Point of zero charge of soils - it's dynamics under fertilizer management practices and nutrient availability

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ABSTRACT

Aims: To study the dynamics of point of zero charge of different soil types and determine the availability of nutrients under the influence of specific fertilizer management practices.
Study design: Completely Randomized Design.
Place and Duration of Study: Department of Soil Science, Assam Agricultural University, Jorhat, Assam; between March 2020 and December 2021.
Methodology: We estimated the point of zero charge (PZC) components, i.e., the point of zero salt effect (PZSE) and point of zero net charge (PZNC) in six surface soil samples [black soil (Vertisol), laterite soil (Alfisol), red soil (Alfisol) of Odisha, and alluvial soils belonging to Entisol, Inceptisol, and Alfisol of Assam, India] through potentiometric titration and ion retention methods respectively. The soils were subjected to four specific fertilizer management practices under laboratory incubation, viz., FYM @ 5 t ha^{-1} (T1), NPK @ 80:40:40 for Odisha soils and 60:20:40 for Assam soils (T2), T1 + T2 (T3) and T3 + Lime requirement/ Gypsum requirement (T4). The PZC components and availability of nutrients were determined at 15 and 30 days after incubation.
Results: The PZSE values of the soils ranged from 2.18 to 4.70, while PZNC values were achieved at relatively lower pH ranging from 2.03 to 4.10. Highest values of PZSE and PZNC were recorded under treatment T2 followed by T3, T4 and T1 for all the incubated soil samples, however there was a decrease in the PZC values with increase in days of incubation. Comparatively, the treatment T4 resulted as the most ideal fertilizer management practice. Besides providing optimum amount of primary and maximum amount of secondary nutrients, T4 regulated the PZC values favouring minimal loss of nutrients and enhanced nutrient use efficiency. The availability of nutrient ions is influenced by the difference between soil solution pH and PZC values of the soil, which recorded to be highest for Vertisol (OS1), followed by Entisol (AS1), Inceptisol (AS2), and Alfisol (AS3, OS2, OS3) soil orders.
Conclusion: The exchange and availability of cationic nutrients get enhanced due to higher CEC in soils with high clay and organic matter percentage. The pH of these soils must therefore be regulated for better availability of anionic nutrients. Highly weathered soil of Alfisol order exhibit optimal CEC over a narrow pH range, favouring better availability of anionic nutrients and hence simultaneously require frequent fertilizer application along with organic manures for the enhanced retention, mobility and availability of nutrients in soil.

Keywords: Point of zero charge, Point of zero salt effect, Point of zero net charge, Fertilizer management practices, Nutrient availability

1. INTRODUCTION

Soil minerals have two types of charge surfaces, i.e., permanent charge and variable charge. A measure of this surface charge of a soil colloid gives rise to the concept of point of zero charge (PZC) [1,2]. The suspension pH at which the particle surface has a zero net charge, i.e., σP = 0, is known as the point of zero charge of a soil and it is one of the most important parameters describing the variable charge surfaces [3]. The PZC components include terminologies like zero point of charge (ZPC), point of zero net proton charge (PZNPC), isoelectric point (IEP), point of zero salt effect (PZSE), and point of zero net charge (PZNC) [4; 5].

The point of zero salt effect (PZSE) is the pH at which the magnitude of the variable surface charge does not change with a change in the electrolyte concentration of the soil solution, when measured at the same temperature. It denotes the pH at which the electrolytic concentration does not affect the pH-dependent charge [6]. The point of zero net charge (PZNC) is used to analyze the changes in ion retention with varying surface charges [7]. It is the pH at which the total concentration of surface anionic sites equals the total concentration of surface cationic sites, thereby forming a fundamental definition of charged mineral surfaces [8]. The PZNC must match the PZSE for systems with no permanent charge, but the PZNC varies from the PZSE for systems with both permanent and variable charges [9]. Several methods have been proposed for the determination of PZSE and PZNC of different soil types [10,11,12].

If the pH of soil lies above its PZC value, the soil surface tends to exhibit net negative charge and is primarily involved in cation exchange, while if the pH lies below its PZC, the soil retains anions electrostatically [13]. PZC controls the net cationic and anionic nutrient retention on the soil surfaces. Furthermore, soil buffering ability not only indicates the stabilization of soil pH but also is an estimate of the amount of amendment needed to effect a required change in soil reaction, which in turn is related to the efficacy of pH stabilization. As a result, a study of soil PZC is necessary while discussing the buffering capacity of various soil types.

The PZC of soil becomes an important parameter to study since the surface charge can be manipulated to take advantage of solid-phase interactions relating to the movement of nutrient ions in the soil system. Since the PZC of different soils vary depending on their pedogenesis and mineralogy, a closer examination of their behaviour and their relationship with different physicochemical properties of soil may contribute to more accurate fertilizer management practices and more efficient reclamation steps can be undertaken for problem soils. It is therefore relevant to investigate the chemistry of surface charges concerning PZC in various soil types and their impact on fertilizer management practices and vice-versa [14,15]. The current study was undertaken to look into the impact of fertilizer management activities on the point of zero charge in different soil types and their subsequent nutrient availability.

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY

Georeferenced surface soil samples (0-15 cm) were collected, processed, and analyzed for various physicochemical properties. The details of the soil samples are given in Table 1.

