Assessment of Geochemistry of Soils for Agriculture at Winder, Balochistan, Pakistan

Shahid Naseem[1], Salma Hamza[2] and Erum Bashir[1]
[1]Department of Geology, University of Karachi, Karachi,
[2]Department of Geology, Federal Urdu University of Arts,
Science and Technology, Karachi,
Pakistan

1. Introduction

Pakistan basically is an agricultural country and this sector approximately contributes 22 percent of GDP. Agricultural products not only facilitate life but are also supplies as raw material to industries and a main source of foreign exchange (Pakistan Agriculture Economy and Policy [PAPE], 2009). In Pakistan, farmers are not aware of the latest development in the field of agro-sciences, although some of them take care about the soil fertility (Iqbal & Ahmad, 2011). Proper management of nutrients and micronutrients will enhance the productivity but thus far very little attention has been paid to evaluate the impact of local geology on the soils for better crop yield.

The Japanese Government in collaboration with the Department of Agriculture, Balochistan in 1993-94 has established agriculture farms in the surrounding areas of Winder Town, Balochistan to boost fruit farming in the area, necessary to fulfill consumer's demand. These farms are situated over the ophiolitic rocks of the Cretaceous age concealed by windblown sediments (Fig. 1). Pillow basalts in association with pelagic sediments are exposed along a North-South alignment in the eastern part of the area (Naseem et al., 2002). The Ferozabad Group of Jurassic age is exposed in the Mor Range and other sedimentary rocks belonging to the Cretaceous and Tertiary ages are exposed in the Pab Range, further east of study area. The dissolution of ophiolites contributes a very discrete assemblage of ions (Neal & Shand, 2002). The abundance of elements largely depends upon the nature of bedrocks, climatic conditions and mobility. The ion distribution is also influenced by the infinite complex surface and subsurface physicochemical environments (Aghazadeh & Mogaddam, 2010). The soil differs from its parent material due to interactions between the lithosphere, hydrosphere, atmosphere and the biosphere (Chesworth, 2008; Danoff-Burg, 2000). The rock in the vicinity of an agricultural field not only provides basic lithology (soil) but also contribute major and trace elements to the soil (Fig. 2). The trace elements in the soil play a dual role in agriculture. Some trace elements are essentially required for the healthy growth of plants, as well as they contribute as essential minerals to human beings. However, some trace elements are not only toxic for plants but also post a health risk to humans (Haluschak et al., 1998).
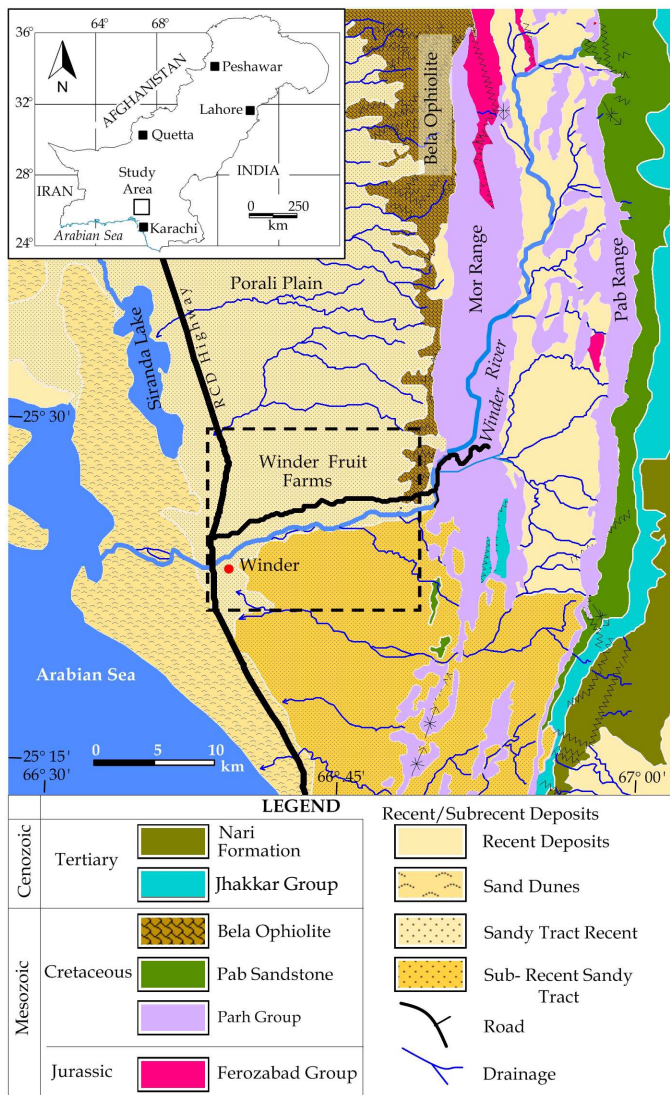
Fig. 1. Geological map of the Winder and adjoining areas (Simplified after Hunting Survey Corporation Ltd. [HSC], 1960). Main study area is marked by broken line cage. Inset showing map of Pakistan.

The majority of the soils of the study area are a mixture of sand, silt and loam. Genetically they are derived from ophiolites, sedimentary rocks and windblown sediments. The soil profile is not well developed having a poor top organic rich horizon. In the foothills of the rocky area, R-horizon is found. The soils developed in the vicinity of the ophiolites are thinner in thickness, medium to coarse grained and are light brown in colour. The western and southern portions of the study area are occupied by saline soil.

Elements from sedimentary rocks (Mor Range)

Fe	Zn
Mg	Cu
Ca	Fe

Fe	Cr
	Ni
Mg	Cu
	Co
Ca	Cd
	Pb

Soil	Secondary Minerals	Primary Minerals	Exposed Rocks
Sand/Silt	Quartz	Quartz	Sandstone
Clay	Clay	Clay	Shale
	Calcite	Calcite	Limestone
Carbonate	Quartz	Feldspar	Pillow basalt
Iron oxide	Clay	Pyroxene	
	Iron oxide	Olivine	
	Serpentine		

Mor Range

Bela Ophiolite

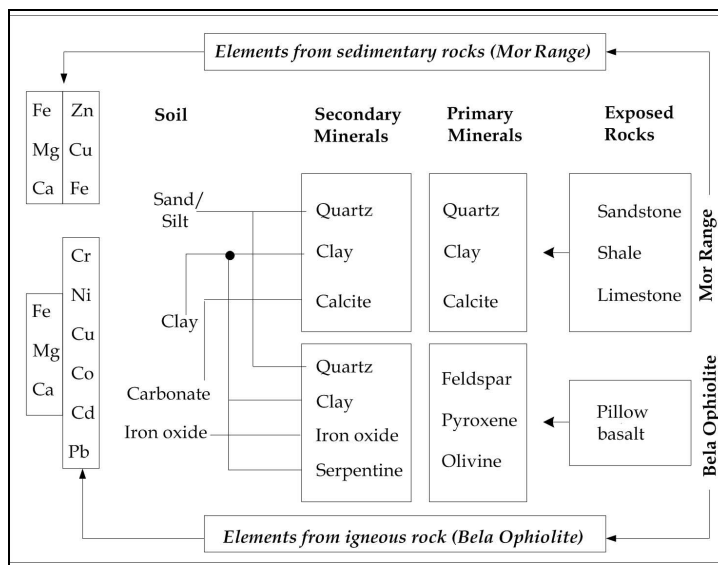Elements from igneous rock (Bela Ophiolite)

Fig. 2. Schematic diagram illustrated contribution of trace elements in soils through rocks of the study area.

