M.Phil

ENVIRONMENTAL STUDIES OF SOILS, WATERS AND PLANTS ASSOCIATED WITH THE MAFIC AND ULTRAMAFIC ROCKS IN KABAL-MINGORA AREA, SWAT, NORTHERN PAKISTAN

By

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Dedicated To
My
Loving parents and teachers who
have always been a source of love
and strength for me

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ABSTRACT

Representative samples of water, soils and plants were collected from Mingora and Kabal areas of the district Swat for their physio-chemical and environmental investigations during this study. The physio-chemical analyses of these samples were performed by using various instruments, including atomic absorption spectrophotometer. Water samples collected from the dug wells, springs, streams and Swat river show variable concentration of physical and chemical parameters. Among the physical parameters pH is ranging from 6.95 to 7.1, electrical conductivity (EC) from 71 μS/cm to 1515 μS/cm, total dissolved solids (TDS) from 37.8 mg/l to 808 mg/l, salinity from 0 to 0.7, resistivity from 0.66 kΩ.cm to 14.1 kΩ.cm and turbidity from 0.03 NTU to 16.2 NTU in the Mingora area while the water of the Kabal area has pH from 6.78 to 7.2, EC from 70.6 μS/cm to 921 μS/cm, TDS from 37.4 mg/l to 491, salinity from 0 to 0.4, resistivity from 1.085 kΩ.cm to 78.34 kΩ.cm and turbidity from 0 kΩ.cm to 4.56 kΩ.cm. Among the light element cations Ca varies from 1 mg/l to 126 mg/l, Mg from 1 mg/l to 99 mg/l, Na from 2 mg/l to 223 mg/l and K from <1 mg/l to 22 mg/l in the water of Mingora area while in the water of Kabal area, Ca, Mg, Na and K are ranging from 6 mg/l to 58 mg/l, 5 mg/l to 53 mg/l, 2 mg/l to 118 mg/l and 1 mg/l to 28 mg/l respectively. Among the heavy and trace elements in the water of Mingora area, Fe varies from 29 μg/l to 682 μg/l, Cu from 22 μg/l to 129 μg/l, Pb from 3 μg/l to 9 μg/l, Zn from 52 μg/l to 1913 μg/l, Ni from 6 μg/l to 199 μg/l, Cr from 17 μg/l to 396 μg/l, Co from 33 μg/l to 74 μg/l and Mn from 30 μg/l to 2198 μg/l while the water of Kabal area has Fe in the range of 66 μg/l to 280 μg/l, Cu 17 μg/l to 129 μg/l, Pb 2 μg/l to 9 μg/l, Zn 47 μg/l to 890 μg/l, Ni 8 μg/l to 19, Cr 14 μg/l to 45 μg/l, Co 30 μg/l to 57 μg/l and Mn 20 μg/l to 87 μg/l.

The soil samples from both Mingora and Kabal areas have variation in both the light element oxides and the heavy and trace elements. Among the light element oxides CaO varies from 119% to 8.99%, MgO from 0.6% to 29.23%, Na_2O from 1.03% to 2.42% and K_2O from 0.36% to 2.38% in the soils of Mingora area while the soils of Kabal area have CaO, MgO, Na_2O and K_2O in the range of 2.16% to 8.11%, 0.70% to 4.66%, 1.07% to 2.68% and 0.49% to 3.59% respectively. Among the heavy and trace elements Fe is ranging from 12499 mg/l to 38763 mg/l, Cu from 9 mg/l to 87 mg/l, Pb from 34 mg/l to 98 mg/l, Zn from 10 mg/l to 142 mg/l, Ni from 207 mg/l to 2341 mg/l, Cr from 311 mg/l to 5647 mg/l, Co from 12 mg/l to 32 mg/l, Cd from 2 mg/l to 4 mg/l and Mn from 36 mg/l to 111 mg/l in the soils of Mingora area while in the soils of Kabal area, Fe, Cu, Pb, Zn, Ni, Cr, Co, Cd and Mn is varying from 20921 mg/l to 43613 mg/l, 0 mg/l to 184 mg/l, 34 mg/l to 93 mg/l, 12 mg/l to 405 mg/l, 136 mg/l to 302 mg/l, 123 mg/l to 679 mg/l, 4 mg/l to 32 mg/l, 2 mg/l to 4 mg/l and 45 mg/l to 105 mg/l respectively.

Both the light element cations and heavy and trace elements have greater variability in about ten families and their species of various plants collected from the Mingora and Kabal areas. Among the light elements Ca varies from 287 mg/l to 20645 mg/l, Mg from 25 mg/l to 7119 mg/l, Na from 22 mg/l to 341 mg/l and K from 906 mg/l to 26044 mg/l. Among the heavy and trace elements Fe is ranging from 1625 mg/l to

10056 mg/l, Cu from to 7 mg/l to 68 mg/l, Pb from to 2 mg/l to 9 mg/l, Zn from 4 mg/l to 43 mg/l, Ni from 27 mg/l to 289 mg/l, Cr from 39 mg/l to 358 mg/l, Co from 5 mg/l to 9 mg/l, Cd from 0.089 mg/l to 0.389 mg/l and Mn from 5 mg/l to 374 mg/l.

The quality of water in the Mingora and Kabal areas was evaluated by comparing the physio-chemical parameters with various permissible limits. It was found that among the physical parameters, pH, EC, TDS, salinity, resistivity and turbidity are within the permissible limits. However, EC in certain dug wells in Mingora area and turbidity in the water from river Swat exceeds the permissible limit. Among the light elements, Ca, Mg, Na and K are generally within the permissible limit. However, Mg contents in the water samples collected from the dug wells and springs within or in the vicinity of the mélange zone in Mingora area are relatively high. Among the heavy and trace elements, Fe, Mn, Pb, Zn, Ni, Cr and Co in most of the waters of both Mingora and Kabal areas are generally within the permissible limit. Nickel and chromium in the waters samples collected from dug wells and springs within or in the vicinity of the mélange zone in Mingora area are remarkable high and are making the water of the area unsafe for drinking purposes.

The soils of the Mingora and Kabal areas were evaluated on the basis of light element oxides and the heavy and traced elements by comparing their concentration with the normal agricultural soil. All the light element oxides (i.e., CaO, MgO, Na_2O and K_2O) in the soils of both Mingora and Kabal areas are exceeding those of normal agricultural soil. However, the CaO and MgO are remarkably high within or in the premises of mélange zone in Mingora area. All the heavy and trace elements, except Zn and Mn, in the Mingora and Kabal areas are exceeding those of normal agricultural soil. Ni and Cr in the soil samples collected from within or in the vicinity of mélange zone are multifold high as compare to the normal agricultural soil and are considered as hazardous for the ecosystem of the region.

Greater variability in the adsorption/absorption rate of all the light, heavy and trace elements from the soils by the various plants species has been noticed in the Mingora and Kabal area. High concentrations of Fe in *Asteraceae*, Mn in the *Cannabinaceae,* Cu in *Poaceae*, Pb in *Simarubaceae* and *Papilionaceae*, Zn in *Cannabinaceae,* Ni in *Papilionaceae* and *Poaceae* and Cr in *Papilionaceae* and *Poaceae* have been observed. The concentrations of Co and Cd are very low in all the plants. The multifold enrichment of Cr and Ni in the *Papilionaceae* and Poaceae as compared to the other plants of the study area suggests that these plants have the ability to uptake and translocate Cr (VI) and Ni in their tissues. Therefore, these plant species could be used as biogeochemical indicator for chromite deposits and are also considered as hazardous the inhabitants of the area.

It is concluded from this study that the lithologies of the area have played a major role in the enrichment of various light, heavy and trace elements in the waters, soils and plants of the area. The increase in Ca can be attributed to the massive amphibolites exposed in Kabal area. Very high concentration of Mg, Ni and Cr in these media can be attributed to the mafic and ultramafic rocks of the mélange zone in the Mingora area.

This increasing of Ni and Cr concentration in the waters, soils and plants could be having carcinogenic effects on the ecosystem of the area as of their transferring from forage to the animals and then to the inhabitants of the area through meat and milk of these animals. Detail investigations are suggested to be carried in this regard in the area of study.

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CHAPTER 1

INTRODUCTION

Environment is the circumstances or conditions that surrounds an organism or group of organisms, or the complex of social or cultural conditions that affect an individual or community (Cunningham & Saigo, 1999). Environment provides us natural resources on which our life sustains e.g., soil, water, air, major and minor elements. More than 99% of the human body is made of six major elements i.e., oxygen, carbon, hydrogen, nitrogen, calcium and phosphorus. Other elements do occur in the body, as they do in rocks, but only at very low concentrations, as trace elements. (Montgomery, 1995). Now a days there is growing concern for the conservation and preservation of environmental resources for future generation as the population on this planet keeps on growing. Prominent among the natural resources are soil, water and forest. It would be these natural resources, which would be used to supply food, shelter and clothing needs to the increasing population. (Khattak, 1997). In the globally changing scenario, environment is the main focusing factor and a huge threat for the entire community. The increased use of natural resources for human needs generated solid waste, toxic effluents and air emissions eventually adversely affecting human and its environment (Kakar et al., 2005).

Environmental pollution is the introduction of substances into environment that are responsible to cause hazards to human health, harm to living resources and ecosystem, damage to structure or amenity, or interference with genuine use of the environment. Currently environmental pollution may be attributed largely to the abuse of natural resources mainly for industrial development. The global atmosphere and hydrosphere are continuously intoxicated by the incorporation of poisonous gases, noise, heat, industrial effluents and different types of garbage. Linked with environmental pollution are air pollution, water pollution and soil pollution (Cunningham & Saigo, 1999).

Of all the gifts of nature, none is more indispensable to man than soil, lying over the rocky core of the earth at different depths, this complex mixture of animal. vegetable and mineral matter is one of the four requisites for life. Along with sunlight, air and water, soil nourishes all plant life, it provides a habitat for large number of animals and micro-organisms that decompose plant residues, there by helping to cycle the nutrients on which most of the plants growth depends. It supports the growth of arable crops, grassland and trees on which man depends for food, fiber, and wood for fuel and as a building material, all of which supports human life. Without soil, this planet would be as barren as the moon. An increasing world population requires more of these resources (Misra & Mani, 1991).

Soils are helpful in identification of the existence of rocks of special character in the uphill or underneath area respectively. These soils, if produced from the weathering of mafic and ultramafic rocks, are of greater interest in regard to environmental and exploration studies. The mafic and ultramafic rocks are generally enriched in heavy metals such as chromium, nickel, cobalt, cadmium, iron, lead, zinc and copper etc. and similarly the weathered soil of these rocks will also be enriched in the heavy metals and hence their adsorption by plants and dissolution in water of the area could be resulted in the environmental degradation of the area and also helps in the identification of pathfinders for the various types of mineral deposits (Kifayatullah et al., 2001; Shah et al., 2004; Leavitt & Goodell, 1979; Brooks 1983).

The geo-botanical studies of the vegetation growing on the residual soil of mafic and ultramaffic terrains show that vegetation patterns in terms of composition, density, frequency, are distinctly different over mafic and ultramafic terrains than over the other lithologies of the sequence. This can be attributed to an increase in the nickel, chromium and magnesium concentration in specific plants growing over the ultramafic terrain compared with the country rocks (Limae et al., 1997; Shah et al., 2004). These plants, having high concentration of heavy metals, are eaten-up by the grazing animals and thus these heavy metals are transferred to the human beings through meat and milk. The contamination of water due to geogenic sources in the areas where the rocks enriched in the metals are hazardous to living organism. The drainage through acid mines in the sulfide deposits and contamination of surface and ground water of the area by heavy metals is the best example, so the surface and ground water of the area where mafic and ultramafic rocks are exposed are of special interest for possible contamination investigation.

Water pollution is contamination of water by foreign matter that deteriorates the quality of water. It may be the presence of any foreign substance (organic, inorganic, radiological, or biological) in water, which tends to degrade its quality so as to constitute a hazard or impair the usefulness of the water (U.S. Public Health Service, 1962). Water pollution covers pollutions in liquid forms like ocean pollution and river pollution. As the term applies, liquid pollution occurs in the oceans, lakes, streams, rivers, underground water and bays, in short liquid-containing areas. It involves the release of toxic substances, pathogenic germs, substances that require much oxygen to decompose, easily soluble substances and radioactivity etc. that become deposited upon the bottom and their accumulations will interfere with the condition of aquatic ecosystems. For example, the eutrophication: lack of oxygen in water body caused by excessive algae growths because of enrichment of pollutants (Botkin et al, 1995). Elements can be quite mobile in water, and most of the environmental problems are ultimately associated with the contamination of surface and ground water. When water percolates through soil, some of the minerals and organic substances are dissolved in it. Water is a medium in which pollutants can be transported and chemically transformed. Prior to their entrance into living organisms, some pollutants proceed through one additional medium, known as soil (Baig, 1996). Major sources that lead to water pollution include, petroleum products, synthetic agricultural chemicals, heavy metals hazardous wastes, excess organic matter, sediment, air pollution and soil pollution etc. (Botkin et al, 1995).

Pakistan is one of the developing countries having population 132 million (City Report Rawalpindi, 1998). Most of environmental problems in our country are anthropogenic as industries, population and unplanned urbanization is growing at fast rate. This has resulted into high rate of deforestation and expansion of un-metallic roads, poor sewerage system, industries without treatment plants and widespread slums, especially in or around the major cities and industrial estates. Such a scenario is the cause of tremendous environmental pollution in air, water and soils of these areas (Hamidullah et al., 1998).

The Swat Kohistan region in the northern parts of Pakistan is mostly occupied by various metamorphosed basic to intermediate rocks. Along a 70 km course of the Swat River there are three NE-trending belts consisting, from south to north, of amphibolites, pyroxene granulites, and quartz diorites. These rocks extend E-W for more than 250 km between Nanga Parbat and eastern Afghanistan (Jan & Kempe, 1973; Tahirkheli & Jan 1979; Coward et al.; 1982). In the south the amphibolites are thrusted over the Precambrian to Palaeozoic sialic metasediments and younger granitic rocks. The occurrence of blueschists, serpentinites and other ultramafic rocks along this thrust is suggestive of major tectonic activity (Coleman, 1971; Moores, 1973) and the fault is now considered to be an extension of the Indus suture which marks the subduction of the Indian plate under the "Asiatic"mass (Jan, 1977, 1980; Tahirkheli et al., 1979).

The rocks of the study area are mainly a part of the mafic and ultramafic sequences of the Mingora-Shangla melange of the Indus Suture Zone (ISZ). The Indus Suture Zone in the northern Pakistan is consisting of tectonic melanges between the Kohistan island arc and the Indo-Pakistan plate. These melanges are named as Malakand-Mohmand ophiolites melange and Mingora-Shangla melange (Kazmi & Jan, 1997). The Malakand-Mohmand ophiolites melange, known as the Dargai Klippe, stretching from Daragi to Utmankhel for 30 km, consists predominantly of ultramafic rocks with subordinate amount of mafic rocks (Ahmad, 1984). The Mingora-Shangla melange zone has a series of tectonic melanges in Mingora, Shangla, Shamozai, Charbagh and Allai areas. These melanges are mainly composed of mafic and ultramafic rocks, greenschist, greenstone and blueschist (Kazmi & Jan 1997). Mingora and Kabal (study areas) have mafic and ultramafic rocks. The rocks of the area are mainly a part of the mafic and ultramafic sequences of the Mingora-Shangla melange zone of the Indus Suture Zone (ISZ).

SWAT DISTRICT

District Swat which is the entry point to beautiful northern areas of Pakistan covering an area between 34° - 45′ to 35°-55′ north latitude and 72° - 08′ to 72°-50′ east longitude (Fig. 1.1). The total area of the district is 5337 square kilometer. The twin cities of Mingora and Saidu Sharif are district as well divisional Headquarters (DCR, 1998). Swat is divided into two sub divisions i.e., Matta and Babozi subdivision. Mingora is the capital city of Swat. Mingora has been an important trading center for the last 2000 years. It is known for its embroided cloth, shawls, woodwork and precious stones. Emerald mine is located in the premises of Mingora.

Kabal is the tehsil of Babozi subdivision. It is located 10 km in the northwest of Mingora and covering an area of about 40026 hectors between latitude 34°- 45′ to 35° - 55′ and longitude 72°- 08′ to 72° - 50′. The average elevation of the area varies from 700m to 2500m from mean sea level. It is bounded from south by river swat, from north by Matta , from east by Babozi and from west by lower Dir. The population density of tehsil Kabal is 17.90 persons per hectare. Total population of Kabal is 716244, out of which 370141 are male and 346103 are female. The average household size of the area is 9.1 persons. Densely populated villages of tehsil are Kabal, Kotlai, Hazara, Shah Derai, Bala Samai, Kanju, Kala Kaly, Koza Bandai, Deolai, Qalangay, Totano Bandai, and Dardyal. The average growth rate of the area is higher than the national growth rate of 2.61 percent during 2005 (DCR, 1998).

Topography

Topographically Swat is a mountainous area and can be divided into two regions i.e. Swat Kohistan and Swat Valley. Swat Kohistan is the mountainous area on the upper reaches of the Swat River. Swat Valley, is further subdivided into Bar (Upper Swat) and Kuz (Lower Swat). The elevation of swat river valley, at the southern boundaries of the district, is over 600 meters and rises rapidly towards the north. There are several mountain peaks ranging from 4500 to over 6000 meters above sea level. In Swat district, there are numerous scenic spots in the valleys. The valleys are lush green with thickly forested mountains, some of them are permanently under snow throughout the year.

Rivers and Streams

The Swat River rises from the Shandur or Mashabar Range bordering Swat district with Chitral in the north and flows south and south west approximately dividing the district into two halves. The other prominent rivers or nalas are Harnoi khwar. Deolai khwar, Chail khwar and Daral khwar.

Climate

Climatically the area falls within the subtropical and moist temperate zone with heavy rain and snowfall; having sever winter and pleasant summer. The summer season is short and moderate. It is warm in the lower Swat valley like Kabal and Mingora, but cool and refreshing in the upper northern part. The hottest month is June with mean maximum and minimum temperature of 33^0C and 16^0C respectively. The coldest month is January and the mean maximum and minimum temperature is 11^0C and -2^0C respectively. The winter season is long and extends from November to March. Rains and snow occur during this season and the temperature usually falls below freezing point. The amount of rainfall received during winter season is more than that of summer season. The mean annual rainfall is 1004 mm. Maximum rainfall occurs during the months of February (160 mm) and March (238 mm). The highest rainfall recorded during the month of March is about 242 mm (Pakistan Meteorological Department. Karachi). Hails are very frequent during the months of July and August and cause damage to the herbaceous vegetation and aerial parts of the woody species. Snowfall frequently occurs from November to February. Maximum snowfall occurs during December and January. Snowfall is highest at high altitudes of the area like Samai, Goda Manrai, Dardyal, Sarbala while low in the lower areas like Kabal, Dagai, Dadahara, Hazara, Aligrama, Bara Bandai and Ningolai.

Relative Humidity

Relative humidity is an important atmospheric factor governing the distribution of vegetation. Relative humidity of the study area is highest in January, February and March having 71%, 80% and 73% respectively.

Flora

Various species of botanical plants characteristic of different altitudes are found in the district, medicinal herbs such as henbane, beladdonna and banafsha etc. are also found, pine trees grow in the forest areas.

Fauna

Swat is well known for its shooting grounds. During shooting seasons, which is from the 1st October to middle of March, duck partridge, chakor and pheasant are found. The wild mountain sheep (Markhor) is found in the higher regions of the valley. Bear, panther, musk deer, golden fowl, black and brown bear are also found on the surrounding mountains.

Agriculture and Related Sectors

Agriculture: Agriculture is the largest sector of the economy and is the main source of livelihood of the rural population. The topography of the district is such that not all the land is suitable for cultivation. The land holdings are small averaging two acres. Total reported area in the district is 506528 hectares out of which 98845 hectares is cultivated (Director of Agriculture Statistics NWFP.1997-98). Most of the cultivation is being carried out in the southern areas of the district mainly in Mingora, Barikot, Kabal, Matta and Khwazakhela as well as in subvillages of Kabal like Dadahara, Gadi, Dagai, Akhunkaly, Hazara, Aligrama, Kanju, Galoch, Sirsinai, Deoali, Shah Derai, Tutano Bandai, Bara Bandai, Koza Bandai and Ningoali. Land use pattern of Swat district for the year 1997-98 is shown in Table 1.1.

Table 1.2 shows the performance of the agricultural sector of the district in terms of area cultivated and crops production. The soil of the district is very fertile and the area has a lot of potential to become a major source of fruits and vegetables due to its moderate climate. This is especially true in case of out of season vegetables. The onion and potatoes are the main products. Honey farming is another agro-based industry of the region but it has been limited to the scale of a cottage industry and there has been no effort to organize it on a large scale.

Soil: The soil of Mingora and Tehsil Kabal consists of varied soil constituents ranging from silt loam to sandy loam and loam. Soil of the valley has great potential of fertility and with high organic matter.

Irrigation: The main source of irrigation is water canals supplied from Swat River and its tributaries. Among these, Nikpikhel irrigation canal and Fatehpur irrigation canal in Kabal and Fatehpur areas are built. These canals irrigate 1842 and 338 hectares of land respectively.

Horticulture: Among fruits apple, pear, persimmon (wild), walnut, grape, apricot plum and citrus fruit are grown all over the district. The details of fruit orchards are given in Table 1.3.

Food: The staple diet of the people is Roti made of wheat or maize flour. Wheat, rice and maize is their major manure of every day life although they also enjoy rice at festivals and at special occasions. The people are also fond of meat. Tea is very popular in Swat.

Forestry

About 20 percent of land area of the district is under forest. Government has declared these forests as protected forests. Most of the forest is concentrated in the northern areas of Kalam and Madyan. Kail fir, spruce and chir are the varieties planted in the south of the district while in the northern and higher plains, *Deodar* is the most popular variety in addition to those already mentioned. The vegetation of the study area varies with the climatic change, especially the rainfall. Vegetation of the area can be classified into the following types:

Scrub Forests: These forests have actually disappeared due to extensive clearance for cultivation and cutting of trees for meeting the timber and fuel wood requirements of the population. The main species are *Accacia modesta, Olea ferruginea, Dodonea viscose,* *Justacia adahtoda, Punica granatum*, Celtis australis, *Vitex negundo, Zizyphus jujube, Zizyphus nummularia* and *Indigofera gerargiana.*

Chir Forest: Chir forests are found in Tutano Bandai and Shah Dearai blocks. With *Pinus roxburghi* the broad leaved associates are *Quercus incana, Ficus carica, Acacia modesta, Celtis australis, Olea ferruginea*. The undergrowth is dense in open places and consists of *Dodonea viscose, Justacia adhatoda, Myrsine Africana, Rusbus fruticosus, Plectranthus rogosus, Jasminum spp., Zanthoxylum aromatum.*

Blue Pine Forest: These forests are mostly confined to upper Swat, however, small groups of *Deodar* are met within Goda Manri. The broad leaved associates are *Juglans regia, Pyrus pashia, Diospyros lotus*. A few trees of *Populus* and *Ficus spp.* are also present. The undergrowth consists of *Plectranthus rogosus, Rosa moschata, Rubus fruticosus, Cannabis sativa, Oxalis corniculata, Artemisia scoporia, Viola canescene, Ruellia graecizan* and *Robdosia rogosus.*

Oak Forests: *Quercus incana, Quescus ilex*, grow in Taghma village *while Quercus* ilex are also available in Shah Derai. The assocaiation of Oak is *Olea ferruginea, Punica grantum, Berberis lyceum, Gymnosporia royleana.* The undergrowth of the Oaks is scanty and composed of *Artemisia scoparia, Oxalis corniculata, Indigofera gerardiana, Cynodon dactylon, Achyranthus aspera, Tagetes erecta, Tagetes minuta.*

Cultivated Trees: Tree plantation is usually done for timber, fruit and fuelwood. Important trees planted are *Melia azedarach, Robinia pseudocacia, Diospyrus lotus, Pyrus malus, Pyrus communis, Prunus armeniaca, Prunus domestica, Morus alba, Morus nigra.*

The forests of Swat do not only add to the beauty of the area but also play an important part in the economy of the area. Wood is a major source of cooking fuel especially for habituations close to forests. Natural Gas is supplied to Mingora only. Population pressure and new constructions play an important role in the depletion of forests. The situation becomes more chronic during the summer months with the influx of tourists in Swat. Unregulated grazing and soil erosion has limited the regeneration capacity of the forests.

Conservation of forests in swat is a major challenge. Presently two foreign assisted programs are in operation to promote forest development, Malam Jabba Afforestation Program (Italy assisted) and Environment rehabilitation program for Malakand division (Dutch assisted). These programs aim at setting up nurseries, promoting social forestry fencing of forests, construction of forest paths and development of forests without compromising the ecology.

AIMS AND OBJECTIVES

The study, has the following objectives:

- Determination of chemical parameters of soils, waters and plants of the area.
- Identification, characterization and categorization of the soils, waters and plants of the area on the basis of their chemical characteristics.
- Identification of the environmental impacts of mafic and ultramafic rocks on the living organism of the area.
- The identification of bio-indicators for the mineral exploration

GEOLOGY OF THE STUDY AREA

The geology of the Mingora and Kabal areas has been mapped by Afridi et al. (1995) on the scale of 1:50, 000. According to this map (Fig. 1.1) the rocks exposed in the study area belong to the Indian plate, mélange zone and Kohistan island arc. The Indian plate rocks are (1) Swat granite gneisses (Martin et al., 1962; Jan & Tahirkheli, 1969; DiPietro et al., 1996), (2) amphibolites with garnetifrrouces schist, biotite schist hornblende and marbles of Marghazar Formation (Pogue et al., 1992; DiPietro, 1990; 1991), and (3) graphitic phyllites of the Saidu Formation; (Kazmi et al., 1984; Treloar et al., 1989a; 1989 b; Lawrence et al., 1989; DiPietro, 1990; 1991; 1993). The mélange zone rock are chaotic assemblages of serpentinite, green schist, talc-carbonate schist and metabasalts (Kazmi et al., 1984; Jan & Jabeen, 1990; Arif & Jan, 1993). The Kohistan island arc rocks are mainly massive amphibolites of southern or Kamila amphibolite belt

(Jan, 1979; 1988; Bard et al., 1980; Treloar et al., 1990; Shah et al., 1992). Most part of the study area is covered by the quaternary deposits mainly composed of stream channel deposits and also the weathering products of the aforementioned rocks exposures in the area of study (Fig. 1.2).

PREVIOUS WORK

No environment related work in detail has been conducted in the study area before, however, the quality of drinking water in some areas of district Swat was investigated by Imran (2005). Zada (2006) studied the nutrients in a plant (*Lycopersicon esculentum*) and their relationship with the soil of Gharri in district Swat. Extensive geological work has been carried out by various scientists in the past in district Swat and adjoining areas. Afridi et al. (1995) prepared a geological map of the Mingora and adjoining areas. Arif (1994) and Arif et al. (1996), studied the ultramafic rocks from the Swat valley ophiolites and the related emerald mineralization of the study area. Rehman and Zeb, (1970) presented the detail petrographic account of the rocks of the Shah Dheri, Kabal area, Swat. Tariq (1984) studied the rock of the Jawan Pass, Kabal village in Swat district. Khan and Bangash (1983) studied the petrography of the rocks of Mahak area near Mingora, Swat. Shah et al. (1986) investigated the ground water condition of the Nikpikhel area in Mingora, Swat. Kazmi et al. (1984), Treloar et al. (1990) and DiPietro (1990), (1991), (1993) have also worked on the geology of the Mingora and adjoining areas.

Table. 1.1. Land use pattern of district Swat

S. NO.	*LAND UTILIZATION STATUS*	*AREA IN HECTARES*
1.	Total reported area	506528
2.	Cultivated area	98845
	i. Net sown area	91718
	ii. Current fallow	7127
3.	Un-cultivated area	407683
	i. Waste area	6663
	ii. Forest area	135400
	iii. Not available for cultivation	265620

Source: Director of Agriculture Statistics NWFP.1997-98

Table .1.2 . Acreage and production of major crops in Swat District

CROPS		*AREA IN HECTARES*			*PRODUCTION IN TONES*		
		Irrigated	**Rainfed**	**Total**	**Irrigated**	**Rainfed**	**Total**
Kharif							
1.	Maize	18950	42050	61000	40308	40487	80795
2.	Rice	7600		7600	16720		16720
Rabi							
1.	Wheat	14539	36710	51249	29026	35820	64846
2.	Barley	160	794	954	207	712	919

Source: Director of Agriculture Statistics, NWFP.1997-98

Table. 1.3. Area Under Orchards, Swat District

S. NO	ORCHARD	AREA (Ha)	PRODUCTION (TONES)
1.	Apple	2750	20460
2.	Walnut	923	9303
3.	Apricot	570	5804
4.	Plum	500	4851
5.	Persimmon	470	4256
6.	Pear	413	7288

Source: Director Agriculture statistics, NWFP. 1997-98

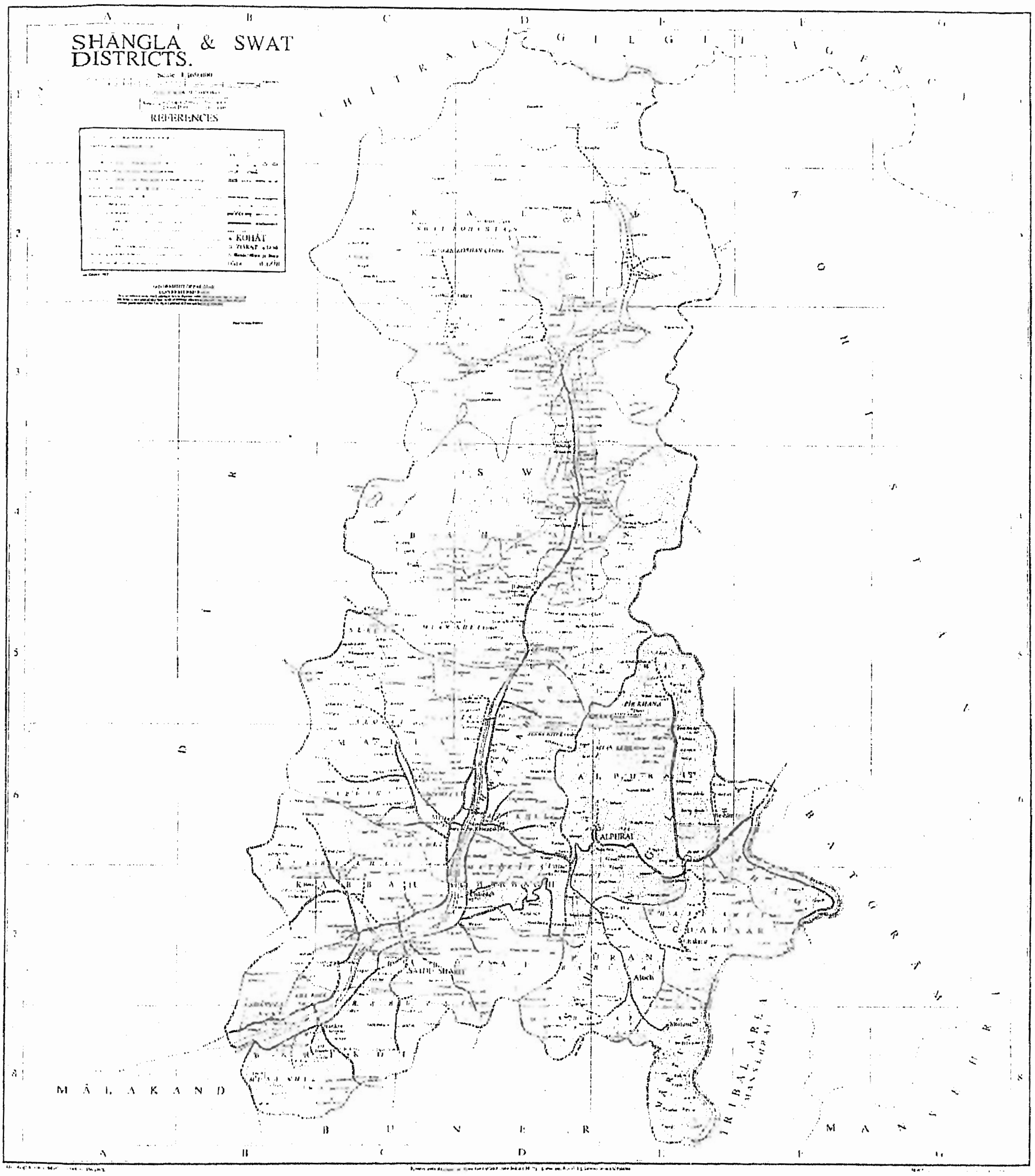

Fig. 1.1. Map showing the geographic locations of District Swat.

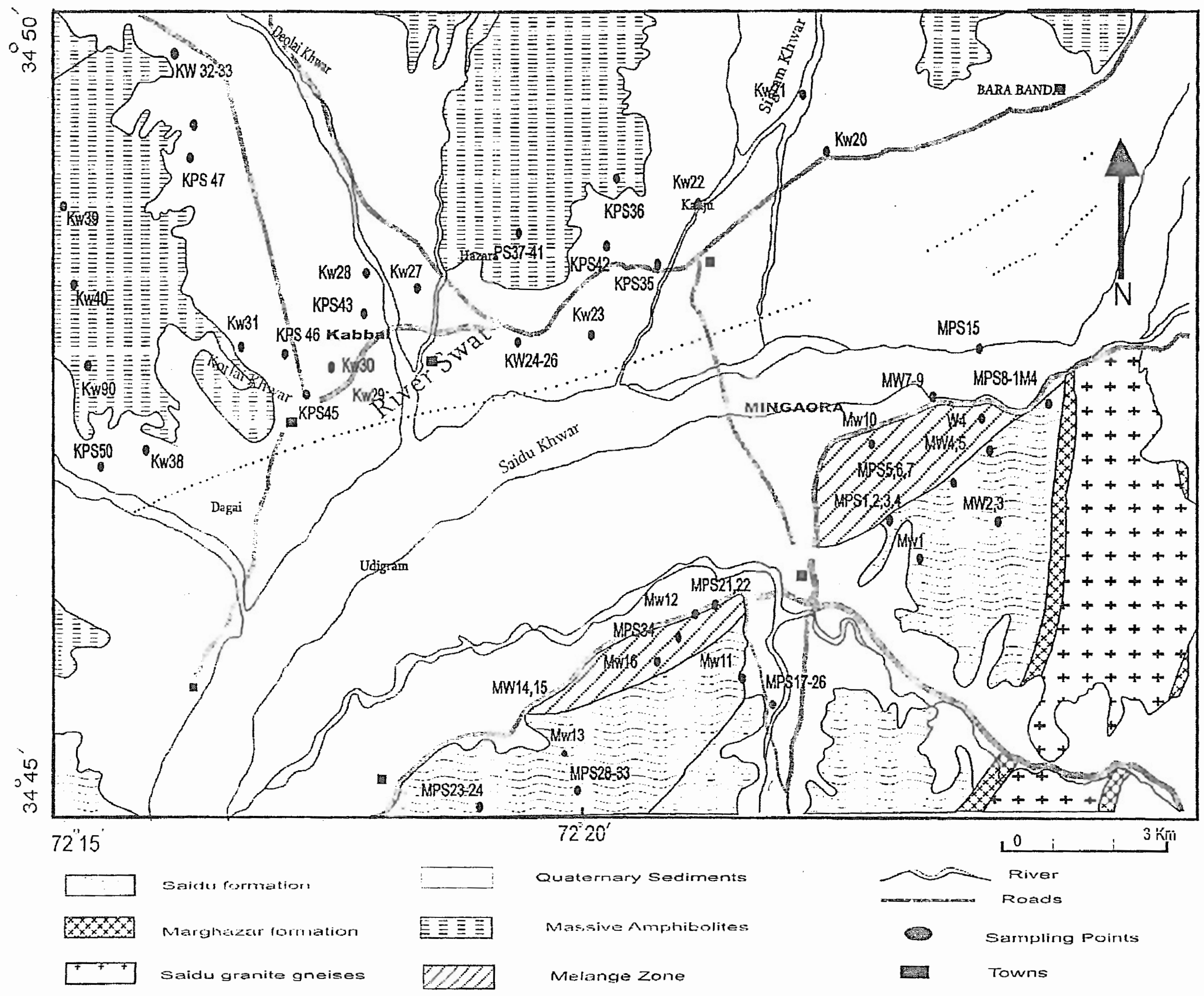

Fig. 1.2. Geological map of the Mingora and Kabal areas of Swat (modified after Afridi et al., 1995). The samples' locations for water, soils and plants are also shown.

complete 48 hours dissolution. The contents of each flask were then filtered through Whatman # 42 filter paper. The filtrate was used for the determination of water-soluble constituents by using various instruments such as Consort Electrochemical analyzer. The same methodology was used as is explained in the following section.

WATER

The following parameters in the water samples were measured on site:

a. pH
b. Electrical Conductivity
c. Temperature
d. Total Dissolved Solids
e. Salinity
f. Resistivity
g. Turbidity

a. Determination of pH: Consort Electrochemical analyzer was used to measure pH in surface and ground water samples. First the Electrochemical analyzer was calibrated with buffer solution of 4.0, 7.0, and 8.0. The electrode was then immersed into each water sample and reading was directly noted from the analyzer. For accuracy the standardization of the instrument was checked by the buffer solution after running few samples.

b. Determination of Electrical Conductivity (EC): Consort Electrochemical analyzer was used for the determination of electrical conductivity of water samples in μS/cm.

c. Determination of Temperature: Temperature of both surface and ground water was determined in the field with the help of a thermometer.

e. Total Dissolved Solids (TDS): TDS values were calculated in mg/l for all water samples by Consort Electrochemical Analyzer.

f. Determination of Salinity: Salinity was measured in mg/l in all water samples by Consort electrochemical analyzer.

g. Determination of Resistivity: The Resistivity in water samples was measured in kΩ.cm by Consort electrochemical analyzer.

h. Turbidity: Turbidity of both surface and ground water samples was measured in NTU by using JENWAY 6035 Turbid meter.

CHEMICAL PARAMETERS

SOIL

Preparation of solution B: 0.5 g of moisture free powder soil samples were taken in teflon beakers. 10 ml hydrofluoric acid (HF) and 4 ml perchloric acid ($HClO_4$) was added to each beaker and after one hour of heating on hotplate, 2 ml perchloric acid was added again and let the contents of the beaker to evaporate. After formation of past, little water and 4 ml perchloric acid again were added and heated for a while so that the paste was dissolved. The contents of each teflon beaker was taken in 250 ml volumetric flask and made to the volume with double- deionized water and kept for the determination of Ca, Mg, Na, K and Fe by using flame atomic absorption spectrophotometer.

Preparation of solution C: 1 g of each moisture free powdered soil sample was taken in a teflon beaker and added 5 ml of hydrofluoric acid (HF) and heated on hotplate for an

CHAPTER 2

METHODOLOGY

FIELD METHODOLOGY

Soil sampling

Representative samples of soil were collected from selected areas of Mingora and Kabal during field. Core samples from a depth of 0 – 20 cm (Horizon A) and 20 – 40 cm (Horizon B) were collected with auger from each site (Fig. 1.2). Soil samples were properly labeled and transferred to polythene bags. The color and texture of these samples were noted with naked eye. Random sampling procedure was followed for different soils of different sites. Samples description is given in Annex -1.

Plant Sampling

Plants growing on the mafic and ultramafic terrains and other barren terrains were collected in the field. All the plants were uprooted, packed in the kraft paper and then collected in the polythene bags (Fig. 1.2). Herbarium sheets were prepared. These plants were identified and the botanical names (Annex-2 & 3) were given to each plant with the help of a plant taxonomist of Botany Department, University of Peshawar.

