Analytical Investigation of Soil Inorganic Elements in Cotton Cultivated Areas of Vehari – Pakistan

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Summary: Soil inorganic elements have their influence on different crop production. Soil samples collected from different areas of Vehari were analysed for moisture contents, pH, Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Cl^-, SO_4^{2-} and silica. Inorganic elements were found to be higher in HCl soluble soil samples than the water-soluble soil sample. pH was observed higher (7.3 – 8.4) than the optimum pH required for normal crop cultivation. The soil samples of study area were also found to be deficient in potassium, magnesium and calcium contents and rich in lithium, sodium, iron, and aluminium levels.

Introduction

During the last two decades, a declining trend in per hectare yield of cotton was observed in Vehari district of Punjab. Cotton (*Gossypium hirsutum* L.) is the best cash crop of this region and requires adequate quantities of nitrogen, phosphorus, and potassium besides several micronutrients like silica, manganese, calcium and zinc. The soil should also be free from toxic salts and ions that are likely to retard the productivity [1-8].

In Pakistan, 90 % soils are deficient in nitrogen and phosphorus, whereas, 50 % soils have insufficient potash in addition to micronutrients [9-10]. The salt affected soil becomes saturated with Na^+, Ca^{2+} and Mg^{2+} cations and their respective anions are chloride, sulphate and carbonates that may likely to depress the potash and nitrate uptake by the plant [11].

The soil profile survey conducted by Muhammad in 1983 [12] showed that as a result of increase in salt concentration and soil pH due to evapotranspiration, a part of calcium, magnesium from soil solution precipitates as calcium carbonate, magnesium sulphate and magnesium silicate. Precipitation of these sparingly soluble salts increases their free concentration in soil solution and thus disturbs the Na^+/K^+, Na^+/Ca^{2+}, and Na^+/Mg^{2+} cation ratio in soil exchange complex. Presence of such salts serves as the parent material for saline and saline sodic soil formation [13]. The fertility of soils in the irrigated area was found to be 68 – 88 % phosphorous deficient, 5 – 52 % potassium deficient, 48 – 75 % zinc deficient whereas boron was quite high i.e. 25 – 50 % [8].

Presence of excessive amount of salts seriously affects the growth and morphology of cotton crop. The cotton displays an irregular, short, thin, ill and stunted growth with bushy habits. Root hairs and membranes are seriously damaged resulting into dead root and such plants can easily be uprooted. They are poor in per hectare cotton production and fiber quality [2-7, 14-15]. To understand the magnitude of the problem, the present studies were carried out to determine the soil inorganic elements in cotton growing area of Vehari district and to identify the soil factors affecting the cotton productivity.

Results and Discussion

Soil is a heterogeneous mixture of minerals, organic matter, water and air and soil fertility standard varies from plant to plant and crop to crop [16]. The soil of the study area was formed by alluvium and kaolin sands of Himaliyas and was deposited by flooding of river Sutlej and Hakra. The predominant part of the soil consists of sandy soils with clayey and loamy patches. In saline soils, high temperature causes salinity, induced drought and injury to plants [2-7]. The study area soil has moisture contents 9.8 – 17.1 %.

The pH is peculiar property of soil that determines the acidity or alkalinity, which affects the chemical reaction between water and soil minerals. In

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cotton growing area of Vehari district, the soil pH ranged 7.3 – 8.4, whereas in Northern areas of Pakistan soil pH is ≅ 4. Above 97 % fields under investigation have shown soil pH 8.0 and above (Table-1) whereas the optimum pH required for normal crop cultivation should be 6.5 – 7.0 [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+} and P^{5+} [16], and also uptake of various plant nutrients is pH dependent. Most of the primary nutrients like nitrogen, phosphorous, potassium and secondary nutrients like calcium, magnesium and sulphur are best utilized by the plants when the soil pH ranges 5.5 – 7.9. The uptake of most of the micronutrients also takes place at low pH [17]. Our soils generally have pH above 8 [18]. Soil pH also influences the activity of microorganisms. At pH 5.5, fungi and algae generally dominate the soil whereas at higher pH levels the bacteria are predominant [19].

