentioned conditions.

Determination of Zinc (Zn)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**213.9nm**
Pretreatment temp	**700˚C**
Atomization temp	**1800˚C**
Energy	**22**
Current	**15mA**
Tube/site	**pyro/platform**
Slit width	**0.7nm**

1000mg/l stock solution was prepared by 1g zinc metal in minimum volume of HCl and diluted upto one liter with double deionized water in a volumetric flask. Further working standards of 50, 100 and 200µg/l were prepared from the same stock solution. After attaining proper conditions and calibration samples were run on instrument through autosampler.

Determination of Nickel (Ni)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**232nm**
Pretreatment temp	**1400˚C**
Atomization temp	**2500˚C**
Energy	**30**
Current	**25mA**
Tube/site	**pyro/platform**
Slit width	**0.2nm**

Stock solution of 1000mg/l was prepared by dissolving 1.273g of Nickel oxide in minimum volume of 10% (v/v) HCl and diluted to one liter with double deionized water in a volumetric flask. Working standard solutions of 50, 100 and 200µg/l were prepared from stock solution. Instrument was calibrated according to the above mentioned conditions. Results were recorded in µg/l.

Determination of Chromium (Cr)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**357.9nm**
Pretreatment temp	**1650˚C**
Atomization temp	**2500˚C**

Energy	**67**
Current	**25mA**
Tube/site	**pyro/platform**
Slit width	**0.7nm**

Stock solution of 1000mg/l was prepared by dissolving 3.735g of potassium chromate (K_2CrO_4) in double deionized water and diluted to one liter with double deionized water in one liter volumetric flask. From this solution, working standards of 50, 100 and 200µg/l were prepared. After proper calibration, samples were run through autosampler and concentration was noted in µg/l.

Determination of Cadmium (Cd)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**228.8nm**
Pretreatment temp	**700˚C**
Atomization temp	**1608˚C**
Energy	**26**
Current	**4mA**
Tube/site	**pyro/platform**
Slit width	**0.7nm**

For making 1000mg/l stock solution 1g of cadmium metal was dissolved in minimum volume of HCl and diluted with 1 % HCl upto one liter. From this, stock working standards of 50, 100 and 200µg/l were prepared. Instrument was calibrated with working standards, and then standards of known concentrations were run in the machine (graphite furnace) to check the accuracy of instrument. All the samples and standards after proper calibration were run through autosampler and concentrations were recorded in µg/l.

Soil Analysis

Preparation of soil solutions

Before the preparation of the solution, the soil samples were air dried. than pulverized to 200 meshes. The mortar was washed and dried after each run. The powder was thoroughly mixed through quartering and coning. Powdered samples were kept in glass bottles for drying in oven at 110 ºC overnight. Solutions were prepared from these oven dried samples.

Solution preparation for Physico-chemical parameters in soil

For measuring physical parameters of soil, 10g of each oven dried sample of soil was taken. To each sample 40ml of deionized water was added and shaken for 10 minutes on electric shaker. Mixture was left overnight and again mixed thoroughly for 10 minutes. After leaving for next 24 hours; again mixture was shaken and finally filtered. Filtrate was used for the determination of physico-chemical parameters.

Stock solution preparation for major elements

From oven dried soil samples, 0.5g of each soil sample was taken in Teflon beakers and10ml of Hydrofluoric acid (HF) and 4ml of Perchloric acid ($HClO_4$) were added. After one hour heating on hot plate, 2ml of Perchloric acid was added and heated continuously until paste was formed. Than again about 10ml of deionized water and 4ml of Perchloric acid were added and heated for 10 minutes. Finally, content of each beaker was diluted to 250 ml with double deionized water. This method was adopted after Jeffery and Hutcheson (1986). This solution was run on the atomic absorption for determination of major elements.

Stock solution preparation for the trace elements

One gram of each dried soil sample was taken in Typhlon beaker and 5ml of HF was added. Teflon beakers were heated for one hour on hot plate, after heating 10ml of aqua regia was added. Beakers were heated to completely dry the sample. On drying 20ml of 2N HCl was added in the dried samples, heated and diluted with 30ml of deionized water (Jeffery and Hutscher, 1986). Solution was run on Atomic Absorption (AA) for determination of Cu, Pb, Zn, Ni, Cr, and Cd.

Solution preparation for Arsenic in soil

5g of air dried soil sample was digested in an acid mixture prepared from 20ml $HNO_{3,}$ 10ml HCl and 2ml HF. Digests were heated at 130˚C on hot plat for 2 hours. After keeping overnight in fuming hood, the contents were filtered. The filtrates were further diluted to 100ml with double deionized water. This solution was run on Mercury Hydride Generation System for Arsenic determination (Abollino et al., 2002).

Determination of Physical Parameters of Soil

Soil color

Soil color was determined in both dry and moist state by comparing it with Munsell soils color Chart.

Soil Texture

Soil texture was determined with hydrometer method. 50g of oven dried soil was taken and 10ml of 1N Sodium Carbonate was added along with deionized water. The mixture was stirred thoroughly in dispersion machine for five minutes. After this, the mixing suspension was transferred to one liter graduated cylinder. Hydrometer was then dipped in suspension and after 40 seconds, the temperature and reading on Hydrometer were noted. The temperature and height were recoded after 2 hours (Ryan, et al., 2001).

pH, Conductivity, Total Dissolved Solids (TDS) in soil

Pysico-chemical parameters such as; pH, conductivity and total dissolve solids (TDS) were determined through the same procedure as was used for water samples from the soil solution prepared for physico-chemical parameters.

Determination of Elements in Soil Samples

Determination of Calcium and Magnesium (Ca + Mg)

Instrumental conditions:

Element	**Ca**	**Mg**
Mode	**Absorption**	**Absorption**
Wavelength	**422nm**	**285.2nm**
Energy	**57**	**58**
Current	**10**	**1.6**
Slit width	**0.7nm**	**0.4nm**
Air flow	**17 L/m**	**17L/min**
Fuel flow	**2L/min**	**2L/min**

Standard stock solutions of 1000mg/l were prepared by dissolving 2.479g of $CaCO_3$ and 4.952g of $MgCO_3$ in 50ml of deionized water and adding drop wise 10ml of HCl, and then diluted to one liter with deionized water for calcium and magnesium respectively. From these stock solutions, working standards of 2.5, 5 and 10mg/l were prepared. Before running, samples 3ml of lanthanum oxide was added to each sample. Instrument was calibrated according to above conditions and the standardization was done by working standards. The samples were than run as unknown on the instruments and result was noted in mg/l.

Determination of Sodium and Potassium (Na + K)

Instrumental conditions:

Element	**Na**	**K**
Mode	**Absorption**	**Absorption**
Wavelength	**589nm**	**766.5nm**
Energy	**57**	**89**
Current	**8**	**12**
Slit width	**0.2nm**	**0.4nm**
Air flow	**17 L/mi**	**17L/min**
Fuel flow	**2L/min**	**2L/min**

Standard stock solutions of 1000mg/l were prepared by dissolving 2.542g of NaCl and 1.910g KCl in deionized water and diluting upto one liter with deionized water in a volumetric flask. Working solutions of different concentration i.e., 2.5, 5 and 10mg/l were prepared from 1000mg/l stock solutions. The samples were diluted with double deionized water where it was required. The instrument was calibrated and standardized before aspirating the samples through the machine. Concentrations were noted in mg/l.

Determination of Iron (Fe)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**248.3nm**
Energy	**40**

Current	**30**
Slit width	**0.2H**
Air flow	**17L/min**
Fuel flow	**2.3L/min**

Stock solution of 1000mg/l was prepared by dissolving Mohr salt [Fe $(NH_4)_2$. $(SO_4)_2$ H_2O] in deionized water and further diluted to one liter with deionized water. Working standards of different concentrations i.e. 2.5, 5 and 10mg/l were prepared from the stock solution. Atomic absorption was calibrated with prepared working standards and concentration of iron was measured in mg/l.

Determination of Manganese (Mn)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**279.5nm**
Energy	**38**
Current	**20**
Slit width	**0.2H**
Air flow	**17L/min**
Fuel flow	**2L/min**

1000mg/l standard was prepared by dissolving 4.054g of $MnSO_4.4H_2O$ in deionized water in volumetric flask and diluted to one liter. This stock solution was used for preparation of working solutions of 2.5, 5, 10mg/l. When proper conditions were attained; instrument was calibrated with working standards. Samples were run and concentration was noted in mg/l.

Determination of Copper (Cu)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**324.8nm**
Energy	**68**
Current	**15**
Slit width	**0.7H**
Air flow	**17L/min**
Fuel flow	**2L/min**

1000mg/l stock solution was prepared by dissolving 1g copper metal in (1:1) HNO_3 and further diluted to one liter with deionized water in a volumetric flask. From the stock, working standards of 2.5, 5 and 10mg/l were prepared. Instrumented was set according to above standardization and calibrated with working standard solutions. Concentrations were noted in mg/l.

Determination of Lead (Pb)

Instrumental conditions:

Mode	**Absorption**

Wavelength	**283.3nm**
Energy	**41**
Current	**10**
Slit width	**0.7H**
Air flow	**17L/min**
Fuel flow	**2L/min**

1000mg/l stock solution was prepared by dissolving 1.598g of Pb $(NO_3)_2$ in 1% of HNO_3 and diluted to one liter with deionized water. Working standards of 2.5, 5 and 10 mg/l were prepared from this 1000mg/l stock solution. Instrument was calibrated and standardized according to above conditions and concentration of Pb was determined in mg/l.

Determination of Zinc (Zn)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**213.9nm**
Energy	**35**
Current	**15**
Slit width	**0.7H**
Air flow	**17L/min**
Fuel flow	**2L/min**

1000mg/l stock solution was prepared by 1g of zinc metal in minimum volume of HCl and diluted upto one liter with deionized water in a volumetric flask. Further working standards of 2.5, 5 and 10mg/l were prepared from the same stock solution. After attaining proper conditions and calibration, samples were run on instrument and the concentrations were noted in mg/l.

Determination of Nickel (Ni)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**232nm**
Energy	**30**
Current	**25**
Slit width	**0.2H**
Air flow	**17L/min**
Fuel flow	**2L/min**

Stock solution of 1000mg/l was prepared by dissolving 1.273g of Nickel oxide in minimum volume of 10% (v/v) HCl and diluted to one liter with deionized water in a volumetric flask. Working solution of 2.5, 5 and 10mg/l were prepared from stock solution. Instrument was calibrated and standardized according the above mentioned conditions. Results were recorded in mg/l.

Determination of Chromium (Cr)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**357.9nm**
Energy	**30**
Current	**25**
Slit width	**0.7H**
Air flow	**17L/min**
Fuel flow	**2.5L/min**

Stock solution of 1000mg/l was prepared by dissolving 3.735g of potassium chromate (K_2CrO_4) in deionized water and diluted to one liter with same water in volumetric flask. From this solution working standards of 2.5, 5 and 10mg/l were prepared. After proper calibration and standardization, samples were run and concentration was noted in mg/l.

Determination of Cadmium (Cd)

Instrumental conditions:

Mode	**Absorption**
Wavelength	**279.5nm**
Energy	**39**
Current	**4**
Slit width	**0.2H**

Air flow	**17L/min**
Fuel flow	**2L/min**

For making 1000mg/l stock solution, 1g of cadmium metal was dissolved in minimum volume of HCl and diluted with 1 % HCl upto one liter. From this stock working standards of 2.5, 5 and 10mg/l were prepared. All the required conditions were set on machine. Instrument was calibrated with working standards, and then standards of known concentrations were run to check the accuracy of instrument. After proper calibration samples were run and concentration was recorded in mg/l.

Determination of Arsenic (As) in Water and Soil on Mercury Hydride System

Instrumental conditions

Wavelength	**193.7nm**
Slit wide	**0.7H**
Radiation source	**Electrodeless discharge lamp for As**
Pre reaction purge time	**50 sec**
Reaction time	**25 sec**
Post reaction purge time	**40 sec**

Arsenic was determined on Mercury Hydride Generation system (MHS). The following solutions were prepared;

1. 0.25mol/L (1% w/v) NaOH was prepared by dissolving 10g NaOH in double deionized water and diluted to one liter. **0.15M (1.5% v/v) HCl**

2. 5mol/L HCl was prepared by taking **206ml** concentrated HCl and diluting upto one liter with double deionized water. **0.8mol/L $NaBH_4$** solution was prepared by taking 3g Sodium borohydride and dissolving it in 100ml of 10% NaOH. Pottasium iodied (KI) was prepared by 3g KI and 5g Ascorbic acid in 100ml of deionized water.

As determination with Pottasium iodied (KI) for pre reduction of As (IV) to As (III)

In order to reduce interference, As (IV) was reduced to As (III) with KI solution. 10ml of 5mol/L HCl and 1ml KI were added to 10ml of each sample. These samples were left for 30min in bottles to reduce As (IV) to As (III). Same procedure was followed for the blank and standards. After 30 minutes, samples were run on MHS. Total inorganic arsenic was determined in µg/l.

CHAPTER 4

WATER CHEMISTRY

Water is a very complicated and important medium upon which, all the living molecules depend and without it no life exists. These unique properties of the water are due to hydrogen bonding, making it best solvent. Due to high dissolution power, it provides basic medium for the transport of nutrients and other hazardous substances (Trivedi and Raj, 1992).

Throughout history water has greatly influenced the well being of humans both qualitatively and quantitatively. Great civilizations were habituated along the water resources and were disappeared due to water shortage. Water has also added destruction to the humans through floods and water born diseases which are able to kill million of people. In nature the water is circulated through Hydrological cycle. (Trivedi and Raj, 1992).

Although major part of the water on the earth is confined in the oceans and ice caps, the two principle sources of water are surface water and ground water, used by the habitants.

Surface Water

Surface water includes all the sources of water (rivers, lakes, streams, canals and springs etc) on the earth except of oceans and seas. Sunlight can penetrate the surface water and is well aerated. Due to availability of oxygen and sunlight, photosynthesis plays important role in alteration of surface water chemistry. The bottom boundary of surface water is called bed sediments (Perk, 2006).

Surface Water Pollution

Surface waters are in contact with humans, animals and soil microbes, because of this, it is more likely to contain harmful chemicals and microbes than ground water (Srivastava, 2004). Water from domestic run off contains variety of contaminants like nitrogen, phosphorus, heavy metals and organic compounds. Direct point sources of surface water pollution are mine drainage, effluents from industrial and municipal sewage. Pollutants in the surface water partially get accumulated in the bed sediments which can be again released to water (Perks, 2006).

Ground water

Ground water is almost found everywhere but the question is its accessibility. It may be so close to surface or hundreds of feet deep (Srivastava, 2004). Ground water is recharged either through infiltration of surface water or percolation of water from unsaturated zone. This replenishment of the ground water is called recharge. The porous structure of soil sediments conduct the water.The only and most differing parameter in the ground waters is temperature (Perks, 2006; Srivastava, 2004).

Ground water pollution

Generally sources of the ground water pollution are same as for soil and surface water, because the dissolved pollutants in soil and surface water infiltrate or percolate to ground water (Perk, 2006). Direct input of contaminated water through deep well injection also contributes to deep water contamination (Perks, 2006). Most of the chemical substances are removed during percolation of the water through the soil horizons. Ground water mostly contains no microbes, but usually some bacteria, due to filtering nature of the soil (Srivastava, 2004).

Classification of Water Pollutants

In spite of such great significance, water is the most suffered medium of the modern ages by pollution and contamination. Quality of surface water is dependant on both natural and anthropogenic sources. The anthropogenic sources constitute as constant polluting source (Singh et al., 2004) and deteriorating water quality both in surface and ground water sources through atmospheric pollution, effluent discharge, use of agriculture, chemical eroded soil and land use (Niemi, 1990). Water pollution can be defined any physical or chemical change in water that an adversely affect organisms. Any substance that disallows the normal use of water is regarded as pollutant. The excess of naturally occurring substances is also considered as pollution. Water pollution is a broad phenomenon, as it varies with the use; nature and quantity of water, e.g., nitrogen in the irrigated water will not be so hazardous than in drinking water (Trivedi and Raj, 1992). Nature and complexity of water pollutants varies with sources generating these pollutants. Trivedi and Raj (1992) have classified water pollutants into following categories:

a) Oxygen demanding waste

Oxygen demanding wastes are primarily organic materials that are oxidized by bacteria**.** Their oxidation leads to the depletion of oxygen in aquatic system. This depletion affects the fish and other aquatic life, besides these wastes imparts annoying odor, color and scum to aquatic life.

b) Disease causing agents

The main sources of such agents are, municipal and sanitary wastes, slaughtering plants and waste dumping. Disease causing agents are mostly bacteria and microorganisms; however, water may also be a breeding place for terrestrial disease causing species e.g., mosquitoes.

c) Plant nutrients

Although nutrients are essential for all living things, but their excess in any environment results in many problems. Excessive nutrient levels accelerate the plants and algal growth resulting in Eutriphication. The organic matter on decay increases the oxygen demand of the system besides other problems.

d) Organic compounds

Sources of organic chemicals are diverse, including detergents, pesticides, industrial products and the decomposition products of the other organic matters. Some of the organics and their biproducts are more dangerous, e.g., phenol has been found toxic to fishes at level less than 1mg/l.

e) Oil

Water is mostly affected by oil during its production, distribution and use in the domestic works. Incidental leakage from ships and oil plants has badly influenced water resources.

f) Inorganic chemicals and mineral substances

This category of pollutants includes inorganic salts, mineral acids and metals. Presence of these elements disrupts the aquatic ecology greatly. The major associated problems are change in the pH, increasing corrosivety, disturbing osmotic balance of salts in the aquatic flora and fauna, persistent heavy metals accumulation and rendering water unsafe for irrigation purposes.

g) Sediments

Sediments are naturally added to water by erosional processes from various sources. These sediments fill the stream channels; power plants and machines are eroded; increase turbidity; reduce light penetration and disrupt habitats of aquatic lives.

h) Radioactive materials

Different types of radioactive waste are released from nuclear plants; industries, mining and refining, medical and scientific research utilizations. Hazardous elements leached from the tailings and reach soil and water. Many of the radioactive elements show similar behavior to other plants nutrients and get absorbed: finally reaching to higher food levels.

i) Heat

Normal water has an average (15-22˚C) temperature. Rise in water temperature is mainly due to thermal waste water used for cooling purposes in plants. High temperature alters the physical, chemical and biological characteristics of the water system, reducing or eliminating life forms. It may also accelerates spawning activity and as a consequence starvation of new spawning. In heated water the dissolved oxygen is lowered: rate of chemical reactions are increased and no hatchings from the eggs of various animals.

Physico- Chemical Properties of Water

The geochemical data of the waters of Mardan District have been given in table 4.1 to 4.4 and are graphically presented in Figures 4.1 to 4.13. Various concentrations and the related variation of physical parameters, anions, cations and the heavy and trace elements in the present studied water samples have been described below:

Water classification

Piper diagram was used to classify the waters of Mardan District. Classification was made on the bases of pH, TDS, Na^+, Ca^+, Mg^{+2}, K^+, SO_4^{-2}, Cl^- and HCO_3^- concentration. In case of surface water dominant cations were Na^+ and K^+ while in anions, HCO_3^- was dominant. Surface water lies in the field of $NaHCO_3$ (Fig. 4.14a). Similarly shallow and deep ground water falls in the fields of $NaHCO_3$ and $NaCaHCO_3$ category (Fig. 4.14b and c respectively). Water from the study area is alkaline type with prevailing (Hydrogen) Carbonatic nature.

Temperature (T)

Temperature is the most important parameter for the aquatic environment, because it controls all the physical, chemical and biological properties. Density, viscosity, surface tension, vapor pressure all are temperature dependent. Saturation values of substances and gases, biological oxygen demands, photosynthesis, microbial activities, all are temperature dependent (Trivedi and Raj, 1992).

Temperature of surface water varied from 18 to 30°C with average value of 25°C (Table 4.1a). Values of temperature in shallow ground water sources (Table 4.1b) varied from 20 to 27°C with average value of 23°C. Similarly deep ground water sources varied from15 to 26°C with an average value of 23°C (Table 4.1c). Majority of the surface waters showed values about 20C°, however, high values were found in stream water from Shahbaz Garhi (30°C), Saidabad (30°C), Bakhshali (30°C) and Malakabad (30°C) (Table 4.1a).

pH

It is the –log of hydrogen ion concentration or is the intensity factor of acidity. pH values can also be defined as the exponent to the base 10 of hydrogen ion concentration. For natural water these values range from 4-9, however, higher values represent bicarbonate and carbonates of alkali and alkaline earth elements (Nollet, 2000).

The average pH value in surface water of District Mardan was 7.3. Shallow and deep ground water showed the average pH values of 7.0 and 7.3 respectively (Table 4.1a and 4.1b respectively). All the water samples were within permissible limit of 6.5 to 8.5 suggested by WHO (2004) and USEPA (2009). Water samples collected from different sources showed less variation although, general trend of alkaline nature was observed among samples. Highest value of pH (8.4) was observed in water from hand pump at Takker village (Table 4.1b).

Electric Conductivity (EC)

Electrical conductivity is the reciprocal of electric resistance, and is directly proportional to the ionic species. In order to measure the amount of TDS in water electric conductance is used as basic factor. Higher EC indicates high concentration of dissolved solids. Results of EC are expressed in millisiemens/meter (Peavy et al., 1985).

Electric conductivity in surface water ranged from 132 to 1876µS/cm with an average value of 522µS/cm (4.1a). Permissible limit of EC by WHO (1996) is <1400µS/cm for drinking water. Highest values of EC were found in water samples from Sangi Murmur (809µS/cm) and Saidabad (1876µS/cm) (Table 4.1a). Shallow ground water of the study area showed relatively higher EC values, ranged from 154 to 2200µS/cm, with an average value of 791µS/cm. Samples with higher EC were observed from Garakol (1442µS/cm), Jhandai (1373µS/cm), Takht Bhai (1123µS/cm), Jalala (2200µS/cm), Chin Banda (912µS/cm), Kundur (1451µS/cm) and Garhi Kapora (1879µS/cm) (Table 4.1b). Electric conductivity in the samples of deep ground water ranged from 260 to1496µS/cm with an average value of 656µS/cm. deep ground water samples with high EC value were from Par Hoti (1496µS/cm), Jalala (1148 µS/cm) and Chankari stop (913µS/cm) (Table 4.1c).

Total Dissolved Solids (TDS)

Dissolved solids in water can be of both inorganic and organic nature. Metals and minerals in nature are dissolved due to solvent nature of water. These dissolved substances may impart undesirable taste, color and odor to water. Some of the metals and dissolved substances posses health problems e.g., dissolved organics may be carcinogenic (Peavy et al., 1985).

Water samples from surface water sources showed an average value of 242mg/l, with minimum value of 70mg/l and maximum of 430mg/l (Table 4.1a). Permissible limit for TDS is 1000mg/l and 500mg/l by WHO (2004) and USEPA (2009) respectively. Average TDS value in samples from shallow ground water source was 430mg/l, and ranged from 82 to 1220mg/l. One water sample, sample No. W-30 from the hand pump of Jalala was having 1220mg/l TDS concentration which exceeded the permissible limit (Table 4.1b). Water samples from deep ground sources observed average value of 367mg/l. TDS values were in range of 142 to 805mg/l, and were therefore, found within the permissible limit of WHO, however, it exceeded the USEPA permissible limit (Table 4.1c).

Turbidity

Turbidity refers to the expression of optical property (Tyndall effect) in which the scattering of light occurs due to suspended particles present in the water. Turbidity reduces the light penetration, hence affecting the biological and chemical activities. The magnitude of the light scattering depends upon the size, shape and refractive index of particles. Turbidity is caused by clay, silt, organic matter, phytoplankton and microorganisms. (Trivedi and Raj, 1992).

Surface water samples of the study area were having turbidity in range from 0.10 to 25.00NTU with average value of 7.85NTU. High value (25.00NTU) was found in sample from Bakhshali (Table 4.1a). In shallow ground water samples turbidity ranged from 0.10 to 23.00NTU with average value of 4.26NTU (Table 4.1b). Highest values were found in the water of hand pumps of Jhandai (23.00NTU), Chil (14.80NTU) and Garhi Kapora (15.00NTU). However, the values of turbidity in deep water samples ranged from 0 to 27.70NTU with average turbidity of 2.60NTU (Table 4.1c).

Sulfates (SO_4^{-2})

Sulfur plays important role in the biosphere. The major ions in which sulfur is found are sulfates, sulfite and sulfide. Among all these, sulfates have received great attention because of its mobility, availability to the plants and microorganisms. Sulfates are also significant in precipitation reaction and its reactivity with positive charged surfaces in the soil (Nolett, 2000).

Sulfate concentration in the surface water varied from 1 to 30mg/l with average content of 15mg/l (Table 4.2a), from 3 to 206mg/l in shallow ground water with average content of 42.88mg/l (Table 4.2b) and from 2 to 250mg/l in deep ground water samples with average value of 52mg/l (Table 4.2c). Permissible limit for SO_4^{-2} by WHO[b] (1996) is 500mg/l and USEPA (2009) is 250mg/l in drinking water. Sulfate concentrations in all water samples from the study area were within permissible limits.

Nitrates (NO_3^-)

Nitrates are stable compounds in the nitrogen cycle. Nitrates are highly soluble specie in the water but weekly retained in the soil, as a result, it gets percolated to the ground water. The presence of the nitrate in the water system indicates contamination, microbial activities and pesticides residue (Nolett, 2000). Although nitrates are found in the natural water however, its level has been elevated by anthropogenic sources like nitrogenous fertilizer, wastewater discharge, sewage disposal, landfills and atmospheric pollutants (Lck, 1996). Elevated level of nitrate poses serious threat to environment in the form of eutriphication (Allaby, 1989). The serious human health problems arise when nitrates are reduced to nitrite, which further oxidize iron of hemoglobin and forms methamoglobin causing “Blue baby” syndrome (Burden, 1961).

Concentration of NO_3^- in surface water samples ranging from <0.3 to 4.10mg/l, with average content of 1.71mg/l (Table 4.2a), from <0.3 to 10.30mg/l in shallow ground water with average value of 2.33mg/l (Table 4.2b) and from <0.3 to 7.80mg/l in deep ground water with an average value of 2.75mg/l (Table 4.2c). WHO (2004) has set limit of less than 50mg/l while that of USEPA (2009) is 10mg/l; therefore all the samples were having NO_3^- within permissible limits.

Chloride (Cl^-)

In nature Chlorides are found as salts of sodium (NaCl), potassium (KCl) and Calcium ($CaCl_2$). They form ionic components of water. Their concentration is unaffected by biological and chemical processes of water. In ground and surface water chlorides are added through run off containing inorganic fertilizers, road salts, septic tanks effluents, industrial discharges and sea water intrusions in coastal areas (WHO^a, 1996). The amount of chloride in fresh water is usually less than 10mg (Nollet, 2000). Health impacts due to chlorides is mainly associated with the type of cation, however, a healthy individual can tolerate large intake. The two important impacts on humans are congestive heart failure due to impaired metabolism of NaCl and hypertension using due to NaCl at level above 2.5mg/l (WHO^a, 1996).

Chloride contents in the surface water varied from 1 to 18mg/l (Table 4.2a), with average value of 6mg/l, from 3 to195mg/l in shallow ground water with average value of 37mg/l (Table 4.2b) and from 2 to 96mg/l in deep ground water samples with average content of 30mg/l (Table 4.2c). Maximum acceptable limit of Cl in drinking water by WHO (2004) and USEPA (2009) is 250mg/l, therefore all the samples were found within permissible limit.

Carbonates (CO_3^{-2}) and Bicarbonates (HCO_3^-)

Carbonates and bicarbonates impart alkalinity to the water, which is the ability of water to neutralize acid. Alkalinity is a function of carbonate, bicarbonates and hydroxyl ion. Measures of these parameters are important in the interpretation and control of the water and wastewater treatment process. Generally soft waters are prone to acids however, the presence of the carbonates and bicarbonates ions help in buffering the system (Nolett, 2000).

Samples from the surface sources were having HCO_3^- in a range of 130 to 460mg/l with average content of 294mg/l (Table 4.2a), from 100 to 1000mg/l in shallow ground water with average content of 450mg/l (Table 4.2b) and from 200 to 800mg/l in deep ground water with average value of 448mg/l (Table 4.3c). WHO (1996) has set permissible limit of 250mg/l for HCO_3^-, therefore, majority of the samples contained elevated concentrations of HCO_3^-.

Light Elements

Calcium (Ca)

Calcium is the most common alkaline earth metal, found in $^{+}2$ oxidation state. Calcium is important constituent of igneous rocks minerals e.g., plagioclase, pyroxene and amphibole. As large numbers of minerals contain Ca therefore, this element is plentiful in soil and water. Besides natural sources fertilizers also contribute to Ca in soil and water (Perk, 2006).

Impacts on humans

Human body stores its 99 % of Ca in bones and teeth; remaining 1 % regulates important physiological functions like vascular and muscular contraction, nerve transmission and blood clotting. Inadequate Ca intake may results in nephrolithiasis (kidney stone), colorectal cancer, osteoporosis, hypertension and obesity (WHO, 2005). High intake calcium is suggested to reduce the chances of Ca resorption and bone loss (Gulliement et al, 2000), however, some studies conclude that elevated Ca reduce the absorption of other essential elements (WHO^a, 2009).

Surface water of the study area contained 39mg/l of average Ca content with a range of 6 to 85mg/l (Table 4.3a). Sample from the stream at Jamal Garhi (85mg/l) showed Ca above WHO (2004) permissible limit of 75mg/l (Fig.4.1a). Majority of shallow ground water samples were found with elevated level of Ca, with a range of 3 to137mg/l and average content of 63mg/l (Table 4.3b, Fig.4.1b). Calcium content in the deep ground water varied from 2 to 111mg/l with average value of 41mg/l (Table 4.3c). Samples from Mian Kali (111mg/l) and Jalalabad (76mg/l) were having high Ca content (Fig.4.1c).

Magnesium (Mg)

Magnesium forms about 2.5% of the earth’s crust. Two common sources of Mg are dolomite and magnesite minerals. Due to high reactivity, Mg readily combines with other elements therefore, not occurs in free state (Uttley, 2000). Magnesium is also important component of nuts, beans, green leaf vegetables and sea foods (Pressman and Buff, 2000).

Impacts on humans

Magnesium is the most abundant cation in human body. Magnesium forms cofactor of 350 enzymes and involved in protein synthesis and nucleic acid synthesis. Severe Mg deficiency leads to Hypomagnesaemia and reduce insulin sensitivity resulting in mellitus diabetes (WHO[a], 2009). High concentration of Mg helps against hypertension and cardiovascular diseases (Simons-Morton et al., 1997).

Average concentration of Mg in surface water was 9mg/l with a range of 0 to 39mg/l (Table 4.3a). WHO (2004) suggested limit for Mg in drinking water is 50mg/l and all the samples from surface water were within permissible limit (Fig. 4.2a). Shallow ground water samples were having Mg in range of 0 to 35mg/l with average content of 13mg/l (Table 4.3b). All of the shallow water samples were having Mg within permissible limit (Fig.4.2b). Deep ground water samples had Mg in range of 2 to 56mg/l with an average value of 17mg/l (Table 4.3c). Deep water samples also contained Mg below permissible limit except samples from Jalala (55mg/l) and Sowkai (56mg/l) (Fig.4.2c).

Sodium (Na)

Sodium is the sixth abundant element on Earth’s crust (2.83%). Salts of Na are readily soluble in water and are, therefore, found in both surface and ground water. Sodium forms essential component of all most every food product in the form of sodium chloride. Its shortages may lead to dehydration, convulsion, muscle paralysis, decreased growth and general numbness. Salts of Na are used in water treatment processes, in road de icing, paper and soap industry: glass, pharmaceuticals, chemicals and food processing (NAS, 1980).

Impacts on humans

In human body the sodium balance is controlled through complex system by Nervous and Hormonal system (DNHW, 1992). High intake of table salt results in high blood pressure, arteriosclerosis, oedema (fluid accumulation in body) and hypetension. Other associated problems with high intake of Na include acute stress and body pain. In acute stress condition Aldosterone is released which cause body inflammation and Na accumulation in kidney tissues (Wilson, 1992).

Sodium concentration in surface water of the study area ranged from 50 to 565 mg/l with an average content of 271mg/l (Table 4.3a). Majority of the samples were having Na above the WHO (2004) limit of 200mg/l. High concentrations of Na were found in surface water from Par Hoti (278mg/l), Sangi Murmur (247mg/l), Sangi Murmur(565mg/l), Shahbaz Garhi (280mg/l), Mandut (344mg/l), Saidabad (560mg/l) , Saidabad (311mg/l), Parkho (282mg/l), Lund Khawr (262mg/l), Toru (315mg/l) and near Risalpur (328mg/l), (Fig.4.3a). Shallow ground water sources had average Na concentration of 318mg/l with minimum concentration of 91mg/l and maximum of 616mg/l (Table 4.3b). Samples with relatively elevated concentration were from Garakol (321mg/l), Jhandai (489mg/l), Pump Korona (368mg/l), Takkar(355mg/l), Jalala (459mg/l), Shergarh (437mg/l), Lund Khwar (414mg/l), Chin Banda (550mg/l), Pirabad near Jamal Garhi (367mg/l), Ghundo (616mg/l), Khairabad (372mg/l) and Kundur village (526mg/l) (Fig.4.3b). Sodium concentration in samples from deep ground water sources ranged from 131 to 586mg/l with an average value of 331mg/l (Table 4.3c). Samples with elevated concentrations of Na were found in Hoti Kali (324mg/l), Chankari stop (529mg/l), Gujar Garhi(422mg/l), Takht Bhai (373mg/l), Jalala (586mg/l), Jamal Garhi (562mg/l), Sheikh Maltoon Town (357mg/l), Torru (292mg/l), Sowkai (472mg/l), (Fig.4.3c).

Potassium (K)

Potassium is essential element and present in all animals and plants tissues. Wastewater from different industries has potassium at several hundred to several thousand mg/l. Groundwater normally contains low K concentration, but in sandy soil leaching of wastewater results in higher values (Kumar and Kookna, 2006).

Impacts on humans

Potassium play important role in the regulation of various important body functions e.g., normal functioning of nerve cells, heart beat, kidney functions, muscles contraction and secretion of juice in stomach (Akhter et al., 2003). Adverse health impacts from high potassium intake in water include chest tightness, nausea, vomiting, diarrhea, hyperkalamia, shortening of breath and heart failure (WHO[a], 2009).

The concentration of K ranged from 1 to 3mg/l in surface water with average value of 2mg/l (Table 4.3a), from 0 to 10mg/l in shallow ground water with average value of 3mg/l (Table 4.3b) and from 1 to10mg/l with average value of 5mg/l in deep ground water samples respectively (Table 4.3c). WHO (2004) suggested a permissible limit of 10 to15 mg/l for K in drinking water. All the samples of surface, shallow and deep water were found within permissible limit.

Heavy and Trace Elements

Iron (Fe)

Iron is the fourth most abundant element on earth's crust and is involved in various important environmental processes. Two dominants form of iron are, Ferrous ion (Fe^{+2}) less water soluble than Ferric ion (Fe^{+3}). Under some geological conditions like in mafic, ultramafic rocks and meteorites, elemental Fe may be found. Due to its electron donor capacity Fe occurs in many compounds (Read, 1970).

Impacts on humans

Fe is the main component of haemoglobin and myglobin, its deficiency results in anemia. Iron has significant role in glucose metabolism and transportation of oxygen and electrons (Peter, 2000). Folic acid is supposed to reduce the risk of colon and rectum cancer (Willett, et al,. 1990). Excessive intake of Fe can cause small intestine infection (Bhattacharjee, 2001) and secondary hemochromtosis in which iron gets accumulated in liver and heart, even death in young children (Bothwell et al,.1979).

Average concentration of Fe in surface water was 98.57µg/l with a range of <0.05 to 497.50µg/l (Table 4.4a). According to USEPA (2009), the permissible limit for Fe in drinking water is 300µg/l. Samples with concentrations above permissible limits were having 497.50µg/l of Fe from Sirai (W-35) and 356.00µg/l from Bakhshali (W-14), (Fig.4.5a). Shallow ground water contained Fe in range of <0.05 to 1627.00µg/l with an average value of 160.85µg/l (Table 4.4b). Samples with high concentration of Fe were 956.25µg/l from Takkar village (W-27) and 1627.00µg/l (W-51) in Chingai Baba spring water (Fig.4.5b). Concentration of Fe in deep ground water samples ranged from <0.05 to 116.70µg/l with average value of 40.88µg/l (Table 4.4c; Fig.4.5c). Distribution map (Fig.4.15a) for Fe concentration showed homogenous distribution of low Fe content in Mardan District except a small area with high Fe content along the eastern boundary (Fig.4.15a).

Manganese (Mn)

Manganese is found in association with other elements in about 100 different kinds of minerals, but not found in pure state (ATSDR, 2000) The common state of occurrence is Mn^{+2} and Mn^{+4} in some compounds. Known compounds of Mn are acetates, chloride, oxides, sulfates and permanganate. Manganese and its compounds are much stable in water, sediments and soil having half life greater than 200 days in aquatic environment (Cover, 1997).

Impacts on humans

Manganese is an essential mineral to living beings but elevated value of Mn proves detrimental to them (Cover, 1997). Mn is present in all aquatic environments, however due to reducing conditions; ground water has relatively high Mn concentration (ATSDR, 2000). Exposure to dust having Mn leads to fever, chills, back pain, blurred vision and Mn pneumonia and direct ingestion results in gastrointestinal irritation (Cover, 1997).

Surface water of study area had Mn in the range of 2 to 71µg/l with an average concentration of Mn is 23µg/l (Table 4.4a). Samples from Mandat (W-8), Bakhshali (W-14), and Malakabad (W-15) were having 62µg/l, 60µg/l and 71µg/l Mn respectively above the USEPA (2009) and WHO (2004) permissible limits of 50µg/l for drinking water (Fig.4.6a). Shallow ground water showed Mn in a range of 2 to 78µg/l with average content of 19µg/l (Table 4.4b). All the water samples from shallow ground sources contained Mn within the permissible limit except one sample No.W-6 from Zando Kali (78 µg/l), (Fig.4.6b). Similarly Mn in deep ground water of the study area varied from 2 to 132µg/l with average value of 30µg/l (Table 4.4c). One sample (W-3) had 132µg/l of Mn above permissible limit (Fig.4.6c). Figure 4.15b showed the distribution pattern of Mn concentration in the water of Mardan District. It was cleared from the map that major part of the District had uniform distribution of Mn except a cluster of relatively high concentration was found in the southern part (Fig.4.15b)

Copper (Cu)

Copper is present on the earth in iron sulfide and copper sulfides ores in low concentration, through metallurgical process Cu is extracted (Sievers and Meyer, 2003). Its major uses include electrical equipments, coins, utensils, building materials, fungicides, algaecides and fertilizers etc. Aquatic environment contains Cu in Cu^+ states in the form of complexes or particulates (ATSDR, 2002).

Impacts on humans

Cu is an essential element for many physiological processes but elevated concentrations may pose threats to biological communities. In humans low dose results in simple food poisoning, however, large amount causes heptocellular toxicity, methaemoglobinemia, intravascular haemolysis, kidney failure and gastrointestinal bleeding (Agarwal et al., 1993). In another genetic disorder “Wilson disease” body fails to absorb Cu which ultimately gets accumulation in different body tissues of liver, eyes and brain, damaging these organs (NDDIC, 2009).

Copper was found in surface water within the range of 5 to 4838µg/l and average value of 400µg/l (Table 4.4a). According to WHO (2004) and USEPA (2009), permissible limit for Cu is 2000µg/l and 1000µg/l respectively. Only one sample (W-35) from Upper Swat Canal branch near Sirai showed high value of 4838µg/l (Fig.4.7a). Shallow ground water had an average Cu concentration in a range of 1 to 2496µg/l with average value of 282µg/l (Table 4.4b). Samples from Chin Banda (W-36) and Chingai Baba (W-51) had Cu above permissible limit with concentration of 2496µg/l and 2236µg/ respectively (Fig.4.7b). Copper concentration in the deep water ranged from 18 to 846µg/l with average value of 113µg/l (Table 4.4c). Cu concentration in all deep water samples was found within permissible limit of WHO (Fig.4.7c). Distribution of Cu in the water samples of Mardan District was showed in Figure 4.15c, based on GIS. Only a small area in Sirai in the northern part of Mardan District showed relatively high concentration of Cu (Fig.4.15c).