Water Sampling

Representative water samples were collected from dug-wells, tube-wells, springs, streams and Swat River in the study area in cleaned polyethylene bottles (Fig. 1.2). The polyethylene bottles were washed with distilled and double-deionized water and then rinsed with water to be collected as sample. Two water samples were collected from each site. One bottle was filled with water having no air bubble (air-tight), while the other bottle was added with few drops of nitric acid after it was filled with the water from the same spot. Various parameters of water such as temperature, pH, dissolved oxygen, alkalinity and electric conductivity were determined on spot by using various

d. Determination of Dissolved Oxygen (DO): In both surface and ground water dissolved gases are present. Major gases of concern are oxygen and carbon dioxide. The DO was measured in water samples by using JENCO DO meter, model 9173.

e. Total Dissolved Solids (TDS): TDS values were calculated in mg/l for all water samples by Consort Electrochemical Analyzer.

f. Determination of Salinity: Salinity was measured in mg/l in all water samples by Consort electrochemical analyzer.

g. Determination of Resistivity: The Resistivity in water samples was measured in kΩ.cm by Consort electrochemical analyzer.

h. Turbidity: Turbidity of both surface and ground water samples was measured in NTU by using JENWAY 6035 Turbid meter.

CHEMICAL PARAMETERS

SOIL

Preparation of solution B: 0.5 g of moisture free powder soil samples were taken in teflon beakers. 10 ml hydrofluoric acid (HF) and 4 ml perchloric acid ($HClO_4$) was added to each beaker and after one hour of heating on hotplate, 2 ml perchloric acid was added again and let the contents of the beaker to evaporate. After formation of past, little water and 4 ml perchloric acid again were added and heated for a while so that the paste was dissolved. The contents of each teflon beaker was taken in 250 ml volumetric flask and made to the volume with double- deionized water and kept for the determination of Ca, Mg, Na, K and Fe by using flame atomic absorption spectrophotometer.

Preparation of solution C: 1 g of each moisture free powdered soil sample was taken in a teflon beaker and added 5 ml of hydrofluoric acid (HF) and heated on hotplate for an hour. To this solution added 15 ml of aqua regia and let the contents of Teflon beaker to evaporate. Then added 20 ml of 2 N hydrochloric acid (HCl), and heated for a while. Then this solution was diluted to 30 ml with double – deionized water and filtered in a test tube. This solution was kept for the determination of Fe, Cu, Pb, Zn, Ni, Cr, Co and Cd by using flame atomic absorption spectrophotometer.

PLANTS

Preparation of solution D: After identification, and nomenclature of each plant, all the plants were dried and cut into small pieces and then pulverized in the chopper (Grinder). Two g of each dried and pulverized plant sample was taken Pyrex beaker separately. 10 ml of nitric acid (HNO_3) was added to each beaker and kept for 24 hours and then heated slowly on hot plate to evaporate HNO_3. Four ml of perchloric acid was added to each beaker and again heated slowly till the evaporation of perchloric acid. For intensive extraction 10 ml of aqua regia (3:1 of HCl and HNO_3) was added to all samples. Once again heated slowly on hot plate till the evaporation of aqua regia. Then the contents of each beaker were filtered and the filtrate was made to the final volume of 50 ml. This solution of each plant sample was kept for the determination of major and trace elements by using atomic absorption spectrophotometer.

Determination of various elements by Atomic Absorption

For the determination of light elements i.e., Ca, Mg, Na and K, solution B of soil, solution D of plants and the acidified water samples were used. The solutions were further diluted where needed.

A. Light Elements

a. Determination of Calcium (Ca) and Magnesium (Mg): For the determination of calcium and magnesium, 1000 mg/l standard solution was prepared by dissolving 2.479 g of $CaCO_3$ and 4.952 g of $MgCO_3$ in 50 ml of deionized water, 10 ml of conc. HCl was added and after this the solution was made up to in 1000 ml volumetric flask with deionized water. This was a standard of 1000 mg/l of Ca and Mg. Three working standards i.e., 2.5, 5, and 10 mg/l were prepared from 1000 mg/l standard stock solution.

For the determination of Ca and Mg concentrations the atomic absorption was calibrated under the following instrumental standard conditions:

Element	Ca	Mg
Mode	Absorption	Absorption
Wavelength	422nm	285.2nm
Slit width	0.4nm	0.4nm
Air flow	51/min	51/min
Fuel flow	51/min	to best flame
Burner height	10mm	10mm

After preliminary standardization of the atomic absorption by the working standard solutions, the concentrations of Ca and Mg were determined in soil, water and plant samples.

b. Determination of Sodium (Na) and Potassium (K): Standard stock solution of 1000 mg/l of Na and K was prepared by dissolving 2.542 g of NaCl and 1.91 g of KCl in deionized water, and the volume was made up to 1000 ml in a volumetric flask. Working standards of 2.5, 5, and 10 mg/l respectively were prepared from 1000 mg/l standard stock solution.

For the determination of Na and K concentrations the atomic absorption was calibrated under the following instrumental standard conditions:

Element	Na	K
Mode	Emission	Emission
Wavelength	589 nm	766 nm
Slit width	0.2 nm	0.4 nm
Air flow	51/min	51/min
Fuel flow	11/min	11/min
Burner height	20 mm	20 mm

After preliminary standardization of the atomic absorption by the working standard solutions, the concentrations of Na and K were determined in soil, water and plant samples.

B. Heavy and trace elements

a. **Determination of Iron (Fe):** 1000 mg/l standard stock solution of Fe was prepared by dissolving 3.511g of Mohr's Salt [$Fe(NH_4)_2 (SO_4)_2.H_2O$)] in deionized water in a volumetric flask of 1000 ml and made the volume in volumetric flask. Working standards of 2.5, 5, and 10 mg/l were prepared from 1000 mg/l stock solution. The instrument was calibrated by using following standard instrumental conditions:

Mode	Absorption
Wavelength	248.3 nm
Slit width	0.2 nm
Fuel flow	1.21/min
Air flow	51/min
Burner height	10 mm

After standardizing the instrument by working standards, the concentration of Fe was determined in soil and plant solutions in mg/kg.

b. **Determination of Copper (Cu):** 1000 mg/l standard stock solution of copper was prepared by dissolving 1.00 g of copper metal in (1:1) HNO_3 and deionized water in a1000 ml in a volumetric flask. Further working standard fractions of 2.5, 5 and 10 mg/l were prepared from 1000 mg/l standard stock solution. The instrument was calibrated under the following standard conditions:

Mode	Absorption
Wavelength	325.8 nm
Slit width	0.4 nm
Fuel flow	11/min
Air flow	51/min
Burner height	10mm

After standardizing the instrument by working standards, the concentration of Cu was determined in soil and plant solutions in mg/kg.

c. Determination of Lead (Pb): 1000 mg/l standard stock solution was prepared by dissolving 1.598 g of lead nitrate in 200 ml of deionized water containing 1.5 ml of conc. HNO_3 and the volume was made to 1000 ml in the volumetric flask with deionized water. Further working standards of 2.5, 5 and 10 mg/l were prepared from 1000 mg/l standard stock solution. The instrument was calibrated under the following standard conditions:

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

After standardizing the instrument by working standards, the concentration of Pb was determined in soil and plant solutions in mg/kg.

d. Determination of Zinc (Zn): 1000 mg/l standard stock solution was prepared by dissolving 1.00 g of Zinc metal in 20 ml (1:1) HCl and was diluted to 1000 ml in a volumetric flask with deionized water. Further working standards of 2.5, 5 and 10 mg/l were prepared from 1000 mg/l standard stock solution. The instrument was calibrated under the following standard conditions:

Mode	Absorption
Wavelength	213.9 nm
Slit width	0.2 nm
Fuel flow	1 l/min
Air flow	5 l/min

Burner height	10 mm

After standardizing the instrument by working standards, the concentration of Zn was determined in soil and plant solutions in mg/kg.

e. **Determination of Nickel (Ni):** 1000 mg/l standard stock solution was prepared by dissolving 1.273 g of Nickel Oxide in a minimum volume of 10% v/v HCl and diluted with de-ionized water upto 1000 ml. Working standards of 2.5, 5 and 10 mg/l were prepared from 1000 mg/l standard stock solution. The instrument was calibrated under the following standard conditions.

Mode	Absorption
Wavelength	232.0 nm
Slit width	0.2 nm
Fuel flow	1l/min
Air flow	5l/min
Burner height	10 mm

After standardizing the instrument by working standards, the concentration of Ni was determined in soil and plant solutions in mg/kg.

f. **Determination of Chromium (Cr):** 1000 mg/l standard stock solution was prepared by dissolving 2.828 g of anhydrous potassium dichromate in 200 ml of deioinized water containing 1.5 ml of conc. HCl and was diluted to 1000 ml in a volumetric flask. Further fractions of 2.5, 5 and 10 mg/l were prepared from 1000 mg/l standard stock solution. The instrument was calibrated under following standard conditions:

Mode	absorption
Wavelength	357.9 nm
Slit width	0.2 nm
Fuel flow	4.5l/min

Air flow	5.01/min
Burner height	10 mm

After standardizing the instrument by working standards, the concentration of Cr was determined in soil and plant solutions in mg/kg.

g. **Determination of Cobalt (Co):** For Cobalt determination in samples first standard stock solution was prepared. 1000 mg/l standard stock solution of Co was prepared by dissolving 1.407 g of Cobalt Oxide (Co_2O_3) in 20 ml of hot conc. HCl. When cooled, the solution was diluted to a volume of 1000 ml in a volumetric flask. From this 1000 mg/l stock solution working standards of 2.5, 5 and 10 mg/l respectively were prepared. Cobalt in soil and plant samples was determined by calibrating the instrument under following standard instrumental conditions:

Mode	Absorption
Wavelength	240.7nm
Slit width	0.4 nm
Fuel flow	1.21/min
Air flow	51/min
Burner height	10 mm

After standardizing the instrument by working standards, the concentration of Co was determined in soil and plant solutions in mg/kg.

h. **Determination of Manganese (Mn):** For Mn determination in samples first standard stock solution was prepared. 1000 mg/l standard stock solution of Mn was prepared by dissolving 1.000 g of manganese metal in a minimum volume of (1+1) HNO_3. Diluted this solution to 1000 ml with 1% (v/v) HCl in a volumetric flask. From this 1000 mg/l stock solution working standards of 2.5, 5 and 10 mg/l respectively were prepared. Mn in soil and plant samples was determined by calibrating the instrument under following standard instrumental conditions:

Mode	Absorption
Wavelength	279.5
Slit width	0.2 nm
Fuel flow	2.0/min
Air flow	51/min
Burner height	10 mm

After standardizing the instrument by working standards, the concentration of Mn was determined in soil and plant solutions in mg/kg.

Determination of Trace elements in Water

Trace elements were determined in both surface and ground water samples by Graphite furnace Atomic Absorption spectrophotometer, in the following way:

a. Determination of Iron (Fe): For determining Fe concentration in water samples 1000 mg/l standard stock solution was prepared by dissolving 1 gram of pure iron metal in minimum quantity of HCl and was made to the volume in one liter volumetric flask with deionized water. Working standards of 2.5, 5 and 10 µg/l were prepared from standard stock solution. Fe concentration in all water samples was determined on the graphite furnace atomic absorption spectrophotometer under following standard instrumental conditions.

Mode	Absorption
Wavelength	248.3 nm
Slit width	0.2 nm
Tube/site	Pyro/Platform
Matrix modifier	0.05mg $(NO_3)_2$
Pretreatment T °C	1400
Atomization T °C	2400

After standardizing the instrument by working standards, the concentration of Fe was determined in water in mg/l.

b. Determination of Copper (Cu): For determination of Cu, first of all 1000 mg/l standard stock solution was prepared by dissolving 1 g of copper metal in 30 ml of (1:1) HNO_3. This solution was diluted to one liter with deionized water. Working standards of 2.5, 5 and 10 μg/l were prepared from the standard stock solution. Then instrument was calibrated under the following instrumental conditions:

Mode	absorption
Wavelength	324.8 nm
Slit width	0.7 nm
Tube/site	Pyro/Platform
Matrix modifier	Nil
Pretreatment T °C	1200
Atomization T °C	2300

After standardizing the instrument by working standards, the concentration of Cu was determined in water in mg/l.

c. **Determination of Lead (Pb):** For the determination of lead in water samples, first of all 1000 mg/l of Pb standard stock solution was prepared by dissolving 1.598 g of lead nitrate ($Pb(NO_3)_2$) in 200 ml of de-ionized water in volumetric flask. Then added 10 ml of conc. HNO_3 and diluted the resulting solution to 1000 ml with deionized water in volumetric flask. This solution contained 1000 mg/l of lead. Three different working standards of 2.5, 5 and 10 μg/l were prepared from standard stock solution. The instrument was calibrated under the following standard conditions:

Mode	Absorption
Wavelength	283.3 nm
Slit width	0.7 nm

Tube/site	Pyro/Platform
Matrix Modifier	0.2 mg $NH_4H_2PO_4$
Pretreatment T °C	1200
Atomization T °C	2300

After standardizing the instrument by working standards, the concentration of Pb was determined in water in mg/l.

d. Determination of Zinc (Zn): For the determination of Zinc in water samples, first of all 1000 mg/l of Zn standard stock solution was prepared by dissolving 100 mg of zinc metal in 20 ml of (1:1) HCl and diluted to 1000 ml with de-ionized water in volumetric flask. Then added 10 ml of conc. HNO_3 and diluted the resulting solution to 1000 ml with de-ionized water in volumetric flask. This solution contained 1000 mg/l of Zn. Three different working standards of 2.5, 5 and 10 μg/l were prepared from standard stock solution. The instrument was calibrated under the following standard conditions:

Mode	Absorption
Wavelength	213.9 nm
Slit width	0.7 nm
Tube/site	Pyro/Platform
Matrix Modifier	0.2 mg $NH_4H_2PO_4$
Pretreatment T °C	1200
Atomization T °C	2300

e. Determination of Nickel (Ni): 1000 mg/l stock solution of Ni was prepared by dissolving 1 gram of Ni metal in a minimum volume of (1:1) HNO_3 and diluting to 1 liter with deionized water. From 1000 mg/l standard stock solution, working standards of 2.5, 5 and 10 μg/l were prepared respectively. The instrument was properly calibrated with working standards and then all water samples were run on graphite furnace atomic absorption spectrophotometer for determination of Ni concentration under following standard conditions:

Mode	Absorption
Wavelength	232.0 nm
Slit width	0.2 nm
Tube/site	Pyro/Platform
Matrix modifier	0.05 mg $(NO_3)_2$
Pretreatment T °C	1400
Atomization T °C	2500

After standardizing the instrument by working standards, the concentration of Ni was determined in water in mg/l.

f. Determination of Chromium (Cr): For determination of Cr, first of all 1000 mg/l standard stock solution was prepared by dissolving 3.735 g of K_2CrO_4 in deionized water and diluting to one liter with deionized water. Working standards of 2.5, 5 and 10 μg/l were prepared from the standard stock solution. Then instrument was calibrated under the following instrumental standard conditions:

Mode	absorption
Wavelength	357.9 nm
Slit width	0.7 nm
Tube/site	Pyro/Platform
Matrix modifier	0.05mg $(NO_3)_2$
Pretreatment T °C	1600
Atomization T °C	2500

After standardizing the instrument by working standards, the concentration of Cr was determined in water in mg/l.

g. Determination of Cobalt (Co): 1000 mg/l standard stock solution of Co was prepared by dissolving 1.0 g of Cobalt metal in 30 ml of (1:1) HCl and was diluted to one liter with deionized water. Then working standards of 2.5, 5 and 10 µg/l were prepared from standard stock solution respectively. Then instrument was calibrated under the following instrumental standard conditions:

Mode	absorption
Wavelength	240.7 nm
Slit width	0.2 nm
Tube/site	Pyro/Platform
Matrix modifier	0.05mg $(NO_3)_2$
Pretreatment T °C	1400
Atomization T °C	2500

After standardizing the instrument by working standards, the concentration of Co was determined in water in mg/l.

CHAPTER 3

WATER CHEMISTRY

INTRODUCTION

We live on the water planet. A precious film of water – most of it is salt water- covers about 71% of the earth's surface. Most of the organisms on the earth are made up mostly of water. For example, a tree is about 60% water by weight, and humans and most animals are about 65% of water (Miller, 1994).

Water is the single most important agent sculpturing the earth surface. Mountains may be raised by the action of plate tectonics and volcanism but they are shaped primarily by water. Streams carve valleys, level plains, and move tremendous amounts of sediments from place to place (Montgomery, 1995).

Significance of water

Fresh water is a vital resource for agriculture, manufacturing, transportation, and countless other human activities. Water also plays a key role in moderating climate, and diluting pollutants. Water is such a good solvent that it dissolves a part of nearly every thing it meets; gases from the atmosphere, salts of many different kinds from rocks and minerals of soil, organic coloring matter from decaying vegetation, even traces of silica, the nearly insoluble substances that is the chief component of ordinary white sand. Even rain water contains dissolved oxygen and nitrogen, with much smaller quantity of carbon dioxide, all three derived from the atmosphere. It also contains minute amounts of every accidental impurity that air itself contains; solid particles of dust, ash and soot, together with traces of common salt, ammonium salts, sulphuric acid, and perhaps as many as a dozen other identifiable organic impurities. The accidental impurities in water are sometimes even beneficial. For example, dissolved oxygen relieves de-aerated water of its flate taste, and is needed to support the life of aquatic organisms, from microscopic plants or animals upward to fish. Any impurity that makes water unfit to drink, or less fit for any other use, is said to contaminate the water. (Deming, 1975)

Water is truly a wondrous substance that connects us to one another, to other forms of life, and to the entire planet. Despite its importance, water is one of the earth's most poorly managed resources. We waste and pollute it; we also charge too little for making it available, thus encouraging even greater waste and pollution of this vital renewable resource ((Miller, 1994).

Water contamination and pollution

Pollution means the presence of any foreign substance (organic, inorganic, radiological, or biological) in water, which tends to degrade its quality so as to constitute a hazard or impair the usefulness of the water (U.S. Public Health Service, 1962). Water pollution is contamination of water by foreign matter that deteriorates the quality of water. Water pollution covers pollutions in liquid forms like ocean pollution and river pollution. As the term applies, liquid pollution occurs in the oceans, lakes, streams, rivers, underground water and bays, in short liquid-containing areas. It involves the release of toxic substances, pathogenic germs, substances that require much oxygen to decompose, easy-soluble substances, radioactivity, etc. that become deposited upon the bottom and their accumulations will interfere with the condition of aquatic ecosystems. For example, the eutrophication: lack of oxygen in a water body caused by excessive algae growths because of enrichment of pollutants. Major sources that lead to water pollution include, petroleum products, synthetic agricultural chemicals, heavy metals hazardous wastes, excess organic matter, sediment, air pollution and soil pollution etc (Daniel & Edward, 1995).

Chemical aspects of water pollution: During past few years the pollution of water resources has become a major subject of investigation in all industrialized countries. The concern of the effect of pollution caused by water on the environment and on the man himself, has now started to arise in developing countries too, where both rural and urban communities require large supplies of water to cope with the ever increasing demands of expanding population. This is specifically true for cities and towns that draw water from streams, which in turn, become the water supplies for down-stream users.

Human health may be affected by ingesting polluted water directly or in food, by using it for agriculture and industry. Ingestion is, however, only one possible pathway to exposure. Man can be exposed to water pollutants through other types of direct contact, e.g. in recreation or the use of water for personal hygiene. In addition to the possible effects of ingestion and other direct water contacts, chemical water pollutants may influence Man's health indirectly by disturbing the aquatic ecosystems or by accumulating in aquatic organisms used in human food. The assessment of pollutant level in water depends on source, body burden and locality (WHO, 1971). Chemical pollutants that chiefly affect human health includes nitrites, nitrates, phosphates, fluorides, arsenic, mercury, cadmium, lead and other toxic metals (Schmidt & Knotek, 1970; McClure, 1970; Alder, et al, 1970; Schwartz, 1967; Lutz et al, 1967).

Due to increasing siltation (emanating from physical disruption), biological contamination (by agents of human diseases and animal and plant pests) and chemical pollution (arising out of industrial effluents and agricultural chemicals etc.) in Pakistan the quality of water is under constant deterioration. Researches of the National Institute of health, Islamabad and Pakistan Medical Research Council have revealed that a large proportion of diseases in Pakistan are caused by the consumption of polluted water. (Environmental Profile of Pakistan, 1983).

Classification of water pollutants: Generally water pollutants include oxygen demanding wastes (sewage), disease causing agents, plant nutrients, oil, inorganic chemicals and mineral substances, sediments, radioactive materials, heat and synthetic organic compounds (pesticides and detergents).

Inorganic constituents: This category of water pollutant include inorganic salts, mineral acids and heavy metals like mercury (Hg), lead (Pb) and arsenic (As) (cumulative poison).

The sources of inorganic constituents are:

- Smelting processes wastes
- Metallurgical processes
- Mining operations
- Natural processes

Inorganic chemicals enter water from municipal and industrial wastewater and urban runoff. These kill fish and interfere with suitability of water for drinking and industrial use. Most of the inorganic constituents concentrate in food chain. A prominent example has been the occurrence of mercury in water. A number of industrial processes like chlorine alkali plants make use of Hg, some of which is eventually disposed off in waste water effluents. Anaerobic bacteria in bottom mud can convert inorganic mercury into methyl mercury (CH_2Hg+), which can be concentrated in living things and lead to mercury poisoning (Tyagi & Mehra, 1990).

Acid mine drainage has been the primary source of pollutants that increase acidity. The actual pollutants present in mine drainage, have been a sulfuric acid (H_2SO_4) and soluble compound of iron. During mining operations, in deep mines, the strata between the coal seam and the, surface have been disturbed. Fissures appear through which water drains into the mine in from many surface areas. This water containing the harmful pollutants is eventually discharged into surface streams, either naturally or through man made processes (Tyagi & Mehra, 1990).

Effects

Major effects of inorganic chemicals are given below:

- Aquatic life destruction: At pH below 4.0 all vertebrates, most invertebrates and many microorganisms get destroyed. This pH lowering is due to addition of sulphuric acid to water.

- Corrosion: Water having pH lower than 6.0 can bring about excessive corrosion of plumbing systems, boats, piers, and related structures.
- Agricultural crop damage: Acidity and alkalinity of irrigation water cause agricultural crop damage. Problems may arise if the pH drops below 4.5. Such acidic water increases the solubility of such substances as Fe, Al, and Mg salts. These ions, at the resulting high concentrations, have been some time's toxic to plants (Tyagi & Mehra, 1990).

WATER QUALITY

PHYSIOCHEMICAL PARAMETERS

pH

Measurement of pH is one of the most frequently used tests in water chemistry; particularly every phase of water supply is pH dependent. pH refers to a scale of intensity of acidity or alkalinity. It is a measurement of the concentration of H^+ ions in water, pH below 7 is termed as acidic and above 7 is termed as basic. Normal water usually has pH value in the range of 6.5- 8.5 (Greenberg., Trussell & Clesceri, 1992).

pH in all the water samples of the study area are presented in Table 3.1 and graphically shown in Fig. 3.1. It is clear from the table that the pH is ranging from 6.78 to 7.2 and are considered in the normal range. No significant change in the pH has been noticed between the water samples collected from the Mingora and Kabal areas. The low pH value (6.78) is recorded in sample No. KW21, collected from pumping well having depth of 15-18 feet at Kanju village in Kabal area. The average amount of pH in the water samples of Mingora and Kabal area is 7.00 and 6.99 respectively.

Electrical Conductivity (EC)

EC is measure of the ability of an aqueous solution to conduct electricity. This ability depends upon the presence of ions, their total concentration, mobility, valence relative concentration, and temperature. Electrical conductivity indicates the chemical behavior and chemical quality of surface and ground water of an area. It alters remarkably with change in temperature. It increases about 2% for each 1^0C increase in temperature (Allen, 1989).

Electrical conductivity of water samples of Kabal and Mingora is varying from 70.6 µS/cm to 1515 µS/cm respectively. In Mingora, the lowest EC is in sample No. MW18 (71 µS/cm) while the highest EC is noted in sample No. MW14 (1515 µS/cm) collected a 40 feet deep dug well at Qambar area (Table 3.1; Fig. 3.2). In Kabal the lowest EC is reported in sample No. KW19 (70.6 µS/cm) and highest in sample No. KW38 (921 µS/cm) (Table 3.1; Fig. 3.2). The average amount of EC in the waters of Mingora and Kabal area is 663.1 µS/cm and 458 µS/cm respectively. It is clear from the data in Table 3.1 and Fig. 3.2 that electrical conductivity in the water of Kabal area is relatively low as compared to that of Mingora area.

Temperature

The surface water temperatures are subjected to large variations than ground water temperatures. The temperature of ground water is effected by exposure of the well to sun light, depth of the water table and the surrounding atmospheric pressure. Temperature of groundwater is generally higher than the air temperature during winters and lower than air temperature during summers. The recorded temperature for Mingora and Kabal areas is ranging from 19 °C to 33.3 °C respectively. In Mingora 22 °C temperature is recorded for sample No. MW43 collected from Swat River at Kanju bridge towards Mingora (The water was speedy and clear) and 32 °C for sample No. MW44 collected from Swat River at Landakai. The temperature of water samples of Kabal area is ranging from 19 °C for sample No. KW19 collected from the tributary of Swat River at Ningulai, to 33.3 °C for sample No. KW37 collected from a spring (Table 3.1). The average temperature of the waters of Mingora and Kabal areas is 26.3 °C and 25.3 °C respectively. It is clear from the data that there is no significant change in the water samples of Mingora and Kabal areas as for as the temperature is concerned.

Dissolved Oxygen (DO)

Dissolved Oxygen in water is one of the essential elements for aquatic life. If organic matter such as untreated human or animal waste is added to water, DO levels decreases as microorganisms use DO to decompose organic matter. Dissolved Oxygen values for water samples of both Mingora and Kabal area are given in Table 3.1 and graphically presented in Fig. 3.3. DO is ranging from 0.13 ppm to 3.75 ppm in sample Nos. MW45 and MW1 respectively in the Mingora area (Table 3.1; Fig. 3.3). Sample No. MW45 was collected from a tap at Berarai, Khwazakhela. While sample No. MW1 was collected from a tap, used as a source of drinking water at Rajabad village of Maluk Abad Union council, Mingora. Dissolved Oxygen in water of Kabal are is lowest in the sample No. KW27 (0.1 ppm) and highest in the sample No. KW19 (3.1 ppm). Sample No. KW27 was collected from stream having muddy water at Hazara. While sample No. KW19 was collected from a tributary of Swat River at Ningulai. The average amount of DO in the waters of Mingora and Kabal area is 2.62 ppm and 2.35 ppm respectively. It is clear from the Table 3.1 and Fig. 3.3 that the DO values in the waters of both Mingora and Kabal are similar.

Total Dissolved Solids (TDS)

TDS are made up primarily by inorganic salts with small concentration of organic matter. Contributing ions are mainly carbonate, bicarbonate, chloride, sulfate, nitrate, sodium, potassium, calcium and magnesium. Major contribution to TDS in water is the natural contact with rocks and soil with minor contribution from pollution. In some cases considerable impact from snow and ice control of roads is also witnessed. Total dissolved solids contents of 500 mg/l are a desirable limit, which has been extended to upper limit of 1000 mg/l in drinking waters.

TDS in water samples are limited to the solids in solution. High content of solids in water has been inversely correlated with increased morbidity and mortality rates (possibility of potential danger of soft water mainly on cardiovascular diseases). According to WHO, the aesthetic water contains < 1000 mg/l of TDS while drinking water contain <1200 mg/l. Drinking water having increased amount of TDS is unpalatable.

The results of total dissolved solids (TDS) are given in Table 3.1 and are graphically presented in Figure 3.4. TDS values in the waters of Mingora are ranging from 37.8 mg/l in sample No. MW18 collected from River Swat near River Pearl Hotel to 808 mg/l in sample No MW14 collected from dug well, having 40 feet depth, at Qambar village. In water samples collected from Kabal area the TDS is ranging from 37.4 mg/l in sample No. KW19 collected a tributary of Swat at Ningulai to 491 mg/l in sample No. KW38 collected from a dug well at Landy village. The average amount of TDS in the waters of Mingora and Kabal areas is 353 mg/l and 244 mg/l respectively. It is clear from the Table 3.1 and Figure 3.4 that the water form Kabal area is having lower amount of total dissolved solids as compared to that of Mingora area.

Salinity

Salinity of water is its acid neutralizing capacity. Salinity of surface and ground water is a function of carbonate, bicarbonate and hydroxide contents.

Salinity in the water samples of Mingora is ranging from negligible amount to 0.7. While in Kabal waters salinity ranging from 0.2 to 0.4 (Table 3.1). In this respect the Mingora value is more saline as compared to that of Kabal. The average amount of salinity in the waters of Mingora and Kabal areas is 0.32 and 0.2 respectively.

Resistivity

Resistivity was measured for both surface and ground water of Mingora and Kabal areas and the results are given in Table 3.1 and presented graphically in Figure 3.5.

It is ranging from 0.66 kΩ.cm in water sample No. MW14 collected from a dug well, 40 feet deep in Qambar village to 14.1 kΩ.cm in sample No. MW18, collected from Swat River near River Pearl Hotel (Table 3.1). In the water of Kabal area the resistivity is ranging from 1.085 kΩ.cm in sample No. KW38, collected from a dug well at Landay village, to 78.34 kΩ.cm in sample No. KW21 collected from a pumping well having depth of 15-18 feet at Kanju village. The average resistivity of the waters of Mingora and Kabal areas is 3.78 kΩ.cm and 5.874 kΩ.cm respectively. The resistivity of Mingora and Kabal area are more or less the same except in few samples.

Turbidity

Turbidity is one of the important drinking water quality parameter. Turbidity in water samples was measured by Consort Electrochemical Analyzer and the results are given in Table 3.1 and graphically presented in Figure 3.6. The turbidity in water of Mingora area varies from 0.03 NTU to 16.2 NTU while that of Kabal area is ranging from negligible amount to 4.56 NTU (Table 3.1; Fig. 3.6). The average turbidity of the waters of Mingora and Kabal area is 2.27 NTU and 0.70 NTU respectively.

LIGHT ELEMENTS

Calcium (Ca)

The presence of calcium in water supplies results from passage through or over deposits of limestone, dolomite, gypsum and gypsiperous shale. The calcium content may range from zero to several hundreds milligrams per liter, depending on the source and treatment of the water. Chemical softening treatment, reverse osmosis, electrodialysis, or ion exchange is used to reduce calcium and associated hardness (Allen, 1989).

The concentrations of Ca in both surface and ground waters of Mingora and Kabal areas are given in table 3.2 and graphically presented in Figure 3.7. Ca is varying from 0.81 mg/l in sample No. MW5, collected from spring water at Maluk Abad to 126.35 mg/l in sample No. MW11, collected from a dug well, having depth of about 30 feet in Rahim Abad in Mingora area. In the water of Kabal area, Ca is ranging from 6.26 mg/l in Sample No. KW19 to 58.15 mg/l in sample No. KW27. The waters of both the areas have similar contents of Ca, except in sample Nos. MW11 and MW12 collected from dug well having depth of about 30 feet at Rahim abad, and dug well having depth of 30 feet at filling station in Rahim Abad respectively. The average concentration of Ca in the water of Mingora is 34.17 mg/l and in that of Kabal area is 41.37 mg/l.

Magnesium (Mg)

Magnesium ranks eighth among the elements in order of abundance and is a common constituent of natural water. Important contributors to the hardness of water, magnesium salts break down when heated, forming scales in boilers. Its concentrations greater than 125 mg/L have a cathartic and diuretic effect. The methods for softening are similar to those of calcium (Allen, 1989).

The concentration of Mg in the water samples collected from Mingora and Kabal areas are given in Table 3.2 and are graphically presented in Figure 3.7. It varies from 0.51 mg/l in sample No. MW10 to 99.35 mg/l in sample No. MW5. Lowest Mg concentration is present in tube well water of Kanra Baba, Mingora while the highest concentration is found in the spring water at Maluk Abad towards Fizagat in Mingora. At Kabal Mg concentration in water is ranging from 5.07 mg/l in sample No. KW24 in ground water of Aligrama to 56.10 mg/l in sample No.KW38 in groundwater of Landy village. The average concentration of Mg in the Mingora and Kabal area is 26.41 mg/l and 14.05 mg/l respectively. It is clear from the Table 3.2 and Figure 3.8 that the water of Mingora area is relatively enriched in Mg as compare to that of Kabal area.

Sodium (Na)

Sodium (Na+) comes in the body mainly by taking salt (NaCl) and backing soda ($NaHCO_3$). The presence of the sodium in the body is important as it controls equilibrium, balances and controls water balance. Low sodium diets are recommended for treating hypertension (WHO, 1999).

Sodium is also the most important and abundant element in natural waters. Nearly all sodium compounds are readily soluble, and since it does not take part in precipitation reactions in solutions. Concentration of sodium varies widely, depending upon the origin of water ranging from few ppm to 100000 ppm. In seawater, where sodium is most abundant, the concentration is about 1000 ppm. Some of the sodium compounds, ion excessive concentration are harmful to man and may be injurious to fish and other aquatic life. Probably, the most adverse effect of high sodium concentration is related to irrigation. All natural waters have measurable quantity of Na. Its quantity in ground water varies from about 0.2mg/l in humid and snow-fed regions to over 100,000 mg/l brines in contact with salt beds (Karanth, 1993).

The concentrations of Na in the water samples of Mingora and Kabal area are shown in Table 3.2 and are graphically presented in Figure 3.7. Sodium is ranging from 1.61 mg/l in sample No. MW43 to 223.05 mg/l in sample No MW6 in waters of Mingora (average = 14.77 mg/l) and 2.01 mg/l in sample No. KW19 to 117.70 mg/l in sample No. KW31 (average = 21.13 mg/l) in the water of Kabal area. Very high concentration of Na is reported in the sample No. MW6 (223.05 mg/l), collected from a well having depth of 60 feet at a car washing service station near emerald mines in Mingora area and in sample Nos. KW26 (105.70 mg/l), KW31 (117.70 mg/) and KW38 (110.95 mg/l) collected from a 40 feet deep dug well at Aligrama, dug well in a Silk Mill in Kabal village and a dug well at Landay respectively in the Kabal area.

Potassium (K)

It is similar in many respects to sodium but differs significantly in several aspects as it is found in very low concentration in water as compared to sodium, thus low concentration in water favors the biological process. The proper balance between potassium and sodium must be maintained (Allen, 1989).

The principal sources of potassium are the feldspars, orthoclase and microcline ($KAlSi_3O_3$). Potassium rocks are less soluble than sodium, calcium and magnesium. Potassium is the essential constituent for plants and animals. However for plants, it is required in trace quantities and excessive concentrations are harmful to a normal plant growth, and it is recognized that this constituent should be balanced with other mineral requirements. Potassium is also found in natural waters. Its concentration varies from (1mg/l or less to about 10- 15 mg/l) in potable waters, and from 100mg/l to over several thousand mg/l in some brines and hot springs (Allen, 1989).

The concentration of K in the waters of Mingora and Kabal areas are reported in Table 3.2 and is graphically presented in Figure 3.7. Potassium contents in sampled water varying from 0.13 mg/l in sample No. MW15 in tube well water of Qambar to 21.65 mg/l in sample No. MW13 (average = 5.35 mg/l) in Mingora area. In Kabal area the K contents are ranging from 0.56 mg/l in sample Nos. KW41 and KW42 to 27.85 mg/l in KW26, collected from dug well at Aligrama and tube well at Meelagah and dug well at Kotali respectively with an average amount of 3.58 mg/l. The water from Mingora area is relatively enriched in K as compare to that of Kabal area.

HEAVY AND TRACE ELEMENTS

Heavy metal concentration in waters can be attributed to both natural and anthropogenic sources. The most significant sources of metals are weathering of rocks and volcanic activities from which the released metals find their way into the water bodies. A large quantity of metals also suspends into the atmosphere from where they can reach the waters through dry deposition and with rainfall. The natural sources of atmospheric heavy metal contamination include mainly the dried water droplets from oceans, dust particles from volcanoes, erosion from soil, weathering of rocks and forest fires. Biodegradation of dead animals and plants also contribute significantly to background levels of metals in waters (Agarwal, 2002).

Heavy and trace elements selected for the present study are Iron (Fe), Copper (Cu), Lead (Pb), Zinc (Zn), Nickel (Ni), Chromium (Cr) Cobalt (Co) and Manganese (Mn). Brief description of the target heavy and trace elements is given below.

Iron (Fe)

Iron with manganese occur quite frequently in natural waters and presents no health hazards at concentrations normally found in natural waters. Iron in very small quantity may cause color problems. Iron concentrations of 0.3 mg/l can cause color problems. Additionally, some bacteria use iron compounds as energy source, and the resulting slime growth may produce taste and odor problems (WHO, 1999).

The concentration of Fe in the waters of both Mingora and Kabal areas are given in the Table No. 3.3 and are graphically represented in Figure 3.8. Fe concentration varies from 29 μg/l in the water sample MW7 collected from a tube well at Hayat Abad to 886 μg/l in sample No. MW43 collected from Swat River at Kanju Bridge with an average amount of 212 μg/l in Mingora area. Fe concentration is ranging from 66 μg/l in sample No. KW25, collected from dug well above marble processing unit, having depth of 40-50 feet at Aligrama to 930 μg/l in sample No. KW19 collected at Ningulai from River Swat tributary with an average amount of 207 μg/l in Kabal area.

Copper (Cu)

Copper is a very common metal that occurs naturally in the environment and spreads through natural phenomena. It enters the air, mainly through release during the combustion of fossil fuels. Copper in air remain for an eminent period of time, before it settles when it starts to rain. Most copper compounds settle and are bound to either water sediment or soil particles Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. Copper can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms (Gurdeep & Trivedi, 1992).

Humans widely use copper. For instance it is applied in the industries and in agriculture. The production of copper has lifted over the last decades and due to these copper quantities in the environment have expanded. Copper can be found in many kinds of food, in drinking water and in air. Because of that humans absorb large quantities of copper each day by eating, drinking and breathing (Agarwal, 2002). The absorption of copper is necessary, because copper is essential for human health. High concentration of copper causes prominent health problems. Occupational exposure to copper often occurs, where its contagion can lead to a flu-like condition known as metal fever. This condition is usually pass after two days and is caused by over sensitivity. Long-term exposure to copper causes irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhoea (Agarwal, 2002).

Copper and its compounds have high acute and chronic toxicity to aquatic life. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants. Chronic toxic effects may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behavior (Environmental Bureau of Investigation, 1997).

The Cu concentration in the waters of both Mingora and Kabal areas are given in Table 3.3 and Figure 3.8. In Mingora its concentration varies from 22 μg/l in sample No. MW12 of dug well having 30 feet depth a filling station, Rahimabad, to 129 μg/l in sample No. MW17 collected from a in stream at Marghazar with an average amount of 43 μg/l. While in Kabal 17 μg/l Cu is noticed in sample No. KW21, collected from a well, having depth of 15-18 feet at Kanju village, and 129 μg/l in sample No. KW41 of tube well, from Melagah in Kabal area with average amount of 41.2 μg/l. Cu concentration in the water samples of Mingora and Kabal areas are similar to greater extent.

Lead (Pb)

Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. Lead pipes are used as drains from the baths. Alloys include pewter and solder. Tetraethyl lead ($PbEt_4$) are used for its anti knocking quality in gasoline. Lead is one of the metals that have the most damaging effects on environment. It occurs naturally in the environment (Agarwal, 2002). Lead is highly toxic and is naturally available in all environmental media in small concentrations. Mining, smelting and processing of lead and lead-containing metal ores generate the majority of lead emissions from stationary sources (JICA, 2000). However, most lead concentrations that are found in the environment are a result of human activities.

