MAJOR ELEMENTS CONCENTRATIONS IN CALCAREOUS SOILS

Shahida Nasreen Zakir*, Samina Siddiqui**, Nasreen Ghaffar*

ABSTRACT

Major elements status in soils derived from alluvium, piedmont and loess parent materials remained in scarcity. This study was conducted to evaluate the major elements concentrations in soils derived from various parent materials and then to classify such soils in calcareous, moderate and non-calcareous soils. Soils were analyzed for total content of Al, Ca, Fe, K, Mg, Na, P, Si and Ti with Atomic Absorption Spectrophotometery and UV-VIS Spectormetry. Total Ca content in loess soils is 12% thus categorized in calcareous soils whereas alluvium and piedmont alluvium soils with Ca content ranged from 0.9 to 5.2% hence are classified into moderate and non-calcareous. There was an inverse relationship between Ca and P concentrations in calcareous soils. Calcium content is around 12% whereas P content is 0.000012% in calcareous soils of this study. The low content of P than Ca in calcareous soils of this study revealed the contention that P is bound with Ca hence is unavailable to plants. Calcareous soil has more than 15% of CaCO3 at pH ranged from 7.5 to 8.4. Iron was also found to be low in calcareous soils. Such soils are required an improved nutrient management in such a manner that soil contact of P, K and Fe can be minimized.

KEYWORDS: *Loess, Alluvium, Piedmont, Calcareous, Major elements*

INTRODUCTION

Major elements distribution in soils primarily depends on the parent material from which soil is derived. When parent material is calcite, soils are high in Calcium (Ca) naturally. Such soils usually contain $CaCO_3$ more than 15% and are known as calcareous soils whereas soils contain less than 1% of Ca are classified as non-calcareous soils[1]. Calcium carbonate are highly soluble at alkaline pH thus such soils have nearly 100% base saturation. Calcite or limestone is not the only natural source from which calcareous soils are derived but other surficial sources such as glacial tills, Aeolian and glaciolacustrine are also contributing significantly for calcareous soils[2]. Calcareous soils are usually found in semiarid and arid regions of the world[3]. Calcareous soils with pH 7.0-8.5 decreases the availability of nitrogen, potassium and magnesium[4]. Potassium forms insoluble compounds in calcareous soils and is unavailable to plants. Potassium deficiency was commonly observed in calcareous soils at pH greater than 7.5[5]. Calcareous soils are usually deficient in available K and P for plant growth and appropriate nutritional management is required for these soils[6]. Phosphorus content in soils ranged from 2.1 to 4.0 mg per kg and potassium was from 81 to 120 mg per kg of calcareous soils of Pakistan[7]. Phosphate rock is used to prepare phosphate fertilizer. When P is added to the calcareous soil in the form of a phosphate fertilizer, a significant proportion is adsorbed with Ca and forms di-calcium phosphate in calcareous soils[8]. The P deficiency in calcareous soils is commonly observed throughout the world. Appropriate nutrient management is required for calcareous soils. Like P, Fe deficiency is commonly observed in calcareous soils because under alkaline condition Fe is oxidized to ferric ion which is insoluble hence become unavailable to plants[9]. Contrary to that in acidic soils phosphate fixation as $FePO_4$ and $AlPO_4$ is usually occur due to precipitation[10]. Lime induce Fe chlorsis is commonly observed in calcareous soils[11].

The nutrient management in calcareous soils remained a problem more likely because of high solubility of nitrogen, phosphorus, magnesium, potassium, manganese, zinc, copper and iron in such soils[12]. Hence their availability reduces in such soils. Therefore when mineral fertilizer such as nitrogen or phosphorus is applied with irrigation as ammonium-N, urea or diammonium phosphate to avoid contact of such elements with soil. Apart from mineral fertilizer crop tolerance to calcareousness must be used to minimize the Fe deficiency. However the later improved management with tolerant species is very expensive more likely because of increased quantity of K and Mg fertilizer is required for such soils.

Macronutrient availability to plants cannot be directly assessed from their total content. However, total content can provide background information about their levels in the soils.