Lead (Pb)

In water Pb is found either in dissolved form or as a waterborne particle. Lead occurs in $^{+}1$, $^{+}2$ oxidation states; its high persistence and stability make it more significant regarding health (Murugesan et al., 2006; Kobya et al., 2005). Generally all sources of water are free of Pb contamination, but corrosion of pipes makes water susceptible for Pb contamination. Alkalinity, temperature, pH and DO are major controlling factors in Pb corrosion (AWWA, 1996).

Impacts on humans

Lead has both carcinogenic and teratogenic properties and adversely effects young children through lowering their Neuropsychological and Neurobehavioral development (Needlemen and Bellinger, 1991). After entering human body 99% of Pb gets bound to red blood cells, remaining 1% with plasma. In adults its toxicity ranges from carcinogenesis to high blood pressure and also dental caries scores (Curzen and Bibby, 1970). Similarly Pb is capable of crossing placenta resulting in prematurity, intra usterine death and low weight birth (Papanikolaou et al., 2005).

In surface water of study area, average concentration of Pb was found as 9.424µg/l with a wide range of <0.05 to 34.670µg/l (Table 4.4a). Permissible limit of Pb in drinking water set by WHO (2004) and USEPA (2009) is 10µg/l and 15µg/l respectively. Surface samples with concentration above 10µg/l were found in water sample No.W-8 from Mandat (29.220µg/l), sample No.W-14 from Bakhshali (12.750µg/l), sample No.W-26 from Takkar (22.940µg/l) and sample No.W-35 from Sirai (34.670µg/l) (Fig.4.8a). Average lead concentration in shallow ground water is

3.660µg/l with minimum value of <0.05µg/l and maximum value of 30.210µg/l (Table 4.4b). Samples with higher content were sample No.W-27 from Takkar (30.120µg/l) and sample N0. W-51 from Chingai Baba (25.170µg/l), (Fig.4.8b). Deep ground water samples showed Pb within range of <0.05 to 34.690µg/l and average value of 5.030µg/l (Table 4.4c). Only one sample (W-55) from Toru (34.690µg/l) had Pb above permissible limit (Fig.4.8c). GIS based Pb distribution map of water was prepared in Figure 4.15d. This map showed relatively high Pb content along the northern, western and southern boundaries of the District (Fig.4.15d).

Zinc (Zn)

Zn forms the 23rd most abundant element of Earth's crust. Its common ores are Sphalrite, Wurzite, Smithsonite and Hemimorphite etc. (Elinder, 1986). About half of the Zn produced is used in galvanization of steel; other applications include batteries, paints, plastic, cosmetics; Zinc carbamates are used in pesticide manufacturing (Elinder, 1986).

Impacts on humans

Zn is an essential element and is present in about 200 enzymes of living organisms (O'Dell, 1984). Mostly low concentration of Zn is found in natural water but, due to leaching from supply pipes tape water may has higher concentration. Toxic effects of high Zn intake or inhalation are fever, nausea, gastrointestinal problems, skin irritation, damage to pancreas and bleeding (Elinder, 1986).

Concentration of Zn in surface water samples varied from <0.5µg/l to 3058µg/l with an average value of 416µg/l (Table 4.4a). According to WHO (2004) and USEPA

(2009), permissible limit of Zn in drinking water is 3000 µg/L and 5000 µg/l respectively. Only one sample (W-26) from Swat Canal in Takkar with a concentration of 3058µg/l showed relatively high concentration (Fig.4.9a). Shallow ground showed average concentration of 744µg/l with a range from <0.5µg/l to 4175 and deep ground water showed average concentration of 280µg/l with a range from 1 to 1297µg/l (Table 4.4b and c respectively). Zinc concentrations in shallow and ground water were generally within permissible limits, however, one sample No.W-27 from Takkar showed Zn in high concentration (Fig.4.9b and c respectively). GIS based contour map of Zn in Figure 4.15e showed Zn distribution in Mardan District. Zinc concentration was homogenously distributed in the whole District as notified from the map. However, a cluster showing relatively higher content was found near Takkar village at the western boundary of Mardan District (Fig.4.15e).

Nickel (Ni)

Ni is mostly found in $^{+}2$ oxidation state. Metallic Ni is insoluble in water but in soluble in slight acidic waters. In aquatic environment Ni is found in the form of various salts, such as acetates, nitrates, chlorides and sulphates, where its carbonates and hydroxides are less water soluble (Morgan and Flint, 1989).

Impacts on humans

Various compounds of Ni are reported to be Nephrotoxic, Heptotoxic, Immunotoxic and terotogens (Ross, 1995). Similarly allergic dermatitis is a common problem with Ni exposure. Dust from Ni refineries containing sulfides and oxides of Ni is the major cause of lung and nasal cancer, however, this problem is not reported in case of metallic Ni (Liesegang et al., 1993).

Average Ni concentration in surface water samples was found as 6.66µg/l with a range from 1.40 to 22.39µg/l (Table 4.4a). WHO (2004) and USEPA (2009) has set permissible limit for Ni as 20µg/l and 100µg/l respectively in drinking water, Only one sample (W-15) from Malkabad was having Ni concentration (22.39µg/l) above WHO permissible limit (Fig. 4.10a). Shallow and deep ground water showed Ni concentration in the range of 1.27 to 19.01µg/l and 0.81 to 20µg/l with average concentrations 4.87µg/l of 3.48µg/l respectively (Table 4.4b and c respectively). All most all samples from shallow and deep ground water were having Ni concentration below WHO (2004) (Fig.4.10b and c respectively). GIS based distribution map of Ni for water of Mardan District was prepared as showed in Figure 4.15f. From this map, it is cleared that low Ni concentration was homogenously distributed. However, relatively high concentration was found along eastern, western, northern and southern boundaries (Fig.4.15f).

Chromium (Cr)

Chromium does not occur free in nature and its most common form is chromate**.** Natural water contains chromium in two oxidation states Cr^{+3} and Cr^{+6}, however, Cr^{+6} is found at higher concentration as its salts are more soluble than those of Cr^{+3} . In surface waters the average concentration of Cr range from 0.5-2µg/l and ground water having concentration less than 1µg/l (USEPA, 1987).

Impacts on humans

Naturally soil and water has little amount of Cr but elevation in concentration can be result of anthropogenic sources. Chromium is used in the manufacturing of chrome colors, cements, fungicides, wood preservatives, electroplating and tannery industries (Kotas and Stasicka, 2000). Both forms of Cr differ in their geochemical and toxicology properties, as Cr^{+3} are essential to mammals for lipid and protein metabolism. On other hand salts of Cr^{+6} are toxic (Kornhauser et al., 2002). It has been reported that chromate at level of 1-5gm can cause sever health problems like gastrointestinal problems, haemorrhagic diathesis and even death due to cardiovascular disorders. Genotoxic effects (chromosomal aberrations) and lung cancer is observed in the workers due to their exposure to Cr^{+6} (Janus and Krajnc, 1990).

Chromium concentration in the surface water ranged from <0.05 to 10.17µg/l with average content of 3.95µg/l (Table 4.4a). It ranged from <0.05 to 40.27µg/l in shallow ground water with average content of 8.08µg/l (Table 4.4b) and in deep ground water it ranged from <0.05 to 18.63µg/l with average value of 6.77µg/l (Table 4.4c). The permissible limit of Cr in drinking water is set as 50µg/l and 100µg/l by WHO (2004) and USEPA (2009) respectively. In this respect all the water samples showed Cr concentration within the permissible limit. Chromium distribution map for Mardan District was prepared by GIS in Figure 4.15g. It was noticed that almost homogenous distribution of low concentration was found throughout the whole District, except at western boundary near Jalala where relatively high concentration of Cr was notified (Fig.4.15g).

Cadmium (Cd)

Cadmium is metal with $^{+}2$ oxidation state. It is found in sulfide ores along zinc and lead due to its similar behavior like zinc. Cadmium has no significant nutritional value but is important in many industrial applications such as fertilizers production, electrodes, batteries, pigments in plastics and PVC products etc. (Toppi and Gabbrielli, 1999).

Impacts on humans

Human kidney is the most sensitive organ to Cd toxicity. Chronic oral exposure results in itai-itai disease and Tubular Proteinaria in which the resorption capacity of tubules is reduced resulting excretion of low weight protein, glucose, enzymes and Amino acids. Sometimes lose of essential constituents results in many physiological changes like bone disease called Osteoporosis (Krajnc et al., 1987).

Average concentration of Cd in surface water was as found 0.764µg/l with a range of <0.002 to 2.691µg/l (Table 4.4a). Cadmium in shallow and deep ground waters ranged from 0.057 to 4.304µg /l and <0.002 to 1.44µg/l with an average concentration of 1.371µg/l and 0.593µg/l respectively (Table 4.4b and c respectively). According to WHO (2004) and USEPA (2009) the permissible limits of Cd in drinking water are 3µg/l and 5µg/l respectively. In this respect all water samples had Cd contents within permissible limit (Fig.4.12a, b and c respectively). The Cd concentration map (Fig.4.15h) based on GIS showed no specific distribution pattern. The whole District had low concentration however; the areas near Spainkai and Lund Khawar in the northern part of District were having relatively high Cd contents in the water (Fig.4.15h).

Arsenic (As)

Arsenic a ubiquitous element, forming 20th most abundant element of earth. It is part of about 200 different minerals, 60% of those are in the form of arsenates (Onisha, 1969). Inorganic arsenic is found in As (III) which is most toxic and mobile form than As (IV): Organic As is mainly found in Methylated form (Bowell, 1994).

Impacts on humans

Chronic arsenicosis is the most prevalent problem especially in south Asian countries. Its chronic effects in human beings commonly include skin diseases (e.g., pigmentation, dermal hyperkeratosis, skin cancer), and many cardiovascular, neurological, hematological, renal and respiratory disorders which may effect lungs, bladder, liver, and kidney (Morton and Dunette, 1994; Smith et al., 1999), as arsenic is accumulated in hair, nails, skin and bones (Karagas et al., 2000).

Surface water sources from the study area showed As concentrations in the range of 0.284 to 1.579µg/l with average concentration of 0.751µg/l (Table 4.4a; Fig.4.13a). Concentration of As in shallow ground water sample varied from 0.000 to 7.780µg/l with average value of 0.893µg/l (Table 4.4b) and from 0.0459 to 2.896µg/l with an average content of 0.864µg/l in deep ground water respectively (Table 4.4c). WHO (2004) has set a permissible limit of 10µg/l and 5µg/l by USEPA (2009). Only one sample from Dug well of Garhi Kapora (7.780µg/l) had high value of As. The distribution map of As in the Mardan District was showed as GIS based contour diagram (Fig.4.15i). It was clearly indicated that the area in premises of Ghari Kapora in the southern part of District was having relatively high concentration of Arsenic (4.15i).

Table 4.1a. Physical parameters of Surface water of Mardan District

Sample	Source	Location	Temp ˚C	pH	Conductivity µS/cm	TDS mg/l	Turbidity NTU
W-1	Kalpani Nalla	Par hoti bridge	28	6.9	542	288	3.60
W-4	Seasonal stream	Sangi Murmur	29	7.1	583	307	8.00
W-5	Seasonal stream	Sangi Murmur	26	7.0	809	430	0.10
W-7	Seasonal stream	Shahbaz Garhi	30	6.8	489	261	8.60
W-8	Irrigational	Mandat	30	7.0	501	269	11.50
W-11	Stream	Saidabad	30	7.2	678	365	2.20
W-13	Seasonal stream	Bakhshali	28	7.1	460	246	5.30
W-14	Irrigational	Bakhshali	29	6.8	132	70	25.00
W-15	Irrigational	Malakabad	30	7.2	203	110	24.00
W-18	Kalpani Nalla	Kul	21	7.7	506	262	14.00
W-21	Seasonal stream	Saidabad (Takht bhai)	20	8.0	1876	282	3.40
W-22	Seasonal stream	Saidabad	22	7.3	455	240	4.70
W-26	Swat canal	Takkar	20	7.3	243	122	7.50
W-28	Jalala stream	Parkho	23	7.8	503	265	8.90
W-32	Seasonal stream	Lund Khwar	24	7.3	436	246	7.90
W-35	Swat canal	Sirai	18	7.5	176	100	0.60
W-44	Seasonal stream	Jamal Garhi	21	7.3	473	250	7.40
W-47	Kalpani Nalla	Rustam	27	7.7	387	206	0.70
W-54	Kalpani Nalla	Toru	21	7.4	500	263	3.50
W-59	Kalpani Nalla	Near Risalpur	23	7.5	500	270	10.00
Minimum			***18***	***6.8***	***132***	***70***	***0.10***
Maximum			***30***	***8.0***	***1876***	***430***	***25.00***
Average			***25***	***7.3***	***522***	***242***	***7.85***
WHO				***6.5-8.5***	***<1400***	***1000***	***5***

Table 4.1b. Physical parameters of Shallow ground water of Mardan District

Sample	Source	Location	Temp ˚C	pH	Conductivity µS/cm	TDS mg/l	Turbidity NTU
W-6	Dug well	Zando kali	27	6.9	850	451	13.40
W-12	Dug well	Garakol	26	7.2	1442	767	0.20
W-16	Hand pump	Gujar Garhi	23	7.0	647	344	8.60
W-19	Hand pump	Jhandai	22	7.5	210	270	23.00
W-20	Dug well	Jhandai	22	7.0	1373	736	1.20
W-23	Hand pump	Pump Korona	25	6.7	740	400	0.40
W-24	Hand pump	Takht Bhai	24	6.8	1123	605	0.10
W-27	Hand pump	Takkar	23	8.4	209	112	0.20
W-30	Hand pump	Jalala	25	7.0	2200	1220	1.70
W-31	Hand pump	Sergarh	24	7.1	639	343	0.30
W-33	Hand pump	Lund Khawr	23	6.8	660	352	0.90
W-34	Hand pump	Chil	24	6.8	420	225	14.80
W-36	Dug well	Chin Banda	22	7.0	912	482	3.30
W-37	Hand pump	Pir Abad (Jamal garhi)	25	6.8	695	370	13.80
W-38	Dug well	Jamal Garhi	23	6.7	746	396	0.60
W-39	Hand pump	Katlang	22	6.8	608	327	0.40
W-41	Hand pump	Ghundo	23	6.7	630	333	1.60
W-46	Hand pump	Spainkai	22	6.8	429	233	1.40
W-48	Hand pump	Rustam	20	6.9	241	206	0.70
W-49	Artesian well	Rustam	25	7.6	317	125	0.40
W-51	Spring	Chingai Baba	24	6.3	154	82	0.10
W-52	Hand pump	Khairabad	20	7.0	578	305	0.10
W-56	Hand pump	Kundr	25	7.4	1451	755	1.50
W-57	Dug well	Garhi Kapora	24	7.7	1879	1000	15.00
W-58	Hand pump	Chandur	24	7.3	625	332	2.70
Minimum			***20***	***6.3***	***154***	***82***	***0.10***
Maximum			***27***	***8.4***	***2200***	***1220***	***23.00***
Average			***23***	***7.0***	***791***	***430***	***4.26***
WHO				***6.5-8.5***	***<1400***	***1000***	***5***

Table 4.1c. Physical parameters of Deep ground water of Mardan District

Sample	**Source**	**Location**	**Temp ˚C**	**pH**	**Conductivity µS/cm**	**TDS mg/l**	**Turbidity NTU**
W-2	Bore water	Hoti kali	26	7.2	542	288	4.80
W-3	Bore water	Hoti kali	25	7.2	1496	805	27.70
W-9	Tube well	Chankari stop	15	7.3	913	495	0.20
W-10	Tube well	Chankari stop	25	7.5	904	496	1.30
W-17	Tape water	Gujar Garhi	20	7.6	567	310	0.30
W-25	Tape water	Takht Bhai	23	7.6	590	340	0.20
W-29	Bore water	Jalala	25	7.2	1148	612	0.90
W-40	Bore water	Katlung	25	7.0	535	281	0.70
W-42	Tape water	Mian Kali	21	7.2	488	258	0.10
W-43	Tape water	Babuzai	22	7.2	430	230	0.20
W-45	Tape water	Jamal Garhi	20	7.3	808	430	0.30
W-50	Tube well	Jalal ababd	23	6.7	492	261	0.60
W-53	Bore water	Sheikh Multon	22	8.0	738	395	1.20
W-55	Bore water	Toru	24	7.5	260	142	0.00
W-60	Tape water	Sowkai	26	7.9	325	168	0.50
Minimum			***15***	***6.7***	***260***	***142***	**0.00**
Maximum			***26***	***8.0***	***1496***	***805***	**27.70**
Average			***23***	***7.3***	***656***	***367***	**2.60**
WHO				***6.5-8.5***	***<1400***	***1000***	***5***

Table 4.2a. Anions concentration in Surface water of Mardan District

Sample	Source	Location	Sulfate mg/l	Nitrate mg/l	Chloride mg/l	Bicarbonate mg/l
W-1	Kalpani Nalla	Par hoti bridge	25	2.30	1	200
W-4	Seasonal stream	Sangi Murmur	16	<0.30	7	400
W-5	Seasonal stream	Sangi Murmur	30	<0.30	8	460
W-7	Seasonal stream	Shahbaz Garhi	13	3.10	18	300
W-8	Irrigational	Mandat	14	<0.30	13	320
W-11	Seasonal stream	Saidabad	18	2.40	6	460
W-13	Seasonal stream	Bakhshali	9	2.30	6	300
W-14	Irrigational	Bakhshali	2	3.70	4	160
W-15	Irrigational	Malakabad	2	<0.30	4	200
W-18	Kalpani Nalla	Kul	24	<0.30	12	360
W-21	Seasonal stream	Saidabad (Takht bhai)	18	0.30	5	340
W-22	Seasonal stream	Saidabad	18	<0.30	5	260
W-26	Swat canal	Takkar	8	2.60	4	140
W-28	Jalala stream	Parkho	17	4.10	3	340
W-32	Seasonal stream	Lund Khwar	14	<0.30	6	280
W-35	Swat canal	Sirai	7	<0.30	4	130
W-44	Seasonal stream	Jamal Garhi	6	0.20	6	300
W-47	Kalpani Nalla	Rustam	7	3.50	7	280
W-54	Kalpani Nalla	Toru	19	0.90	6	300
W-59	Kalpani Nalla	near Risalpur	26	1.70	10	340
Minimum			***2***	***<0.30***	***1***	***130***
Maximum			***30***	***4.10***	***18***	***460***
Average			***15***	***1.71***	***6***	***294***
WHO			***250***	***50***	***250***	***250***

Table 4.2b. Anions concentration in Shallow ground water of Mardan District

Sample	Source	Location	Sulfate mg/l	Nitrate mg/l	Chloride mg/l	Bicarbonate mg/l
W-6	Dug well	Zando kali	42	2.50	16	440
W-12	Dug well	Garakol	52	<0.30	25	500
W-16	Hand pump	Gujar Garhi	18	2.60	15	440
W-19	Hand pump	Jhandai	29	<0.30	6	340
W-20	Dug well	Jhandai	187	<0.30	130	600
W-23	Hand pump	Pump Korona	20	<0.30	6	360
W-24	Hand pump	Takht Bhai	206	6.50	86	480
W-27	Hand pump	Takkar	12	<0.30	5	160
W-30	Hand pump	Jalala	162	10.30	154	820
W-31	Hand pump	Shergarh	27	2.90	10	380
W-33	Hand pump	Lund Khawr	19	3.10	5	360
W-34	Hand pump	Chil	5	1.90	14	320
W-36	Dug well	Chin Banda	14	3.10	6	640
W-37	Hand pump	Pir Abad (Jamal garhi)	8	<0.30	14	460
W-38	Dug well	Jamal Garhi	10	<0.30	12	700
W-39	Hand pump	Katlang	12	2.70	13	460
W-41	Hand pump	Ghundo	11	<0.30	12	440
W-46	Hand pump	Spainkai	8	<0.30	4	340
W-48	Hand pump	Rustam	3	<0.30	18	200
W-49	Artesian well	Rustam	9	<0.30	11	240
W-51	Spring	Chingai Baba	5	1.80	3	100
W-52	Hand pump	Khairabad	10	0.30	3	460
W-56	Hand pump	Kundr	75	<0.30	195	620
W-57	Dug well	Garhi Kapora	112	1.00	140	1000
W-58	Hand pump	Chandur	16	0.60	29	400
Minimum			***3***	***<0.30***	***3***	***100***
Maximum			***206***	***10.30***	***195***	***1000***
Average			***43***	***2.33***	***37***	***450***
WHO			***250***	***50***	***250***	***250***

Table 4.2c. Anions concentration in Deep ground water of Mardan District

Sample	Source	Loaction	Sulfate mg/l	Nitrate mg/l	Chloride mg/l	Bicarbonates mg/l
W-2	Bore water	Hoti kali	250	5.80	96	460
W-3	Bore water	Hoti kali	135	7.80	73	500
W-9	Tube well	Chankari stop	70	4.00	50	440
W-10	Tube well	Chankari stop	69	<0.30	34	540
W-17	Tape water	Gujar Garhi	38	<0.30	11	340
W-25	Tape water	Takht Bhai	19	2.80	5	400
W-29	Bore water	Jalalal	66	<0.30	26	880
W-40	Bore water	Katlung	2	<0.30	2	460
W-42	Tape water	Mian Kali	15	1.50	8	400
W-43	Tube well	Babuzai	13	<0.30	14	360
W-45	Tape water	Jamal Garhi	33	2.30	28	660
W-50	Tube well	Jalal abad	11	1.50	5	320
W-53	Bore water	Sheikh Multon	60	1.10	89	340
W-55	Bore water	Toru	2	0.30	2	200
W-60	Tape water	Sowkai	8	0.90	3	240
Minimum			***2***	***<0.30***	***2***	***200***
Maximium			***250***	***7.80***	***96***	***880***
Average			***61***	***2.75***	***30***	***448***
WHO			***250***	***50***	***250***	***250***

Table 4.3a. Light elements concentration in Surface water of Mardan District

Sample	Source	Location	Ca mg/l	Mg mg/l	Na Mg/l	K mg/l
W-1	Kalpani Nalla	Par hoti bridge	46	38	278	3
W-4	Seasonal stream	Sangi Murmur	50	10	247	3
W-5	Seasonal stream	Sangi Murmur	24	6	565	1
W-7	Seasonal stream	Shahbaz Garhi	28	7	280	3
W-8	Seasonal stream	Mandat	10	7	344	3
W-11	Seasonal stream	Saidabad	15	8	560	2
W-13	Seasonal stream	Bakhshali	33	6	215	3
W-14	Irrigational	Bakhshali	46	5	145	1
W-15	Irrigational	Malakabad	19	1	157	3
W-18	Kalpani Nalla	Kul	49	18	324	2
W-21	Seasonal stream	Saidabad (Takht bahi)	43	39	50	2
W-22	Seasonal stream	Saidabad	74	10	311	2
W-26	Swat canal	Takkar	51	2	184	2
W-28	Jalala stream	Parkho	22	0	282	2
W-32	Seasonal stream	Lund Khwar	57	9	262	2
W-35	Swat canal	Sirai	6	0	146	1
W-44	Seasonal stream	Jamal Garhi	85	6	228	2
W-47	Kalpani Nalla	Rustam	44	0	197	3
W-54	Kalpani Nalla	Toru	34	2	315	2
W-59	Kalpani Nalla	near Risalpur	43	6	328	3
Minimum			***6***	***0***	***50***	***1***
Maximum			***85***	***39***	***565***	***3***
Average			***39***	***9***	***271***	***2***
WHO			***75***	***50***	***200***	***15***

Table 4.3b. Light elements concentration in Shallow ground water of Mardan District

Sample	Source	Location	Ca mg/l	Mg mg/l	Na mg/l	K mg/l
W-6	Dug well	Zando kali	44	7	427	10
W-12	Dug well	Garakol	20	19	321	4
W-16	Hand pump	Gujar Garhi	85	17	269	3
W-19	Hand pump	Jhandai	27	19	489	5
W-20	Dug well	Jhandai	82	11	219	6
W-23	Hand pump	Pump Korona	129	4	368	4
W-24	Hand pump	Takht Bhai	118	25	193	2
W-27	Hand pump	Takkar	28	3	355	3
W-30	Hand pump	Jalala	51	35	459	7
W-31	Hand pump	Shergarh	39	13	437	2
W-33	Hand pump	Lund Khawr	55	15	414	2
W-34	Hand pump	Chil	75	6	158	1
W-36	Dug well	Chin Banda	59	31	550	3
W-37	Hand pump	Pir Abad (Jamal garhi)	84	19	367	1
W-38	Dug well	Jamal Garhi	137	20	181	2
W-39	Hand pump	Katlang	82	16	227	2
W-41	Hand pump	Ghundo	109	4	616	1
W-46	Hand pump	Spainkai	85	2	147	0
W-48	Hand pump	Rustam	80	3	186	4
W-49	Artesian well	Rustam	37	10	190	2
W-51	Spring	Chingai Baba	8	0	210	1
W-52	Hand pump	Khairabad	47	3	372	2
W-56	Hand pump	Kundr	38	16	526	3
W-57	Dug well	Garhi Kapora	3	10	120	1
W-58	Hand pump	Chandur	50	7	91	3
Minimum			***3***	***0***	***91***	***0***
Maximum			***137***	***35***	***616***	***10***
Average			***63***	***13***	***318***	***3***
WHO			***75***	***50***	***200***	***15***

Table 4.3c. Light elements concentration in Deep ground water of Mardan District

Sample	Source	Location	Ca mg/l	Mg mg/l	Na mg/l	K mg/l
W-2	Bore water	Hoti kali	40	25	324	10
W-3	Bore water	Hoti kali	25	21	210	10
W-9	Tube well	Chankari stop	46	8	131	6
W-10	Tube well	Chankari stop	59	9	529	6
W-17	Tape water	Gujar Garhi	13	7	422	5
W-25	Tape water	Takht Bhai	17	23	373	5
W-29	Bore water	Jalala	46	55	586	5
W-40	Bore water	Katlung	71	12	200	1
W-42	Tape water	Mian Kali	111	2	158	1
W-43	Tape water	Babuzai	72	10	164	1
W-45	Tape water	Jamal Garhi	36	24	562	6
W-50	Tube well	Jalal ababd	76	3	188	3
W-53	Bore water	Sheikh Multon	2	9	357	3
W-55	Bore water	Toru	4	2	292	5
W-60	Tape water	Sowkai	5	56	472	3
Minimum			***2***	***2***	***131***	***1***
Maximum			***111***	***56***	***586***	***10***
Average			***41***	***18***	***331***	***5***
WHO			***75***	***50***	***200***	***15***

Table 4.4a. Trace and heavy elements concentration in Surface water of Mardan District

Sample	Source	Location	Fe µg/l	Mn µg/l	Cu µg/l	Pb µg/l	Zn µg/l	Ni µg/l	Cr µg/l	Cd µg/l	As µg/l
W-1	Kalpani Nalla	Par hoti	8.47	2	23	<0.05	6	8.85	4.90	0.089	1.455
W-4	Seasonal stream	Sangi Murmur	<0.05	2	5	<0.05	14	1.88	1.43	1.135	0.302
W-5	Stream stream	Sangi Murmur	8.70	2	20	<0.05	70	2.10	<0.05	<0.002	0.316
W-7	Stream stream	Shahbaz Garhi	5.98	49	37	<0.05	78	1.82	<0.05	<0.002	1.480
W-8	Irrigational	Mandat	19.75	62	195	29.220	72	2.50	<0.05	0.248	1.579
W-11	Stream stream	Saidabad	3.17	18	29	0.110	<0.5	5.47	0.70	2.691	0.521
W-13	Seasonal stream	Bakhshali	<0.05	2	11	<0.05	47	1.69	<0.05	<0.002	0.967
W-14	Irrigational	Bakhshali	356.00	60	611	12.750	62	13.15	0.31	0.876	0.833
W-15	Irrigational	Malakabad	195.00	71	1258	22.940	738	22.39	0.05	1.135	1.047
W-18	Kalpani Nalla	Kul	20.84	18	22	<0.05	31	1.64	<0.05	0.150	0.561
W-21	Stream stream	Saidabad (Takht bahi)	9.76	30	34	0.772	92	9.49	3.27	0.823	1.013
W-22	Stream stream	Saidabad	24.53	11	48	0.374	911	4.29	1.89	<0.002	0.414
W-26	Swat canal	Takkar	186.90	35	319	23.530	3058	12.95	2.26	0.697	0.400
W-28	Jalala stream	Parkho	4.15	33	316	0.246	14	2.93	2.03	0.206	0.361
W-32	Stream stream	Lund Khwar	<0.05	17	15	0.868	565	4.60	3.39	0.111	0.494
W-35	Swat canal	Sirai	497.50	4	4838	34.670	1185	14.86	4.98	1.147	0.328
W-44	Seasonal stream	Jamal Garhi	<0.05	4	26	1.741	20	1.40	8.66	1.114	0.284
W-47	Kalpani Nalla	Rustam	27.94	9	123	3.632	885	6.91	5.34	0.274	0.717
W-54	Kalpani Nalla	Toru	<0.05	8	30	0.529	34	2.32	9.87	<0.002	0.613
W-59	Kalpani Nalla	near Risalpur	109.80	14	40	0.556	30	1.56	10.17	<0.002	1.337
Minimum			***<0.05***	***2***	***5***	***<0.05***	***<0.5***	***1.40***	***<0.05***	***<0.002***	***0.284***
Maximum			***497.50***	***71***	***4838***	***34.670***	***3058***	***22.39***	***10.17***	***2.691***	***1.579***
Average			***98.57***	***23***	***400***	***9.424***	***416***	***6.66***	***3.95***	***0.764***	***0.751***
WHO			***300***	***50***	***2000***	***10***	***3000***	***20***	***50***	***3***	***10***
USEPA			***300***	***50***	***1300***	***15***	***5000***	***100***	***100***	***5***	***5***

Table 4.4b. Trace and heavy elements concentration in Shallow ground water of Mardan District

Sample	Source	Location	Fe µg/l	Mn µg/l	Cu µg/l	Pb µg/l	Zn µg/l	Ni µg/l	Cr µg/l	Cd µg/l	As µg/l
W-6	Dug well	Zando kali	48.05	78	37	0.344	1013	3.07	<0.05	<0.002	0.717
W-12	Dug well	Garakol	11.60	2	32	0.354	<0.5	3.54	0.34	<0.002	1.454
W-16	Hand pump	Gujar Garhi	5.87	6	71	<0.05	2750	1.96	<0.05	0.812	0.372
W-19	Hand pump	Jhandai	20.75	37	27	<0.05	45	2.63	0.26	1.164	1.606
W-20	Dug well	Jhandai	4.55	10	13	<0.05	23	BDL	6.14	1.114	0.489
W-23	Hand pump	Pump Korona	<0.05	28	8	0.922	1275	1.58	3.29	0.328	0.139
W-24	Hand pump	Takht Bhai	28.99	33	9	0.456	68	2.82	0.14	1.722	0.092
W-27	Hand pump	Takkar	956.25	2	953	30.210	4175	16.78	10.91	0.351	2.420
W-30	Hand pump	Jalala	0.06	2	58	<0.05	6	1.93	40.27	0.197	1.316
W-31	Hand pump	Shergarh	<0.05	2	1	0.045	2171	11.21	5.04	<0.002	0.317
W-33	Hand pump	Lund Khawr	7.80	12	47	0.584	638	2.47	3.04	4.149	0.205
W-34	Hand pump	Chil	<0.05	11	30	0.546	924	3.27	5.54	0.412	0.000
W-36	Dug well	Chin Banda	14.28	2	2496	1.572	63	1.49	3.29	<0.002	0.398
W-37	Hand pump	Pir Abad	3.02	31	54	1.368	86	3.33	3.23	1.437	0.044
W-38	Dug well	Jamal Garhi	<0.05	2	16	0.791	27	4.72	*3.92*	0.870	0.227
W-39	Hand pump	Katlang	5.14	16	65	<0.05	36	1.42	3.43	<0.002	0.013
W-41	Hand pump	Ghundo	<0.05	2	31	0.210	82	7.51	6.66	2.127	0.039
W-46	Hand pump	Spainkai	<0.05	13	15	0.904	52	1.27	5.34	4.304	0.173
W-48	Hand pump	Rustam	78.41	22	197	4.278	748	1.86	5.41	0.415	1.309
W-49	Artesian well	Rustam	23.42	16	255	0.646	204	3.63	6.42	2.477	0.056
W-51	Spring	Chingai Baba	1627.00	19	2236	25.170	1034	19.01	11.26	0.057	0.000
W-52	Hand pump	Khairabad	6.23	6	62	0.235	2144	4.05	8.30	<0.002	0.295
W-56	Hand pump	Kundr	<0.05	33	171	0.487	11	2.71	9.51	<0.002	0.849
W-57	Dug well	Garhi Kapora	8.11	19	119	<0.05	27	2.44	9.90	<0.002	7.780
W-58	Hand pump	Chandur	46.40	71	41	0.415	256	1.76	10.02	<0.002	2.005
Minimum			***<0.05***	***2***	***1***	***<0.05***	***<0.5***	***1.27***	***<0.05***	***<0.002***	***0.000***
Maximum			***1627.00***	***78***	***2496***	***30.210***	***4175***	***19.01***	***40.27***	***4.304***	***7.780***
Average			***160.85***	***19***	***282***	***3.660***	***744***	***4.87***	***8.08***	***1.371***	***0.893***
WHO			***300***	***50***	***2000***	***10***	***3000***	***20***	***50***	***3***	***10***
USEPA			***300***	***50***	***1300***	***15***	***5000***	***100***	***100***	***5***	***5***

Table 4.4c. Trace and heavy elements concentration in Deep ground water of Mardan District

Sample	**Source**	**Location**	**Fe µg/l**	**Mn µg/l**	**Cu µg/l**	**Pb µg/l**	**Zn µg/l**	**Ni µg/l**	**Cr µg/l**	**Cd µg/l**	**As µg/l**
W-2	Bore water	Hoti kali	13.38	19	23	<0.05	10	5.06	4.39	0.446	1.078
W-3	Bore water	Hoti kali	16.31	132	68	<0.05	256	4.08	3.08	0.544	0.869
W-9	Tube well	Chankari stop	<0.05	17	18	<0.05	30	0.81	4.66	<0.002	0.278
W-10	Tube well	Chankari stop	40.85	90	51	0.121	6	1.16	4.31	0.236	0.363
W-17	Tape water	Gujar Garhi	13.99	14	39	<0.05	92	3.61	<0.05	0.022	0.694
W-25	Tape water	Takht Bhai	<0.05	50	21	0.263	1068	1.82	3.61	0.591	0.656
W-29	Bore water	Jalala	5.17	23	79	<0.05	1	1.32	18.63	0.419	0.787
W-40	Bore water	Katlung	<0.05	10	43	0.586	48	1.79	6.34	1.030	0.111
W-42	Tape water	Mian Kali	<0.05	13	22	0.508	1297	3.28	4.99	0.057	0.049
W-43	Tape water	Babuzai	<0.05	2	50	0.168	610	4.26	4.68	0.209	0.05
W-45	Tape water	Jamal Garhi	99.55	2	30	0.782	25	3.79	6.42	1.437	0.398
W-50	Tube well	Jalal ababd	55.16	6	35	<0.05	27	1.83	7.25	0.351	0.166
W-53	Bore water	Sheikh Multon	<0.05	10	42	<0.05	60	2.97	7.90	1.198	2.869
W-55	Bore water	Toru	116.70	32	327	34.690	448	12.53	9.34	1.331	2.184
W-60	Tape water	Sowkai	6.80	24	846	3.109	225	3.91	9.11	1.028	1.600
Minimun			***<0.05***	***2***	***18***	***<0.05***	***1***	***0.81***	***<0.05***	***<0.002***	***0.049***
Maximum			***116.70***	***132***	***846***	***34.690***	***1297***	***12.53***	***18.63***	***1.437***	***2.869***
Average			***40.88***	***30***	***113***	***5.030***	***280***	***3.48***	***6.77***	***0.022***	***0.864***
WHO			***300***	***50***	***2000***	***10***	***3000***	***20***	***50***	***3***	***10***
USEPA			***300***	***50***	***1300***	***15***	***5000***	***100***	***100***	***5***	***5***

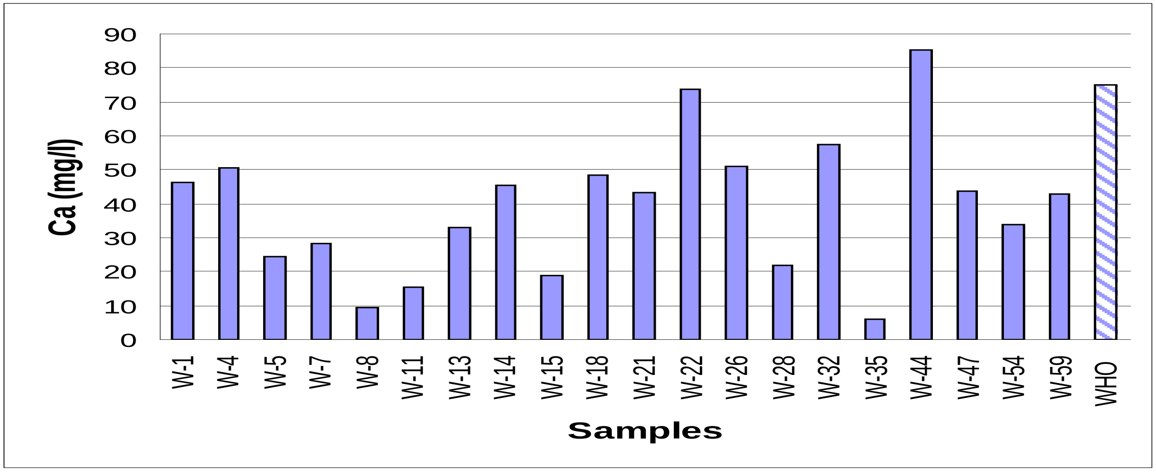

Fig. 4.1a. Calcium (Ca) concentration (mg/l) in Surface water of Mardan District

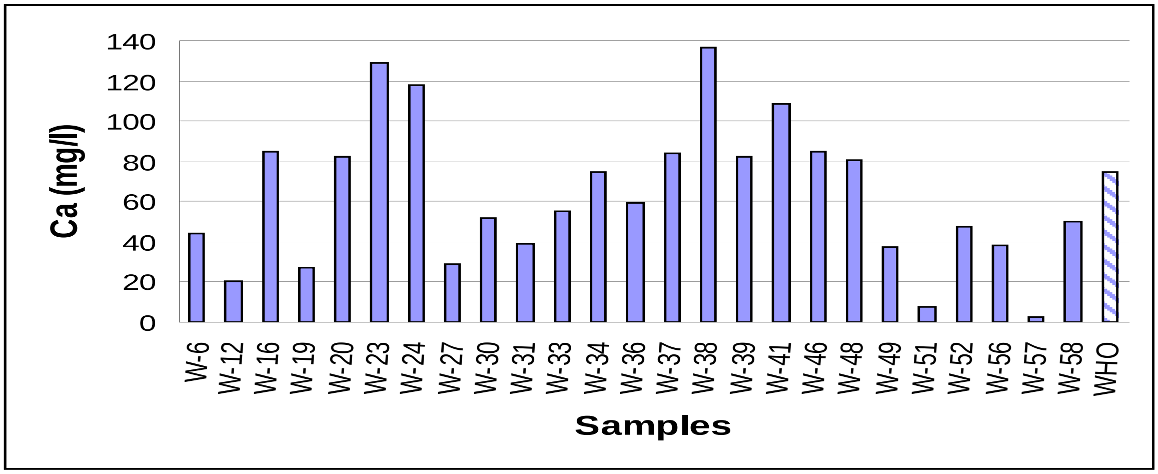

Fig. 4.1b. Calcium (Ca) concentration (mg/l) in Shallow ground water of Mardan District