Lead accumulates in the bodies of water and soil organisms. These will experience health effects from lead poisoning. Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present. Soil organisms suffer from lead poisoning, too. It can enter the human body through uptake of food. Lead can enter (drinking) water through corrosion of pipes. This is more likely to happen when the water is slightly acidic. It causes several unwanted effects, such as: disruption of the biosynthesis of hemoglobin and anemia, a rise in blood pressure, kidney damage, miscarriages and subtle abortions (Agarwal, 2002).

The concentrations of Pb in the water from Mingora and Kabal areas are given in the Table 3.3 and Figure 3.8. It is ranging from 56 µg/l to 117 µg/l (average 89 µg/l) in Mingora and from negligible amount to 116 µg/l (average 84 µg/l) in Kabal area. The average concentration of Pb in the waters of Mingora and Kabal areas is more or less similar (Table 3.3).

Zinc (Zn)

Zinc is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. Normally its level does not exceeds 0.01 to to 0.05 mg/l in surface and ground water respectively. Zinc is not considered to be a toxic element but imparts an undesirable astringent taste to water and may appear opalescent and develop a greasy film on boiling, when its concentration exceeds 3 mg/l, reducing the acceptability and aesthetic value of water. Absorption of low concentration of zinc causes loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis (Agarwal, 2002).

The concentration of Zn in the waters of Mingora and Kabal areas have been determined and the results are shown in Table 3.3 and are graphically presented in Figure 3.8. Zn is ranging from 52 µg/l to 1913 µg/l (average 214 µg/l) in the waters of Mingora area and 47 µg/l to 890 µg/l (average 130 µg/l) in the Kabal area. Very high amount of Zn has been reported in the sample No. MW10 (810 µg/l) and sample No. MW45 (1913 µg/l) of the Mingora area and in sample Nos. KW20 (810 µg/l) and KW35 (447 µg/l), collected from a stream at Kanju village, and a dug well in a service station at Sersenai village in the Kabal area respectively.

Nickel (Ni)

Nickel is silvery white, hard, malleable, and ductile metal. Nickel is released into the environment by power plants and trash incinerators. It is then settled to the ground or fall down after reactions with raindrops. It usually takes a long time for nickel to be removed from air (Agarwal,. 2002). Nickel can also end up in surface water when it is a part of wastewater streams. The larger part of all nickel compounds that are released to the environment is adsorbed to sediment or soil particles and become immobile as a result. In acidic ground, however, nickel is more mobile and often rinse out to the groundwater (Agarwal, 2002).

Microorganisms can suffer from growth decline due to the presence of nickel, but they usually develop resistance to nickel after a while. But nickel is not only favorable as an essential element; it can also be dangerous when the maximum tolerable amounts are exceeded (Agarwal, 2002). This can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that live near refineries. Nickel is not known to accumulate in plants or animals. As a result nickel is not bio magnifying in the food chain (Agarwal, 2002). Humans may be exposed to nickel by inhalation, drinking water and eating food. Skin contact with nickel-contaminated soil or water may also result in nickel exposure. In small quantities nickel is essential, but an uptake of large quantities (greater than 1.0 mg/m^3) can cause: sickness and dizziness after exposure to nickel gas, lung embolism, respiratory failure and birth defects etc. (Agarwal, 2002).

Nickel concentration was determined in both surface and ground waters of Mingora and Kabal areas and the results are given in Table 3.3 and graphically presented in Figure 3.8. Its concentration in Mingora area is ranging from 204 μg/l to 344 μg/ (average = 282 μg/l) while Kabal area water is showing Ni concentration of negligible amount to 327 μg/l (average = 260 μg/l). The water from both the areas is having similar concentration of Ni.

Chromium (Cr)

Chromium enters the air, water and soil in the chromium (III) and chromium (VI) form through natural processes and human activities. The main human activities that increase the concentrations of chromium (III) are steel, leather, chromal plating, welding and chrome pigment production. The main human activities that increase chromium (VI) concentrations in water are chemical, leather tanning, electroplating and other chromium (VI) applications in the industry (Agarwal, 2002). Most of the chromium in air eventually settles and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it can not move towards groundwater. In water chromium absorbed on sediment and become immobile. Only a small part of the chromium that ends up in water is eventually dissolved (Agarwal, 2002). Chromium (III) is an essential element for organisms and its deficiency develops glucose tolerance. Chromium (VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer (Agarwal, 2002).

Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can occur (Agarwal, 2002).

The toxic effects of high levels of chromium are perforation of the nasal septum, skin ulcers and liver and kidney damage.

The concentration of Cr has been determined in the waters of Mingora and Kabal area and the results are given in Table 3.3 and are graphically presented in the Figure 3.8. It is ranging from 187 µg/l in sample No MW1 collected from a tap at Rajabad/Maluk Abad Union council to 396 µg/l in sample No. MW5 from a flowing spring at Maluk abad towards Fizagat with an average amount of 312 µg/l in the water of Mingora area. In Kabal area, the concentration of Cr varies from 185 µg/l in sample No. KW23 from a spring at Deerai Baba to 585 µg/l in sample No. KW32 from a dug well at Sersenai with an average amount of 313 µg/l. In this respect, the water of Kabal area is enriched in Cr relative to that of Mingora.

Cobalt (Co)

The concentration of Co in the waters of Mingora and Kabal area are given in Table 3.3 and are graphically represented in Figure 3.8. Co is ranging from 33 µg/l to 74 µg/l (average = 46 µg/l) in the water of Mingora area and 30 µg/l to 57 µg/l (average =

41 μg/l) in the water of Kabal area. The Co concentrations in the waters of both Mingora and Kabal area are more or less similar.

Manganese (Mn)

Manganese usually occurs together with iron. In surface waters, Mn occurs in both dissolved and suspended forms. Anaerobic ground water often contains high levels of dissolved Mn. The divalent (Mn^{+2}) predominates in most water at pH 4-7, but more highly oxidized forms may occur at higher pH values or result from microbial oxidation (US EPA, 1984). At concentrations exceeding 0.1 mg/l, Mn ion imparts an undesirable taste to water, beverages and stains plumbing fixtures and laundry (Griffon, 1960).

Mn is an essential element, its deficiency lead to impaired growth, skeletal abnormalities, reproductive deficits and defects in lipid and carbohydrate metabolism (US EPA, 1984; WHO 1981; Hurley and Keen, 1987). Although no specific manganese- deficiency syndrome has been described in humans, as association between manganese deficiency and disorders like anemia and bone changes in children have been suggested (Pier, 1975). In humans, chronically exposed to elevated levels in the workplace, neurological effects of inhaled Mn have been documented. Weakness, muscle pain, apathy, slow speech, slow clumsy movement of limbs and monotonous tone of voice etc characterize the syndrome known as "manganism". The minimal exposure level producing neurological effects is not certain but is probably in the range of 0.1 –1 mg/m^3 (Agency for Toxic Substances and Disease Registry, 1992).

The concentration of Mn was determined in water samples of Mingora and Kabal areas and the results are given in Table 3.3 and are graphically presented in Figure 3.8. Mn concentration varies from 30 μg/l in sample Nos. MW2, MW3 and MW45, collected from a spring at Maluk Abad, from a well near Mingora emerald mine area and from a tap at Birarai to 2198 μg/l in sample No. MW6, collected from a 60 feet dug well at car washing service station near Fizagat mine area with an average amount of 150 μg/l in Mingora area. In Kabal area it is ranging from 20 μg/l in sample No. KW42, collected from a dug well at Kotlai to 87 μg/l in sample No. KW28, collected from main Stream Hazara and Guljabba with an average amount of 38 μg/l .

Table 3.1. Physiochemical parameters of water samples of Mingora and Kabal areas.

S. Codes	Source	pH	EC µS/cm	Temp C°	DO ppm	TDS mg/l	Salinity	Resistivity kΩ.cm	Turbidity (NTU)
Mingora									
MW1	Tap water	7.01	241	27.4	3.75	129	0.1	4.16	1.22
MW2	Spring water	7.00	650	28.1	2.65	347	0.3	1.533	0.54
MW3	Well water	7.02	815	25	2.92	433	0.4	1.228	0.47
MW4	Spring water	7.00	564	27.3	3.03	301	0.3	1.772	0.2
MW5	Flowing water from spring	6.99	798	25	2.95	425	0.4	1.253	0.11
MW6	Well water	6.95	1102	25	2.56	587	0.5	0.908	3.8
MW7	Tube well	7.05	218	28.1	2.76	116	0.1	4.58	0.48
MW8	Dug well	7.00	238	25	2.64	126	0.1	4.21	0.13
MW9	Dug well	7.01	189	25	2.87	109	0.1	5.3	0.58
MW10	Tube well	6.99	316	27.1	3.07	168	0.2	3.17	0.22
MW11	Dug well	6.95	1503	23	2.45	800	0.7	0.667	1.08
MW12	Dug well	6.99	1466	26.5	3.01	781	0.7	0.683	1.07
MW13	Dug well	7.02	1302	26.8	2.93	695	0.6	0.769	0.28
MW14	Dug well	6.98	1515	26	2.3	808	0.7	0.66	4.68
MW15	Tube well	7.10	1160	25.2	2.82	618	0.6	0.861	0.03
MW16	Dug well	6.99	1120	27.9	2.63	591	0.5	0.893	0.3
MW17	Stream water	7.00	179	26.1	2.45	95.6	0.1	5.57	2.38
MW18	River water	7.02	71	25.8	3.09	37.8	0	14.1	16.2
MW43	River water	6.95	71	22	2	38.1	0	14.03	6.88
MW44	Swat River	6.98	102	32	1.96	53.9	0.1	9.85	3.63
MW45	Tap water	7.05	305	28.9	0.13	163	0.2	3.27	3.45
Average		**7.00**	**663.1**	**26.3**	**2.62**	**353**	**0.32**	**3.78**	**2.27**
Kabal									
KW19	River Water	6.97	70.6	19	3.1	37.4	0	14.18	4.56
KW20	Stream water	6.97	256	26	2.38	190	0.2	2.81	2.08
KW21	Pumping well	6.78	262	24	2.34	78	0.2	78.34	2.43
KW22	Stream water	7.00	465	26	2.6	248	0.2	2.15	0
KW23	Spring water	7.02	450	28	2.66	239	0.2	2.22	0

ontinued from Table 3.1.

Codes	Source	pH	EC µS/cm	Temp C°	DO ppm	TDS mg/l	Salinity	Resistivity kΩ.cm	Turbidity (NTU)
W24	Dug well	7.01	403	21	2.76	215	0.2	2.48	0.29
W25	Dug well	7.02	408	23	2.92	218	0.2	2.45	0.53
W26	Dug well	7.00	907	21	2.89	484	0.4	1.103	0
W27	Stream water	7.20	314	30	0.1	167	0.2	3.19	0.45
W28	Stream water	7.11	306	30	2.6	162	0.2	3.27	0.32
W29	Pumping well	7.08	502	20	2.16	268	0.2	1.991	0.05
W30	Tube well	7.07	478	20	2.36	255	0.2	2.09	0.06
W31	Dug well	6.96	561	32	2.8	300	0.3	1.775	0.1
W32	Dug well	6.95	504	28.7	2.3	269	0.2	1.992	0.12
W33	Dug well	6.96	516	20	2.28	274	0.3	1.94	0
W34	Dug well	7.00	475	20	2.34	251	0.2	2.11	0.31
W35	Dug well	6.99	458	20	2.2	244	0.2	2.18	1.17
W36	Spring	6.99	549	32.4	2.22	293	0.3	1.822	0.36
W37	Spring	7.02	535	33.3	1.7	285	0.3	1.87	0.26
W38	Dug well	6.99	921	23	2.28	491	0.4	1.085	0.25
W39	Spring water	6.97	390	32.7	1.99	208	0.2	2.56	2.68
W40	Stream	6.92	317	26	2.26	169	0.2	3.15	0.13
W41	Tube well	6.99	440	20	2.53	235	0.2	2.27	0.19
W42	Dug well	6.86	514	31.7	2.55	273	0.3	1.951	0.42
Average		**6.99**	**458**	**25.3**	**2.35**	**244**	**0.2**	**5.874**	**0.70**

Table. 3.2. Light element cations in water samples of Mingora and Kabal areas.

Sample Code	Source	Ca mg/l	Mg mg/l	Na mg/l	K mg/l
Mingora					
MW1	Tap water	24.65	34.18	5.10	2.33
MW2	Spring water	22.37	53.35	6.08	2.54
MW3	Dug well water	29.79	59.45	13.87	6.74
MW4	Spring water	2.09	67.95	3.39	1.03
MW5	Flowing water from spring	0.81	99.35	3.53	2.53
MW6	Dug well water	56.95	11.97	223.05	6.82
MW7	Tube well	23.10	14.45	4.88	1.62
MW8	Dug well	26.92	8.90	5.82	2.94
MW9	Dug well	23.52	16.23	4.96	2.45
MW10	Tube well	34.00	0.51	5.68	1.96
MW11	Dug well	126.35	35.69	2.88	8.42
MW12	Dug well	123.55	12.09	2.66	7.79
MW13	Dug well	43.56	20.80	2.56	21.65
MW14	Dug well	56.12	28.81	3.08	20.35
MW15	Tube well	17.23	20.62	2.87	0.13
MW16	Dug well	30.21	18.56	2.62	6.45
MW17	Stream water	23.90	13.02	4.21	11.50
MW18	River water	5.77	12.09	1.77	1.12
MW43	River water	6.13	12.01	1.61	1.57
MW44	Swat River	12.87	8.12	2.55	1.33
MW45	Tap water	27.65	6.43	7.09	1.15
Average		**34.17**	**26.41**	**14.77**	**5.35**
Kabal					
KW19	River Water	6.26	9.34	2.01	1.16
KW20	Stream water	30.79	7.37	9.21	2.82
KW21	Pumping well	45.65	21.74	9.72	0.94
KW22	Stream water	37.48	12.75	12.74	3.05

Continued from Table 3.2.

Sample Code	**Source**	**Ca mg/l**	**Mg mg/l**	**Na mg/l**	**K mg/l**
KW23	Spring water	49.46	9.09	7.89	1.47
KW24	Dug well	44.44	5.07	8.81	2.91
KW25	Dug well	42.48	6.55	7.31	3.96
KW26	Dug well	34.45	8.23	105.70	27.85
KW27	Stream water	58.15	10.67	11.28	26.23
KW28	Stream water	33.80	5.19	7.09	1.17
KW29	Pumping well	53.90	13.56	8.56	1.24
KW30	Tube well	48.39	14.71	7.08	1.25
KW31	Dug well	49.56	20.36	117.70	1.09
KW32	Dug well	48.56	17.66	9.20	0.86
KW33	Dug well	50.05	17.85	9.73	0.89
KW34	Dug well	42.02	15.37	7.44	1.24
KW35	Dug well	41.35	16.05	6.90	0.81
KW36	Spring	56.00	16.53	11.05	1.66
KW37	Spring	53.80	17.38	11.17	1.21
KW38	Dug well	19.71	56.10	110.95	1.58
KW39	Spring water	34.23	10.92	7.19	0.76
KW40	Stream	31.41	5.46	5.74	0.75
KW41	Tube well	43.30	10.59	6.42	0.56
KW42	Dug well	37.67	8.84	6.35	0.56
Average		**41.37**	**14.05**	**21.13**	**3.58**

Table. 3.3. Heavy and trace elements in water samples of Mingora and Kabal areas.

S.No	Source	Fe µg/l	Cu µg/l	Pb µg/l	Zn µg/l	Ni µg/l	Cr µg/l	Co µg/l	Mn µg/l
Mingora									
MW1	Tap water	88	40	77	222	277	187	61	46
MW2	Spring water	100	30	56	55	271	326	45	30
MW3	Well water	182	33	100	63	344	340	43	30
MW4	Spring water	68	24	88	54	204	355	48	35
MW5	Flowing water from spring	96	35	80	56	324	396	54	100
MW6	Well water	137	37	101	91	300	370	74	2198
MW7	Tube well	29	61	98	91	282	209	37	82
MW8	Dug well	166	38	92	79	262	302	42	38
MW9	Dug well	94	37	76	82	282	310	33	39
MW10	Tube well	101	72	77	810	292	303	48	38
MW11	Dug well	149	36	95	67	268	387	56	44
MW12	Dug well	57	22	81	52	270	229	40	47
MW13	Dug well	173	31	61	52	254	208	34	37
MW14	Dug well	68	33	115	135	299	323	54	44
MW15	Tube well	125	32	90	218	317	364	45	42
MW16	Dug well	167	29	117	190	284	361	45	38
MW17	Stream water	165	129	87	75	279	297	36	41
MW18	River water	731	42	114	64	289	354	45	68
MW43	River water	886	35	88	58	276	262	35	63
MW44	Swat River	697	33	67	65	267	306	38	69
MW45	Tap water	175	68	114	1913	278	364	47	30
Average		**212**	**43**	**89**	**214**	**282**	**312**	**46**	**150**
Kabal									
KW19	River Water	930	37	86	73	281	363	44	80
KW20	Stream water	87	26	86	890	285	303	37	41

Continued from Table 3.3.

S.No	**Source**	**Fe µg/l**	**Cu µg/l**	**Pb µg/l**	**Zn µg/l**	**Ni µg/l**	**Cr µg/l**	**Co µg/l**	**Mn µg/l**
KW21	Pumping well	192	17	81	113	293	272	30	37
KW22	Stream water	193	33	105	60	312	348	47	32
KW23	Spring water	155	24	104	52	257	185	34	37
KW24	Dug well	114	31	81	113	225	371	43	36
KW25	Dug well	66	41	63	185	262	201	37	34
KW26	Dug well	187	30	102	47	260	202	31	37
KW27	Stream water	88	35	113	57	313	319	39	31
KW28	Stream water	479	44	113	71	0	348	48	87
KW29	Pumping well	146	32	96	75	313	357	48	40
KW30	Tube well	83	29	89	56	227	390	53	35
KW31	Dug well	165	32	68	57	264	274	34	38
KW32	Dug well	101	79	63	111	303	585	33	32
KW33	Dug well	138	33	102	61	316	383	57	34
KW34	Dug well	153	34	86	55	0	195	31	31
KW35	Dug well	800	30	116	447	274	368	53	27
KW36	Spring	142	35	0	56	297	351	52	31
KW37	Spring	131	29	84	55	268	327	40	30
KW38	Dug well	118	31	96	48	318	282	37	31
KW39	Spring water	188	33	0	72	327	323	38	34
KW40	Stream	119	113	102	57	250	224	32	40
KW41	Tube well	93	129	104	85	308	258	34	25
KW42	Dug well	100	32	81	217	287	292	49	20
Average		**207**	**41.2**	**84**	**130**	**260**	**313**	**41**	**38**

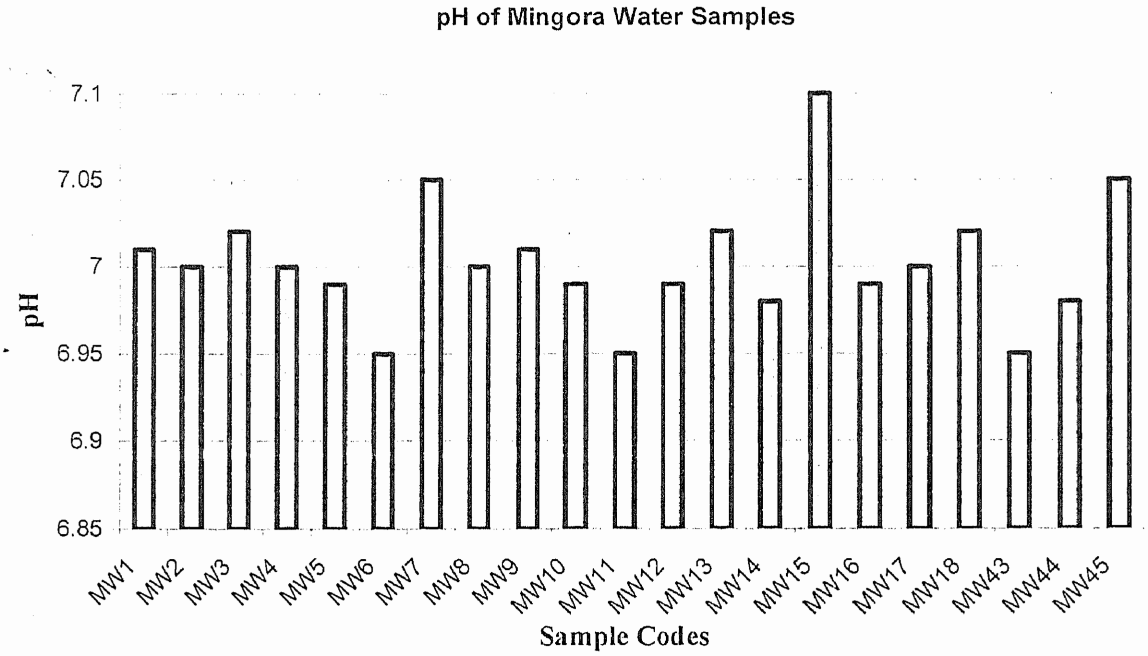

Fig. 3.1 a. Variation of pH in the surface and ground water of Mingora area.

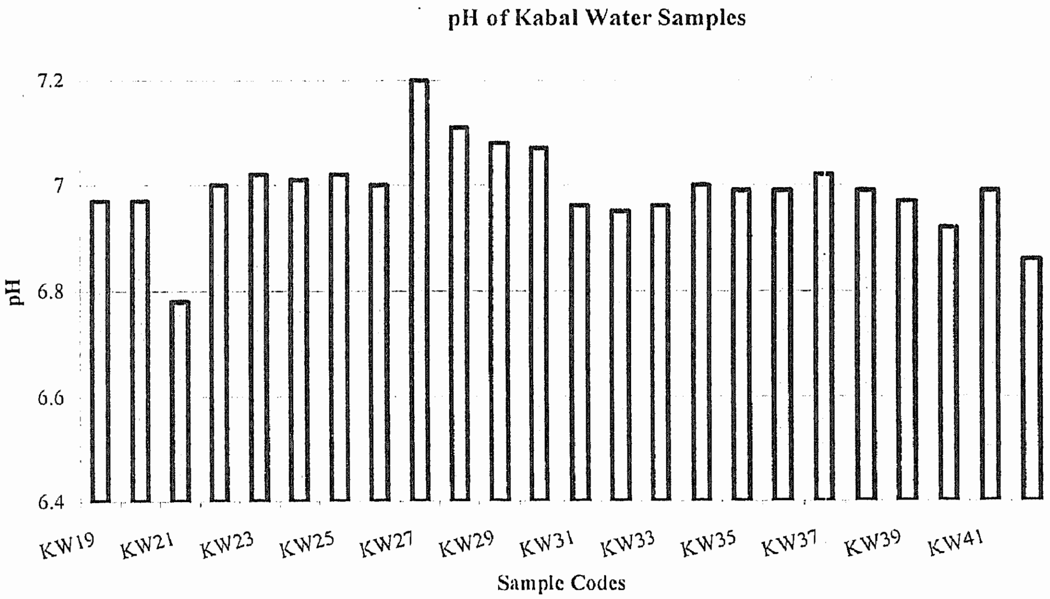

Fig. 3.1 b. Variation of pH in the surface and ground water of Kabal area.

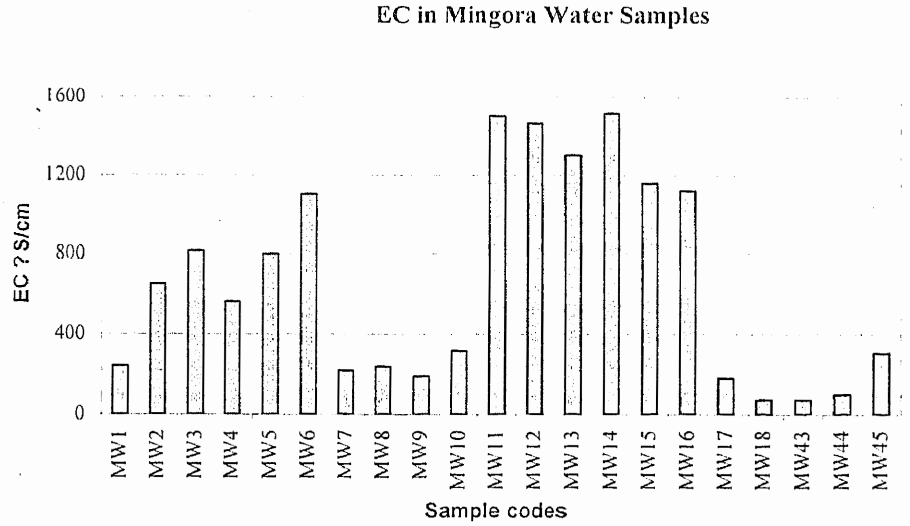

Fig. 3.2 a. Electrical Conductivity of the surface and ground water in Mingora area.

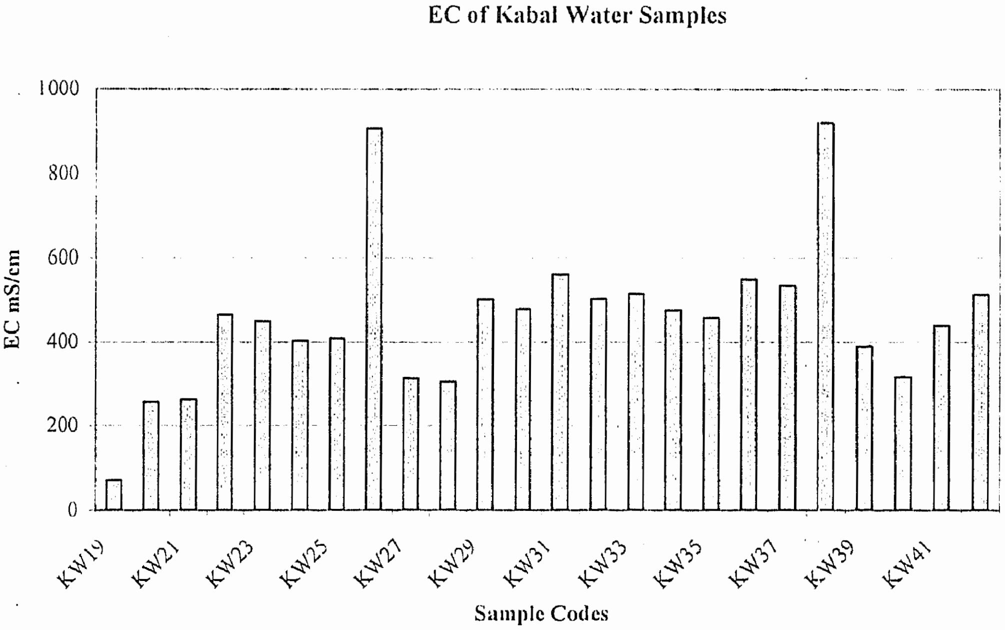

Fig. 3.2 b. Electrical conductivity in the surface and ground water of Kabal area.

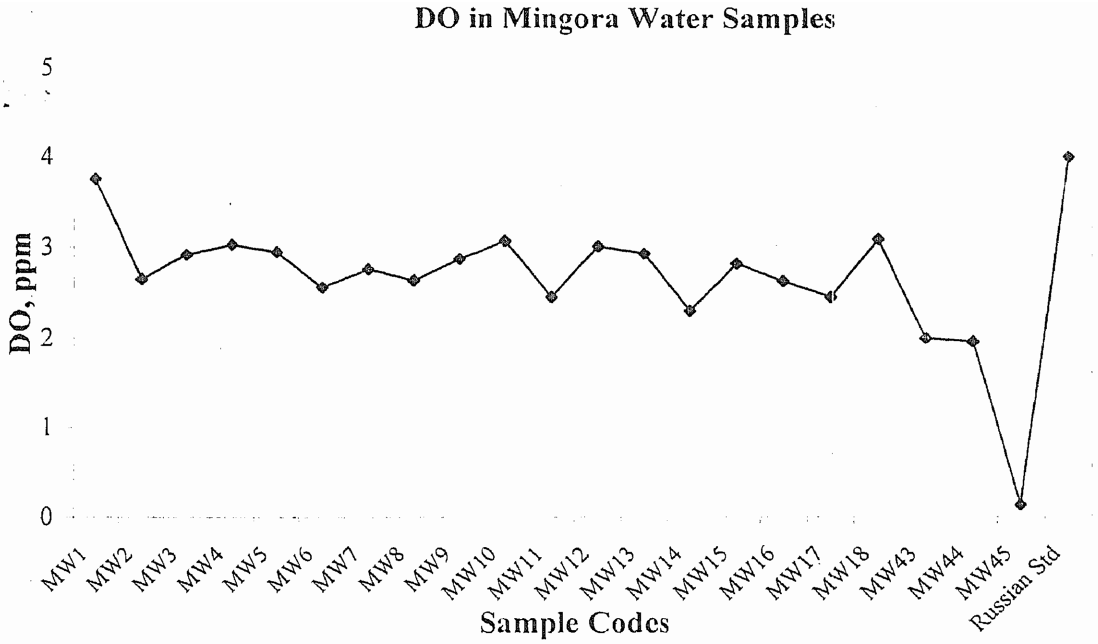

Fig. 3.3 a. Dissolved oxygen in surface and ground water of Mingora area.

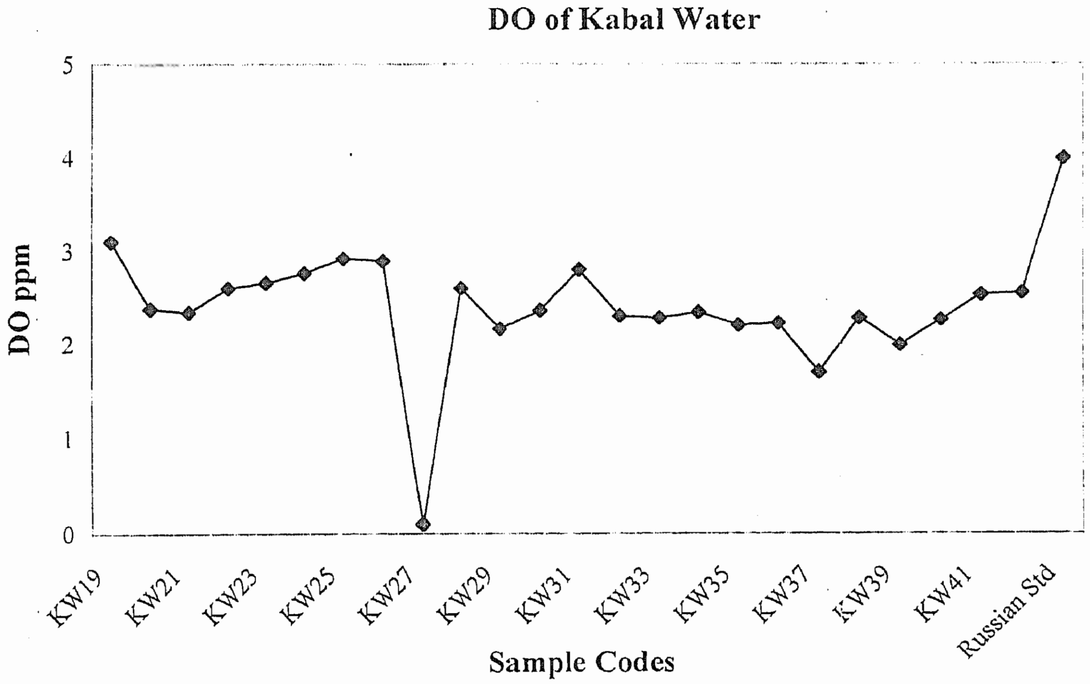

Fig. 3.3 b. Dissolved oxygen in the surface and ground water of Mingora area.

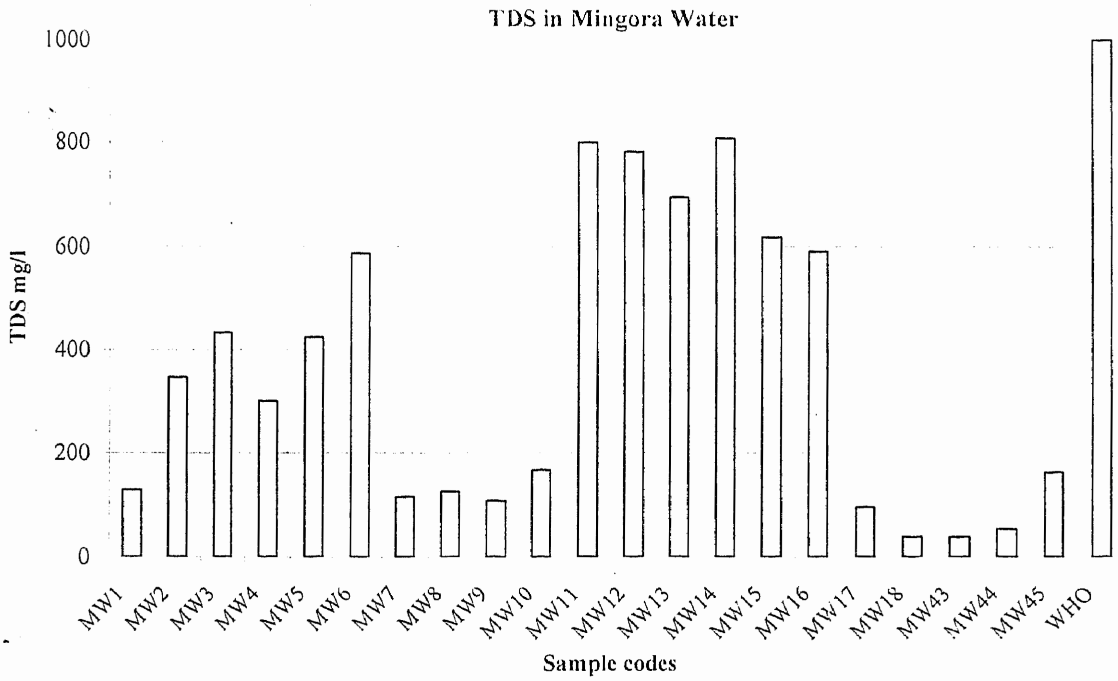

Fig. 3.4 a. Total dissolved solids in the water of Mingora in comparison with WHO standards.

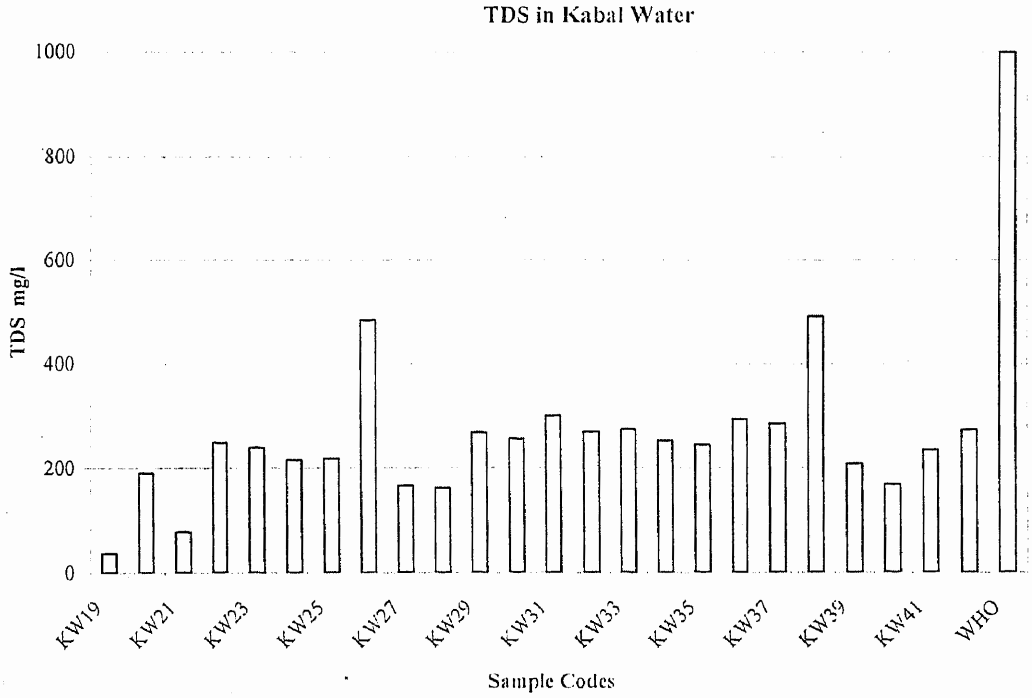

Fig. 3.4 b. Total dissolved solids in the surface and ground water of Kabal area in comparison with WHO standards.

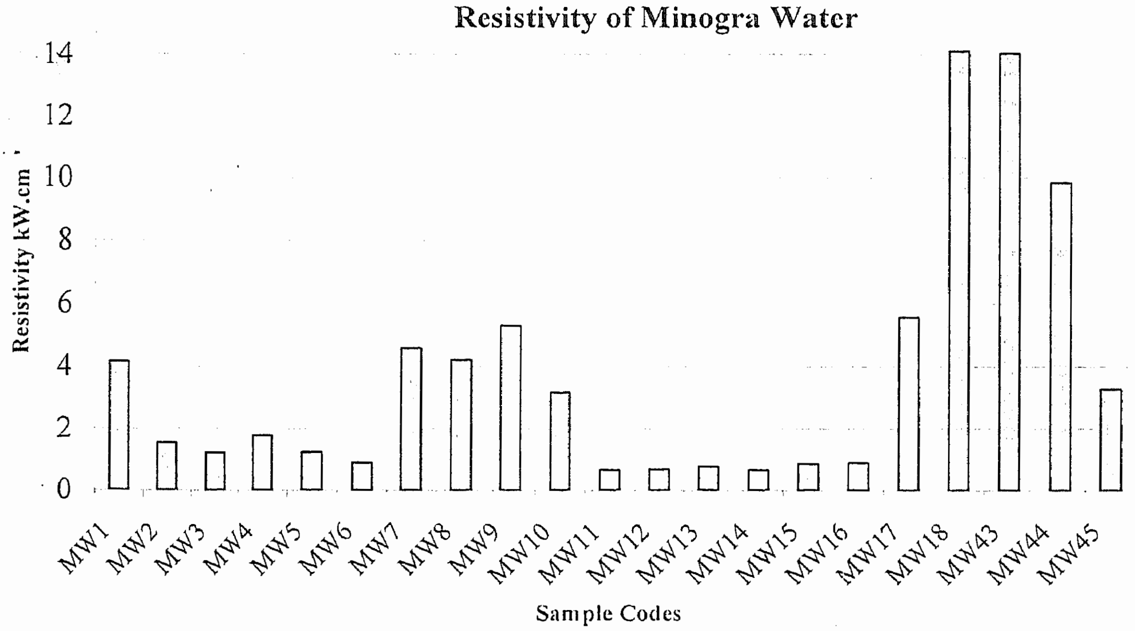

Fig. 3.5 a. Resistivity of the surface and ground water of Mingora area.