* *Department of Environmental Sciences, University of Peshawar, Pakistan*
** *Center of Excellence in Geology University of Peshawar, Pakistan*

Total content of major elements in calcareous soils is usually used to provide information about the nutritional status of calcareous soils. Calcium content can be used as a reference element and the content of all other elements was compared with their value in world reported value of calcareous soils. Calcareous soils are classified into deficient, marginal or sufficient in major elements by comparing the mean of major elements with the world reported value for calcareous soils.

METHOD AND MATERIALS

Soil samples were collected randomly from 0-15cm and 15-30cm from 32 sites within Peshawar Basin. Soils are well drained and used for cultivation of sugarcane, wheat, maize and seasonal vegetables.

Soil sample collection and analysis

Surface litter was removed with a spade and soil samples were collected up to a depth of 0-15 cm and 15-30 cm. Representative soil samples were brought to the laboratory and composite samples were broken down and mixed thoroughly by hand. The soils were partially dried just to allow sieving through 2 mm mesh size.

The soil samples were analyzed for organic matter content, pH and EC[13].

Major elements extraction

For determination of Ca, Fe, K, Mg, Mn, Na, P, Ti triplicate subsamples of oven dried soil (0.5g) were removed from bulk soil samples and were transferred to 120 mL Teflon vessel. About 10 mL of HF and 4 mL of $HClO_4$ were added in the Teflon vessel were placed on a hot plate for 90 min. Samples were allowed to cool at 22^{o}C and 2 mL of $HClO_4$ was added to Teflon vessel for re-digestion and were placed on hot plate for further 30min. Thereafter, 4 mL of $HClO_4$ was added into the vessel which was placed on the hotplate for further dryness. The aliquots were diluted with 250 mL distilled water and were filtered with Whatmann No 2 and were transferred to plastic bottles before analyzing it by Atomic Absorption Sepctrophotomer. In order to determine the concentration of Ca and Mg in the soils, 2 mL of aliquots was taken from the digested samples and 3 mL of La_2O_3 was added and was diluted with 25 mL of distilled water. The samples were taken in the 30 mL plastic bottles and were placed in the laboratory for further analysis.

Total phosphorus in soil was determined by using simple Kjeldahl digestion as described by Taylor[14].

RESULTS AND DISCUSSION

Physicochemical characteristics

Table 1 shows the physiochemical parameters of alluvium, piedmont and loess soils. The pH ranged from 7.5 to 7.9 in alluvium and piedmont alluvium soils and 7.6 to 8.5 in loess soils. The organic matter content remained the same in all soils and was less than 0.5% in any of the soils. The alluvium soil is sandy loam, piedmont is silty clay loam and loess soils are silty loam soil.

Table 2 shows the mean percentage of major elements in alluvium, piedmont alluvium and loess soils. In alluvium soil Al, Na, and Ti contents are high than piedmont alluvium and loess soil. In piedmont alluvium K, P, and Si are more than both soils, while Ca, and Mg are more in loess soil. The Fe concentration remain the same for piedmont alluvium and loess soil.

Table 3 represents the total Ca content in loess soils is 12% thus categorized in calcareous soils whereas piedmont alluvium and alluvium soils with Ca content ranged from 5.2 to 0.9% hence are classified into moderate and non-calcareous.

Table 4 represents the distribution of major elements in horizons (A and B) of alluvium, piedmont and loess soil profile. The Al, Ca, Mg and Na contents were greater in both horizons of loess profile than alluvium and piedmont soil profiles. Iron and Ti content remained similar in both horizons of all soil profiles. Potassium (K) and phosphorus (P) content were low in loess soils than alluvium and piedmont soils. Silica (Si) and Titanium (Ti) also remained same in both horizons of all soil profiles but was significantly different in the both horizons of piedmont alluvium soil profile than A and B horizons of alluvium and loess soil profiles.

Seasonal variations in the distribution of major elements in alluvium, piedmont alluvium and loess soils within Peshawar Basin is presented in Tables 5a to c. There was no significant difference in the mean content of any of the major elements in all three soils in both seasons during 2003 and 2004. Nevertheless there is a trend that greater content of all major elements in any of the soil was noted in summer than winter of both seasons (because of evaporation than leaching). The contents of all elements apart from Al in all soils increased downwards in winter than summer of both years (More leaching than evaporation). Contrary to that the content of all major elements decreased downwards during summer than winter of both years. However, Si and Ti content remained same during summer and winter of both years.