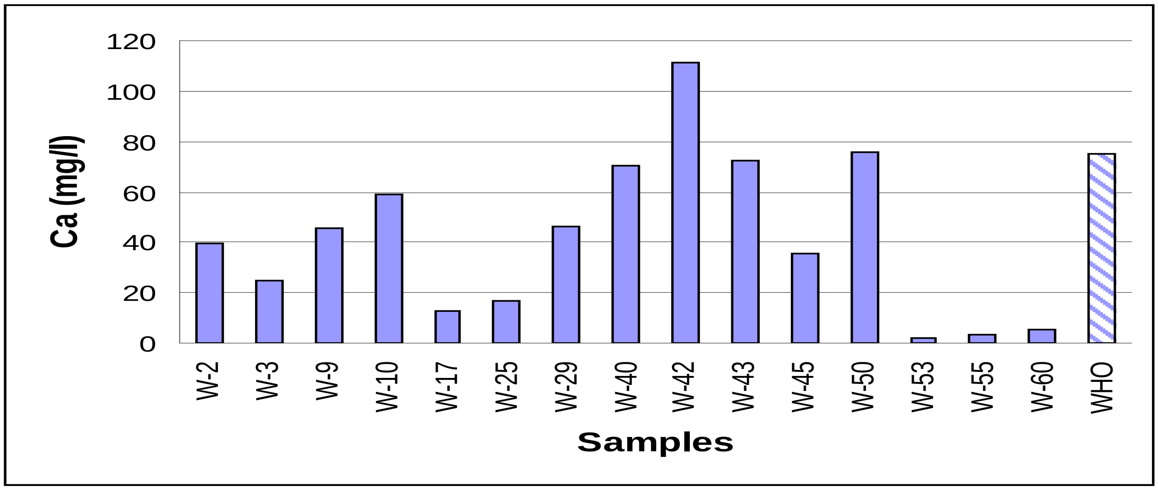

Fig. 4.1c. Calcium (Ca) concentration (mg/l) in Deep ground water of Mardan District

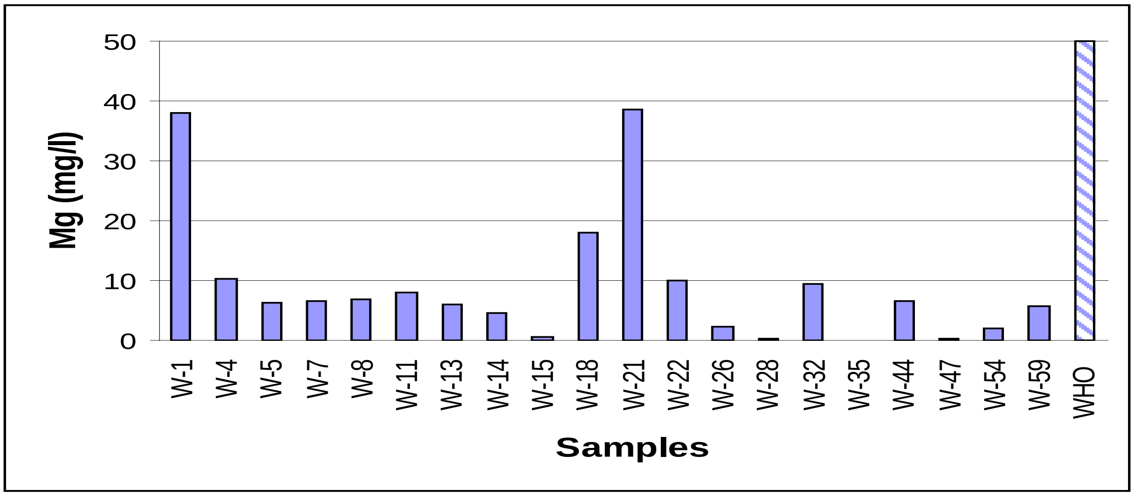

Fig. 4.2a. Magnesium (Mg) concentration (mg/l) in Surface water of Mardan District

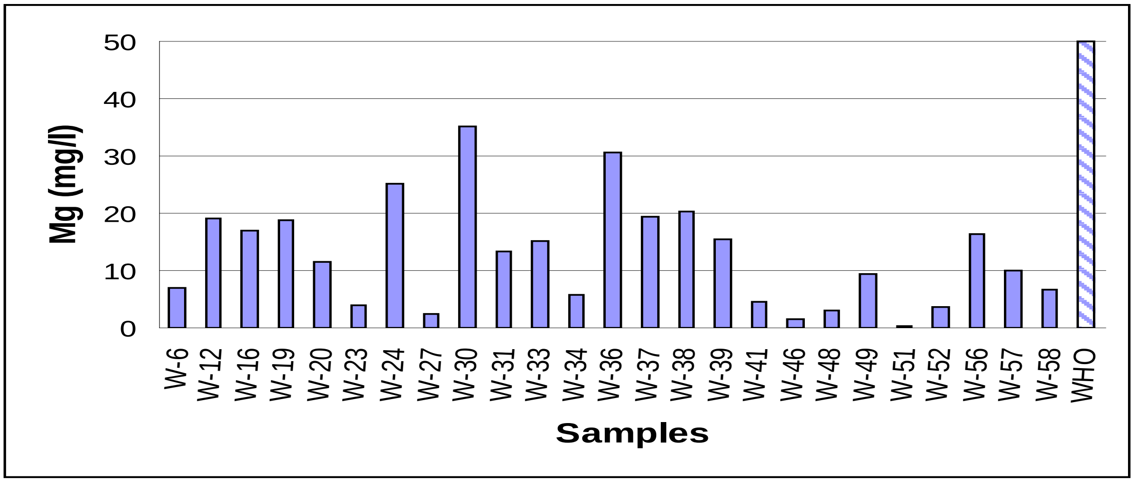

Fig. 4.2b. Magnesium (Mg) concentration (mg/l) in Shallow ground water of Mardan District

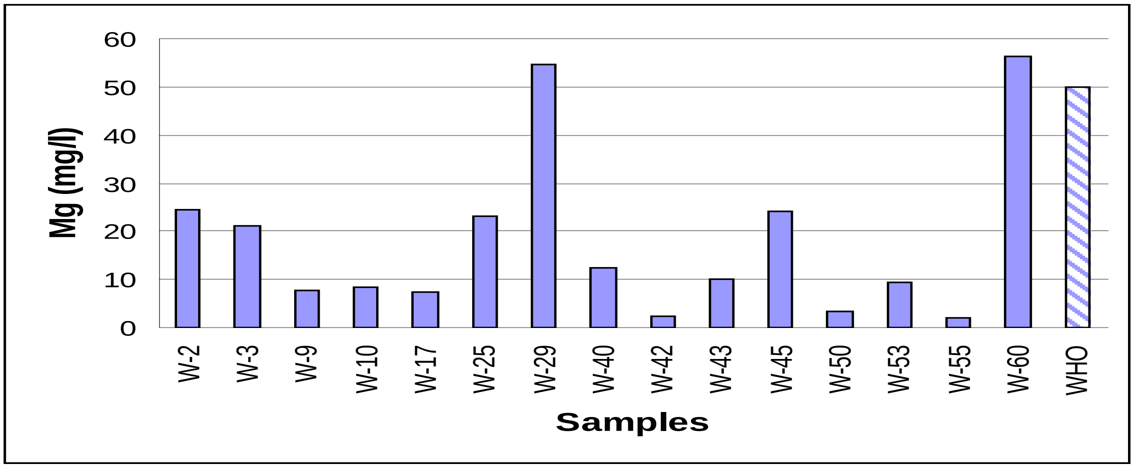

Fig. 4.2c. Magnesium (Mg) concentration (mg/l) in Deep ground water of Mardan District

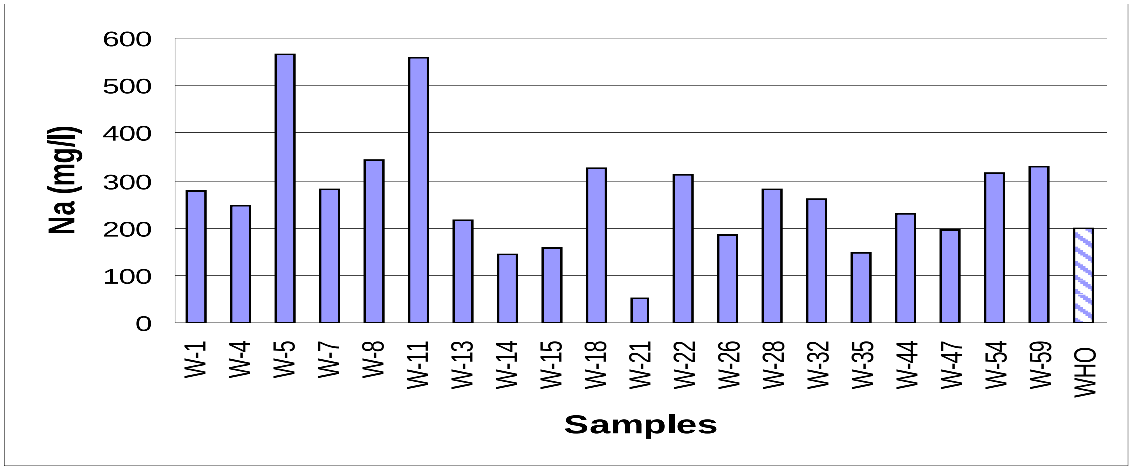

Fig. 4.3a. Sodium concentration (mg/l) in Surface water of Mardan District

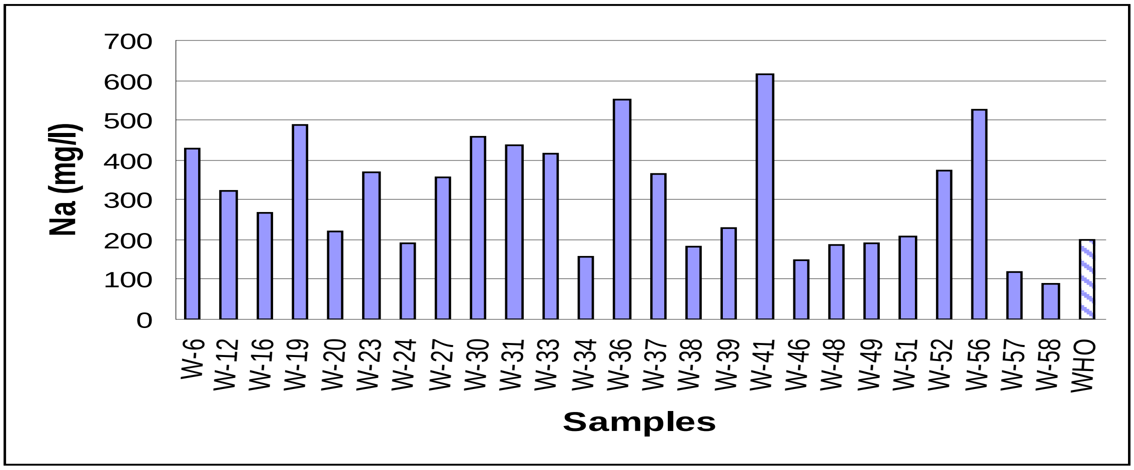

Fig. 4.3b. Sodium (Na) concentration (mg/l) in Shallow ground water of Mardan District

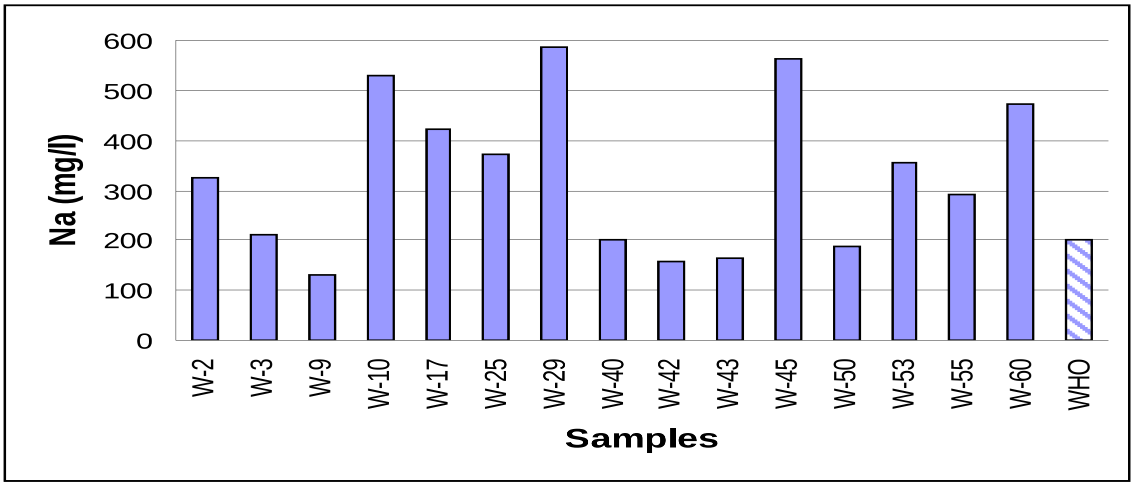

Fig. 4.3c. Sodium (Na) concentration (mg/l) in Deep ground water of Mardan District

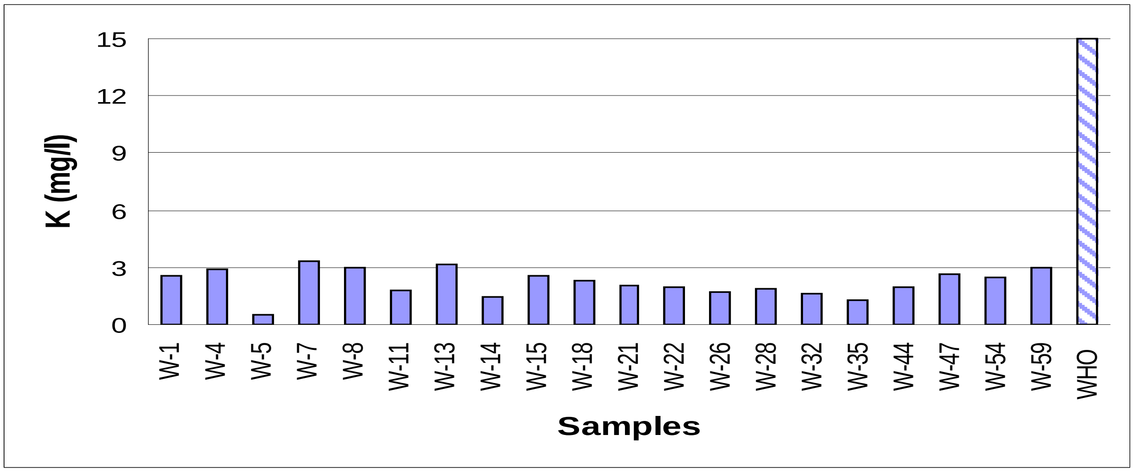

Fig. 4.4a. Potassium (K) concentration (mg/l) in Surface water of Mardan District

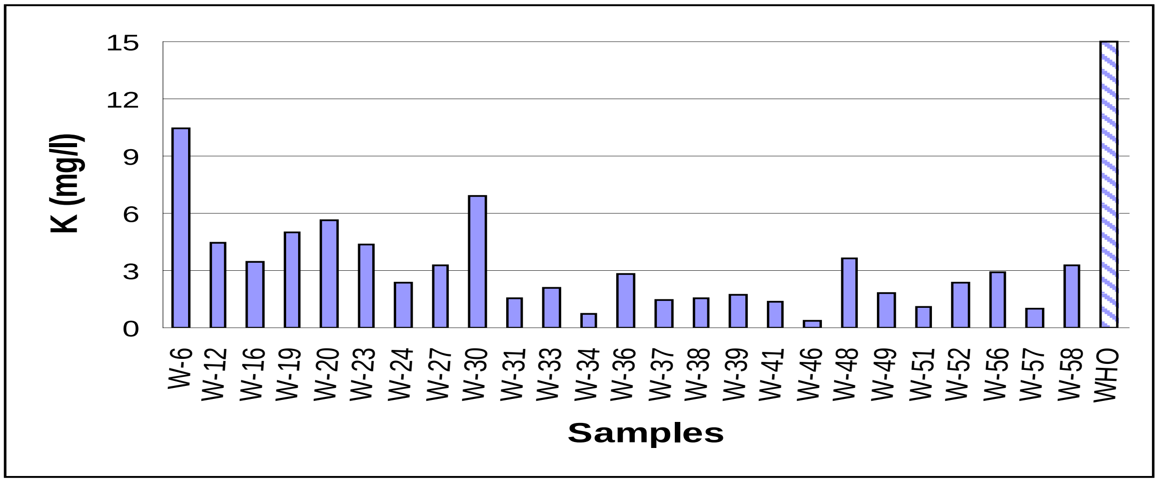

Fig. 4.4b. Potassium (K) concentration (mg/l) in Shallow ground water of Mardan District

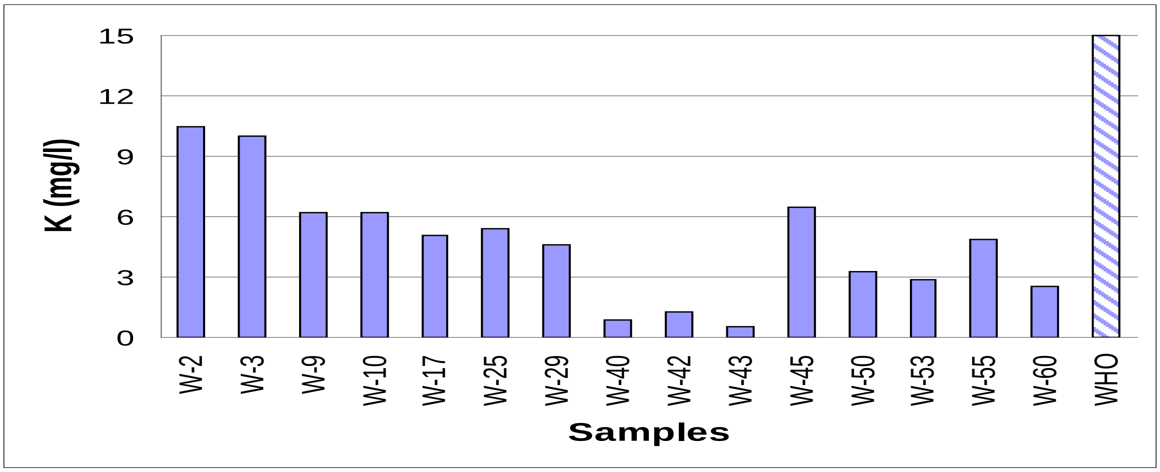

Fig. 4.4c. Potassium (K) concentration (mg/l) in Deep ground water of Mardan District

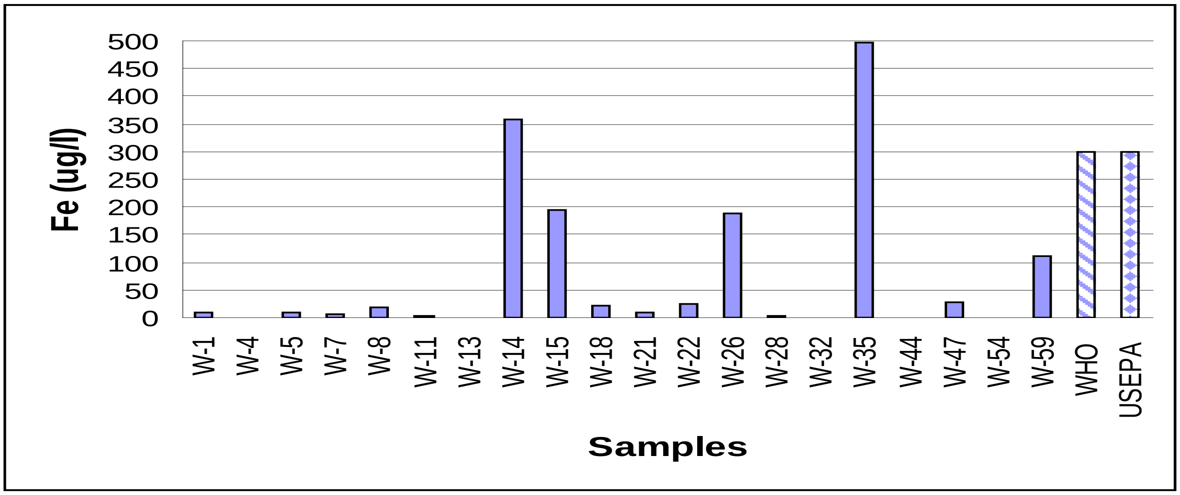

Fig. 4.5a. Iron (Fe) concentration (µg/l) in Surface water of Mardan District

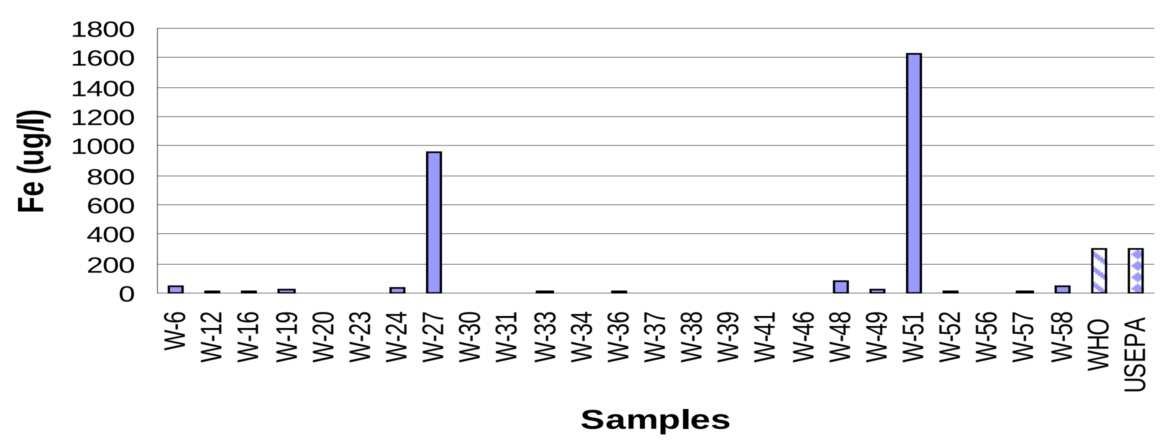

Fig. 4.5b. Iron (Fe) concentration (µg/l) in Shallow ground water of Mardan District

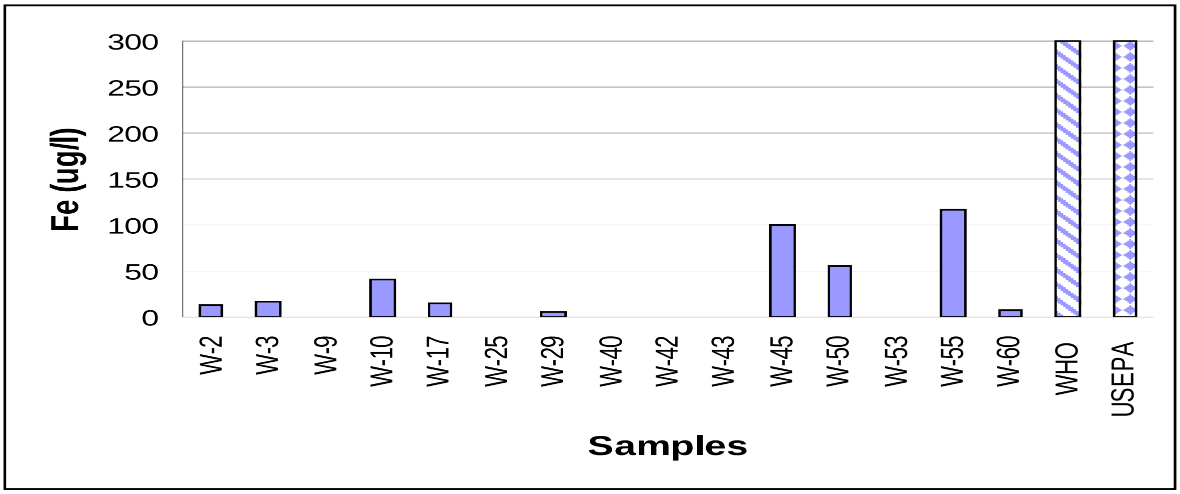

Fig. 4.5c. Iron (Fe) concentration (µg/l) in Deep ground water of Mardan District

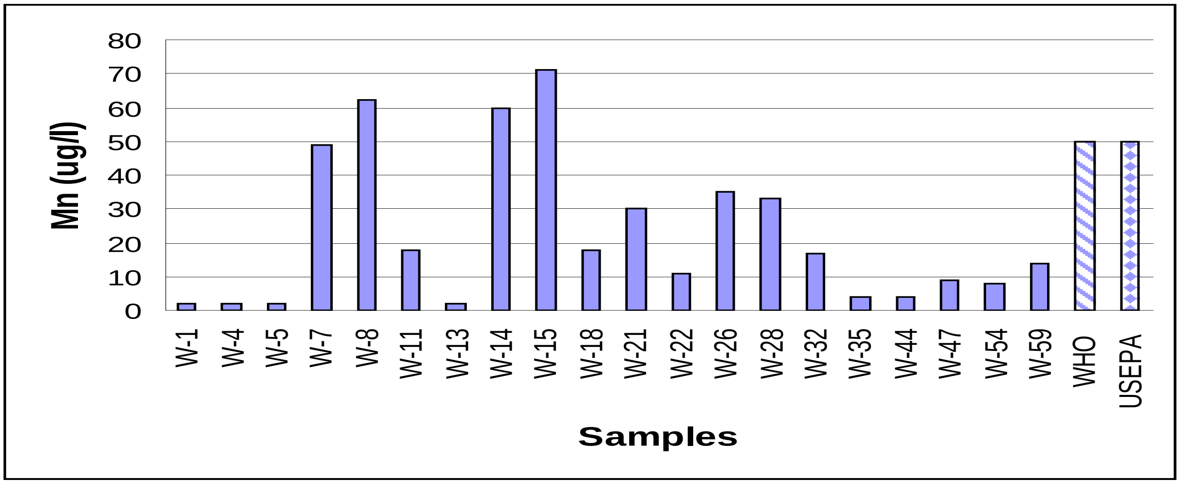

Fig. 4.6a. Manganese (Mn) concentration (µg/l) in Surface water of Mardan District

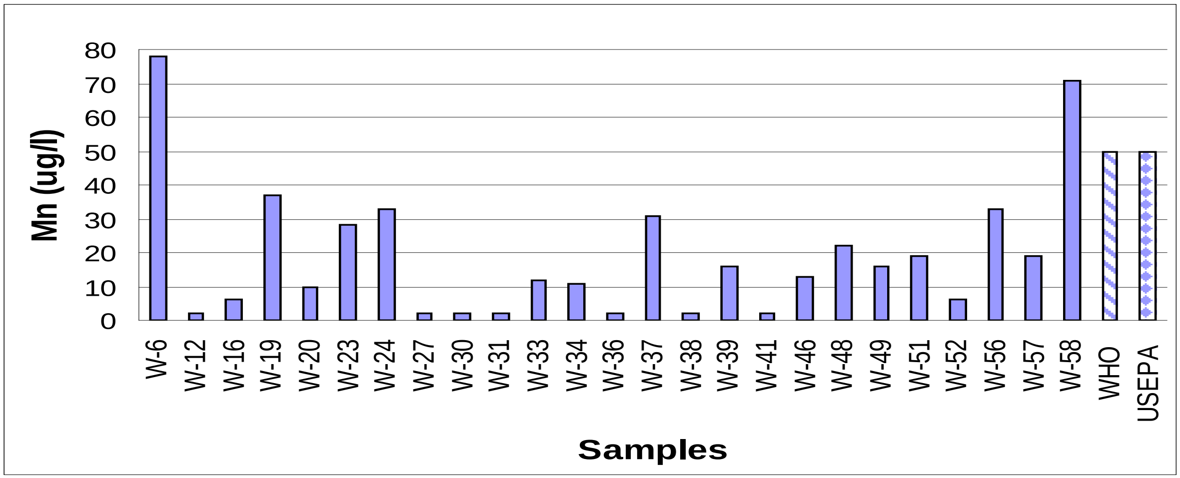

Fig. 4.6b. Manganese (Mn) concentration (µg/l) in Shallow ground water of Mardan District

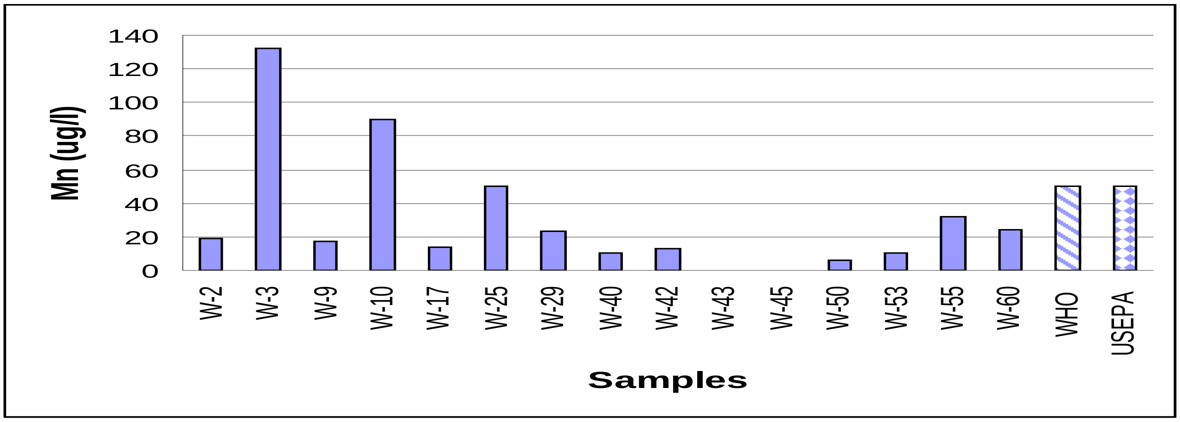

Fig. 4.6c. Manganese (Mn) concentration (µg/l) in Deep ground water of Mardan District

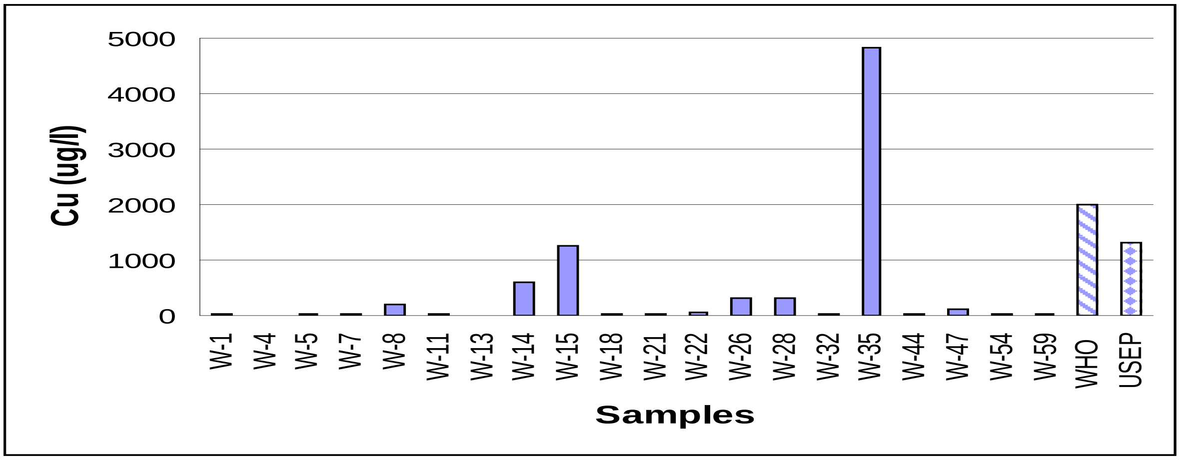

Fig. 4.7a. Copper (Cu) concentration (µg/l) in Surface water of Mardan District

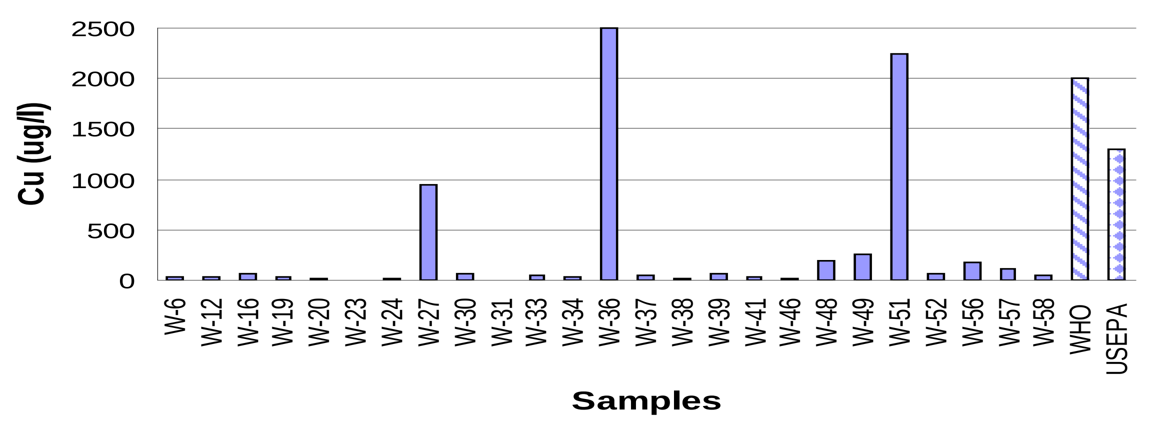

Fig. 4.7b. Copper (Cu) concentration (µg/l) in Shallow ground water of Mardan District

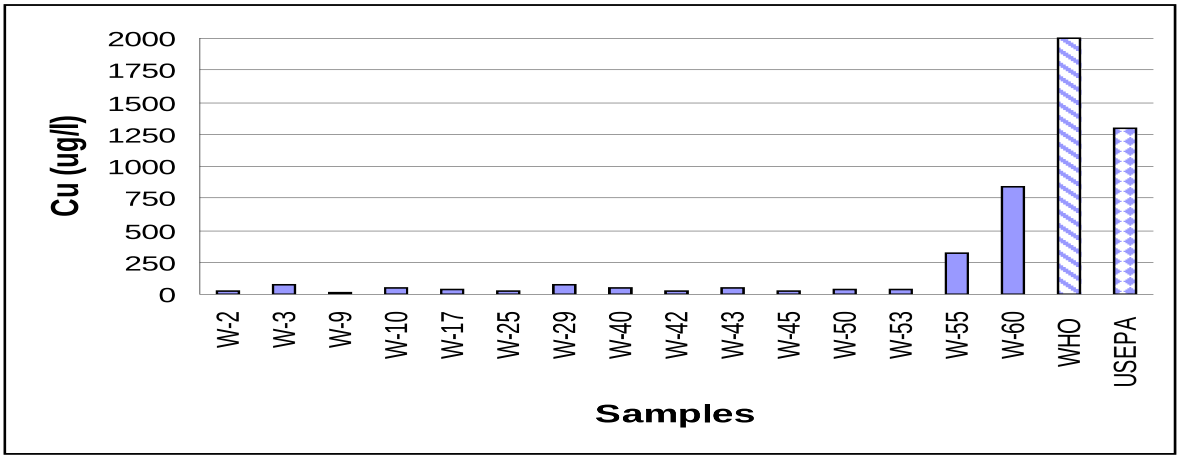

Fig. 4.7c. Copper (Cu) concentration (µg/l) in Deep ground water of Mardan District

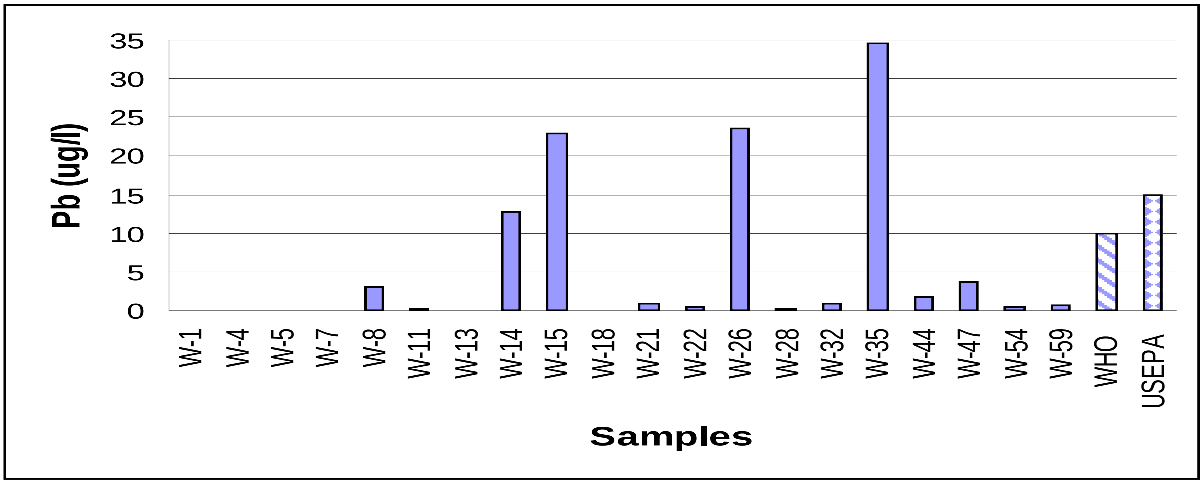

Fig. 4.8a. Lead (Pb) concentration (μg/l) in Surface water of Mardan District

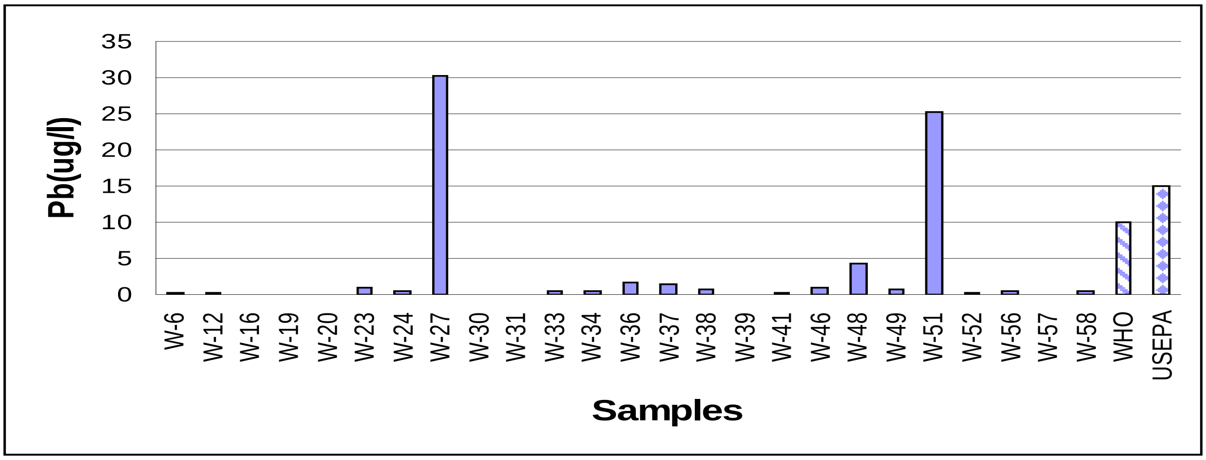

Fig. 4.8b. Lead (Pb) concentration (μg/l) in Shallow ground water of Mardan District

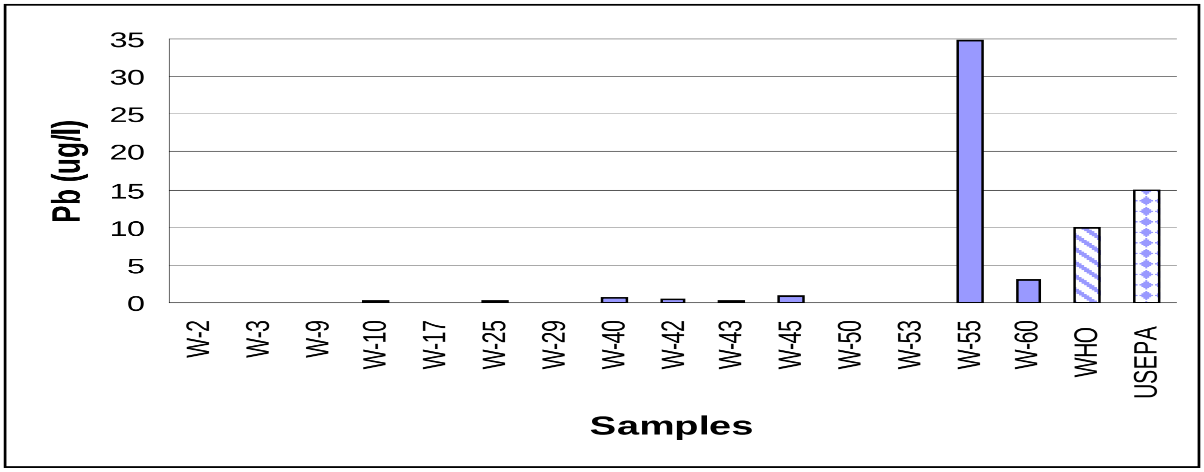

Fig. 4.8c. Lead (Pb) concentration (μg/l) in Deep ground water of Mardan District