Seventy-two representative soil samples were collected from Winder town and adjoining areas. The pH and electrical conductivity (EC) of soil samples were measured using a Denver Instrument Model 50. Soil organic matter was determined by the ignition method. The texture of the soils was determined with a set of sieves of different diameters. The XRD of soil samples were made using a Bruker D-8 Advance X-ray diffracto-meter, Cu and K-radiation. Estimation of major and trace elements were made through water extraction (Gupta, 2004) using AAS (Hitachi Model, Z-5000).

The objective of the study is to describe the geochemistry of the soil in relation to it potential for agriculture purposes. The major and trace elements are discussed considering its soil quality, impact of bed-rock and bioavailability of these elements in the soil. Prime irrigation qualities are elaborated to appraise its suitability for irrigation in the Winder Agriculture Farms. Possibly present study helps farmers of the area for better irrigation planning.

2. General geology

The study area lies in the southern extremity of Mor-Pab ranges, comprises of ophiolite and sedimentary rocks. The Bela Ophiolite is linked with 400km long Alpine-Himalayan Mesozoic Ophiolite Belt. It is a harzburgite sub-type ophiolite, which is common in Tethyan Domain. It has characteristics of both suprasubduction zone and mid-ocean ridge settings and is also intruded by hotspot-derived magmas (Sheth, 2008; Khan et al., 2007). It is represented by tholeiitic basalts, mafics and ultramafics. Gnos et al. (1998) divided the Bela Ophiolite into two distinct units on the basis of age and tectonic setup. The upper unit (ophiolite) is exposed in the northern part of the belt between Sonaro and Wadh. The lower unit (ophiolite accretionary wedge and trench sediments) is well exposed from Sonaro to the coast of Karachi in the south. The study area is the part of lower unit of Bela Ophiolite and intermittently exposed along the western contact of Mor Range.

Rocks of the Mor Range consists of Ferozabad Group, comprised of Kharrari, Malikhor and Anjira formations (Shah, 2009). It consists of mainly siliciclastic and carbonate rocks of Lower-Middle Jurassic age. The rocks of the Ferozabad Group were deposited on the shelf flank of a rift system resulting from the breakup of Gondwanaland and the separation of the Indian Craton from Madagascar and Africa (Gnos et al., 1997). The stratabound replacement type (MVT) deposit is confined to the allochemical limestone beds of the Kharrari and Malikhor formations. Sedimentary exhalative mineralization (Sedex) is common in the topmost Anjira Formation. Sulphide mineralization comprises sphalerite, galena, pyrite and marcasite with minor chalcopyrite (Ahsan & Mallick, 1999). The outcrops of Cretaceous sedimentary rocks (Sembar, Goru, Parh, Fort Munro, Mughal Kot and Pab formations) are present in the Pab Range (Kazmi & Abbasi, 2008).

3. Soil character and classification

The top layer of the earth's surface made up of organic material and particles of broken rocks that have been altered by chemical and environmental processes. It is generally composed of many parallel distinctive horizons (soil profile) responsible for the agricultural growth. In the study area, soils reveal variable profiles according to the geology of the area. Mostly windblown sediments are present (Fig. 3), thinning towards east, where the ophiolitic rocks are present. In the western part, windblown and fine soil is present (Fig. 3A). In the vicinity of Winder River and its Tributaries, river driven materials are common (Fig. 3B). In the foothills of rocky area, R-horizon is found. Based on the United States Department of Agriculture (USDA) and the National Cooperative Soil Survey classification system, in the study area, majority of the soils are Entisols, which are formed in the areas of very dry or cold climate, having low soil moisture and poor soil organic matter, however some of the wind-blown soils are Aridisols, which develops in very dry environments.
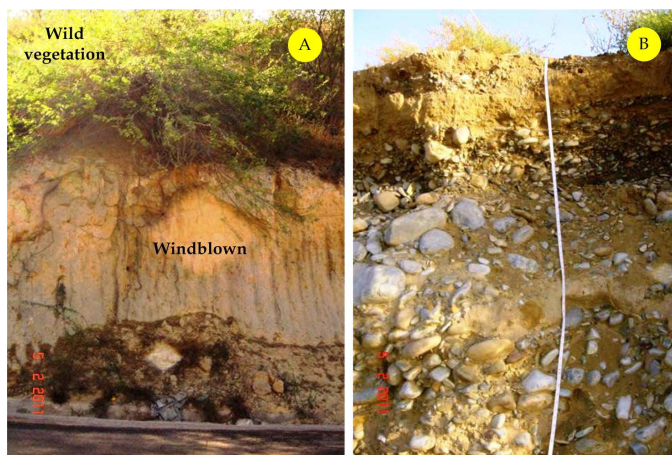

Fig. 3. Different types of soils present in the study area; A. Windblown silty soil, and B. Winder River channel.

Briggs et al. (1998) used sand, silt and clay fractions in the classification of agriculture soils. The information of soil through this scheme is valuable to infer texture, structure, porosity,

adhesion and consistency of the soil. In addition, it largely determines the water retention and transmission properties of soils (Singh & Dhillon, 2004). The USDS sand-silt-clay triangular diagram (Fig. 4) displays 27.77% (20 out of 72) soil in the study area as sandy loam, followed by 20.83% sand, while 13.88% are silt loam. This indicates that soil of the study area is the mixture of sand and loam. Sand may drain too rapidly, while in a clay individual pore spaces are too small for adequate water holding; where clay and silt proportions are high, root penetration is difficult. Generally, loam textures are best for crop growth (Singh & Dhillon, 2004). The combination of both sandy and loamy soil is suitable for agriculture.
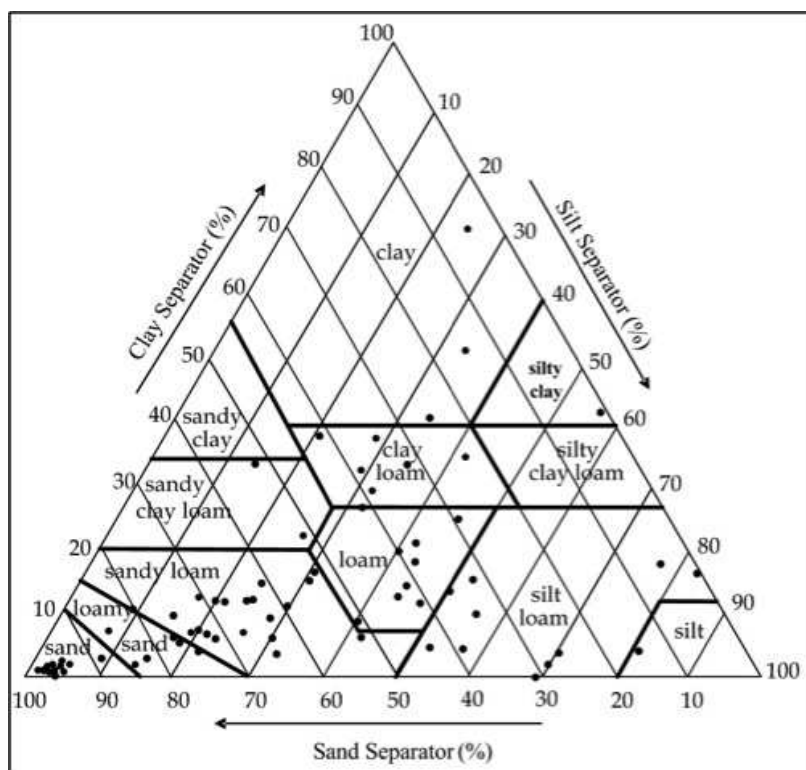