Table 1. Description of collected soil samples

Sample	Location	Longitude and Latitude	Soil Type	Soil Colour	Soil Order
OS1	Kalahandi, Odisha	19°98'46.02" N 83°13'78.52" E	Black Soil	10YR2.5/1	Vertisol
OS2	Khordha, Odisha	20°16'35.29" N 85°71'67.45" E	Laterite Soil	7.5YR5/6	Alfisol

OS3	Dhenkanal, Odisha	20°69'46.09" N 85°75'51.33" E	Red Soil	5YR4/8	Alfisol
AS1	Dergaon, Golaghat, Assam	26°40'67.07" N 93°59'61.67" E	Alluvial Soil	10YR7/3	Entisol
AS2	ICR Farm, AAU, Jorhat, Assam	26°42'19.47" N 94°11'26.18" E	Alluvial Soil	10YR7/4	Inceptisol
AS3	Titabor, Jorhat, Assam	26°58'92.37" N 94°19'17.12" E	Alluvial Soil	10YR8/3	Alfisol

2.1 Point of Zero Salt Effect (PZSE)

For the estimation of PZSE, a suitable amount of soil was made homoionic by centrifuging it at 3000 rpm with 1N NaCl for 10 minutes. The residue was air-dried. About 4 g of Na-saturated soil was taken along with 0.002M NaCl in 8 separate beakers. The pH was adjusted to span the expected PZC value (2 to 9) and the final volume was made to 20 ml with 0.002M NaCl. The beakers were kept covered to prevent evaporation. After 4 days of equilibration, the pH of the suspension in 0.002M NaCl was recorded and designated as pH0.002M. Further, 0.5 ml of 2M NaCl was added in each beaker to make the final concentration of the suspension to 0.05M. The pH in 0.05M NaCl was recorded after 3 hours of intermittent shaking and designated as pH0.05M. The ΔpH was computed as the difference between the pH0.002M and pH0.05M as follows:

$$\Delta \mathrm{pH} = \mathrm{pH}0.05\mathrm{M} - \mathrm{pH}0.002\mathrm{M}$$

The PZSE was evaluated by plotting potentiometric titration curves by taking the ΔpH values along the Y-axis and the pH0.002M values along the X-axis. The pH at which the ΔpH curve intersected the pH0.002M axis was considered to be the value of PZSE [16].

2.2 Point of Zero Net Charge (PZNC)

For the assessment of PZNC, the determination of CEC and AEC for charged surfaces as a function of pH and ionic strength was accomplished by the estimation of K^+ and Cl^- ion retention in the soils through the ion adsorption method [7]. About 1.5 grams of soil was centrifuged with 15 ml of 0.1N KCl. The pH of the suspension was adjusted to the span of expected PZC values (pH 2 to 7). The sample was kept covered at room temperature for three days with intermittent shaking for 2 hours, twice daily. After 3 days of equilibration, the supernatant was discarded and the soil sample was centrifuged with 25 ml of 0.1N KCl for 20 minutes at 3500 rpm and the supernatant was discarded. The addition of 25 ml of 0.1N KCl was repeated four times with subsequent centrifugation and removal of the supernatant. After the final washing, the residue was extracted with 25 ml of 0.5N NH_4NO_3 solution to replace the adsorbed K^+ and Cl^- ions. Potassium (K^+) in the extract was determined by a flame photometer. Chlorine (Cl^-) was determined by titrating against $AgNO_3$ in presence of potassium chromate (K_2CrO_4) as the indicator. The amounts of K^+ and Cl^- ions extracted were expressed as equivalent amounts of negative (CEC, K^+) and positive (AEC, Cl^-) charges, respectively. The same procedure was repeated for all the pH values (2 to 7).

The PZNC is marked by the pH at which the cation adsorption becomes equal to the anion adsorption. It was obtained by locating the point of intersection or crossover point by plotting the measure of CEC (K^+) and AEC (Cl^-) along the Y-axis against the pH values in the span of 2 to 7 along the X-axis for each soil sample [7].

2.3 Incubation Study

An incubation study was conducted with soil samples in which 200 gram of each sample was treated with four different fertilizer management practices (Table 2), to monitor their impact on the point of zero charge of the soils after 15 and 30 days of fertilizer application. The treated soil samples were incubated (three replications each), at room temperature in covered plastic containers maintained with moisture content at field capacity (0.3 bar), as determined from the pressure plate apparatus for the respective soil types. Sub sample were drawn at 15 and 30 days after treatment (DAT), shade dried, ground and were analyzed for their fertility status and PZC components (PZSE and PZNC) at both the DAT using standard procedures.

Table 2. Details of the fertilizer management practices

Treatment No.	Treatment Details
T_1	Farmyard Manure (FYM) (5 tons ha^{-1})
T_2	N, P_2O_5, K_2O (*)
T_3	FYM (5 tons ha^{-1}) + N, P_2O_5, K_2O (*)
T_4	FYM (5 tons ha^{-1}) + N, P_2O_5, K_2O (*) + Lime/Gypsum Requirement

**Location specific fertilizer dose i.e. 80:40:40 kg ha^{-1} N, P_2O_5, K_2O for Odisha soils (OS_1, OS_2, OS_3) and 60:20:40 kg ha^{-1} N, P_2O_5, K_2O for Assam soils (AS_1, AS_2, AS_3)*

3. RESULTS AND DISCUSSION

The various physicochemical properties and fertility status of the untreated soil samples have been given in Table 3 and 4 respectively.