The average contents of sodium in the soil of Vehari area was found to be 36.08 ppm and ranged 22.0 – 61.0 ppm (Table-1). The sodium concentration (1150-2300 ppm) in soil solution is known to cause detrimental effect on the growth of most crop plants [16]. Physiologically sodium helps osmo-regu-lation, heat expansion and may act as a potassium substitute. However, high sodium concentra-tion causes 'ionic toxicity' and imbalances in the Na^+/K^+, Na^+/Ca^{2+}, Na^+/Mg^{2+} ratio and may cause salt injury to crop [16].

Vehari soils are deficient in potassium contents and the mean potassium contents were found to be 35.78 ppm (range 25.8 – 46.5 ppm). The optimum levels required for crop cultivation are known to be 180 – 300 ppm and below 60 ppm deficiency symptoms may appear [20, 21]. Potassium is the major nutrient after nitrogen and phosphorous which is considered essential for plant growth. Potassium is an enzyme activator, increases photo-synthesis and reduces the crop lodging [22-23]. Potassium leaching and availability has become a limiting factor for crop production in many soils of Pakistan. The release and fixation of potassium is controlled by several factors such as properties of 2:1 soil type clay/mineral, structural configuration, and interlayer charge density [24]. The problem of potassium deficiency was of lesser extent in irrigated areas where it ranges from 5 – 52 % [8, 24].

The soil from Vehari area was also deficient in calcium contents (Table-1). The mean calcium in water-soluble soil was found to be 40 – 55 ppm and ranged between 16 – 74 ppm and in HCl soluble soil; the mean value was found to be 318.9 ppm and ranged between 12 – 800 ppm. Calcium deficiency symptoms generally occur below 500 ppm [14]. Increasing sodium salt may lead to precipitation of calcium with carbonates and bicarbonates [11]. 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 [16].

The Vehari soil was also found deficient in magnesium (Table-1). The soil magnesium contents in water-soluble soils were found to range between

Table-1: Water Soluble and *Water HCl soluble Soil Samples

Sample Code	Sample depth in feet	Moisture %age	pH	*(Li^+) (ppm)	Na^+ (ppm)	K^+ (ppm)	Ca^{2+} (ppm)	Mg^{2+} (ppm)	*(Fe^{3+}) (ppm)	*(Al^{3+}) (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	Silica % age
S – 1	Surface	13.8	7.4	(18)	22.0	39.3	29.6, (408)	12.4, (220)	(2.17)	(0.197)	8.0	14.1	(83.5)
S – 2	Surface	11.5	8.0	(5)	53.0	27.7	74.0, (250)	22.4, (38.4)	(3.25)	(0.3)	25.5	16.0	(68)
S – 3	Surface	9.8	8.0	(14)	25.5	35.4	40, (250)	33.9, (34.4)	(0.325)	(0.3)	21.1	16.4	(68)
S – 4	1	10.7	8.0	(5)	39.5	43.2	64.0, (254)	11.2, (44.6)	(3.16)	(1.37)	12.1	16.1	(71)
S – 5	1	12.3	8.2	(14)	27.5	36.3	16.0, (552)	-, (28)	(3.55)	(1.21)	32.7	7.2	(77.9)
S – 6	1	12.2	8.2	(2)	30.5	26.4	63.4, (345)	22.3, (110)	(0.53)	(2.11)	14.3	15.0	(73.1)
S – 7	2	14.6	8.1	(18)	61.0	33.1	36.0, (800)	13.9, (139.2)	(3.12)	-	18.0	19.3	(8.1)
S – 8	2	15.6	8.3	(20)	31.0	35.1	40.0, (424)	38.0, (-)	(0.95)	(0.7)	2.1	17.3	(86.1)
S – 9	2	15.91	7.3	(5)	31.5	46.5	60.3, (101.1)	24.4, (18.7)	(1.36)	(0.91)	9.5	16.2	(79)
S – 10	2	14.1	8.2	(4)	31.8	34.6	47.3, (205)	32.1, (60.7)	(1.8)	(0.5)	46.0	12.3	(76.1)
S – 11	2	12.8	8.1	(20)	28.5	40.0	35.8, (407)	13.8, (111.2)	(1.21)	(0.731)	5.6	14.1	(82.1)
S – 12	3	11.9	8.3	(10)	47.5	36.1	16.0, (12)	-, (-)	(0.77)	(1.98)	17.2	16.5	(72.6)
S – 13	3	17.1	8.4	(2)	36.5	25.8	26.4, (296)	16.0, (72)	(3.43)	(1.09)	14.9	5.4	(81)
S – 14	3	10.5	8.3	(13)	28.5	30.8	29, (300.4)	5.9, (46.2)	(2.8)	(1.37)	16.0	17.3	(73)
S – 15	3	11.1	8.4	(18)	47.0	46.4	30.4, (179)	11.3, (35.5)	(0.512)	(1.19)	16.1	7.5	(81.21)
Range	Surface-3	9.8 – 17.1	7.3 – 8.4	(2 – 20)	22.0 – 61.0	25.8 – 46.5	16 – 74 (12 – 800)	5.9 – 38.0 (18.7 – 139.2)	(0.325 – 3.55)	(0.3 – 2.11)	2.1 – 46.0	5.4 – 19.3	(8.1 – 86.1)
Average Values	---	12.9	8.08	(11.2)	36.08	35.78	40.55 (318.9)	19.82 (73.75)	(1.93)	(0.997)	17.27	14.05	(72.05)
SD	---	± 2.103	± 0.314	(± 6.585)	± 10.843	± 6.325	± 17.189 (±182.93)	± 9.587 (±55.172)	(± 1.157)	(± 0.573)	± 10.655	± 4.012	(± 17.922)

