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CHARGE CHARACTERISTICS OF THE PRODUCTIVE AND SALT-AFFECTED CALCAREOUS SOILS OF PAKISTAN

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Sllils GIIT\ both the positivI: and negative charges. To accomplish quantitative information for arid lands of Pakistan. samples lrorn the A and B horizons of normal (Ustalfic Haplatgids) and salinesodic (Aquic Haplargids) soils were collected. Positive and Ill:gativl: charucs WLrI: determined by saturating the samples with KCI solution followed by desorption with Na,SO~ solution. The zero point of charge (ZPC) was determined by salt-titration method. Negative charge for the A and B horizons of normal soil was (l.!17 and o.O? crnol kg '. while corresponding values were 5.20 and 5.55 cmol kg' for the saline -sodic soil. Positive charge ill the A and B horizons of normal soil was I. X5 and 2.60 cmol, kg while charge values were 2.32 and 3.17 cmol kg tor the A and B horizons of salt-affected soil., respectively. Negative and positive charge was higher at higher soil pH The ZPC values were l,1.<)5and 7.0() tor the A and B horizons of the normal soil., while these were 7.60 and 7.35 for the A and B horilOns of the salt-affected soil. respectively.l At ZPC, permanent charge was 4.80 and 3.47 cmol, kg' for the A and B horizons of normal soil and 2.88 and 2.38 cmol, kg' for the A and B horizons of the salt-affected soil., respectively. Variable charge (pl l-dcpendcnu at ZPC was 1.85 and 2.60 cmol, kg' for the A and B horizons of normal soil. while 2.32 and 3.17 cmol, kg' for the A and B horizons of salt-affected soil. respectively. Although the native soils arc dominated by illite type clay minerals. the results indicated the presence of some other minerals carrying pl-l-depcndent negative and positive charges both in thl: llorll1-t1as wL11as salinL-smlic soil.

Key words: calcareous soils. charge characteristics, xalt-al'lccu«!

I~TRODllCTION

Pakistan soils, contain dominantly illitc type clay minerals IR~ll1lh~1ci al.. 1<)<)3)which arc expected to have both the properties of const.uu and variable charge surfaces. Much of the work pertaining to the charge characteristics has been conducted in temperate regions. \VhLIT in general, soils arc characterized hv surfaces bearing a constant charge (van Raij and Pecch, 1<)72). Oltcnly. the negative charge increases with an increase in plL. Such increase is more in I: I than that in 2: I tYPL clay minerals (Schoficld and Sarnson, 1<)53).

Charge on soi I colloids induces ion exchange properties which arc important for the sustainable utilization of soils for agriculture. Physical and chemical properties are directly or indirectly related to the nature and magnitude of surface charges of soil colloids. Such properties as cation exchange. fixation of uutrient ions (K . NH~. H,PO~. SO~'. LtC.). adsorption of heavy metals and/or agro-chcmicals. soil acidity/alkalinity and aggregate stability arc important ones. Charge characteristics arc related and important in clav mineralogy and pcdogcncsis (Katuaruzzaman. I<)XI). Sorption of ioniz.ihlc and V~IPOur phase of organic and inoruanic compounds or ions is primarily conlrolled by organic component and swelling clays. However, sorption of Ilrganil: compounds is further affected by carbon conLnls. particle xizc distribution. clay mineral composition. pll, CEC and specific surface area (Shimizu *cl al..* 1<)<)l). Among these. CEC and type of clays arc the most important. However increased sorption of heavy metals or organic molecules in soil appears favourable to slow down the groundwaicr pollution/contamination rate.

TIlL zero point of charge (ZPC) of soils, helps to predict the response of a soil to the changes in its surroundings. like soil solution concentration and composition. The literature revealed very limucd information about the changes III the ZPC dUL to pl l., EC, and/or nature and concentration 01 electrolytes in soils, particularly like those of Pakistan'. HLncL. preliminary investigations were undertaken on calcareous soils belonging to tile Hafizabad (Ustalfic Haplargids) and Khurrianwala (Aquic Haplargids) soil series to assess the positive and negative charges. permanent and variable charges and ZPC.