Table 3. Physicochemical properties of the soil samples

Soil	Textural Class	BD (gcm^{-3})	Moisture content at FC (%)	pH (H_2O)	OC (%)	Exchangeable Bases [cmol(p^+)kg^{-1}]			
						Na^+	K^+	Ca^{2+}	Mg^{2+}
OS1	c	1.22	32.91	7.93	0.95	0.11	0.19	13.00	3.00
OS2	ls	1.60	14.64	5.71	0.21	0.09	0.16	1.39	1.10
OS3	sl	1.46	17.98	5.32	0.33	0.12	0.17	1.24	0.96
AS1	sil	1.27	27.23	5.04	0.86	0.14	0.15	0.35	0.30
AS2	sil	1.36	20.11	5.43	0.47	0.06	0.12	1.95	1.25
AS3	cl	1.31	23.41	5.13	0.62	0.09	0.14	1.53	1.16

Table 4. Fertility status of the soil samples

Soil	Available Nutrients (kg ha^{-1})				Ex. Al [cmol (p$^+$)kg^{-1}]	CaCO$_3$ (%)	Free Sesquioxides (g kg^{-1})	
	N	P$_2$O$_5$	K$_2$O	S			Fe-Oxide	Al-Oxide
OS1	197.25	9.53	173.76	34.97	0.08	5.2	10.27	3.02
OS2	158.36	18.29	144.48	28.65	0.10	<1	20.84	11.42
OS3	163.07	16.23	148.64	30.39	0.15	<1	25.61	7.92
AS1	275.97	12.88	133.76	71.68	1.15	<1	12.04	4.17
AS2	231.42	24.73	103.92	49.28	1.05	<1	15.32	6.65
AS3	238.34	19.06	123.04	62.72	1.13	<1	21.47	11.33

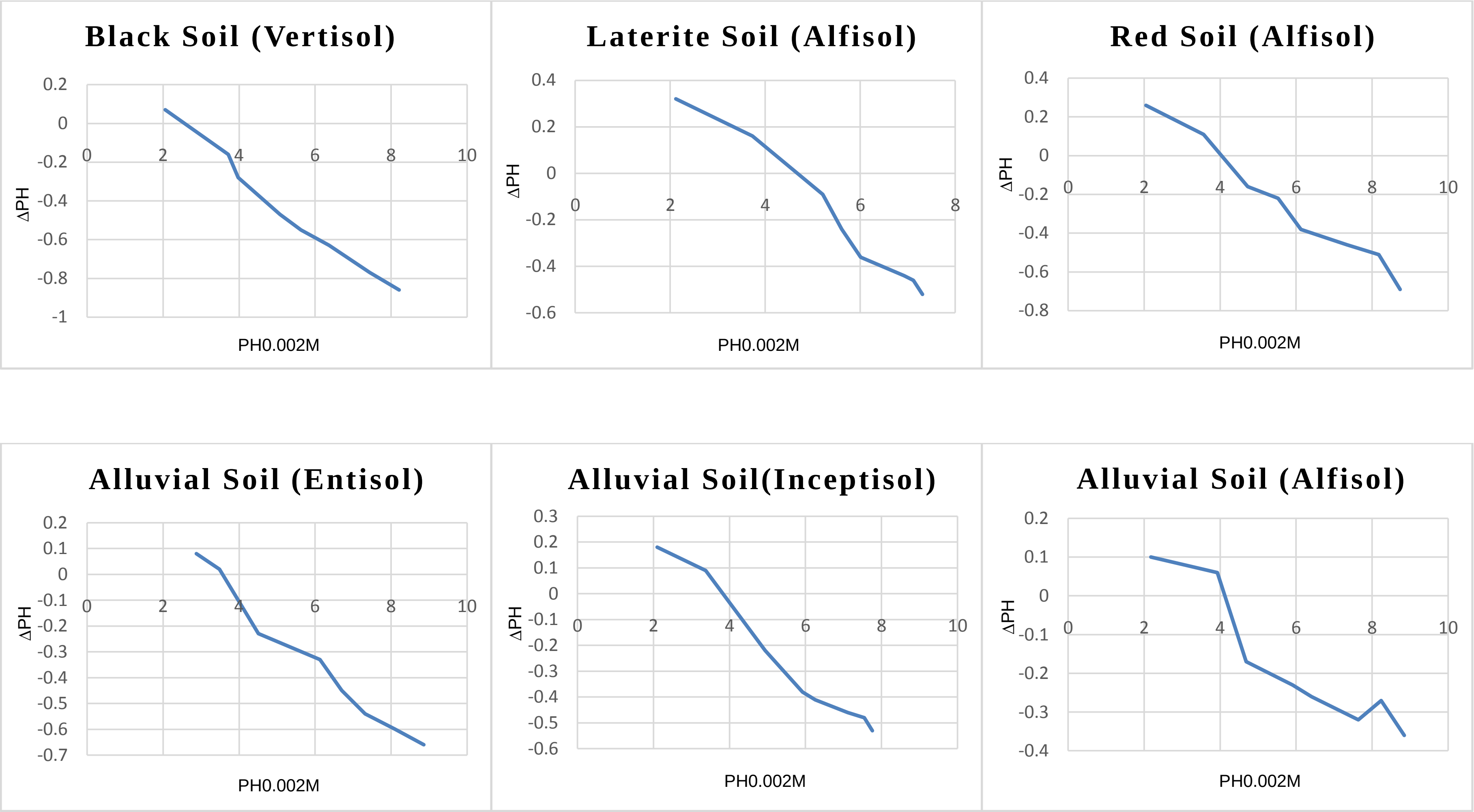
3.1 Point of Zero Salt Effect (PZSE)

The point of zero salt effect (PZSE) is mostly indicative of the soil reaction, degree of weathering and sesquioxides content in the soil. The pH in different electrolyte concentrations and the Δ pH for a series of pH ranges (2-9) are given in Table 5 and the graphical determination of PZSE points from potentiometric titration curves for the untreated soils are presented in Figure 1. In general, the PZSE for untreated soils of both the states are found to be equivalent, nevertheless, variation was seen in different soil orders.