Fig. 4. Classification of soils of Winder area on sand-silt-clay ternary diagram (Class boundaries after USDA textural triangle).

4. Soil geochemistry

4.1 pH and alkalinity

The pH is one of the most important soil properties that affect the availability of elements. The majority of food crops prefer a neutral or slightly acidic soil (pH 7). Some plants however, prefer more acidic (*Manilkara zapota*) or alkaline (*Zizyphus jujuba*) conditions (Dave's, 2010). Many nutrient cations such as Zn, Fe and Cu are available for uptake by plants below pH 5.0; however at variable pH, elements show different availability. In more alkaline conditions, elements availability decreases (Sutton, 2003) and symptoms of nutrient

deficiency may result, including thin plant stems, yellowing (chlorosis) or mottling of leaves and slow or stunted growth (McKenzie, 2003). In the study area, the pH range 7.06-9.20, indicates alkaline soil, which is obvious in the presence of carbonate rocks in the area.

4.2 Electrical conductivity (EC)

The accumulation of soluble salts in the soil is termed as water extractable salts and can be assessed by measuring the electrical conductivity (EC) in soil saturation extracts (Reluy et al., 2004). The EC is an important determinant of the suitability of the soil for plant growth (Gana, 2000). Singh & Dhillon (2004) classify soil with reference to salinity; soils having EC <2000 μS is termed as Non-saline, between 2000-6000 are Moderately saline, while EC >6000 are Highly saline. In the study area, only 4 samples (5.55%) are Non-saline, 44.44% samples have Moderately saline while rest of the samples are Highly saline.

4.3 Cation exchange capacity (CEC)

It is the total number of negative charges per unit weight of the soil. The quantity of positively charged ions (cations) that a clay mineral or similar material can accommodate on its negatively charged surface is expressed as milli-ion equivalent per 100g at 7pH, or more commonly as milliequivalent (meq) per 100g or cmol/kg (Troeh & Thompson, 2005). Thus, CEC is the measure of soil fertility and nutrient retention capacity. The CEC of the clay mainly depends upon the mineralogy and different members of clay can hold variable amount of cations. In the studied samples, relation between clay percent and trace elements is poor. The correlation coefficient (Fig. 5) between clay content and trace elements (Cu, Cr and Ni) exhibits negative relationship. The data also reveals that relatively high amount of elements are more in those soil samples in which clay content is between 10-20%. The distribution of trace elements is low (Table 1) in contrast to world average (Alloway, 2005). Probably the low amount is due to sandy soil and alkaline pH.
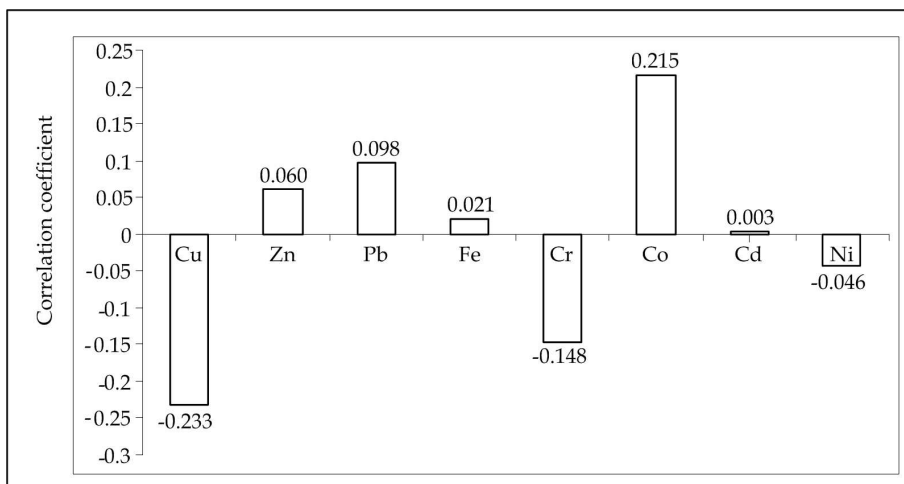

Fig. 5. Correlation coefficient between clay content and trace elements of the soils of the study area.

Element	Range in agriculture soil	World Average in agriculture soil	Average in soil of study area
Na	750-7500	6300	631
K	400-30000	8300	96
Ca	7000-500000	13700	1273
Mg	20-10000	5000	334
Fe	5000-500000	38000	28.05
Cu	1-20	13-24	2.66
Pb	3-189	32	5.12
Ni	0.2-450	20	3.12
Zn	17-125	64	1.02
Co	0.1-70	7.9	0.97
Cd	0.01-2.5	0.06-1.1	0.49

Table 1. Concentrations of selected major and trace elements in the agriculture soils (After Alloway, 2005) and their comparison with the soils of study area. All values are in mg/kg.

4.4 Water content (WC)

Water content is the quantity of water contained in the soil. It helps to maintain dissolved salts and to promote soil stratification (Hussain, 2007). It is simply express as ratio of mass of water hold in the soil (Wesley, 2010). Normally, it ranges between 15-80%. Soil with high amount of clay minerals generally contains high amount of water. It is measured by weighing a soil sample before and after it has been dried in an oven at a temperature $105^{\circ}C$ till constant weight.

The soils of the study area have 11-74% WC with a mean value of 31%, indicating good reflection of soil texture. Nearly 14% soils have WC <15%. Mostly these soils are present in the northern barren area; however few of them are windblown soil. Soils with high WC >50% are less (6.94%) and present in the main farm area.