*Values in parenthesis are Water-HCl soluble soil samples

0.00 – 30 ppm with an average of 17.17 ppm. Whereas in HCl soluble soil samples the contents of magnesium was ranged between 0.00 – 139.2 ppm with an average contents of 63.91 ppm. Magnesium deficiency generally occurs below 60 ppm [14]. 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 [16]. Magnesium present in dark coloured mineral soil in dolomitic limestone consists of calcium, magnesium and carbonates. The amount of exchangeable magnesium is less than the exchangeable calcium in most soil complexes [14].

The mean contents of lithium in HCl soluble soil samples was found to be 11.2 ppm (range 2 – 20 ppm). Lithium is not essential but is present in arid soils. At levels over 3 parts per million, toxicity may occur, but varies from species to species of growing crops [25-26].

The mean contents of iron in HCl soluble soil samples were found to be 1.93 ppm (range 0.325 – 3.55 ppm). The young leaves of plants, growing in iron deficient soils, become yellow in the areas between the veins. The veins usually remain green, unless deficiency is severe, in which case the veins also turn yellow, and the whole leaf can eventually become white. It is the active iron (Fe^{+2}) component of total iron that is critical for iron nutrition of plants [27-28].

The mean contents of aluminium in HCl soluble soil samples were found to be 0.93 ppm and ranged between 0 – 2.11 ppm. Aluminium is present as $[AlSiO_4]^-$ network in the soil and hydrolysis by basic pH and remain insoluble as $Al(OH)_3$, which is soluble in HCl [29-31].

The mean contents of silica in HCl soluble soil samples were found to be 72.05% (range 8.1 – 86.1%). Silica SiO_4^{4-}, SiO_3^{2-} network is broken down at high pH and is soluble in water as Na^+, K^+ salt. This gives free silicate ions in soil.

Experimental

The Vehari district has large variations in temperature. During summer, the day and night temperature ranges between 45 °C and 25 °C respectively and average rainfall is of 11.4 mm [32]. Fifteen soil samples, from surface to depth of 3 feet, were randomly collected from Neeli Bar areas of district Vahari, because main bioactivity lies up to these depths. Stones and gravel were removed from the soil samples, which are than air dried, grinded and sieved by 2 mm pore size sieve. The samples were preserved by using the method as described by Rowell [33]. The samples were analysed for different cations and anions like Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Cl^-, SO_4^{2-} and silica.

Chemical reagents

All the reagents and chemicals used were of analytical reagent grade from Merck and Fluka. All the solution of Standards and Samples were prepared in deionised water using E.mil glasswares. Metler PM 460 electric balance, Milwaukee pH meter and Corning – 460 flame photometer were used.