Table 5. The pH measured in 0.002M and 0.05M NaCl, their difference (△pH) and PZSE of the soil samples

	pH	OS1	OS2	OS3	AS1	AS2	AS3
pH 0.002M	**2**	2.06	2.12	2.05	2.88	2.1	2.18
	3	3.72	3.73	3.57	3.49	3.38	3.93
	4	3.98	5.21	4.73	4.51	4.94	4.69
	5	5.08	5.61	5.53	6.13	5.92	5.91
	6	5.63	6.01	6.13	6.7	6.26	6.41
	7	6.37	6.92	7.34	7.32	7.11	7.64
	8	7.44	7.12	8.18	8.1	7.55	8.24
	9	8.21	7.31	8.74	8.86	7.76	8.85
pH 0.05M	**2**	2.13	2.44	2.31	2.96	2.28	2.28
	3	3.56	3.89	3.46	3.51	3.47	3.99
	4	3.7	5.12	4.57	4.28	4.72	4.52
	5	4.61	5.37	5.31	5.8	5.54	5.68
	6	5.08	5.65	5.75	6.25	5.85	6.15
	7	5.74	6.48	6.88	6.78	6.65	7.32
	8	6.67	6.66	7.67	7.5	7.07	7.97

	9	7.35	6.79	8.05	8.2	7.23	8.49
ΔpH	**2**	0.07	0.32	0.26	0.08	0.18	0.1
	3	-0.16	0.16	0.11	0.02	0.09	0.06
	4	-0.28	-0.09	-0.16	-0.23	-0.22	-0.17
	5	-0.47	-0.24	-0.22	-0.33	-0.38	-0.23
	6	-0.55	-0.36	-0.38	-0.45	-0.41	-0.26
	7	-0.63	-0.44	-0.46	-0.54	-0.46	-0.32
	8	-0.77	-0.46	-0.51	-0.6	-0.48	-0.27
	9	-0.86	-0.52	-0.69	-0.66	-0.53	-0.36
PZSE		**2.18**	**4.70**	**4.00**	**3.60**	**3.80**	**4.16**



Black Soil (Vertisol)

Laterite Soil (Alfisol)

Red Soil (Alfisol)

Alluvial Soil (Entisol)

Alluvial Soil(Inceptisol)

Alluvial Soil (Alfisol)

Figure 1. Point of zero salt effect (PZSE) of the soil samples

3.2 Point of Zero Net Charge (PZNC)

The point of zero net charge (PZNC) takes into account the contribution of both the variable as well as the permanent charge components towards soil PZC. The solution pH at which the net cation exchange capacity (CEC) equals the net anion exchange capacity (AEC), gives the PZNC. Relevant values of the CEC, AEC, and PZNC of untreated soil samples are presented in Table 6 and the ion retention curves for PZNC determination are presented in Figure 2. The AEC values were remarkably lower than CEC values with an increase in soil pH and vice-versa.

Table 6. The CEC, AEC and PZNC of the soil samples

	pH	OS1	OS2	OS3	AS1	AS2	AS3
CEC $[cmol(p^+)kg^{-1}]$	**2**	1.39	2.27	2.59	2.14	2.03	2.42
	3	4.91	3.61	3.62	3.18	2.59	4.39
	4	6.82	4.16	4.25	5.93	4.77	5.01
	5	10.57	5.23	6.91	7.41	6.81	9.05
	6	15.70	7.48	7.72	10.54	9.38	14.47
	7	16.45	9.33	9.83	16.92	14.73	18.75
AEC $[cmol(p^+)kg^{-1}]$	**2**	1.42	4.89	4.04	2.84	2.99	4.95
	3	1.37	4.47	3.95	2.42	2.64	4.89
	4	1.31	4.29	3.18	2.04	2.29	4.72
	5	0.97	3.84	2.64	1.87	1.82	3.78
	6	0.73	3.07	2.32	1.62	1.58	3.22
	7	0.54	2.93	2.01	1.54	1.27	2.73
PZNC		**2.03**	**4.10**	**3.23**	**2.50**	**2.97**	**3.61**