4.5 Soil organic matter (SOM)

Soil organic matter (SOM) is related to the productivity of a soil. Soil organic matter comprises of an accumulation of partially disintegrated and decomposed plant and animal residues and other organic compounds synthesized by the soil microbes as the decay occurs (Brady, 1990). The SOM can be divided into two major groups: Particulate Organic Matter (active fraction) and Humus (transitioning organic matter) with increasingly stable/complex compounds. The amount of SOM can vary from <1% in coarse-textured sandy soils to >5% in fertile cultivated soils. The SOM plays an important role in providing nutrients, stabilization of soil structure, water retention, cation exchange and pH buffering. The quantitative determination of SOM has high variability and ambiguities. Dry combustion and acid-dichromate methods are commonly employed for the measurement of SOM. In the present work, dry ignition method as described by Hussain (2007) is utilized. In the study area, SOM ranged between 0.35-12% with an average of 2% (Table 2). In the cultivated areas, it is high while in the rocky and wind-blown soil it is recorded low. The arid climate of the study area and sandy soil also hinder for high SOM.

	Minimum	Maximum	Average	SD	Median
pH	7.06	9.2	8.06	0.39	8
EC mS	1	22	8	5.29	5.67
TDS g/kg	1	15	5	3.68	4
Ca mg/kg	500	3507	1273	750	985
Mg mg/kg	100	2431	334	339	300
Na mg/kg	50	6875	631	1299	269
K mg/kg	13	475	96	67.87	81
Cl mg/kg	100	2747	938	691	798
SO_4 mg/kg	21	3149	803	679	700
WC %	11	74	31	13.61	28
SOM %	0.35	12	2	1.81	2
Ca:Mg	0.82	30.06	5.97	5.72	4.29
Ca:K	2.63	175	19.14	21.97	15.03
Mg:K	0.63	121	5.78	14.24	3.43
Ca epm	25	175	64	37.43	49.15
Mg epm	8	200	28	27.92	24.17
Na epm	2	299	27	56.5	11.68
K epm	0.32	12.13	2.45	1.73	2.07
ESP %	1	82	17	17.33	10.79
Cu mg/kg	0.03	8.8	2.66	2.73	1.1
Zn mg/kg	0.03	16.7	1.02	2.67	0.25
Pb mg/kg	0.08	10.55	5.12	4.14	7.55
Fe mg/kg	0.8	197.6	28.05	45.7	5.35
Cr mg/kg	0.07	9.8	4.69	2.61	4.45
Co mg/kg	0.05	2	0.97	0.38	1.05
Cd mg/kg	0.13	1.8	0.49	0.46	0.35
Ni mg/kg	0.52	13.3	3.12	2.9	1.78

ESP = Exchangeable Sodium Percentage (see Section 4.7 for definition)

Table 2. Statistical analysis of physical and chemical parameters of soils of Winder area.

4.6 Calcium (Ca) and magnesium (Mg)

Calcium improves the soil crust, structure and quality as well as reduces soil salinity, erosion and phosphorous loss. It also promotes root and leaf development, and helps to create a healthy environment for the plant growth. Calcium at optimum level will reduce disease in most plants (Dick, 2007). Imbalance of Ca will lead to tight, hardpan soils, which will restrict the flow of air and water through the soil profile (Trotter, 2011). Magnesium

deficiency causes the loss of healthy green colour of leaves because of shortage of chlorophyll in plant. Magnesium is a mobile element in the plant, so the concentration of Mg usually decreases from top to bottom of plant. It also decreases according to plant maturity. Ca/Mg ratio is an important parameter to evaluate soil for agriculture purpose. A good soil has Ca:Mg between 5-8 with 6.5 as an ideal condition (Spectrum, 2011). In the presence of different rock exposures, the ratio varies. In the study area, 15 out of 72 samples i.e. 20.83% soils are within the ideal limit (5-8). Fourteen samples (19.44%) have high Ca:Mg exceeding 8. The majority of the samples 59.73% (43 samples) have low Ca:Mg (Fig. 6). This observation shows a good agreement with the geology of the area. Soils derived from ophiolites have nearly above range of ratio (Robinson et al., 1997). The present study also shows compatibility with the work of Naseem et al. (2005, 2009) carried out in the Khuzdar, north of the study area. The Ca/Mg ratio map shows that the Winder farm area has low values with few high ratio spots (Fig. 7A). The diagram shows decrease of Ca/Mg ratio in the east as well as in the west direction. High supply of Mg from ophiolitic rocks (east) and seawater from western side are mainly responsible for low Ca/Mg ratio in the study area.
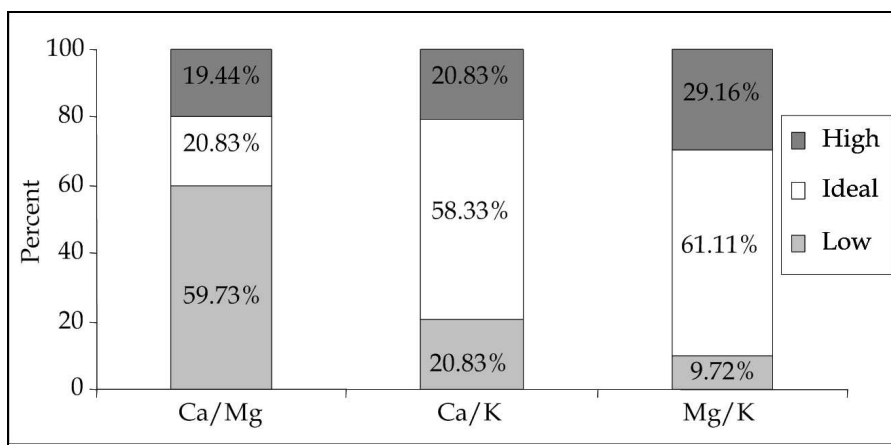

Fig. 6. Comparison of Ca/Mg, Ca/K and Mg/K ratios of soils of the Winder area, showing distribution percents of low, near ideal and high conditions.

In the study area, most of the sedimentary rocks consist of limestone such as, Parh Limestone, Malikhore and Kharrari formations. Soil becomes acidic when certain basic elements, especially Ca are removed by the percolation of rain water (Ca is very soluble in water) which carry the dissolved Ca down deep into the soil and by crops and plants removing the Ca as they grow and develop. The study area has hot and dry climate. In drier areas, the Ca remains undissolve and is not carried deep into the soil. As the Ca and some other elements build up, the soil becomes basic or alkaline (Holley, 2009).

4.7 Potassium (K) and sodium (Na)

Potassium (K) is an essential nutrient for plant growth and occupies third position after nitrogen and phosphorus. It enhances disease and drought resistance in plants. It also helps to develop fruit size, flavor and texture. Soil K is found in three forms; relatively unavailable, slowly available and readily available. Generally, 90-98% of the total K in soils