MATERIALS AND METHODS

Soil samples WLIT collected from the A and B horizons of nonsalinc-nonsodic (Hafizabad) and saline-sodic (Khurrianwala) soil SLriLS (Table I). Particle-size analysis was carried out by the Bouyoucos method. The pH of the saturated soil paste (pl'U. EC of the saturation extract (ECJ. soluble ions. exchangeable cations. lime and cation exchange capacity (CECl WLIT determined (U. S. Salinity Lab. Staff., 1<)54). Organic carbon was determined by the method of Nelson ami Sommcrs. I<)X6. ThL mineralogy of < 0.0()2 mm particles quoted in Table 2 was estimated according to Ranjha *('I'0/. (1<)<)3).*

Determination **of Total Positive and Negative Charges:** These WLIT dctcnnincd by measuring the adsorbcd K' and Cl from IN KCI solution as a function of pH and salt concentration (Schofield, 1949). In each centrifuge tube, 2.5 g soil sample was mixed with 25 ml *IN* KCI solution and pH of each sample was adjusted at 6, 8 or 10 with KOH or HCI. Next day after readjusting the respective pH, the samples were centrifuged and supcrnatant liquid was discarded. This step was repeated four times. every time adjusting the pH of each sample as was maintained in the first step. Then KCI was removed by washing the samples four times with 95 % ethanol. Adsorbcd K' and Cl were desorbed by using 25 ml *IN* Na~S04 soluuon four times and supernatant was collected in a 100 ml volumetric flask After making volume with *IN* Na$_2$S04, K' was measured by name photometer and Cl' by titration with standard AgNO,. Potassium and chloride expressed as cmol k.~ soil represented negative and positive charges, respectively.

Determination of the Zero Point of Charge: The ZPC was measured by the salt-titration method as described by Kinniburgh *et al.(* 1(75) and later modified by Sakurai (1989). In plastic centrifuge tubes (50 ml), 2 g soil was placed and a kw ml of water were added for soaking. For having a range of pH from 2 to 8.5. additional water and/or o.IN HCI was added ııı obtain a final volume of l-lO plus HCI equal to 20 ml. These suspensions were allowed to equilibrate for four days. stirring :'i-C) times daily, and pH of this equilibrated suspension (pl-l,) was measured. Then to each centrifuge tube. 0.5 ml *2N* NaCl solution was added. After reciprocal shaking for about 3 hours. again pH was recorded and designated as pH,. By subtracting pH, from pH 2' 6 pH was calculated. Then 6 pH was plotted against pH, LO determine the ZPC.

Determination of Permanent and Variable Charges: Permanent and pl-l-dependent charges were determined by the direct measurement of adsorbed KT and Cl from *IN* KCI solution at ZPC (Kamaruzzaman, 1981). Potassium and chloride ions were determined as described above. The pH was adjusted equal to respective ZPC of soils under test. The types of charges were calculated as follows:

Permanent charge = Total negative charge minus total positive charge, all expressed in cmol, kg' soil. i.e. adsorbed KT_ adsorbed Cl .

Variable charge = Total positive charge. expressed as crnol, kg soil, i.e. adsorbed Cl .

The statistical analysis of the data was accomplished in MSTAT-C, version 1988 and graphs were drawn in Sigma plot version 5.1.

RESULTS AND DISCUSSION

Positive, Negative and Net Charge on Soils: The charge distribution on soils (Tables 3 & 4) shows simultaneous adsorption of both the cations and anions i.e. a stearic arrangement of charges but there was net negative charge at £111 the pH values. The stearic arrangement of charges may help to avoid complete cancellation of opposite charges because positive and negative charges are spatially separated on soil particles (van Raij and Peech, 1972; Espinoza *et al.. 1975).* The negative charge ranged from 5.12 to 6.17 cmol kg! in the Hafizabad soil and from 5.04 to 6.09 cmol, kg' in the Khurrianwala soil (Table 3). The positive charge in nonsaline-nonsodic soil varied from 1.85 to 3.40 crnol kg' . while in saline-sodic soil it varied from 2.15 to 3.75 cmol, kg' (Table 4). As the pH increased, there was a consistent increase in negative charge but a gradual decrease in positive charge. However, the correlation between pH and negative or positive charge remained statistically similar and was, in general. negative. There was net negative charge in nonsaline-nonsodic soil which ranged from 2.41 to 3.55 cmol, kg' and in saline-sodic soil, it varied from 1.33 to 3.94 cmol, kg' (Table 5).