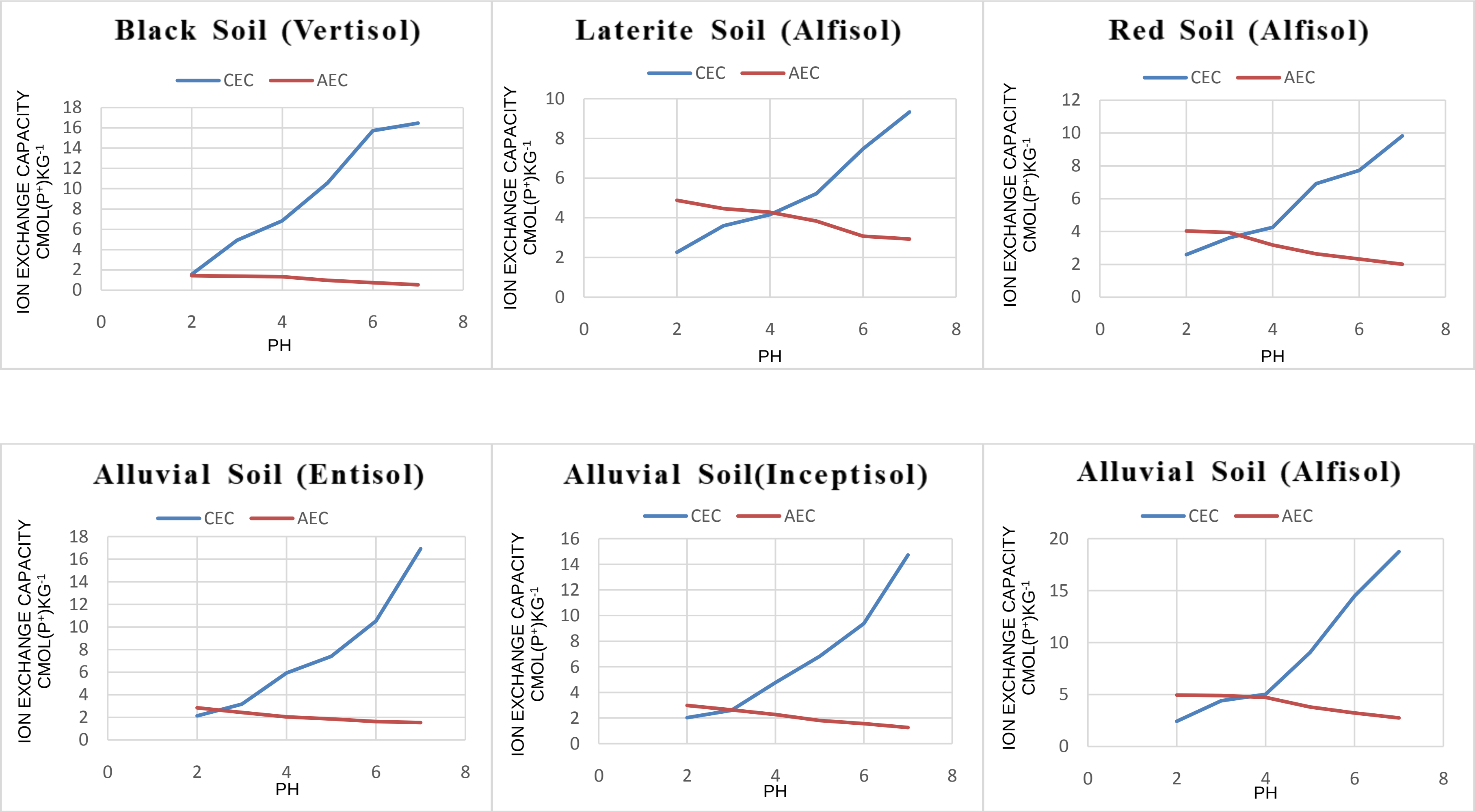


Figure 2. Point of zero net charge (PZNC) of the soil samples

A closer observation through the results revealed that for the alluvial soils of Assam, the PZSE and PZNC was in the order Entisol < Inceptisol < Alfisol and for Odisha soils, the lowest PZC components were noted in the order Vertisol (black soil) < Alfisol (red soil) < Alfisol (laterite soil). The general trend of PZC components for all the samples were significantly in line with the respective sesquioxide contents and soil weathering stages (as evidenced by the soil order), i.e., more weathered soils showed higher PZC values and vice-versa (Figure 3). These findings were in close association with the findings of [17].

