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Evaluation of Physico-Chemical Characteristics of Soil Samples Collected from Harrapa-Sahiwal (Pakistan)

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The soil of different sites of the Harappa museum situated at Sahiwal district was collected and investigated for pH, electrical conductivity, organic matter, micronutrients and macronutrients. The soil is saline sodic. pH was found to be in the range of 7.62-8.27 which is slightly neutral to basic. Electrical conductivity was in the range 8.9-12.0 mS/cm while percentage of organic matter was 0.276-1.035. The elements like Na, K, Ca, Mg, Zn, Ni, Cu, Mn, Mo, Se, B, P, N, S, Cl were found in the range, Na (1035-9050 mg/kg), K (3050-6000 mg/kg), Ca (153-260 mg/kg), Mg (259-689 mg/kg), Zn (31-85 mg/kg), Ni (7.3-17.8 mg/kg), Cu (70-91 mg/kg), Mn (3.1-20.3 mg/kg), Mo (16.1-24.4 mg/kg), Se (0.01-0.062 mg/kg), B (6.7-16.6 mg/kg), P (164-696 mg/kg), N (5.76-13.38 mg/kg), S (62-281.3 mg/kg), Cl (102.3-200 mg/kg), respectively. The overall contents of the above parameters were found to be above permissible limits. The main purpose of the study is to report physico-chemical composition of soil of archaeological interest and to provide guidelines for the restoration and rehabilitation of vegetation.

Key Words: Soil, Metal ions, Permissible limits, Sahiwal, Pakistan.

INTRODUCTION

Soil is the unconsolidated mineral on the surface of the earth that serves as a natural medium for the growth of plants. It is formed from rocks by physical, chemical and biological weathering[1]. Soil consists of various constituents such as minerals, organic matter, water and air[2-4]. An average soil is 45 % mineral, 25 % water, 25 % air and 5 % organic matter[5]. Soil is the basic medium providing majority of food items to the living organisms but its degradation has become a major global concern for the last few years as a result of increasing demands of land for food production.

In Pakistan 90 % soils are deficient in nitrogen and phosphorous, whereas, 50 % soils have insufficient potash in addition to micronutrients[6,7]. The previous studies show that as a result of increase in salt concentration and pH of the soil due to

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evapotranspiration, a part of calcium, magnesium from soil solution precipitates as $CaSO_4$, $MgSO_4$ and magnesium silicate[8,9]. The presence of such salts serves as the parent material for saline and saline sodic soil formation[10].

Harappa is the one of the ancient city of Pakistan, about 35 km (22 miles) southeast of Sahiwal district. The precise location of Harappa site is 30º latitude and 72º longitude. The ancient city (Harappa) existed from about 3300 BCE until 1600 BCE and is believed to had as many as 40,000 residents-considered large for its time. The city is found to be very modern with respect to its living style and constructions[11]. The climate of the area is mainly arid and dry semi-arid of sub-tropical continental type with mean annual rain fall in the month July to September. The remaining one third rainfalls is received in winter during months of December to February as mild showers. The maximum temperature in extreme winter is 74.5 ºF and minimum is 35 ºF while maximum and minimum temperature in hot summer is 107.2 and 73.5 ºF, respectively. Trespassing, grazing and cutting of trees for fuel wood are the anthropogenic activities causing disturbance not only to the archaeological remains but also to the thriving thorn forest community in this area. Sharif[12] reported restoration and conservation of indigenous vegetation at Harappa. As many disturbance factors particularly anthropogenic activities such as over grazing and fuel-wood gathering are extremely affecting the remnants of indigenous vegetation so it was necessary to protect the vegetation from these hazards by replacement of indigenous soil with imported one. For this purpose an attempt has been made to analyze the soil samples collected from Harappa museum under the control of Archaeological department to report and provide guidelines for the suitability and physico-chemical composition of soil for the restoration and rehabilitation of vegetation in this particular area.

EXPERIMENTAL

During the studies eight soil samples at the depth of 0-15 cm were collected from different sites surrounding the Harappa museum situated at sahiwal district. The samples were analyzed for different cations and anions like Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Mo, PO_4^{2-}, SO_4^{2-}, Cl^-, B, Se using different laboratory methods[13,14]. The soil samples were also analyzed for pH, EC and % organic matter.

All the reagents and chemicals used were of AR grade procured from E. Marck, BDH and Radiel-de-Hein. All the solutions of standards and samples were prepared in freshly prepared deionized water.