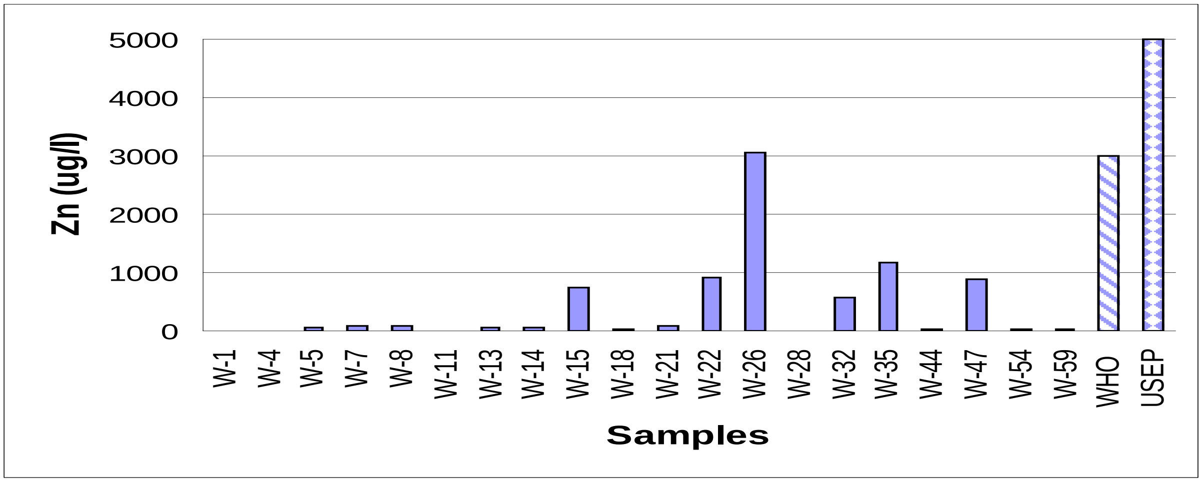

Fig. 4.9a. Zinc (Zn) concentration (µg/l) in Surface water of Mardan District

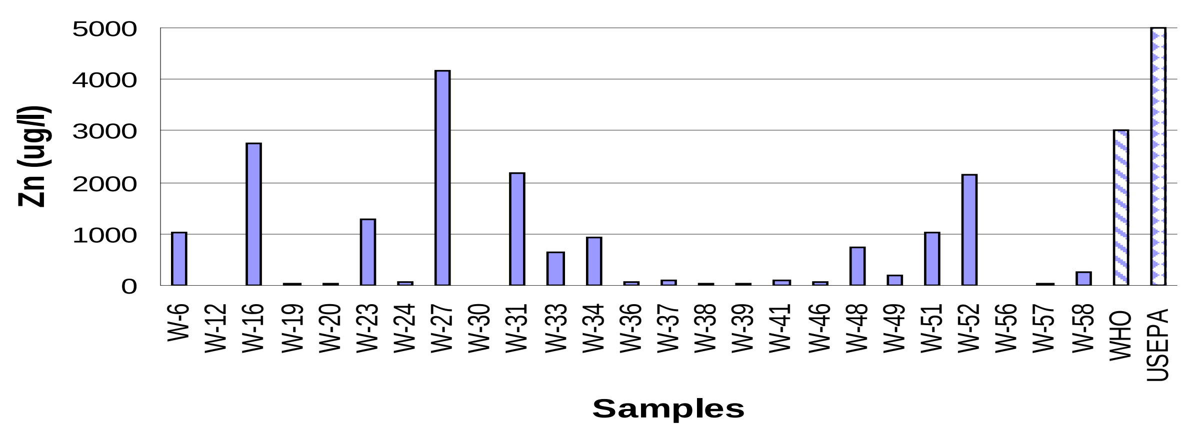

Fig. 4.9b. Zinc (Zn) concentration (µg/l) in Shallow ground water of Mardan District

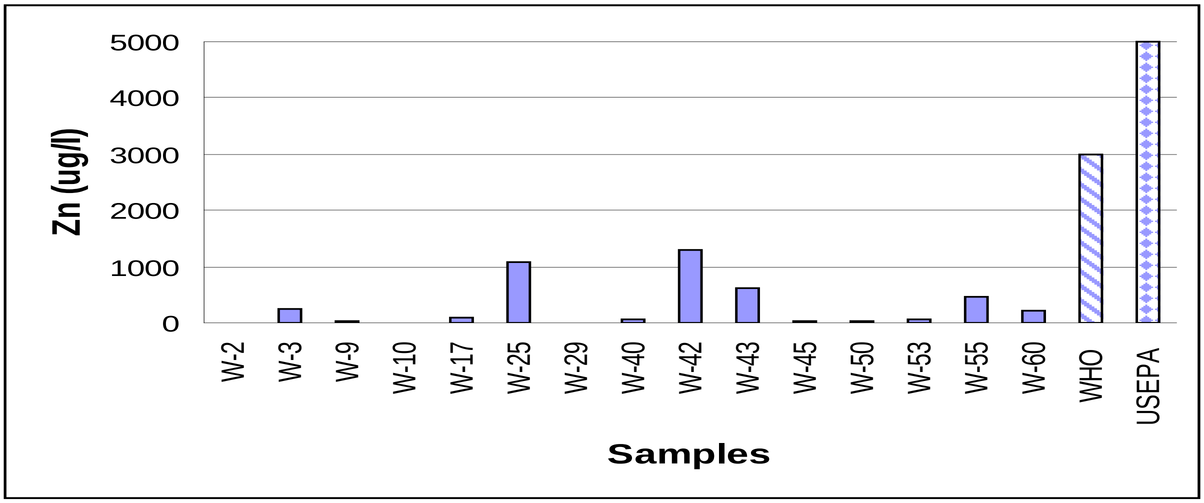

Fig. 4.9c. Zinc (Zn) concentration (µg/l) in Deep ground water of Mardan District

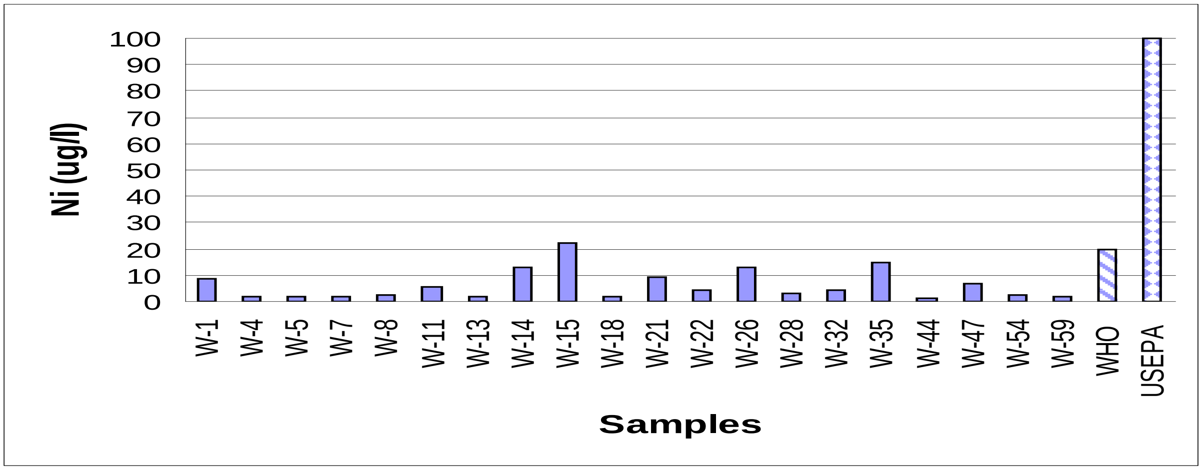

Fig. 4.10a. Nickel (Ni) concentration (μg/l) in Surface water of Mardan District

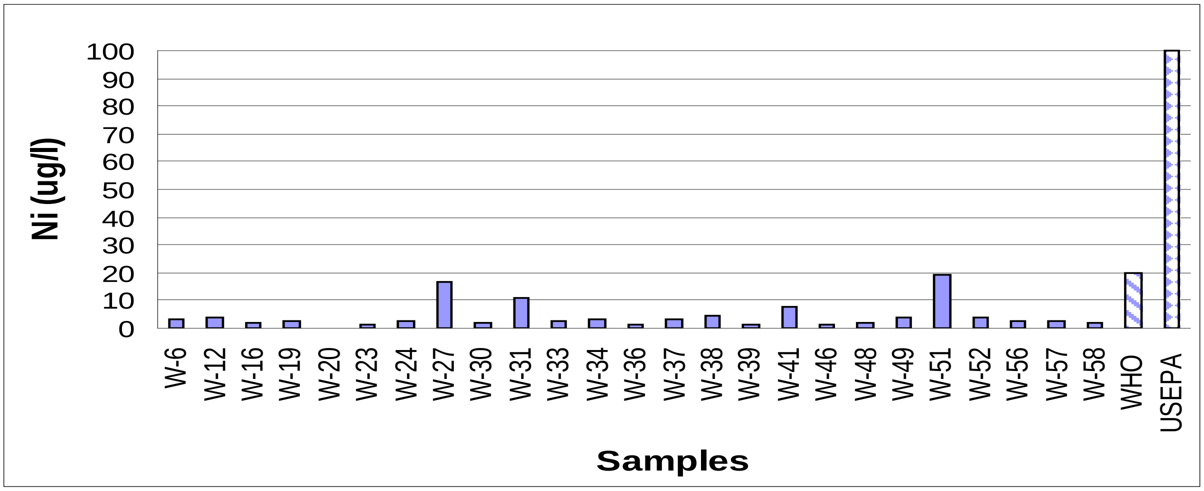

Fig. 4.10b. Nickel (Ni) concentration (μg/l) in Shallow ground water of Mardan District

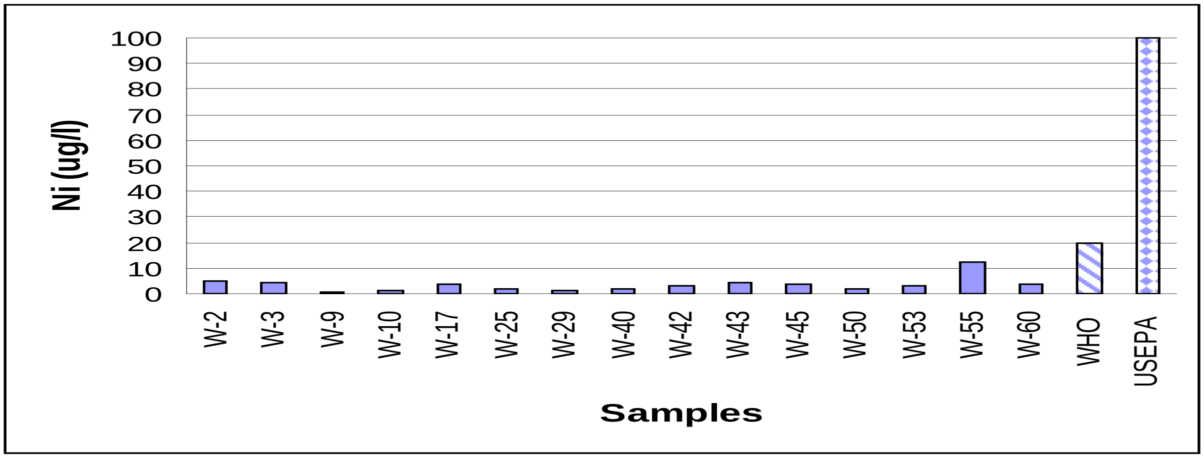

Fig. 4.10c. Nickel (Ni) concentration (μg/l) in Deep ground water of Mardan District

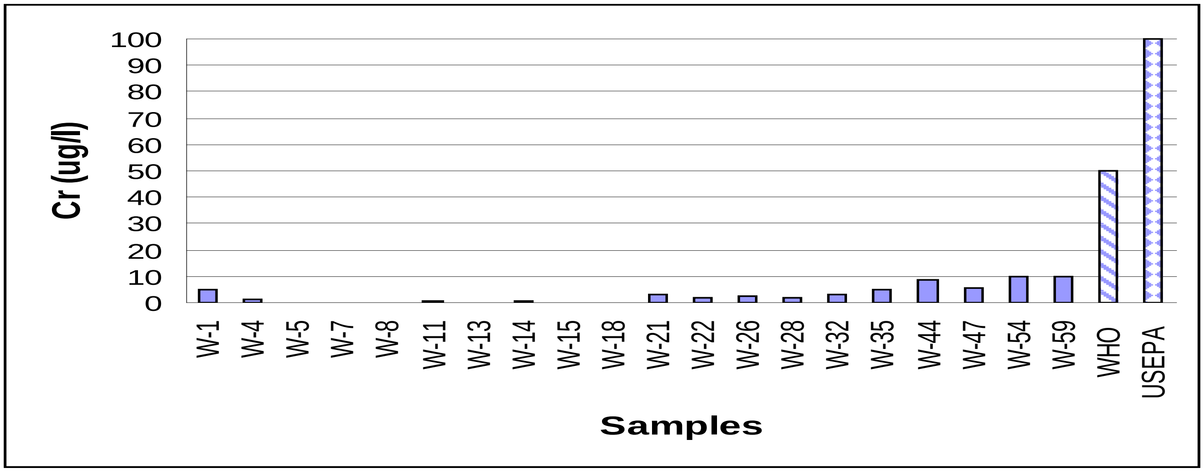

Fig. 4.11a. Chromium (Cr) concentration (µg/l) in Surface water of Mardan District

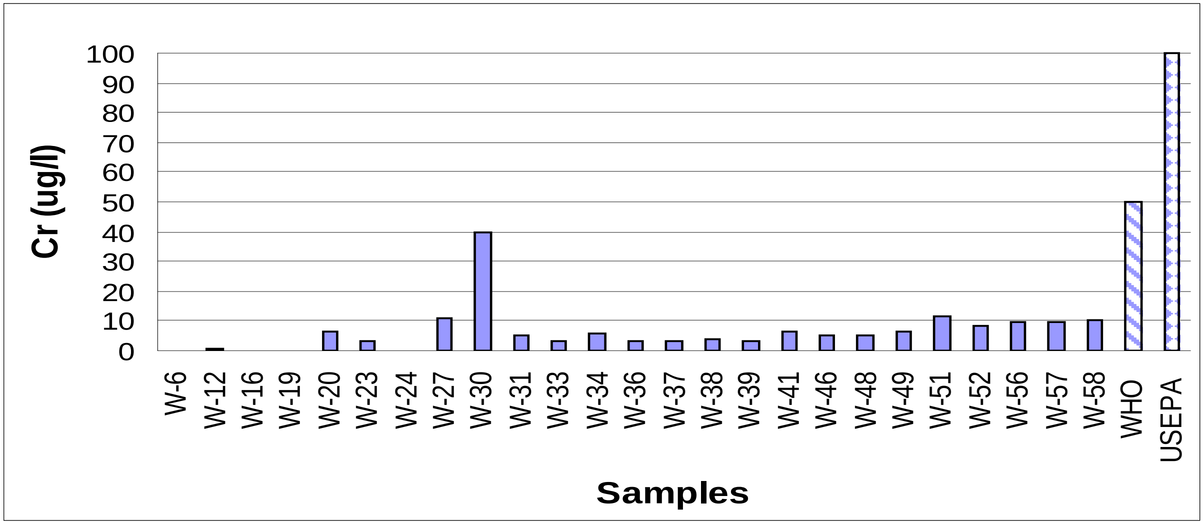

Fig. 4.11b. Chromium (Cr) concentration (µg/l) in Shallow ground water of Mardan District

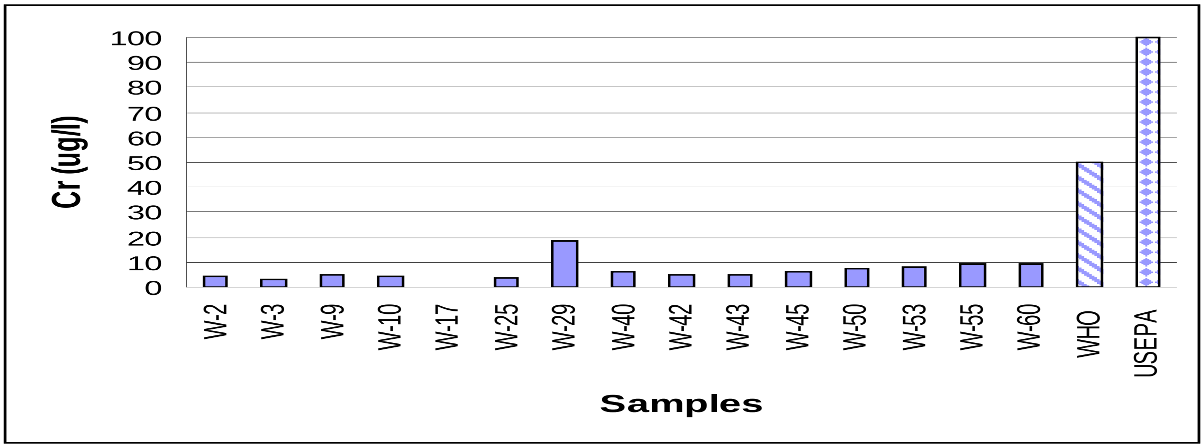

Fig. 4.11c. Chromium (Cr) concentration (µg/l) in Deep ground water of Mardan District

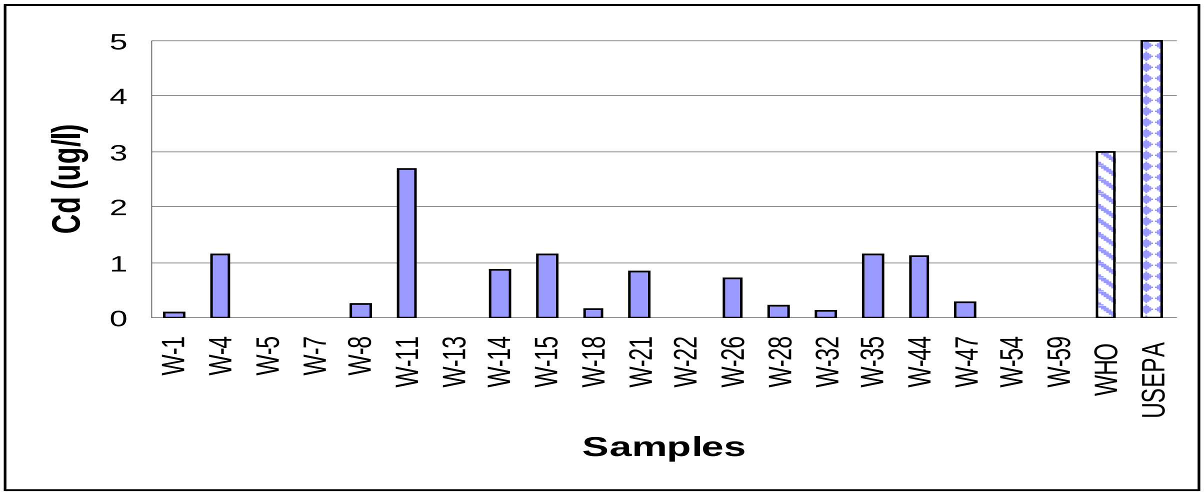

Fig. 4.12a. Cadmium (Cd) concentration (µg/l) in Surface water of Mardan District

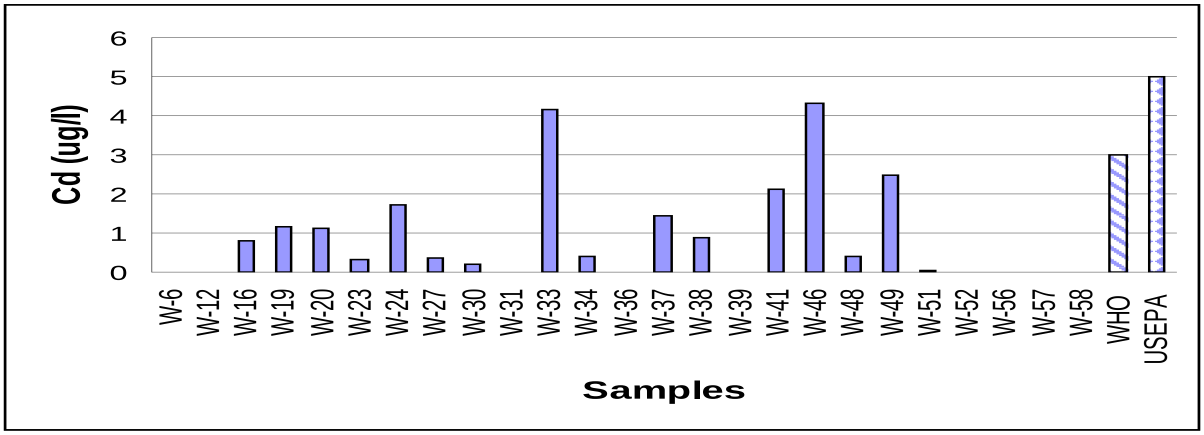

Fig. 4.12b. Cadmium (Cd) concentration (µg/l) in Shallow ground water of Mardan District

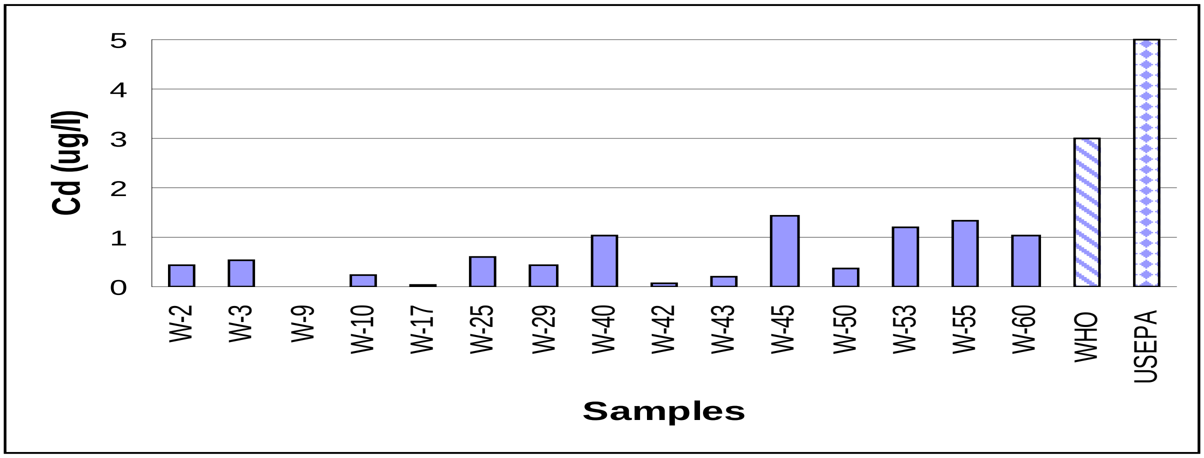

Fig. 4.12c. Cadmium (Cd) concentration (µg/l) in Deep ground water of Mardan District

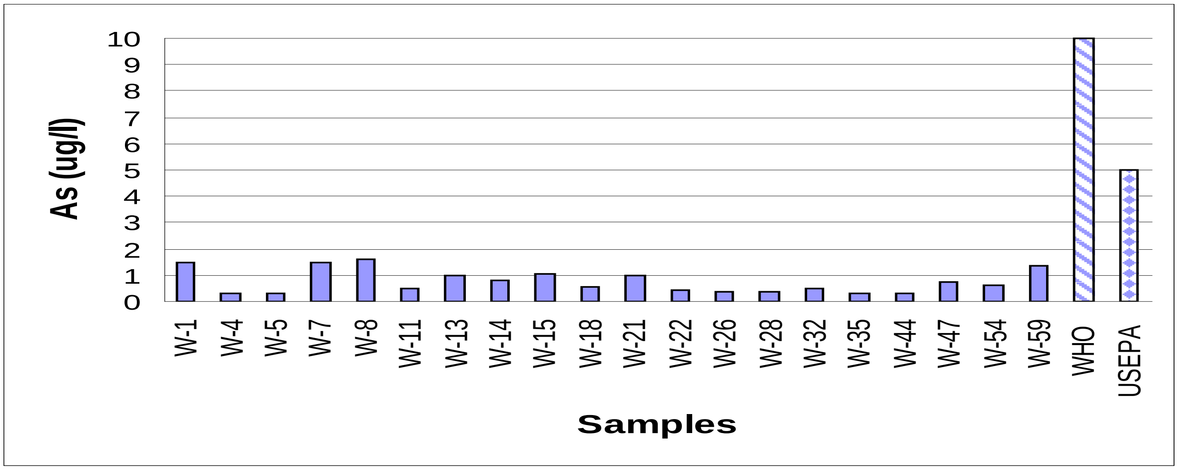

Fig. 4.13a. Arsenic (As) concentration (µg/l) in Surface water of Mardan District

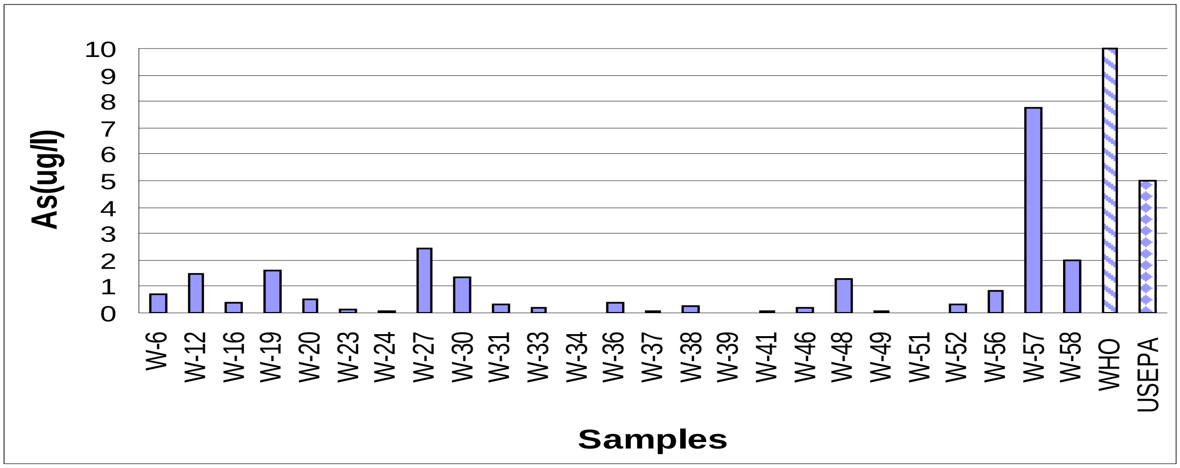

Fig. 4.13b. Arsenic (As) concentration (µg/l) in Shallow ground water of Mardan District

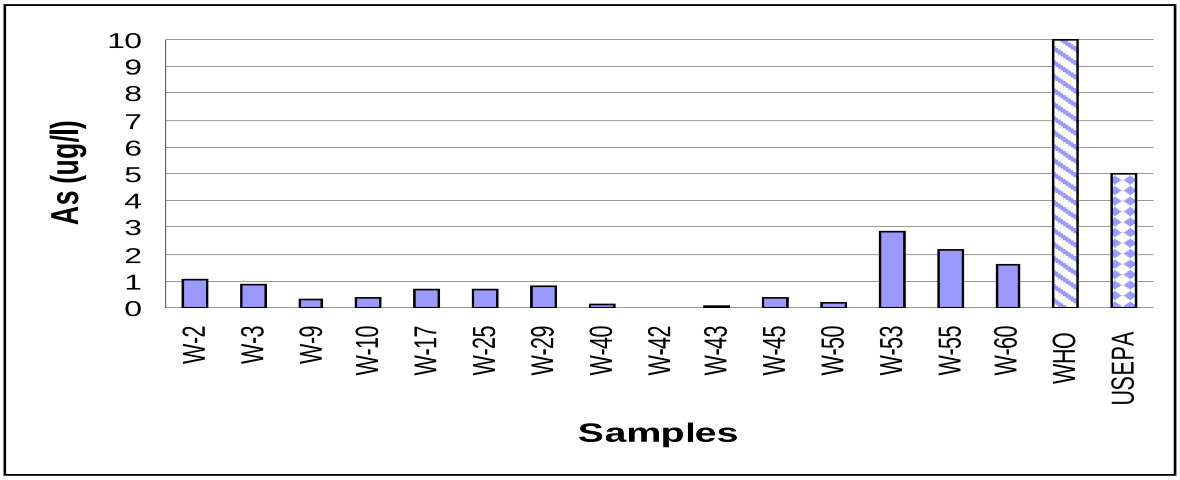

Fig. 4.13c. Arsenic (As) concentration (µg/l) in Deep ground water of Mardan District

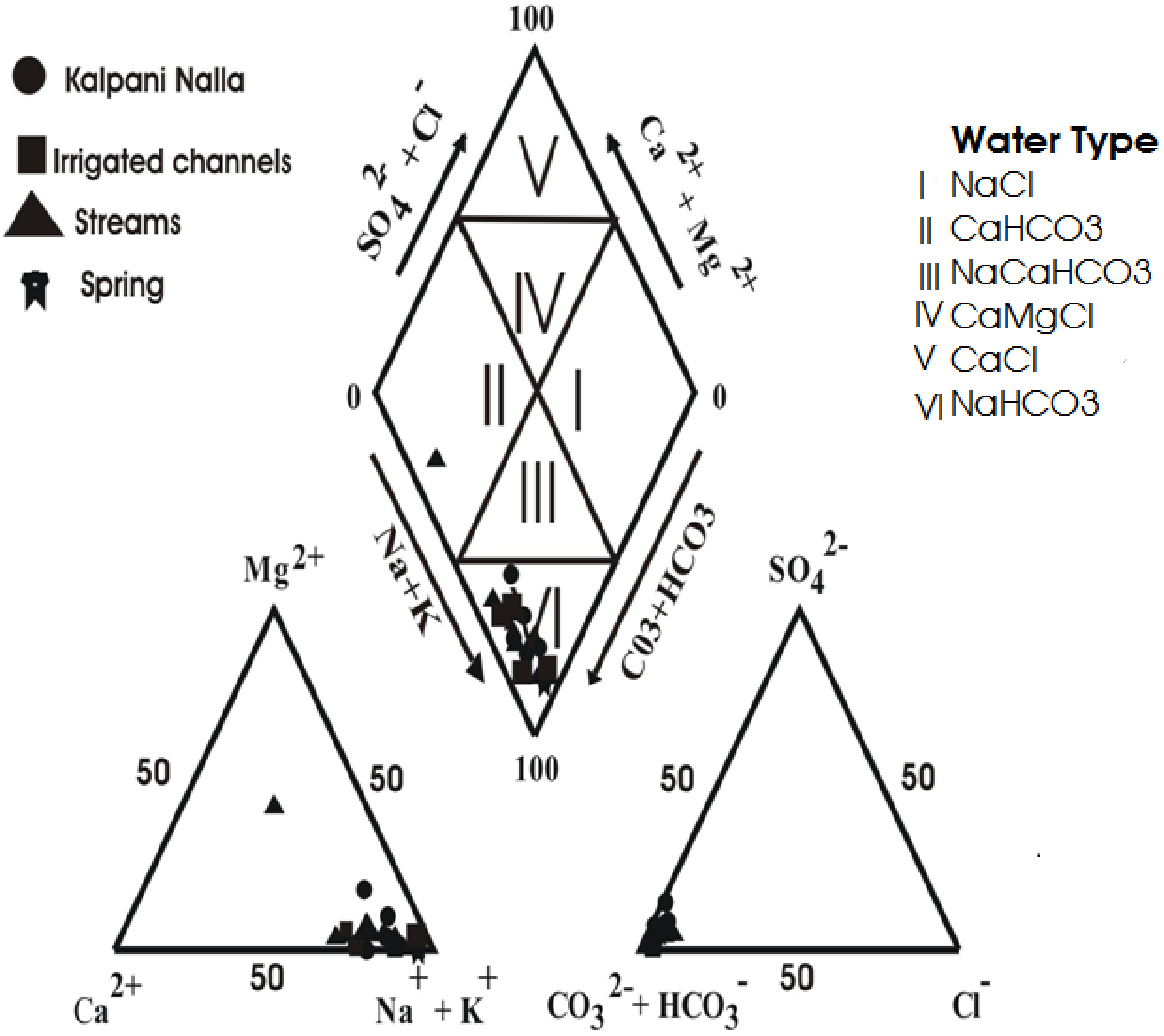

Fig.4.14a. Piper diagram showing Surface water classification of Mardan District

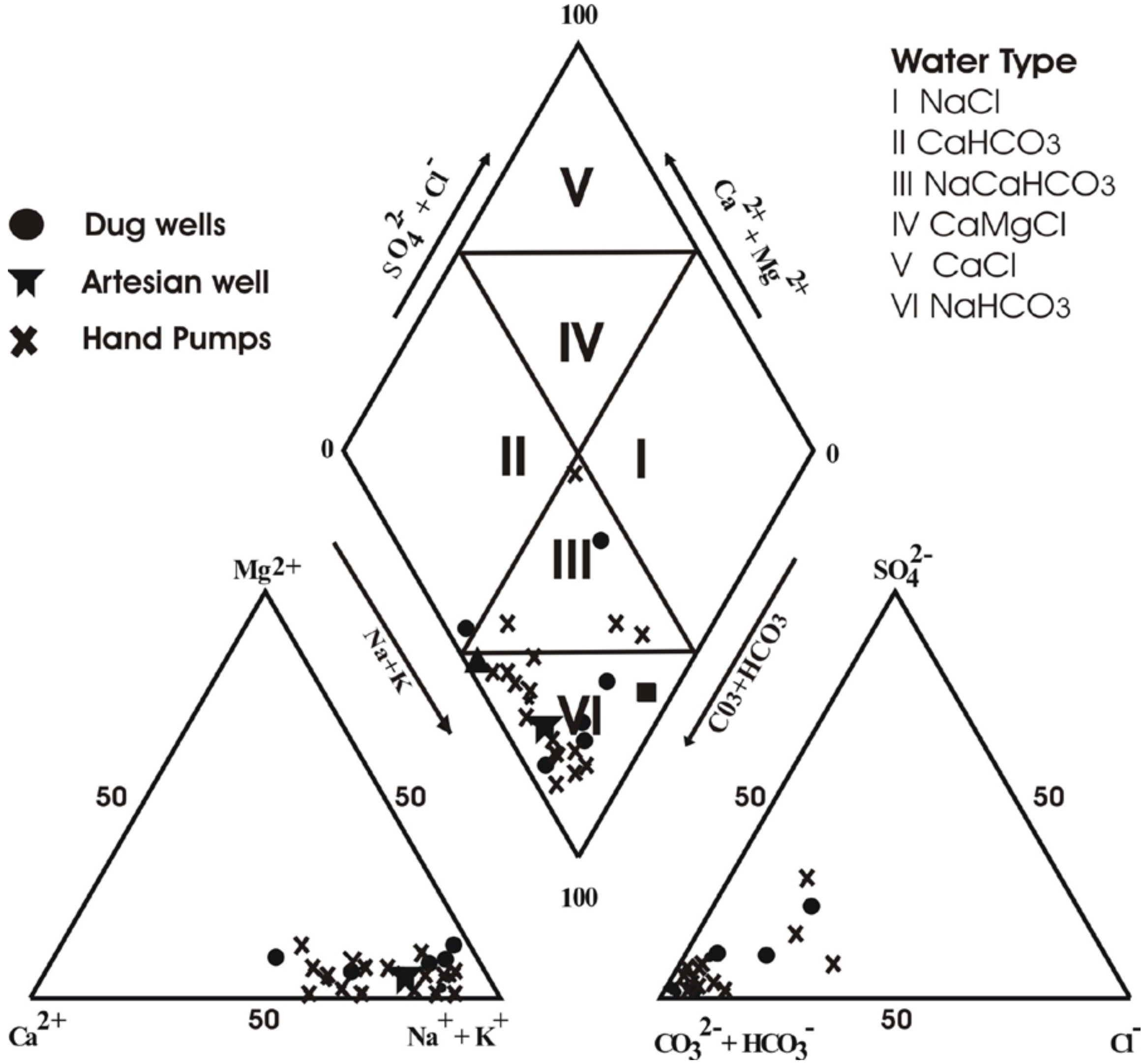

Fig.4.14b. **Piper diagram showing Shallow ground water classification of Mardan District**

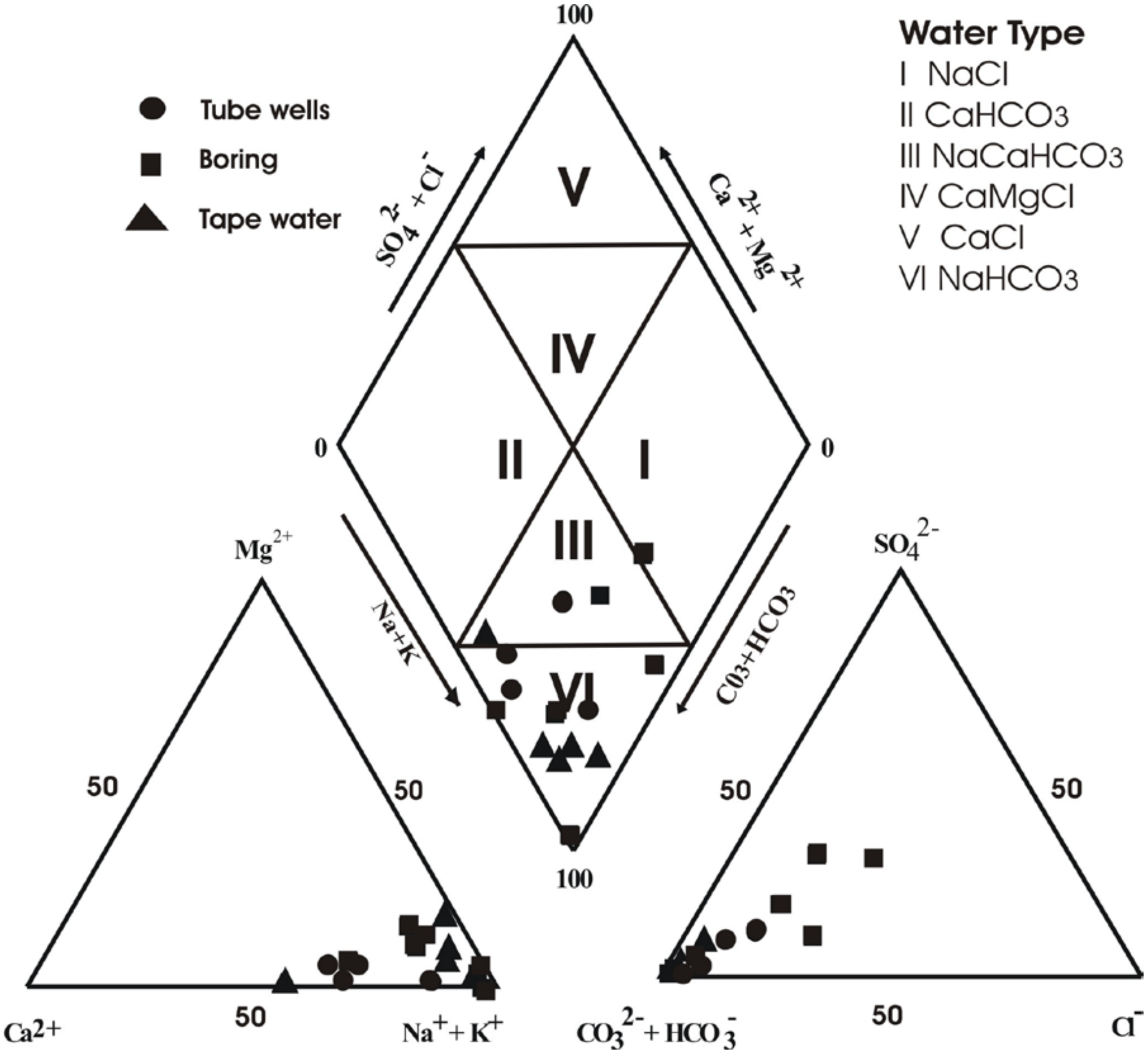

Fig.4.14c. Piper diagram showing Deep ground water classification of Mardan District