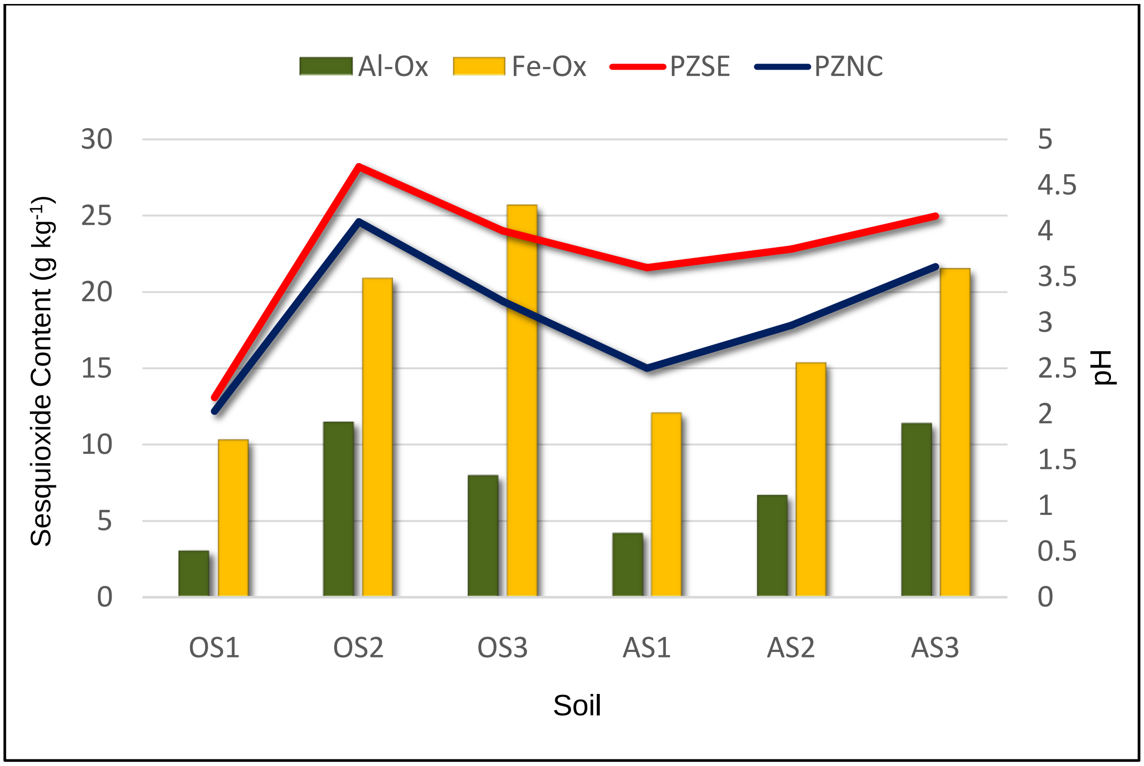


Figure 3. Relation between sesquioxides content in soil and PZC components

In all the samples, the PZSE points were achieved at a comparatively higher pH as compared to the PZNC points (Figure 4), which was because PZNC generally takes into account both the permanent and variable charge components of the soil system as against PZSE which is regulated only by the variable charge components. Since the permanent charge components are mostly negative in nature, the attainment of net charge neutralization in case of PZNC takes place relatively at lower pH in the soils [18]. Different pH points for PZSE and PZNC in every soil depict that all the samples under study had a mixture of both permanent and variable charge components [9] however with differential magnitude.

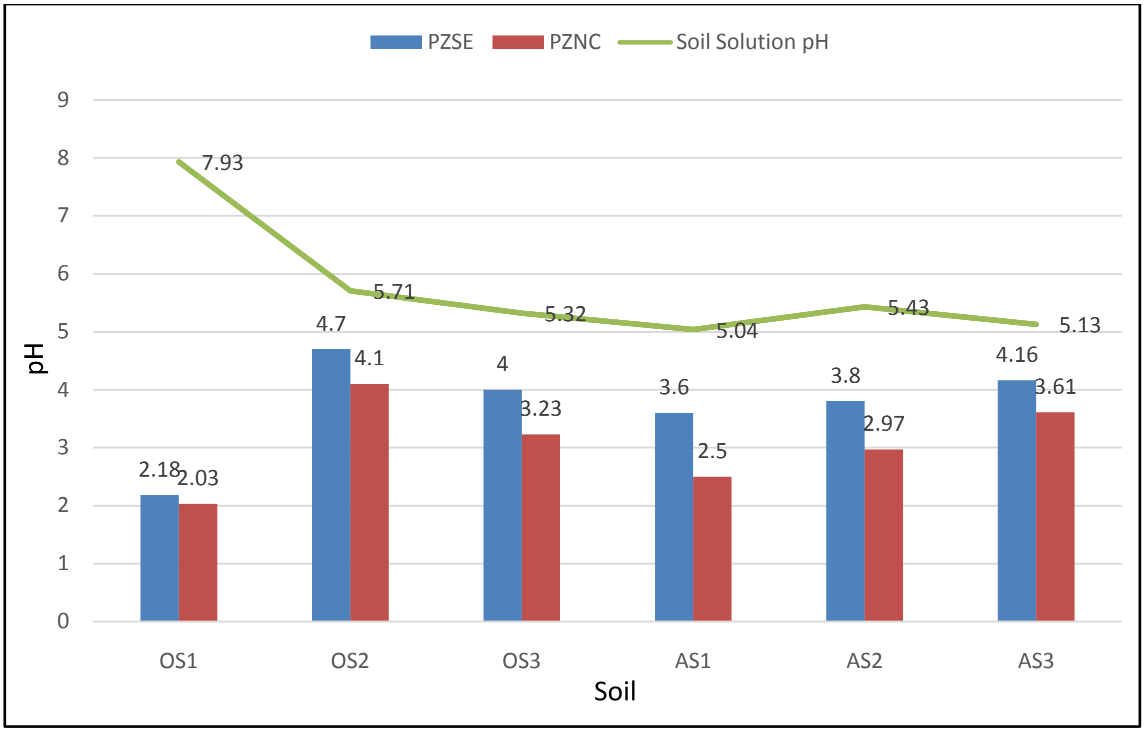


Figure 4. Variation in PZC components and solution pH of the untreated soil samples

For black soil (Vertisol)(OS1), the PZSE lay close to the PZNC point (Figure 4). Despite having limited amount of variable charged components, the permanent structural charges and high organic matter contributed towards such results. For the alluvial soil of the order Entisol, a high difference between the PZSE and PZNC points was recorded, probably due to the presence of high amounts of organic matter contributing to variable negative charges to the soil system [19]. On the other hand, a considerable difference was observed between the PZSE and PZNC points for the samples laterite (OS2) and red soil (OS3) of Alfisol order and alluvial soils of order Inceptisol (AS2) and Alfisol (AS3), owing to their better stages of weathering, indicating the presence of a fair amount of variable charge along with the permanent structural charges.

3.2 Correlation between PZC Components and Physicochemical Properties of Soil

Of all the studied parameters, the factors that showed high values Pearson's correlation coefficient (r) were clay content, organic carbon, and free iron and aluminium oxides, exchangeable Ca^{2+} and available P_2O_5 (Table 7). A significant correlation of the above-discussed parameters with soil PZC has also been reported by [20].