In normal soil, negative charge was more than that in saline-sodic soil (Table 3). This could be attributed to high EC< of saline-sodic soil whereby some electrolytes such as Na + and Ca'+, might be antagonizing K+ saturation of exchange complex (Lindsay, 1979). In addition, negative adsorption of anions i.e. ligand exchange that could give rise to a covalent bond between anion and structural cation (Dixon *et al., 1977),* might have decreased magnitude of the measured negative charge at high EC,. (Table 2). Moreover, higher clay in Hafizabad soil also carried more positive charge. Previous studies have shown absence of allophanes and oxide minerals in Pakistan soils including Hafizabad and Khurrianwala soils (Akhtar, 1989). However, the positively charged gibbsite [AI, Mg, (OH)d^{T} and/or brucite [(AI, Mg, (OHl"I" $^{+}$ like layers in chlorite (Akhtar, 1989) and other complex ions or ion pairs (Ca HCO/, CaH$_2$PO/, MgHCO, +) at high EC, could be considered sources of positive charges in these native soils (Rasool, 199.1). It has also been reported that weathering of illite and smectites during soil formation under sodic conditions (sodic parent material) leads to the formation of 14A components of random disarray in soils of Pakistan (Ismail, 1970; Razzaq and Herbillon, 1979: Akhtar, 1989) and at other places. Possibility of formation of such minerals could also be a source of positive charges and hence lower net negative charge.

Negative charge was significantly more in the A horizon than that in the B horizon of the normal soil (Table 3). This might be due to higher organic carbon in the A horizon than that in the B horizon, although clay contents were almost similar in both the horizons (Table 1) of this soil profile. However, no significant difference was observed in the values of negative charge for the A and B horizons of the salt-affected soil. The higher values of CEC might be due to the presence of zeolitic or feldspathoidic minerals which released non-exchangeable sodium during the extraction with ammonium

Table 1. Characteristics of the Hafizabad and Khurrianwala soil series

Soil property	Hafizabad soil series		Khurriauwala soil series	
	A horizon	B horizon	A horizon	B horizon
pH,	7.83	8.20	9.97	8.55
EC", dS m⁻¹	4.02	3.24	14.63	4.35
Saturation extract analysis				
CO_3^{2-} "	Absent	Absent	2.00	Absent
HCO_3^- "	4.38	2.63	10.50	2.13
Cl "	23.13	16.88	80.00	23.75
SO_4^{2-} "	18.49	14.49	87.50	22.12
Ca^{2+} "	8.00	6.00	2.75	3.75
Mg^{2+} "	4.60	3.67	0.85	5.70
Na^+ "	33.04	26.09	174.00	33.48
K^+ "	0.46	0.31	2.68	107
SAR	13.00	11.80	130.00	10.00
Exchangeable ions*				
Na^+, cmol, kg⁻¹	2.66	2.61	8.61)	4.57
K^+ "	0.38	0.34	1.20	0.87
Ca^{2+} + Mg^{2+} "	8.62	7.22	0.54	:U8
CEC	1166	10.17	7.83	7.82
ESP	n.oo	2500	89.00	5800
$CaCO_3$ (%)	4.32	3.54	5.40	4.78
Organic carbon (%)	0.52	0.24	0.25	0.15
Textural class	Clay loam	Clay loam	Clay loam	Sandy clay loam

*The sum of exchangeable cations was more than CEC when determined exchangeable Ca^{2+} + Mg^{2+} by titration method which appeared due to the presence of $CaCO_3$ and/or zeolite clay minerals. This type of composition might be very true for the A horizon soil of the Khurrianwala series where EC, was 14.63 dS m⁻¹ (Bohn *et al.*, 1985).

Table 2. Clay mineralogy of ≤ 2 µm soil particles

Soil series	Horizon	Type of clay minerals				
		Illite	Smectite	Chlorite	Vermiculite	Kaolinite
Hafizabad	A	3	traces	1	traces	2
Hafizabad	B	3	traces	1	traces	2
Khurrianwala	A	3	traces	1	-	2
Khurrianwala	B	3	1	1	-	2

(Source: Ranjha, 1993).

Table 3. pH affects total negative charge (cmol$_c$ kg⁻¹) of soils

pH	Hafizabad soil series		Khurriauwala soil series		Mean	r
	A horizon	B horizon	A horizon	B horizon		
6	5.56 cd	5.12 d	5.04 d	5.08 d	5.20 C	-0.671^{NS}
8	6.13 a	5.42 cd	5.44 cd	5.35 cd	5.58 B	-0.527^{NS}
10	6.17 a	5.65 bc	6.09 ab	5.52 cd	5.86 A	+0.2001'O~
Mean	5.95 A	5.40 B	5.52 B	5.53 B		

Figures sharing the same letter(s) in columns, rows or means are statistically similar at P = 0.05; No. of observations for computing r between pH and negative charge was 16.