is relatively unavailable in the form of primary minerals (muscovite, biotite, and feldspars); nearly 1-10% is the slowly available from clays and hardly 0.1-2% are readily available as exchangeable K (Buchholz & Brown, 1993).
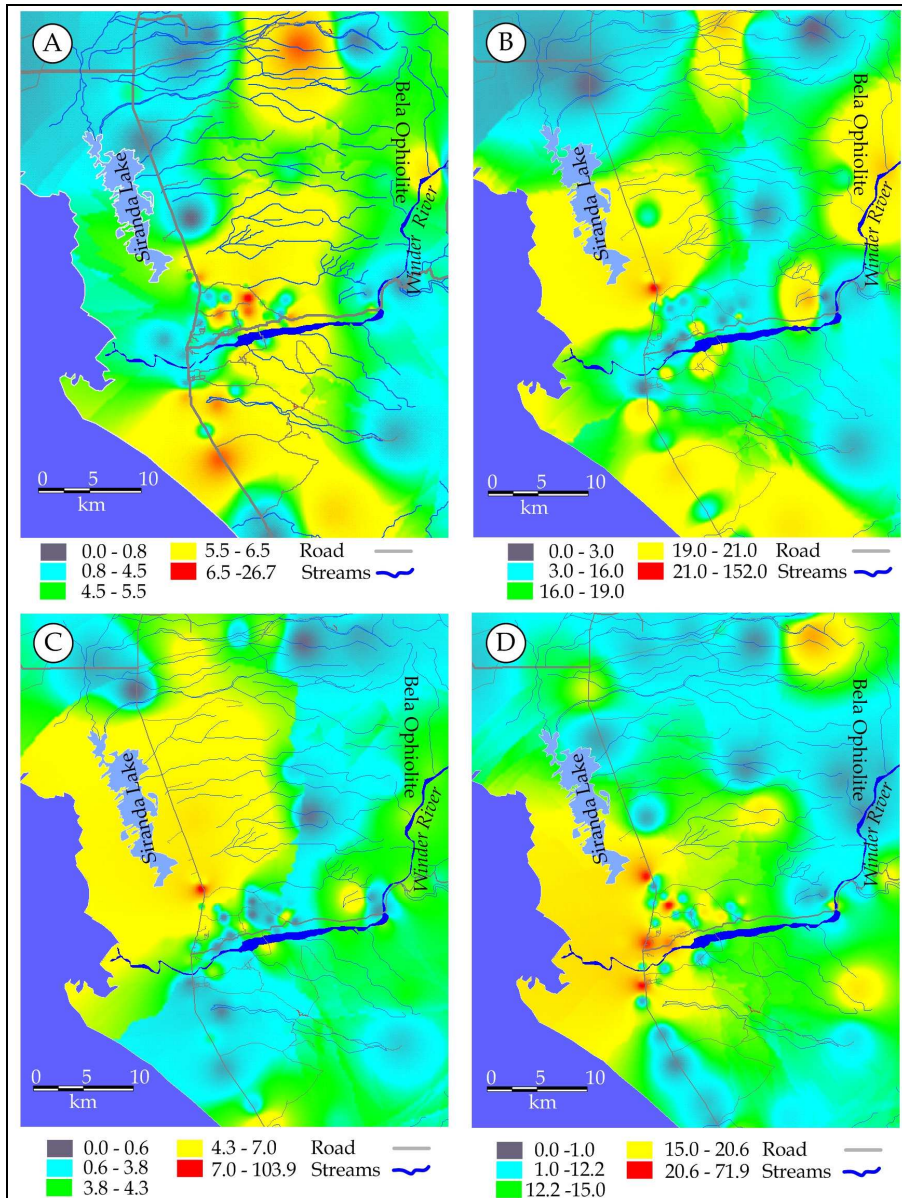

Fig. 7. Equal value range interpolation of A: Ca/Mg; B: Ca/K; C: Mg/K ratios; D: ESP in the soils of Winder and adjoining areas, based on inverse distance weighted (IDW) technique.

The level of K in the soil is termed low when it is <60mg/kg; medium (60-100) and high, when the readily available K is >100mg/kg. In the study area, nearly 29.17% soils have low K, 27.8% medium while rest have K >100mg/kg. Potassium in combination to Ca and Mg is also very significant to assessed quality of agriculture soils. The Ca/K ratio around 13:1 is approaching ideal condition. In the study area, nearly 58% samples fulfill the requirement, while the rest are either low or high (Fig. 6). The Ca/K ratio is ideal near farm areas and either side are low in K and high in Ca due to rock type (Fig. 7B). Similarly, Mg/K relationship in a ratio 2:1 is ideally fit for yielding good fruits. Here, the situation is similar, 61.11% samples are close to model ratio (Fig. 6). In and around fruit farms, the ideal condition exists with few low patches (Fig. 7C). Possibly the high Mg/K ratio is due to the presence of low K and high Mg-bearing tholeiitic basalt as one of the soil parent material in the area (Naseem et al., 1996-97). The high Ca/K ratio is due to the exposure of carbonate rocks. The other minor causes for high ratio are due to sandy soil, poor chemical weathering due to arid climate and continuous crop production since long time.

The primary problem posed by high sodium (Na) is not a toxicity hazard, but has a dispersive effect on agriculture soils, thus reduction of soil permeability and soil aeration. It can cause the clay particles to separate from each other; the particles will clog the soil pores, and cause variation in the permeability of the soil. This effect is more serious in fine textured soils than in coarse textured (Natural Resources Conservation Service [NRCS], 2007).

The amount of Na in the soil can be conveniently appraised by Exchangeable Sodium Percentage (ESP). It is calculated as follows:

$$ESP = Exchangeable \{(Na)/ (Ca + Mg + K + Na)\} \times 100$$

ESP measures the amount of soil exchange capacity occupied by Na ions and expressed as percentage. At higher ESP values, more exchangeable Na is available, and greater the potential for negative plant-soil impacts. An ESP >15% indicates that soil Na will probably limit permeability. The University of New South Wales [UNSW] (2007) has categorized soils on the basis of ESP into five classes (Table 3).

ESP Classes	ESP Values	Soil of Winder Area
Non-sodic	<6	22.2%
Sodic soil	6-10	25%
Moderately Sodic	10-15	11%
Strongly Sodic	15-25	14%
Very Strongly Sodic	>25	22.2%

Table 3. Soil classification of Winder area on the basis of ESP values (After UNSW, 2007).

The distribution of ESP in the study area illustrates high values close to Arabian Sea, which is the good source of Na in the soils (Fig. 7D). However, the farm area is safe except few high concentration zones.

4.8 Sulphate (SO_4^{2-}) and chloride (Cl^-)

Sulphur (S) is described as secondary plant nutrient and essentially required for crops. It is a major component of plant proteins and having an important role in the synthesis of

chlorophyll. The deficiency of S in plants appears in the youngest leaves as pale-yellow colour (Rajendram et al., 2008). Sulphur exists in the soil predominantly as bound organic S (~94%); with small amounts (~3% each) existing as sulphate-S (SO_4-S) and extractable organic S (OS). Plant-available S is taken up by plants only in the sulfate (SO_4) form, through the roots because agricultural crops rarely respond to other types. Thus, most agriculture soil estimates plant-available S by extraction and determination of sulfate-S (Hayes, 2007).

The soils of Winder area show concentration of SO_4 in between 21-3149 with an average 803mg/kg (Table 2). According to Alloway (2005), the range of SO_4 in agriculture soil is between 90-30,000mg/kg; while ~2,000mg/kg is considered best for crop. All soil samples of the study area have low SO_4-S. The SO_4 is mainly due to sulphide mineralization in the rocks of Mor Range and to some extent from Bela Ophiolite.