Table 7. Pearson's Correlation Coefficient between PZC components and soil parameters

Soil Parameters	**Pearson's Correlation Coefficient (r)**	
	PZSE	**PZNC**
Sand	0.823^{**}	0.906^{**}
Silt	-0.310	-0.577^{*}
Clay	-0.816^{**}	-0.718^{**}

pH	-0.785**	-0.543*
BD	0.787**	0.830**
Moisture Content at FC	-0.884**	-0.857**
OC	-0.816**	-0.846**
Ex. Na^{+}	-0.262	-0.390
Ex. K^{+}	-0.447	-0.261
Ex. Ca^{2+}	-0.869**	-0.637**
Ex. Mg^{2+}	-0.739**	-0.452
Ex. Al	0.165	-0.056
Av. N	-0.190	-0.411
Av. P_2O_5	0.653**	0.595**
Av. K_2O	-0.493*	-0.313
Av. S	0.001	-0.220
Fe-Ox	0.727**	0.775**
Al-Ox	0.854**	0.968**

** indicates 0.05 level of significance and ** indicates 0.01 level of significance*

3.2 Effect of Fertilizer Management practices on Soil PZC

There was an increase in PZSE and PZNC pH points for all the treated soil samples under incubation (Figure 5). Both PZSE and PZNC values decreased at 30 DAT in comparison to 15 DAT for all the samples (Table 8). After application of acidic fertilizers ionic strength of the soil solution increased and the suspension pH decreased causing more protonation resulting in an increased soil PZC [21]. With time, due to complex reactions taking place in the soil system involving specific and non-specific adsorption and ion exchange mechanisms, the soil PZC components probably decreased.

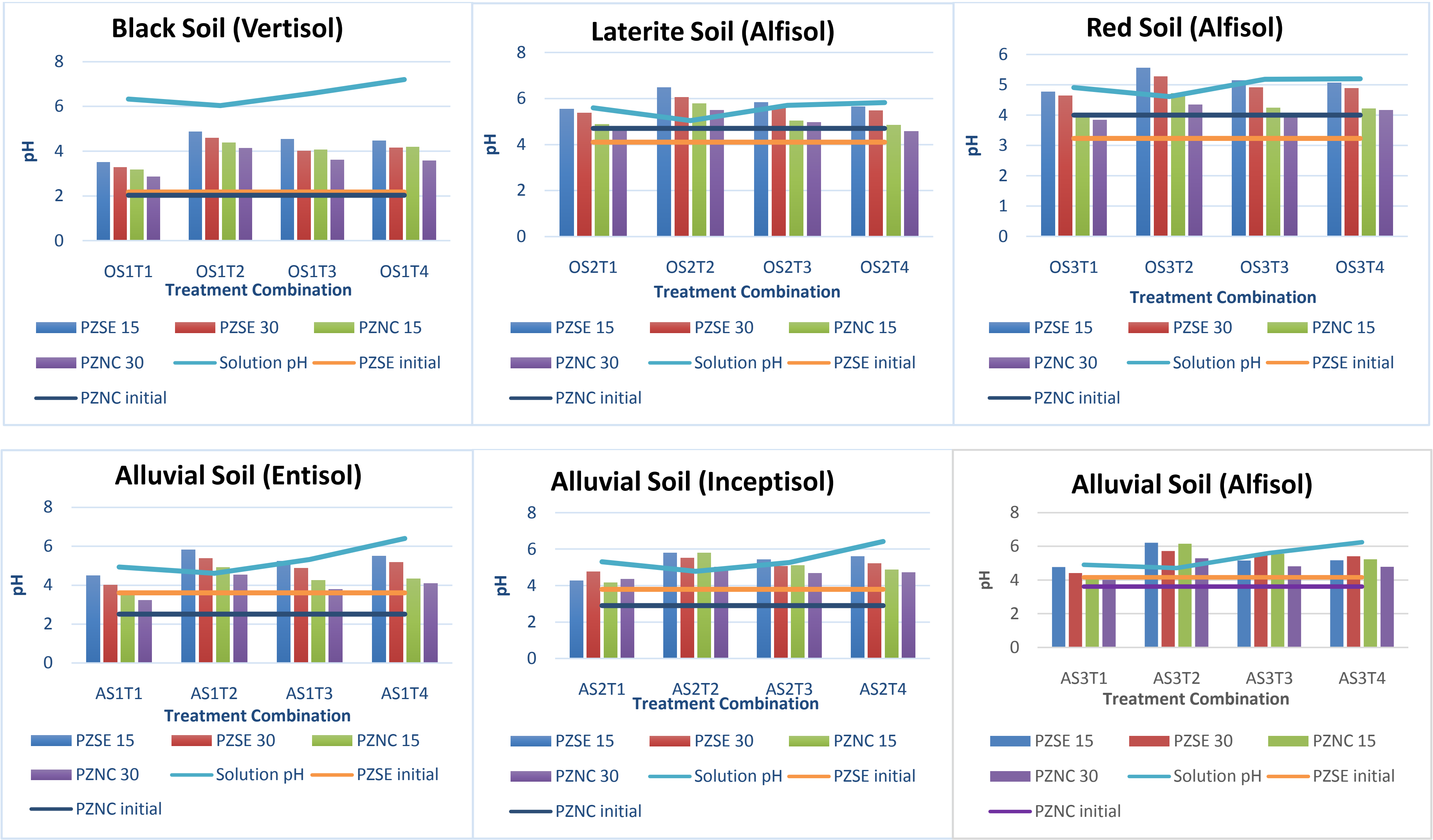


Figure 5. PZC components and solution pH of treated soils under incubation

(PZSE initial and PZNC initial are the PZC values of respective soils before treatment application)