DISCUSSION

Peshawar soils are derived from alluvium, piedmont alluvium and loess parent materials. Total Ca content in loess soils is 12% thus categorized in calcareous soils whereas piedmont alluvium and alluvium soils with Ca content ranged from 5.2 to 0.9% hence are classified into moderate and non-calcareous. This suggests that most of the calcareous soils of this study are derived from calcite rocks. Calcareous soils with high Ca content may reduce the availability of some essential nutrients such as K and P to plants[15]. This is more likely because Ca is replaced by P through precipitation processes and forms insoluble phosphate. The latter phenomena can be estimated from the total concentrations of Ca and P in calcareous soils. The results of this study revealed that there was an inverse relationship between Ca and P concentrations in calcareous soils. Calcium content is around 12% whereas P content is 0.004% in calcareous soils of this study. The low content of P than Ca in calcareous soils of this study revealed the contention that P is bound with Ca hence is unavailable to plants (Also the) Ca content increases because of formation of ocacalcium phosphate (OCP). Rahmatullah et al.[16] reported that total P content in calcareous soils ranged from 92.5 to 862.5 mg-kg^{-1}. They found that most of the P is bound to Ca in calcareous soils. In another study Wang et al.[17] and Rehimi et al.[18] reported that Ca bound P content in calcareous soils ranged from 3.7-20.6 and 8 mg-kg^{-1}. When Ca is freely available in alkaline

Table 1: Physiochemical characteristics of alluvium, piedmont alluvium and loess soils of Peshawar district.

Soils	pH$_{H_2O}$	Organic matter (%)	Texture
Alluvium	7.5-7.9	0.41	Sandy loam
Piedmont alluvium	7.5-7.9	0.45	Silty clay loam
Loess	7.6-8.5	0.42	Silty loam

Table 2: Major elements (%) in the alluvium, piedmont alluvium and loess soils within Peshawar Basin.

Soils	Elements (%)								
	Al	Ca	Fe	K	Mg	Na	P	Si	Ti
Alluvium	11.55	0.9	3.10	1.6	0.9	1.39	1.2	22.2	0.46
Piedmont alluvium	9.30	5.20	3.3	1.86	1.12	1.34	0.5	24.4	0.43
Loess	8.37	12	3.3	1.6	1.5	1.21	0.04	22.6	0.40

* Means followed by different letters within rows are significantly different at the 5% level of probability.

Table 3: Classification of soils in calcareous, moderate and non-calcareous soils according to Ca content in the soils[6].

Soils	Ca Content (%)	Classification
Loess	12	Calcareous soils >10%
Piedmont	5.20	Moderate calcareous soils
Alluvium	0.9	Non calcareous soils

Table 4: The major elements distribution in the A and B horizons of alluvium, piedmont and loess soils of Peshawar Basin.

Soils	Alluvium		Piedmont alluvium		Loess	
Horizons	A	B	A	B	A	B
Elements %						
Al	13	10	9.1	9.4	8.4	8.46
Ca	0.70	1.1	4.25	6.20	11.0	13.50
Fe	3.02	3.10	3.0	3.56	3.02	3.82
K	1.32	2.0	1.94	1.78	1.56	1.61
Mg	0.93	0.84	1.11	1.01	1.50	1.42
Na	1.38	1.39	1.34	1.19	1.22	1.11
P	1.0	1.4	0.4	0.6	0.03	0.05
Si	22.0	22.8	23.8	24.4	22.3	22.6
Ti	0.44	0.48	0.40	0.46	0.38	0.42

* Means followed by different letters within rows are significantly different at the 5% level of probability.

Table 5 a: The seasonal variations in the distribution of mean contents of major elements of alluvium soils Peshawar Basin.