Chloride (Cl) is recent addition in the list of micronutrient, needed in small quantities for crop growth. Chloride functions in photosynthesis and chemically balances the K concentration that increases in the guard cells during the opening and closing of stomata. On the other hand, high Cl may reduce the ability of roots to extract water and nutrients from the soil. Thus high Cl in the soil is major constraints to crop production (Dang et al., 2008). Chloride is taken up by plants as the Cl^- ion. In the soil, it is found as anion because it is highly soluble and most mobile.

In the study area, the rock containing appreciable amount of Cl is lacking. The soils in the surroundings of Winder show 100-2747 with an average 938mg/kg (Table 2). The Cl concentration of studied samples is much higher than world average of 100mg/kg (Flowers, 1988). Probably closeness to coastal area and arid climate is mainly responsible for elevated Cl content in the area. Additionally, it is supported from high ESP in the soil of the study area (Fig. 7D).

4.9 Trace elements

The natural concentration of trace elements in soils is a result of weathering that releases trace elements from their host minerals during soil formation (Kabata-Pendias, 1993). A close relationship between the metal content of the parent material and soils has been observed in a number of studies (Singh & Steinnes, 1994). The mobility, solubility and bioaccumulation of trace elements depend on the properties of the trace elements as well as the quality of soil, pH and other factors. The estimated amount of trace elements in the soil is also depends upon the medium of extraction. It varies for different extractors and noted minimum for simple water (Kabata-Pendias, 2004). For the present study, water extraction was used, which is close to bioavailability for plants. The bioavailability of trace elements in the soil is decisive for agriculture purposes.

The speciation of trace metals ultimately determines their bioavailability and their mobility in the soil (Pelfrêne et al., 2009). A number of trace elements (Cu, Zn, Pb, Fe, Cr, Co, Cd and Ni) are contributed through the weathering of igneous and sedimentary rocks in the study area. In order to assess the role of rock in dispersing the elements, a graph is constructed to illustrate mutual relationship (Fig. 8). It is important to note the concentration trend is quite similar except the level of enrichment. The concentration level of Cu, Zn, Cr & Co is high in the rocks and nearly 1% is transformed in the soils of the study area. Lead and Cd show relatively high proportion in the soil, while Fe and Ni are hardly half percent in the soils of the study area (Fig. 8).
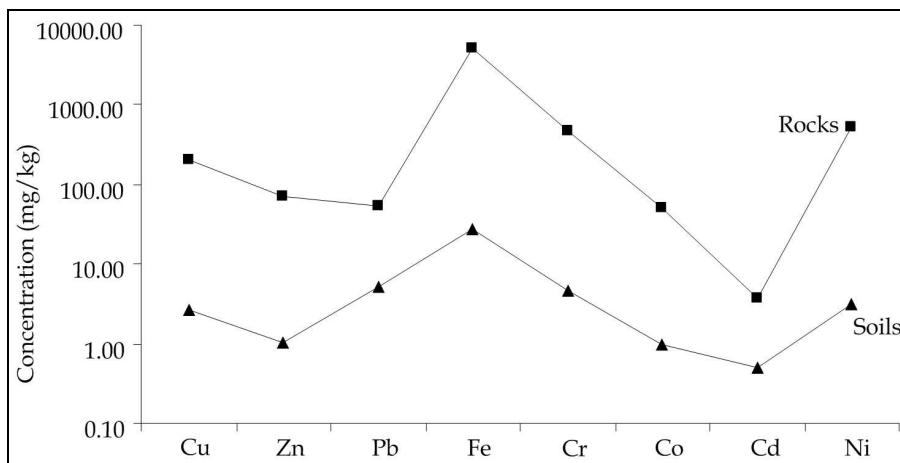
Fig. 8. Average concentration of trace elements in the rocks and the soils of the study area.

The migration of an element from rock to soil or water is termed as its mobility, i.e. the ease with which an element is move from one phase (rock) to other phase (soil). The migration can be assessed numerically from the following expression (Rose et al., 1979), modified for extractable elements of soil.

$$\text{Coefficient of Aqueous Migration } (K) = 100 \times s / t \times r$$

Where s is the concentration of the trace element in the soil (mg/kg); t is total water soluble salts (mg/kg) and r is the concentration of the trace element in the rock (%).

The assessment of trace elements indicates that Fe is immobile, Cu, Zn, Cr, Co and Ni are semi-mobile while Pb and Cd are moderately mobile elements (Fig. 9). The present situation of trace elements abundance in the soil is best demonstrated through the study of K, which is in fact influenced by the climatic condition, distance from the rock and the nature of the element. In the following paragraph, occurrence and distribution of some of the important trace elements of the soils of the study area is discussed to correlate linkage between rocks-soils-plants.

4.9.1 Chromium (Cr)

Chromium is mainly derived from the ultramafic rocks (1600-3400mg/kg), and range in the soil from 1.4-1100 mg/kg (av. 54mg/kg), depending on the soil type and other physicochemical parameters (Kabata-Pendias & Pendias, 1992). Chromium is generally found as two species Cr^{+3} and Cr^{+6} in soils. The former (Cr^{+3}) is common and serve as a micronutrient and a non-hazardous species, much less toxic than Cr^{+6} (Fendorf, 1995). The major part of the absorbed Cr is retained in the roots however it is relatively low in the leaves (5-30 mg/kg). Organic matter reduces Cr^{+6} to Cr^{+3}, which is less bioavailable to plant, because geochemically, Cr^{+3} is inert. The presence of Cr in the soil of the Winder area is best reflection of ophiolitic rocks. Its abundance is measured in the range of 0.07-9.8mg/kg (Table 2). The average value is (4.69mg/kg) beyond the world average (54mg/kg) probably due to sandy soil and organic matter in the study area.
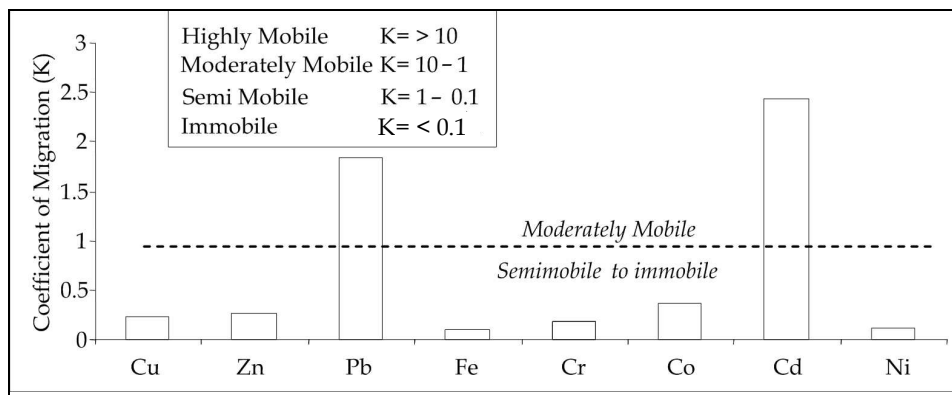
Fig. 9. Coefficient of migration (K) of trace elements calculated from average concentration in the rocks and soils (Categories after Rose et al., 1979).