Sample preparation: Soil samples were dried in electric oven, ground, homogenized separately and passed through 0.5 mm mesh sieve. 10 g of soil was taken in a 250 mL round bottom flask along with 30 mL of aqua-regia and refluxed for 0.5 h, cooled and then filtered through Whattman No. 42 filter paper by using suction pump. The filtrate was then diluted upto 100 mL with deionized water[14].

Determination of pH and EC: A saturated paste of 2 mm sieved soil was prepared by adding 150 g of soil sample in 500 mL capacity beaker using deionized water[15-17]. Then the paste of soil samples was introduced to HANNA 211 microprocessor pH meter and Cyber scan 500 conductometrer.

Determination of % organic matter: The organic matter in each soil sample was determined by the method approved by soil survey of Pakistan. 1 g of soil sample was taken in the titration flask along with 10 mL of 1 N potassium dichromate and 20 mL of sulfuric acid (98.5 %), the mixture was allowed to stand for 1 h, then added 150-200 mL deionized water, 10 mL of orthophosphorus acid and 10-20 drops of barium diphenylamine sulphonate as indicator and finally titrated against 0.2 N ammonium ferrous sulphate until a sharp green end point[15]. The % organic matter was calculated by using the following formula.

$$\text{Organic matter (\%)} = \frac{(\text{mL of for reagent B for blank} - \text{mL of reagent B for sample}) \times \text{N}}{\text{wt : (g) of soil sample}} \times 100$$

where B = 0.2 N ammonium ferrous sulphate.

Determination of metals: Sodium and potassium were determined by flame emission spectrophotometer JENWAY PFP 7 and all the other metals were determined by atomic absorption spectrophotometer PerkinElmer Analyst 200.

Determination of non-metals: Phosphates were determined by colorimetric method using 'ammonium dihydrogen phosphate' as standard solution and "molybdate" was complexing agent. Chloride ions were determined by $AgNO_3$ titration (argentomentric titration). Sulphate ions were estimated gravimetrically using $BaSO_4$ precipitates[16]. Boron was estimated by using colorimetric method in which quinalizarin forms blue colored complex with boron in acidic medium.

RESULTS AND DISCUSSION

pH is an important property of soil that determines the acidity or alkalinity, which effects the chemical reactions between water and soil minerals[18]. pH of all the soil samples was found within the permissible limits (Table-1). There is a strong relationship between soil pH and nutrient availability. Alkaline soils with pH ranging 7-8 are generally deficient in Zn^{2+}, Fe^{3+}, P^{5+} and also uptake of various plant nutrients is pH dependent[19]. Most of the primary nutrients like nitrogen, phosphorous, potassium and secondary nutrients like calcium, magnesium and sulfur are best utilized by the plants when the pH rang is 5.5-7.9. The uptake of most of the micronutrients also take place at low pH[20]. In Pakistan the soils have generally pH above 8[21]. At pH 5.5, fungi and algae generally dominate the soils where at higher pH levels the bacteria are predominates[22].

The electrical conductivity (EC) which may create salinity problem over a long period of time was found in the range of 8.42-12.0 mS/cm whereas the permissible limit is 4 mS/cm (Table-1)[23].

More than 1 % organic matter was found in sample No. 6 and 8, whereas only 25 % samples were found within the permissible limits (Table-1). Such a low concentration of organic matter may also be responsible for the infertility of soil. Walkly[24] studied and interpreted the result of percentage organic carbon as follow.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF SOIL SAMPLES COLLECTED FROM HARAPPA

Sample No	pH	EC (mS/cm)	Organic matter (%)	mg/kg		
				P	S	Cl
1	7.95	8.9	0.414	28.3	425.0	125.0
2	7.93	10.4	0.276	11.3	1445.0	170.2
3	8.27	9.5	0.414	22.5	1460.0	150.0
4	8.13	10.3	0.483	14.4	1096.0	110.0
5	8.14	8.4	0.345	34.8	960.0	107.5
6	7.62	11.0	1.520	18.4	713.0	102.3
7	7.97	9.8	0.345	20.6	620.0	200.0
8	7.90	12.0	1.035	8.2	312.0	197.0
Mean	7.98	10.0	0.604	19.8	878.8	145.2

Very low	> low	> medium	> medium high	> high
0.20	0.21-0.40	0.41-0.60	0.61-0.80	0.80

So according to above standards the soils of Harappa museum site is found to be placed in the class of medium as an average.