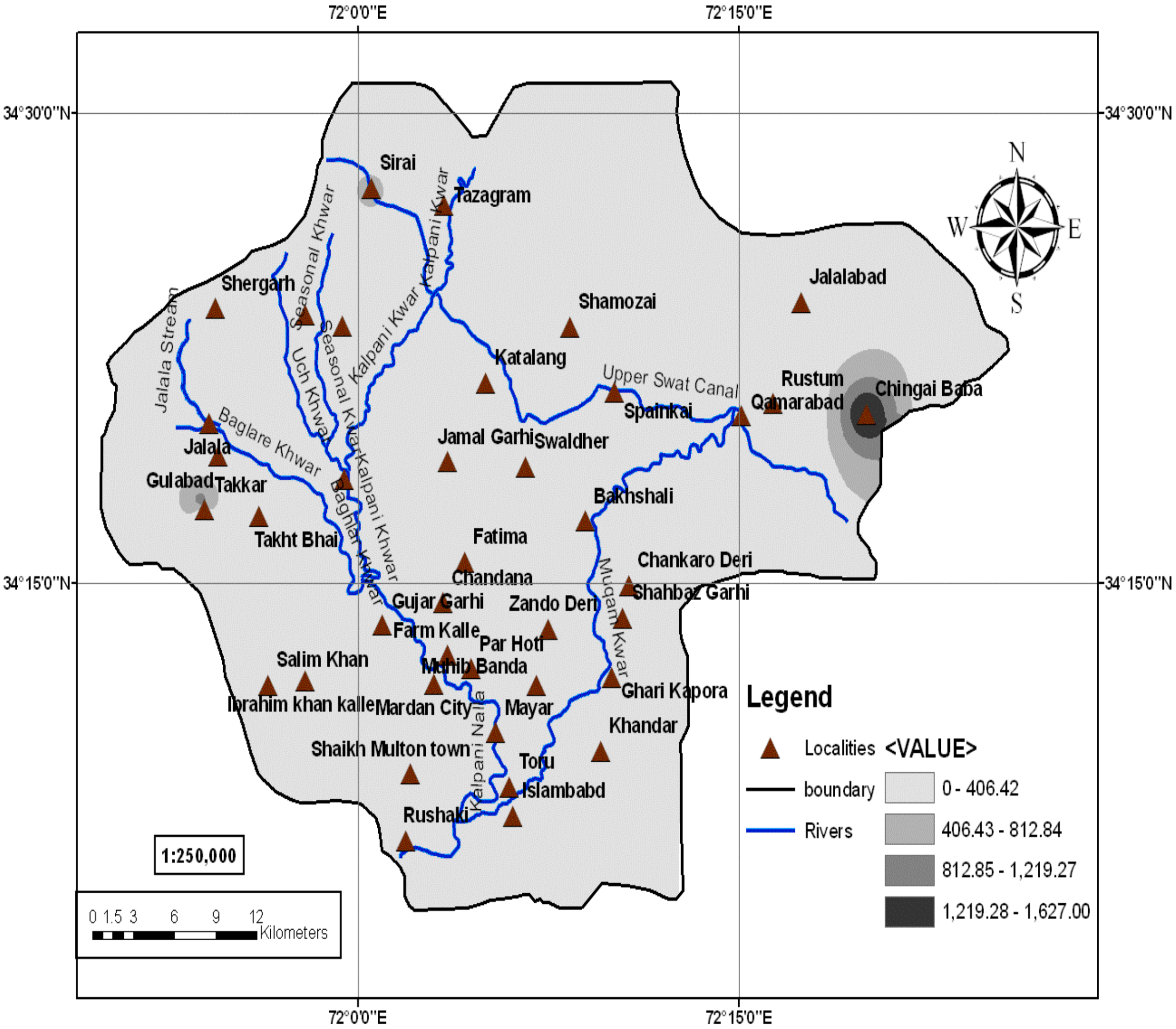

Fig.4.15a. Map showing the Iron (Fe) concentration (µg/l) in water of Mardan District

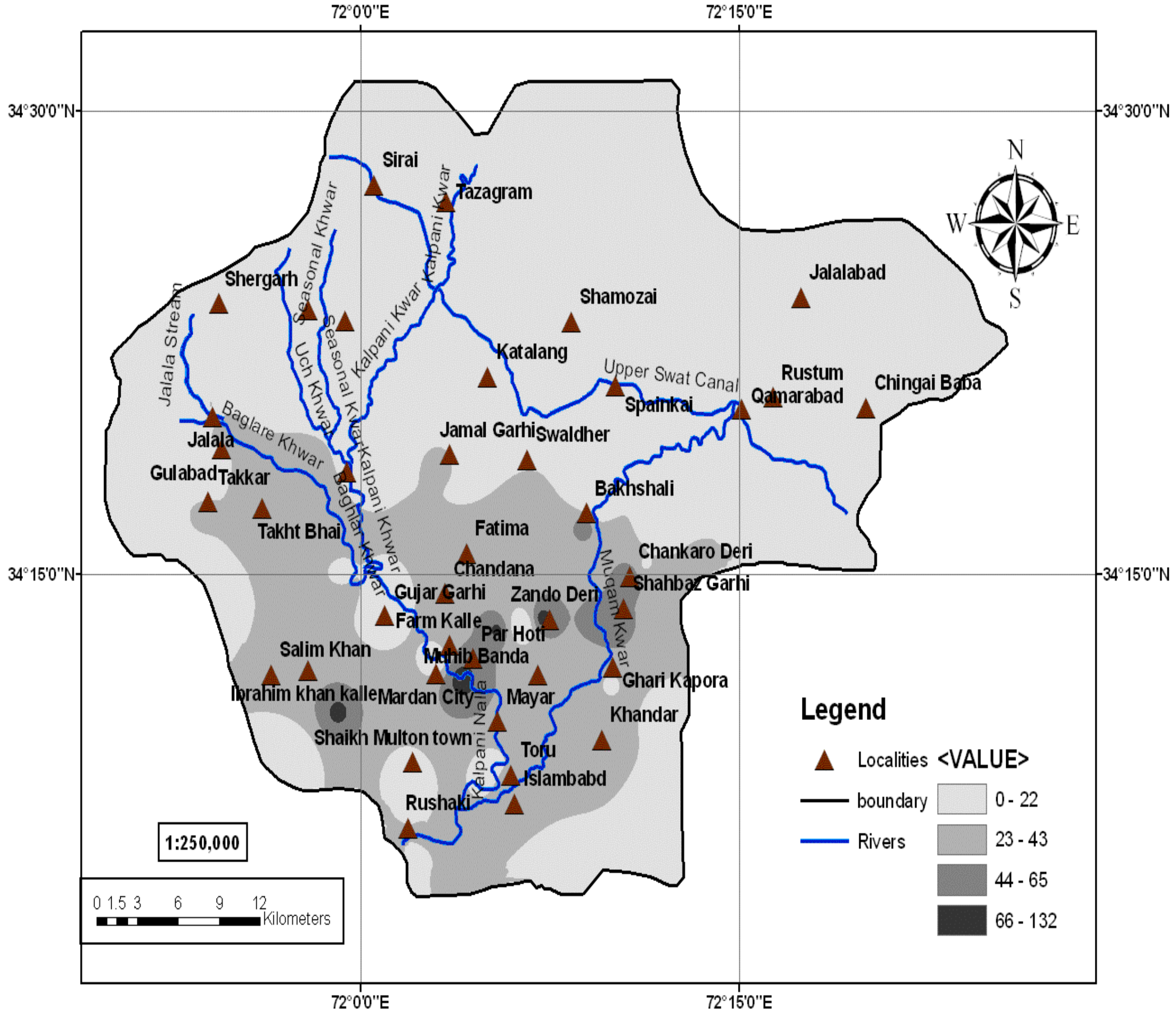

Fig.4.15b. Map showing the Manganese (Mn) concentration (µg/l) in water of Mardan District

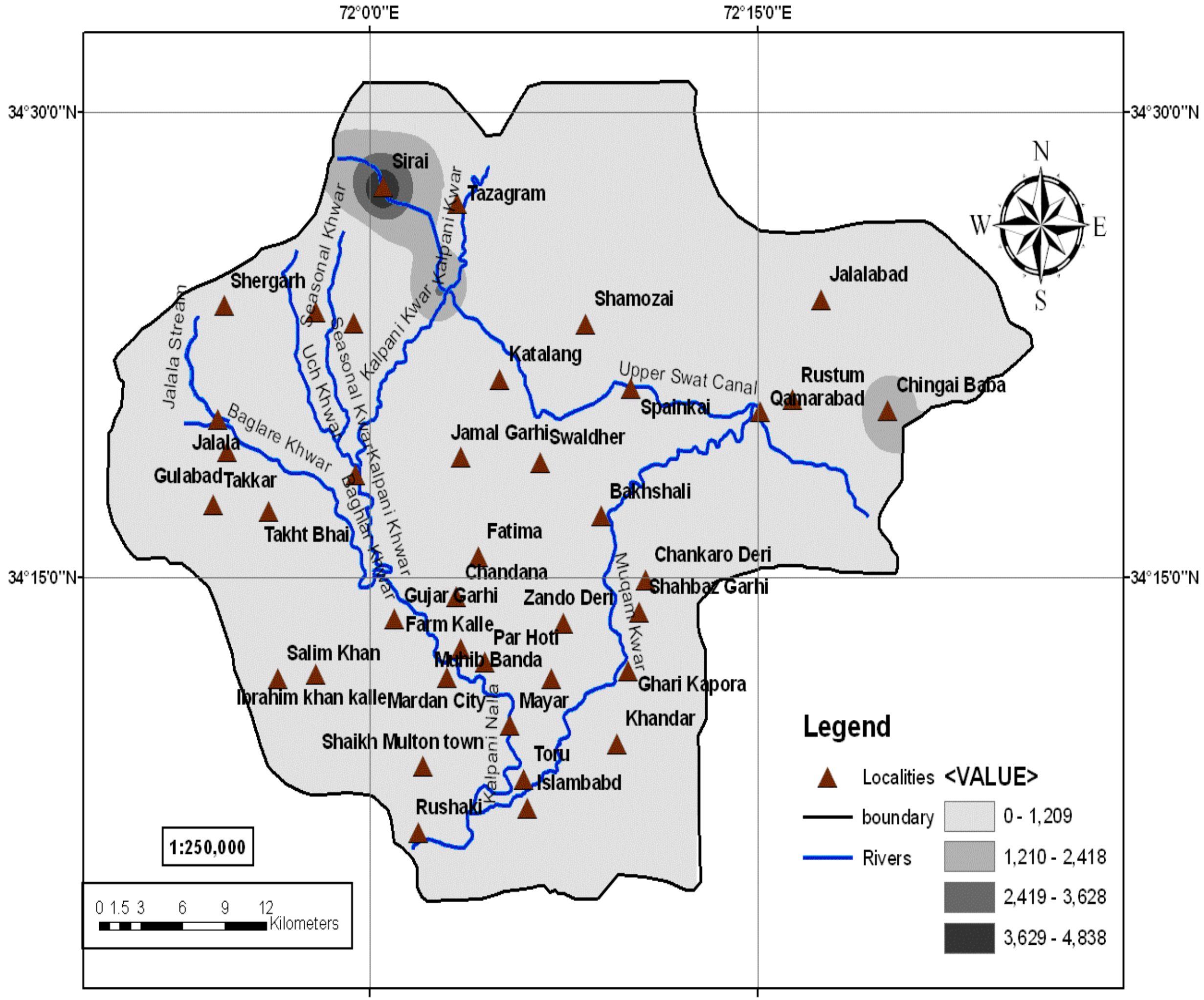

Fig.4.15c. Map showing the Copper (Cu) concentration (µg/l) in water of Mardan District

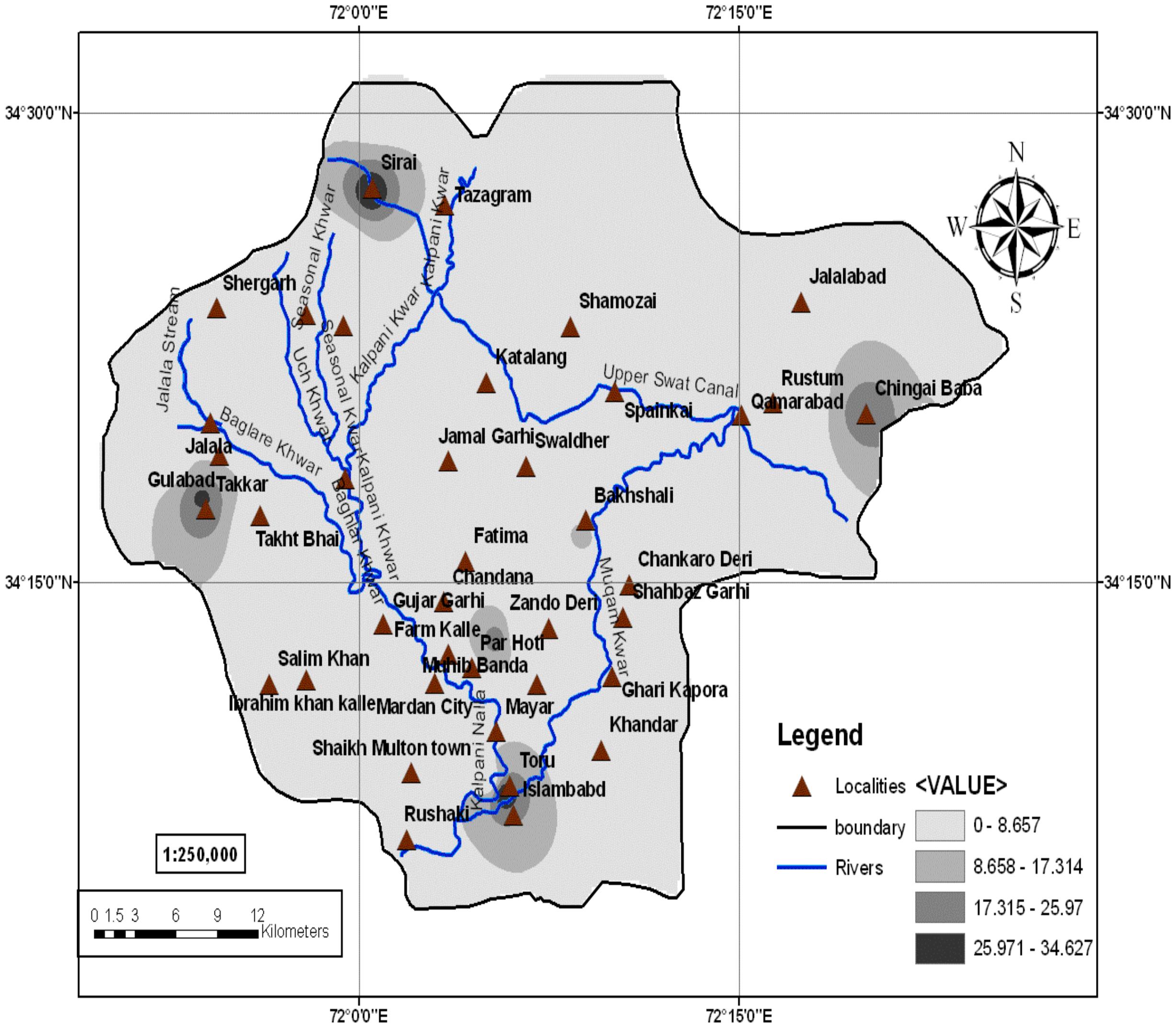

Fig.4.15d. Map showing the Lead (Pb) concentration (µg/l) in water of Mardan District

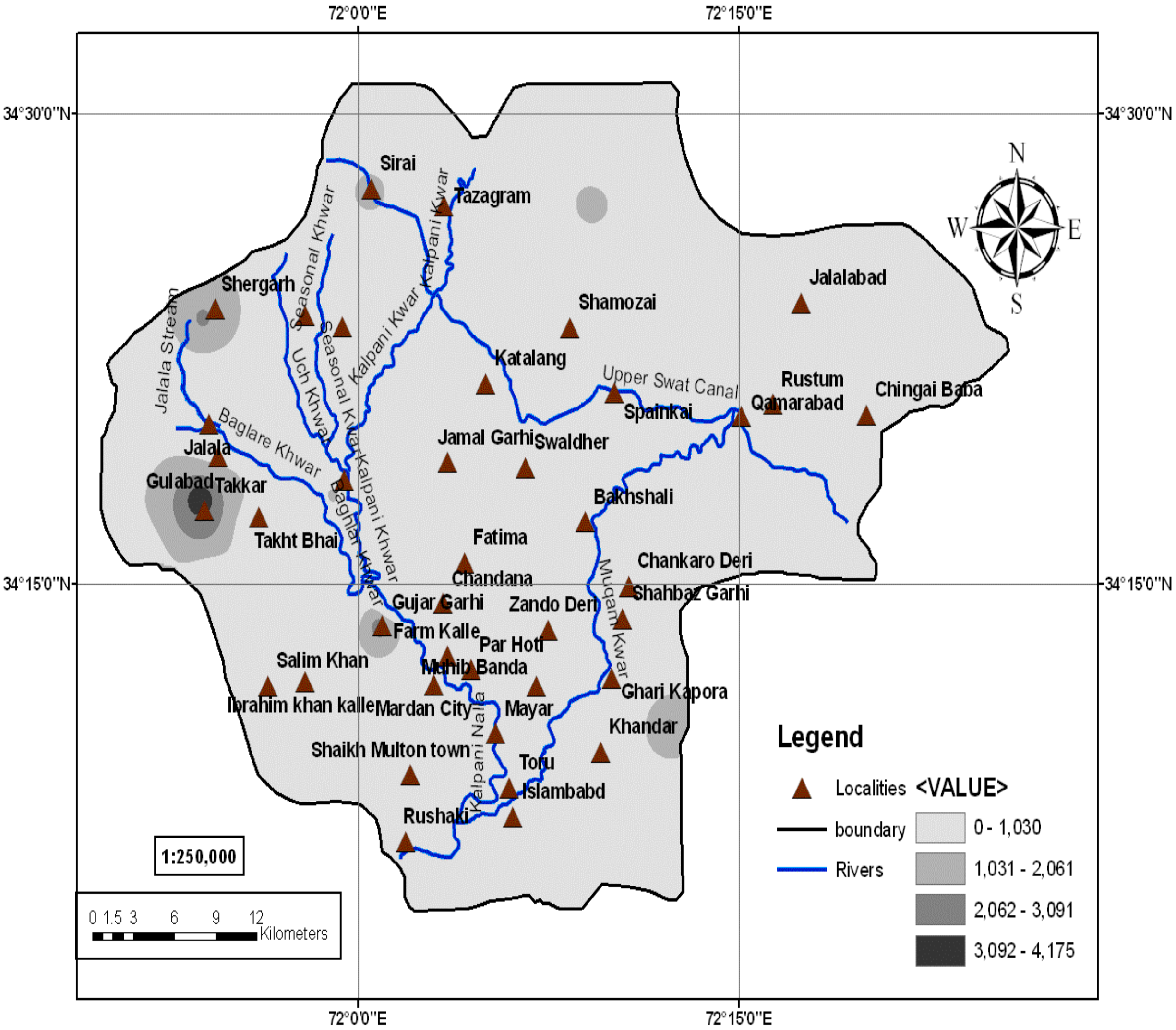

Fig.4.15e. Map showing the Zinc (Zn) concentration (µg/l) in water of Mardan District

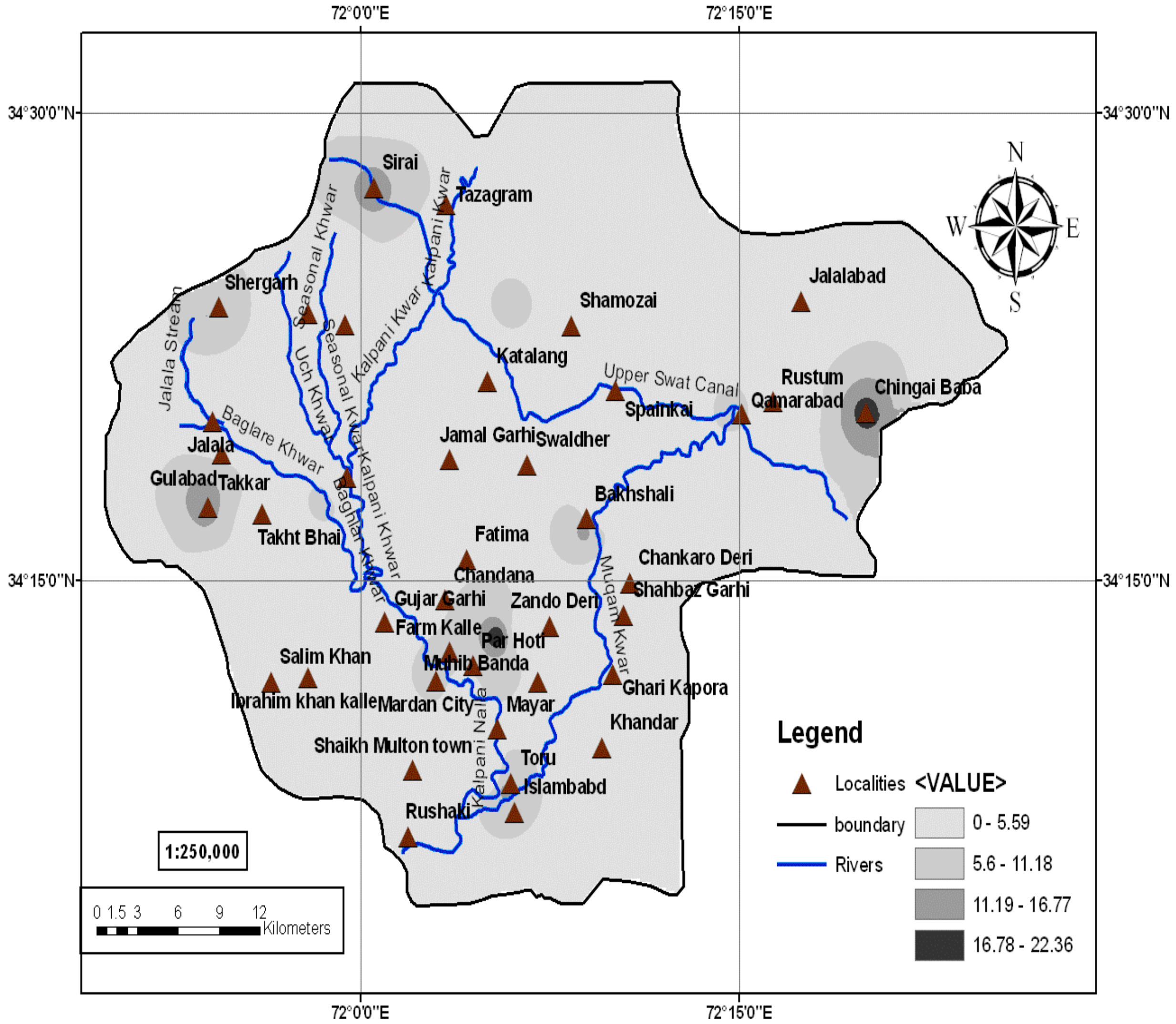

Fig.4.15f. Map showing the Nickel (Ni) concentration (µg/l) in water of Mardan District

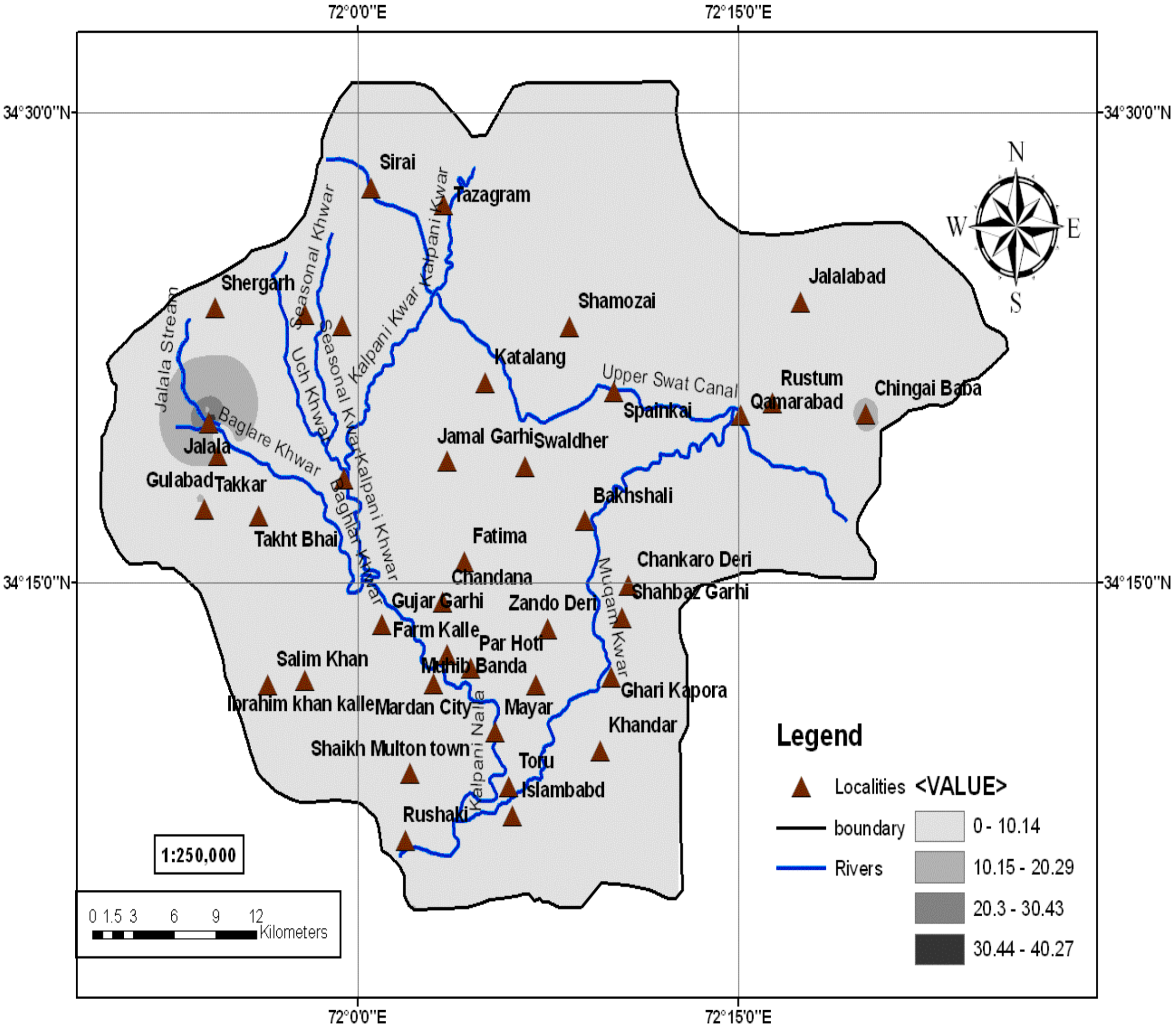

Fig.4.15g. Map showing the Chromium (Cr) concentration (µg/l) in water of Mardan District

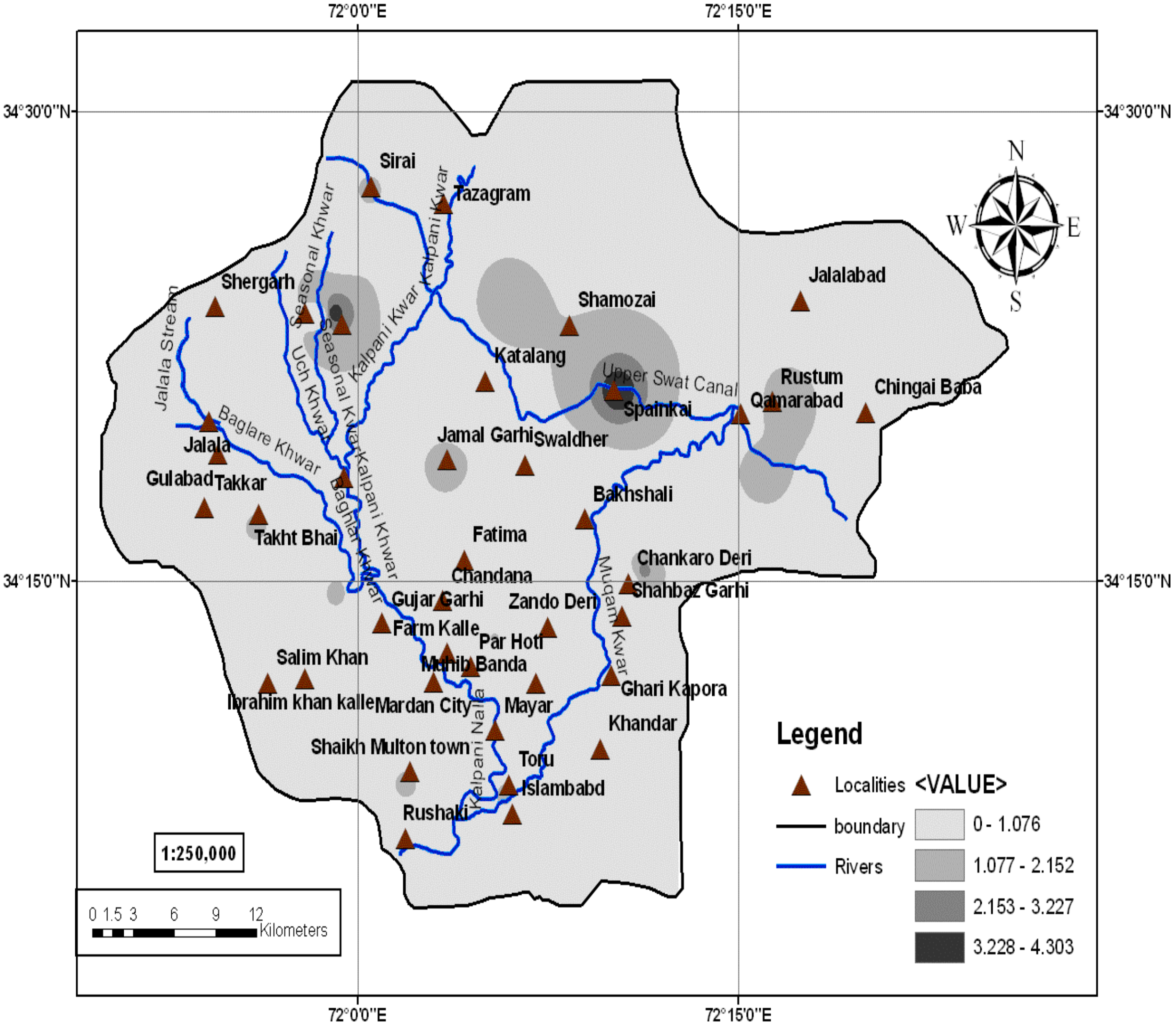

Fig.4.15h. Map showing the Cadmium (Cd) concentration (µg/l) in water of Mardan District

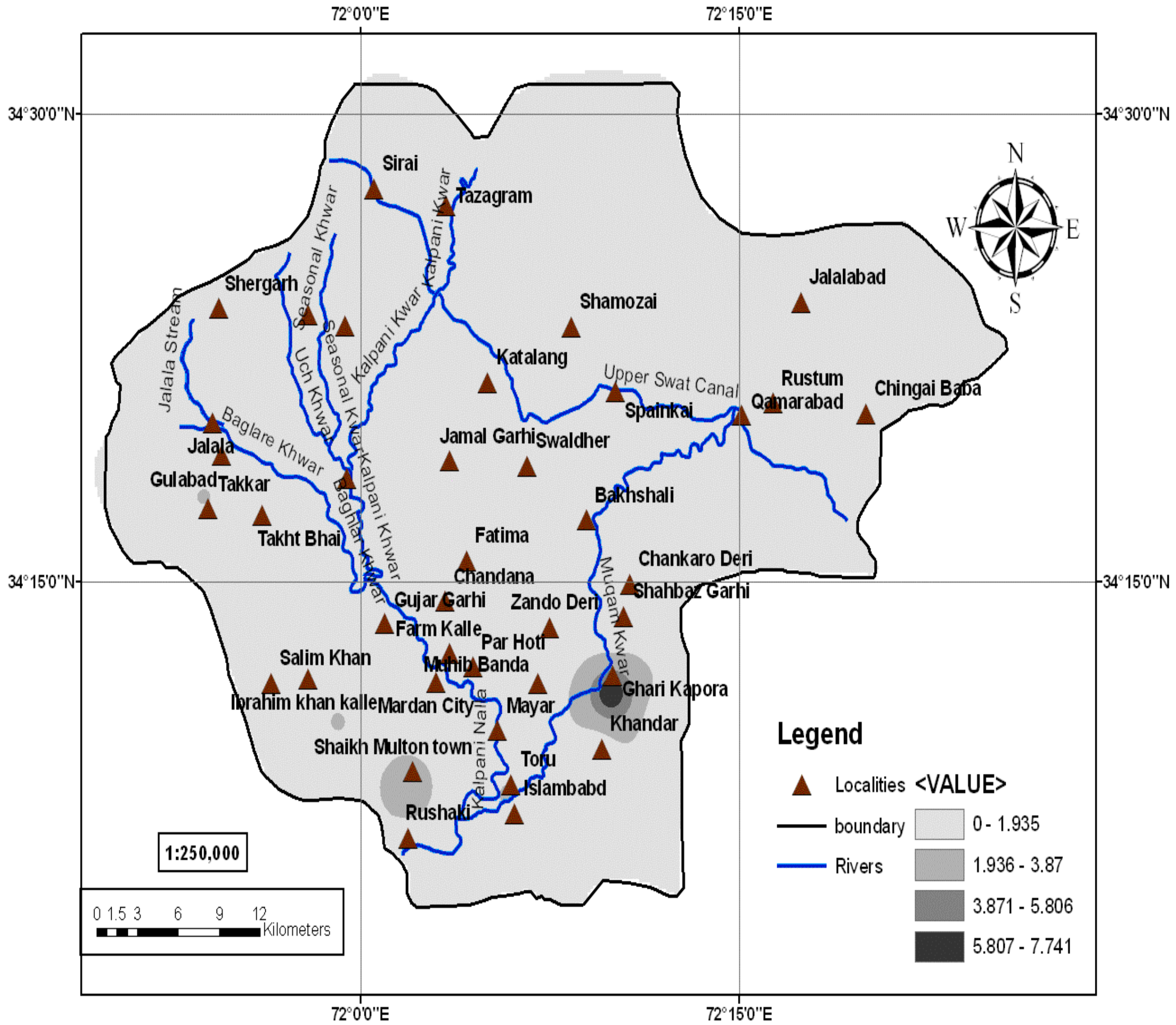

Fig.4.15i. Map showing the Arsenic (As) concentration (µg/l) in water of Mardan District

CHAPTER 5

SOIL CHEMISTRY

Soil is a mixture of weathered rocks minerals; and, small living organisms including plants, animals and bacteria. Soil also contains water and air. The general proportion is of 95 % inorganic and 5% organic constituents. Soil provides media to trap solar energy in the form of plant biomass and then transfer it to higher level organisms later on. All the biogeochemical cycles are operated on the soil, recycling essential elements in the environment. Soil differs from the regolith (rock fragments). In terms it supports and bears living flora and fauna (Mckenzie and Susan, 2004). Vertical distribution of matter in the soil is called horizons while the vertical arrangement of horizons form soil profiles (Wild, 1996).

Soil Formation

The complex phenomena of soil formation can be simplified in two steps: weathering and addition of organics (Wild, 1996). Weathering is a biochemical process by which the parent rock is broken down into fragments by the action of water, gases and living mater (Mckenzie and Susan, 2004). After exposure of surface through various chemical interactions e.g., hydrolysis of orthoclase, oxidation of ferrous iron, hydration and carbonation minerals are released (Wild, 1996). During all the mentioned process parent minerals are destructed and the elements pass from into suspension and solutions. Besides chemical dissolution, living organisms contributes to the weathering by the release of two compounds: carbonic acid and organic chelates and their decomposition add organics (Kabat-Pendias and Pendias, 1992).

Major Constituents of the Soil

Soil Water

Amount of water in the form of soil moist is estimated to range from 0.001 to 0.0005% of the total water content of the earth (Bohn et al., 2001). Greater part of soil water is runoff or percolating water, so this liquid part is not pure as it contains various solutes and dissolved gases. The concentration of these solutes and gases differs according to their solubility, conditions of formation of soil, water content, organics and gases etc (Wild, 1996).

Soil Air

Air in the soil is not of uniform nature but a mixture of nitrogen, oxygen and carbon dioxide. Concentration of nitrogen remains constant (79%) while oxygen and nitrogen dioxide fluctuates (Hausenbuiller, 1972). In soil rich with flora and fauna, carbon dioxide is much higher than oxygen due to respiration of plants and soil organisms and the reduce diffusion of gases. Due to limited oxygen supply respiration and organic decay is affected and availability of released nutrients is lowered down. Movement of air constituents in soil takes place through diffusion and mass flow (Hausenbuiller, 1972).

Soil Organics

Plants, bacteria, fungi and other living organisms forms the organic and living part of the soil. Solar energy trapped in the biomass is converted to organics on decomposition (Mckenzie and Susan, 2004). Addition of sewage sludge and organic manure are also source of soil organics. The upper 10cm soil layer usually contains 1-3 % carbon in the form of organics. Soil organics can be divided in 1) light fraction (light color, visible, low density) and 2) Humus (dark color, high density), (Hausenbuiller, 1972).

Soil Inorganics

Nature of the mineral in the soil depends on the parent rock, degree of weathering and physical nature of the soil (Wild, 1996). In nature only 8 minerals forms the major portion of earth crust, major portion of which are silicate minerals (Hausenbuiller, 1972). On the basis of formation, minerals are of two types: Primary minerals are derived from rocks without any transformation while the secondary minerals are altered by air, water and other chemical reactions (Mckenzie and Susan, 2004).

Physico- Chemical Properties of the Soils of study area

Soil pH

Soil pH is of primary importance as all the chemical and biological activities are highly dependant on pH. Lowering of pH, enhances the metals solubility and hence their extraction from soil (Castilha and Chardan, 1995). Decrease in pH poses negative impacts on soil microbial activities. On one side concentration of metals get increased upto dangerous limit in plants, while on other the availability of essential nutrients are hindered (Wang et al., 2006).

Average soil pH of the samples was 7.6 with a range of 5.9 to 8.1. Highest value was observed in soils of the Chin Banda and lowest in the soil from Farum Korona. However, generally the pH of soils of Mardan District was normal (Table 5.1).

Electric Conductivity (EC) and Total Dissolved Solids (TDS)

Total dissolved solids and EC both are significant from agricultural point of view. High electric conductivity of the soil indicates more dissolve substances. For example increase in soil salinity speed up soil erosion and retard the plant growth (Szaboles, 1989). Sources of soluble salts in the soil include weathering of primary minerals and native rocks, atmospheric deposition, saline irrigational water, addition of inorganic and organic fertilizers (Sparks, 2003).

Electric conductivity in studied soils varied from 209 to 510µS/cm with an average conductivity of 287µS/cm. Soil samples from Farum Korona (445µS/cm) and Shahabaz Garhi (510µS/cm) were having relatively higher values (Table 5.1). Total dissolved solids in the soil samples varied from 110 to 265mg/kg with an average of 152mg/Kg. The values of TDS in soil samples were found normal (Table 5.1).

Soil Texture

Texture is the relative proportion of clay, silt and sand in the soil. On the bases of texture, soil is called as clay, silty clay, sandy clay etc. Texture gives clue about soil capacity to hold water and minerals. Soil texture is relatively a permanent property until some outside phenomena e.g., erosion, deposition and flood etc. changes it (Hausenbuiller, 1972).

Average percentage of three components, sand, clay and silt were found as 28.24%, 10.24% and 61.55% respectively. On the basis of dominant silt component, the soils of the study area were mainly “Silty Loam”. One sample from Rustam was falling in the category of “Sandy Loam” having 63.5 % of sand (Table 5.2).

Soil Color

Color is an important property to the pedogenic environment and history of soil formation (Murry and Tedrow, 1992). Soil color provides clue for the extent of weathering, amount of organics and state of aeration. Change in color of soil indicates the formation of secondary minerals. Similarly red, yellow and brown colors are due to Fe compounds or highly weathered minerals in the soil. Color imparted due to organics depends upon quantity, nature and grain size of organic material (Hausenbuiller, 1972).

Color of the studied soils showed little variations. Dominant colors were pale yellow, olive brown, light brown and brownish gray in dry condition. In the moist form dark brown and dark grayish colors were dominant in most of the samples (Table 5.2).