Soil sample preparation

25 g of dried soil was taken in a 500 ml beaker, stirred with 100 ml deionised water for 30 minutes and filtered through 'Whattman 42' filter paper. The volume of the filtrate was made up to 1000 ml. This is called water-soluble soil sample (A) and was used for quantitative estimation of Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^-.

The insoluble soil sample from above was dried at 100 °C, weighed and dissolved in concentrated HCl, filtered through crucible and volume was made up to 100 ml with deionised water. This is called HCl soluble soil sample (B) and was used for quantitative estimation of Ca^{2+}, Mg^{2+}, Li^+, Fe^{3+} and Al^{3+}.

Moisture percentage and soil pH

10 g soil sample was taken in a dried preweighed nickel crucible and heated in an oven at 110 °C until constant weight. Moisture contents were calculated by using the formula;

% age of H_2O in soil sample = weight of soil / weight of dry soil × 100

pH was determined by pH meter of supernatant water.

Determination of lithium, sodium and potassium

Lithium, sodium, and potassium were determined by using 'Corning – 40 flame photometer. A calibration plot for lithium, sodium, and potassium with the help of Corning standards in the range of 10 – 30 ppm ± 0.1 %, 10 – 70 ppm ± 0.1 % and 20 – 50 ppm ± 0.1 % were prepared respectively, and from this 'absorbance' verses 'concentration' plot, the concentrations of the unknown samples were calculated.

Determination of calcium and magnesium

Calcium and magnesium were determined by complexometric method, using EDTA as titrant. Ecriochorm Black T and Murexide as indicator. The measurement of calcium and magnesium were made with the standard deviation of ± 0.8 % [34-35].

Determination of chloride and sulphate

Chloride ions were determined by $AgNO_3$ titration (argentometric titration). Sulphates ions were estimated gravimetrically using $BaSO_4$ precipitates [34-35].

Determination of iron and aluminium

Iron and aluminium levels in soil samples were estimated by precipitating with NH_4Cl/NH_4OH buffer solution and precipitates of $Fe(OH)_3$, $Al(OH)_3$ were complexed with oxine solution of 8-hydroxyquinoline. The precipitates obtained were filtered, dried and calculated the amount of iron and aluminium respectively [34-35].

Conclusions

The difference in mineral contents estimated in water-soluble soil and HCl-soluble soil is very informative. The pH of our soils is normally 7 – 9; where Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} can easily convert into their corresponding hydroxides which are least soluble. However, in case of those soils where pH is relatively low ≅ 4, these minerals are found in soluble form and clear evidence comes from the difference in mineral content for the same plant species when grown in different soils having different pH. This difference can easily be chalked out when some soil samples are first treated with water shows less mineral content and high mineral content upon treatment with acid.

References

1. M. A. Arain,, M. Ahmad and M. A. Khan, *Pak. J. Bot.*, **32**, 93 (2000).
2. A. R. Reddy, K. R. Reddy, and H. F. Hodges, *Indian Jour. of Experimental Biology,* **35,** 1002 (1997).
3. K. R. Reddy, H. F. Hodges, and J. M. McKinion, *Australian Jour. of Plant Physiology*, **24,** 707 (1997).
4. K. R. Reddy, H. F. Hodges, and J. M. McKinion, *World Resource Review*, **10,** 23 (1997).
5. V. R. Reddy, K. R. Reddy, and Z. Wang, *Soil Science and Plant Nutrition,* **43,** 1125 (1997).
6. V. R. Reddy, Z. Wang, and K. R. Reddy, *Environmental and Experimental Botany*, **38,** 39 (1997).
7. V. R. Reddy, K. R. Reddy, and Z. Wang, In: Developments in Plant and Soil Science: Plant Nutrition for Sustainable Food Production and Environment, Vol.78, Pp: 867 – 872. Kluwer Academic Publishers (1997).
8. M. S. Zia, M. S. Baig, and M. B. Tahir, *Science Vision*, **4,** 56 (1998).
9. M. I. Bajwa, Soil fertility management for sustainable agriculture. *Proc. 3 rd. National Congress of Soil Science,* March 20 – 22, Lahore. Pp: 7 – 25, (1990).
10. M. Zai, N. Khan, M. J. Khan, *Jour. Chem. Soc. Pak.* **23,** 23 (2001).
11. S. Muhammad, Salt affected and water logged soil in Pakistan. *Indo-Pak workshop on soil Salinity and Water Management,* Feb. 10 – 14, PARC, Islamabad, (1990).
12. S. Muhammad , Salt affected soils and their reclamation, presidential address, Section Agriculture and Forestry, *29th Science Conference,* December 26 – 30, University of Karachi. Pp: 15, (1983).
13. Anonymous, Diagnosis and improvement of saline and alkaline soil. *Agriculture Hand Book. 60.* USDA, (1954).
14. R. L. Donahue, R. W. Miller, and J. C. Shickluna, *An introduction to soils and plant growth.* Prentice Hall Inc. Englewood Cliffs, New Jersey. Pp: 626, (1977).
15. J. Levitt, *Response of plant to environmental stress.* Vol. 2. Academic press, New York, (1980).
16. H. Marschner, Mineral nutrition of higher plants. Academic Press, London. Pp: 674, (1986).
17. R. E. Lucas, and J. E. Davis, *Soil Science,* **92,** 177 (1961).
18. M. A. R. Bhatti, *Pak. Food and Agricultural Review.* **5,** 12 (1999).
19. G. Trolldenier, *Plant and soil.,* **38,** 267 (1973).
20. E. A. Kirkby, and K. Mengel, *Principles of plant nutrition.* International Potash Institute, P. O. Box CH-3048 Worblausen, Bern, Switzerland. Pp: 607, (1987).
21. M. T. Saleem, The need to review