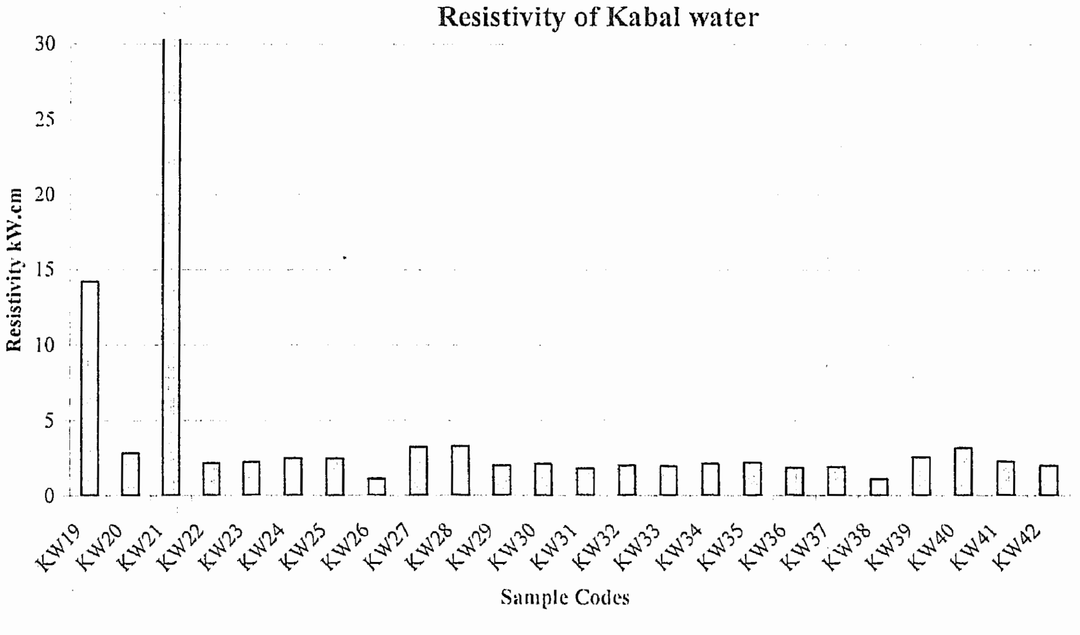

Fig. 3.5 b. Resistivity of the surface and ground water of Kabal area.

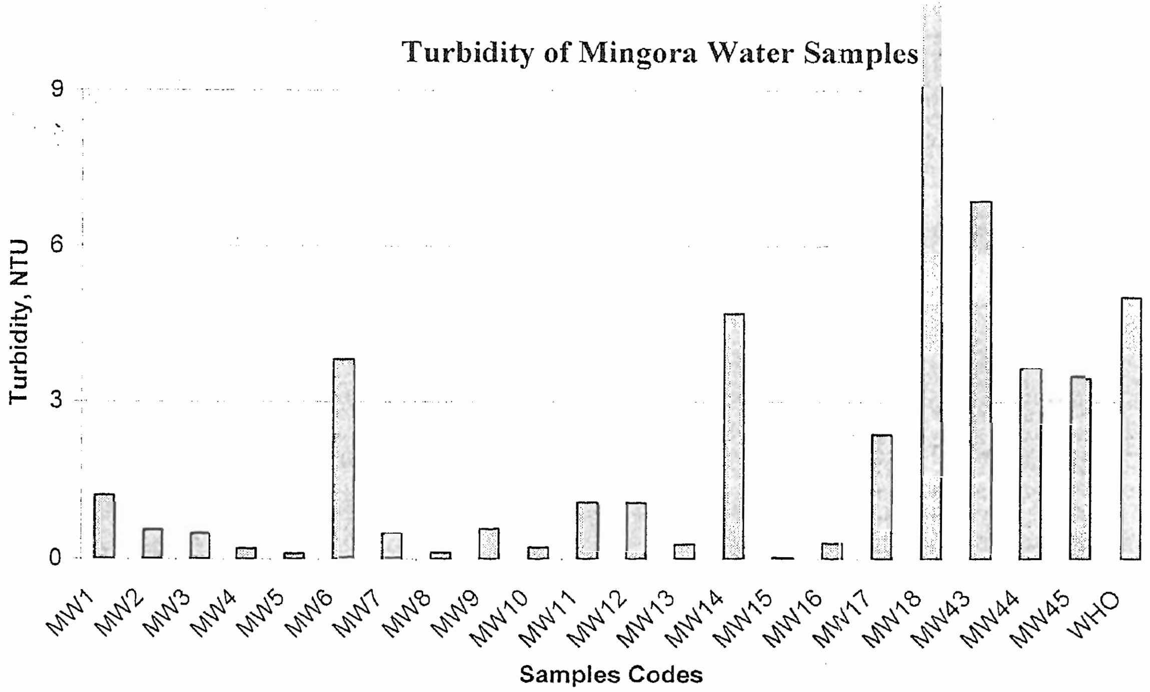

Fig. 3.6 a. Variation of turbidity in the surface and ground water of Mingora area in comparison with WHO standards

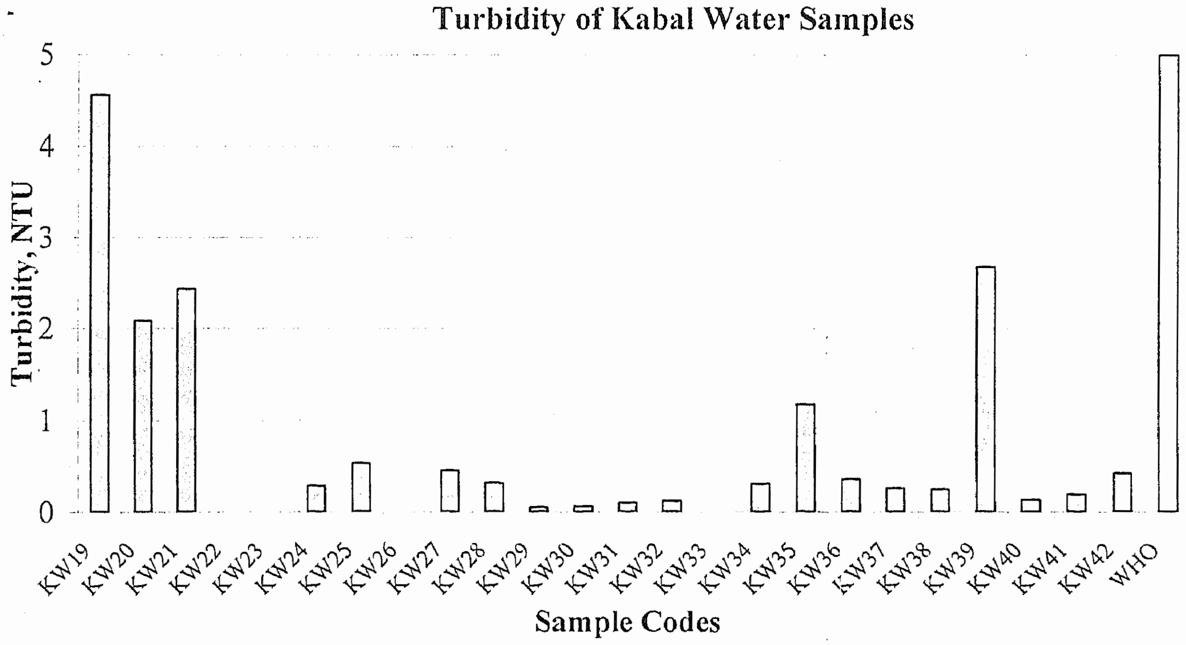

Fig. 3.6 b. Turbidity in the surface and ground water of Kabal area in comparison with WHO standards

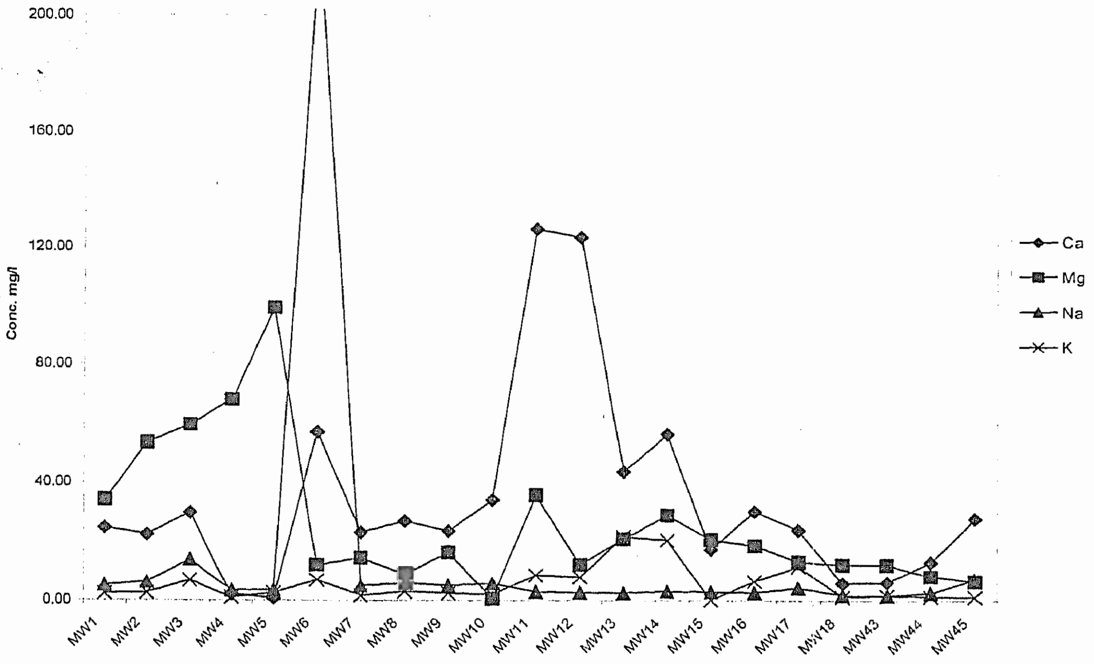

Fig. 3.7 a . Light element cations in the surface and ground water of Mingora area.

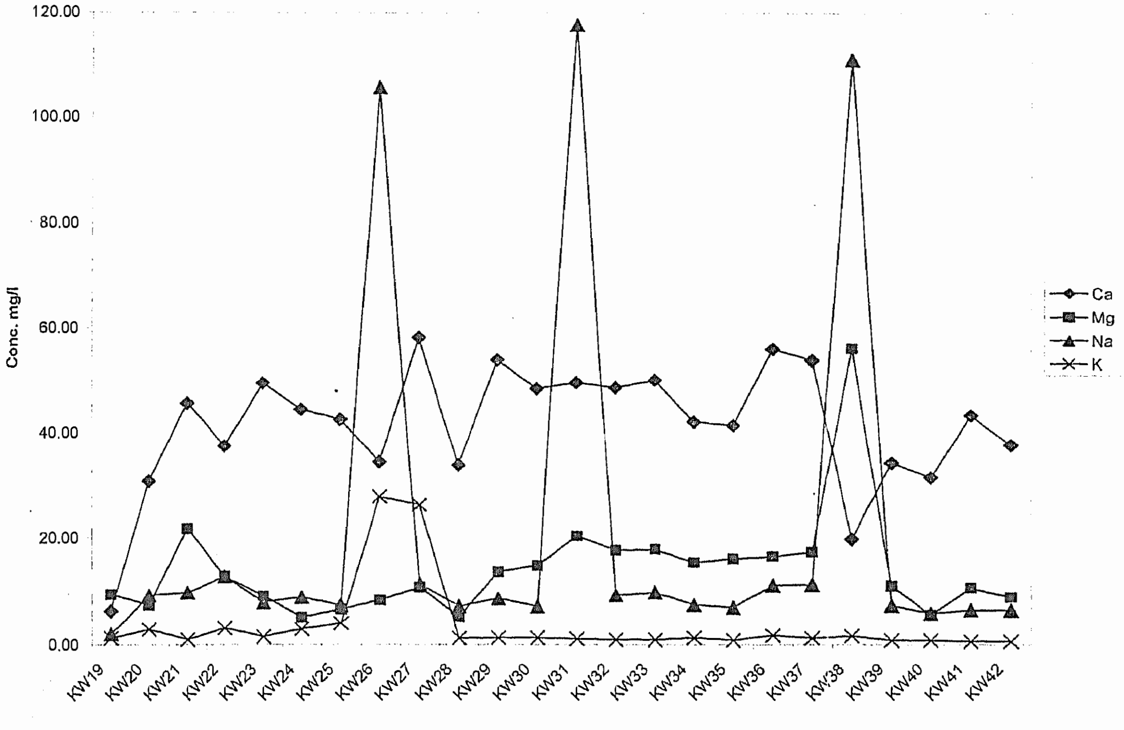

Fig. 3.7 b. Light element cations in surface and ground water of Kabal area.

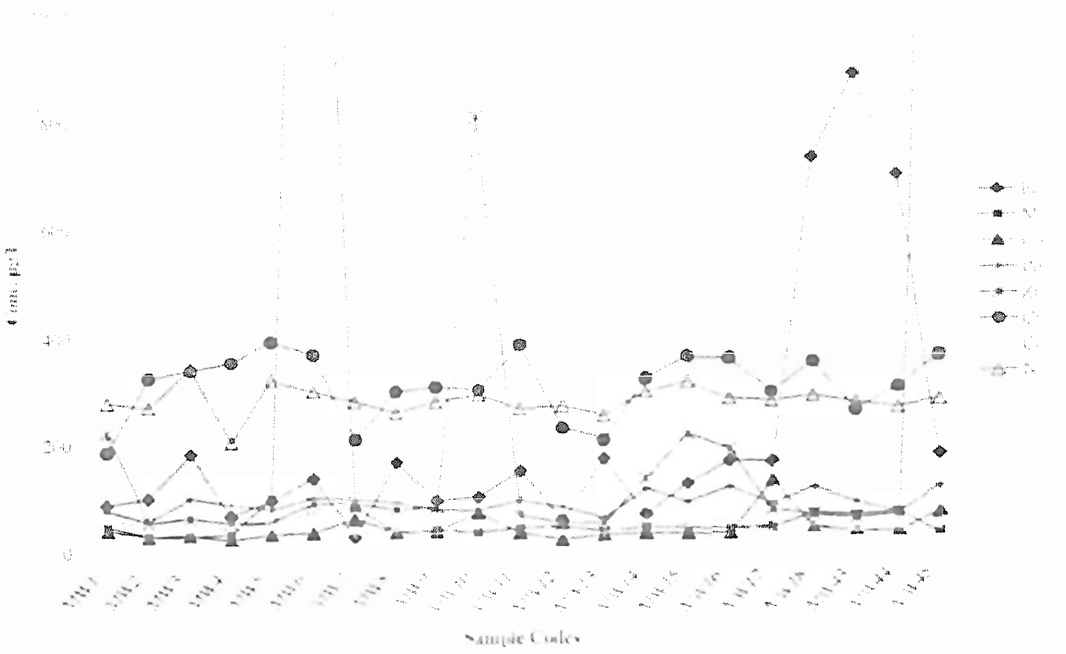

Fig. 3.8 a. Trace elements concentration in the surface and ground water of Mingora area.

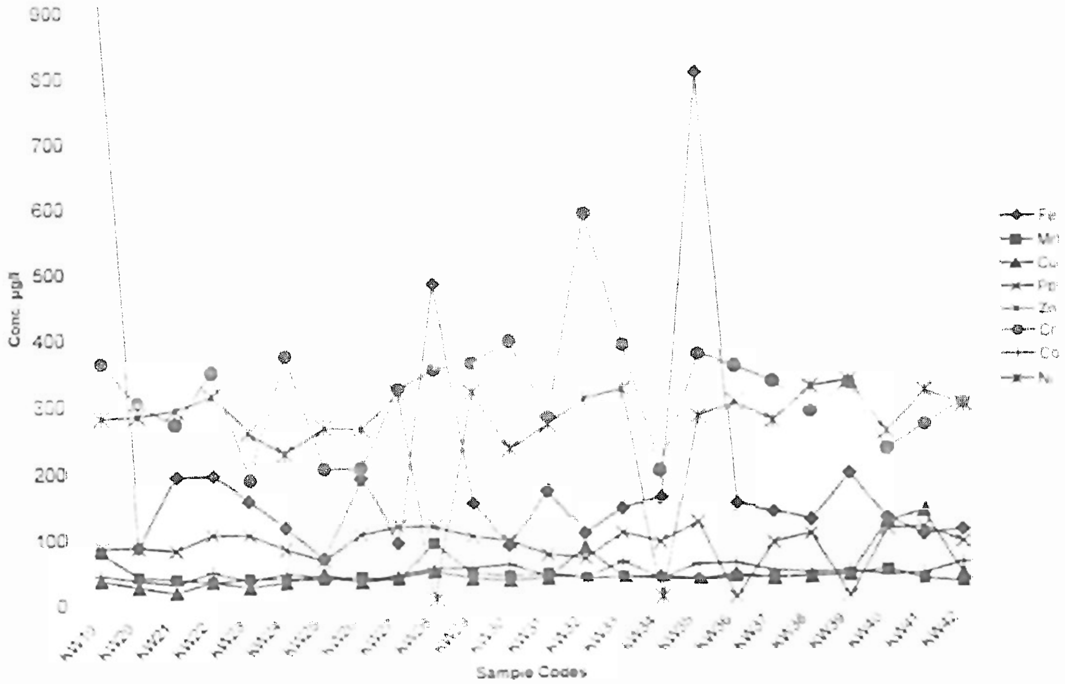

Fig. 3.8 b. Trace elements concentration in the surface and ground water of Kabal area.

CHAPTER 4

PEDO-GEOCHEMSITRY

INTRODUCTION

Mafic rock is igneous rock that is dominated by the silicates pyroxene, amphibole, olivine, and mica. These minerals are high in magnesium and ferric oxides, and their presence gives mafic rock its characteristic dark color. Mafic rock is commonly contrasted with felsic rock, in which light-colored minerals predominate. Common mafic rocks include basalt and its coarse-grained intrusive equivalent, gabbro (Encyclopædia Britannica, 2006)

Ultramafic rocks occupy a small portion (<1%) of the earth's land surface, but are locally abundant in ophiolite belts along tectonic plate margins (Brooks, 1987; Coleman and Jove, 1991). The rocks of the study area are mainly a part of the mafic and ultramafic sequences of the Mingora-Shangla melange of the Indus Suture Zone (ISZ) (Kazmi and Jan, 1997). The weathering and erosion of these rocks have deposited soils in the low laying areas of the region, which is focus of this study.

Engineering geologists define soil very broadly to include all unconsolidated material overlying bedrock. While soil scientists restrict the term soil to those materials capable of supporting plant growth and distinguish it from regolith, which encompasses all unconsolidated material at the surface whether fertile or not. (Montgomery, 1995).

Soil composition and characteristics

Soil is an essential natural medium for the growth of land plants, whether or not it has discernible soil horizons. It is formed from rocks by physical, chemical and biological weathering. Soil consists of various constituents such as minerals, organic matters, water and air. Half of the soil volume is solid space, 45% mineral matters and

5% organic materials. In porous soil about 25% of the volume is water and 25% is air (Lal and Stewart, 1992)..Soil is the basic medium-providing majority of food items to the living organisms but its degradation has become a major global concern in recent years as a result of increasing demands on land for food production and waste disposal. Soil is polluted by various factors such as over using of pesticides and fertilizers and dumping of solid wastes and industrial effluents. The wastewater of industrial processes contains different physical, chemical and biological pollutants, which give rise environmental and public health concerns in numerous areas of the world. Polluted soil can affect the normal growth of plant, because it contains a lot of toxic metals such as Cu, Cd, Ni, Zn, Pb Cr and Hg (Lal and Stewart, 1992).

Soils formed from ultramafic rocks contain an abundance of Fe, Mn, Cr, Ni, and Mg, and low concentrations of the plant-essential nutrients Ca and K. The resulting vegetation is commonly xeromorphic and characteristically stunted (Lee, et al, 2001).

Soil Formation

Physical, chemical and biological weathering of various types of rocks is responsible for the formation of both transported and residual soil. These soils are helpful in identification of the existence of rocks of special character in the uphill or underneath area respectively. These soils if produced from the weathering of the mafic and ultramafic rocks are of greater interest in regard to environmental and exploration studies. The mafic and ultramafic rocks are generally enriched in heavy metals such as chromium, nickel, cobalt, cadmium, iron, lead, zinc and copper etc. and similarly the weathered soil of these rocks will also be enriched in the heavy metals and hence their adsorption by plants and dissolution in water of the area could be resulted in the environmental degradation of the area and also helps in the identification of pathfinders for the various types of mineral deposits (Kifayatullah et al., 2001; Shah et al., 2004; Leavitt and Goodell, 1979; Brooks 1987).

The processes of soil formation on ultramafic rocks are generally different from those on acidic rock, largely due to high concentrations of Fe and Mg. Soils formed on serpentinite generally produce more exaggerated effects than other types of ultramafics (Kruckeberg, 1984). Soil profile development is generally slow and poor, with average pH between 6-7.5. Soil moisture holding capacity is generally low. Cation exchange capacity is typically high, as is the Mg/Ca ratio. Ultramafic soils are often lacking in nitrogen, phosphorous and sometimes molybdenum; they are moderate to high in cobalt, chromium, iron and nickel (Rabenhorst et al., 1982; Alexander et al., 1989; Graham et al., 1990). Because soil development is poor and slopes are steep, ultramafic soils are not stable. This affects the establishment of pioneering vegetation and, as a consequence, further slows soil development.

Crop and timber productivity is highly variable, but mostly very poor. Land use is mostly restricted to livestock grazing and wildlife values. Food crops and livestock are susceptible to picking up and even concentrating heavy metals. Timber can be harvested from sites that are not so severe that they exclude tree growth, but regeneration after harvest is often difficult and growth is poor. Ultramafic sites in forested regions are often classified as non-productive, especially as the amount of serpentine increases. Many ultramafic soils have been found to benefit from the addition of calcium (Kruckeberg, 1992).

Soil Profile

Soils are stratified into different layers called, soil horizons, which give information about the history and usefulness of the soil. Thickness, color, texture and composition of each horizon is used to classify the soil. The soil surface is usually covered with a layer of leaf litter, crop residues or other fresh or partially decomposed organic material. This is called O-horizon. Under the organic layer is A-horizon or topsoil, consisted of mineral particles mixed with organic material. Its thickness range from several meters to zero (in some deserts). This layer contains most of the living organisms and organic material in the soil, and it is in this layer that most plants spread their roots to absorb water and nutrients. The surface horizon often blends into another horizon i.e. E-horizon which is subject to leaching by water percolating through it. Beneath the surface horizons are the subsurface horizons usually having lower organic content and higher concentrations of mineral particles. This zone is known as B-horizon where soluble compounds and clay particles carried by water percolating down, are accumulated. Beneath the subsoil is the parent material which is know as C-horizon. It is made of relatively un-decomposed mineral particles and un-weathered rock fragments with very little organic material. Weathering of this layer produces new soil particles and permits downward expansion of the horizons above (Cunningham & Saigo, 1999)

Distribution and Environmental effects of trace metals in soils

Soils enriched in trace metals often pose environmental and human health problems and thus attract the attention of researchers from a wide range of disciplines. In order to reach a greater understanding of these metals as pollutants it is important to understand their natural sources as well. While most people probably associate metal rich soils with hazardous waste pollution, there are many cases where soils, rocks and waters are naturally enriched in trace metals (Alloway, 1990; McBride, 1994). Concentrations vary between different rock types, climates, and geochemical conditions, but ultramafic rocks are known for high natural occurrences of trace metals, Co, Cr, and Ni in particular (Dinelli et al., 1997; Lottermoser, 1997). Ultramafic rocks are exposed at the surface in areas where sections of the upper mantle have been abducted in orogenic regions (Robinson et al., 1996). The most common types of these rocks are harzburgite, lherzolite, and dunite—all are naturally or geochemically enriched in heavy metals (Lottermoser, 1997; Winter, 2001). Typically ultramafic rocks and associated soils contain Ni and Cr at concentrations of 1500 to 5000 ppm and Co from 100 to 200 ppm (McGrath and Smith, 1990; Venturelli et al., 1997; Robinson et al., 1999). At these high concentrations metals can migrate into surface or groundwater and cause potential ecological and health concerns (Wesolowski, 2003).

Potential hazards associated with trace elements pertain to their accumulation in soils which may (1) lead to a plant toxicity condition or (2) result in increased uptake of metals into the food chain. Ten elements of primary concern are arsenic, boron, cadmium, copper, mercury, molybdenum, nickel, lead, selenium, and zinc. Of these cadmium has the most dangerous long-term effects on human health. Many of these are amplified in the food chain.

The distribution of heavy metals in natural soils can affect the plant species growing in an area. These species have, therefore, been used successfully as tracers in mineral prospecting and environmental degradation in many areas. The mechanism of accumulation of a substance or its enrichment, in relation to its environment, often involves additional energy consumption and increased enzyme activity (Brook, 1983). Lower and higher plants are included as the accumulative organisms. A biological absorption coefficient value, or the ratio between the concentration of a given element in plant and soil, decreases exponentially with the increase of concentration in soil (Brook, 1983). A vegetable species can also develop natural barriers against excess concentrations of an element, according to the need and tolerance for it (Kovalesky, 1969). Due to several factors such as drainage, pH the nature of clay minerals, antagonistic effects of other ions and the presence of complexing agents, very little of the total contents of some elements in the soil can be utilized by plants (Brook, 1983).

Sources of Trace metals in Soil

There are several sources of trace elements in the environment, both natural and anthropogenic. Soil parent material (rocks) is the natural source while commercial fertilizers, liming materials, sewage sludge, animal wastes, pesticides, irrigation water, coal combustion residues, metal smelting industries, auto emissions, and others anthropogenic sources. (Adriano, 1986).

Fate of Trace Elements in Soils

There are four main processes for the solution phase concentration of trace elements:

- Ion exchange on layered silicates
- Precipitation reactions
- Sorption to hydrous oxide surfaces
- Complex formation with soil organic matter

Ionic exchange: Layered silicates in the soils provide permanent charges and pH dependent charges which retain trace metal cations by non-specific electrostatic forces. These elements compete with Ca and Mg for the available exchange sites. Trace elements are retained to higher concentrations when in lower pH systems. At a higher pH, metal hydrolysis is more prevalent and is the dominant reaction. Cd, Cu, Cr, Pb, Hg, Ni and Zn are the main trace elements that are of greatest concern on a waste treatment facility (Hagedorn, 1996).

Precipitation reactions: When an element undergoes a precipitation reaction, a certain sequence happens in the process as the concentration of the element in solution increases.

- elements are absorbed on the particle surfaces.
- the reactants are supersaturated in the reaction.
- crystal growth

The major classes of precipitates found in soils are silicates, oxides, carbonates, phosphates and sulfates. These precipitates form salts in the system, which are not beneficial to the soil system or the waste treatment system. Precipitation reactions are completely reversible and still have some dissolution properties even in stable solid phases (Hagedorn, 1996).

Sorption to Hydrous Oxide surfaces: This process involves the altering of the surface charge using adsorbtion or chemisorption. Trace elements in the form of cations and anions will form short directional bonds with oxide surfaces (Hagedorn, 1996).

Complex formation with soil organic matter: Soil organic matter has many functional groups contained in it that can serve as exchange sites. Groups found in soil organic matter and react with trace elements will most likely contain either COOH groups or OH groups. These functional groups help drive the complex reactions in the organic matter. Trace metal compounds are tied up by the highly reactive oxygen groups and hold the metals in place.

Adverse effects of soil trace elements

Trace elements cause a variety of problems. Human health effects, effects c animal health, plants and aquatic ecosystems are of great concern. A trace element ca have an adverse effect on any organism if the dose high is administered (Pierzynski al., 2000).

Human Health: The primary routes of exposure of humans to trace elements in soil are through food and direct ingestion of soil particles. Soil is the primary recipient of global emissions of trace elements (Pierzynski and et al., 2000).

Cd and Pb can have profound human health effects, but means of exposure a quite different due to their chemical behavior in the soil environment and tl concentration ranges at which they occur in contaminated soils. Cd is readily taken up b plants and food chain transfer is the primary route of exposure. Two symptoms of C toxicity are renal dysfunction and *itai-itai* disease (Pierzynski et al., 2000).

QUALITY OF SOIL

PHYSIOCHEMICAL PARAMETERS

Both Kabal and Mingora Soil extracts were analyzed for pH, electric conductivity, temperature, total dissolved solids (TDS), Salinity and Resistivity. Most the soils showed normal pH values. The physiochemical results of soil are given in tab 4.1.

pH: With the increase in pH value of soil, the capacity for most trace elements is increased, with the maximum under neutral and slightly alkaline conditions (Adriano, 1986). pH values of Mingora soil extracts is ranging from 6.82 to 7.19 (average = 6.99) while in Kabal soil extracts, pH varies from 6.87 to 7.13 (average = 7.00).

Electrical Conductivity: In Mingora soil samples conductivity ranged from 179.7µS/cm to 983 µS/cm. In Kabal soils its concentration ranged from 212 µS/cm to 586 µS/cm.

Temperature: Temperature of Mingora soil extracts is ranging from 23.2 °C to 27.3 °C (average 25 °C). while Kabal soil extracts have temperature in the range of 23 °C to 27.7 °C (average = 24.4 °C).

Total Dissolved Solids (TDS): TDS were calculated in all soil extracts. Its concentration is ranging from 95.5 mg/l to 523 mg/l (average = 224 mg/l) in Mingora soils while in Kabal soils TDS concentration varies from 113 mg/l to 311 mg/l (average = 177 mg/l).

Salinity: Salinity in Mingora soils extract varies from 0.1 to 0.5 (average = 0.2) while in Kabal soils it is ranging from 0.1 to 0.3 (average = 0.2).

Resistivity: Resistivity of Mingora soils varies from 1.018 kΩ/cm to 5.56 kΩ/cm (average = 2.80 kΩ/cm) while Kabal soils have resistivity in the range of 1.711 kΩ/cm to 5.08 kΩ/cm (average = 3.22 kΩ/cm).

LIGHT ELEMENT OXIDES

The light element oxides (i.e., CaO, MgO, Na_2O and K_2O) have been determined in the soils of Mingora and Kabal areas and the results are presented in Table 4.2 and 4.3 respectively.

Calcium Oxide (CaO)

The concentration of Ca in the earth's crust is about 3.6%. the average concentration in soils is about 1.37% (Lindsay, 1979). Ca content is variable in soils, and is largely influenced by parent material and rainfall. Levels in calcareous soils vary from less than 1% to more than 25% (Tisdale et al., 1985), while in mineral soil it varies from 0.5% to 2% (Allen (1989).

The concentration of CaO is ranging from 1.19% to 8.99% (average = 3.11%) in Mingora soils. Lowest concentration of CaO occurs in mountainous soil of Rahim Abad in sample No. MS-17, while maximum concentration occurs in sample No. MS-19 collected from the mountainous soil of Rahim Abad, Mingora. CaO concentration in Kabal soils ranging from 2.16% to 8.11% (average = 4.81%). There is no significant change in the concentration of CaO in both the soils of Mingora and Kabal area.

Magnesium Oxide (MgO)

The concentration of Mg in the earth' crust is about 2.1%, and the average content of Mg in soils is 0.5%. This reflects the removal of Mg from soils during weathering (Lindsay, 1979). Mg is notably high in serpentine minerals which form soils having a distinctive amount of Mg (Proctor & Woodell, 1975).

MgO is ranging from 0.6% to 29.23% (average =10%) in the soils of Mingora area while MgO in the soil of Kabal area varies from 0.70% to 4.66% (average 2.22%). The highest concentration is present in the Sample No. MS-14 collected from Hayat Abad, Fizagat in Mingora area. While the lowest concentration is present in the sample No. MS-21-B, collected from agricultural soil of Rahim Abad in the Mingora area. I Kabal area, the lowest concentration occurs in the sample No. KS-50-B, collected from Landay village and the the higher concentration is reported in the sample No. KS-52, collected from Meelagah-Kotlai. It is clear from the Tables 4.2 and 4.3 that the soils of certain areas of Mingora area highly enriched as compare to that of Kabal area.

Sodium Oxide (Na_2O)

The concentration of Na_2O in the soil of Mingora area varies from 1.03% to 2.42% (average = 1.54%). While its concentration in the soil of Kabal area is ranging from 1.07% to 2.68% (average = 1.60%) at Kabal. The maximum concentration of Na_2O is present in the sample No. MS-16-A collected from agricultural soil of Kanra Baba, and the minimum concentration is present in the sample No. MS-19 collected mountainous area of Rahim Abad, in the Mingora area. In Kabal area, the maximum content of Na_2O is reported in sample No. KS-35-A, collected from Kanju village and minimum contents are reported in sample No. KS-53, collected from Meelagah-Kotlai. The Na_2O concentrations in both the soils of Mingora and Kabal area are more or less similar (Table 4.2 & 4.3)

Potassium Oxide (K_2O)

The concentration of K_2O in the soil of Mingora area is ranging from 0.36% to 2.38% (average = 1.47%). While in Kabal area the K_2O contents of the soil varies from 0.49% to 3.59% (average = 1.56%). The K_2O contents of the soils of Mingora and Kabal area are similar (Table 4.2 & 4.3).

HEAVY AND TRACE ELEMENTS

The concentration of heavy and trace elements (i.e., Fe, Cu, Pb, Zn, Ni, Cr, Co and Mn) has been determined in the soil of Mingora and Kabal areas (see chapter 2). The results are given in the Table 4.2. and 4.3.

Iron (Fe)

Iron is one of the major constituents of the lithosphere and comprises about 5%, being concentrated in mafic rocks. Global abundance of Fe is calculated to be about 45%. In soils, Fe mostly occur in the forms of oxides and hydroxides as small particles or associated with the surfaces of other minerals. While, in soil horizons rich in organic matter, Fe is mainly in chelated form (Kabata-Pendias and Pendias, 2001).

The most important oxidation states of iron are Fe^{2+} and Fe^{3+}. The human body contains 60-70 mg/kg of Fe. This is approximately twice the level of the total body zinc and more than 20 times that of copper. Most of the body iron exists in complex forms bound to protein, either as porphyrin or haeme compounds. Haemoglobin iron occupies a dominant role in all animals (60-70% of body iron in man). The highest concentrations of Fe are in liver, spleen, kidney and heart. (Himmelhoch, et al., 1966).

The concentration of Fe in the Mingora area is ranging from 12499 mg/kg to 38763 mg/kg with an average amount of 25395 mg/kg while in the soils of Kabal area the Fe varies from 20921 mg/kg to 43613 mg/kg with an average amount of 29721 mg/kg. It is clear from the Table 4.2 and 4.3 that the soils of Kabal area are relatively enriched in iron as compare to that of the Mingora area.

Copper (Cu)

Copper is a reddish metal that occurs naturally in rock, soil, water, sediment, and air. Its average concentration in the earth's crust is about 50 mg/kg. Copper also occurs naturally in plants and animals. It is an essential element for all known living organisms including humans and other animals. (Environmental Bureau of Investigation, 1997).

Soil generally contains between 2 - 250 mg/kg copper, although concentrations close to 7000 mg/kg have been found near copper production facilities. Another common source of copper in soil results from spreading sludge from sewage treatment plants. This copper generally stays strongly attached to the surface layer of soil (Environmental Bureau of Investigation, 1997).

Cu in the earth's crust is most abundant in mafic and intermediate rocks and has a tendency to be excluded from carbonate rocks. Cu is considered among the more mobile of the heavy metals in hypergenic processes. Cu in soil exhibits a great ability to chemically interact with mineral and organic components of soil. Cu ions can readily precipitate with various anions such as sulfide, carbonate and hydroxide. Thus Cu is rather immobile element in soils and shows relatively little variation in total content in soil profiles, but it is abundant in soil. However the mobile and available forms of Cu in soils are of great importance in agronomic practice (Kabata-Pendias & Pendias, 2001).

The common characteristic of Cu distribution in soil profiles is its accumulation in the top horizons. Cu concentration in surface soils reflects the bioaccumulation of the metal and also anthropogenic sources of the element. (Kabata-Pendias & Pendias, 2001).

Exposure to copper can occur by breathing air, drinking water, eating food, and by skin contact with soil, water, and other copper-containing substances. Most copper compounds found in air, water, sediment, soil, and rock are bound to dust and dirt or imbedded in minerals and are not easily bioavailable. Some copper in the environment is less tightly bound to particles and may be taken up by plants and animals (Environmental Bureau of Investigation, 1997). Soluble copper compounds (most commonly used in agriculture) are more likely to have harmful impacts. When soluble copper compounds are released into lakes and rivers, they generally become attached to particles in the water within approximately a day, and are then less of a threat to the environment although the particular conditions of the watershed determines the form (Environmental Bureau of Investigation, 1997). Food naturally contains copper. People ingest about 1 mg of copper every day. Copper rapidly enters the bloodstream and is distributed throughout the body after ingestion. Other foods eaten with copper can affect the amount of copper that enters the bloodstream. The human body is efficient in blocking high levels of copper from entering the bloodstream. Vomiting or diarrhea may follow ingestion of high levels of copper preventing copper from entering the blood. Copper is excreted through feces and urine. It takes several days for copper to be excreted (Environmental Bureau of Investigation, 1997).

The soil of Mingora area has copper in the range of 9 mg/kg to 87 mg/kg in the sample No. MS-9 and MS-19 respectively. The average amount of Cu in the soil of Mingora is 45 mg/kg. The soil of Kabal area is having Cu in the range of 25 mg/kg to 184 mg/kg in the sample No. KS-35-A and KS-53 respectively. The high amount of Cu has been reported in the soil of Meelagah in Kotlai village. The average concentration of Cu in the soil of Kabal are is 53 mg/kg. The soil of Kabal area is having more Cu relative to Mingora.

Lead (Pb)

The average abundance of Lead in the earth's crust is about 15 mg/kg. The terrestrial abundance of Pb indicates a tendency for Pb to concentrate in the acid series of magmatic rocks and argillaceous sediments in which the common Pb concentrations range from 10-40 mg/kg, while in ultramafic rocks and calcareous sediments its range is from 0.1 to 10 mg/kg. 100-to 500 mg/kg of Pb concentrations in soils is considered to be toxic to plants (Kabata-Pendias & Pendias, 2001).

Lead is highly toxic and is naturally available in all environmental media in small concentrations. It is probably the most serious atmospheric pollutant and is a serious cumulative body poison. A significant part of lead particles from emission sources is in the sub-micron size, which can be transported over large distances. Mining, smelting and processing of lead and lead-containing metal ores generate the majority of lead emissions from stationary sources. Decreasing use of leaded gasoline and increasing use of coal will probably result in its replacement by mercury as the most troublesome atmospheric pollutant (JICA, 2000).

Health Effects: The main pathways of lead to humans are ingestion and inhalation. Chronic exposure to lead causes weight loss, constipation and teeth loss. Children up to about six years of age constitute the population group that is at the highest risk from lead exposure through ingestion. The USEPA and EU set lead concentration in ambient air as 1.5 $\mu g/m^3$ and 2 $\mu g/m^3$ respectively, based on quarterly average. (JICA, 2000).

The Pb concentration in the soil of Mingora area is ranging from 34 mg/kg to 98 mg/kg with an average amount of 60 mg/kg while the soils of Kabal area have its concentration in the range of 34 mg/kg to 93 mg/kg with an average amount of 52 mg/kg. In most of the soil samples in both Mingora and Kabal area the concentration of Pb is below 80 mg/kg, however, in few samples in both the areas the Pb exceeds this limit.

Zinc (Zn)

Zinc is one of the most common elements in the earth's crust. It is found in the air, soil, and water and is present in all foods. In its pure elemental form, zinc is a bluish-white shiny metal. It also exists as a variety of salts and combines with other elements, such as chlorine, oxygen, and sulfur, to form zinc compounds (Environmental Bureau of Investigation, 1997). Most zinc ore found naturally in the environment is in the form of zinc sulfide. It is an essential element for life when present in trace amounts. Too little zinc in the diet can lead to poor health, reproductive problems, and lowered ability to resist disease. Too much zinc can be harmful to health.