4.9.2 Nickel (Ni)

Nickel is the most abundant (2000mg/kg) trace element of the ultramafic rocks and decreases in mafic rock (150mg/kg). Primary Ni minerals (Millerite, pentlandite, niccolite etc.) will release Ni^{2+} upon weathering into soil which is stable in the soil. In the study area, Ni is mainly derived from ophiolitic rocks and ranged between 0.52-13.3mg/kg in the soils of Winder area (Table 2). The average is lower than the world median of Ni, which is about 20mg/kg (Alloway, 2005). There is no harm of Ni in the plants through soil in the study area because the average Ni is ~3mg/kg. The present study shows good correlation matrix of Ni with Fe ($r = 0.843$) and Cd ($r = 0.788$), moderate with Zn ($r = 0.578$) and inverse ($r = -0.568$) to Pb (Table 4), reflecting origin of Ni from sulphide phase of Bela Ophiolite. Sometimes recent windblown sediments also contribute substantial amount of Ni-Cr in the soil, as it was noted by Varkouhi et al. (2006) in the neighboring country Iran.

Bioavailability of Ni decreases in alkaline pH. Furthermore, presence of Fe-Mn oxides and high organic matter also lower its availability to plants (National Research Council of Canada [NRCC], 1981). Despite the toxicity, Ni is easily translocated within plants and commonly accumulates in high quantities in leaves, exhibiting chlorosis (Kabata-Pendias & Pendias, 1992).

	Zn	Pb	Fe	Cr	Co	Cd	Ni
Cu	0.314	-0.010	0.455	0.460	0.079	0.471	-0.046
Zn		-0.316	**0.710**	0.152	0.223	**0.67**	**0.578**
Pb			**-0.567**	0.453	0.245	-0.383	**-0.568**
Fe				0.053	0.004	**0.911**	**0.843**
Cr					0.337	0.239	0.163
Co						0.09	-0.118
Cd							**0.788**

Table 4. Correlation matrix of important trace elements of soil of Winder area.

4.9.3 Iron (Fe)

Iron is the common element which may be contributed through both the different segments of ophiolites and sedimentary rocks of the study area. The water soluble Fe is in the range of 0.8-197.6mg/kg (av. 28.05). The mutual relationship among Ni-Fe-Cr in the form of triangular diagram (Fig. 10A) exhibit two separate populations, one is dominated by Cr and other by Fe. Chromium is signature for soils that developed from ultramafic rocks (Garnier et al., 2006), while high Fe is related with either mafic or sedimentary rocks.
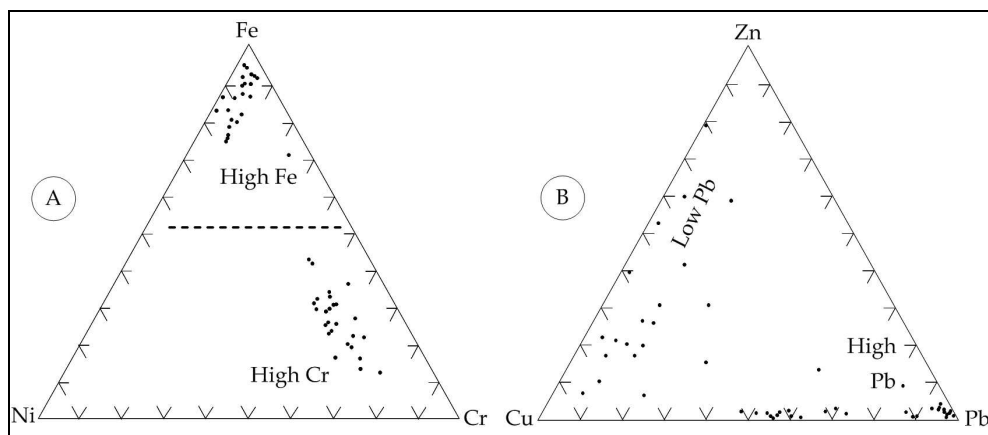
Fig. 10. Mutual relationships among A) Ni-Fe-Cr and B) Cu-Zn-Pb showing two populations of soil samples in the study area.

4.9.4 Copper (Cu)

Copper is found in relatively high levels in mafic rocks (60-120 mg/kg), which are widely exposed as pillow lavas in the study area. In the Winder area, the level of concentration of Cu in the soils is between 0.03-8.8mg/kg. The average (2.66mg/kg) is lower than world average 13-24mg/kg (Yusuf, 2007). In spite of Cu- mineralization in the ophiolitic rocks, the soils of the study area are deficient in Cu. Probably, basic pH and calcareous sandy soil reduces the mobility of Cu (Irha et al., 2009). It is an important biophile element and found as organic complex. This complexing is of great significance in maintaining adequate Cu in solution for plant use. Plants need Cu in small quantities (5-10mg/kg) for photosynthesis, and metabolism. However, Cu >100mg/kg in the soil is lethal for most common plants.

4.9.5 Zinc (Zn)

It is an essential micronutrient, required for the healthy growth of the plants. Zinc helps in chlorophyll formation and promotes formation of acetic acid in the root to prevent decaying. It motivates plant growth and prevents mottling and other disorders in the leaves (Andersen, 2000). The concentration level is 0.03-16.7; av. 1.02mg/kg in the soils of the study area (Table 2). Although, the Zn can be supply both from ophiolite and sedimentary rocks of the area, but the level is much lower than the world average (64mg/kg). Possibly the poor availability in the soil is due to long-time farming in the area.

4.9.6 Lead (Pb)

There are multi sources of Pb in the rocks of the study area, but most commonly it is derived from the ophiolites. Lead is a non essential toxic element for plants. In general, plants do not favor to absorb much Pb from soil and the translocated Pb is accumulated in the leaf. Symptoms of toxicity appear on leaf nearly in the range of 30-300mg/kg (Kabata-Pendias & Pendias, 1992). It varies between 0.08 to 10.55mg/kg in the soils of study area (Table 2). Comparing to the mean abundance in the soil (32mg/kg), the soils of the study area is quite low (av. 5.12). Despite the low abundance, Pb is one of the dominant elements in contrast to Cu and Zn (Fig. 10B). However, Cu-Zn relation in the same diagram display scattered population in which Pb is low. Probably the separate population represents two different sources. Low Pb in the soils is due to low mobility (Irha et al., 2009), especially in the arid climate. It is important to note that Pb has inverse relationship with Fe and Ni, indicating replacement with each other in the soils of Winder area (Table 4). Lead usually occurs in the soil as Pb^{2+}/Pb^{4+} and accumulates in the surface horizons of soils.

4.9.7 Cobalt (Co)

The ultramafic (100-200mg/kg) and mafic rocks (35-50mg/kg) contain elevated amount of Co and these rocks are widely exposed in the study area. The overall range for cobalt in soils on a world-wide basis is 0.1-70mg/kg (Kabata-Pendias & Pendias, 1992) and the average amount is 8mg/kg (Tisdale et al., 1985). In the Winder area soils, it ranges 0.05-2mg/kg (av. 0.97mg/kg). Despite the presence of mafic-ultramafic rocks in the area, it is measured very low. Alkaline and calcareous soil, organic matter and high Fe reduce the mobility of Co.