recommendations for efficient use of fertilizers in Pakistan. International Forum on Soil Taxonomy and Agrotechnology Transfer, Lahore, Soil Survey of Pakistan and SMSS USA. Pp: 130 (1986).

22. D. M. Malik, R. A. Chaudhry, and G. Hassan, Crop response to potassium application. *Proc. of the workshop on the role of potassium in improving fertilizer use efficiency*. Planning and Development division. GOP, Islamabad. Pp: 71 (1989).
23. M. Rashid, M. I. Bajwa, and A. A. Shah, Wheat responses to potash application in some selected areas of Pakistan. *Proc. Natl. Cong. Soil Science*, March 20 – 22. Pp: 131 (1990).
24. G. N. White, S. B. Feldman, and L. W. Zelazny, Rate of nutrient release by mineral weathering. *Tech. Bull. 254* National Council of Paper Industry for Air and Stream Improvement Inc., 260 Mad. Avenue, N. Y. 10016, USA (1988).
25. M. S. Akhtar, and J. B. Dixon, *Clay Res.* **12,** 22 (1993).
26. M. S. Akhtar, T. Steenhuis, B. Richards, and M. McBride. Treansport of a metal (lithium) and a nonadsorbing tracer in a silty loam and a sand loam soil. *Vedos Research* (2002).
27. I. Cakmak, and C. Engels, Role of mineral nutrients in photosynthesis and yield formation. In: Crop Nutrition: Ed. Z. Rengel. The Haworth Press, New York pp. 141 (1999).
28. B. Erenoglu, S. Eker, I. Cakmak, R. Derici and V. Romheld, *J. Plant Nutrition* **23** (2000).
29. I. Cakmak, and W. J. Horst, *J. Plant Physiol.* **138,** 400 (1991).
30. I. Cakmak, and W. J. Horst, *Physiol. Plant.* **83,** 463 (1991).
31. W. Horst, J. Asher, I. Cakmak, P. Suzulkiewicz, and A. H. Wissemeier, *Plant Physiol.*, **98,** 1222 (1992).
32. M. I. Makhdum, M. N. Malik, F. Ahmad, F. I. Chaudhry and S. Din., *J. Res. Sci.* **12,** 147 (2001).
33. D. L. Rowell, Soil science methods and application. Longman Scientific and Technical Group, U. K. Pp: 350 (1994).
34. J. Bassett, R. C. Denney, G. H. Jeffery and J. Mendham, *Vogel's text book of quantitative inorganic analysis*, The English language book society and Longman, New York, p: 325 – 6, 335 – 8 (1978).
35. M. H. S. Wattoo, J. Iqbal, T. G. Kazi and M. A. Jakhrani, *Pak. J. Biol. Sci.*, **3,** 960 (2000).