Zinc is one of the most commonly used metals in the world. Its major uses are for galvanizing steel, producing alloys, and for serving as an ingredient in rubber, ceramics. and paints. Zinc compounds are also used to preserve wood and in manufacturing and dyeing fabrics. Zinc chloride is the major ingredient in smoke from smoke bombs. Zinc compounds are used by the drug industry as ingredients in some common products, such as sun blocks, diaper rash ointments, deodorants, athlete's foot preparations, acne and poison ivy preparations, and anti-dandruff shampoos (Environmental Bureau of Investigation, 1997).

Most zinc enters the environment as the result of human activities, such as mining, purifying of zinc, lead, and cadmium ores, steel production, coal burning, and burning of wastes. Zinc may enter the environment in the discharge from galvanizing plants, as a leachate from galvanized structures and natural ores, and from municipal waste treatment plant discharges. Zinc compounds that may be found at hazardous waste sites include zinc chloride, zinc oxide, zinc sulfate, and zinc sulfide (Environmental Bureau of Investigation, 1997).

The level of zinc in soil increases mainly from disposal of zinc wastes from metal manufacturing industries and coal ash from electric utilities. In air, zinc is present mostly as fine dust particles which eventually settles over land and water. Rain and snow aid in removing zinc from air. Most of the zinc in soil is bound to the soil and does not dissolve in water. However, depending on the characteristics of the soil, some zinc may reach groundwater. Zinc may be taken up by animals by drinking or eating soil and other animals containing zinc (Environmental Bureau of Investigation, 1997).

Zinc can enter the body through the digestive tract by ingestion of zinc-containing food or water. Zinc can also enter through inhalation of zinc dust or fumes from zinc-smelting or zinc-welding operations. The amount of zinc that passes directly through the skin is relatively small. Zinc is stored throughout the body. Zinc increases in blood and bone most rapidly after exposure. Zinc may stay in the bone for many days after exposure. Normally, zinc is excreted through urine and feces.

Health Effects: Average daily zinc intake through diet generally ranges from 7 to 16.3 mg/kg. Food may contain levels of zinc ranging from approximately 2 mg/kg (e.g., leafy vegetables) to 29 mg/kg (meats, fish, poultry). Zinc is also present in most drinking water. High-level exposure to zinc may also result from taking too many zinc dietary supplements. Fetuses and nursing children may be exposed to the zinc in the blood or milk of their mothers.

Large doses of zinc (10-15 times higher than the RDA) taken by mouth even for a short time may cause stomach cramps, nausea, and vomiting. Ingesting high levels of zinc for several months may cause anemia, damage the pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol. Harmful health effects generally begin at levels from 10-15 times the RDA (in the 100 to 250 mg/day range). Inhaling large amounts of zinc (as zinc dust or fumes from smelting or welding) can cause a specific short-term disease called metal fume fever. This is believed to be an immune response affecting the lungs and body temperature. Very little is known about the long-term effects of breathing zinc dust or fumes. High exposure to zinc dust can cause cough with phlegm. Skin irritation will probably occur in people exposed to some zinc compounds. Metal particles can irritate the eyes. (Environmental Bureau of Investigation, 1997).

The concentration of Zn is ranging from 10 mg/kg to 142 mg/kg (average = 58 mg/kg) in the soil of Mingora area. Its concentration in the soil of Kabal area is ranging from 12 mg/kg to 405 mg/ l (average = 72 mg/kg). The maximum Zn contests are reported in the sample No. MS-21-A, collected from the agricultural soil of Rahim Abad in Mingora area and in sample No. KS-59-B collected from Kotlai village in Kabal area. However, high concentration of Zn contests are noticed in the sample Nos. MS-6, MS-15-B, MS-16-A and MS-21-A collected from soils of Mingora area and in sample Nos. KS-38, KS-45-B, KS-57-A, KS-58-B, KS-59-A and KS-59-B in the soil of Kabal area.

Nickel (Ni)

Pure nickel is a hard, silvery white metal and is a very abundant element. Nickel combined with other elements occurs naturally in the earth's crust, primarily combined with oxygen (oxides) or sulfur (sulfides) and is found in all soils. Because nickel attaches to particles that contain iron or manganese, it is often present in soil and sediments.

Health Effects: Exposure to nickel occurs through breathing air or smoking tobacco containing nickel, eating food containing nickel (the major source of exposure for most people), drinking water which contains nickel, handling coins and touching other metals containing nickel (Environmental Bureau of Investigation, 1997).

A minor amount of nickel is essential for humans, although a lack of nickel has not been found to affect the health of humans. The most common adverse health effect of nickel in humans is an allergic reaction. People can become sensitive to nickel when jewelry or other things containing this metal come into direct contact with the skin. Once a person is sensitized to nickel, further contact with it will produce a reaction. Symptoms include burning, itching, redness and bumps or other rashes. A rash may spread to other areas and last for weeks after exposure stops, but usually improves in about a week. Less frequently, some people who are sensitive to nickel have asthma attacks following exposure to nickel. Eye or skin contact may cause irritation. Lung effects, including chronic bronchitis and reduced lung function, have been observed in workers who inhaled large amounts of nickel. High exposure can cause cough, shortness of breath and fluid in the lungs, which is sometimes delayed for 1 to 2 days after exposure (Environmental Bureau of Investigation, 1997).

Single high or repeated lower exposures may damage the lungs, with scarring of lung tissues, and may cause damage to heart muscle, liver and/or kidney. Fumes from heated nickel can cause a pneumonia-like illness, with cough and shortness of breath. Higher exposures can cause a build-up of fluid in the lungs (pulmonary edema), a medical emergency, with severe shortness of breath. Exposure to nickel can cause a sore or hole in the "bone" dividing the inner nose (septum). Nickel and certain nickel compounds may reasonably be anticipated to be carcinogens. Cancers of the lung, nasal sinus, and throat have resulted when workers breathed dust containing high levels of nickel compounds while working in nickel refineries or nickel processing plants. Carcinogens may also have the potential for causing reproductive damage in humans. Nickel may damage the developing fetus (Environmental Bureau of Investigation, 1997).

The Ni concentration in the soil of Mingora area is ranging from 207 mg/kg to 2341 mg/kg with an average amount of 788 mg/kg while the soil of Kabal area has Ni contents in the range of 136 mg/kg to 302 mg/kg with an average amount of 211 mg/kg. The Mingora soil is relatively more enriched as compare to the soil of Kabal area. In certain areas of Mingora the soil has very high amount (> 1000 mg/kg) of nickel (Table 4.2).

Chromium (Cr)

Chromium is widely distributed in the earth crust and it has an average concentration f 125 mg/kg in the continental crust. Cr is inherited from parent rocks and, therefore, its higher concentration in soils is derived from mafic and volcanic rocks. Soils on ultramafic rocks are known to contain as much as 0.2 to 0.4% Cr, and these soils are said to be infertile (Kabata-Pendias & Pendias, 1999). Sandy soils are usually poorest in Cr. Chromium shows highly variable oxidation states i.e., Cr^{2+} and Cr^{6+} and it forms complex anionic and cationic ions (e.g., $Cr(OH)^{2+}$, $CrO^{2-}{}_{4}$, $CrO^{3-}{}_{3}$). The immobility of soil Cr may be responsible for an inadequate Cr supply to plants. Cr^{6+} in soils is toxic to plants and animals (Kabata-Pendias & Pendias, 2001).

Cr content of surface soil is increased due to pollution from various sources, e.g., industrial wastes and municipal sewage sludge. Liming, P application and organic matter are known to be effective in reducing chromate toxicity in Cr-polluted soils. If contamination is by Cr^{6+}, acidification and then reducing agents (e.g. S and leaf litter) could be used to speed the Cr^{6+} reduction (Grove & Ellis, 1980).

Health Effects: Chromium is an essential nutrient required for normal sugar and fat metabolism and works primarily by ensuring insulin acts correctly. It is present in the entire body but with the highest concentrations in the liver, kidneys, spleen and bone. Cr^{6+} is more readily absorbed from the gastrointestinal tract than Cr^{3+} and is able to penetrate cellular membranes. It is considered as human carcinogen. 0.05 mg/kg is considered to be unlikely to give rise to significant risks to health (WHO, 1993). Chronic exposure to high Cr levels has been correlated to lung cancer in man and liver and kidney damage in animals (Himmelhoch, et al., 1966).

The Cr concentration in the soils of Mingora area are ranging from 311 mg/kg to 5647 mg/kg with an average amount of 973 mg/kg while the soils of Kabal area are having Cr in the range of 123 mg/kg to 679 mg/kg with an average amount 314 mg/kg. It is clear from Tables 4.2 and 4.3 that the soil of Mingora is highly enriched in the Cr as compare to that of the soil of Kabal area. In Kabal area the Cr concentration is generally less than 1000 mg/kg. In Mingora area the concentration of Cr in the soil is less than 1000 mg/kg but in certain samples (i.e., MS-5, MS-6, MS-9, MS-10, MS-11, MS-12, and MS-14) it exceeds 1000 mg/kg. Among these two samples such as MS-11 and MS-14 have the concentration of Cr reaching upto 4035 mg/kg and 5647 mg/kg respectively.

Cobalt (Co)

Cobalt, a natural element present in certain ores of the earth's crust, is essential to life in trace amounts. It exists in the form of various salts. Pure cobalt is an odorless, steel-gray, shiny, hard metal. Everyone is exposed to low levels of cobalt in air, water, and food. An average of 2 g/l in drinking water has been estimated. Cobalt has both beneficial and harmful effects on health (Environmental Bureau of Investigation, 1997).

Important natural sources of cobalt in the environment are soil, dust, and seawater. It is also released to the environment from burning coal and oil. The water solubility of cobalt and its salts range from highly soluble to practically insoluble and it can be transferred from the soil to underground water and also the plants grown on it. Cobalt and its salts are highly persistent in water, with a half- life greater than 200 days (Environmental Bureau of Investigation, 1997).

Health Effects: Effects on the lungs, including asthma, pneumonia, and wheezing, have been found in workers who breathed high levels of cobalt in the air.

Drinking large quantity of Co causes nausea, vomiting, and serious effects on the heart. Exposure can cause a severe allergic lung reaction with coughing, wheezing, chest pain and shortness of breath. The International Agency for Research on Cancer has determined that cobalt is a possible carcinogen to humans. Repeated exposure can cause scarring of the lungs (fibrosis) even if no symptoms are noticed. Cobalt dust may irritate eye, nose, mouth, throat and the skin, causing a rash or burning feeling on contact. High levels of Co can irritate the lungs, causing a build up of fluid (pulmonary edema). Cobalt compounds may cause mutations (genetic changes) in living cells. Exposure to ionizing radiation is associated with an increased risk of developing cancer. Some isotopes of Co emit ionizing radiation (Environmental Bureau of Investigation, 1997).

Cobalt occurs in the range of 12 mg/kg to 32 mg/kg with an average amount of 19 mg/kg in the soil of Mingora area. While in the soil of Kabal area it varies from 4 mg/kg to 32 mg/kg with an average amount of 17 mg/kg. The soils of both the areas have more or less the same concentration of Co (Table 4.2 & 4.3).

Cadmium (Cd)

Cadmium is a soft, ductile, silver-white, metal. It is naturally occurring in soils, water and plants (Adriano, 1986). Soils derived from igneous rocks contain lowest Cd (<0.1 to 0.3 mg/kg), soils derived from metamorphic rocks contain intermediate Cd concentration (0.1-1.0 mg/kg), and soils derived from sedimentary rocks contain the largest quantity of Cd (0.3 – 11 mg/kg) (Page and Bingham, 1973). Cd is quite immobile in the soil profile. It always occurs in combination with zinc. Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. Cadmium strongly adsorbs to organic matter in soils. When cadmium is present in soils, it can be extremely dangerous, as the uptake through food will increase. Soils with low pH values enhance the cadmium uptake by plants. This is a potential danger to the animals dependent upon the plants for survival.

Human uptake of cadmium takes place mainly through food. Cadmium is first transported to the liver through the blood. There, it is bonded to proteins to form complexes that are transported to the kidneys. It accumulates in kidneys, where it damages nephrons. Other health effects caused by cadmium are: diarrhoea, stomach pains and severe vomiting, bone fracture, reproductive failure and possibly even infertility and damage to the central nervous system etc.(Agarwal, 2002).

The Cd concentration in the soils of Mingora area varies from 2 mg/kg to 4 mg/kg with an average amount of 3 mg/kg while the soils of Kabal area have Cd in the range 2 mg/kg to 4 mg/kg with an average amount of 3 mg/kg. It seems that both the soils of Mingora and Kabal area have generally Cd up to 3 mg/kg.

Manganese (Mn)

Manganese is one of the most abundant trace elements in the lithosphere, and it is ranging from 350 to 2000 mg/kg in rocks. Its highest concentrations are usually associated with mafic rocks. Mn exists mostly as ions Mn^{+2} and Mn^{+3} or Mn^{+4} but its +2 oxidation state is most frequent in the rock forming silicate minerals. The cation Mn^{+2} is known to replace the sites of some divalent cations (Fe^{+2}, Mg^{+2}) in silicates and oxides. Mn is essential in plant nutrition and controls the behavior of several other micronutrients. It has considerable effect on pH of soil (Kabata-Pendias & Pendias, 2001).

Health Effects: The human body manganese content is estimated to be 12-20 mg/kg. Its high contents in the human body may cause health related hazards. In patients with rheumatoid arthritis the Mn level in the red blood cells is significantly raised (Himmelhoch, et al., 1966).

The value of Mn in soils of Mingora varies from 36 mg/kg to 111 mg/kg with an average amount of 65 mg/kg while its concentration in soil of Kabal area is ranging from 45 mg/kg to 105 mg/kg with an average amount of 69 mg/kg. Both the soils of Mingora and Kabal area have more or less similar amount of Mn.

Table. 4.1. Physiochemical parameters of the soils of Mingora and Kabal areas.

S.No	pH	Electrical Conductivity µS/cm	Temp °C	TDS mg/l	Salinity	Resistivity kΩ/cm
Mingora						
MS-1	7.12	458	23.2	243	0.2	2.18
MS-2	6.99	983	24.7	523	0.5	1.018
MS-3	7.04	582	25.2	309	0.3	1.717
MS-4	6.99	911	25.8	484	0.4	1.098
MS-5	7	217	24.5	115	0.1	4.62
MS-6	7.02	179.7	26	95.5	0.1	5.56
MS-7	7.1	262	24.9	139	0.1	3.81
MS-8	6.99	279	23.9	148	0.1	3.59
MS-9	6.98	455	24.9	242	0.2	2.2
MS-10	7.01	296	25.8	157	0.1	3.38
MS-11	7.01	342	26.1	182	0.2	2.92
MS-12	7.02	282	25.8	149	0.1	3.53
MS-13-A	7	419	24.9	222	0.2	2.39
MS-13-B	7.01	386	26.6	205	0.2	2.59
MS-15-A	6.94	309	25.8	165	0.2	3.22
MS-15-B	7.06	229	24	122	0.1	4.36
M-16-A	6.99	287	23.6	153	0.1	3.47
MS-16-B	6.98	253	24	134	0.1	3.96
MS-17	7	539	24	286	0.3	1.855
MS-18	6.84	339	24.3	180	0.2	2.95
MS-19	6.94	416	26.1	221	0.2	2.4
MS-20	6.97	416	24	221	0.2	2.41
MS-21-A	7.02	406	24.5	214	0.2	2.47
MS-21-B	6.98	284	25.2	151	0.1	3.52
MS-22	7.02	963	24.3	512	0.5	1.038
MS-25	7.19	448	23.5	238	0.2	2.23
MS-26	6.82	532	23.7	283	0.3	1.881
MS-29	6.96	557	24.5	296	0.3	1.796
MS-31-A	6.84	497	27.3	266	0.2	2
MS-33	6.98	316	27.1	168	0.2	3.17
MS-34-A	6.99	320	24	170	0.2	3.13
MS-34-B	6.96	308	26.4	184	0.2	3.25
Average	**6.99**	**421**	**25**	**224**	**0.2**	**2.80**

Continued from Table 4.1.

S.No	pH	Electrical Conductivity µS/cm	Temp °C	TDS mg/l	Salinity	Resistivity kΩ/cm
Kabal						
KS-35-A	6.87	524	24.2	278	0.3	1.912
KS-35-B	6.98	299	24.3	159	0.1	3.34
KS-36-A	6.97	383	24	203	0.2	2.62
KS-36-B	7	431	23	229	0.2	2.33
KS-37	7	292	24.9	155	0.1	3.43
KS-40	ND	ND	ND	ND	ND	ND
KS-41	7.13	236	27.7	125	0.1	4.23
KS-42-A	6.97	212	24.3	113	0.1	5.08
KS-42-B	7.01	282	23.3	150	0.1	3.54
KS-43-A	7.13	330	23.7	176	0.2	3.02
KS-43-B	6.98	314	24.7	166	0.2	3.19
KS-44-A	6.97	364	26.7	194	0.2	2.75
KS-44-B	7.01	323	24.7	172	0.2	3.1
KS-45-A	6.97	316	24	169	0.2	3.16
KS-45-B	6.96	271	24.3	143	0.1	3.69
KS-47-A	6.9	470	24.1	250	0.2	2.14
KS-47-B	7	242	25.3	129	0.1	4.13
KS-48-A	7.01	473	23.6	252	0.2	2.11
KS-48-B	7.04	268	26.2	133	0.1	3.72
KS-49-A	6.99	393	24	210	0.2	2.54
KS-49-B	7.02	408	24.1	217	0.2	2.46
KS-50-A	7.01	323	24.4	172	0.2	3.1
KS-50-B	7.06	255	26.1	136	0.1	3.91
KS-51	6.97	224	24.1	118	0.1	4.48
KS-52	7	409	23.9	217	0.2	2.45
KS-53	7.01	354	24.7	188	0.2	2.83
KS-55	7.03	380	24	201	0.2	2.63
KS-57-A	7	586	23.1	311	0.3	1.711
KS-57-B	6.98	247	27.4	132	0.1	4.03
KS-58-A	7	347	23.8	185	0.2	2.86
KS-58-B	6.98	231	24.9	122	0.1	4.34
KS-59-A	7.01	235	24.5	125	0.1	4.26
KS-59-B	7.03	258	24.1	136	0.1	3.89
Average	**7.00**	**334**	**24.6**	**177**	**0.2**	**3.22**
Reference soil	7.03	316	23.9	167	0.2	3.62

Table. 4.2. Light element oxides and trace and heavy metals in the soils of Mingora area (oxides are in wt % and the trace and heavy metals are in mg/kg)

Sample Code	CaO	MgO	Na_2O	K_2O	Fe	Cu	Pb	Zn	Ni	Cr	Co	Cd	Mn
MS-1	4.26	2.6	1.07	1.81	25590	64	62	10	436	446	16	2	86
MS-2	2.22	2.02	1.4	2.38	21143	83	81	44	468	371	16	3	96
MS-3	3.27	1.88	2.4	1.77	22245	69	82	47	318	409	15	3	86
MS-4	2.18	1.99	1.43	2.25	23921	65	90	50	360	457	14	3	105
MS-5	3.33	29.11	1.8	0.41	26520	57	62	59	1368	1568	32	3	53
MS-6	2.91	22.71	1.46	0.36	24521	49	60	104	1929	1245	30	3	47
MS-7	2.6	16.75	1.42	0.47	25313	16	52	26	1596	657	29	3	63
MS-8	1.78	28.31	1.06	1.23	22841	53	38	23	1467	879	22	3	43
MS-9	1.47	22.02	1.38	1.09	19841	29	34	25	1314	1231	18	2	40
MS-10	3.02	19.52	1.93	0.62	23213	9	55	81	1563	1269	21	3	43
MS-11	3.01	27.16	1.54	0.52	34567	41	56	17	1836	4035	25	3	50
MS-12	2.28	22.09	1.25	0.52	23479	62	49	15	1440	1425	22	3	46
MS-13-A	3.49	2.05	1.76	1.39	25298	55	59	81	270	486	18	3	72
MS-13-B	3.27	2.17	1.76	2.27	27848	46	54	68	216	357	15	3	63
MS-14	2.89	29.23	1.34	0.65	38763	34	67	18	2341	5647	26	4	55
MS-15-A	3.9	1.85	1.24	2.2	28384	75	53	63	259	372	18	3	73
MS-15-B	3.53	1.89	1.57	1.42	27821	42	54	128	242	364	15	3	67
MS-16-A	2.62	1.87	2.42	2.3	25628	57	98	134	221	407	15	3	55
MS-16-B	2.53	1.95	1.88	1.77	26216	52	55	78	242	311	16	3	54
MS-17	1.19	0.86	1.98	1.3	12499	73	52	40	501	643	15	3	36

Continued from Table 4.2.

Sample Code	**CaO**	**MgO**	**Na_2O**	**K_2O**	**Fe**	**Cu**	**Pb**	**Zn**	**Ni**	**Cr**	**Co**	**Cd**	**Mn**
MS-18	7.04	3.27	1.67	1.65	25343	48	47	44	421	554	15	3	111
MS-19	8.99	3.79	1.03	1.39	28455	87	39	28	207	338	12	3	87
MS-20	3	3.21	1.31	1.81	29951	71	48	43	210	366	13	3	94
MS-21-A	1.4	1.06	1.24	2.21	23756	47	81	142	329	637	19	4	62
M-S-21-B	1.43	0.6	1.12	2.21	25748	45	55	45	259	338	18	3	65
MS-22	3.2	1.3	1.51	2.13	21356	60	89	95	673	490	16	3	41
Average	3.11	9.66	1.54	1.47	25395	44.69	60.46	58.00	787.92	973.15	18.88	3.00	65.12

ND = Not detected; MS = Mingora Soil

Table. 4.3. Light element oxides and trace and heavy metals in the soils of Kabal area (oxides are in wt % and the trace and heavy metals are in mg/kg).

Sample Code	CaO	MgO	Na_2O	K_2O	Fe	Cu	Pb	Zn	Ni	Cr	Co	Cd	Mn
KS-35-A	7.39	3.33	1.39	1.51	34804	47	49	106	270	349	14	3	79
KS-35-B	8.11	3.82	1.14	0.67	33124	61	50	42	229	381	20	4	83
KS-36-A	4.63	3.05	1.51	1.91	31406	55	56	51	240	447	18	3	78
KS-36-B	4.25	2.9	1.33	3.59	31001	68	56	88	262	360	19	4	81
KS-37	5.51	1.98	1.39	0.99	35033	60	45	39	146	140	17	4	99
KS-38	2.45	1.65	1.98	1.34	26897	48	57	135	253	324	13	2	72
KS-39	5.34	1.89	1.65	0.87	28921	54	42	89	156	187	24	3	105
KS-40	4.56	1.76	1.21	0.97	36542	54	36	43	167	123	12	3	78
KS-41	4.73	1.62	1.92	0.94	35186	47	47	70	136	158	19	4	91
KS-42-A	4.12	1.92	1.9	1.32	33379	52	42	13	177	213	17	3	84
KS-42-B	3.93	2.02	1.88	1.48	34084	60	51	12	184	217	20	4	85
KS-43-A	5.24	2.11	1.89	0.97	27135	25	47	33	264	469	14	3	58
KS-43-B	6.37	3.64	1.64	0.71	27176	37	53	49	298	445	18	3	80
KS-44-A	2.71	1.62	1.18	1.72	25620	35	45	67	238	329	15	3	53
KS-44-B	2.16	1.47	1.16	1.6	22391	37	47	47	231	323	15	3	49
KS-45-A	6.51	1.72	1.82	1.42	27173	33	52	63	177	299	14	3	62
KS-45-B	6	2.14	1.78	1.99	27821	38	62	146	188	438	16	3	67
KS-46	4.56	1.76	1.54	1.34	26980	73	52	63	177	299	16	3	61
KS-47-A	3.44	1.05	1.51	1.83	24375	46	39	52	233	272	15	3	56
KS-47-B	3.59	1.14	1.79	2.16	25579	33	42	43	210	232	13	3	61
KS-48-A	3.72	2.95	1.54	1.59	27825	49	46	78	242	363	15	3	69

Continued from Table 4.3.

Sample Code	**CaO**	**MgO**	**Na2O**	**K2O**	**Fe**	**Cu**	**Pb**	**Zn**	**Ni**	**Cr**	**Co**	**Cd**	**Mn**
KS-48-B	4.05	2.85	1.43	1.84	27799	72	44	50	302	454	18	3	66
KS-49-A	3.97	1.8	1.86	2.33	25961	49	46	78	244	363	12	3	50
KS-49-B	3.85	1.53	1.18	2.31	23524	31	56	40	180	363	15	3	49
KS-50-A	6.54	0.74	1.24	2.72	20921	29	57	59	168	233	13	3	45
KS-50-B	6.98	0.7	2.68	1.99	20974	36	59	42	220	335	13	3	50
KS-51	6.03	2.98	1.07	0.54	43613	60	44	26	140	322	22	4	75
KS-52	6.39	4.66	1.89	0.54	42450	161	56	39	300	679	32	4	76
KS-53	5.75	4.41	1.82	0.49	33379	184	41	28	184	274	21	3	61
KS-54	3.67	1.89	1.89	2.12	26431	32	46	38	143	261	14	3	66
KS-55	6.01	3.26	1.88	1.21	37725	86	52	27	201	336	24	2	61
KS-56	4.23	2.34	1.89	0.67	27456	42	34	67	187	145	29	3	78
KS-57-A	6.18	3.02	1.86	1.5	36180	61	34	245	188	320	21	3	86
KS-57-B	5.65	2.78	1.12	1.64	35756	61	93	44	231	404	21	3	84
KS-58-A	2.91	0.93	1.08	2.4	22399	43	52	59	233	295	15	4	52
KS-58-B	2.77	1.05	1.13	2.66	23351	43	74	123	259	311	15	3	54
KS-59-A	4.58	2.11	1.68	1.48	29843	56	51	130	241	334	4	3	66
KS-59-B	3.95	1.63	1.79	1.73	29190	38	83	405	198	272	15	3	68
Average	**4.81**	**2.22**	**1.60**	**1.56**	**29721**	**53**	**52**	**72**	**211**	**314**	**17**	**3**	**69**
Reference soil	1.99	3.89	1.91	1.24	2510	17	8	14	31	30	2	0.674	90

ND = Not detected; KS = Kabal Soil

Table 4.4. Light element oxides and trace and heavy metals in reference soils of Mingora (oxides are in wt % and the trace and heavy metals are in mg/kg)

Sample Code	**CaO**	**MgO**	**Na_2O**	**K_2O**	**Fe**	**Cu**	**Pb**	**Zn**	**Ni**	**Cr**	**Co**	**Cd**	**Mn**
MS-24	2.42	1.07	1.54	0.5	2321	18	13	17	15	18	2	0.651	ND
MS-26	1.94	0.07	1.47	2.13	2603	7	5	2	42	56	2	0.603	86
MS-27	2.08	1.32	1.14	0.37	2531	11	11	10	48	45	3	0.775	72
MS-28	3.7	2.44	1	1.53	3141	15	19	13	31	28	2	0.606	72
MS-29	2.79	2.12	1.45	1.5	2235	22	17	19	23	32	1	0.7	65
MS-30	1.88	1.96	1.18	1.07	2135	21	15	18	30	34	2	0.7	46
MS-31	3.45	1.85	1.22	1.58	2391	18	15	10	23	29	2	0.754	67
MS-33	4.24	1.31	1.07	1.76	2683	13	24	8	34	34	2	0.549	111
MS-34-A	1.14	1	1.92	1.77	2279	21	11	16	12	10	2	0.848	70
MS-34-B	1.34	1.08	1.78	1.65	2134	8	12	13	31	38	2	0.745	64
Average	2.50	1.42	1.38	1.39	2445	15.4	14.2	12.6	28.9	32.4	2	0.57	72.56

ND = Not detected; MS = Mingora Soil

CHAPTER 5

BIOGEOCHEMISTRY

INTRODUCTION

The field of biogeochemistry involves scientific study of the chemical, physical, geological, and biological processes and reactions that govern the composition of the natural environment (including the biosphere, hydrosphere, pedosphere, atmosphere, and lithosphere), and the cycles of matter and energy that transport the Earth's chemical components in time and space (Widipedia, 2006).

The distribution of heavy metals in natural soils can affect the plant species growing in an area. These species have, therefore, been used successfully as tracers in mineral prospecting and environmental degradation in many areas. The mechanism of accumulation of a substance or its enrichment, in relation to its environment, often involves additional energy consumption and increased enzyme activity (Brook, 1983). Lower and higher plants are included as the accumulative organisms. A biological absorption coefficient value, or the ratio between the concentration of a given element in plant and soil, decreases exponentially with the increase of concentration in soil (Brook, 1983). A vegetable species can also develop natural barriers against excess concentrations of an element, according to the need and tolerance for it (Kovalesky 1969). Due to several factors such as drainage, pH the nature of clay minerals, antagonistic effects of other ions and the presence of complexing agents, very little of the total contents of some elements in the soil can be utilized by plants (Brook, 1983).

Around the world, ultramafic outcrops are characterized by altered vegetation forms: endemism, indicator species, edaphic races (Kruckeberg, 1992). Why do ultramafic support such unique plant species communities? This question has been scientifically investigated since the beginning of the 20th century and physical, chemical and biological components have been isolated to determine a cause. Much of the scientific work has gone into determining plant response to ultramafic chemistry including tissue analysis, nutrient cultures and field and greenhouse trails with fertilizers. There are several vegetation studies to determine patterns in plant communities (e.g., Cooke 1994). The synthesis of these varied works gives the impression that there is no single factor that describes the effect(s) of ultramafic rocks on plants. Instead, there must be a host of factors, that may or may not be present on a given site, that culminate to create the "serpentine effect" (Kruckeberg, 1992).

As in all organisms, metal cations are crucial for nutrition in plants. Several metals, such as copper, iron, zinc, and manganese, act as important cofactors for many enzymes and are essential for both mitochondrial and chloroplast functions. However, when supplied in excess, these essential cations can become toxic, like heavy metals with no generally established function, such as cadmium, lead, or mercury (Clemens, 2001; Hall and Williams, 2003).

Macro and micronutrients in plants

Macronutrients are the elements, which are required in relatively large quantities e.g. Na, K, Ca, Mg etc for the proper growth of plants and proper functioning of human body.

Micronutrients are the trace and heavy elements required in minor quantities (e.g. Cu, Zn, Cr etc.) for proper growth of plants as well as proper functioning of human body. The excess or reductions of these micronutrients or trace metals may negatively affect plant as well as human life.

Review of effects of Trace metals in Plants

The reaction of plants to chemical stresses are caused by deficiencies and excesses of trace elements, cannot be defined exactly because plants have several biochemical mechanisms that have been resulted in adaptation to tolerance of new or chemically imbalanced environments. Therefore, plant responses to trace elements in the soil and ambient air always needs to be investigated for the particular soil-plant system (Kabata-Pendias &d Pendias, 2001).

Plants reveal various tendencies in the uptake of trace elements. Three general uptake characteristics can be distinguished: accumulation, indication and exclusion. To a large extent, this depends on the specific ability of plants and huge differences in metal uptake between plant species. Also between genotypes of a species, great variabilitiess have been demonstrated in many studies (Simon, 1999). The most common plants tested for phytoremediation have been listed by Felix et al. (1999) such as *Alysssum murale, Thlaspi caerulescens, Nicotiana tobaccum, Zea mays, Brassica juncea, and Salix viminalis*. The ability of several agricultural crop species, such as mustard, radish, turnip, rape, and amaranth, to accumulate higher amounts of some metals like Cd, Cr, Cu, Ni and Zn has been well investigated (Simon, 1999).

Plants able to take up metals above established background concentrations and more than other species from the same soils are called hyperaccumulators. These are mainly populations of species found in soils rich in metals either due to geochemical parameters or due to pollution. Hyperaccumulators usually have a low biomass because they use more energy in the mechanisms necessary to adapt to the high metal concentrations in the tissues. Plants that highly accumulate metals are used in phytoremediation programs (Brooks, 1998; Prasad, 1997).

A number of plants are known as medicinal herbs, used for curing illness. Although a curative agent is mainly associated with organic compounds such as glycosides or alkaloids, trace elements can have additional impact. Most medicinal plants belong to a kind of weed that can accumulate a greater amount of trace elements than other plants. A good example is dandelion often used in herb medicine and also as a nutritional plant. However, dandelion grown in a polluted environment, takes up many more trace metals than other plants, from both ariel and soil sources (Kabata-Pendias & Krakowiak, 1998)

In general the chemical composition of plants reflects the elemental composition of the growth media. The extent to which this relation exists, is highly variable and is governed by many different factors. The common concentrations of trace elements in plants growing on various non-polluted soils show quite a large variation for each element. It is observed that sea plants contain more Al, As, Br, Cl, I, Sr, V and Fe (on a dry matter basis) than terrestrial plants (Hou et al., 1998).

Sources of trace elements and their uptake by plants: The main sources of trace elements in plants are their growth media, e.g., nutrient solutions or soils. One of the most important factors that determines the biological availability of a trace element is its binding to soil constituents. Generally plants readily take up the species that are dissolved in soil solutions in either ionic or chelated or complexed forms. Much have been written on the absorption of trace elements from solutions by Moore (1972), Loneragan (1975), Mengel and Kirkby (1978), Wild and Jones (1988), etc. this absorption can be summarized as follow:

- It usually operates at very low concentrations in solutions.
- It largely depends on the concentrations in the solution, especially at low ranges.
- The rate depends strongly on the occurrence of H^+ and other ions.
- The intensity varies with the plant species and stage of development.
- The processes are sensitive to some properties of the soil environment such as temperature, aeration, etc.
- It may be selective for a particular ion.
- The accumulation of some ions can take place against a concentration gradient.
- Mycorrhizae play an important role in cycling between external media and roots.

Generally the uptake of trace elements by plants is effected, in addition to plant specific ability, by soil factors like pH, water regime, clay content, organic matter content, cation exchange capacity, nutrient balance and concentration of other trace elements. Also, climatic conditions are shown to influence the rate of trace metal uptake, which may be partly an indirect impact due to the water flow phenomenon. Generally higher ambient temperature influences a greater uptake of trace elements by plants. The metal absorption in plants is through root and foliar uptake (Kabata-Pendias & Pendias, 2001)

Phytotoxicities: Vegetation can be used as a useful indicator of heavy metal contamination in an environment in that root uptake of metals can integrate environmental levels across both spatial and temporal scales. Heavy metal accumulation by vegetation can be further magnified within ecosystem via food webs (Pugh et al., 2002).

Phytotoxicities refer to reduce yields or death of plants by substances in soil. Symptoms for trace element-induced phytotoxicities include stunting, chlorosis, necrosis, and death of the plant. Trace elements mostly associated with phytotoxicities are Cu, Ni, and Zn. Copper will generally remain on leaf surfaces for 1-2 weeks, or until it is washed off by rain or overhead irrigation. It is always present at a background level, but can be of concern in situations of heavy agronomic use of copper compounds. Phytotoxicity problems are of concern for two primary reasons. First, the reduction in soil quality induced by elevated trace elements concentrations that reduce both the quantity and quality of food produced from that soil. The second reason relates to areas where vegetation is sparse because of trace element phytotoxicities so that wind and water erosion can occur uninhibited. These conditions often exist around sites where metal mining or smelting once took place (Pierzynski, et al., 2000).

Plants collected from mafic and ultramafic terrains of Mingora and Kabal were investigated for trace and heavy metals as well as light element cations. Plant species of ten families were collected from the Mingora and Kabal areas (Annex-2). The representative photographs of various plants are given in Plate 1 to Plate 10 (Annex-3). About 47 samples of plants, including reference plants, were analyzed for the macro and micronutrients (Chapter 2) and the results are given in Table 5.1 and 5.2.

MACRONUTRIENTS OR LIGHT ELEMENT CATIONS IN STUDIED PLANTS

Calcium (Ca)

Calcium itself is relatively non-toxic to plants although it is well known that disorders like chlorosis can be induced in some species by excessive liming of soil. Calcium deficiencies may occur in aluminum saturated acidic and magnesium serpentine soils.

Calcium concentration in all plants is ranging from 287 mg/kg in sample No. MP-15 (*Oryza sativa*), collected from Hayat Abad in Mingora area to to 20645 mg/kg in sample No. MP-22 (*Cannabis sativa*), collected from Rahim Abad, Mingora.

Magnesium (Mg)

Magnesium is macronutrient with distinctive functions in plants where it is a structural component of chlorophyll pigments. Unlike Ca^2+, levels of free Mg^2+ are not unduly low cytoplasm where it activates a much wider range of enzyme systems and is involved in ATP- dependent reactions. (Allen, 1989).

Mg content in studied plants is ranging from 11 mg/kg in sample No. MP-4 (*Otostegia limbata)* of Labiateae, collected from Maluk Abad, Mingora, to 7119 mg/kg in sample No. MP-13 *(Debergeasia sulicifolia)* of Utricaceae at Mingora mines area towards Fizagat.

Sodium (Na)

Amount of Na is ranging from 22 mg/kg in sample No. KP-38 (*Saccharum spp.)* of Poaceae, collected from Deerai Baba, Kanju, to 287 mg/kg in sample No. MP-19 *(Isodon rugosus*) of Labiateae, collected from mountainous area of Rahim Abad, Mingora. However, higher amount (380 mg/kg) of Na is reported in the reference sample of Polygonaceae.

Potassium (K)

Potassium concentration in selected plant families is ranging from 69 mg/kg to 26044 mg/kg. Low K contents are observed in MP-3 of Sapindaceae collected from Maluk Abad in Mingora area, while highest K (26044 mg/kg) is found in *Zea mays* of Poaceae, collected from agricultural field in Kabal area.

MICRONUTRIENTS OR TRACE AND HEAY METALS IN STUDIED PLANTS

The concentration of Fe, Cu, Pb, Zn, Cr, Ni, Co, Cd and Mn were determined in all selected plant families, including Poaceae, Papilionaceae, Polygonaceae, Labiateae, Aesteraceae, Sapindaceae, Utricaceae, Cannabinaceae, Simarubaceae and Amaranthaceae. All the plants were grouped into their respective families. Following are results of the above-mentioned trace elements in plants.

Poaceae

Iron (Fe): Fe concentration in Poaceae species is ranging from 1719 mg/kg in sample No. KP54 (*Dicanthium annulatum*), collected from Meelagah-Kotlai to 5744 mg/kg in sample No. KP-46 (*Zea mays*), collected from Kabal village. 456 mg/kg of Fe concentration is reported in reference sample. The average concentration of Fe (3079 mg/kg) in Poaceae is much higher than reference sample.

Copper (Cu): Cu concentration in Poaceae species is ranging from 7 mg/kg in sample No. MP15 (*Oryza sativa*), collected from Hayat Abad in Mingora to 68 mg/kg in sample No. KP57 (*Zea mays*) Meelagah-Kotlai in Kabal area. 6 mg/kg of Cu concentration is reported in reference sample. The average Cu concentration (30 mg/kg) in Poaceae is higher than the reference sample.

Lead (Pb): Pb concentration in Poaceae species is ranging from 3 mg/kg in sample Nos. KP-38 (*Saccharum species)* and KP-35 (*Zea mays*), collected from Deerai Baba, Knaju and Kanju village respectively to 9 mg/kg in sample No. MP-12 (*Saccharum species),* collected from emerald mine area, Fizagat. The concentration of Pb in reference sample is reported as 3 mg/kg. The average concentration of Pb (5 mg/kg) is higher than the reference sample.

Zinc (Zn): Zn concentration in Poaceae species is ranging from 4 mg/kg in sample No. MP-15 (*Oryza sativa)*, collected from Hayat Abad in Mingora area to 43 mg/kg in sample No. KP57 (*Zea mays)*, collected from Meelagah- Kotlai in Kabal area. 4 mg/kg of Zn is reported in reference sample. The average Zn concentration (19 mg/kg) in Poaceae is higher than the reference sample.