Seasons	Winter 2003	Winter 2003	Winter 2004	Winter 2004	Summer 2003	Summer 2003	Summer 2004	Summer 2004
Horizons	A	B	A	B	A	B	A	B
Al	12.5 (1.2)*	13.6 (2)	12.1 (2)*	14.6 (2.5)	9.5 (1.1)	10.5 (1.2)	9.5 (1.1)	10.5 (1.2)
Ca	0.65 (0.05)	0.75 (0.04)	0.55 (0.15)	0.85 (0.14)	0.9 (0.05)	1.3 (0.06)	0.9 (0.05)	1.3 (0.06)
Fe	2.9(0.3)	3.3(0.4)	1.9 (0.25)	4.6 (0.35)	2.8 (0.3)	3.4 (0.5)	2.8 (0.3)	3.4 (0.5)
K	1.4(0.2)	1.6(0.3)	1.0 (0.22)	2 (0.13)	1.5 (0.05)	1.7 (0.04)	1.5 (0.05)	1.7 (0.04)
Mg	0.86(0.05)	1.0(0.04)	0.66 (0.03)	1.2 (0.02)	0.7 (0.05)	0.9 (0.06)	0.7 (0.05)	0.9 (0.06)
Na	1.38(0.4)	1.37(0.2)	1.1 (0.23)	1.45 (0.22)	1.38 (0.4)	1.39 (0.3)	1.38 (0.4)	1.39 (0.3)
P	1.2 (0.05)	1.0 (0.03)	1.1 (0.02)	1.3 (0.01)	1.2 (0.01)	1.2 (0.01)	1.1 (0.01)	1.3 (0.005)
Si	21.0 (1.5)	23.0 (1.4)	22.5 (3.2)	23.0 (4.1)	22.0 (2.4)	23.6 (2.6)	22.0 (2.4)	23.6 (2.6)
Ti	0.40 (0.05)	0.48 (0.03)	0.44 (0.02)	0.44 (0.01)	0.40(0.03)	0.56(0.05)	0.40(0.03)	0.56(0.05)

* Means in paranthesis represent standard errors.

calcareous soils, Na content increases. This is in agreement with the findings of this study that increase in Ca content increases the soil pH hence indirectly increases the Na content and soils are converted into saline soils. The latter soils are unsuitable for growing crops. In addition to that in sandy soils where leaching is more than adsorption and most of the Na is leached down, during flooding salts were brought to the soil surface and causes surface salinity[15].

Iron deficiency in calcareous soils is wide spread most probably because of lime induce iron chlorois[19]. Iron deficiency in calcareous soils with greater content of Ca and P is observed. However, K deficiency is commonly

Table 5 b: The seasonal variations in the distribution of mean contents of major elements of piedmont alluvium soils of Peshawar district.

Seasons	**Winter 2003**	**Winter 2003**	**Summer 2003**	**Summer 2003**	**Winter 2004**	**Winter 2004**	**Summer 2004**	**Summer 2004**
Horizons	A	B	A	B	A	B	A	B
Elements								
Al	8.0 (1.0)*	10.6 (1.2)	9.2 (0.8)	9.6 (0.6)	8.6 (0.5)	10.0 (1.0)	9.3 (0.52)	9.3 (0.62)
Ca	4.8 (0.8)	5.5 (0.5)	6.0 (0.5)	4.2 (0.2)	4.9 (0.2)	5.5 (0.3)	6.2 (0.6)	4.0 (0.5)
Fe	2.8(0.2)	3.4(0.3)	2.0 (0.2)	4.7 (0.3)	2.9 (0.5)	3.5 (0.6)	3.0 (0.5)	3.6 (0.6)
K	1.8(0.2)	1.92(0.3)	1.9 (0.22)	1.66 (0.13)	1.86 (0.05)	2.4 (0.04)	1.9 (0.05)	2.8 (0.04)
Mg	1.12(0.3)	1.32(0.2)	1.34 (0.03)	1.0 (0.02)	1.12 (0.05)	1.44 (0.06)	0.88 (0.05)	1.64 (0.06)
Na	1.37(0.4)	1.37(0.2)	1.0 (0.23)	1.55 (0.22)	1.48 (0.4)	1.49 (0.3)	1.48 (0.4)	1.49 (0.3)
P	0.4 (0.01)	0.6 (0.01)	0.6(0.01)	0.4(0.01)	0.5(0.01)	0.5(0.01)	0.4(0.01)	0.6(0.01)
Si	24.0 (1.4)	24.4 (1.5)	26.0 (2.2)	28.0 (3.1)	24.0 (1.4)	28.8 (1.6)	26.0 (1.4)	28.8 (1.6)
Ti	0.40 (0.05)	0.46 (0.03)	0.47 (0.02)	0.46 (0.01)	0.42(0.03)	0.58(0.05)	0.42(0.03)	0.58(0.05)

*Means in paranthesis represent standard errors.