Biological function of Co is not very clearly understood but it is considered essential for the plants in minor quantities. The low abundance of Co in the soils of the study area possibly does not impart threat of Co in human beings through food.

4.9.8 Cadmium (Cd)

Cadmium is commonly found as sulphide mineral (Greenockite, CdS) in the mafic rock, ranges between 0.13-0.22mg/kg (Kabata-Pendias & Pendias, 1992). The weathering of rock release Cd ions, which are than accumulated in the soil in the range from 0.06-1.1mg/kg. Cadmium is phytotoxic element; it can be absorb through root and can be store in the range of 5-30mg/kg in the leaves at sub-toxic level, but it can accumulate less in the edible parts of the plant (Alloway, 1990).

The range of Cd in the soils of the study area is 0.13-1.8 with an average 0.49mg/kg, which is close to the world average 0.35 (Coskun et al., 2006). The possibilities of potential health hazards of Cd to consumers of fruits grown is minimum because the bioavailability of Cd decreases in the presence of soil carbonates and basic pH (Oluwatosin et al., 2008), as it is common in the study area. The strong correlation matrix with Fe ($r = 0.911$) and Ni ($r = 0.788$) will suggest its origin from ophiolitic rocks (Table 4).

5. Soil mineralogy

The XRD mineralogical studies of the soils of the study area revealed high quartz and calcite along with variable proportions of clay minerals and iron oxides. High quartz is not suspected from basalt country rock, so the large amounts of quartz in the soils of the study area may have contributed from windblown sediments, as indicated by Prone (2003) for the

soils of Thailand. The minor mineral content of the soil is more valuable because they reflect the nature of parental rocks. These include gismondine, albite, orthoclase, anorthite, palygorskite, hercynite and rutile. Descriptions of uncommon soil minerals such as gismondine, palygorskite, chlorite-serpentine and hercynite are given below:

Gismondine is a low temperature zeolite formed by the alteration of Ca-bearing (anorthite) basaltic rocks. It is a low-silica zeolite, associated with nepheline and olivine basalt and leucite tephrite (Dyer et al., 2006; Katsuki et al., 2008). Zeolites have large vacant spaces or cages in their structures that allow space for large cations such as Na, K, Ca and Ba. The alumino-silicate structure is negatively charged and attracts the positive cations and hence the members of zeolite are capable to hold many trace elements in high quantities. It is a hydrated calcium aluminosilicate with the formula $Ca_2Al_4Si_4O_{16}\ 9H_2O$.

Palygorskite is a crystalline hydrated magnesium phyllosilicate $(MgAl)_2Si_4O_{10}4H_2O)$ with a fibrous habit. Its structure and absorbed cations provide it with a large specific surface area and moderate cation exchange capacity, which is very beneficial for the adsorption of heavy metals from solution (Frini-Srasra & Srasra, 2010). There are two sources of palygorskite in the soil. It is an alteration product of magnesium silicates and on the other hand it is also derived from the soil of arid regions and reported from Cretaceous-Tertiary sedimentary rocks (Daoudi, 2004). Despite the presence of both sources, the occurrence of palygorskite in the soils of the study area is less. The associated minerals in the soil indicate an igneous source.

Hercynite $(FeAl_2O_4)$ is a member of the spinel group, commonly associated with ophiolite and other high grade metamorphic minerals like chromite, magnetite, ilmenite, sillimanite and andalusite (Guiraud et al., 1996). It is only reported from one locality and strengthens the idea that the soils of Winder area have influence of Bela Ophiolite.

6. Conclusion

The trace elements geochemistry of the soils of the Winder area shows relevance mainly with Bela Ophiolite of Cretaceous age along with sedimentary rocks of Mor and Pab ranges belong to Cretaceous and Tertiary ages. The Cr, Ni, Cu, Co and Cd in the soil are mainly supplied by ophiolitic rocks while high Fe and Zn can be contributed both from ophiolite and sedimentary rocks of the area. The average values of these elements are lower than world average probably due to basic pH, calcareous sandy soil and organic matter in the study area. The XRD mineralogy revealed high quartz and calcite along with variable proportions of clay minerals and iron oxides. Gismondine, albite, orthoclase, anorthite, palygorskite, hercynite, chlorite-serpentine and rutile are as minor minerals, confirming their alliance with the rocks of Bela Ophiolite.

Texturally, Entisols types of soil with some Aridisols are common. The soils on the sand-silt-clay ternary diagram are classified as sandy loam, sand and silt loam reflects the mixture of sand and loam in the study area which is suitable for agriculture. The average water content (WC) of the soils is 31%. The soil organic matter (SOM) ranged between 0.35-12% with an average of 2%; relatively high in cultivated areas and low in the rocky and wind-blown soil. The assessed Ca/Mg ratio is low while Ca/K and Mg/K ratios are ideal near farm areas while on either side these ratios vary from low to high due to rock exposures, sandy soil, poor chemical weathering and continuous crop production since long time. The distribution of ESP in the study area illustrates high values close to Arabian Sea; however, the farm areas are safe except few high concentration zones. The chloride concentration is much higher than world average while SO_4-S is low. Trace elements demonstrate Fe>Pb>Cr>Ni>Cu>Zn>Co>Cd

abundance trend in the soil of the study area. The concentration level of these trace elements is low in contrast to world average, thus there is little harm suspected from the toxic trace element in the area.

The study of major and trace element geochemistry of an agriculture soil, located close to rocks exposure, is recommended for the proper management of nutrients and micronutrients as this will not only enhance the productivity and quality of the crops but also mitigate an environmental threat to humans through the food chain.

7. References

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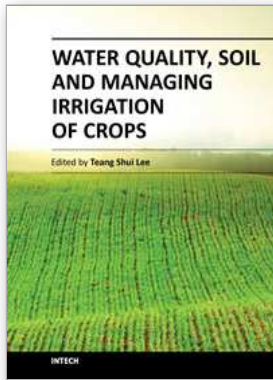
Water Quality, Soil and Managing Irrigation of Crops
Edited by Dr. Teang Shui Lee

The book entitled Water Quality, Soil and Managing Irrigation of Crops comprises three sections, specifically: Reuse Water Quality, Soil and Pollution which comprises five technical chapters, Managing Irrigation of Crops with four, and Examples of Irrigation Systems three technical chapters, all presented by the respective authors in their own fields of expertise. This text should be of interest to those who are interested in the safe reuse of water for irrigation purposes in terms of effluent quality and quality of urban drainage basins, as well as to those who are involved with research into the problems of soils in relation to pollution and health, infiltration and effects of irrigation and managing irrigation systems including basin type of irrigation, as well as the subsurface method of irrigation. The many examples are indeed a semblance of real world irrigation practices of general interest to practitioners, more so when the venues of these projects illustrated cover a fair range of climate environments.

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