Nickel (Ni): Ni concentration in Poaceae species is ranging from 31 mg/kg in sample No. KP38 (*Saccharum spp.)*, collected from Deerai Baba to 289 mg/kg in sample No. MP6 (*Saccharum spp.*), collected from Maluk Abad within emerald mine area. Ni concentration of 4 mg/kg is reported in reference sample. The average concentration of Ni (80 mg/kg) in Poaceae is higher than the reference sample.

Chromium (Cr): Cr concentration in Poaceae species is ranging from 56 mg/kg in sample No. KP54 (*Dicanthium annulatum),* collected from Meelagah-Kotlai to 358 mg/kg for MP6 (*Saccharum spp.*), collected from Maluk Abad within emerald mine area. 5 mg/kg of Cr concentration is reported in reference. The average Cr concentration (122 mg/kg) in Poaceae is higher than the reference sample.

Cobalt (Co): Co concentration in Poaceae species is ranging from 5mg/kg in sample Nos. KP38 (*Saccharum spp.)* and KP54 (*Dicanthium annulatum*), collected from Deerai Baba and Meelagah-Kotlai respectively to 9 mg/kg in sample No. KP35 (*Zea mays),* collected from Kanju village. Co concetration of 0.89mg/kg is reported in reference sample. The average concentration of Co (6 mg/kg) in Poaceae is higher than the reference sample.

Cadmium (Cd): Cd concentration in Poaceae species is ranging from 0.089 mg/kg in sample No. KP35 (Zea mays), collected from Kanju village to 0.389 mg/kg in sample No. KP46 (Zea mays), collected from Kabal village. 0.093 mg/kg of Cd is reported in reference sample. The average Cd concentration (0.241 mg/kg) in Poaceae is higher than the reference sample.

Manganese (Mn): Mn is an essential minor nutrient for plants. It is involved in enzyme activation and in some of the reactions required for photosynthesis and nitrogen metabolism. Mn deficiencies can occur on calcarious soils and toxicities on acid sites in species not adapted to these habitats. Concentration of few mg/kg in solution can effect a sensitive species(Allen, 1989). Mn concentration in Poaceae species is ranging from 13 mg/kg in sample No. KP-35 (Zea mays), collected from Kanju village to 115 mg/kg in sample No. KP-54 (*Dicanthium annulatum)*, collected from Meelagah-Kotlai. 30 mg/kg of Mn is reported in reference sample. The average concentration of Mn (49 mg/kg) in Poaceae is higher than reference.

Papilionaceae

Iron (Fe): Fe concentration in Paplionaceae species is ranging from 1625 mg/kg in sample No. MP-11 (*Indigofrra gerardiana*) to 1863 mg/kg in sample No. MP-14 (*Lespediza juncea*), collected from emerald mine area, Fizagat. Fe concentration of 439 mg/kg is reported in reference sample. The average concentration of Fe (1744 mg/kg) is much higher than the reference sample.

Copper (Cu): Cu concentration in Paplionaceae species is ranging from 9 mg/kg in sample No. MP-14 (*Lespediza juncea)*, collected from emerald mine area, Fizagat to 14 mg/kg in sample No. MP-11(*Indigofrra gerardiana*), collected from emerald mine area, Fizagat. 3 mg/kg of Cu is reported in reference sample. The average concentration of Cu (11 mg/kg) in Papilionaceae is higher than the reference sample.

Lead (Pb): Pb concentration in Papilionaceae species is ranging from 2 mg/kg in sample No. MP-11 (*Indigofrra gerardiana*), collected from emerald mine area, Fizagat to 2 mg/kg in sample No. MP-14 (*Lespediza juncea)*, collected emerald mine area, Fizagat. 2 mg/kg of Pb is reported in reference sample. The average concentration of Pb (2 mg/kg) in Papilionaceae is similar to that of reference sample.

Zinc (Zn): Zn concentration in Paplionaceae species is ranging from 8 mg/kg in sample No. MP-14 (*Lespediza juncea*) to 13 mg/kg in sample No. MP-11 (*Indigofrra gerardiana*), collected from emerald mine area, Fizagat. 4 mg/kg of Zn is reported in reference sample. The average concentration of Zn (10 mg/kg) in Paplionaceae is higher than reference sample.

Nickel (Ni): Ni concentration in Paplionaceae is ranging from 269 mg/kg in sample No. MP-14 (*Lespediza juncea*) to 278 in sample No. MP-11 (*Indigofrra gerardiana*), both collected from emerald mine area, Fizagat. 6 mg/kg of Ni is reported in reference sample. The average concentration of Ni (274 mg/kg) in Papilionaceae is higher than reference sample.

Chromium (Cr): Cr concentration in Paplionaceae is ranging from 256 mg/kg in sample No. MP-14 (*Lespediza juncea*) to 285 mg/kg in sample No. MP-11 (*Indigofera gerardiana*), collected from emerald mine area, Fizagat. Cr concentration of 6 mg/kg is reported in reference sample. The average concentration of Cr (271 mg/kg) in Paplionaceae is higher than the reference sample.

Cobalt (Co): Cobalt concentration in Paplionaceae is 6 mg/kg in sample Nos. MP-14 (*Lespediza juncea*) and MP-11 (*Indigofera gerardiana*), collected from emerald mine area, Fizagat. 4 mg/kg of Co is reported in reference sample. The average concentration of Co (6 mg/kg) in Paplionaceae is higher than reference sample.

Cadmium (Cd): Cd concentration in Paplionaceae species is ranging from 0.178 mg/kg in sample No. MP-14 (*Lespediza juncea*) to 0.223 mg/kg in sample No. MP-11 (*Indigofera gerardiana*), collected from emerald mine area, Fizagat. 0.104 mg/kg of Cd is reported in reference sample. The average concentration of Cd (0.201 mg/kg) in Paplionaceae is higher than reference sample.

Manganese (Mn): Mn concentration in Papilionaceae species is ranging from 5 mg/kg in sample No. MP-14 (*Lespediza juncea)*, collected from emerald mine area, Fizagat to 18 mg/kg in MP-11 (*Indigofera gerardiana)*, collected from area of mines towards Fizagat. 32 mg/kg of Mn concentration is reported in reference sample. The average concentration of Mn (12 mg/kg) in Papilionaceae is lower than the reference sample.

Polygonaceae

Iron (Fe): Fe concentration in Polygonaceae species is ranging from 1731 mg/kg in sample No. MP-9 (*Rumex hastatus)*, collected from emerald mine area, Fizagat to 4194 mg/kg in sample No. KP52 (*Rumex hastatus)*, collected from Meelagah-Kotlai. 679 mg/kg of Fe is reported in reference sample. The average concentration of Fe (3275 mg/kg) in Polygonaceae is much higher than the reference.

Copper (Cu): Cu concentrations in Polygonaceae species is ranging from 8 mg/kg in sample No. MP-9 (*Rumex hastatus)*, collected from emarld mine area, Fizagat to 12 mg/kg in sample No. KP37 (*Rumex hastatus),* collected from Deerai Baba, Kanju. 3 mg/kg of Cu concentration is reported in reference sample. The average concentration of Cu (10 mg/kg) is higher than the reference sample.

Lead (Pb): Pb concentration in Polygonaceae species is ranging from 2 mg/kg in sample Nos. MP-9 (*Rumex hastatus*) and KP-52 (*Rumex hastatus*), collected from emarld mine area and Meelagah-Kotlai respectively to 3mg/kg in sample No. KP-37 (*Rumex hastatus*), collected from Deerai Baba, Kanju. 2 mg/kg of Pb is reported in reference sample. The average concentration of Pb (2 mg/kg) in Polygonaceae is similar to that of reference sample.

Zinc (Zn): Zn concentrations in Polygonaceae species is ranging from 7 mg/kg in sample No. MP-9 (*Rumex hastatus)*, collected from emerald mine area, Fizagat to 11 mg/kg in sample No. KP37 (*Rumex hastatus),* collected from Deerai Baba, Kanju. 4 mg/kg of Zn concentration is reported in reference sample. The average concentration of Zn (9 mg/kg) in Polygonaceae is higher than the reference sample.

Nickel (Ni): Ni concentration in Polygonaceae is ranging from 28 mg/kg in sample No. KP-37 (*Rumex hastatus),* collected from Deerai Baba, Kanju to 40mg/kg MP-9 (*Rumex hastatus),* collected from emerald mine area, Fizagat. 14 mg/kg of Ni concentration is reported in reference sample. The average concentration of Ni (36 mg/kg) in Polygonaceae is higher than the reference sample.

Chromium (Cr): Cr concentration in Polygonaceae is ranging from 48 mg/kg in sample No. MP-9 (*Rumex hastatus),* collected from emerald mine area, Fizagat to 61 mg/kg in sample No. KP52 (*Rumex hastatus),* collected from Meelagah-Kotlai. 15 mg/kg of Cr is reported in reference sample. The average concentration of Cr (55 mg/kg) in Polygonaceae is higher than the reference.

Cobalt (Co): Co concentration in Polygonaceae species reported is 6 mg/kg in all the samples. 0.79 mg /l of Zn concentration is reported in reference sample. The average concentration of Zn (6 mg/kg) in Polygonaceae is higher than the reference sample.

Cadmium (Cd): Cd concentrations in Polygonaceae species is ranging from 0.221 mg/kg in sample No. MP-9 (*Rumex hastatus),* collected from emarld mine area, Fizagat to 0.242 mg/kg in sample No. KP37 (*Rumex hastatus),* collected from Deerai Baba, Kanju. 0.111 mg/kg of Cd concentration is reported in reference sample. The average concentration of Cd (0.234 mg/kg) in Polygonaceae is higher than the reference sample.

Manganese (Mn): Mn concentration in Polygonaceae species is ranging from 39 mg/kg in sample No. MP-9 (*Rumex hastatus),* collected from emerald mine area, Fizagat to 99 mg/kg in sample No. KP37 (*Rumex hastatus),* collected from Deerai Baba, Kanju. 35 mg/kg of Mn concentration is reported in reference sample. The average concentration of Mn (71 mg/kg) in Polygonaceae is higher than the reference sample.

Labiateae

Iron (Fe): Fe concentration in Labiateae species is ranging from 4163 mg/kg in sample No. MP-18 (*Teucrium quadrium)*, collected from mountainous area of Rahim Abad, Mingora to 8163 mg/kg in sample No. MP-19 (*Isodon rugosus)*, collected from the same area as of MP-18. In reference plant species Fe concentration ranged from 421 mg/kg to 879 mg/kg. The average concentration of Fe (6802 mg/kg) in Labiateae is higher than the reference sample.

Copper (Cu): Cu concentration in Labiateae is ranging from 15 mg/kg for MP-18 (*Teucrium quadrium)*, collected from mountainous area of Rahim Abad to 29 mg/kg in sample No. MP-19 (*Isodon rugosus)*, collected from the same area as that of MP-18. In reference plants of Labiateae Cu concentration varied from 3 mg/kg to 4 mg/kg. The average concentration of Cu (23 mg/kg) in Labiateae is higher than the reference samples.

Lead (Pb): Pb concentration in Labiateae species reported is 5 mg/kg. While in reference samples of Labiateae, Pb concentration of 3 mg/kg is reported. The average concentration of Pb (5 mg/kg) in Labiateae is higher than the reference sample.

Zinc (Zn): Zn concentration in Labiateae species is ranging from 14 mg/kg in sample No. MP-18 (*Teucrium quadrium)*, collected from mountainous area of Rahim Abad to 26 mg/kg in sample No. MP-19 (*Isodon rugosus),* collected from the same area as that of MP-18. . Its concentration in reference samples is ranging from 4 mg/kg to 5 mg/kg. The average concentration of Zn (21 mg/kg) in Labiateae is higher than the reference samples.

Nickel (Ni): Ni concentration in Labiateae species is ranging from 27 mg/kg in sample No. MP-18 (*Teucrium quadrium)* collected from mountainous area of Rahim Abad, Mingora to 70 mg/kg in sample No. MP-4 (*Otostegia limbata)*, collected from Maluk Abad, Mingora. In reference plants Ni concentration is ranging from 8 mg/kg to 9 mg/kg. The average concentration of Ni (40 mg/kg) in Labiateae is higher than the reference samples.

Chromium (Cr): Cr concentration in Labiateae species is ranging from 40 mg/kg in sample No. MP-18 (*Teucrium quadrium)* collected from mountainous area of Rahim Abad, Mingora to 56 mg/kg in sample No. MP-19 (*Isodon rugosus),* collected from the same area as that of MP-18. Cr concentration in reference samples is ranging from 8 mg/kg to 10 mg/kg. The average concentration of Cr (49 mg/kg) in Labiateae is higher than the reference samples.

Cobalt (Co): Co concentration in Labiateae species is ranging from 7 mg/kg in sample Nos. MP-4 (*Otostegia limbata*), MP-17 (*Salvia moorcroftiana)* and MP-18 (*Teucrium quadrium)*, collected from Maluk Abad and Rahim Abad, Mingora respectively to 9 mg/kg in sample No. MP-19 collected from Rahim Abad, Minogra. While in reference plants of Labiateae the concentration of Co is ranging from 0.987 mg/kg to 1.21 mg/kg. The average concentration of Co (8 mg/kg) in Labiateae is higher than the reference samples.

Cadmium (Cd): Cd concentration in Labiateae species is ranging from 0.213mg/kg in sample No. MP-18 (*Teucrium quadrium)*, collected from mountains of Rahim Abad to 0.257 mg/kg in sample No. MP-4 (*Otostegia limbata*), collected from Maluk Abad. Cd in reference samples is ranging from 0.117 mg/kg to 0.103 mg/kg. The average concentration of Cd (0.238 mg/kg) in Labiatea is higher than reference samples.

Manganese (Mn): Mn concentration in Labiateae species is ranging from 72 mg/kg in sample No. MP-18 (*Teucrium quadrium)*, collected from mountains of Rahim Abad to

134 mg/kg in sample No. MP-17 *(Salvia moorcroftiana)*, collected from Rahim Abad, Minogra. Mn concentration in reference samples is ranging from 40 mg/kg to 65 mg/kg. The average concentration of Mn (117 mg/kg) in Labiateae is higher than the reference samples.

Asteraceae

Iron (Fe): Fe concentration in Aesteraceae speices is ranging from 4269 mg/kg in sample No. MP-5 *(Xanthium strumarium)*, collected from Maluk Abad within limits of emerald mines to 10056 mg/kg in sample No. KP55 *(Xanthium strumarium)*, collected from Meelagah-Kotlai. 987 mg/kg of Fe concentration is reported in reference sample. The average concentration of Fe (7163 mg/kg) in Aesteraceae is higher than the reference sample.

Copper (Cu): Cu concentrations in Aesteraceae is ranging from 16 mg/kg in sample No. KP-55 *(Xanthium strumarium)*, collected from Meelagah-Kotlai to 28 mg/kg in sample No. MP-5 *(Xanthium strumarium)*, collected from Maluk Abad within limits of emerald mines. 3 mg/kg of Cu concentration is reported in reference sample. The average concentration of Cu (22 mg/kg) in Aesteraceae is higher than the reference sample.

Lead (Pb): Pb concentration in Aesteraceae species is ranging from 5 mg/kg in sample No. MP-5 *(Xanthium strumarium)*, collected from Maluk Abad within limits of emerald mines to 7 mg/kg in sample No. KP-55 *(Xanthium strumarium)*, collected from Meelagah-Kotlai. 4 mg/kg of Pb is reported in reference sample. The average concentration of Pb (6 mg/kg) in Aesteraceae is higher than the reference.

Zinc (Zn): Zn concentration in Aesteraceae species is ranging from 15 mg/kg in sample No. KP-55 *(Xanthium strumarium)*, collected from Meelagah-Kotlai to 25 mg/kg in sample No. MP-5 *(Xanthium strumarium)*, collected from Maluk Abad within limits of emerald mines. 5 mg/kg of Zn concentration is reported in reference sample. The average concentration of Zn (20 mg/kg) in Aesteraceae is higher than the reference sample.

Nickel (Ni): Ni concentration in Aesteraceae species is ranging from 28 mg/kg in sample No. KP-55 (*Xanthium strumarium*), collected from Meelagah-Kotlai to 53 mg/kg in sample No. MP-5 (*Xanthium strumarium*), collected from Maluk Abad within limits of emerald mines. 5 mg/kg of Ni concentration is reported in reference sample. The average of concentration of Ni (40 mg/kg) in Aesteraceae is higher than the reference sample.

Chromium (Cr): Cr concentration in Aesteraceae species is ranging from 48 mg/kg in sample No. KP-55 (*Xanthium strumarium*), collected from Meelagah-Kotlai to 54 mg/kg in sample No. MP-5 (*Xanthium strumarium*), collected from Maluk Abad within limits of emerald mines. 5 mg/kg of Cr is reported in reference sample. The average concentration of Cr (51 mg/kg) in Aesteraceae is higher than the reference sample.

Cobalt (Co): Co concentration in Aesteraceae species is ranging from 7 mg/kg in sample No. MP-5 (*Xanthium strumarium*), collected from Maluk Abad within limits of emerald mines to 9 mg/kg in sample No. KP-55 (*Xanthium strumarium*), collected from Meelagah-Kotlai. 1.11 mg/kg of Co is reported in reference sample. The average concentration of Co (8 mg/kg) in Aesteraceae is higher than the reference sample.

Cadmium (Cd): Cd concentration in Aesteraceae species is ranging from 0.245 mg/kg in sample No. KP-55 (*Xanthium strumarium*), collected from Meelagah-Kotlai to 0.268 mg/kg in sample No. MP-5 (*Xanthium strumarium*), collected from Maluk Abad within limits of emerald mines, Mingora. 0.134 mg/kg mg/kg of Co is reported in reference sample. The average concentration of Co (0.257 mg/kg) in Aesteraceae is higher than the reference sample.

Manganese (Mn): Mn concentration in Aesteraceae species is ranging from 48 mg/kg in sample No. MP-5 (*Xanthium strumarium*), collected from Maluk Abad within limits of emerald mines, Mingora to 96 mg/kg in sample No. KP-55 (*Xanthium strumarium*), collected from Meelagah-Kotlai. 45 mg/kg of Mn is reported in reference sample. The average concentration of Mn (72 mg/kg) in Aesteraceae is higher than the reference sample.

Sapindaceae

Iron (Fe): Fe concentration in Sapindaceae species is ranging from 806 mg/kg in sample No. MP-3 (*Dodonaea viscose*), collected from Raja Abad/Maluk Abad to 6225 mg/kg in sample No. MP-8 (*Dodonaea viscose)*, collected from emerald mine area towards Fizagat. 724 mg/kg of Fe concentration is reported in reference sample. The average Fe concentration (3160 mg/kg) in Sapindaceae is higher than the reference sample.

Copper (Cu): Cu concentration in Sapindaceae species is ranging from 17 mg/kg in sample No. KP- 51-B (*Dodonaea viscose)*, collected from Meelagah-Kotlai in Kabal area to 20 mg/kg in sample No. MP-3 (*Dodonaea viscose*), collected from Raja Abad/Maluk Abad. 4 mg/kg of Cu concentration is reported in reference sample. The average concentration of Fe (19 mg/kg) in Sapindaceae is higher than the reference sample.

Lead (Pb): Pb concentration in Sapindaceae species is ranging 4 mg/kg in sample No. MP-8 (*Dodonaea viscose)*, collected from emerald mine area towards Fizagat to 5mg/kg in sample Nos. MP-3 (*Dodonaea viscose)* and KP-51-B (*Dodonaea viscose),* collected from Raja Abad/Maluk Abad and Meelagah-Kotlai respectively. 2 mg/kg of Pb concentration is reported in reference sample. The average concentration of Fe (5 mg/kg) in Sapindaceae species is higher than the reference sample.

Zinc (Zn): Zn concentration in Sapindaceae species is ranging from 15 mg/kg in sample No. KP- 51-B (*Dodonaea viscose)*, collected from Meelagah-Kotlai in Kabal area to 19 mg/kg in sample No. MP-3 (*Dodonaea viscose*), collected from Raja Abad/Maluk Abad. 2 mg/kg of Zn concentration is reported in the reference sample. The average concentration of Zn (17 mg/kg) in Sapindaceae is higher than the reference sample.

Nickel (Ni): Ni concentration in Sapindaceae species is varying from 30 mg/kg in sample No. MP-3 (*Dodonaea viscose*), collected from Raja Abad/Maluk Abad to 42 mg/kg in sample No. MP-8 (*Dodonaea viscose)*, collected from emerald mine area towards Fizagat. 4 mg/kg of Ni concentration is reported in the reference sample. The average concentration of Ni (34 mg/kg) in Sapindaceae is higher than the reference sample.

Chromium (Cr): Cr concentration in Sapindaceae species is ranging from 35 mg/kg l in sample No. MP-3 (*Dodonaea viscose*), collected from Raja Abad/Maluk Abad to 55 mg/kg in sample No. MP-8 (*Dodonaea viscose)*, collected from emerald mine area towards Fizagat. 5 mg/kg of Cr concentration is reported in the reference sample. The average concentration of Cr (45 mg/kg) in Sapindaceae is higher than the reference sample.

Cobalt (Co): Co concentration in Sapindaceae species is ranging from 6 mg/kg in sample No. MP-3 (*Dodonaea viscose*), collected from Raja Abad/Maluk Abad to 7 mg/kg in sample Nos. MP-8 (*Dodonaea viscose*) and KP-51-B (*Dodonaea viscose*), collected from emerald mine area towards Fizagat and Meelagh-Kotlai respectively. 1.21 mg/kg of Co concentration is reported in the reference sample. The average concentration of Co (7 mg/kg) in Sapindaceae is higher than the reference sample.

Cadmium (Cd): Cd concentration in Sapindaceae species is ranging from 0.214 mg/kg in sample No. MP-8 (*Dodonaea viscose*), collected emerald mine area towards Fizagat to 0.245 mg/kg in sample No. MP-3 (*Dodonaea viscose*), collected from Raja Abad/Maluk Abad. 0.118 mg/kg concentration of Cd is reported in reference sample. The average concentration of Cd (0.226 mg/kg) is Sapindaceae is higher than the reference sample.

Manganese (Mn): Mn concentration in Sapindaceae species is ranging from 21 mg/kg in sample No. MP-3 (*Dodonaea viscose*), collected from Raja Abad/Maluk Abad to 65 mg/kg in sample No. MP-8 (*Dodonaea viscose*), collected emerald mine area towards

Fizagat. 28 mg/kg concentration of Mn is reported in reference sample. The average concentration of Mn (45 mg/kg) is Sapindaceae is higher than the reference sample.

Utricaceae

Iron (Fe): Fe concentration in Utricaceae species is ranging from 1706 mg/kg in sample No. MP-13 (*Debergeasia sulicifolia)*, collected from emerald mine area towards Fizagat to 1738 mg/kg in sample No. MP-2 (*Debergeasia sulicifolia)*, collected from Raja Abad/ Maluk Abad. 678 mg/kg of Fe concentration is reported in reference sample. The average concentration of Fe (1722 mg/kg) in Utricaceae is higher than the reference sample.

Copper (Cu): Cu concentration in Utricaceae species is ranging from 11mg/kg in sample No. MP-13 (*Debergeasia sulicifolia)*, collected from emerald mine area towards Fizagat to 15mg/kg in sample No. MP-2 (*Debergeasia sulicifolia)*, collected from Raja Abad/ Maluk Abad. 4mg/kg of Cu concentration is reported in reference sample. The average concentration of Cu (13 mg/kg) in Utricaceae is higher than the reference sample..

Lead (Pb): Pb concentration in Utricaceae species is ranging from 5 mg/kg in sample No. MP-13 (*Debergeasia sulicifolia)*, collected from emerald mine area towards Fizagat to 6 mg/kg in sample No. MP-2 (*Debergeasia sulicifolia)*, collected from Raja Abad/ Maluk Abad. 2 mg/kg of Pb is reported in the reference sample. The average concentration of Pb (6 mg/kg) in Utricaceae is higher than the reference.

Zinc (Zn): Zn concentration in Utricaceae species is ranging from 10 mg/kg 1 in sample No. MP-13 (*Debergeasia sulicifolia)*, collected from emerald mine area towards Fizagat to 12 mg/kg in sample No. MP-2 (*Debergeasia sulicifolia)*, collected from Raja Abad/ Maluk Abad. 2 mg/kg of Zn is reported in the reference sample. The average concentration of Zn (11 mg/kg) in Utricaceae is higher than the reference.

Nickel (Ni): Ni concentration in Utricaceae species is ranging from varied from 20 mg/kg in sample No. MP-2 (*Debergeasia sulicifolia)*, collected from Raja Abad/ Maluk

Abad to 30mg/kg in sample No. MP-13 *(Debergeasia sulicifolia)*, collected from emerald mine area towards Fizagat. 5 mg/kg of Ni is reported in the reference sample. The average concentration of Ni (25 mg/kg) in Utricaceae is higher than the reference.

Chromium (Cr): Cr concentration in Utricaceae species is ranging from 46 mg/kg sample No. MP-2 *(Debergeasia sulicifolia)*, collected from Raja Abad/ Maluk Abad to 68 mg/kg in sample No. MP-13 *(Debergeasia sulicifolia)*, collected from emerald mine area towards Fizagat. 6 mg/kg of Cr is reported in the reference sample. The average concentration of Cr (57 mg/kg) in Utricaceae is higher than the reference.

Cobalt (Co): 6 mg/ l of Co concentration is reported in both the samples i.e. MP-2 and MP-13 of Utricaceae. 0.921 mg/kg of Co is reported in the reference sample. The average concentration of Co (6 mg/kg) is Utricaceae is higher than the reference sample.

Cadmium (Cd): Cd concentration in Utricaceae species is ranging from ranged from 0.220 mg/kg in sample No. MP-2 *(Debergeasia sulicifolia)*, collected from Raja Abad/ Maluk Abad to 0.226 mg/kg in sample No. MP-13 *(Debergeasia sulicifolia)*, collected from emerald mine area towards Fizagat. 0.111mg/kg of Cd concentration is reported in the reference sample. The average concentration of Cd (0.223 mg/kg) in Utricaceae is higher than the reference sample.

Manganese (Mn): Mn concentration in Utricaceae species is ranging from 39 mg/kg l in sample No. MP-13 *(Debergeasia sulicifolia)*, collected from emerald mine area towards Fizagat to 70 mg/kg in sample No. MP-2 *(Debergeasia sulicifolia)*, collected from Raja Abad/ Maluk Abad. 32 mg/kg of Mn is reported in the reference sample. The average concentration of Mn (54 mg/kg) in Utricaceae is higher than the reference.

Cannabinaceae

Iron (Fe): Fe in Cannabinaceae species is ranging from 3456 mg/kg in sample No. MP-22 *(Cannabis sativa)*, collected from Rahim Abad, Mingora to 9925 mg/kg in sample No. KP-53 *(Cannabis sativa)*, collected from Meelagah-Kotlai, Kabal. 679 mg/kg of Fe concentration is reported in the reference sample. The average concentration of Fe (6691 mg/kg) in Cannabinaceae is higher than the reference sample.

Copper (Cu): Cu concentration in Cannabinaceae species is ranging 27 mg/kg in sample No. KP-53 (*Cannabis sativa)*, collected from Meelagah-Kotlai, Kabal to 33 mg/kg in sample No. MP-22 (*Cannabis sativa)*, collected from Rahim Abad, Mingora. 4 mg/kg of Cu concentration is reported in the reference sample. The average concentration of Cu (30 mg/kg) in Cannabinaceae is higher than the reference sample.

Lead (Pb): Pb concentration in Cannabinaceae species is ranging from 3 mg/kg in sample No. MP-22 (*Cannabis sativa)*, collected from Rahim Abad, Mingora to 4 mg/kg in sample No. KP-53 (*Cannabis sativa)*, collected from Meelagah-Kotlai, Kabal. 3 mg/kg of Pb concentration is reported in the reference sample. The average concentration of Pb (4 mg/kg) in Cannabinaceae is more or less similar to that of the reference sample.

Zinc (Zn): Zn concentration in Cannabinaceae species is ranging from 25 mg/kg in sample No. KP-53 (*Cannabis sativa)*, collected from Meelagah-Kotlai, Kabal to 30 mg/kg in sample No. MP-22 (*Cannabis sativa)*, collected from Rahim Abad, Mingora. 2 mg/kg of Zn concentration is reported in the reference sample. The average concentration of Zn (27 mg/kg) in Cannabinaceae is higher than the reference sample.

Nickel (Ni): Ni concentration in Cannabinaceae species is ranging from 35 mg/kg in sample No. MP-22 (*Cannabis sativa)*, collected from Rahim Abad, Mingora to 39 mg/kg in sample No. KP-53 (*Cannabis sativa)*, collected from Meelagah-Kotlai, Kabal. 5 mg/kg of Ni concentration is reported in the reference sample. The average concentration of Ni (37 mg/kg) in Cannabinaceae is higher than the reference sample.

Chromium (Cr): Cr concentration in Cannabinaceae species is ranging from 48 mg/kg in sample No. MP-22 (*Cannabis sativa)*, collected from Rahim Abad, Mingora to 53 mg/kg in sample No. KP-53 (*Cannabis sativa)*, collected from Meelagah-Kotlai, Kabal. 6

mg/kg of Cr concentration is reported in the reference sample. The average concentration of Cr (51 mg/kg) in Cannabinaceae is higher than the reference sample.

Cobalt (Co): Co concentration in Cannabinaceae species is ranging from 7 mg/kg in sample No. MP-22 (*Cannabis sativa)*, collected from Rahim Abad, Mingora to 9 mg/kg in sample No. KP-53 (*Cannabis sativa)*, collected from Meelagah-Kotlai, Kabal. 0.976 mg/kg of Co concentration is reported in the reference sample. The average concentration of Co (8 mg/kg) in Cannabinaceae is higher than the reference sample.

Cadmium (Cd): Cd concentration in Cannabinaceae species is ranging from 0.276 mg/kg in sample No. KP-53 (*Cannabis sativa)*, collected from Meelagah-Kotlai, Kabal to 0.289 mgl in sample No. MP-22 (*Cannabis sativa)*, collected from Rahim Abad, Mingora. 0.112 mg/kg of Cd concentration is reported in the reference sample. The average concentration of Cd (0.283 mg/kg) in Cannabinaceae is a little higher than the reference sample.

Manganese (Mn): Mn concentration in Cannabinaceae species is ranging from 126 mg/kg in sample No. KP-53 (*Cannabis sativa)*, collected from Meelagah-Kotlai, Kabal to 374 mg/kg in sample No. MP-22 (*Cannabis sativa)*, collected from Rahim Abad, Mingora. 60 mg/kg of Mn concentration is reported in the reference sample. The average concentration of Mn (250 mg/kg) in Cannabinaceae is higher than the reference sample.

Simarubaceae

Iron (Fe): Fe concentration in Simarubaceae species is ranging from 2367 mg/kg in sample No. KP-42 (*Ailanthus altissima (Indian*)), collected from Deerai Baba, Kanju to 3369 mg/kg in sample No. MP-1 (*Ailanthus altissima (Indian))*, collected from Maluk Abad. 568 mg/kg of Fe concentration is reported in the reference sample. The average concentration of Fe (2868 mg/kg) in Simarubaceae is higher than the reference sample.

Copper (Cu): Cu concentrations in Simarubaceae species is ranging from 19 mg/kg in sample No. KP-42 (*Ailanthus altissima (Indian*)), collected from Deerai Baba, Kanju to 25 mg/kg in sample No. MP-1 (*Ailanthus altissima (Indian))*, collected from Maluk Abad. 4

mg/kg of Cu concentration is reported in the reference sample. The average concentration of Cu (22 mg/kg) in Simarubaceae is higher than the reference.

Lead (Pb): Pb concentration in Simarubaceae species is ranging from 6 mg/kg in sample No. MP-1 (*Ailanthus altissima (Indian)),* collected from Maluk Abad to 8 mg/kg in sample No. KP-42 (*Ailanthus altissima (Indian)*), collected from Deerai Baba, Kanju. 3 mg/kg of Pb is reported in the reference sample. The average concentration of Pb (7 mg/kg) in Simarubaceae is higher than the reference.

Zinc (Zn): Zn concentration in Simarubaceae species is ranging from 17 mg/kg in sample No. KP-42 (*Ailanthus altissima (Indian)*), collected from Deerai Baba, Kanju to 22 mg/kg in sample No. MP-1 (*Ailanthus altissima (Indian)),* collected from Maluk Abad. 3 mg/kg of Zn concentration is reported in the reference sample. The average concentration of Zn (20 mg/kg) in Simarubaceae is higher than the reference sample.

Nickel (Ni): Ni concentration in Simarubaceae is ranging from 53 mg/kg in sample No. KP-42 (*Ailanthus altissima (Indian)*), collected from Deerai Baba, Kanju to 64 mg/kg in sample No. MP-1 (*Ailanthus altissima (Indian)),* collected from Maluk Abad. 5 mg/kg of Ni concentration is reported in the reference sample. The average concentration of Ni (59 mg/kg) in Simarubaceae is higher than the reference sample.

Chromium (Cr): Cr concentration in Simarubaceae is ranging from 39 mg/kg in sample No. KP-42 (*Ailanthus altissima (Indian)*), collected from Deerai Baba, Kanju to 43 mg/kg in sample No. MP-1 (*Ailanthus altissima (Indian)),* collected from Maluk Abad. 6 mg/kg of Cr concentration is reported in the reference sample. The average concentration of Cr (41 mg/kg) in Simarubaceae is higher than the reference sample.

Cobalt (Co): Co concentration in Simarubaceae species is ranging from 5 mg/kg in sample No. KP-42 (*Ailanthus altissima (Indian)*), collected from Deerai Baba, Kanju to 7 mg/kg in sample No. MP-1 (*Ailanthus altissima (Indian)),* collected from Maluk Abad.

1.11 mg/kg of Co concentration is reported in the reference sample. The average concentration of Co (6 mg/kg) in Simarubaceae is higher than the reference sample.

Cadmium (Cd): The average Cd concentration in Simarubaceae species is 0.286mg/kg. In the reference sample 0.172 mg/kg of Cd is reported. The average concentration of Cd in Simarubaceae is a little higher than the reference sample.

Manganese (Mn): Mn concentration in both the species of Simarubaceae is 130 mg/kg. While 35 mg/kg of Mn is reported in the reference sample. The average concentration of Mn in Simarubaceae is higher than the reference sample.

Amaranthaceae

Iron (Fe): Fe concentration in Amaranthaceae species is 5363 mg/kg in sample No. KP-39 (*Althernantera pungs)*, collected from Deerai Baba, Kanju. 568 mg/kg of Fe concentration is reported in reference sample. The average concentration of Fe in Amaranthaceae is higher than the reference sample.

Copper (Cu): Cu concentration in Amaranthaceae species reported is 32 mg/kg in sample No. KP-39 (*Althernantera pungs)*, collected from Deerai Baba, Kanju. 19 mg/kg of Cu concentration is reported in reference sample. The average concentration of Cu in Amaranthaceae is higher than the reference sample.

Lead (Pb): Pb concentration in Amaranthaceae species is 4 mg/kg in sample No. KP-39 (*Althernantera pungs)*, collected from Deerai Baba, Kanju. 0.12 mg/kg of Pb concentration is reported in reference sample. The average concentration of Pb in Amaranthaceae is higher than the reference sample.

Zinc (Zn): Zn concentration in Amaranthaceae species is 29 mg/kg in sample No. KP-39 (*Althernantera pungs)*, collected from Deerai Baba, Kanju . 4 mg/kg of Zn concentration is reported in the reference sample. The average concentration of Zn in Amaranthaceae is higher than the reference sample.

Nickel (Ni): Ni concentration in Amaranthaceae species is reported as 19 mg/kg in sample No. KP-39 (*Althernantera pungs)*, collected from Deerai Baba, Kanju. 1 mg/kg of Ni is reported in the reference sample. The average concentration of Ni in Amaranthaceae is higher than the reference sample.

Chromium (Cr): Cr concentration in Amaranthaceae species is reported as 39 mg/kg in sample No. KP-39 (*Althernantera pungs)*, collected from Deerai Baba, Kanju. 21 mg/kg of Cr is reported in the reference sample. The average concentration of Cr in Amaranthaceae is higher than the reference sample.

Cobalt (Co): Co concentration in Amaranthaceae species is reported 6 mg/kg in sample No. KP-39 (*Althernantera pungs)*, collected from Deerai Baba, Kanju. 0.432 mg/kg of Co is reported in the reference sample. The average concentration of Co in Amaranthaceae is higher than the reference sample.

Cadmium (Cd): Cd concentration in Amaranthaceae species is not detected.

Manganese (Mn): Mn concentration in Amaranthaceae species is reported 70 mg/kg in sample No. KP-39 (*Althernantera pungs)*, collected from Deerai Baba, Kanju. 88 mg/kg of Mn is reported in the reference sample. The average concentration of Mn in Amaranthaceae is lower than the reference sample.

Table. 5.1. Macro and micro nutrients in mg/kg in various plant species of Mingora and Kabal area.

S.No.	Plant sp.	Fe	Cu	Pb	Zn	Ni	Cr	Co	Cd	Mn	Ca	Mg	Na	K
Poaceae														
MP6	*Saccharum spp.*	2606	19	5	12	289	358	6	0.233	49	1823	111	86	8125
MP12	*Saccharum spp.*	4706	30	9	19	256	289	6	0.245	54	2603	ND	31	2175
MP15	*Oryza sativa*	1981	7	5	4	37	63	6	0.089	86	287	ND	34	2713
KP38	*Saccharum spp.*	2256	18	3	11	31	73	5	0.238	15	2507	ND	22	7838
MP34	*Zea mays*	1788	12	5	8	45	87	7	0.134	104	7036	ND	251	11175
KP35	*Zea mays*	3432	53	3	33	77	118	9	0.089	13	2260	ND	38	2069
KP43	*Zea mays*	2342	21	4	13	65	78	6	ND	ND	ND	ND	ND	ND
KP45	*Zea mays*	2569	30	6	19	44	72	6	0.24	18	2613	ND	62	7319
KP46	*Zea mays*	5744	48	5	30	63	102	6	0.389	75	6164	1161	74	6306
KP48	*Zea mays*	2469	27	5	17	52	233	7	0.245	27	3810	150	38	12881
KP49	*Zea mays*	3638	29	7	18	57	71	7	0.237	25	2564	ND	233	26044
KP54	*Dicanthium annulatum*	1719	34	5	21	49	56	5	0.245	115	2097	545	ND	ND

Continued from Table 5.1.

S.No.	*Plant sp.*	Fe	Cu	Pb	Zn	Ni	Cr	Co	Cd	Mn	Ca	Mg	Na	K
KP57	*Zea mays*	5519	68	5	43	42	87	6	0.388	44	2529	929	39	12281
KP59	*Zea mays*	2531	22	6	14	45	74	7	0.24	39	4197	790	51	11475
KP0	*Zea mays*	2888	36	5	22	46	69	7	0.356	27	7369	543	125	10363
Average		3079	30	5	19	80	122	6	0.241	49	3418	604	83	9289
Reference. P26	*Zea mays*	456	6	3	6	4	5	0.89	0.093	30	4958	ND	158	937.5
Papilionaceae														
MP11	*Indigofrra gerardiana*	1625	14	2	13	278	285	6	0.223	18	6985	25	69	2244
MP14	*Lespediza juncea*	1863	9	2	8	269	256	6	0.178	5	1303	ND	23	1206
Average		1744	11	2	10	274	271	6	0.201	12	4144	25	46	1725
Reference B2	*Indigofrra gerardiana*	439	3	2	4	6	6	4	0.104	32	9961	ND	64	17788
Polygonaceae														
MP9	*Rumex hastatus*	1731	8	2	7	40	48	6	0.221	39	5089	3502	341	4738

Continued from Table 5.1.