Major Element Oxides

Calcium (CaO)

Calcium is a most important soil nutrient. Amount of Ca present in soil varies greatly from 0.05 to 25% of the whole soil weight. Feldspar minerals are the primary source of Ca in soil, while the Ca from the lime and gypsum is termed secondary (Hausenbuiller, 1972). Limestone derived soils are not very productive because of excessive leaching of Ca (Bohn et al., 2001)

Significance to plants

Crops grow rapidly when Ca is adequate in the soil. Calcium maintains the soil pH neutral for plants and microorganisms survival (Bohn et al., 2001). Ca deficiency results in chlorosis, root damage and malformation of younger leaves (Jain, 2006). Excess in soil calcium may alter the pH and ultimately accumulation of elements in plants is disturbed (Hausenbuiller, 1972). Sometimes excess of Ca results in the formation of different compounds with other elements e.g., with chlorides which disturbs the Osmotic pressure in plant roots (Hausenbuiller, 1972).

Calcium oxides concentration in the soils of studied area ranged from1.26 to 19.56 % with an average content of 8.66%. According to Bohn et al. (2001) the safe limit for CaO in normal agricultural soils is 2.5 %. Soil sample (S-5) with normal CaO (1.26) content was found in Gujrat, while the rest of samples were having higher concentrations (Table 5.3). Soil samples with higher CaO were from Farum Korona (9.14%), Shahbaz Garhi (8.84%), Yaqubabad (10.35%), Gujar Garhi (7.65%), Pump Korona (11.12%), Takht Bhai (16.19%), Takkar (11.61%), Lund Khwur (11.9%), Chil (12.57%), Chin Banda (7.90%), Jamal Garhi (9.96%), Katlung (7.21%), Ghundo (7.87%), Mian Kali(19.56%), Babuzai (13.10%), Spainkai (15.90%), Jalalabad (18.10%) and Toru (11.70%) (Table 5.3; Fig.5.1a).

Magnesium (MgO)

Magnesium is present in all soil types in sufficient amount except sandy soils which are Mg deficient. Soils derived from the serpentine (Mg silicate) rock have higher Mg content. Many primary and secondary minerals of aluminum silicates also contain Mg as major component (Bohn et al., 2001).

Significance to plants

Magnesium is an important plant nutrient and its deficiency affects plants growth badly. Magnesium is a part of chlorophyll and helps in the translocation of starch within plant tissues. It is also significant in the formation of plant oils and fats and for the growth of new cells (Bohn et al., 2001). Magnesium deficiency appears in the form of leaf chlorosis and necrotic patches on leaves (Jain, 2006). Soils with high Mg content experience some problems like high pH, soil crusting and lower hydraulic permeability. In the presence of elevated Mg, availability of Ca is also hindered (Bohn et al., 2001).

The concentration of MgO in studied soils ranged from 0.13 to 2.40% with an average value of 1.59% (Table 5.3). The permissible limit for MgO in normal soils is 1.5% (Bohn et al., 2001). Samples with higher concentration of MgO were from Shahbaz Garhi (1.98%), Yaquabad (2.14%), Salim Khan Kali (2.37%), Gujar Garhi (2.03%), Pump Korona (2.00%), Shergarh (2.06%), Lund Khuwr (2.06%), Chil (2.15%), Garhi Kapora (2.00%) and Chandar (2.28%) (Table 5.3; Fig.5.1b).

Sodium (Na_2O)

Sodium along with K is found in the parent material of many minerals. Soils derived from igneous rock have total 1 to 2% Na, while in sedimentary origin soil, its value ranges from 0.02 to 0.1%. In light sandy soil Na is found below 0.02%. Soil with sodic nature generally has greater than 15% of Na exchange capacity (Draycott et al., 2003).

Significance to plants

Sodium is not required by plants and inhibits the absorption of K. It is estimated that 5-15 % of exchangeable Na has inhibitory effect on water movement (Bohn et al., 2001). Elevated concentrations of Na results in soil swell (Kabata-Pendias and Pendias, 1992). In presence of high Na, plants expand more energy on water take up due to higher osmotic pressure, leaving less potential for plant growth (Bohn et al., 2001). High Na reduces photosynthesis and disrupts the balance of Reactive oxygen species (ROS) (Marschner, 1995).

Average concentration of Na_2O in studied soil samples was 13.26% with a range from 7.92-15.50%. The recommended value of Na_2O for agricultural soil is 1.5% (Bohn et al., 2001). In this respect, all the samples of the study area were having elevated level of Na_2O (Table 5.3; Fig.5.1c).

Potassium (K_2O)

Potassium is the 3rd most used element in fertilizers after nitrogen and phosphorus (Bohn et al., 2001). In soil the minerals having K in abundance are mica, feldspar and illite (Hausenbuiller, 1972). A soil solution mainly has low available K because it is strongly retained by the clay minerals in soil, to overcome its deficiency fertilizer are added to the soil (Bohn et al., 2001).

Significance to plants

Inspite of K abundance in soil, very small amount is available (10%) of the whole K to plants. On the basis of mineral structure, K is categorized in exchangeable and non-exchangeable forms. In plants K remains in ionic form having different functions e.g., synthesis of protein, chlorophyll and carbohydrate, transformation of nitrogen from nitrates, helps in the root absorption, translocation and storage of carbohydrates (Hausenbuiller, 1972). Symptoms of K deficiency are chlorosis and necrosis of leaves and stunted plant growth (Jain, 2006).

The content of K_2O in the studied soil samples varied from 1.18 to 4.13% with average value of 3.14%. The safe limit K_2O content in normal agricultural soils is as 1.5% (Bohn et al., 2001). It was notified that the majority of samples were having K_2O above permissible limits; however the concentration of K_2O was found lower than Na_2O content (Table 5.3; Fig.5.1d).

Iron (Fe_2O_3)

Through out the world estimated concentration of the Fe is about 45%; main sources being mafic rocks. Iron content provides base in the classification of soil types. Although Fe forms many different compounds in soil, however, the available content is very small. Normal soils are supposed to contain 0.5-5% Fe (Kabata-Pendias and Pendias, 1992).

Significance to plants

Iron is a plant micronutrients and its deficiency leads to severe impacts on growth and yield (Marschner, 1995). Iron has important part in Nitrate and Sulphate reduction, chlorophyll formation, metabolism and catalytic functions (Kabata-Pendias and Pendias, 1992). During Fe deficiency, the uptake of Mn and Zn is accelerated (Alam et al., 2001).

Average concentration of Fe_2O_3 in the agricultural fields of study area was 3.57% with a range of 1.66 to 4.97%. Permissible limit of Fe_2O_3 for normal agricultural soils by Bohn et al. (2001) is 5.77%. Most of the studied soil samples were having Fe_2O_3 concentration within normal range (Table 5.3; Fig.5.1e).

Manganese (MnO)

Mn is a common most trace element on earth, usually association with mafic rocks. In minerals, Mn is present in various ionic forms but Mn^{+2} is common in silicates minerals. Its hydroxides and oxides are capable of making association with heavy metals (Kabata-Pendias and Pendias, 1992).

Significance to plants

Manganese is essential for plants especially for electron transport in photosynthesis (Bartlett, 1986) and as a cofactor of various enzymes (Marschner, 1995). Mn also helps plants in the assimilation of nitrogen. Chloroplast shows sensitivity towards Mn deficiency, growth and osmotic pressure are also affected (Kabat-Pendias and Pendias, 1992). On other hand excess Mn is toxic and its symptoms are brown patches on leaves and uneven chlorophyll distribution in leaves. During Mn stress free radicals oxidize membrane lipids causing cells death (Tanaka, 1994). High Mn level also impairs enzymes and growth hormones (Foy, 1983).

Manganese Oxide concentration in studied soils ranged from 0.07 to 1.38 % with an average concentration of 0.21%. The safe limit for MnO in agricultural soils is <0.1% (Bohn et al., 2001). Soil samples collected from Chankari Dehri (0.25 %) and Sowkai (1.38%) contained high concentration of MnO while the rest of soil samples were having normal MnO content (Table 5.3; Fig.5.1f).

Trace and Heavy Elements

Copper (Cu)

Major source of Cu on earth is mafic and ultramafic rocks. Cu is found in the form of simple and complex sulfides. Through weathering Cu is released easily and readily forms compounds with different anions. Despite of limited mobility, Cu is present in all soil solutions in both free and ionic state (Kabata-Pendias and Pendias, 2001). Cu concentration in the soils varies from 2-50mg/kg (Alloway, 1995).

Significance to plants

Cu forms integral part of several plant enzymes and its average concentration in plants tissue range from 1-5mg/kg (Alloway, 1995). Major biochemical functions in which Cu is involved are photosynthesis, respiration, nitrogen reduction and fixation, protein metabolism, immune against diseases and fertility (Kabata-Pendias and Pendias, 1992). Ionic forms of Cu are more toxic than organic complexes (Florence, et al,. 1984). Some toxic effects of high Cu content to plants are, to change the permeability of cell membrane, peroxidies the lipid content of chloroplasts, damage DNA and reduce photosynthesis (Woolhouse and Walker, 1981; Sandmann and Boger, 1980). Iron deficiency and root elongation are also reported in wheat in presence of excess Cu (Michaud et al., 2008).

Copper concentration in studied soils ranged from 12 to 45mg/kg with average concentration of 28mg/kg. Safe limit of Cu content in normal agricultural soil is 20mg/kg (Bohn et al., 2001). Soil samples with higher concentration of Cu were from Farum Korona (31mg/kg and 36mg/kg), Yaqubabad (39mg/kg), Ibrahim Khan Kali (38mg/kg), Pump Korona (35mg/kg), Takht Bhai (35mg/kg), Takkar (27mg/kg), Jalala (38mg/kg), Shergarh(40mg/kg), Chill (27mg/kg), Chin Banda (28mg/kg), Chandar (35mg/kg), Katlung (35mg/kg) and Sowkai (45mg/kg) (Table 5.4; Fig.5.2a). Distribution map for the Cu concentration in the soils of Mardan District was prepared by GIS as showed in Figure 5.3a. Uneven distribution of Cu was notified from the figure with low Cu content at the eastern boundary. However rest of the Mardan District was having high Cu content with clusters found at the western boundary near Shergarh and Jalala; at the southern boundary near Salim Khan kalli and Rushaki and at the central part near Katlang (Fig.5.3a)

Lead (Pb)

On earth Pb occurs in two forms, primary and secondary: primary is of geogenic origin while secondary Pb comes from radioactive decay of U and Th. The common natural state of Pb is galena. Pb gets accumulated on the surface soil due to its low solubility and high adsorption to minerals or by forming organic complexes (Adriano, 1986). The estimated half life of Pb in soil is about 740-5,900 years (Alloway and Ayres, 1997).

Significance to plants

All most all plants have Pb but many studies suggest its no significant biological role. Major phytotoxic impacts on plants are reduction in enzymatic, photosynthesis activities and plant growth (Stiborova et al., 1987). Pb contamination also affects the growth and population of Arbuscular Mycorrhizal Fungi (AMF), a symbiotic soil fungus (Khan et al., 2000).

The average concentration of Pb in studied soils was 27mg/kg with a range of 4 to 56 mg/kg. According to Bohn et al. (2001), safe limit of Pb for normal agricultural soils is 10mg/kg. All most all the soil samples were having Pb content above permissible limit except one sample (W-21) from Jamal Garhi (Fig.5.2b). Lead distribution map was prepared by GIS and showed in Figure 5.3b. It is showed that high Pb content was homogenously distributed through the whole study area; however, cluster with relatively elevated Pb content was showed near Shahbaz Garhi at the southern part of Mardan District (Fig.5.3b)

Zinc (Zn)

Zn is found in all magmatic rocks uniformly, with slight increase in mafic rocks. Common form is zinc sulfide. During weathering Zn is released as Zn^{+2} that are readily adsorbed by soil minerals and organic component. Anthropogenic sources of Zn are metal industry and agricultural practices (Kabata-Pendias and Pendias, 1992). Average Zn content in the soil is 50mg/kg (MortvEd. 2000).

Significance to plants

Plants take Zn in the forms of complex ions, hydrated ions and Zn-organic chelates (Grahm et al,. 1987). Zinc is considered important in protein and carbohydrate metabolism, and also involved in the synthesis of growth hormone Auxin (Jain, 2006). Zinc also develops resistance in plants against extreme conditions, and bacterial and fungal attacks. Zn is not considered as highly phytotoxic, however; new leaves chlorosis and retarded growth are consequences of Zn phytotoxicity (Kiekens, 1990; Fontes and Cox, 1998). It also hindered the uptake of Fe and redish color appears due to deficiency (Lee et al., 1996).

Zinc concentration in the studied soil samples varied from 4 to 275mg/kg with an average value of 96mg/kg. According to Bohn et al. (2001), safe limit for Zn in normal soils is 50mg/kg. Samples with high Zn value were found in Farum Korona (70mg/kg and 80mg/kg respectively), Shahbaz Garhi (127mg/kg), Chankari Stop (107), Ibrahim Khan Kali (101mg/kg), Gujar Garhi (120mg/kg), Gujar Garhi (110mg/kg), Jalala (208mg/kg), Shergarh (120mg/kg), Chin Banda (275mg/kg), Jamal Garhi (141mg/kg), Katlung (122mg/kg), Ghundo (76mg/kg), Mian Kali (81mg/kg), Babuzai (74mg/kg), (99mg/kg) Spainkai, Toru (105mg/kg), Garhi Kapora (100mg/kg) , Chandar (91mg/kg) and Sowkai (133mg/kg) (Table 5.4; Fig.5.2c). Distribution of Zn in the studied soils was demonstrated in Figure 5.3c. High Zn content with homogenous distribution was notified from the map with a cluster of relatively elevated Zn towards northern part (Fig.5.3c)

Nickel (Ni)

In nature mafic rocks are the main source of Ni having its proportion from 1400-2000mg/kg. Primary minerals of terrestrial rocks having Ni are sulfides, arsenites, antimonides and ferromagnesian minerals; Ni also occurs in carbonate, silicates and phosphates. After weathering, Ni becomes mobilized but its ions are stable in soil. Due to strong affinity of organics to absorb Ni, it is also found in coal and oil (Kabat-Pendias and Pendias, 1992).

Significance to plants

Although many studies show that Ni is not essential to plants but supposed to be a part of enzymes in higher plants. Symptoms of toxicity on plants include necrosis, chlorosis, wilting and restarted growth (Madhava Rao and Sresty 2000; Pandey and Sharma, 2002). Under high Ni stress ROS (reactive oxygen species) in plants are disturbed (Gratao et al., 2005) which cause injuries to macromolecules (lipids, proteins and nucleic acids), (Kekrer, 2000).

Soils from the study area contained Ni in the range of 20 to 81mg/kg with average value of 49mg/kg. Safe limit for Ni content in normal agricultural soils by Bohn et al. (2001) is 40mg/kg. Samples having high Ni concentration were from Farum Korona (65mg/kg and 68mg/kg), Gulshanabad (53mg/Kg), Yaquabad (81mg/Kg), Ibrahim Khan Kali (62mg/kg), Gujar Garhi (62mg/kg and 60mg/kg), Jhandai (60mg/kg), Pump Korona (64mg/kg), Takht Bhai (58mg/kg), Jalala (69mg/kg), Shergarh (66mg/kg), Katlung (58mg/kg), Chandar (51mg/kg) and Sokai (54mg/kg), (Table 5.4; Fig.5.2d). GIS based Ni distribution map was prepared in Figure 5.3d. It was noticed in the map that the eastern boundary contained Ni within safe limit. However, high content was found in the central part with clusters of elevated levels along western and southern boundaries (Fig.5.3d).

Chromium (Cr)

Soils derived from mafic and ultramafic rocks have Cr from 0.2 to 0.4 %, while higher concentration is found in argillaceous sediments. Chromium has variable range of oxidation states, forming complexes through its anions and cations. The two common states of Cr are Cr^{+3} and Cr^{+6} in soil (Kabata-Pendias and Pendias, 1992). Normal range of Cr in soil is 9.9-121mg/kg (Archer and Hodgson, 1987).

Significance to plants

Cr has no nutritional value to plants and its elevated level hinders plant growth and cause leaf chlorosis (Sharma et al., 1995). Plants grown on Cr spiked soils also show greater metal accumulation (Ali et al., 2004).

Chromium content in the studied soils varied from 25 to 84mg/kg with an average concentration of 60mg/kg (Table 5.4). According to Bohn et al. (2001), the Cr concentration in the normal agricultural soils is generally 20mg/kg. Majority of the soil samples were having high Cr contents as compared to normal agricultural soil (Fig.5.2e). The distribution map of Cr in the soils was prepared with the help of GIS. It was noted that the whole District was having high Cr values. However, cluster with relatively higher values were recorded in the western, southern and central parts (Fig.5.3e) of Mardan District.

Cadmium (Cd)

Cadmium is considered important because of its ecotoxicity to environment. Magmatic rocks have very low Cd while it is concentrated in argillaceous and shale deposits (0.3ppm). Average content of Cd in soil is 0.06-1.1mg/kg. Cd is readily soluble and shows strong affinity towards sulfur, therefore, is adsorbed by sulfide in the soil. Anthropogenic sources of Cd in soil are phosphorus fertilizers, sewage sludge and aerial deposition (Kabata-Pendias and Pendias, 1992).

Significance to plants

In plants Cd is easily translocated from root tissues to above ground parts. Cd has ability to affect physiological activities and productivity (Florijin and Van Beusichem, 1993). Reduction in photosynthesis, plant growth, chlorophyll content and oxidative stress development are the major phytotoxic effects of Cd (Zhou and Huang, 2001; Yi and Ching, 2003; Zhou et al., 2003).

Agricultural soil of the study area showed average Cd concentration of 2.33mg/kg of Cd with a range of 0.15 to 3.06mg/kg. All the soil samples from the study area were having concentration above the normal Cd value of 0.06mg/kg of Bohn et al. (2001) (Table 5.4; Fig.5.2f). The GIS based distribution map of Cd in the soils of Mardan District was prepared (Fig.5.3f). The distribution pattern of Cd indicated that the whole Mardan District was having high Cd concentration, with clusters of elevated concentration in the northern, western and central parts (Fig.5.3f).

Arsenic (As)

All types of rocks constitutes As but relatively concentrated in argillaceous sediments. About 200 minerals contains As, majority of which are Arsenates. It forms compounds with Fe, Pb and Cu e.g., Arsenopyrite (FeAsS). Although elemental As is less mobile due to its strong association with clay and organics, but its ions have more mobility (Kabata-Pendias and Pendias, 1992). Complexation reaction on mineral oxides (Inskeep et al., 2002) and small textural fraction of soil control As activity (Lombi et al., 2000).

Significance to plants

Arsenic has no important biological role hence, is considered non essential elements to plants (Marin et al., 1993). Contaminated soils around the world have average As concentration of 26.5mg/kg (Hingston et al, 2001).Two As compounds, sodium arsenate and arsenic trioxide (used in herbicides) cause metabolic inhibition (Kabata-Pendias and Pendias, 1992). Root elongation is markedly reduced in As contaminated soils (Cao et al, 2007).

Arsenic was present in the soil samples of the study area in the range of 1.55 to 26.13mg/kg with an average amount of 5.14mg/kg. All the samples contained As within permissible limit of 8.4-9mg/kg for silty and loam soils (Kabata-Pendias and Pendias, 2001), except one sample (S-11) collected from Gujar Garhi (Table 5.4; Fig.5.2g). Arsenic distribution map of the studied soil was prepared by GIS as showed in the Figure 5.3g. The As distribution was generally homogenous in the soils throughout the District. However, small cluster of relatively high concentration was found in the south-western part (Fig.5.3g)

Table 5.1. Physical parameters of Soils of Mardan District

Sample	Locations	pH	Conductivity µS/cm	TDS mg/l
S-1	Farum Korona	5.9	445	231
S-2	Farum Korona	7.3	305	158
S-3	Shahbaz Garhi	7.4	510	265
S-4	Chankari Dheri	6.2	266	138
S-5	Gujrat	7.2	277	146
S-6	Gulshanabad	7.7	345	178
S-7	Malakabad	7.8	279	154
S-8	Yaqubabad	8.0	371	196
S-9	Salim Khan kalli	7.6	360	190
S-10	Gujar Garhi	7.5	276	146
S-11	Gujar Garhi	7.7	246	132
S-12	Jhandai	8.0	300	160
S-13	Pumo Korona	7.8	277	148
S-14	Takht Bhai	7.8	255	137
S-15	Takkar	7.7	256	136
S-16	Jalala	8.0	249	132
S-17	Shergarh	7.9	266	141
S-18	Lund Khwur	7.7	259	140
S-19	Chil	7.9	237	125
S-20	Chin Banda	8.1	295	157
S-21	Jamal Garhi	7.4	246	135
S-22	Katlung	7.5	240	126
S-23	Ghundo	7.6	225	119
S-24	Mian Kali	7.5	247	131
S-25	Babuzai	7.5	271	143
S-26	Sphinkai	7.6	235	127
S-27	Rustum	7.7	257	135
S-28	Jalalabad	7.6	242	129
S-29	Chigai Baba	7.7	209	110
S-30	Toru	8.0	247	134
S-31	Garhi Kapora	7.7	287	152
S-32	Chandar	7.4	327	176
S-33	Sowkai	7.5	358	184
Minimum		***5.9***	***209***	***110***
Maximum		***8.1***	***510***	***265***
Average		***7.6***	***287***	***152***

Table 5.2. Texture and Color of Soils of Mardan District

Sample	Locations	Sand %	Clay %	Silt %	Texture	Color in Dry	Color in moist
S-1	Farum Korona	21.50	21.70	56.70	Silty Loam	L.brownish gray	D.grayish brown
S-2	Farum Korona	30.30	5.00	64.60	Silty Loam	L.yellow brown	Grayish brown
S-3	Shahbaz Garhi	27.50	5.70	66.80	Silty Loam	L.brownish gray	D.grayish brown
S-4	Chankari Dheri	30.60	5.00	64.30	Silty Loam	Brown	Dark brown
S-5	Gujrat	29.50	17.76	53.00	Silty Loam	Brown	V.gray dark brown
S-6	Gulshanabad	33.50	15.70	50.70	Silty Loam	Brown	V.gray dark brown
S-7	Malakabad	29.50	5.70	64.70	Silty Loam	L.brownish gray	D.grayish brown
S-8	Yaqubabad	21.52	17.70	60.70	Silty Loam	L.brownish gray	D.grayish brown
S-9	Charsadda road	18.24	5.00	76.80	Silty Loam	L.yellow brown	dark brown
S-10	Gujar Garhi	21.50	17.76	60.70	Silty Loam	L.yellow brown	V.dark brown
S-11	Gujar Garhi	30.24	5.00	64.70	Silty Loam	L.olive brown	Dark brown
S-12	Jhandai	13.50	5.70	81.00	Silt	L.yellow brown	L.olive brown
S-13	Pumo Korona	22.20	23.00	54.70	Silty Loam	L.yellow brown	D.grayish brown
S-14	Takht Bhai	33.50	5.70	60.70	Silty Loam	L.yellow brown	D.grayish brown
S-15	Takkar	17.50	5.70	76.70	Silty Loam	Pale yellow	L.olive brown
S-16	Jalala	17.50	15.70	66.70	Silty Loam	L.olive brown	Olive brown
S-17	Shergarh	34.24	9.00	56.70	Silty Loam	L.olive brown	D.grayish brown
S-18	Lund Khwur	31.50	5.70	62.70	Silty Loam	Pale yellow	Olive brown
S-19	Chil	30.20	15.00	54.70	Silty Loam	L.yellow brown	D.grayish brown
S-20	Chin Banda	41.50	5.70	52.80	Silty Loam	L.yellow brown	Olive brown
S-21	Jamal Garhi	30.00	13.00	57.00	Silty Loam	L.yellow brown	D.grayish brown
S-22	Katlung	19.50	9.80	71.00	Silty Loam	L.yellow brown	D.grayish brown
S-23	Ghundo	17.50	15.80	66.70	Silty Loam	light gray	Olive brown
S-24	Mian Kali	14.24	9.00	76.70	Silty Loam	Pale yellow	L.olive brown
S-25	Babuzai	17.50	15.70	66.70	Silty Loam	L.yellow brown	D.yellow brown
S-26	Sphinkai	16.20	11.00	72.70	Silty Loam	L.yellow brown	Olive brown
S-27	Rustum	63.50	5.70	31.00	Sandy Loam	L.olive brown	Olive brown
S-28	Jalalabad	44.00	5.00	50.70	Silty Loam	L.yellow brown	Olive brown
S-29	Chigai Baba	54.00	9.00	37.00	Silty Loam	L.yellow brown	Olive brown
S-30	Toru	50.30	5.00	47.00	Silty Loam	L.yellow brown	D.grayish brown
S-31	Garhi Kapora	17.50	5.70	76.70	Silty Loam	L.yellow brown	D.grayish brown
S-32	Chandar	20.00	15.00	65.00	Silty Loam	L.brownish gray	Dark gray
S-33	Sowkai	32.24	5.00	62.70	Silty Loam	L.yellow brown	Olive brown
Minimum		***13.50***	***5.00***	***31.00***			
Maximum		***63.50***	***23.00***	***81.00***			
Average		***28.24***	***10.24***	***61.55***			

Sample	Locations	CaO%	MgO%	Na_2O%	K_2O%	Fe_2O_3%	MnO%

S-1	Farum Korona	9.14	0.13	13.06	3.88	4.11	0.10
S-2	Farum Korona	6.99	2.40	12.80	3.53	3.95	0.12
S-3	Shahbaz Garhi	8.84	1.98	13.38	3.91	3.50	0.10
S-4	Chankari Dheri	5.60	1.52	13.95	2.90	4.80	0.25
S-5	Gujrat	1.26	1.14	15.50	4.13	3.12	0.09
S-6	Gulshanabad	3.60	1.51	13.20	3.90	3.19	0.09
S-7	Malakabad	4.38	1.33	13.54	3.88	2.79	0.08
S-8	Yaqubabad	10.35	2.14	12.87	4.08	3.76	0.12
S-9	Salim Khan kalli	3.83	2.37	15.24	4.07	3.84	0.12
S-10	Gujar Garhi	7.65	2.03	15.20	3.42	4.00	0.13
S-11	Gujar Garhi	9.50	1.66	13.04	2.66	3.34	0.11
S-12	Jhandai	5.90	1.87	12.81	2.60	3.55	0.11
S-13	Pumo Korona	11.12	2.00	7.92	2.67	3.86	0.10
S-14	Takht Bhai	16.19	1.17	12.13	2.10	3.09	0.07
S-15	Takkar	11.61	1.87	14.14	3.40	4.80	0.12
S-16	Jalala	3.00	1.72	12.28	2.60	2.47	0.11
S-17	Shergarh	4.23	2.06	13.00	3.47	4.20	0.12
S-18	Lund Khwur	11.90	2.06	13.40	3.62	4.97	0.10
S-19	Chil	12.57	2.15	12.80	2.40	2.94	0.11
S-20	Chin Banda	7.92	1.51	13.00	2.57	3.01	0.11
S-21	Jamal Garhi	9.96	1.57	13.05	3.32	3.50	0.08
S-22	Katlung	7.21	1.40	12.76	3.34	4.42	0.11
S-23	Ghundo	7.87	1.65	12.87	3.13	3.58	0.10
S-24	Mian Kali	19.56	1.55	12.60	3.35	3.60	0.08
S-25	Babuzai	13.10	1.64	13.12	3.60	3.89	0.10
S-26	Sphinkai	15.90	1.69	12.96	2.50	4.08	0.11
S-27	Rustum	5.06	0.28	14.22	1.86	1.66	0.57
S-28	Jalalabad	18.10	0.72	14.76	2.96	2.63	0.65
S-29	Chigai Baba	2.73	0.67	13.99	3.55	2.05	0.09
S-30	Toru	11.70	1.76	14.02	2.87	3.40	0.08
S-31	Garhi Kapora	6.65	2.00	13.04	3.66	3.60	0.11
S-32	Chandar	3.37	2.28	13.01	3.37	4.06	0.12
S-33	Sowkai	5.49	1.35	14.02	1.18	4.60	1.38
Minimum		***1.26***	***0.13***	***7.92***	***1.18***	***1.66***	***0.07***
Maximium		***19.56***	***2.40***	***15.50***	***4.13***	***4.97***	***1.38***
Average		***8.66***	***1.59***	***13.26***	***3.14***	***3.57***	***0.21***
Bohn’s Stnd		***2.5***	***1.5***	***1.5***	***1.5***	***5.77***	***<0.1***

Table 5.3. Major elements oxides in Soils of Mardan District

Table 5.4. Total trace and heavy elements concentration in Soils of Mardan District

Sample	Locations	Cu mg/kg	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cr mg/kg	Cd mg/kg	As mg/kg
S-1	Farum Korona	31	25	70	65	64	0.15	4.63
S-2	Farum Korona	36	35	80	68	70	2.43	5.48
S-3	Shahbaz Garhi	28	56	127	42	52	2.19	3.02
S-4	Chankari Dheri	17	34	107	28	25	2.52	4.25
S-5	Gujrat	18	36	52	41	48	2.43	5.46
S-6	Gulshanabad	23	30	69	53	58	3.06	3.31
S-7	Malakabad	24	29	70	45	56	2.55	3.48
S-8	Yaqubabad	39	38	79	81	80	2.73	5.97
S-9	Salim Khan kalli	38	17	101	62	69	2.28	4.28
S-10	Gujar Garhi	32	27	120	62	70	2.49	4.42
S-11	Gujar Garhi	32	28	110	60	60	2.73	26.13
S-12	Jhandai	25	28	9	60	65	2.79	5.25
S-13	Pumo Korona	35	30	8	64	65	2.40	3.46
S-14	Takht Bhai	35	33	36	58	84	3.06	5.46
S-15	Takkar	27	30	4	46	58	2.25	3.66
S-16	Jalala	38	27	208	69	74	2.73	5.06
S-17	Shergarh	40	31	120	66	77	2.91	5.64
S-18	Lund Khwur	25	19	70	36	47	2.10	6.01
S-19	Chil	27	20	75	42	58	2.67	5.44
S-20	Chin Banda	28	32	275	38	58	2.82	4.03
S-21	Jamal Garhi	24	4	141	38	55	1.77	5.30
S-22	Katlung	35	27	122	58	75	2.55	4.00
S-23	Ghundo	24	22	76	43	54	2.07	5.71
S-24	Mian Kali	25	27	81	40	57	2.79	1.55
S-25	Babuzai	24	26	74	40	55	2.07	4.03
S-26	Sphinkai	23	20	99	42	58	2.16	5.79
S-27	Rustum	12	16	65	20	28	1.89	3.08
S-28	Jalalabad	17	17	103	23	44	1.71	5.60
S-29	Chigai Baba	21	27	181	23	30	2.07	2.82
S-30	Toru	28	22	105	62	61	2.16	5.45
S-31	Garhi Kapora	24	25	100	41	64	1.95	4.09
S-32	Chandar	35	29	91	51	70	2.25	5.09
S-33	Sowkai	45	21	133	54	77	2.04	2.51
Minimum		***12***	***4***	***4***	***20***	***25***	***0.15***	***1.55***
Maximium		***45***	***56***	***275***	***81***	***84***	***3.06***	***26.13***
Average		***28***	***27***	***96***	***49***	***60***	***2.33***	***5.14***
Bohn's Stnd		***20***	***10***	***50***	***40***	***20***	***0.06***	***4-9***