Table 5 c: The seasonal variations in the distribution of mean contents of major elements of loess soils of Peshawar Basin.

Seasons	**Winter 2003**	**Winter 2003**	**Summer 2003**	**Summer 2003**	**Winter 2004**	**Winter 2004**	**Summer 2004**	**Summer 2004**
Horizons	A	B	A	B	A	B	A	B
Elements								
Al	8.37 (1.0)*	8.74 (1.2)	9.2 (0.8)	8.4 (0.6)	8.6 (0.5)	9.2 (1.0)	8.8 (0.52)	8.0 (0.62)
Ca	14 (1.0)	10 (1.3)	12 (1.2)	14 (2)	12 (1.6)	14 (1.8)	12 (1.2)	14 (1.3)
Fe	3.0(0.5)	3.6(0.3)	2.2 (0.2)	4.4 (0.5)	2.8 (0.6)	3.3 (0.5)	3.0 (0.4)	3.6 (0.4)
K	1.6(0.2)	1.6(0.3)	1.8 (0.22)	1.66 (0.13)	1.66 (0.05)	2.6 (0.04)	2.0 (0.05)	3.2 (0.04)
Mg	1.5(0.3)	2.0(0.2)	1.34 (0.03)	1.0 (0.02)	1.12 (0.05)	1.44 (0.06)	0.88 (0.05)	1.64 (0.06)
P	0.0038 (0.0001)	0.0042 (0.0001)	0.0038 (0.0001)	0.0042 (0.0001)	0.0035 (0.0001)	0.0047 (0.0001)	0.0042 (0.0001)	0.0044 (0.0001)
Na	1.37(0.4)	1.37(0.2)	1.0 (0.23)	1.55 (0.22)	1.48 (0.4)	1.49 (0.3)	1.48 (0.4)	1.49 (0.3)
Si	26.0 (1.4)	20.0 (1.5)	24.0 (2.2)	28.0 (3.1)	22.0 (1.4)	23.6 (1.6)	24.6 (1.4)	19.2 (1.6)
Ti	0.41 (0.05)	0.45 (0.03)	0.38 (0.02)	0.42 (0.01)	0.42(0.03)	0.38(0.05)	0.32(0.03)	0.48(0.05)

*Means in paranthesis represent standard errors.

reported in Fe deficient calcareous soils[20]. The range of total Fe content in calcareous soils of this study is within the reported value for calcareous soils in India (4000-273000 mg-kg^{-1})[21]. Olomu et al.[19] reported that Fe content was 18 mg-kg^{-1} in calcareous soil.

High Fe content in soils causes Mn deficiency in soils. Although Mn deficiency is not widespread in alkaline soils but commonly observed in sandy soils with high leaching capacity, calcareous soils, clay with greater content of montmorillonite and waterlogged soils.

Manganese deficiency in soils cannot be estimated from total concentrations but it is reported that Mn content less than 20 mg-kg^{-1} causes Mn deficiency in soils. Manganese average content in the calcareous soils of this study is up to 1000 mg-kg^{-1}. Manganese content in calcareous soils ranged from 2 to 11500 mg-kg^{-1}.

Unlike P and K, Al and Si are stable elements and an important constituent of clay mineral. Calcareous soils sandy in texture having low content of Al. However the calcareous soils of this study were silty loam in texture and were low in Al than any of the other soils (Table 1). Aluminum and Silica (Si) content was 8 and 24% in all soils whereas in calcareous soils of this study Al was ranged from 8.4% whereas Si was up to 22% (Table 2). Both Al and Si remained within the average concentration of such elements in soil.

The distribution of all major elements in relation to depth in both soils remained same except for a few exceptions.

Major elements distribution in winter and summer over a period of two years revealed the contention that greater content of all major elements except for Si and Ti in summer than winter. This is more likely because of evaporation than leaching.

CONCLUSIONS

Calcareous soils are dominant in the study area and were found to be enriched in Ca and Mg, Sodium (Na) content was also greater in such soils. Nonetheless, Al and Si content remained same in such soils. Phosphorus was found to be deficient in calcareous soils than non-calcareous soils of this study. The distribution of all major elements in relation to depth in both soils remained same except for a few exceptions. Calcareous soils required appropriate nutrient management including appropriate dozes of mineral fertilizers.

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