S.No.	***Plant sp.***	**Fe**	**Cu**	**Pb**	**Zn**	**Ni**	**Cr**	**Co**	**Cd**	**Mn**	**Ca**	**Mg**	**Na**	**K**
KP37	*Rumex hastatus*	3900	12	3	11	28	57	6	0.242	99	7833	1788	ND	5719
KP52	*Rumex hastatus*	4194	11	2	10	39	61	6	0.239	76	7004	3689	276	3375
Average		3275	10	2	9	36	55	6	0.234	71	6642	2993	308	4610
Reference B3	*Rumex hastatus*	679	3	2	4	14	15	0.79	0.111	35	8210	ND	380	8506
Labiateae														
MP4	*Otostegia limbata*	8081	24	5	22	70	45	7	0.257	132	11893	11	77	4638
MP17	*Salvia moorcroftiana*	ND	ND	4	ND	31	54	7	0.232	134	15320	918	97	906
MP18	*Teucrium quadrium*	4163	15	5	14	27	40	7	0.213	72	8905	ND	126	1350
MP19	*Isodon rugosus*	8163	29	5	26	34	56	9	0.249	131	11896	ND	287	4338
Average		6802	23	5	21	40	49	8	0.238	117	12003	464	147	2808
Reference B6	*Isodon rugosus*	879	4	3	5	8	10	1.21	0.117	36	11063	ND	26	5400
Reference B9	*Otostegia limbata*	421	3	3	4	9	8	0.987	0.103	40	4967	ND	21	2131

Continued from Table 5.1.

S.No.	*Plant sp.*	Fe	Cu	Pb	Zn	Ni	Cr	Co	Cd	Mn	Ca	Mg	Na	K
Asteraceae		650	3.5	3	4.5	8.5	9	1.0985	0.11	38	8015	ND	23.5	3765.5
MP5	*Xanthium strumarium*	4269	28	5	25	53	54	7	0.268	48	9931	1508	101	9119
KP55	*Xanthium strumarium*	10056	16	7	15	28	48	9	0.245	96	11354	832	ND	6456
Average		7163	22	6	20	40	51	8	0.257	72	10643	1170	101	7788
Reference B5	*Xanthium strumarium*	987	3	4	5	5	5	1.11	0.134	45	1864	1788	208	17419
Sapindaceae														
MP3	*Dodonaea viscose*	806	20	5	19	30	35	6	0.245	21	4476	1533	107	68.75
MP8	*Dodonaea viscose*	6225	ND	4	ND	42	55	7	0.214	65	5454	5909	92	2512.5
KP51-B	*Dodonaea viscose*	2450	17	5	15	30	45	7	0.218	50	5948	ND!	98	5350

Continued from Table 5.1.

S.No.	Plant sp.	Fe	Cu	Pb	Zn	Ni	Cr	Co	Cd	Mn	Ca	Mg	Na	K
Average		3160	19	5	17	34	45	7	0.226	45	5292	3721	99	2643.75
Reference B1	*Dodonaea viscose*	724	4	2	2	4	5	1.21	0.118	28	6854	ND	65	6112.5
Utricaceae														
MP13	*Debergeasia sulicifolia*	1706	11	5	10	30	68	6	0.226	39	6779	7119	134	3494
MP2	*Debergeasia sulicifolia*	1738	15	6	12	20	46	6	0.22	70	7579	529	136	3344
Average		1722	13	6	11	25	57	6	0.223	54	7179	3824	135	3419
Reference B10	*Debergeasia sulicifolia*	678	4	2	2	5	6	0.921	0.111	32	513	2513	97	3119
Cannabinaceae														
MP22	*Cannabis sativa*	3456	33	3	30	35	48	7	0.289	374	20645	946	278	5013
KP53	*Cannabis sativa*	9925	27	4	25	39	53	9	0.276	126	13545	3505	77	7594
Average		6691	30	4	27	37	51	8	0.283	250	17095	2225	177	6303
Reference B8	*Cannabis sativa*	679	4	3	2	5	6	0.976	0.112	60	14695	ND	ND	ND

Continued from Table 5.1.

S.No.	*Plant sp.*	Fe	Cu	Pb	Zn	Ni	Cr	Co	Cd	Mn	Ca	Mg	Na	K
Simarubaceae														
MP1	*Ailanthus altissima (Indian)*	3369	25	6	22	64	43	7	0.286	130	16466	291	172	5994
KP42	*Ailanthus altissima (Indian)*	2367	19	8	17	53	39	5	ND	ND	ND	ND	ND	ND
Average		2868	22	7	20	59	41	6	0.286	130	16466	291	172	5994
Reference B4	*Ailanthus altissima (Indian)*	568	4	3	3	5	6	1.11	0.172	35	17673	411	211	4950
Amaranthaceae														
KP39	*Althernantera pungs*	5363	32	4	29	19	39	6	ND	70	6826	ND	ND	ND
Reference P27	*Althernantera pungs*	568	19	0.12	4	1	21	0.432	0.105	88	7438	4463	ND	5506

ND = Not determined; MP = Plants of Mingora; KP; Plants of Kabal

CHAPTER 6

DISCUSSION

Trace metal pollution of water, soil and plants is one of the rising issues from human as well as animal health's point of view. Water, soil and plants are interconnected to each other and human is directly dependent on them for their survival. Trace metals environmental pollution is one of the global as well as national issue. The aim of the preset study was to assess the geochemical and environmental consequences of heavy metal pollution in water, soil and plants in Mingora and Kabal areas of the District Swat. For materializing the aforementioned planned study, physiochemical parameters, especially trace and heavy metals, in soil and plants of the Mingora and Kabal area were studied for their environmental impact on the ecosystem of the region. The data obtained during this study was compared with the standard values (safe limits) as proposed by WHO and Allen, 1989 for drinking water, soils and plants in relation to human health concerns and discussed in detail as under.

Water

Water is generally used for domestic, irrigation and industrial purposes. For every use it should have certain acceptable quality. Like water for domestic use should have no smell, taste and odor, and it should be free of pollutants which are detrimental to ecosystem and the existing infrastructures. Therefore, it should have a specific range of physiochemical parameters. The irrigation water doesn't have such restrictions as domestic water has because the plants are tolerant to a wide range of water quality. However, the high concentration of boron and dissolved solids is detrimental and the balance of sodium and calcium is crucial for soil structure. The water quality for industry varies with the type of industry. The quality of ground water from chemical composition point of view is related to the soluble products from rock weathering and decomposition of other agencies, which are responsible for the temporal and spatial changes in both surface and ground water.

The quality of water varies with the local geology, agricultural activities, leaching and runoff, industrial and municipal wastes. Ground water has more mineral contaminants like arsenic, nitrates and barium etc. than the surface water because as water percolates in the rocks, it excavange various chemical parameters from the rocks. But surface water occasionally contains more biological pollutants and more natural organic pollutants. However, both ground and surface water contain industrial wastes of organic and inorganic derivation.

The concentration of various trace and heavy elements (i.e., Fe, Cu, Pb, Zn, Ni, Cr, Co and Mn) which have significant health and environmental concerns, have been determined in both surface and ground water of Mingora and Kabal areas of district Swat.

The water quality evaluation in the area of study is carried out to determine its potability in terms of drinking, domestic and agricultural purposes. This assessment was based on the WHO (1996) standards and the values suggested by Allen (1989) for natural waters.

Among the physio-chemical parameter the pH values of both Mingora and Kabal waters are within WHO permissible limits for drinking water (i.e., <8). The electrical conductivity (EC) is generally within the permissible limit (<1400 MS/cm) of WHO (1996). However, in certain dug wells of Mingora area the EC is exceeding the permissible limit. The increased concentration of EC in Mingora water demonstrates more dissolved solids in water. The dissolved oxygen (DO) is within the permissible limit (<5mg/l) of WHO (1996) in both the waters of Mingora and Kabal areas. The turbidity in the dug wells, tube wells and spring waters of both Mingora and Kabal areas is within the permissible limit (< 5 NTU) of WHO (1996). However, the water of river Swat collected near Pearl Hotel has three times higher turbidity. This water is also used for drinking purposes. The physio-chemical parameters of the waters from both Mingora and Kabal area are generally safe for drinking and other domestic and agricultural use.

The light element cations (i.e., Ca, Mg, Na and K) in the waters of Mingora and Kabal areas are compared with the permissible limits of WHO (1996) for drinking water and the quality of water is evaluated below.

Calcium is generally found within the permissible limit (100 μg/l) of WHO (1996) for drinking water and Allen (1986) for natural water. The water samples collected from the dug wells in Rahimabad of Mingora area have Ca higher (123.55 & 126.35 mg/l) than that of the permissible limit. This increase can be attributed to the contact of local seams of $CaCO_3$ in the area.

Magnesium concentration in waters of both Mingora and Kabal areas is generally within the permissible limit (50 mg/l) of WHO (1996) for drinking water. However, the water samples collected from the dug well and springs in the vicinity of emerald mines in Mingora area are having Mg concentration higher than the permissible limit. One dug well in the Kabal area is also having Mg contents (56 mg/l) higher than the permissible limit. The high concentration of Mg in these waters can be attributed to the percolation of these waters through the ultramafic rocks of the melange zone.

Sodium contents of the waters of both Mingora and Kabal areas are far below the WHO (1996) maximum permissible limit (200 mg/l). One dug well in the Mingora area, having 223.05 mg /l of Na, exceeding the permissible limit. This increase can be localized and can be considered harmless.

Potassium contents in all the surface and ground waters of the Mingora and Kabal areas are far below the maximum permissible limit of WHO (1996). By comparing the waters of Mingora and Kabal areas, it is clear that various lithologies in the areas have played an important role in the increase of Ca and Mg in the water of certain areas. The general increase of Mg in the waters of Mingora area and Ca in the waters of Kabal area can be attributed to the occurrence of ultramafic rocks in the former and amphibolites in the later. Generally the waters of both Mingora and Kabal areas is safe for drinking purposes as far as the light element cations are concerned.

The heavy and trace element concentrations (Fe, Cu, Pb, Zn, Ni, Cr, Co and Mn,) in the waters of both Mingora and Kabal area are evaluated in regard to the maximum permissible limit of WHO (1996) in the following section.

Iron concentration in the spring and underground waters of Mingora and Kabal areas is within the permissible limit (300μg/l) of WHO (1996) for drinking water. However, the Swat river in both Mingora and Kabal areas is having high amount (up to 930 μg/l) of Fe. One dug well from Sersenai village in Kabal area exceeds the permissible limit. This can be attributed to the corrosion effect of borehole material or to a local redox environment change in groundwater. All the water samples, however, are having Fe within the range (50-1000 μg/l) for natural water (Allen 1989).

Copper concentration in the water of Mingora and Kabal areas are far below the maximum permissible limit (1000 μg/l) of the WHO (1996) for drinking water. The Cu contents in maximum water samples of both Mingora and Kabal areas are within the range (2-50μg/l) for natural water (see Allen, 1989). However, few samples exceeds Cu that of natural water in both Mingora and Kabal areas (Table 3.3; chapter 3).

Lead concentration in the waters of both Mingora and Kabal areas is generally below the maximum permissible limit (50 μg/l) of WHO (1996) for drinking water. The two water samples from the dug wells of petrol station at Rahimabad (Mingora) and of service station at Sersenai (Kabal) are having 2 fold high concentration of Pb as compare to the maximum permissible limit of WHO (1996). This can be attributed to the contamination from the automobiles washing and petrol leakage in the ground. However, the waters of Mingora and Kabal area are having high concentration of Pb as compare to that of natural water (see Allen, 1989).

Zinc contents of water from Mingora and Kabal areas are generally within the permissible limit (500 μg/l) of WHO (1996) for safe drinking water. Two samples collected from tube well at Kanra Baba and from tape water at Berarai area having higher contents 810μg/l and 1913μg/l of Zn respectively in the Mingora area (Table 3.3;

chapter 3). In Kabal area, one sample collected from the stream at Kanju area is having high amount (890 μg/l) of Zn. The high concentration of Zn in these water could be due to the contact of the water with localized sulfide seems. The water of the study area however, is having high concentration of Zn as compare to that of natural water (5-50μg/l) (see Allen, 1989).

Nickel concentration in the waters of Mingora and Kabal area is generally within the permissible limit (50 μg/l) of WHO (1996) for safe drinking water and also of natural water (5-100μg/l) (Allen, 1989). However, the water samples collected from the spring and dug wells in the vicinity of emerald mines in the Mingora area are having many fold high concentration (277-344 μg/l) of Ni as compare to that of WHO (1996). This high concentration of Ni in these areas can be attributed to the occurrence of ultramafic rocks within the mélange zone through which the water is percolating and, therefore, absorbing Ni.

Chromium concentration in the waters of Mingora and Kabal area is generally within the permissible limit (50 μg/l) of WHO 1996). However, many fold high Cr concentration (287-396 μg/l) is noticed in the water samples collected from the springs and dug wells in the vicinity of the emerald mines in the Mingora area. The high concentration of Cr in these waters can be attributed to the occurrence of ultramafic rocks within the mélange zone in the Mingora area. The Ni and Cr have similar distribution pattern in both the Mingora and Kabal areas.

As no availability of maximum permissible limit of Co for safe drinking water in the WHO (1996) report, therefore, the concentration of Co in the waters of the study area can not be evaluated in regard to health hazards. However, the data indicate that the waters of the study area have high amount of Co as compare to the natural water (0.5 – 2.5 μg/l) reported by Allen (1989).

Manganese concentration in the waters of Mingora and Kabal areas are generally within the maximum permissible limit (100µg/l) of WHO (1996) for drinking water and also in the range (1-80 µg/l) for natural water (Allen, 1989). One sample collected at the service station near Fazagat in Mingora area is having multi times higher amount (2198 µg/l) of Mn. The source of contamination in this well water could be from the service station.

Soils

Soils are the ultimate and most important sink of heavy and trace elements in the terrestrial environment which may retain contaminants in clay particles and hence have a great capacity for receiving, purifying and decomposing wastes and pollutants of different kinds (Boon and Soltanpour, 1992). These metals can be contributed in soils from various sources such as (1) natural geological materials from weathering of rocks and minerals (i.e., geogenic source) and (2) domestic sewage, garbage, agricultural return flows and industrial effluents generated by human activities (i.e., anthropogenic source) (Fazeli et al., 1998). Soil obtained through these sources is generally altered by chemical, physical and biological processes which support rooted plant life. These chemical changes are of greater importance in regard to agricultural and environmental point of view. There are certain cations in the soil that are essential for the growth of plants kingdom. But certain plants have greater capability f adsorbing high concentration of heavy and trace metals from the soil, which pose greater threat for the contamination of food chain (Doming, 1994; Christensen, 1995).

For last three decades, remarkable advancement in the biogeochemical research has indicated that heavy and trace elements have played a significant role in the health and productivity of plants. Similarly, the total concentration of heavy and trace elements, their chemistry, mobility and availability to food chain provide the basis for understanding the number of health related hazards in crops, animals and human beings. Plants accumulate these metals from the soil in variable proportion and result in transfer of these metals is humans through food chain. Therefore, the chemistry of soils and plants has greater effects on the ecosystem of any region.

Soils of both Mingora and Kabal areas have been evaluated in regard to physiochemical parameters, light elements oxides and heavy and trace elements and their effects on the ecosystem of the region.

Among the physiochemical parameters the range of pH, electrical conductivity, total dissolved solids, salinity and resistivity is within the safer limit for agricultural purpose. The light element oxides (i.e., CaO, MgO, Na_2O and K_2O) of the soils of Mingora and Kabal areas have been compared with the normal agricultural soil of Bohn et al. (2001). The CaO contents of the majority of soil samples of both Mingora and Kabal areas are exceeding the normal agricultural soil (2.50%) (Table 4.2, Chapter 4; Table 6.1, Fig. 6. 1a). This increase in soils of Mingora area can be attributed to talc-carbonate racks occurring in the melange zone while the high concentration in soils of Kabal area is due to the weathering of the amphibolites exposed in the area. The MgO contents of majority of the soil samples of both Mingora and Kabal area are higher than that of the normal agricultural soil (1.50%) of Bohn et al. (2001) (Table 4.2, Chapter 4; Table 6.1, Fig. 6. 1a). Some soil samples collected from the mélange zone or its vicinity in Mingora are having many fold higher amount (16.75 to 29.23%) of MgO. The high amount of MgO in the soils of Mingora area can be attributed to the weathering of ultramafic rocks of the melange zone while that of Kabal area is due to the weathering of amphibolites. The concentration of Na_2O and K_2O in most of the soils of both Mingora and Kabal areas also exceeds that of the normal agricultural soil of Bohn et al (2001).

The heavy and trace elements of the soils of Mingora and Kabal areas are compared among themselves and also compared with the normal agricultural soils of Bohn et al. (2001). The environmental effects of these elements on the ecosystem of the region are discussed here.

Iron concentration in the soils of Mingora and Kabal areas are lower than that of the normal agricultural soil (38600 mg/l) of Bohn et al. (2001) (Table 4.2, chapter 4; Table 6.1, Fig. 6.1b). Fe is the most important metal is energy transformation during the synthesis of plants' cells and its deficiency in soil is the world wide problem with many crops since the large number of cultivated soils are low in Fe contents (Kabata-Pendias & Pendias, 2001). However, in the soils rich in soluble Fe fraction, an excessive Fe up lake can produce toxic effects in plants (Kabata-Pendias & Pendias, 2001). The studied soils have optimum amount of Fe and, therefore, have no adverse effect as far as the plants' growth is concerned.

Manganese contents of the soils of Mingora and Kabal areas are also lower than that of normal agricultural soil (~850 mg/l) of Bohn et al. (2001) (Table 4.2, chapter 4; Table 6.1, Fig. 6.1b). Mn is, therefore, not considered as hazardous in the soils of the study area.

Copper concentrations in the majority of soil samples of Mingora and Kabal areas are exceeding that of the normal agricultural soil (~20 mg/L) of Bohn et al. (2001) (Table 4.2, chapter 4; Table 6.1, Fig.6.1b). The soil of Kabal area is, however, enriched in Cu relative to that of Mingora area. The occurrence of copper in small amount (4-20 mg/l) is generally beneficial for the normal growth of the plant while Cu concentration less than 4 mg/l is considered deficient and more than 20 mg/l is considered toxic (Jones, 1972; Adriano, 1986; 2001). The higher concentration (>20 mg/l) in the soils of Mingora and Kabal areas could be hazardous as far as the normal growth of plants in concerned.

Lead contents in almost all the soil samples of Mingora and Kabal areas are many fold higher than that of the normal agricultural soils (~10 mg/l) of Bohn et al. (2001) (Table 4.2, chapter 4; Table 6.1, Fig.6.1b). The soil of Kabal area on average is, however, enriched in Pb as compare to Mingora area. Total Pb contents of soil is not a good indicator of Pb phytoavailability until the availability of extractable Pb for plant uptake is known (Adriano, 1986; 2001). During uptake, Pb is concentrated in the roots as compared to other parts of the plants. However, Pb phytotoxicity is low as compared to the other trace elements (Chino, 1981; Adriano, 1986; 2001; Kabata-Pendias & Pendias, 2001) The high concentration of Pb in the soil of Mingora and Kabal areas could be considered as producing Pb phytotoxicity in the plants of the area.

Zinc contents of the majority of the soil samples of Mingora and Kabal areas are within the limit (50 mg/l) for normal agricultural soils of Bohn et al. (2001) (Table 4.2, chapter 4; Table 6.1, Fig.6.1b). However, at some places the soils also contain higher amount of Zn. The two soil samples, collected from Kotlai village, in Kabal area, are having multifold higher amount (245 mg/l and 405 mg/l) of Zn. Zinc is very important element for the normal growth of plants and its deficiency can highly effect the nutritious quality of plants but its high concentration in the soils could be toxic for the plants (Adriano, 1986; 2001; Kabata-Pendias & Pendias, 2001). Therefore, it is suggested that the soils of Mingora and Kabal area are generally not having any toxic effects of Zn on plants, but the soils of Kotlai village need further investigation regarding Zn toxicity and its possible source of enrichment.

Nickel contents of the soils of both Mingora and Kabal areas suggest that these soils are highly enriched in Ni as compared to that of normal agricultural soil (~40 mg/l) of Bohn et al. (2001) (Table 4.2 & 6.1 ; Fig. 6.1b). The soils within the mélange zone or in its vicinity in the Mingora area are having anomalous values (318 to 1929 mg/l) of Ni. This can be attributed to the formation of this soil due to the weathering of ultramafic rocks within the mélange zone. The soils of Kabal area (on average basis) are relatively less enriched as compare to that of Mingora area (Table 4.2, chapter 4; Table 6.1, Fig.6.1b). Nickel is beneficial for the plant growth if present in normal amount in soil, however, the soil with high concentration, especially derived from the ultramafic rocks, can produce toxicity symptoms in plants (Misra, 1974; Adriano, 1986; 2001; Kabata-Pendias & Pendias, 2001). Therefore, the soils of Mingora area can be considered more toxic for plant kingdom as far as the Ni concentration in the soils of the area is concerned.

Chromium concentration in the soils of Mingora and Kabal areas has similar distribution as that of nickel. It is many fold higher than that of normal agricultural soil

(~20 mg/l) (Table 4.2, chapter 4; Table 6.1, Fig.6.1b) . In the soils of mélange zone and its vicinity it is highly anomalous (357 to 5647 mg/l). The source of this enrichment could be the ultramafic rocks in mélange zone. Cr. Shows highly variable oxidation state (from II to VI). However, naturally occurring Cr compound have principal valences of III (chromic) and VI (Chromate). The Cr (VI) is much less stable than Cr (III) and can very easily be mobilized in both acid and alkaline soils. However, the C(111) can only be mobilized in the acidic soils (Adriano, 1986; Kabata-Pendias & Pendias, 2001). Cr has stimulatory effects on the growth of the plants and could be toxic in these soils which are derived from the ultramafic rocks (Adriano, 1986; 2001). The soils of Mingora and Kabal areas, as have been derived fro the ultramafic rocks, could produce toxic effect in the plant kingdom of the area.

Cobalt contents in the soils of Mingora and Kabal areas is higher than that of the normal agricultural soil (~8 mg/l) of Bohn et al. (2001) (Table 4.2, chapter 4; Table 6.1, Fig.6.1b). Co is of greater nutritional concern and, therefore, its presence in soil is essential for the biological activities (Kabata-Pendias & Pendias, 2001). The soils of Mingora and Kabal area are, therefore, safe as far as the Co toxicity is concerned.

Cadmium concentrations in the soils of Mingora and Kabal areas are exceeding that of normal agricultural soil (~ 0.05 mg/l) of Bohn et al. (2001) (Table 4.2, chapter 4; Table 6.1, Fig.6.1b). Soil contamination with Ca is believed to be a most serious health risk. However, the Cd concentration (<4 mg/l) in the studied soil is not considered as hazardous for the plant Kingdom of the area (Adriano, 1986; 2001; Kabata-Pendias & Pendias, 2001).

Plants

Plants play an important role in cycling the heavy and trace elements from the soil and contaminating the food chain to greater extent and hence threatening the ecosystem of the region. Plants are receptacle to heavy and trace metals in variable proportion depending on the physiological reactions of each plant species (Tiffin, 1977). Therefore, plants are acting as intermediate reservoirs through which trace elements move from soil to human beings and animals and are resulting in health related hazards. The chemistry of Plants are also effectively used for geochemical exploration and prospecting of metallic ores (Vernadsky, 1998; Warren, 1975; Dobrovolsky, 1994; Kovalevsky, 1991; Hawkes & Web, 1962; Rose et al. 1979).

Various plants have been collected from the Mingora and Kabal areas, which are generally wild in nature on the soils derived from mafic and ultramafic rocks. Similar plants have been collected from the other areas where the soil has no input from the mafic and ultramafic rocks and are, therefore, used as reference samples. These different groups of plant species were analyzed for heavy and trace elements (Table 5.1, chapter 5; Table 6.2) and the results are discussed in regard to their environmental degradation, if any.

Iron concentration in the *Asteraceac* is reaching to maximum (10056 mg/l) with an average amount of 7163 mg/l. The minimum Fe concentration is present in the *Utricaceae* (average ~1722 mg/l) and *Papilionaceae* (average=1744 mg/l). The Fe concentration is found in the decreasing order of *Asteraceac>Labiateae> Cannabinaceae>Polygonaceae>Sapindaceae>Poaceae>Simarubaceae>Papilionaccae* > *Utricaceae*> (Table 6.2). The variable amount of Fe has been reported in the plants because the ability to absorb Fe is not always constant but is depending on the changing conditions of soil and climate (Kabata-Pendias & Pendias, 2001). The fodder plants have Fe contents in the range of 18 to 1000 mg/l while the nutrition of the grazing animals is usually met with Fe concentration ranging from 50 to 100 mg/l in the forage (Kabata-Pendias & Pendias, 2001. Fe toxicity is also varying in the plants species and in certain species the injuries of leaves or necrotic spots have been reported (Kabata-Pendias & Pendias, 2001). The iron concentration in some plants (i.e., *Asteraceae, Labiateae* and *Cannabinaceae*) of Mingora and Kabal area is many fold higher than amount of Fe in reference plants and therefore, considered harmful for the ecosystem of the region.

Manganese occurs in maximum concentration (374 mg/l) in the *Cannabinaceae* plant (average ~ 250 mg/l) while the minimum amount (5 mg/l) of Mn is noticed in *Papilionaceae* (Table 6.2). The decreasing trend of Mn in the studied plants is observed as:*Cannabinaceae>Simarubaceae>Labiateae>Polygonaceae>Asteraceac>Utricaceae> Poaceae>Sapindaceae> Papilionaccae* (Table. 6.2). Greater variability in the concentration of Mn is observed in the studied plants. Wide variation in the Mn contents (30 to 500 mg/l) among plant species grown on the same soil has also been discussed by Loneragan (1975). A relatively small variation (15 to 25 mg/l) has been observed in Mn content of cereal grains throughout the world (Kabata-Pendias & Pendias, 2001). The critical deficiency level for most of the plants is ranging from 15 to 25 mg/l, whereas the toxic level of Mn in plants is variable depending on both plant and the associated soil (Kabata-Pendias & Pendias, 2001). Mn contents of the plants of Mingora and Kabal areas are not reaching the toxic concentration and are, therefore, posing no environmental problem to the ecosystem.

Copper concentrations in the plants of Mingora and Kabal areas have been observed as maximum (68 mg/l) and minimum (7 mg/l) with an average amount of 30 mg/l in the *Poaceae* (Table 6.2). Cu contents in these plants are in the decreasing order of *Poaceae>Cannabinaceae>Labiateae>Simarubacea>Asteraceac>Sapindaceae> Utricaceae> Polygonaceae> Papilionaceae* (Table 6.2). Cu deficiency in plants exhibits large genetic differences and the Cu < 2 mg/l is considered in adequate for many of the plants (Kabata-Pendias & Pendias, 2001). Copper in very small amount of 5 to 20 mg/l in plant tissue is adequate for normal growth of plant while more than 20 mg/l is considered as toxic for many plants (Jones, 1972). In this regard *Poaceae* and C*annabinaceae* are having Cu in the toxic level while rest of the plants are having Cu in the permissible limit.

Maximum lead contents of 8 mg/l (average=7 mg/l) and minimum Pb contents of 2 mg/l (average ≃ 2 mg/l) are found in Simarubaceae and Papilionaceae respectively (Table 6.2). The decreasing order of Pb contents in these plants is as; Simarubaceae > Utricaceae>*Asteraceac*>Poaceae>*Labiateae>Sapindaceae*>Cannabinaceae>*Polygonace* *ae>Papilionaceae* (Table 6.2). Pb in the concentration of 2 to 6 g/l is sufficient for the normal growth of the plant (Broyer et al., 1972). Background level of Pb in the forage plants is averaging to 2.5 mg/l (Kabata-Pendias & Pendias, 2001). Phytotoxicity of Pb is relatively low compared with the other trace elements (Adriano, 1986). Pb concentration in the plants of Mingora and Kabal areas is relatively high as far as the normal concentration of Pb in various plants is concerned, but it pose no threat to the ecosystem of the region (Adriano, 1986; Kabata-Pendias & Pendias, 2001).

Zinc is found highly variable in some of the families of the plants. Its maximum (43 mg/l) and minimum (4 mg/l) amounts have been found in *Poaceae* (Table 6.2) On average the order of decreasing concentration of Zn in these plant is as: *Cannabinaceae>abiateae>Asteraceae>Poaceae>Simarubaccae>Sapindaceae>Utricaceae>Papilionaceae>Polygonaceae* (Table 6.2). Zinc plays an important role in the metabolism within plants (Lindsay, 1972; Price et al., 1972). Zinc is not considered to be highly phytotoxic. However, the toxicity limit for Zn depends on the plant species and genotypes as well as on the growth stage (Pendias & Pendias, 2001). Upper toxic limit in most of the plants is ranging from 100 to 500 mg/l (Macnicol & Beckelt, 1985). According to Jones (1972), the optimum requirement of Zn for plants varies greatly and, therefore, it is difficult to establish a single critical value. However, plants with Zn contents below 20 mg/l are suspected of Zn deficiency with normal values ranging from 25 to 150 mg/l of Zn (Jone, 1972). Zn contents of plants in Mingora and Kabal areas are generally deficient in Zn and, therefore, no any environmental threats can be expected in the region in this regard.

Nickel concentration in the plants of Mingora and Kabal areas is found maximum (289 mg/l) in *Poaceae* and minimum (20 mg/l) in *Utricaceae* (Table 6.2). Most of the plants species show variable Ni concentration. However, more or less constant and high amount of Ni is noticed in the *Papilionaceae* (Table 6.2). Ni concentration in these plants is decreasing on average in the order as: *Papilionaceae>Poaceae>Simarubaceae>Labiateae>Asteraceae>Cannabianaceae>Sapindaceae>Polygonaceae>Utricaceae* (Table 6.2). The phytotoxic Ni concentrations are ranging widely among plant species and have been reported for various plants to be from 40 to 246 mg/l (Gough et al., 1979) and < 1 to 300 mg/l (Mishra & Kar, 1974). The Ni concentration in the two plant families (i.e., *Papilionaceae* and *Poaceae*) is considered to be in the toxic range while the other plants are not having Ni contents to the alarming level in the Mingora and Kabal areas.

Chromium in the plants of Mingora and Kabal areas has maximum amount (358 mg/l) in *Poaceae* and minimum amount (39 mg/l) in *Simarubaceae* (Table 6.2). However, the highest average amount of Cr is found in *Papilionaceae* with the lowest variability in Cr concentration (Table 6.2). Cr on average is decreasing in these plants in the order of *Papilionaceae> Poaceae> Pohygonaceae> Utricaceae> Cannabinaceae> Asteraceae> Sapindaceae> Simarubaceae* (Table 6.2). The toxicity limit is generally reported as 1 to 10 mg/l (Macnicol & Beckett, 1985). Adriano (1986) suggested that for many plant species Cr proved to be toxic at about 5 mg/l. In this regard all the studied plants of Mingora and Kabal area have manifold high concentration of Cr as compared to that of recommended level for toxicity in plants. Therefore, the effects of Cr on the ecosystem of the region could be hazardous.

Cobalt and cadmium concentrations in the plants of Mingora and Kabal areas are low and are not considered as toxic as far as the maximum toxic level of these metals in various plants are concerned (Adriano, 1986; 2001; Kabata-Pendias & Pendias, 2001).

The total average uptake of the heavy and trace elements by various plants of the Mingora and Kabal area have the relation: Fe >Cr>Ni>Mn>Cu>Zn>Co>Pb>Cd in *Poaceae* while in rest of all the plants similar relation of Fe> Mn>Cr>Ni>Cu> Co> Pb>Cd has been noticed. The existence of heavy and trace elements in soils of Mingora and Kabal areas have the relation: Fe>Cr>Ni>Zn>Mn>Cu>Pb>Co>Cd in the former and Fe>Cr>Ni>Mn>Pb>Zn>Cu>Co>Cd in the latter. This suggests the variable uptake rate of various metals from the soils occur in different plants because of their different adsorbing/absorbing capacity for these elements (Shah et al., 2004). The high uptake of Fe, Cr and Ni is consistent in all plants. However, *Papilionaceae* and *Poaceae* are having maximum accumulation of Cr and Ni in their tissues. This can be attributed to the enrichment of Cr and Ni in the soils due to the weathering of the mafic and ultramafic rocks of the region and also the ability of absorbing these metals from the soil by these plants. According to Barttett and James (1979) and Gough et al. (1986), Cr in the soil is usually oxidized from Cr (III) to Cr (VI) and then it is available for uptake in plants. The multifold enrichment of Cr and Ni in the *Papilionaceae* and Poaceae as compared to the other plants of the study area suggests that these plants have the ability to uptake and translocate Cr (VI) and Ni in their tissues (Kafayatullah et al., 2001).

Enrichment and depletion of the heavy and trace elements have been established in the plants generally self-grown in the soils derived from mafic and ultramafic rocks of the Mingora and Kabal areas relative to the reference plants grown on the soil having no input from the mafic and ultramafic rocks (Fig.6.2). The data suggest that all the plants are variably enriched in Fe, Cu, Pb, Zn, Ni, Cr, Co, Cd and Mn (Fig.6.2). However, it is well observed that *Papilionaceae* and *Poaceae* have multifold high concentration relative to the other plant species grown on the same soil (Fig.6.2) further suggests that these plants have high ability to uptake and translocate Cr and Ni in their tissues.

The inter-element correlation in the soils and plants of the Mingora and Kabal areas have been calculated and the results are given in Table 6.3 and 6.4 respectively. Table 6.3 exhibits that a negligible correlation (r=<0.82) of elements exists in the soil while no correlation (r= <0.35) of elements in the plant is noticed (Table 6.4). The plant-soil correlation was also established by calculating the correlation coefficient for heavy and trace element concentration in the soils and plants of the Mingora and Kabal area and the results are shown in Figure 6.3. It is clear from this figure that no correlation (r=<0.17) exist for Cr, Pb, Zn and Fe (Fig. 6.3). However, weak correlations for Cr (r= 0.620) and for Ni (r= 0.713) have been noticed (Fig. 6.3). No correlation in Cr, Pb, Zn and Fe can be attributed to the greater variation of these elements in the soil and also the variable uptake rate of the different plants (see Bloemen et al., 1995; Kabata-Pendias & Pendias, 2001; Kafayatullah et al., 2001; Shah et al., 2004).

The biogeochemical studies shows that the ability of various plants to absorb/adsorb greater amount of various heavy and trace elements from the soil has provided significant clues for both mineral prospecting and environmental degradation (Hawkes and Webb, 1962; Levinson 1974; Rose et al., 1979; Adriano, 1986; 2001; Kabata-Pendias & Pendias, 2001; Bohn et al., 2001). It has been noticed during this study that most of the heavy and trace elements (i.e., Fe Mn, Cu, Pb, Zn, Co, Cd) in the soils of the Mingora and Kabal areas though enriched relative to the normal soils but their effects on the plant kingdom can not be considered hazardous. However, the variable increase of Cr and Ni in the plants species, especially in *Papilionaceae* and *Poaceae,* grown on the soils derived from mafic and ultramafic rocks can be applicable not only to mineral exploration but also to environmental and toxicological concern because the Cr, particularly Cr (VI) and Ni can be toxic. The Cr and Ni toxicology and their carcinogenic effects on both animals and human beings are well reported (Furst, 1971, Thornton, 1987; Adriano, 1986; 2001; Kabata-Pendias & Pendias, 2001; Bohn et al., 2001).

The increased concentration of Cr and Ni reported in the soils and plants during this study is indicative of the fact that the possibilities of transferring of these metals from foliage to the animals and then to the inhabitants of the area through meat and milk of these animals. In this regard detailed studies involving the biochemist, geochemist, and epidemiologists need to be carried out in order to unravel the toxicity caused by these elements in the area of study.

Table 6.1. Comparison of the average light element oxides and heavy and Trace elements of the soils of Mingora and Kabal areas with that of reference soils and normal soils

	Mingora	Kabal	Reference	Normal soil
Light element oxides				
CaO	3.11	4.81	2.50	2.50
MgO	10	2.22	1.42	1.50
Na2O	4	4.31	3.08	1.50
K2O	1	1.56	1.39	1.50
Heavy and trace elements				
Fe	25395	29721	2445	3860
Mn	65	69	73	850
Cu	45	53	9	20
Pb	60	52	12	10
Zn	58	72	10	50
Ni	788	211	23	40
Cr	973	314	33	20
Co	19	17	2	8
Cd	3	3	0.573	0.05

Table 6.2. Ranges and averages of the various heavy and trace elements in the plants of Mingora and Kabal area.