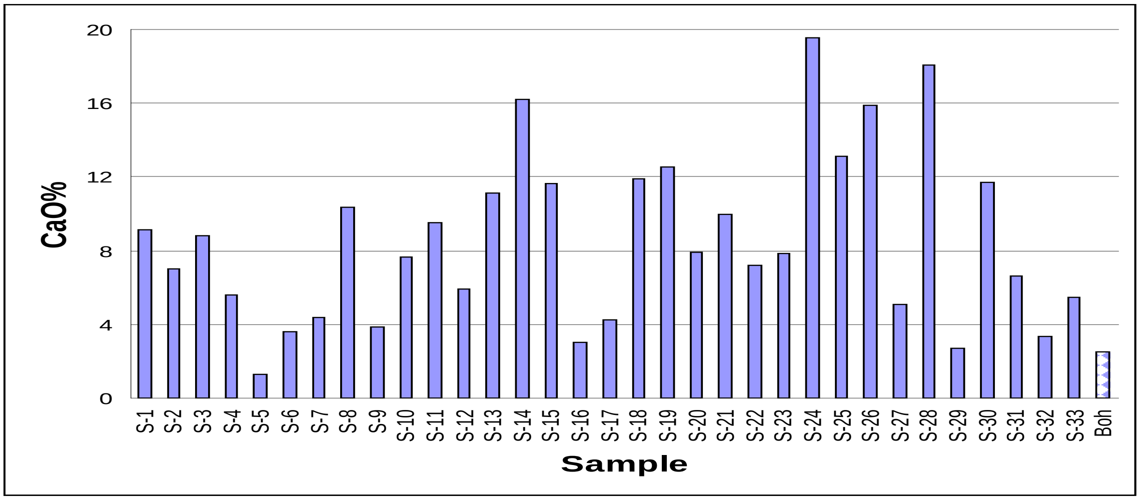

Fig. 5.1a. CaO concentration (%) in Soils of Mardan District

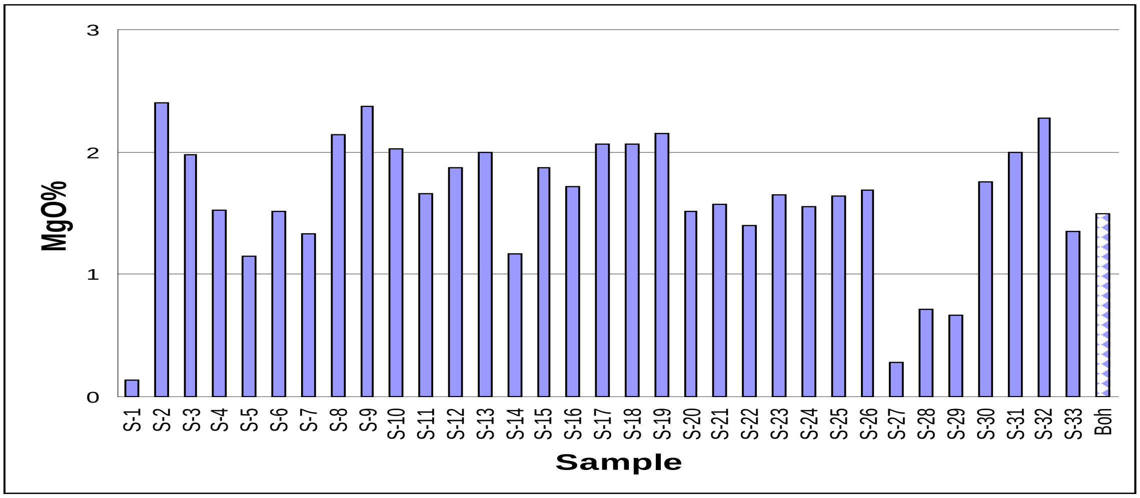

Fig. 5.1b. MgO concentration (%) in Soils of Mardan District

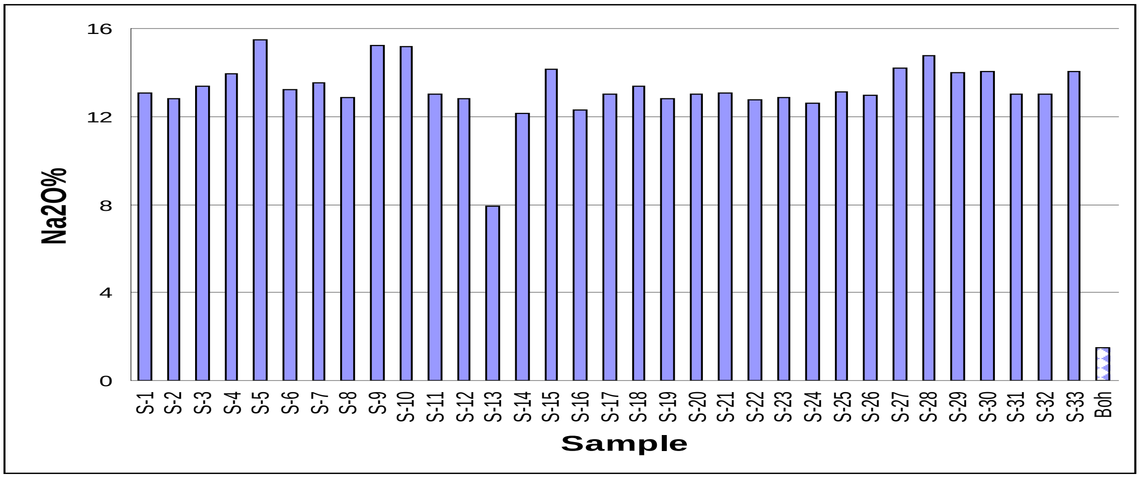

Fig. 5.1c. Na_2O concentration (%) in Soils of Mardan District

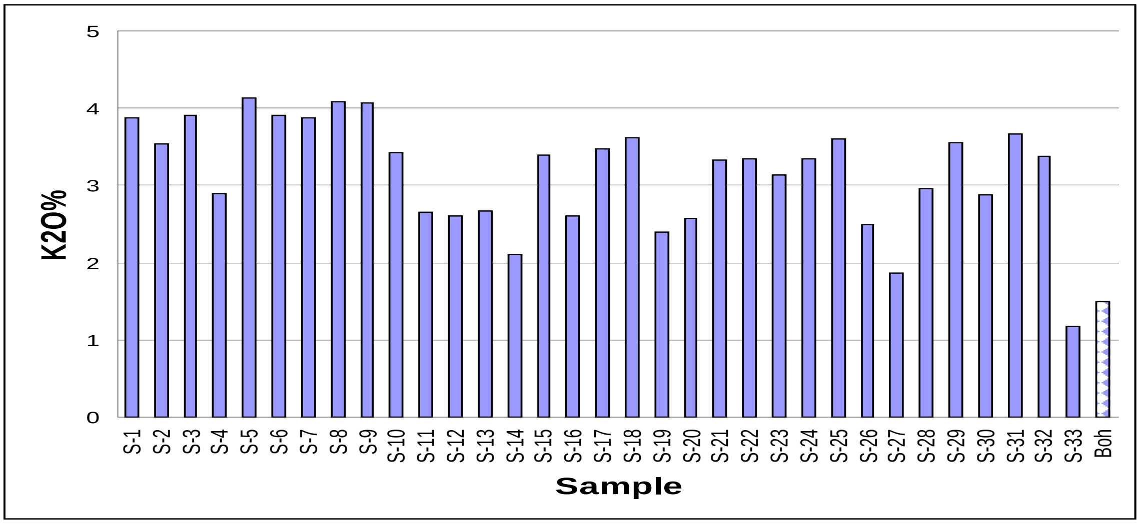

Fig. 5.1d. K_2O concentration (%) in Soils of Mardan District

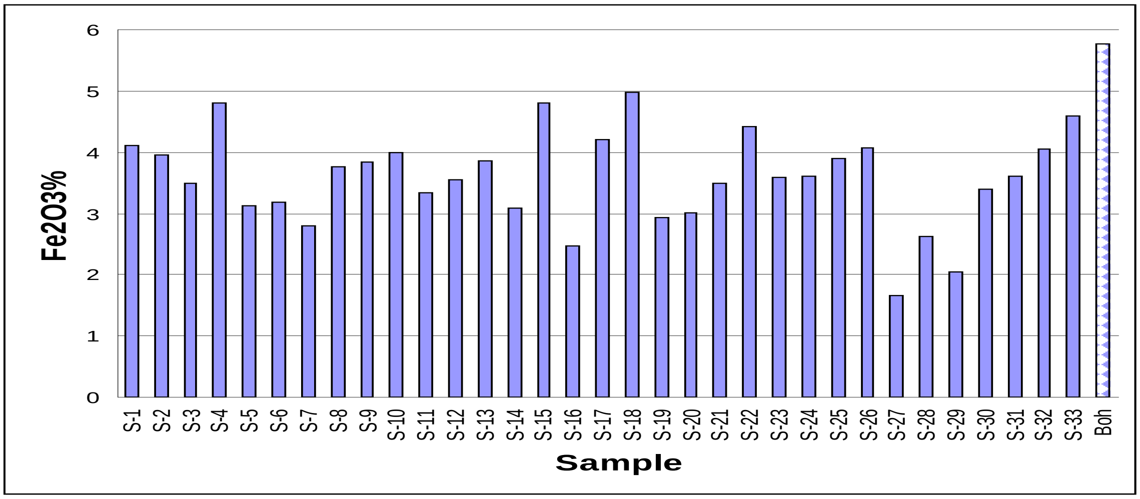

Fig. 5.1e. Fe_2O_3 concentration (%) in Soils of Mardan District

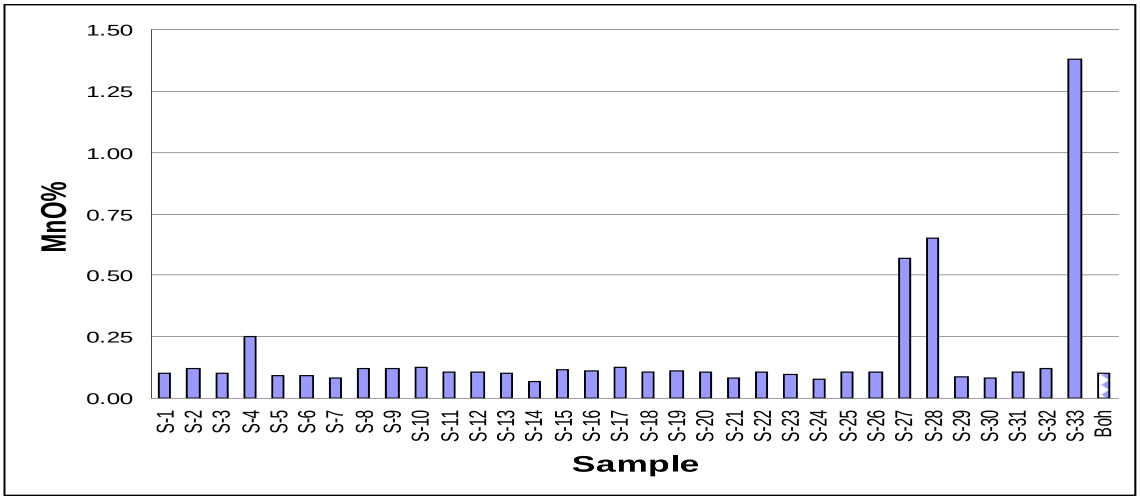

Fig. 5.1f. MnO concentration (%) in Soils of Mardan District

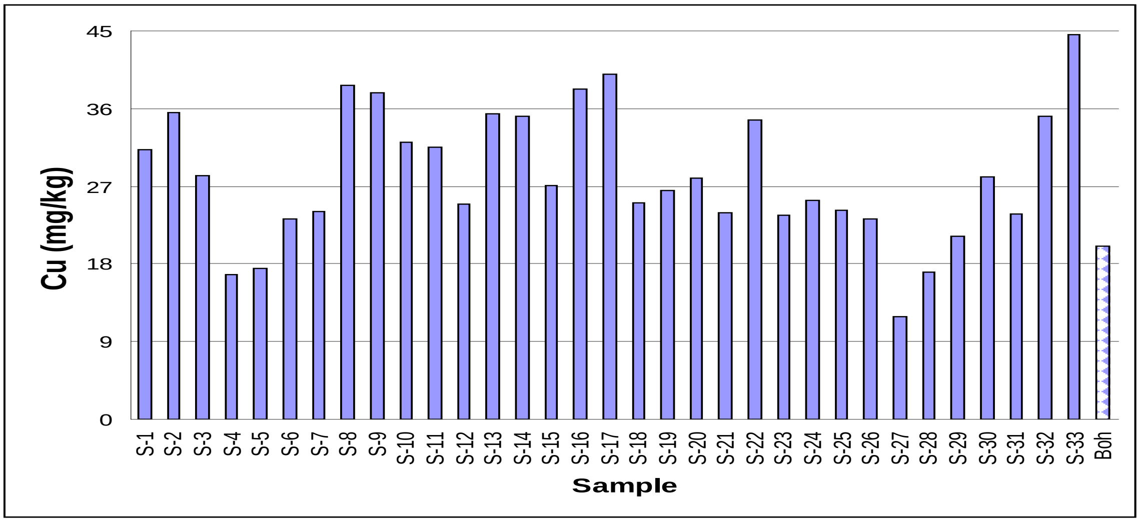

Fig. 5.2a. Copper (Cu) concentration (mg/kg) in Soils of Mardan District

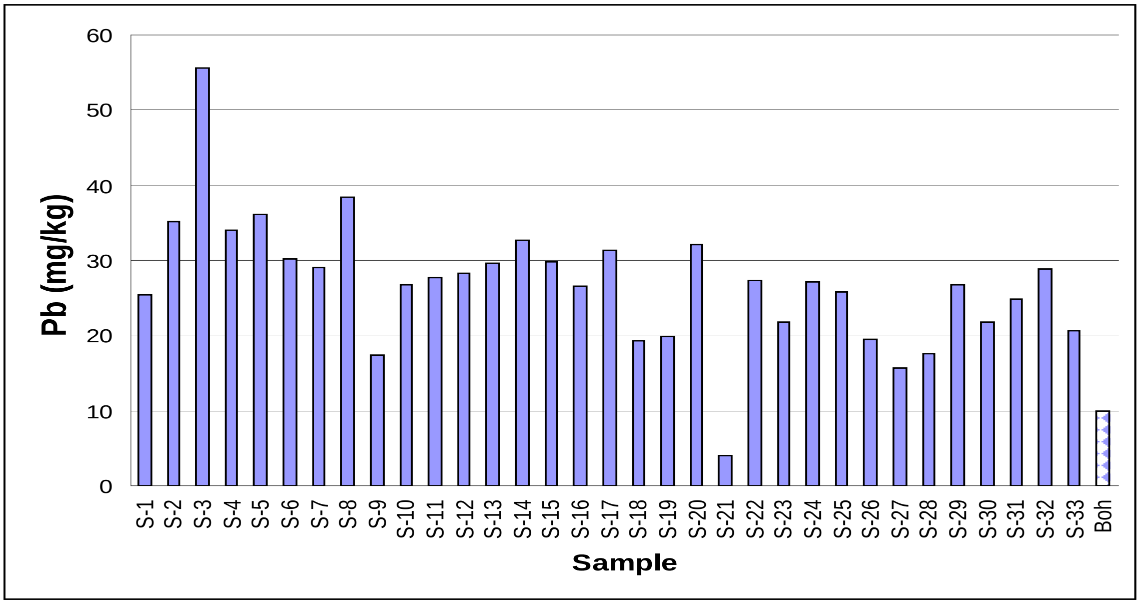

Fig. 5.2b. Lead (Pb) concentration (mg/kg) in Soils of Mardan District

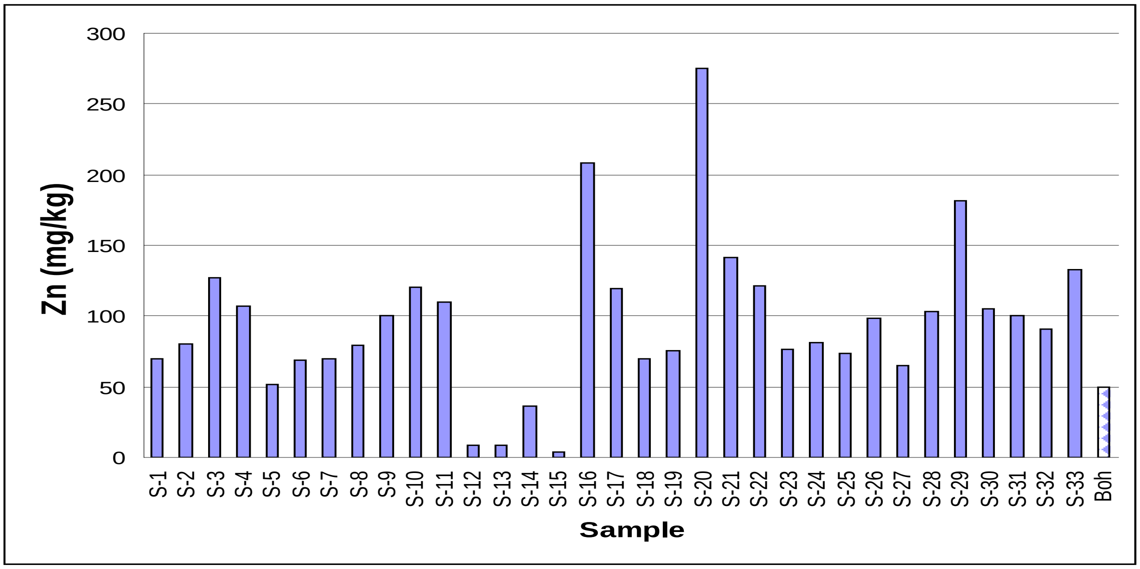

Fig. 5.2c. Zinc (Zn) concentration (mg/kg) in Soils of Mardan District

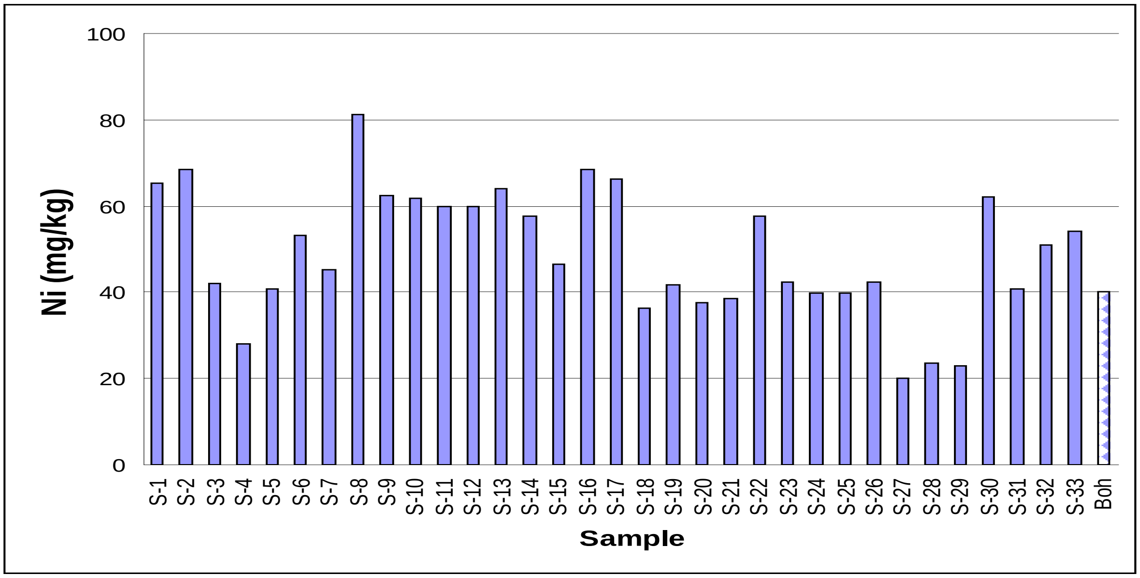

Fig. 5.2d. Nickel (Ni) concentration (mg/kg) in Soils of Mardan District

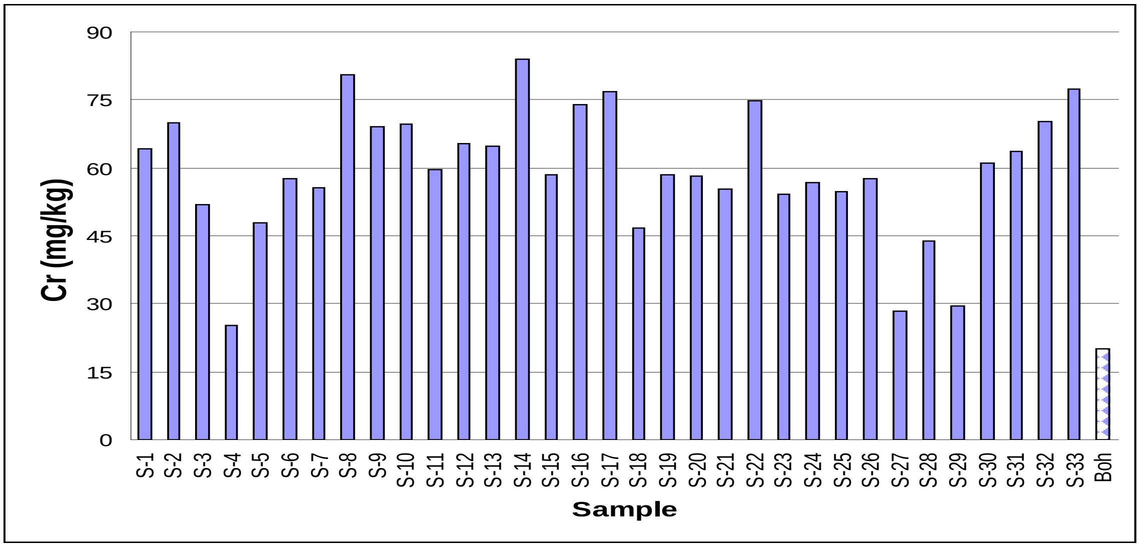

Fig. 5.2e. Chromium (Cr) concentration (mg/kg) in Soils of Mardan District

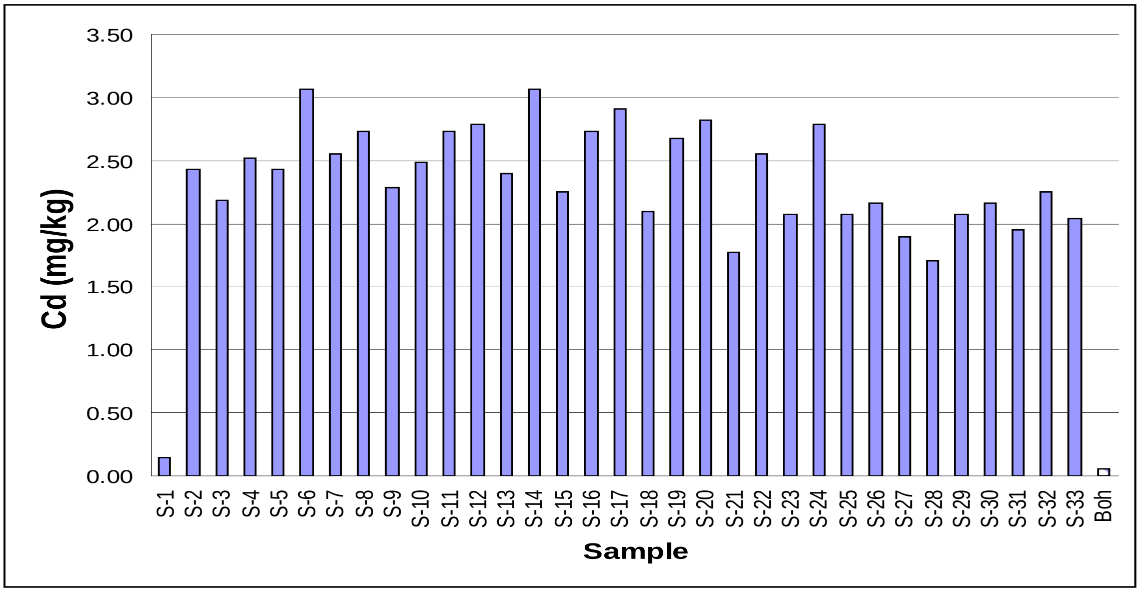

Fig. 5.2f. Cadmium (Cd) concentration (mg/kg) in Soils of Mardan District

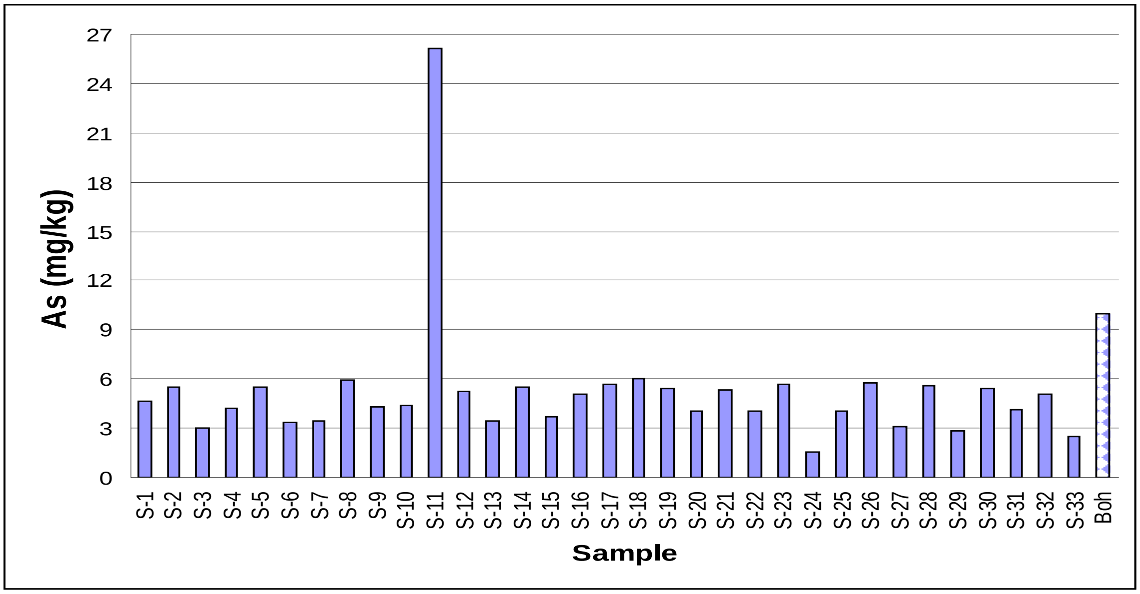

Fig. 5.2g. Arsenic (As) concentration (mg/kg) in Soils of Mardan District

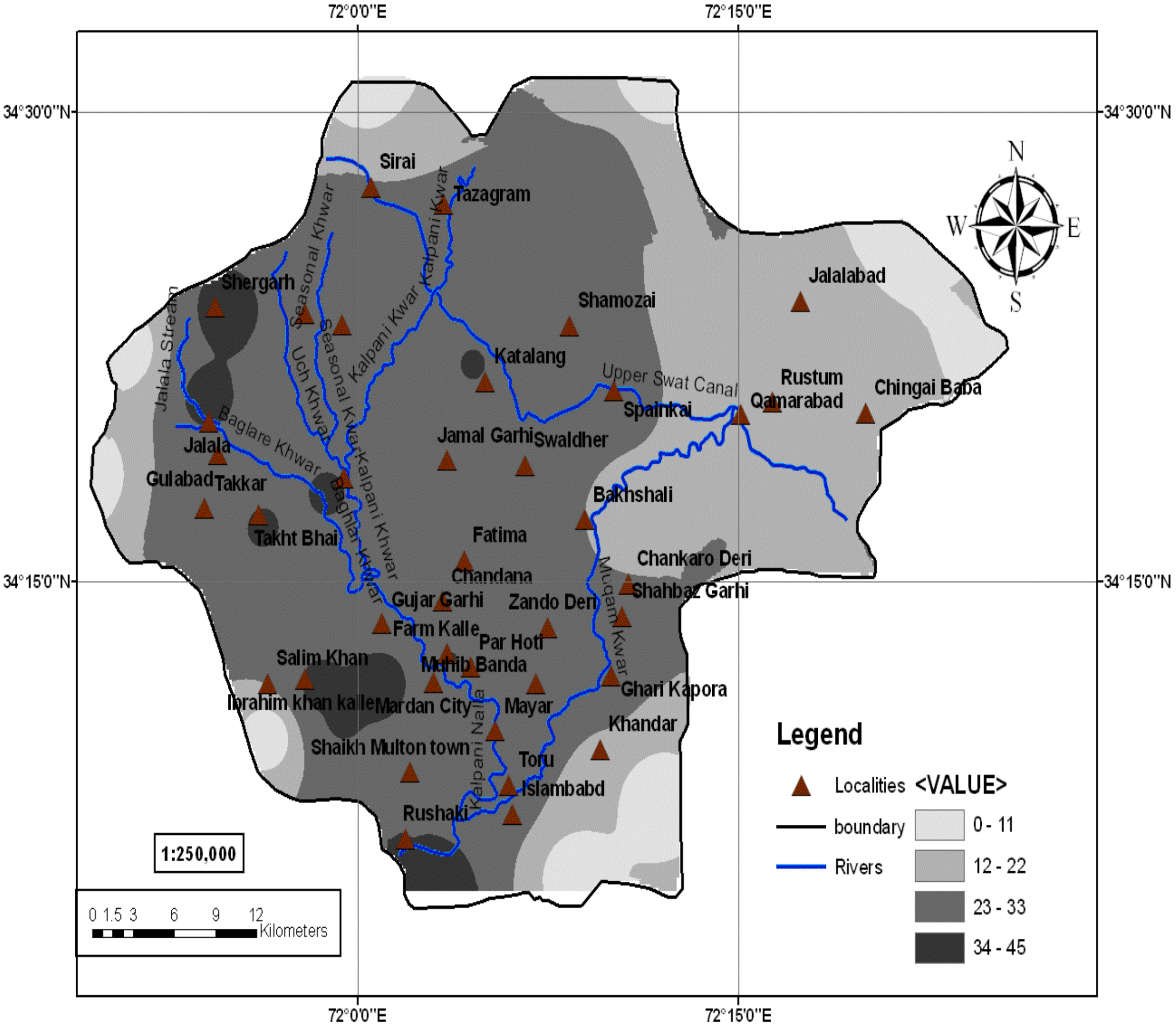

Fig.5.3a. Map showing Copper (Cu) concentration (mg/kg) in Soils of Mardan District

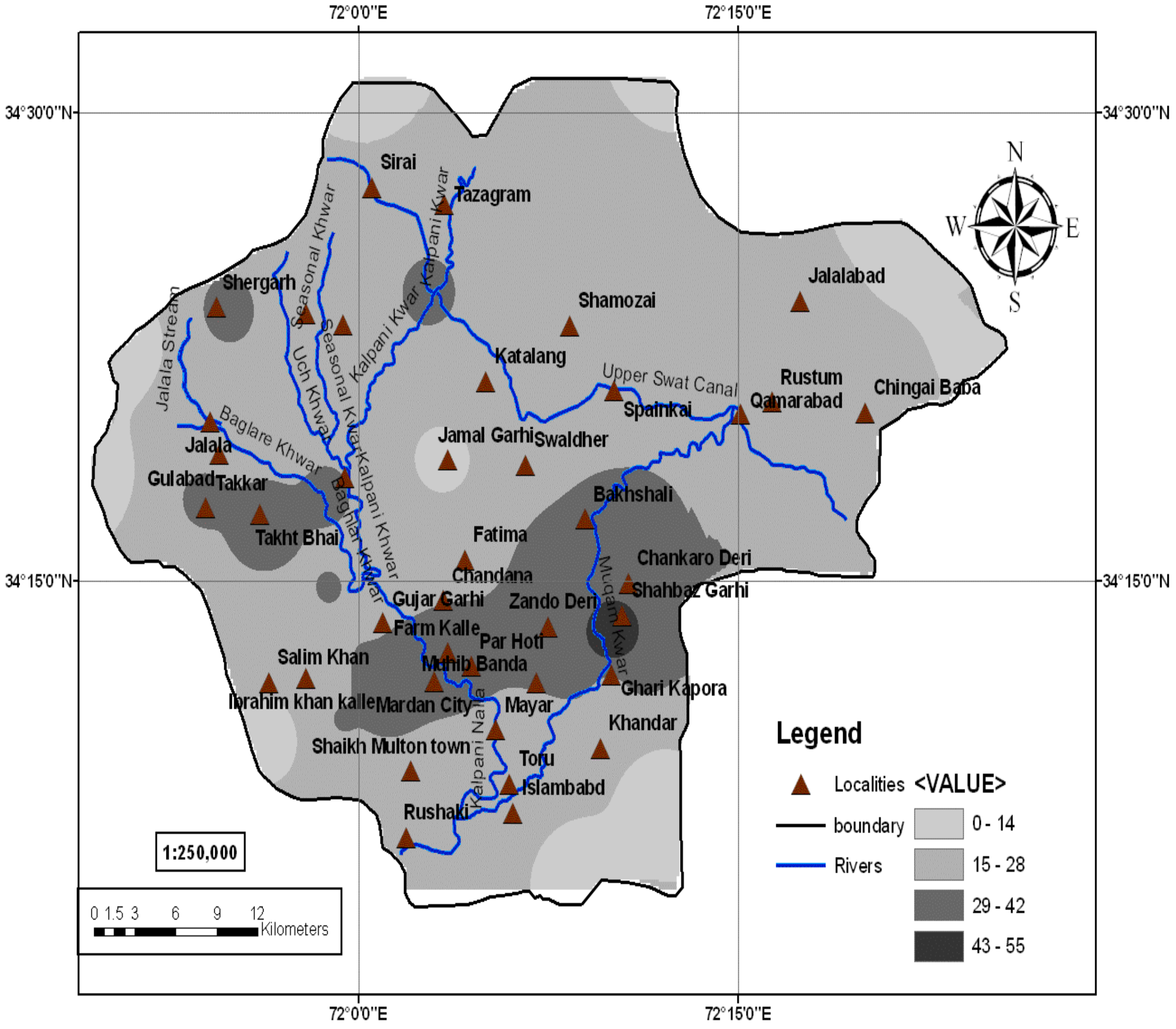

Fig.5.3b. Map showing Lead (Pb) concentration (mg/kg) in Soils of Mardan District

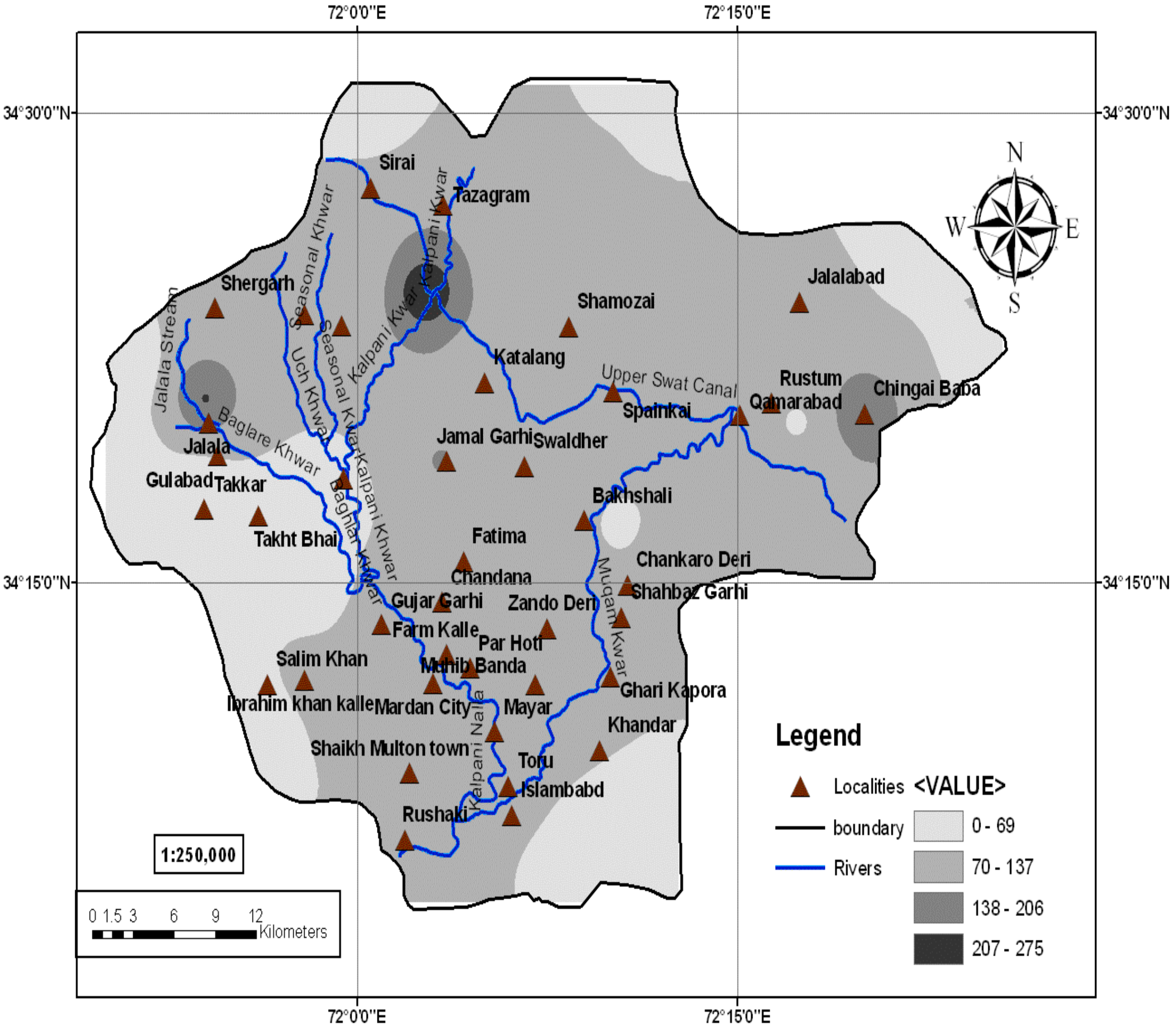

Fig.5.3c. Map showing Zinc (Zn) concentration (mg/kg) in Soils of Mardan District

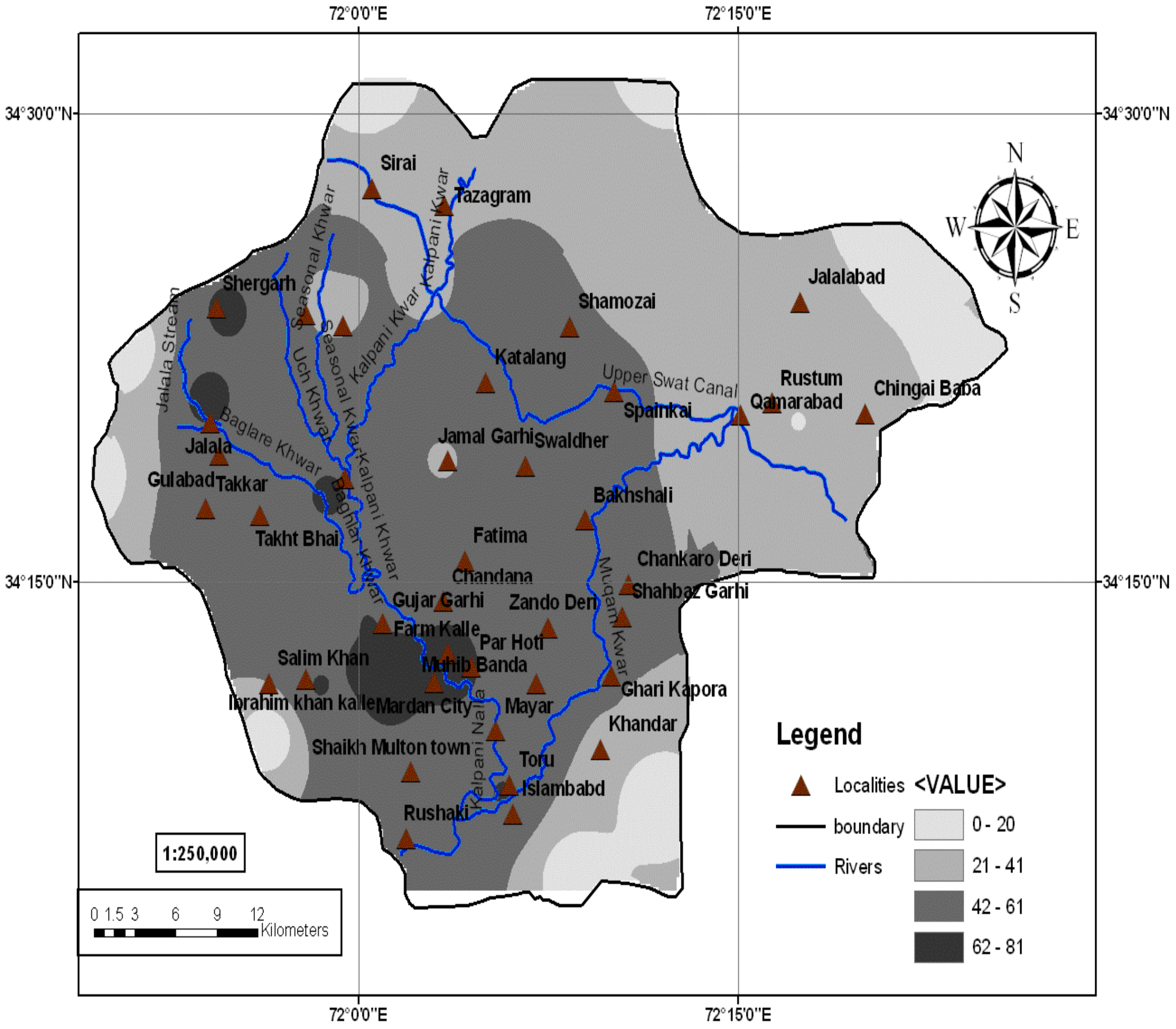

Fig.5.3d. Map showing Nickel (Ni) concentration (mg/kg) in Soils of Mardan District

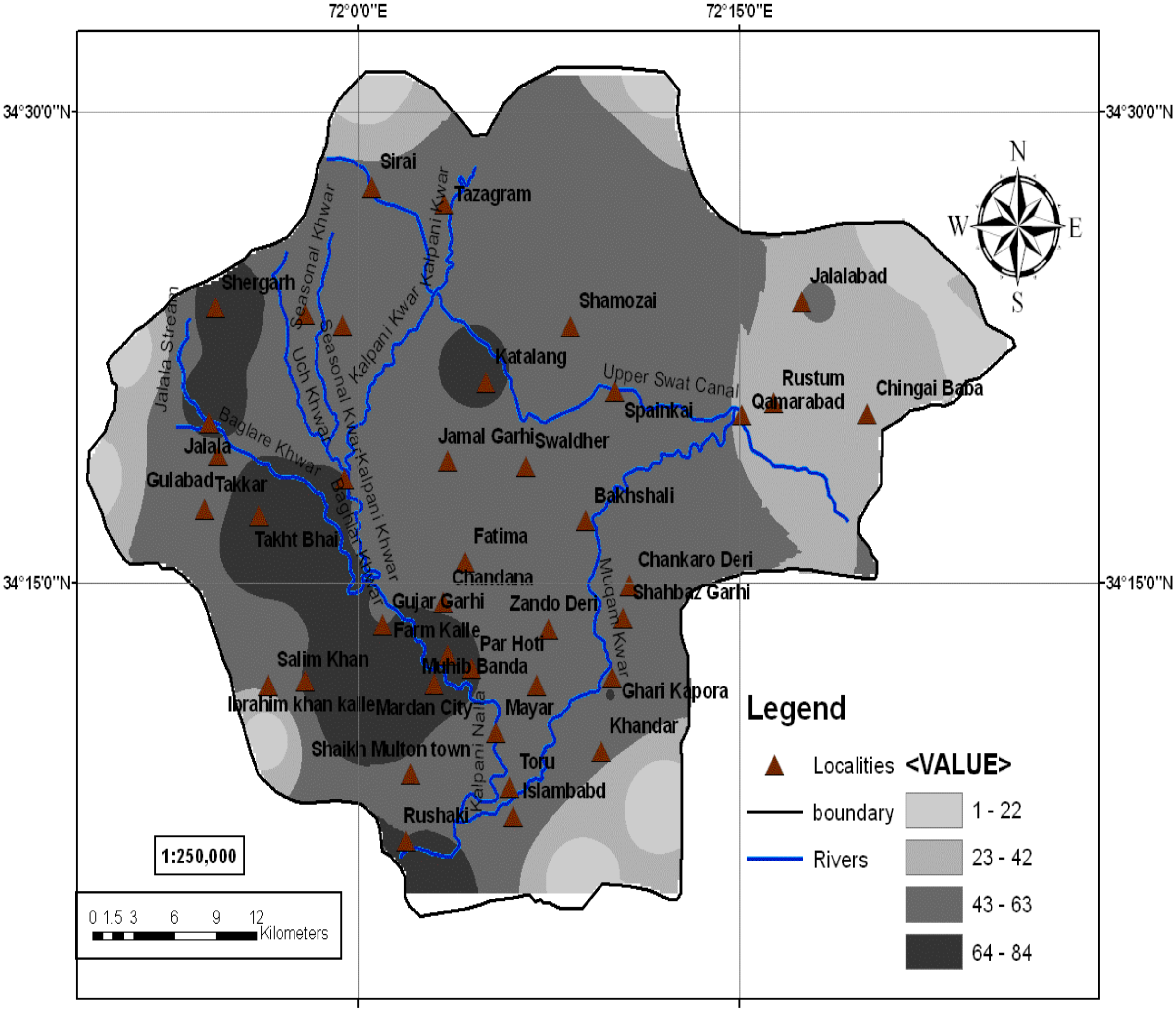

Fig.5.3e. Map showing Chromium (Cr) concentration (mg/kg) in Soils of Mardan District

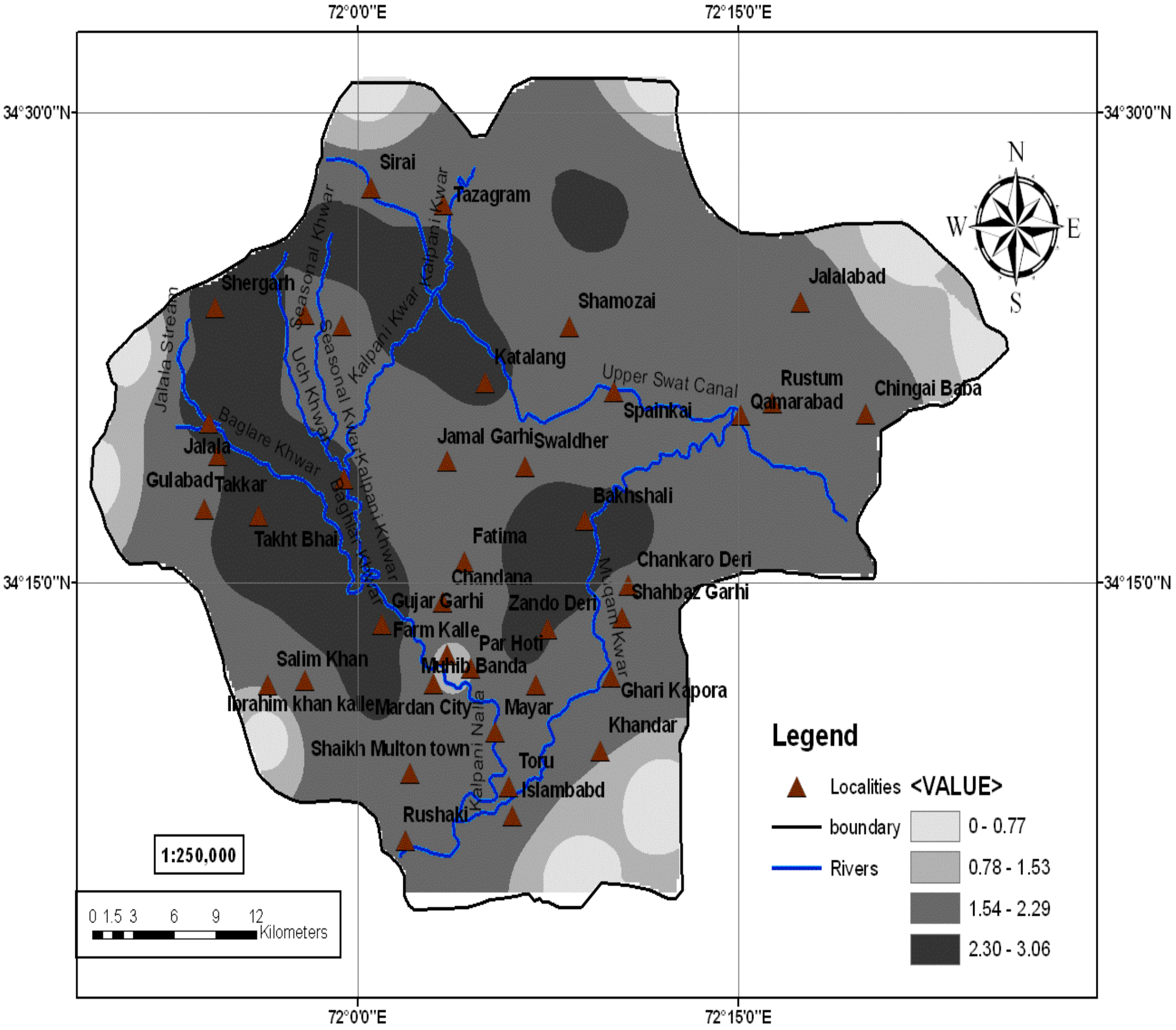

Fig.5.3f. Map showing Cadmium (Cd) concentration (mg/kg) in Soils of Mardan District