fable 4. pH affects total positive charge (cmol. kg 1) of soils

pH	Hafizabad soil series		Khurrianwala soil series		Mean	r
	A horizon	B horizon	A horizon	B horizon		
6	3.15 abd	1.85 g	2.25 efg	3.75 a	2.75~s	-0.283 "
8	3,40abc	2.15fg	2.60dc£	3.00bcd	2.79~s	-O.322~s
10	2.85cd~	2.IOfg	2.15fg	3.55 ab	2.66 "	-0.34 7~s
M~an	3.13 A	2.03 B	2.33 B	3.43 A		

Figures sharing the same lettert s) in columns, rows or means are statistically similar at P 0.05: No. of observations for computing r between pH and positive charge were 16.

Table 5. pi I affects nelnegative charge (cmol. kg') of the soils

pl1	llafizabad soi I series		Khurrianwala soil series		Mean
	A horizon	B horizon	A horizon	B horizon	
6	2,41 cd	3.27 ab	2.79 bed	1.33 c	2.50 B
8	2.73 bed	3.26 ab	2.84 bc	2.34 cd	2.79 B
10	3.32 ab	3.55 ab	3.94a	1.97 de	3.20 A
Mean	2.82 B	3.60 A	3.19 AB	1.88 e	

Figures sharing the same letter(s) in columns, rows or means are statistically similar at p,~ (L05.

Table 6. Variable and permanent charge (cmol.kg")^{1} at zpe of soils

Soi I series	Horizon	ZI'C	+ive charge (e I adsorbed)	-ive charge (K adsorbed)	Variable charge	Permanent charge
Hafizabad	A	6.95	1.85	6.67	1.85	4.82
Hafizabad	B	7.00	2.60	6.07	2.60	3.47
Khurrianwala	A	7.60	2.32'	5.20	2.32	2.88
Khurrianwala	B	7.35	3.17	5.55	3.17	2.38

acetate (Waraich , IS17~). Since the soil clay is dominated by illite type minerals, the fixation of added K is highly expected and thus K in the extract remained lower leading to less negative charge estimation.

Zero Point of Charge (ZPC): The ZI'C was determined by plotting pH$_{1}$ versus $_{6}$ pH. The values of ZfC for the A and B horizons of normal soil were 6.95 and 7.00, respectively, while the corresponding values for the salt-affected soil were 7.35 and 7.60 perhaps due to low organic matter in salt-affected soil. IL has been reported that the presence of organic matter tends to lower the zpe values (van Raij and Peech, 1972). The A horizons of both the soils have lower ZfC than that of the B horizons. It could thus be concluded that normal soil was capable of storing larger amounts of cations than the salt-affected one against leaching, hence the application of organic matter to salt-affected soil during reclamation will help minimize the leaching losses of nutrients in addition to improving the physical properties of soils. The ZfC values for all the cases were lower than the soil pl=l,. The zpe > pl-l, indicates that the soils had more OH ions adsorbed on the surface than H+ ions because of an alkaline reaction. Earlier Dolui *et at.* (1990) used ZfC to characterize the surface charge of soils dominated by hydrous oxides of iron and aluminium where ZI-C ranged from 2.0 to 2.4 and these values were less than the pH of soil under natural condition.

Permanent and pH-Dependent Charges: In the Hafizabad soil series, permanent charge was 4.~2 and 3.47 cmol, kg', while the pH-dependent charge was 1.85 and 2.60 cmol, kg for the A and B horizons, respectively (Table 6). In the Khurrianwala soil series, permanent charge was 2.88 and 2.38 while variable charge was 2.32 and 3.17 cmol.kg' ^{1} for the A and B horizons, respectively. IL is obvious that in both the soil series, permanent negative charge was more compared to variable charge. This scenario was natura] since soils under investigation have dominance or permanent charge colloids (Table 2), like 2: I type silicate clay minerals. Such mineralogical make lip has to carry more permanent charge as reported by Ranjha *et al.* (1993) for many Pakistani soils including the soils investigated here.

Conclusions: The negative charge of soils increased significantly with an increase in pH. Such an increase in charge was more in normal than that in salt-affected soil. The pH showed non-significant. correlation with negative and positive charges for both the horizons of normal and salt-affected soils. The zpe of salt- affected soil tended to be higher than that of normal one. In both the soil series, permanent negative charge was more compared to variable charge. Variable charge was higher in the saline-sodic than that in nonsaline-nonsodic soil. This aspect needs further investigations to quantify the expected importance for achieving cost-effective amelioration of salt-affected soils of Pakistan.

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