Chloride: Chloride is essential in water balance, osmotic pressure regulation as well as in acid base equilibrium. Mostly it may be required for cell division in leaves and roots. The concentration of chloride in soil samples was found to be in the range of 102.3-200 ppm with the average value of 145.2 ppm (Table-1).

Sulphur: Sulphur is an essential component of vitamins, biotin and co-enzyme. The concentration of sulphur was found to be in the range of 312-1460 ppm with the average value of 878.8 ppm (Table-1). Table-1 clearly shows that the concentration of S is highest among P, Cl and S.

Phosphorous: Phosphorous as phosphate, is an integral component of a number of important compounds present in plant cells. It acts as limiting element in soil and is observed primarily as mono-valent phosphate anion -H_2PO_4. The ability of these two forms of ions is controlled by soil pH *i.e.*, monovalent is favored by pH below 7 and divalent form by pH above 7. Phosphorous remains as free phosphate or bound to organic compounds as esters in plants[13]. The phosphorous, as phosphate, in the soil samples was found in the range of 8.2-34.8 ppm with an average value of 19.8 ppm (Table-1).

Sodium: The average contents of sodium in soil samples collected in present study was found to be 186.37 ppm and ranged from 53-340 ppm. The sodium concentration (1550-2300) ppm in soil is known to cause the detrimental effects on the growth of most crop plants[19]. Physiologically sodium helps osmo-regulations, heat expansion and may act as potassium constituent.

However, high sodium concentration causes 'ionic toxicity' and imbalance in the Na^+/K^+, Na^+/Ca^{2+}, Na^+/Mg^{2+} and may cause salt injury to crops[19]. Table-2 shows that the concentration of sodium is highest among observed alkali and alkaline earth metals.

TABLE-2
CONCENTRATION OF METALS (mg/kg) IN THE SOILS SAMPLES COLLECTED FROM HARAPPA

S. No.	Na	K	Ca	Mg	Ni	Cu	Mn	Zn	Mo	Se	B
1	7500	4560.0	225.0	689.0	15.0	70.0	20.3	60.0	20.3	0.058	9.8
2	1035	3500.0	260.0	473.0	12.1	79.0	11.7	10.0	22.4	0.021	7.4
3	7650	3865.0	195.0	612.0	14.3	80.0	8.9	46.0	18.2	0.043	6.7
4	1150	5125.0	160.0	496.0	10.4	78.0	7.3	36.5	16.1	0.053	16.6
5	7500	5415.0	179.0	630.0	9.8	85.4	16.8	85.0	24.4	0.062	12.9
6	9000	6000.0	213.0	640.0	16.6	89.0	3.1	15.0	21.5	0.025	14.8
7	1700	5415.0	153.0	259.0	17.8	90.0	11.9	31.0	19.2	0.060	9.6
8	9050	5415.0	218.0	645.0	7.3	91.0	6.3	53.2	20.0	0.053	7.9
Mean	5573.13	4911.8	200.4	555.5	12.9	82.8	10.8	42.1	20.3	0.046	10.7

Potassium: In the present studies, the mean potassium concentration of soil was found to be 92.32 ppm with a range 61.0-120 ppm (Table-2). The optimum levels required for the crop cultivation are known to be 180-300 ppm while below 60 ppm deficiency symptoms may occur[25,26]. So the soil of present study is found to be deficient in potassium. Potassium is the major nutrient after nitrogen and phosphorous which is considered essential for the plant growth. Potassium is an enzyme activator that increases photosynthesis and reduce crop loading[27,28]. The availability and leaching of potassium has become a limiting factor for crop production in many soils of Pakistan. In real, fixation of potassium is controlled by several factors such as soil type *i.e.*, clay/mineral, structural configuration and interlayer charge density[29].

Calcium: The soil samples were also found deficient in calcium contents (Table-2). The mean concentration of calcium was found to be 20.8 ppm and ranged between 15.3 and 26.0 ppm. Whereas the deficiency symptoms generally occur below 500 ppm[30]. Increasing sodium salt may lead to precipitation of calcium with carbonates and bicarbonates[9]. Physiologically calcium is important in plant nutrition. It regulates the growth, IAA hormone, calmodulin barrier across the cell membrane to regulate the intercellular cation and anion balance[19].

Magnesium: Magnesium plays an active role in plant growth and metabolism. It regulates the ATP enzymes, carbon dioxide fixation, cellular pH control, chlorophyll content, chloroplast pigmentation and many other functions of crop development[19]. The amount of exchangeable Mg is less than the exchangeable soil complexes. Magnesium contents were found in the range of 0.269-0.689 ppm with the average value of 0.635 ppm (Table-2) and are less than permissible limit. The magnesium deficiency occurs below 60 ppm[30].