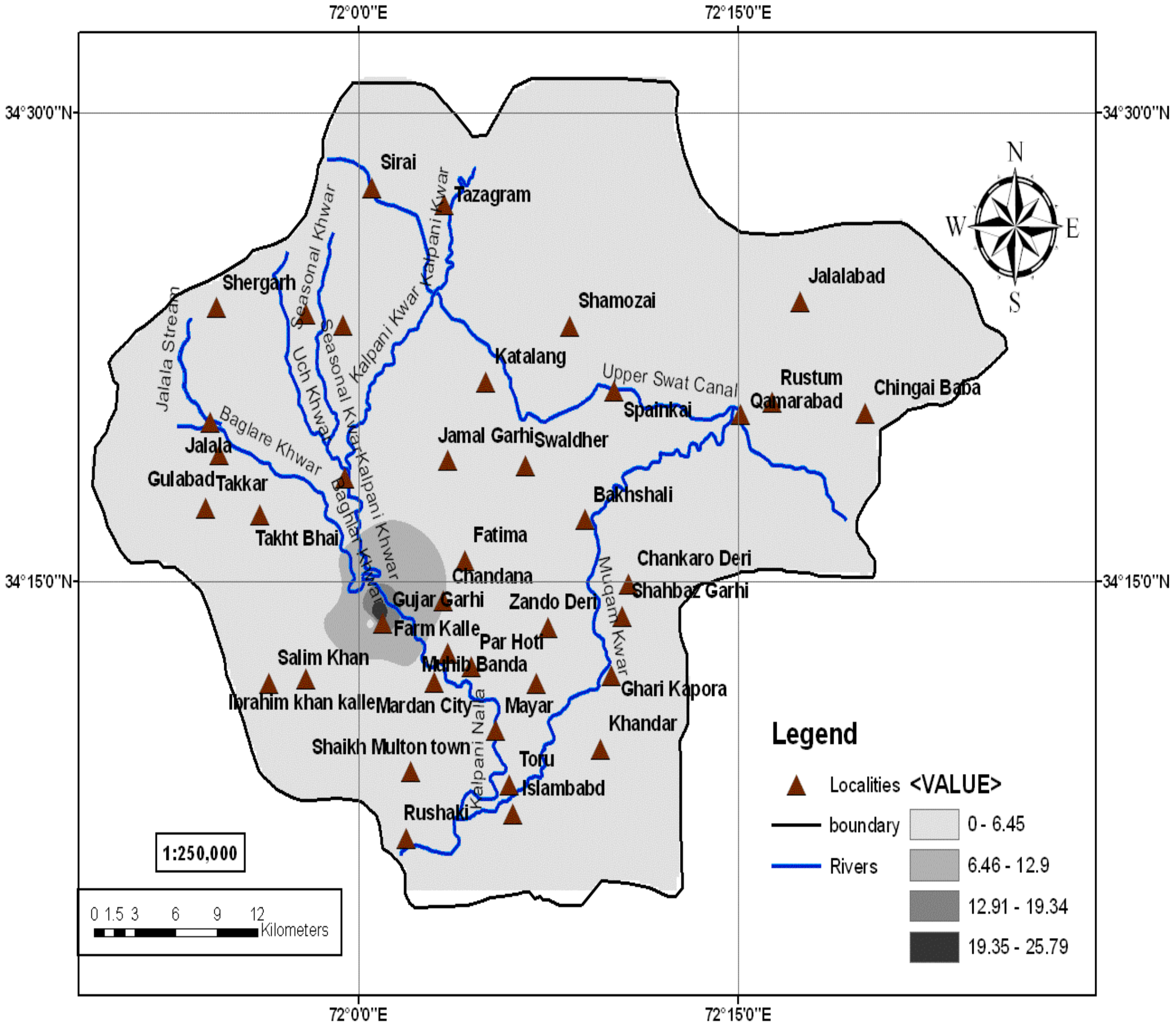

Fig.5.3g. Map showing Arsenic (As) concentration (mg/kg) in Soils of Mardan District

CHAPTER 6

DISCUSSION

District Mardan is a part of Peshawar valley which lies between latitude 34° 05′ to 34° 32′ North and longitude 71° 48′ to 72° 25′ East. It is bounded on the north-east by Buner District, on the north and north-west by Malakand protected area, on the south-east by Swabi, on the south by Nowshera District and on the west by Charsadda. Total population of the District is about 1.6 million having1632 square km^2 area (SDNP, 2003). Geologically Mardan can be differentiated into hilly area and south western plain area (DCR, 1998). In eastern part of the District Salkala Formation, Tanowal Formation and Ambela Granitic complex while in south, outcrops of Shahbaz Garhi are observed. Source of irrigational water in the District mainly comes from the upper and lower Swat Canal and their tributaries. Beside Swat Canals other sources include seasonal streams (Khwars), perennials streams, artesisn wells, tube wells and dug wells. Majority of the surface water is drained to Kabul River (DCR, 1998). Water and soil data from the different localities were studied and anaylised and on the basis of their Physico-chemical analysis following discussion is made:

Water

Among the various physical parameters, temperature and pH of the water samples were within permissible limits suggested by WHO (2004) and USEPA (2009). Turbidity was found relatively high (>5 NTU) in some samples. Turbidity in surface water ranged from 0.01 to 25.00 with average value of 7.85NTU (Table 4.1a). Samples from Bakhshali (25.00NTU) and Malkabad (24.00NTU) showed higher level of turbidity. Samples from shallow ground water showed turbidity in a range of 0.01 to 23.00NTU with an average value of 4.26NTU (Table 4.1b), high turbidity was recorded from Zando Kali (13.40NTU), Chil (14.80NTU) and Pirabad (13.80NTU). Turbidity in deep ground water ranged from 0 to 27.70NTU, highest value was notified in Bore water from Hoti Kali (27.70NTU), (Table 4.1c). Total dissolved solids in the water were within permissible limit (1000mg/l) of WHO (2004) except one sample from a Hand Pump in Jalala (1220mg/l) (Table 4.1b). Water samples from all the three sources showed elevated values of EC (Table 4.1a, b, c, respectively). Surface water had EC in range of 132 to1876µS/cm, elevated values had been recorded in the stream water of Sangi Murmur (809µS/cm) and in village Saidabad (1876µS/cm) near Takht Bhai (Table 4.1a). Relatively high levels of EC were found in Shallow ground water in the range of 154-2200µS/cm with average EC of 791µS/cm. Samples with relatively high EC values were from Garakol, Jhandai, Garhi Kapora and Takht Bhai, Jalala, Chin Banda, and Kundur (Table 4.1b). Deep ground samples from Boring at Par Hoti, Jalala and tube wells of Chankari stop showed high EC level (Table 4.1c). Such results show that water of the study area has a great potential to dissolve salts and minerals.

Among various Anions (SO_4^{-2}, NO_3^-, Cl^- and HCO_3^-), all were found within the permissible limits of WHO and USEPA except HCO_3^-, which was notified with high levels in majority of water samples from all sources (Table 4.2a, b and c, respectively). Such elevated HCO_3^- content may be due to the dissolution of carbonates minerals.

Similarly light elements cations (Ca, Mg, Na and K) were also compared with WHO and USEPA standards. Surface water of the study area had 39mg/l average Ca (Table 4.3a). The shallow water (Dug wells and Hand pumps) of the Mardan District contained relatively high Ca with average value of 63mg/l higher than average of 41mg/l in deep ground water (Table 4.b, c, respectively). Calcium content can be attributed to the percolation of water through limestone and dolomite. High Ca (>75mg/l) content was observed in the water from the Hand pumps and Dug wells of Jamal Garhi, Jahndai, Pump Korona, Takht Bhai, Jalala, Lund Khawr, Chil, Chin Banda, Katlung, Ghundo, Spainkai and Rustum. Sodium in all sort of water was present in level above WHO (2004) limit of 200 mg/l. Sodium content varied from 50 to 565 mg/l in surface water, 91 to 616 mg/l in shallow ground water and 131 to 586mg/l in deep ground water (Table 4.3a, b and c, respectively). In water of the study area high content of Na can be the result of dissolved minerals from the local NaCl and Na_2CO_3 seems. Sedimentary evaporates and high saline conditions in the past can also be responsible for high Na concentration in water. Both Mg and K were observed within permissible limits of WHO (2004), except one sample from Sowkai (56mg/l) with Mg above 50mg/l (Table 4.3c).

On the basis of Cations, Anions and TDS water of the Mardan District has been classified as $NaHCO_3$ type through Piper classification scheme.

In order to assess the health risk associated with heavy and trace elements (Mn, Fe, Cu, Pb, Zn, Ni, Cr, Cd and As) their concentration in water were compared with WHO and USEPA permissible limits.

Average content of Fe in surface water was 98.57µg/l (Table 4.4a). Water samples from Swat Canal at Sirai (497.75µg/l) and in irrigational channel at Bakhshali (356.00µg/l) were having Fe above USEPA (2009) permissible limit of 300µg/l (Fig.4.15a). In shallow ground water average Fe was notified as 160.85µg/l, samples with high concentration were from Takkar village (956.25µg/l) and Chingai Baba (1627.00µg/l), (Table 4.4b; Fig.4.15a). However, deep ground water had low average content with a value of 40.88µg/l (Table 4.4c; Fig.4.15a). High content of Fe in surface and shallow ground water can be attributed to the oxidation of magnetite, hematite and other iron sulfide minerals.

Mn concentration in majority of samples from all types of water was found within permissible limit (50µg/l) of USEPA and WHO (Table 4.4a, b and c, respectively). Samples with relatively higher concentration were from Mandat, Zando kali, Chandar and Hoti kali (Fig.4.15b).

Copper concentration in surface water samples varied from 5 to 4838µg/l, and 1 to 2496µg/l in shallow ground water (Table 4.4b; Fig.4.15c). All the samples from the deep ground water sources were within permissible limit (2000µg/l) of WHO (2004) and USEPA (2009). The raised value of Cu in the surface and shallow ground water could be the leaching of Cu from sulfide seems present in the area.

Like other parts of the Peshawar Basin, Mardan District also showed high concentration of Pb in water above 10µg/l and 15µg/l by WHO (2004) and USEPA

(2009) respectively. Pb in surface water ranged from <0.05 to 34.670µg/l, in shallow ground water <0.05 to 30.21µg/l and <0.05 to 34.69µg/l in deep ground water. High Pb content in localities like Bakhshali, Saidabad near Takht Bhai, Sirai, Takkar, Chingai Baba and Torru can be result of percolation and dissolution of sulfide minerals from sulfide seems in the area.

Other remaining elements which includes Zn, Ni, Cr, Cd and As were found within permissible limits of WHO (2004) and USEPA (2009). Only one sample collected from the irrigational canal at Malkabad (22.39µg/l) had Ni above permissible (20µg/l) limit of WHO (2004). This increase could be the leaching of Ni from the ultramafic rocks exposed in the vicinity.

It has been noted during the present study that the occurrence of some heavy and trace elements such as Fe, Cu, Pb and Ni above the relevant permissible limits in some water samples could be due to the geogenic sources as no industrial or other anthropogenic sources are found in the area which could cause enhancement of these metals. The elevated concentrations of these elements in certain areas need further investigations in regard to the health related problems.

Soils

All the physical parameters (pH, TDS and EC) were notified at normal levels (Table 5.1). Soil samples showed pH value ranged from 5.9 to 8.1, low pH values could be due to the presence of sulfides while the high values could be attributed to the calcite and dolomite presence in the soil. Similarly the average distribution of silt (61.55%), clay (10.24%) and sand (28.24%) indicated the texture was dominantly silty loam (Table 5.2). Various light element oxides, trace and heavy metals concentration was measured and compared with values of normal soil suggested by Bohn et al. (2001).

Agricultural soils of the study area had CaO content in range of 1.26 to 19.56 % with average content of 8.66% (Table 5.3; Fig.5.1a). Value of CaO for normal agricultural soil is 2.5 % (Bohn et al., 2001). All the soil samples from the study area were having elevated level of Ca which may be due to the weathering of limestone and dolomite, and the addition of superphosphate fertilizers to the soil. Although Ca is essential plant nutrient but its abundance may disturb the water and salt balance in the plants. On other hand the average value (1.59%) of MgO in the study area was near to the normal value of 1.5% (Bohn et al., 2001), (Table 5.3; Fig.5.1b).

Soil samples of the study area were highly enriched with NaO, with average content of 13.26% (Table 5.3; Fig.5.1c). Sodium concentration in the soil of study area was far higher than normal value of 1.5% (Bohn et al., 2001). This elevated level of Na alters the soil structure (Kabata-Pendias and Pendias, 1992), as well as harmful for plants as it disturbs the salt-water balance. Sodium content in the soil of Mardan may be due to high concentration of salt that is built up in the soils of Mardan District due to high rate of evaporation of water contributed by the Swat River through irrigational means. The water logging and salinity remained the problem for long time in the Mardan District which has greatly affected the agriculture of the area. This problem has been dealt with by pumping out the saline water by tube wells and SCARP program, but still the problem exists to certain extent.

Average K_2O value in the studied soils was 3.14%, higher than the Bohn et al. (2001) value (1.5%) for normal agricultural soils (Table 5.3; Fig.5.1d). Samples with higher values were from Farum Korona, Shahbaz Garhi, Gujrat, Gulshanabad, Malkabad, Yaqubabad, Ibrahim Khan Kali, Gujar Garhi, Takkar, Shergarh, Lund Khwur, Jamal Garhi and Katlung. The elevated content of K_2O could be due to the decomposition of feldspar, contributed to the studied soils by the granite rocks of alkaline province exposed in the northern parts of Mardan District

Among the heavy and trace elements in the soils of Mardan District, Fe and Mn were found within the limit suggested by Bohn et al. (2001) for normal agricultural soils. The rest of the elements such as Cu, Pb, Zn, Ni, Cr and Cd were found above the limits of normal agricultural soils.

The average concentrations of Cu, Pb, Zn and Cd in the studied soils were found as 28mg/kg, 27mg/kg, 96mg/kg and 2.33mg/kg respectively, which are higher than the values suggested by Bohn et al. (2001) for normal agricultural soil. This enhancement of Cu, Pb and Zn can be attributed by sulfide seems in the soils of the area (Watling, 2006).

The average amount of Ni (49mg/kg) and Cr (60mg/kg) in the studied soils were found higher than that of normal agricultural soils (Bohn et al., 2001). This enrichment in the studied soils could be due to the weathered material contributed by the mafic and ultramafic rocks exposed in the north-western part of Mardan District.

The average amount of As (5.14mg/kg) in the studied soils was found within the range of normal soils (Kabata-Pendias and Pendias, 2001). These low values indicated no significant environmental threats due to As presence in the soils.

It has been notified during this study that the soils of Mardan District have greater input from geogenic sources and no anthropogenic sources are involved in the metal enrichment in the soils. The elevated concentration of various elements in the soils as compare to the normal agricultural soil suggests that there could be environmental impacts on the ecosystem of the area.

Health risk assessment

In the study area, the health risk assessment; Average daily dose (ADD), hazard quotient (HQ) and cancer risk (CR) were calculated for the consumption of drinking (shallow and deep ground water). Table 6.1a and 6.2b have summarized the calculated ADD, HQ and CR values for heavy and trace elements.

Health risk assessment of shallow ground water

The minimum, maximum and average ADD values for trace and heavy elements in shallow ground water were as following; Fe from 0.00 to 4.39E-02mg/kg-day with average value of 3.00E-03mg/kg-day, Mn from 0.00 to 2.11E-03mg/kg-day with average value of 5.00E-04mg/kg-day, Cu from 6.7E-02 to 7.00E-03mg/kg-day with average value of 7.00E-03mg/kg-day, Pb from 0.00 to 8.00E-04mg/kg-day with average value of 7.00E-05mg/kg-day, Zn from 0.00 to 1.13E-01mg/kg-day with average value of 1.90E-02mg/kg-day, Ni from 0.00 to 5.00E-04mg/kg-day with average value of 1.00E-04mg/kg-day, Cr from 0.00 to 1.00E-03mg/kg-day with average value of 2.00E-05mg/kg-day, Cd from 0.00 to 1.00E-04mg/kg-day, with average value of 2.00E-05mg/kg-day and As from 0.00 to 2.00E-04mg/kg-day with average value of 2.30E-05mg/kg-day (Table 6.1a).

The ADD values were used to calculate the HQ of trace and heavy elements in the shallow ground water. The HQ values of these elements were found as; Fe from 0.00 to 17.57 with average value of 1.20, Mn from 0.00 to 0.01 with average value of 0.00, Cu from 0.00 to 1.82 with average value of 0.19, Pb from 0.00 to 0.22 with average value of 0.02, Zn from 0.00 to 0.37 with average value of 0.06, Ni from 0.00 to 0.02 with average value of 0.00, Cr from 0.00 to 0.00 with average value of 0.00, Cd from 0.00 to 0.23 with average value of 0.04, As from 0.00 to 0.70 with average value of 0.07 (Table 6.1a). Majority of trace and heavy elements were found with HQ values <1, indicating no risk as suggested by USEPA approach (1999). However, 7% of samples from the shallow ground water were showing high risk due to HQ values >10 for Fe. Similarly 7% samples were recorded with HQ value >1- <5 for Cu, indicating low risk in accordance with USEPA approach 1999.

The cancer risk values were calculated only for Arsenic in shallow ground water samples. It ranged from 0.00 to 1.10E-04 with average value of 3.47E-05. According to USEPA approach 1999 these values indicate low cancer risk.

Health risk assessment of deep ground water

Values of calculated ADD for different trace and heavy elements were as follows; Fe from 0.00 to 3.20E-03mg/kg-day with average value of 7.00E-04mg/kg-day, Mn from 0.00 to 4.00E-03 mg/kg-day with average value of 8.00E-04mg/kg-day, Cu from 5.00E-04 to 2.30E-02mg/kg-day with average value of 3.00E-03 mg/kg-day, Pb from 0.00 to 9.00E-04mg/kg-day with average value of 7.00E-05 mg/kg-day, Zn from 1.00E-05 to 3.50E-02mg/kg-day with average value of 8.00E-03mg/kg-day, Cd from 0.00 to 3.87E-05mg/kg-day with average value of 1.60E-05mg/kg-day and As from 0.00 to 7.70E-05mg/kg-day with average value of 2.17E-05mg/kg-day. However, Ni showed negligible ADD values (6.1b).

HQ values based on the ADD for trace and heavy elements in deep ground water samples were as follows; Fe from 0.00 to 1.26 with average value of 0.26, Mn from 0.00 to 0.25 with average value of 0.05, Cu from 0.01 to 0.61 with average value of 0.082, Pb from 0.00 to 0.26 with average value of 0.02, Zn from 0.00 to 0.11 with average value of 0.25, Ni from 0.00 to 0.01 with average value of 0.00, Cd from 0.00 to 0.07 with average value of 0.03 and As from 0.00 to 0.25 with average value of 0.07 (6.1b). However, Ni and Cr showed negligible values of HQ (6.1b). It is clear from the

HQ values that majority of sample were having no risk (HQ= <1) in accordance with USEPA approach 1999.

The cancer risk values have been calculated only for Arsenic in the deep ground water samples. It ranged from 0.00 to 1.00E-04 with average value of 4.00E-05, showing low cancer risk as suggested by USEPA approach 1999.

Statistical Analysis

Correlation matrices among various physico-chemical parameters of waters and soils were calculated based on Pearson correlation using SPSS statistical software version 13.1. Among the physio-chemical parameters various parameters pairs showed positive and negative correlations.

Surface water

The correlation matrices of physio-chemical parameters were summarized in Tables 6.2a-6.2c. In surface water metric some pairs of the physio-chemical parameters showed strong correlation such as; EC-TDS (r = 0.548), EC-SO_4 (r = 0.452), EC-Mg (r = 0.686), TDS-SO_4 (r =0.798), TDS-HCO_3 (r = 0.895), TDS-Na (r = 0.741), SO_4-HCO_3 (r = 0.621), SO_4-Na (r = 0.635), HCO_3-Na (r = 0.689), K-As (r = 0.615), Mn-As (r = 0.452), Fe-Cu (r = 0.837), Fe-Ni (r = 0.706), Cu-Ni (r = 0.559). While some pairs showed strong negative correlation like; EC-Fe (r = -0.452), TDS-Mn (r = -0.453), TDS-Fe (r = -0.775), TDS-Cu (r = -0.544), TDS-Zn (r = -0.541), TDS-Ni (r = -0.720), SO_4-Mn (r = -0.444), SO_4-Fe (r = -0.514), SO_4-Ni (r = -0.561), Cl-Ni (r = -0.504), HCO_3-Fe (r = -0.696),

HCO_3-Cu (r = -0.524), HCO_3-Zn (r = -0.591), HCO_3-Ni (r = -0.688), Ca-Cu (r = -0.444), Na-Ni (r = -0.516), K-Fe (r =-0.467), Mn-Cd (r = -0.453), (Table 6.2a).

Shallow ground water

In shallow ground water sources some of physio-chemical parameters pairs showed positive correlation such as; pH-As (r = 0.582), EC-TDS (r = 0.991), EC-SO_4 (r = 0.748), EC-NO_3 (r = 0.472), EC-Cl (r = 0.820), EC-HCO_3 (r = 0.865), EC-Mg (r = 0.562), EC-Cr (r = 0.478), EC-As (r = 0.426), TDS- SO_4 (r = 0.761), TDS- NO_3 (r = 0.487), TDS-Cl (r = 0.821), TDS-HCO_3 (r = 0.860), TDS-Mg (r = 0.589), TDS-As (r = 0.447), SO_4-NO_3 (r = 0.527), SO_4-Cl (r = 0.778), SO_4- HCO_3 (r = 0.547), SO_4-Mg (r = 0.449), NO_3-Mg (r = 0.629), NO_3-Cr (r = 0.550), Cl HCO_3 (r = 0.665), ClAs (r = 0.400), HCO_3-Mg (r = 0.575), HCO_3-As (r = 0.453), K-Mn (r = 0.411), Fe-Cu (r = 0.657), Fe-Pb (r = 0.931), Fe-Zn (r = 0.401), Fe-Ni (r = 0.859), Cu-Pb (r = 0.592), Cu-Ni (r = 0.489), Pb-Zn (r = 0.564), Pb-Ni (r = 0.852). While some pair also showed negative correlation such as; EC-Zn (r = -0.409), EC-Ni (r = -0.405), HCO_3-Fe (r = -0.490), HCO_3-Zn (r = -0.438), HCO_3-Ni (r = -0.473), (Table 6.2b).

Deep ground water

In deep ground water some of the selected physio-chemical parameters showed strong positive correlation such as; pH-As (r = 0.705), EC-TDS (r = 0.999), EC-NO_3 (r = 0.768), pH-HCO_3 (r = 0.686), pH-K (r = 0.564), pH-Mn (r = 0.637), TDS-NO_3 (r = 0.772), TDS-HCO_3 (r = 0.678), TDS-K (r = 0.572), TDS-Mn (r = 0.652), SO_4-NO_3 (r = 0.807), SO_4 –Cl (r = 0.842), SO_4-K (r = 0.805), NO_3-Cl (r = 0.667), NO_3-K (r = 0.884), NO_3-Mn (r = 0.693), Cl-K (r = 0.636), Ca-As (r = 0.797), Mg-Na (r = 0.602), Mg-Cu (r = 0.536), K-Mn (r = 0.583), Fe-Cd (r = 0.686), Pb-Ni (r = 0.956), Pb-As (r = 0.816), Cr-As (r = 0.550). While some of the pairs showed negative correlation like; pH-Ca (r = -0.725), NO_3-Cr (r = -0.704), Ca-As (r = -0.797), (Table 6.2c).

Pearson correlation of related physio-chemical parameters in soils

In order to asses correlation among different physio-chemical parameters in soil, Pearson correlation method was applied. Table 6.3 summarized the correlation of selected physio-chemical parameters. The result showed that some of pairs had strong positive correlation such as; pH-MgO (r = 0.369), Cond-TDS (r = 0.998), Cond-Pb (r = 0.509), TDS-Pb (r = 0.500), MgO-Fe_2O_3 (r = 0.460), MgO-Cu (r = 0.459), MgO-Ni (r = 0.446), MgO-Cr (r = 0.447), MgO-Cd (r = 0.491), Fe_2O_3-Cu (r =0.381), Cu-Ni (r = 0.818, p =0.01),Cu-Cr (r = 0.870), Ni-Cr (r = 0.870). Pairs with negative correlation were found as; pH-Cond (r = -0.345), pH-Cd (r = -0.602), K_2O-MnO (r = -0.590), (Table 6.3).

Table.6.1a. Health risk assessment (ADD, HQ and CR) of trace and heavy elements in Shallow ground water of Mardan District.

	Fe	Mn	Cu	Pb	Zn	Ni	Cr	Cd	As
ADD (mg/kg-day)									
Range	0.00-4.39E-02	0.00-2.11E-03	6.70E-02-7.00E-03	0.00-8.00E-04	0.00-1.13E-01	0.00-5.00E-04	0.00-1.00E-03	0.00-1.00E-04	0.00-2.00E-04
Average	3.00E-03	5.00E-05	7.00E-03	7.00E-05	1.90E-02	1.00E-04	2.00E-04	2.00E-05	2.30E-05
HQ									
Range	0.00-17.57	0.00-0.01	0.00-1.82	0.00-0.22	0.00-0.37	0.00-0.02	0.00-0.00	0.00-0.23	0.00-0.07
Average	1.20	0.003	0.19	0.02	0.06	0.00	0.00	0.04	0.07
CR									
Range	ND	ND	ND	ND	ND	ND	ND	ND	0.00-3.10E-04
Average	ND	ND	ND	ND	ND	ND	ND	ND	3.47E-05

*****ADD (Average daily dose).

*HQ (Hazard quotient).

* CR (Cancer risk).

* ND (Not determined)

Table 6.1b. Health risk assessment (ADD, HQ and CR) of trace and heavy elements in Deep ground water of Mardan District.

	Fe	**Mn**	**Cu**	**Pb**	**Zn**	**Ni**	**Cr**	**Cd**	**As**
ADD (mg/kg-day)									
Range	0.00-3.20E-03	0.00-4.00E-03	5.00E-4-2.3E-02	0.00-9.00E-04	1.00E-05-3.50E-02	0.00-0.00	0.00-5.00E-04	0.00-3.87E-05	0.00-7.70E-05
Average	7.00E-04	8.00E-04	3.00E-03	7.00E-05	8.00E-03	0.00	2.00E-04	1.60E-05	2.17E-05
HQ									
Range	0.00-1.26	0.00-0.25	0.01-0.61	0.00-0.26	0.00-0.11	0.00-0.01	0.00-0.00	0.00-0.07	0.00-0.25
Average	0.26	0.05	0.08	0.02	0.00	0.00	0.00	0.03	0.07
CR									
Range	ND	ND	ND	ND	ND	ND	ND	ND	0.00-1.00E-04
Average	ND	ND	ND	ND	ND	ND	ND	ND	4.00E-05

*****ADD (Average daily dose).

*HQ (Hazard quotient).

* CR (Cancer risk).

* ND (Not determined)

Table 6.2a. Correlation between different parameters in Surface water of Mardan District

	pH	EC	TDS	SO$_4^{-2}$	NO$_3^-$	Cl$^-$	HC0$_3^-$	Ca	Mg	Na	K	Mn	Fe	Cu	Zn	Ni	Cd	Cr	As
pH	1	0.418	-0.012	0.123	-0.086	-0.187	0.114	0.077	0.110	-0.283	-0.105	-0.209	-0.065	0.106	0.114	-0.007	0.343	-0.006	-0.308
EC		1	0.548*	0.452*	-0.222	0.041	0.509*	0.033	0.686**	-0.011	-0.013	-0.141	-0.452*	-0.323	-0.326	-0.218	0.007	0.041	0.107
TDS			1	0.798**	-0.181	0.283	0.895**	-0.027	0.314	0.741**	0.121	-0.453*	-0.775**	-0.544*	-0.541*	-0.720**	-0.019	-0.087	-0.017
SO$_4^{-2}$				1	-0.205	0.196	0.621**	-0.020	0.441	0.635**	0.009	-0.444*	-0.514*	-0.370	-0.372	-0.561*	0.122	-0.336	0.068
NO$_3^-$					1	-0.090	-0.165	-0.127	-0.176	-0.061	0.107	0.175	0.048	-0.171	0.058	0.022	-0.049	-0.028	0.182
Cl$^-$						1	0.385	-0.151	-0.126	0.287	0.305	0.225	-0.281	-0.234	-0.263	-0.504*	-0.191	-0.268	0.397
HC0$_3^-$							1	-0.093	0.099	0.689**	0.096	-0.284	-0.696**	-0.524*	-0.591**	-0.688**	-0.123	0.091	-0.119
Ca								1	0.228	-0.220	0.008	-0.326	-0.280	-0.444*	0.097	-0.241	0.327	-0.184	-0.275
Mg									1	-0.143	0.127	-0.150	-0.307	-0.270	-0.284	-0.027	-0.016	-0.063	0.347
Na										1	-0.097	-0.251	-0.421	-0.322	-0.307	-0.516*	-0.132	0.053	-0.114
K											1	0.107	-0.467*	-0.390	-0.143	-0.168	0.038	-0.196	0.615**
Mn												1	0.259	0.013	0.098	0.466*	-0.453*	0.105	0.452*
Fe													1	0.837**	0.421	0.706**	0.004	0.271	-0.102
Cu														1	0.312	0.559*	0.055	0.266	-0.185
Zn															1	0.502*	-0.022	0.063	-0.285
Ni																1	-0.156	0.377	0.041
Cd																	1	-0.128	-0.047
Cr																		1	-0.290
As																			1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

Table 6.2b. Correlation between different parameters in Shallow ground water of Mardan Distric

	pH	**EC**	**TDS**	**SO$_4^{-2}$**	**NO$_3^-$**	**Cl$^-$**	**HC0$_3^-$**	**Ca**	**Mg**	**Na**	**K**	**Mn**	**Fe**	**Cu**	**Pb**	**Zn**	**Ni**	**Cr**	**Cd**	**As**
pH	1	0.082	0.090	0.066	-0.205	0.213	0.066	-0.517^{**}	-0.009	0.031	0.104	0.002	0.023	-0.047	0.263	0.348	0.130	0.114	-0.157	0.582^{**}
EC		1	0.991^{**}	0.748^{**}	0.472^{*}	0.820^{**}	0.865^{**}	-0.098	0.562^{**}	0.124	0.324	-0.074	-0.355	-0.199	-0.381	-0.392	-0.385	0.478^{*}	-0.240	0.426^{*}
TDS			1	0.761^{**}	0.487^{*}	0.821^{**}	0.860^{**}	-0.109	0.589^{**}	0.148	0.369	-0.058	-0.365	-0.216	-0.391	-0.409^{*}	-0.405^{*}	0.490^{*}	-0.249	0.447^{*}
SO$_4^{-2}$				1	0.527^{**}	0.778^{**}	0.547^{**}	0.037	0.449^{*}	-0.062	0.344	0.029	-0.176	-0.206	-0.206	-0.304	-0.266	0.328	-0.059	0.245
NO$_3^-$					1	0.319	0.314	0.021	0.629^{**}	0.134	0.272	-0.076	-0.056	0.055	-0.119	-0.082	-0.086	0.550^{**}	-0.065	-0.068
Cl$^-$						1	0.665^{**}	-0.155	0.354	0.034	0.237	0.049	-0.182	-0.184	-0.203	-0.344	-0.271	0.497^{*}	-0.204	0.408^{*}
HC0$_3^-$							1	0.033	0.575^{**}	0.090	0.151	0-.109	-0.490^{*}	-0.184	-0.506^{**}	-0.438^{*}	-0.473^{*}	0.314	-0.220	0.493^{*}
Ca								1	0.085	-0.074	-0.117	-0.089	-0.387	-0.311	-0.338	-0.154	-0.356	-0.230	0.279	-0.496^{*}
Mg									1	0.307	0.231	-0.171	-0.372	0.052	-0.373	-0.378	-0.367	0.231	-0.085	-0.039
Na										1	0.288	-0.128	-0.115	0.150	-0.068	0.066	0.091	0.093	-0.058	-.225
K											1	0.411^{*}	-0.141	-0.125	-0.123	0.005	-0.241	0.181	-0.337	0.016
Mn												1	-0.060	-0.176	-0.134	-0.190	-0.217	-0.195	-0.133	0.096
Fe													1	0.657^{**}	0.931^{**}	0.401^{*}	0.859^{**}	0.165	-0.174	0.006
Cu														1	0.592^{**}	0.124	0.489^{*}	0.067	-0.228	-0.052
Pb															1	0.564^{**}	0.852^{**}	0.161	-0.155	0.069
Zn																1	0.553^{**}	-0.039	-0.218	-0.015
Ni																	1	0.122	-0.175	-0.023
Cr																		1	-0.183	0.202
Cd																			1	-0.273
As																				1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

Table.6.2c. Correlation between different parameters in Deep ground water of Mardan District

	pH	**EC**	**TDS**	**SO_4^{-2}**	**NO_3^-**	**Cl^-**	**$HC0_3^-$**	**Ca**	**Mg**	**Na**	**K**	**Mn**	**Fe**	**Cu**	**Pb**	**Zn**	**Ni**	**Cr**	**Cd**	**As**
pH	1	-0.123	-0.110	-0.078	-0.188	0.159	-0.293	-0.725**	0.229	0.441	0.008	0.078	-0.117	0.466	0.197	0.060	0.169	0.053	0.320	0.705**
EC		1	0.999**	0.421	0.768**	0.507	0.686**	-0.046	0.221	0.173	0.564*	0.637*	-0.333	-0.368	-0.549	-0.306	-0.408	0.061	-0.176	-0.162
TDS			1	0.417	0.772**	0.501	0.678**	-0.058	0.210	0.175	0.572*	0.652**	-0.329	-0.378	-0.534	-0.289	-0.411	0.043	-0.185	-0.166
SO_4^{-2}				1	0.807**	0.842**	0.286	-0.115	0.165	0.045	0.805**	0.327	-0.440	-0.253	-0.375	-0.327	-0.027	-0.189	-0.202	0.076
NO_3^-					1	0.667*	0.468	-0.086	0.151	-0.155	0.884**	0.693*	-0.556	-0.310	-0.465	-0.117	-0.132	-0.764**	-0.439	-0.220
Cl^-						1	0.206	-0.242	0.025	-0.008	0.636*	0.270	-0.353	-0.295	-0.352	-0.378	-0.078	-0.194	0.000	0.345
$HC0_3^-$							1	0.224	0.443	0.484	0.292	0.131	-0.211	-0.405	-0.595	-0.284	-0.464	0.421	-0.095	-0.365
Ca								1	-0.315	-0.429	-0.405	-0.195	-0.046	-0.424	-0.496	0.277	-0.375	-0.162	-0.499	-0.797**
Mg									1	0.602*	0.188	0.065	-0.531	0.536*	-0.277	-0.196	-0.175	0.571*	0.210	0.093
Na										1	0.232	0.069	-0.092	0.242	-0.101	-0.333	-0.080	0.503	0.315	0.183
K											1	0.583*	-0.189	-0.139	0.262	-0.349	0.127	-0.173	-0.039	0.059
Mn												1	-0.224	0.001	0.048	0.021	-0.008	-0.285	-0.111	0.008
Fe													1	-0.088	0.621	0.366	0.596	-0.130	0.686*	0.182
Cu														1	0.292	-0.022	0.342	0.272	0.382	0.406
Pb															1	-0.033	0.956**	0.667	0.476	0.816*
Zn																1	0.156	-0.289	-0.185	0.017
Ni																	1	0.048	0.452	0.520
Cr																		1	0.218	0.259
Cd																			1	0.550*
As																				1

*. Correlation is significant at the 0.05 level (2-tailed)

**. Correlation is significant at the 0.01 level (2-tailed).

Table 6.3. Correlation between different parameters in Soils of Mardan District

	pH	**EC**	**TDS**	**CaO**	**MgO**	**Na$_2$O**	**K$_2$O**	**Fe$_2$O$_3$**	**MnO**	**Cu**	**Pb**	**Zn**	**Ni**	**Cr**	**Cd**	**As**
pH	1	-0.345*	-0.324	0.068	0.369*	-0.184	-0.220	-0.344	-0.063	0.172	-0.072	0.099	0.129	0.283	0.602**	0.072
Cond		1	0.998**	-0.200	0.065	0.046	0.313	0.204	0.106	0.316	0.509**	-0.024	0.323	0.235	-0.284	-0.163
TDS			1	-0.189	0.081	0.038	0.326	0.201	0.081	0.319	0.500**	-0.030	0.330	0.247	-0.282	-0.153
CaO				1	-0.021	-0.238	-0.196	0.127	-0.035	-0.101	-0.166	-0.231	-0.122	0.044	-0.075	0.061
MgO					1	-0.200	0.199	0.460**	-0.304	0.459**	0.205	-0.066	0.446**	0.447**	0.491**	0.092
Na$_2$O						1	0.214	-0.069	0.236	-0.310	-0.120	0.178	-0.310	-0.299	-0.162	-0.019
K$_2$O							1	0.154	-0.590**	-0.080	0.311	-0.105	0.128	-0.039	-0.123	-0.102
Fe$_2$O$_3$								1	0.028	0.381*	0.097	-0.246	0.309	0.307	-0.085	-0.018
MnO									1	0.108	-0.244	0.095	-0.187	-0.032	-0.204	-0.125
Cu										1	0.188	0.136	0.818**	0.870**	0.193	0.095
Pb											1	-0.032	0.257	0.135	0.342	-0.028
Zn												1	-0.131	-0.046	0.050	0.017
Ni													1	0.847**	0.207	0.205
Cr														1	0.255	0.069
Cd															1	0.127
As																1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

CHAPTER 7

CONCLUSION

- The physical parameters (T, pH, TDS, EC and turbidity) were found within the permissible limits. However, few water samples showed relatively high concentrations of EC and turbidity.

- Different anions such as NO_3^-, Cl^- and SO_4^- were found within permissible limits. However, HCO_3^- was found higher than the permissible limits.

- Among the light elements Ca and Na were present above the permissible limits. While K, Mg, and Mn were found within permissible limits of WHO and USEPA, except one water sample collected from Malkabad showed high Mn concentration.

- The Fe concentration in water samples was within permissible limits except two surface water samples collected from Sirai and Bakhshali villages; and two shallow ground water samples collected from Takkar and Chingai Baba villages.

- Some water samples from the study area contained Pb above permissible limits like samples from Bakhshali, Saidabad near Takht Bhai, Sirai, Takkar, Chingai Baba and Torru.

- The trace and heavy elements such as Cu, Zn, Ni, Cr, Cd and As in water samples were found within permissible limits of WHO and USEPA. However, Ni showed relatively high concentration in one sample collected from Malkabad.

- No significant health risk was observed on the basis of HQ and CR. However, elevated concentration of certain elements in water samples may cause health problems.

- Stronger positive and negative correlation was observed among pairs of various physio-chemical parameters in water.

- The dominant texture of the soils of the study area was “Silty Loam” with color indicating highly weathered mineral configuration.

- All the physical parameters i.e., pH, EC and TDS of the soils were found within normal range.

- The major elements oxides such as CaO, MgO, Na_2O and K_2O in the soil samples were found multi folds higher than those of the normal agricultural soils, while the Fe_2O_3 and MnO were found within permissible limits.

- All the trace and heavy elements (Cu, Pb, Zn, Ni, Cr and Cd) in the soil samples were found in higher concentrations than those of normal agricultural soils.

- Soil samples showed stronger positive and negative correlation among pairs of physio-chemical parameters.

- The geogenic sources are responsible for that increasing amount of various light, heavy and trace elements in both water and soil samples of the Mardan District.

RECOMMENDATIONS

- As shallow ground water sources have been reported with relatively high values of different parameters so, it is suggested that the old dug wells and hand pumps should be renewed or replaced with deep ground water wells.

- The old pipes supplying drinking water from tube wells should be replaced with the new ones.

- Proper salinity control programmes should be adopted throughout the whole District to reduce salts content in soils and their seepage to ground water sources.

- Fertilizers and other agro chemicals should be used properly in agricultural fields so that accumulation of various hazardous elements can be avoided.

- Monitoring of both water and soils of the District Mardan in regard to environmental health risk assessment should be performed regularly in future.

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