	Poaceae			Papilionaceae			Polygonaceae		
S.No.	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
Fe	1719	5744	3079	1625	1863	1744	3275	4194	3734.5
Mn	13	115	49	5	18	12	71	99	85
Cu	7	68	30	9	14	11	10	12	11
Pb	3	9	5	2	2	2	2	3	2.5
Zn	4	43	19	8	13	10	9	11	10
Ni	31	289	80	269	278	274	28	40	34
Cr	56	358	122	256	285	271	55	61	58
Co	5	9	6	6	6	6	6	6	6
Cd	0.089	0.389	0.241	0.178	0.223	0.201	0.234	0.242	0.238
Ca	287	7369	3418	1303	6985	4144	6642	7833	7237.5
Mg,	111	1161	604	25	25	25	1788	3689	2738.5
Na	22	251	83	23	69	46	276	341	308.5
K	2069	26044	9289	1206	2244	1725	3375	5719	4547

	Labiateae			Asteraceae			Sapindaceae		
S.No.	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
Fe	4163	8163	6802	7163	10056	7163	2450	6225	3160
Mn	72	134	117	72	96	72	45	65	45
Cu	15	29	23	16	28	22	17	20	19
Pb	4	5	5	6	7	6	4	5	5
Zn	14	26	21	15	25	20	15	19	17
Ni	27	70	40	28	53	40	30	42	34
Cr	40	56	49	48	54	51	45	55	45
Co	7	9	8	8	9	8	7	7	7
Cd	0.213	0.257	0.238	0.245	0.268	0.257	0.214	0.245	0.226
Ca	8905	15320	12003	10643	11354	10643	5292	5948	5292
Mg,	464	918	464	832	1508	1170	3721	5909	3721
Na	97	287	147	101	101	101	92	107	99
K	906	4638	2808	6456	9119	7788	2512.5	5350	2643.75

	Utricaceae			Cannabinaceae			Simarubaceae		
	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
Fe	1706	1738	1722	3456	9925	6691	2367	3369	2868
Mn	39	70	54	126	374	250	130	145	137.5
Cu	11	15	13	27	33	30	19	25	22
Pb	5	6	6	3	4	4	6	8	7
Zn	10	12	11	25	30	27	17	22	19.5
Ni	20	30	25	35	39	37	53	64	58.5
Cr	46	68	57	48	53	51	39	43	41
Co	6	6	6	7	9	8	5	7	6
Cd	0.22	0.226	0.223	0.276	0.289	0.283	0.234	0.286	0.26
Ca	6779	7579	7179	13545	20645	17095	1675	16466	9070.5
Mg,	529	7119	3824	946	3505	2225	272	291	281.5
Na	134	136	135	77	278	177	134	172	153
K	3344	3494	3419	5013	7594	6303	4325	5994	5159.5

Table 6.3. Interelement correlations in the soils of Mingora and Kabal areas, Swat, Pakistan

Cu	Pb	Zn	Fe	Cr	Ni	Co	Cd
1	0.196	0.933	0.404	0.046	-0.019	0.267	0.824
	1	0.149	-0.002	-0.005	-0.024	0.007	0.056
		1	0.413	-0.090	-0.102	0.348	0.783
			1	-0.066	-0.067	0.616	0.463
				1	0.920	-0.021	-0.044
					1	-0.052	-0.076
						1	1

Table 6.4. Interelement correlations in the plants of Mingora and Kabal areas, Swat, Pakistan

Cu	Pb	Zn	Fe	Cr	Ni	Co	Cd
1	0.053	-0.009	0.274	-0.331	-0.477	-0.233	0.180
	1	0.090	-0.273	0.145	0.106	0.024	0.032
		1	-0.082	-0.227	-0.205	0.067	0.055
			1	0.148	-0.140	-0.182	0.354
				1	0.799	0.702	0.193
					1	0.587	-0.282
						1	-0.092

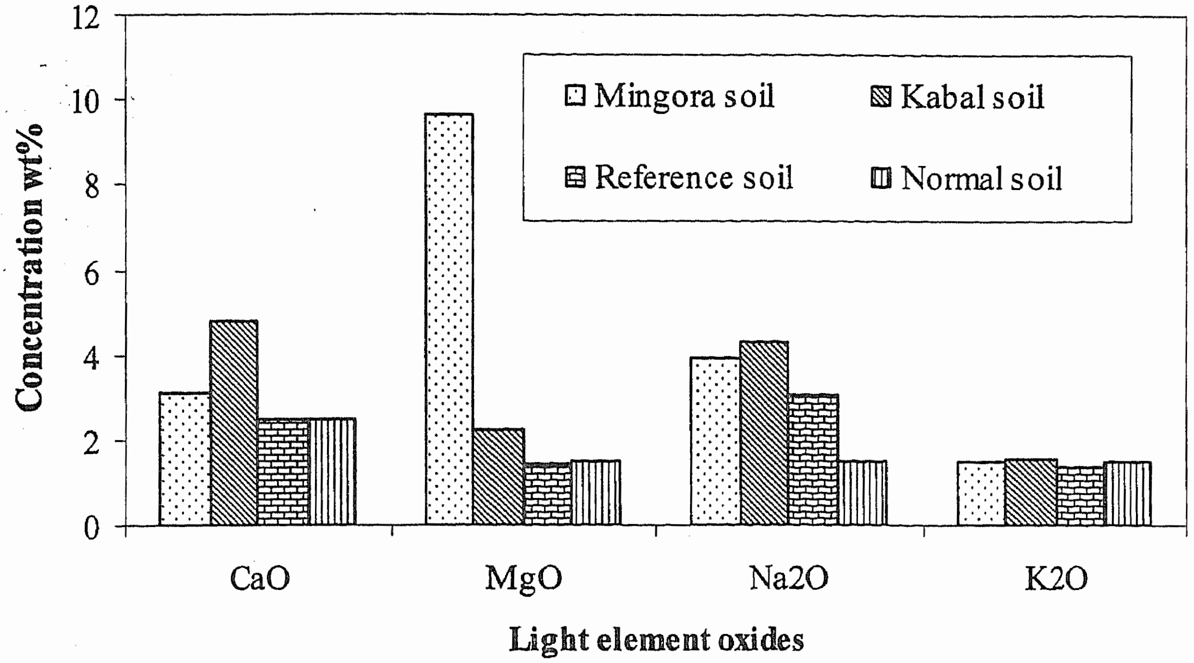

Fig.6. 1a. Comparison of the average concentration of light element oxides in the soils of Mingora and Kabal areas with that of reference soil and normal soils.

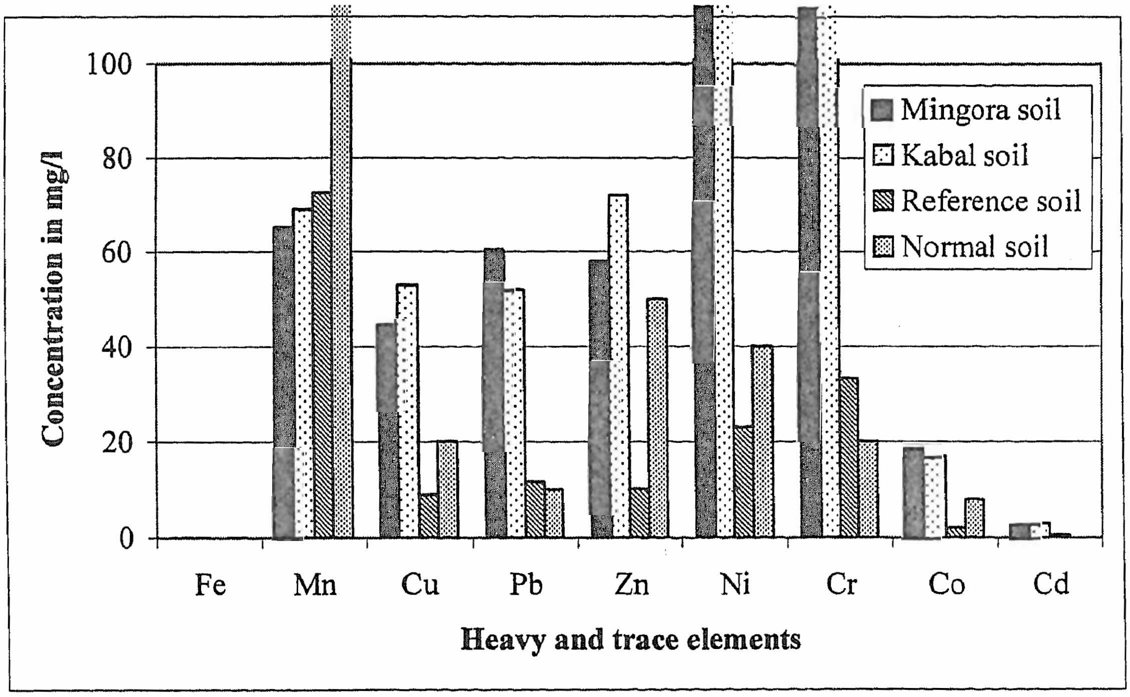

Fig.6. 1b. Comparison of the heavy and trace elements concentrations in the soils of Mingora and Kabal areas with that of reference soil and normal soils.

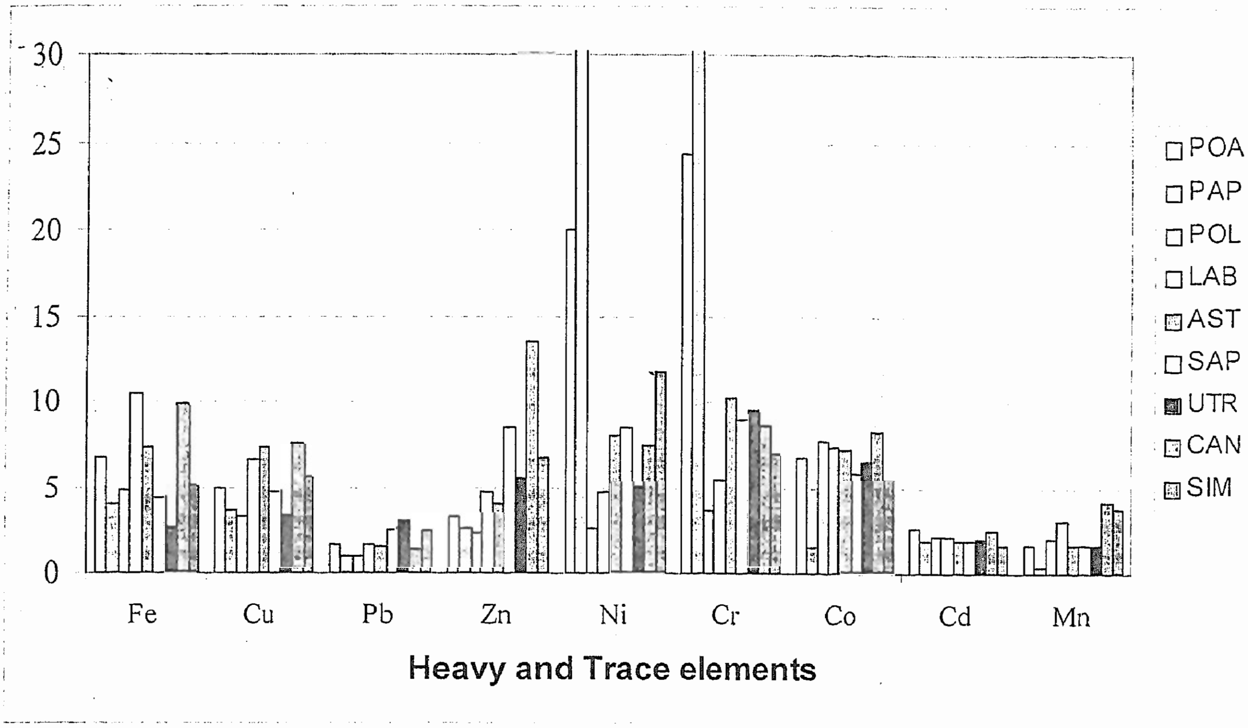

Fig. 6. 2. Enrichment and depletion of various heavy and trace elements in the plants of the Mingora and Kabal area, Swat, Pakistan. POA, Poaceae, PAP, Papilionaceae, POL, Polygonaceae, LAB, Labiateae, AST, Asteraceae, SAP, Sapindaceae, UTR, Utricaceae, CAN, Cannabinaceae, SIM, Simarubaceae.

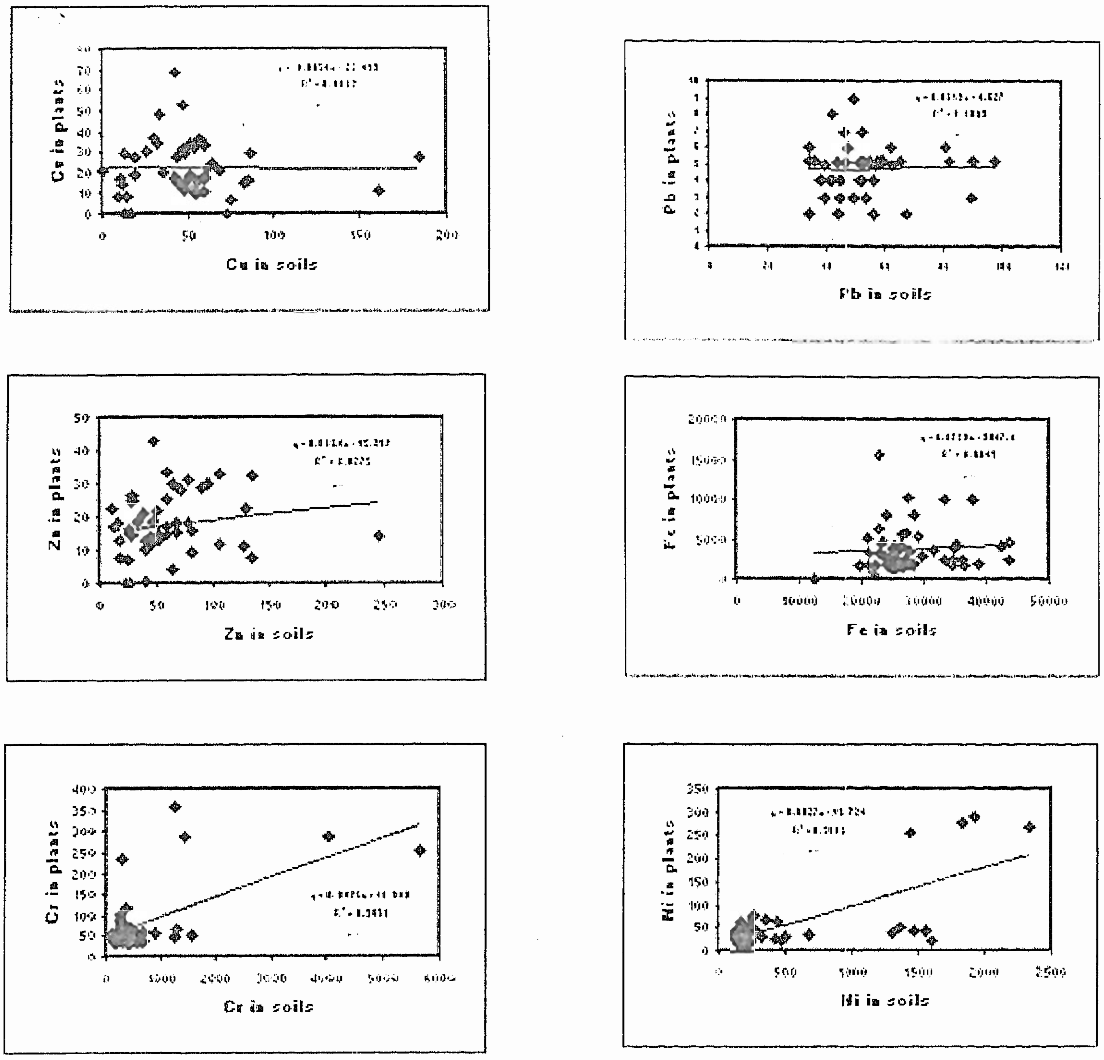

Fig. 6.3. Correlation between concentration of various heavy and trace elements in the Plants and associated soils of the Mingora and Kabal areas, Swat, Pakistan.

CONCLUSIONS

Following are the conclusions of this study:

- The physio-chemical parameters (i.e., pH, EC, TDS, DO, turbidity) of the waters of Mingora and Kabal areas are within the WHO permissible limit for drinking water. However, the water of river Swat has relatively high turbidity.

- Among the light elements Ca, Mg, Na and K are generally within the WHO permissible limit for drinking water. However, Mg in the springs and dug wells within and in the premises of melange zone in the Mingora area are exceeding the permissible limit.

- Among the heavy and trace elements Fe, Cu, Pb, Zn, Co and Mn are within the WHO permissible limit for drinking water. The concentration of Cr and Ni in the Kabal area are generally within the permissible limit but the water of springs and dug wells within or in the premises of mélange zone in Mingora area has many folds high concentration of both these elements.

- The physio-chemical parameters (i.e., pH, EC, TDS, DO, turbidity) of the soils of Mingora and Kabal areas are within the permissible limit of the normal agricultural soil.

- The concentration of light element major oxides (i.e., CaO, MgO, Na_2O, K_2O) in majority of the soils of the Mingora and Kabal areas are generally exceeding that of normal agricultural soils. However, the MgO contents of soils from within and adjacent areas of the melange zone are relatively very high.

- The soils of the Mingora and Kabal areas are generally enriched in Cu, Pb, Zn, Ni, Cr, Co and Cd and are deficient in Fe and Mn. However, Cr and Ni in soils within and adjacent to the mélange zone in Mingora are many-fold higher than that of the normal agricultural soil.

- The concentrations of light, heavy and trace elements in all the studied plants of Mingora and Kabal areas are highly variable. However, the *Papilionaceae* and *Poaceae* have multifold high concentration relative to the other plant species grown on the same soil.

- There is no inter-element correlation within these plants. However, very weak correlation has been noticed in Cr, Pb, Zn.

- The increased concentration of Cr, Ni and Mg in the water, soils and plants of the Mingora can be attributed to the occurrence of mafic and ultramafic rocks within the mélange zone exposed in the area.

- The pedo and bio-geochemistry of the Kabal and Mingora area has greater implications in the geochemical explorationan and environmental degradation in the study area.

- There could be the increase in Cr and Ni concentration in the blood the inhabitants of the area by transferring of these metals from forage to the animals and then through meat and milk to the human-being. Further detailed investigations in the study area are, therefore, proposed.

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ANNEX 1

Description of Water Samples

Sample Code	Lactation	Source	Location
W1, W1-A	Raj Abad/Maluk Abad Union council	Tap water	N 34 46 718 E 72 22 050
W2	Maluk Abad, Mingora	Spring water	N 34 46 897 E 72 21 991
W3	Maluk Abad, Mingora	Well water. Depth of the well was about 50 feet but its surface is about 10 feet and well itself is 40 feet deep. It was near mine area.	
W4, W4-A	Maluk Abad towards Fizagat	Spring water	N 34 47 318 E 72 22 198
W5, W5-A	Maluk Abad towards Fizagat	Flowing water may be from another spring	N 34 47 318 E 72 22 198
W6, W6-A	From car washing service station near at Fizagat near mine area	Well water Depth of well 60 feet	N 34 47 318 E 72 22 198
W7, W7-A	Hayat Abad	Tube well	N 34 47 450 E 72 21 882
W8, W8-A	Hayat Aabad	Dug well	N 34 47 450 E 72 21 882
W9, W9-A	Haya Abad	Dug well	N 34 47 450 E 72 21 882
W10, W10-A	Kanra Baba	Tube well No. 7	N 34 47 287 E 72 21 509
W11, W11-A	Rahim Abad, near road, Mingora	Dug well, having depth of about 30 feet	N 34 46 122 72 20 197
W12, W12-A	Filling station, Rahim Abad	Dug well having 30 feet	N 34 46 196 E 72 20 147
W13, W13-A	Qambar, Mingora	Dug well, 70 feet deep	N 34 45 864 E 72 19 578
W14, W14-A	Qambar, Mingora	Dugu well, 40 feet deep	N 34 45 864 E 72 19 578
W15, W15-A	Qambar, Mingora	Tube well	N 34 45 864 E 72 19 578
W16, W16-A	From petrol pump, Rahimabad	Dug well	N 34 46 119 E 72 20 004
W17, W17-A	Marghuzar	Stream water	
W18, W18-A	Collected from Rivers Swat near River Pear Hotel	River water	
W19, W19-A	Collected at Ningulai from River Swat tributary	River Water	N 34 49 494 E 72 24 288
W20, W20-A	Taken from stream at Kanju towards Kabal. Collected at sunny day	Stream water	N 34 48 379 E 72 20 404

W21, W21-A	Kanju village bazaar towards Kabal	Pumping well having depth of 15-18 feet	N 34 48 396 E 72 20 382
W22, W22-A	Kanju Village	Stream 2	N 34 48 423 E 72 20 083
W23, W23-A	Deerai Baba, Kanju	Spring	N 34 48 229 E 72 19 529
W24, W24-A	Aligrama	Dug well at a Mosque, having depth of 40-50 feet	N 34 48 130 E 72 19 360
W25, W25-A	Aligrama	Collected from Dug well above marble processing unit, having depth of 40-50 feet	N 34 48 130 E 72 19 360
W26, W26-A	Aligrama	Dug well having depth of 40 feet	N 34 48 130 E 72 19 360
W27, W27-A	Hazara towards Kabal	Stream having muddy water	N 34 48 130 E 72 19 360
W28, W28-A	Hazara	Main Stream after passing hazara (Between Hazara and Guljabba)	N 34 48 001 E 72 18 023
W29, W29-A	Near girls School, Guljabba, Kabal	Pumping well	N 34 47 646 E 72 17 475
W30, W30-A	Near girls School, Kabal	Tube well	N 34 47 452 E 72 17 395
W31, W31-A	Kabal	Dug well withing Silk mill on main road	N 34 47 968 E 72 17 044
W32, W32-A	Sarsenai	Dug well at a house	N 34 48 782 E 72 16 810
W33, W33-A	Sarsenai	Dugwell at a filling station, having 90 ft depth	N 34 48 782 E 72 16 810
W34, W34-A	Sarsenai	Dug well having depth of 90 ft	N 34 49 504 E 72 16 564
W35, W35-A	Sarsenai	Dug well at service station	N 34 49 504 E 72 16 564
W36, W36-A	Kabal	Sprig near Police Model Reporting Center at Mosque	N 34 47 532 E 72 17 230
W37, W37-A	Kabal	Spring, about 10 steps farther W36	N 34 47 532 E 72 17 230
W38, W38-A	Landay, Kabal	Dug well	N 34 47 054 E 72 16 685
W39, W39-A	Meelagah-Kotlai	Spring	N 34 47 162 E 72 12 722
W40, W40-A	Meelagah-Kotlai	Stream	N 34 47 148 E 72 13 442
W41, W41-A	Meelagah towards Kabal	Tube well, powered by tractor	N 34 47 100 E 72 13 971
W42, W42-A	Kotlai	Dug well	N 34 46 880 E 72 15 203
W43, W43-A	Mingora	Swat River at Kanju brigde towards Mingora. (Speedy and Clear water)	N 34 47 485 E 72 20 815
W44, W44-A	Landakai	Swat River	N 34 39 823

			E 72 07 985
W45, W45-A	Berarai, Khwazakhela	Tap water	N 34 55 703 E 72 28 490

Description of soil samples, Mingora

Sample code	Appearance	Area	Location
S1	Dark brownish red. Fine to sandy texture	Maluk Abad	N 34 46 850 E 72 21 765
S2	Same soil as of S1	Maluk Abad	N 34 46 842 E 72 21 768
S3		Maluk Abad	N 34 46 852 E 72 21 768
S4	Same as S3 (P4 without soil)		
S5		Maluk Abad (within the emeralds mine limits)	N 34 46 872 E 72 21 964
S6		Maluk Abad (within the emeralds mine limits)	N 34 46 872 E 72 21 964
S 7		Maluk abad (within the emeralds mine limits)	N 34 46 872 E 72 21 964
S8		Area of mine towards Fizagat	N 34 47 332 E 72 22 189
S9		Area of mine towards Fizagat	N 34 47 332 E 72 22 189
S 10		Area of mine towards Fizagat	N 34 47 318 E 72 22 198
S 11	Same as S10, so not collected		N 34 47 318 E 72 22 198
S 12		Area of mine towards Fizagat	N 34 47 318 E 72 22 198
S13- A S13-B	Top soil Subsoil (agricultural soil	Hayat Abad, Fizagat	N 34 47 450 E 72 21 882
S 14			
S 15- A S 15- B	Soil from rice paddies	Hayat Abad, Fizagat	N 34 47 450 E 72 21 882
S 16- A S 16- B	Dark color silt, collected from Agricultural soil	Kanara Baba	N 34 47 273 E 72 21 488
S 17		Rahim Abad mountain	N 34 46 074 E 72 20 186
S 18		Rahim Abad mountain	N 34 46 074 E 72 20 186
S 19		Rahim Abad mountain	N 34 46 074 E 72 20 186
S 20		Rahim Abad mountain	N 34 46 074 E 72 20 186
S 21-A S21- B	Agricultural soil	Rahim Abad	N 34 46 196 E 72 20 147

S22		Rahim Abad	N 34 46 196 E 72 20 147
S33		Qamber, Mingora	N 34 45 734 E 72 19 354
S34- A S34- B	Agricultural soil	Rahim Abad	N 34 46 115 E 72 20 064

Soil Reference samples from baren area, Mingora

S23	From graphitic schist	Odigram	N 34 44 482 E 73 17 244
S 25		Odigram	N 34 44 482 E 73 17 244
S 26	From agricultural field	Odigram	N 34 44 482 E 73 17 244
S29	From Melang zone	Odigram	N 34 45 426 E 072 18 74

Description of soil samples from Kanju- Kabal area

S. Code	**Description**	**Area**	**Location**
S 35- A S35 – B	Agri soil	Kanju village, just after Knaju airport towards Kabal near second stream	N 34 48 423 E 72 20 083
S 36- A S36- B	Agri soil (field of lady finger)	Knaju village	N 34 48 306 E 72 19 620
S37		Knaju, Deerai Baba	N 34 48 216 E 72 19 512
S 40		Deerai Baba, Kanju	N 34 48 211 E 72 19 501
S 41		Deerai Baba, Kanju	N 34 48 211 E 72 19 501
S 42-A S42- B	From horticultural and agri field	Deerai Baba, Knju	N 34 48 229 E 72 19 529
S43 –A S43- B	Agri field, at Hazara	Hazara towards Kabal	N 34 48 001 E 72 18 023
S44	Agri field near Kabal girls school	Kabal	N 34 47 452 E 72 17 395
S45	Agri field at Kabal	Kabal	N 34 47 968 E 72 17 044
S47- A S47- B	Agri field	Kabal	N 34 47 968 E 72 17 044
S48- A S48- B	Agri field at Sirsenai	Sirsenai, Kabal	N 34 49 504 E 72 16 564
S49- A S49- B	Agri field near Police model reporting centre, Kabal	Main bazaar Kabal towards shamozai	N 34 47 532 E 72 17 230
S50-A S50- B	Agri field on roadside at Landay, Kabal	Landay, Kabal	N 34 47 054 E 72 16 685
S51	Collected from kabal mountain, which are strong amphibolites at Meelagah-Kotlai, 14 km Kabal	Meelagah-Kotlai	N 34 47 162 E 72 12 722

	towards west		
S52		Meelagah-Kotlai	N 34 47 162 E 72 12 722
S53	Light in color	Meelagah-Kotlai	N 34 47 162 E 72 12 722
S55	Light in color	Meelagah-Kotlai	N 34 47 162 E 72 12 722
S57- A S57- B	Agri field	End point of Meelagah-Kotlai	N 34 47 148 E 72 13 442
S58	Collected from peach garden	Kotlai, Kabal	N 34 46 880 E 72 15 203
S59-A S59- B	Collected at junction of Kabal and Kotlai at Chakdara road	Kotlai	N 34 46 622 E 72 16 099
Blank 1		From Malamjabba	
Blank 2		Malamjabba	

Description of plant samples

Code	Local name	Description	Location	Area of collection
P1	Shandai	Yellowish green in color, height about 2 feet, multibranched with elongated conical leaves and thin stem	N 34 46 850 E 72 21 765	Maluk abad, Mingora
P2	Beaker	Hieght about 2½ feet, multibranched with violet color small flowers and small sized leaves.	N 34 46 842 E 72 21 768	Raja abad/Maluk abad (Union Council)
P3	Ghwaraskay	Elliptical leaves	N 34 46 852 E 72 21 768	Raja abad/Maluk abad (Union Council)
P4		Small herb, multibranched with small height, light green in color thorny	N 34 46 851 E 72 21 768	Maluk Abad, Mingora
P5	Arhanda	Broad leaved, bright green in color	N 34 46 872 E 72 21 964	Within in the mine limits, Maluk Abad, Mingora
P6	Grass	Long scales like grass	N 34 46 872 E 72 21 964	Within in the mine limits, Maluk Abad, Mingora
P7			N 34 46 872 E 72 21 964	Within in the mine limits, Maluk Abad, Mingora
P8	Ghwaraskay		N 34 47 332 E 72 22 189	Area of mines towards Fizagat
P9	Tarokay		N 34 47 332 E 72 22 189	Area of mines towards Fizagat

P10	Gandery	Yellowish green, small height with about more than 6 inches.	N 34 47 318 E 72 22 198	Area of mines towards Fizagat
P11	Ghwareja	Fern with pink small flowers	N 34 47 318 E 72 22 198	Area of mines towards Fizagat
P12	Grass		N 34 47 318 E 72 22 198	Area of mines towards Fizagat
P13	Beaker	Collected without soil, as soil is same like S11 and S12	N 34 47 318 E 72 22 198	Area of mines towards Fizagat
P14		Collected without soil, as soil is same like S11 and S12	N 34 47 318 E 72 22 198	Area of mines towards Fizagat
P15	Sholy	Whole plant is consisted of scales	N 34 47 450 E 72 21 882	Hayat Abad, Mingora
P16	Gopi		N 34 47 273 E 72 21 488	Kanra Baba
P17				
P18			N 34 46 074 E 72 20 186	Rahim Abad, mountain, Mingora
P19			N 34 46 074 E 72 20 186	Rahim Abad, mountain
P20			N 34 46 074 E 72 20 186	Rahim Abad, mountain
P21	Jowar	Collected from agricultural field, Light green in color	N 34 46 196 E 72 20 147	Rahim Abad, Mingora
P22	Bhang	Dark green color shrub	N 34 46 196 E 72 20 147	Rahim Abad, Mingora
P33	Shimsha	Elliptical leaves. Collected from Melang zone	N 34 45 734 E 72 19 354	Balogram, Mingora
P34	Jowar		N 34 46 165 E 72 20 064	Rahim Abad, Mingora
P35	Jowar	Taken from agricultural field at Kanju village just after Airport toward Kabal near 2nd stream	N 34 48 423 E 72 20 083	Kanju village
P36	Bendai	Thorny stem, 2-3 feet height	N 34 48 306 E 72 19 620	Kanju Village
P37	Taroky	Shrub with bright green	N 34 48 216 E72 19 512	Deerai baba, Kanju
P38	Grass	Collected without soil, as soil was same as of P37.	N 34 48 216 E 72 19 512	Deerai Baba, Kanju
P39		Collected without soil as was same that of P40. Having about 1 foot hight, multibranched.	N 34 48 211 E72 19 501	Deerai Baba, Knaju
P40	Palosa	Thorny fern, dull green leaves.	N 34 48 211 E72 19 501	Deerai Baba, Knaju
P41		Bright green color leaves, short heighted	N 34 48 211 E72 19 501	Deerai Baba, Kanju
P42	Shandai	Collected from direct amphibolites without soil as soil as same to S42	N 34 48 229 E72 19 529	Deerai Baba, Kanju
P43	Jowar	Bright green color, collected from	N 34 48 001	Hazara towards

		agricultural field adjancent to stream.	E 72 18 023	Kabal
P44	Shaltaloo	Short highted tree, with bright green color leaves. Collected without soil, as soil was same as of P43	N 34 48 001 E 72 18 023	Hazara towards Kabal
P45	Jowar	Collected from agricultural field	N 34 47 452 E 72 17 395	Kabal (Near girls School)
P 46	Jowar	Collected from agricultural field near silk mill	N 34 47 968 E 72 17 044	Kabal towards Sirsenari
P47	Shaltaloo	Collected from agri field having maiz and peach orchards	N 34 47 968 E 72 17 044	Sirsenari, Kabal
P48	Jowar	Collected from agri field	N 34 49 504 E 72 16 564	Sirsenari, Kabal
P49	Jowar	Collected from agricultural field	N 34 47 532 E 72 17 230	Kabal
P50	Sharsham	Collected from agricultural field, having bright green color	N 34 47 054 E 72 16 685	Landay, Kabal
P 51	Shaltaloo	Collected from agricultural field without soil as soil was same as for P50	N 34 47 054 E 72 16 685	Landay, Kabal
P 51-B	Ghwarskay	Bright green color shrub with short height. Collected from strong amphibolites.	N 34 47 162 E 72 12 722	Melagah Kotlai, about 14 km west of Kabal
P52	Taroky	Same location as of P51-B	N 34 47 162 E 72 12 722	Melagah Kotlai
P53	Bhang	=	N 34 47 162 E 72 12 722	Melagah Kotlai
P54	Grass	Collected without soil as soil same as of P53	N 34 47 162 E 72 12 722	Melagah Kotlai
P55	Arhanda		N 34 47 162 E 72 12 722	Melagah Kotlai
P 56	Skha bootay	Collected without soil, from same area as of P55	N 34 47 162 E 72 12 722	Melagah Kotlai
P57	Jowar	Collected from agricultural field at ending point of Melagah Kotlai	N 34 47 148 E 72 13 442	Melagah Kotlai
P58	Shaltaloo	Collected from peach orchard field	N 34 46 880 E 72 15 203	Kotlai
P 59	Jowar	Collected from agricultural field	N 34 46 622 E 72 16 099	Junction of Kotlai and Chakdara road
P 60	Shaltaloo	Collected from peach orchards without soil	N 34 46 622 E 72 16 099	Junction of Kotlai and Chakdara road

Reference Samples of Plants

P23	Shandai	From barren soil (graphitic schist)	N 34 44 482 E 72 17 244	Odigram, Mingora
P24	Taroky	Collected without soil, as same soil was there as	N 34 44 482 E 72 17 244	Odigram, Mingora

		S23		
P25	Arhandas	Broad leaved, bright green in color	N 34 44 482 E 72 17 244	Odigram, Mingora
P26	Jowar	From agricultural field	N 34 44 482 E 72 17 244	Odigram, Mingora
P27		Shrub, collected without soil	N 34 44 482 E 72 17 244	Odigram, Mingora
P28	Bhang	Shrub, collected without soil	N 34 44 482 E 72 17 244	Odigram, Mingora
P29			N 34 45 426 E 072 18 74	Odigram, Mingora
P30		without soil	N 34 45 426 E 072 18 74	Odigram, Mingora
P31		without soil	N 34 45 426 E 072 18 74	Odigram, Mingora
P32		without soil	N 34 45 426 E 072 18 74	Odigram, Mingora
Blanks (1-10)				Collected from MalamJabba

ANNEX 2

Scientific Names of Studied Plants

Plant code	Family	Botanical name
P12, P6, P38	Poaceae	*Saccharum species (Grass, long)*
P11	Papilionaceae	*Indigofrra gerardiana*
P9, P37, P52	Polygonaceae	*Rumex hastatus*
P17	Labiateae	*Salvia moorcroftiana (broad leaved)*
P5, P25, P55	Asteraceae	*Xanthium strumarium*
P14	Papilionaceae	*Lespediza juncea*
P3, P8, P33, P51-B	Sapindaceae	*Dodonaea viscose*
P19	Labiatae	*Isodon rugosus/ Plectramthus rugosus (new name)*
P13, P2	Utricaceae	*Debergeasia sulicifolia*
P34, P35, P43, P46, P26, P48, P57, P45, P59, P49, P35, P0	Poaceae	*Zea mays*
P53, P22	Cannabinaceae	*Cannabis sativa*
P58, P51, P47, P60, P44	Rosaceae	*Prunus persica (Peach)*
P54	Poaceaae	*Dicanthium annulatum*
P16	Brassicaceae	*Brassica bortrytis*
Warkhary	Portulaceae	*Portulaca oleraceae*
P40	Mimosaceae	*Acacia modesta*
P7	Solanaceae	*Withania romnifeaea*
P42, P1	Simarubaceae	*Ailanthus altissima (Indian)*
P10	Apocyanaceae	*Nerium indicum*
P18	Labiatae	*Teucrium quadrium*
P50	Brassicaceae	*Brassica campastris*
P41	Moraceae	*Morus nigra*
P4, Blank 9	Labiatae	*Otostegia limbata*
P39	Amaranthaceae	*Arva javanica*
P56	Braginaceae	*Onasma species*
P36	Malvaceae	*Hibiscus esculentus* (Landy finger)
P15	Poacceae	*Oryza sativa*

Additional Reference Samples

Plant Code	Family	Botnical name
P23	Simarubaceae	*Ailanthus altissima (Indian)*
P24	Polygonaceae	*Rumex hastatus*
P25	Asteraceae	*Xanthium strumarium*
P26	Poaceae	*Zea mays*
P27	Amaranthaceae	*Althernantera pungens*
P28	Cannabinaceae	*Cannabis sativa*

P29	Labiateae	*Salvia moorcroftiana* (broad leaved)
P30	Labiatae	*Otostegia limbata*
P31	Labiatae	*Isodon rugosus/ Plectramthus rugosus (*new name*)*
P32	Poaceaae	*Dicanthium annulatum*

Blank plants

Plant code	**Family**	**Botanical name**
Blank 1	Sapindaceae	**Dodonaea viscose**
Blank 2,	Papilionaceae	*Indigofrra gerardiana*
Blank 3	Polygonaceae	*Rumex hastatus*
Blank 4	Simarubaceae	*Ailanthus altissima (Indian)*
Blank 5,	Asteraceae	*Xanthium strumarium*
Blank 6	Labiatae	*Isodon rugosus/ Plectramthus rugosus* (new name)
Blank 8	Cannabinaceae	**Cannabis sativa**
Blank 9	Labiatae	*Otostegia limbata*
Blank 10	Utricaceae	*Debergeasia sulicifolia*
Blank 11,	Poaceaae	*Dicanthium annulatum*
Grass Blank		

Annex-3

Plate 1. *Debergeasia salicifolia*

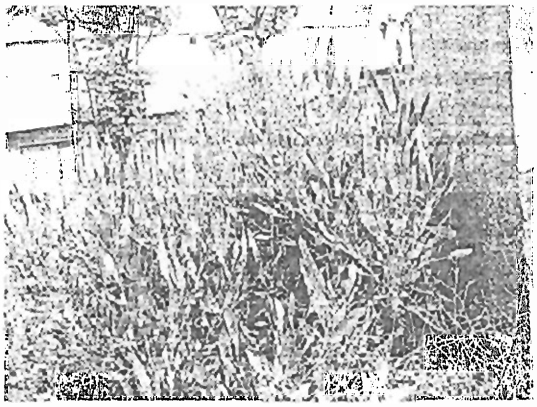

Plate 2. *Dodonaea viscose*

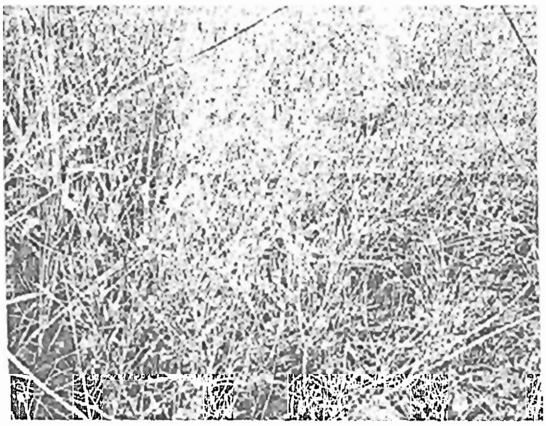

Plate 3. *Rumex hastatus*

Plate 4. *Indigiofera gerardiana*

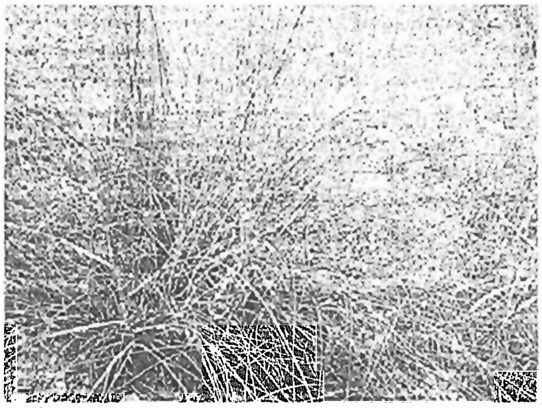

Plate 5. *Saccharum spp.*

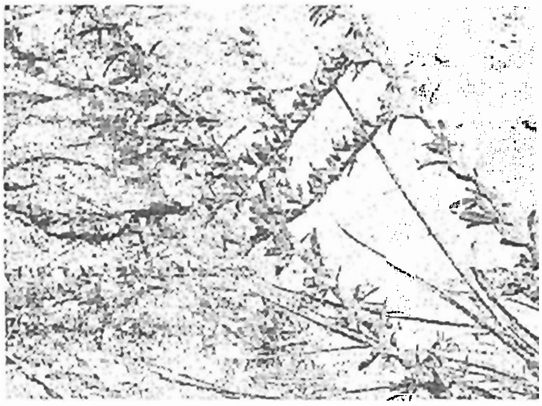

Plate 6. *Otostegia limbata*

Plate 7. *Brassica bortrytis*

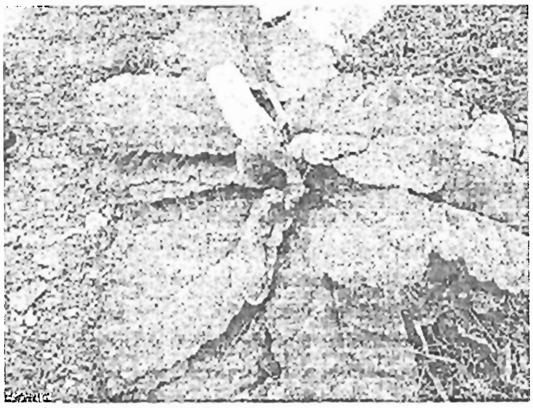

Plate 8. *Salvia morcraftiana*

Plate 9. *Cannabis sativa*

Plate 10. *Zea mays*