Nickel: Organic matter has a strong ability to adsorb the metals; this is why coal and oil contain considerable amounts of nickel. The nickel contents in soil can be as low as 0.2 ppm or as high as 450 ppm in some clay and loamy soils. The average is around 20 ppm. The average value of nickel was found to be 12.9 mg/kg with the range of 7.3-17.8 mg/kg (Table-2). According to international agricultural soil standards (Table-3) all the soil samples were found within the permissible limits (20 mg/kg).

TABLE-3
INTERNATIONAL AGRICULTURAL SOIL STANDARDS

S. No.	Parameters	Units	Permissible limits
1	P	mg/kg	> 7
2	K	mg/kg	> 80
3	Organic matter	w/w (%)	> 0.86
4	pH	Unit less	4-8.5
5	EC	mS/cm	4.0
6	Cu	Mg/kg	100
7	Hg	mg/kg	1.0
8	Cd	mg/kg	1.0
9	Cr	mg/kg	100
10	As	mg/kg	30
11	Pb	mg/kg	500
12	Fe	mg/kg	NGVS
13	Mn	mg/kg	500
14	Ni	mg/kg	20
15	Zn	mg/kg	250

Source: alloway (1990)[17] NGVS: No. guideline value set.

Copper: Copper does not break down in the environment and can be accumulated in plants and animals when it is found in soil. In copper-rich soils only a limited number of plants have a chance of survival. Due to the effects on plants copper is a serious threat to the production of farmlands. Copper can seriously influence, the proceedings of certain farmlands, depending upon the acidity of soil and presence of organic matter. The average value of copper in the soil samples was found to be 82.2 mg/kg with the range of 70-91 mg/kg. According to international agricultural soil standards (Table-3), all the soil samples were found within the permissible limits of 100 mg/kg. So the soil of present studies was found adequate in copper.

Manganese: High concentration of manganese in soils can cause swellings of cell wall, weathering of leaves and brown spots on leaves. In plants Mn^{2+} are transported to the leaves after the uptake from soils. When small amount of manganese is observed in the soil, this causes disturbance in plants mechanisms. The soil of present study was also found to be deficient in manganese. The average concentration of manganese was found to be 10.4 mg/kg with the range of 3.1-20.3 mg/kg. According to international agricultural soil standards (Table-3), all the soil samples were found within the permissible maximum limits of 100 mg/kg.

Zinc: The concentration of zinc was found to be in the range of 10-85 mg/kg with an average value of 42.02 mg/kg whereas the maximum permissible limits are 250 mg/kg (Table-2). Mostly the required level of zinc is 140 mg/kg. So the soil of present study is also deficient in zinc.

Molybdenum: The availability of Mo is reduced in acidic soils. Molybdenum deficiency is usually associated with soils below pH 5. Acidic soils result in an increase in the availability of Mo. Soils high in the free Fe_2O_3 are often deficient in available Mo. Molybdenum disorders are also induced by excess of Mn, Cu and SO_4. The concentration of molybdenum in the soil samples was found to be in range of 16.12-24.4 mg/kg (Table-2) with the average value of 20.26 mg/kg. The desirable maximum level of molybdenum in unpolluted soil is 100 mg/kg. So the soil of present study is also deficient with molybdenum.

Boron: The deficiency of boron in a variety of plants occurs when boron concentration in the dry matter is less than 15 ppm. Adequate level of boron in plants varies from 20-100 ppm. The minimum amount of boron required in the soil is 0.75 ppm. The concentration of boron was found to be in the range of 6.7-16.6 mg/kg with the average value of 10.7 mg/kg (Table-2).

Selenium: The concentration of Se in the soil samples was found to be in the range of 0.0210-0.062 mg/kg with an average value of 0.046 mg/kg. The permissible limits are 2 mg/kg. The concentration of selenium was found to be very small as compared to boron (Table-2).

Conclusion

pH of the soil is in the range 7.62-8.27 which is slightly neutral to basic. Various major and minor metal ions in the soil samples exceed those of normal soils. These high values can have environmental effects on the ecosystem of this area. So in addition to several other anthropogenic effects, the present physico-chemical composition of soil is extremely affecting the remnants of indigenous vegetation at Harappa museum, therefore it is necessary to preserve the existing vegetation and grow new plants of native species through restoration process by replacing local soil with imported one.

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