Table 8. Interaction effect on the PZSE and PZNC in treated soil samples under incubation

Treatment Combination	PZSE		PZNC	
	15 DAT	30 DAT	15 DAT	30 DAT
Black Soil (Entisol)				
OS1T1	3.51	3.28	3.17	2.85
OS1T2	4.87	4.59	4.38	4.14
OS1T3	4.53	4.02	4.07	3.61
OS1T4	4.47	4.15	4.19	3.58
Laterite Soil (Inceptisol)				
OS2T1	5.54	5.38	4.87	4.62
OS2T2	6.47	6.05	5.78	5.49
OS2T3	5.83	5.59	5.03	4.96
OS2T4	5.64	5.47	4.84	4.58
Red Soil (Alfisol)				
OS3T1	4.77	4.64	4.06	3.84
OS3T2	5.56	5.28	4.72	4.35
OS3T3	5.14	4.91	4.24	4.07
OS3T4	5.07	4.88	4.22	4.16
Interaction Effect				
S.Em (±)	0.02	0.02	0.02	0.02
LSD (0.05)	0.07	0.07	0.08	0.08
Alluvial Soil (Entisol)				
AS1T1	4.48	4.00	3.65	3.21
AS1T2	5.81	5.36	4.91	4.52
AS1T3	5.22	4.87	4.25	3.78
AS1T4	5.48	5.17	4.32	4.08
Alluvial Soil (Inceptisol)				
AS2T1	4.26	4.77	4.17	4.35
AS2T2	5.79	5.51	5.79	5.02
AS2T3	5.44	5.06	5.10	4.67
AS2T4	5.61	5.21	4.88	4.72
Alluvial Soil (Alfisol)				
AS3T1	4.77	4.41	4.24	4.01
AS3T2	6.21	5.73	6.15	5.29
AS3T3	5.16	5.49	5.56	4.82
AS3T4	5.18	5.42	5.23	4.79
Interaction Effect				
S.Em (±)	0.03	0.03	0.02	0.02
LSD (0.05)	0.08	0.06	0.07	0.06

When compared between the treatments, the highest PZSE and PZNC were recorded under T2 followed by treatment T3, T4, and T1 (Table 8). An increased electrolyte concentration upon addition of inorganic fertilizers under treatment T2 might be the reason of increased

PZC values while in T1, the addition of organic manures must have increased the variable negative charge sites resulting in lower PZC [22]. Both PZSE and PZNC points recorded lower pH values at 30 DAT as compared to 15 DAT, with a pronounced effect in case of treatment T2, and a minimal effect in treatment T1. A significant negative correlation of organic matter with both PZSE (r = -0.553**) and PZNC (r = -0.587**) stands in support for this explanation. The treatments T3 and T4 gave almost similar results with a slightly lower PZC value under T4, due to Ca addition in the form of lime/gypsum that showed negative correlation with soil PZC (r = - 0.816** for PZSE, r = -0718** for PZNC).

The difference between the initial PZC values before fertilizer treatment and final PZC values of the fertilized samples was highest for black soil (Vertisol) that decreased from 15 DAT to 30 DAT (Figure 5). Such a result confer that these soils allow more availability of anions (anionic nutrients such as NO_3^-, PO_4^{3-}, SO_4^{2-}) immediately after fertilizer application, which slowly decreases with time thereby favouring an increase in CEC in the latter phase and enhancing availability of cationic nutrients such as NH_4^+, K^+, Ca^{2+}, etc. In case of the laterite and red soils of Alfisol order, the difference between initial and final PZC values were found to be very less, indicating the essentiality of frequent fertilizer application for better productivity. For the alluvial soils, the difference between the initial and final PZC values showed a decreasing trend in the order Inceptisol > Alfisol > AS1 Entisol, indicating the buffering capacity of these soils in the reverse order. Thus, the availability of cationic nutrients may be high in Entisol followed by Alfisol and Inceptisol and the opposite for that of anionic nutrients.

In the context of soil PZC, the availability of cationic and anionic nutrients is influenced by the difference between the soil solution pH and the PZC values of the soil. This difference was highest for Vertisol (OS1), followed by Entisol (AS1), Inceptisol (AS2), and Alfisol (AS3, OS2, OS3) soil orders as reflected in Figure 4 for untreated soils and Figure 5 for treated soils under incubation.

A higher difference between the solution pH and PZC indicates the persistence of negative charge potential over a wider pH range (i.e., from the pH corresponding to PZC up to the soil solution pH), thereby providing these samples (OS1, AS1) with good cation exchange capacities [13] favouring better retention of cationic nutrients and reduction in leaching losses. Under such a soil chemical environment, there is an enhanced availability of nutrients ions like N-NH_4^+, K^+, Ca^{2+}, Mg^{2+}, etc.

In the case of other test samples (i.e., OS2, OS3, AS2, and AS3), owing to advanced stages of weathering and high content of sesquioxides, the difference between their PZC values and soil solution pH was observed to be smaller [22]. A smaller difference between these pH points lowers the cation exchange abilities of the samples, favouring a comparative increase in the availability of anionic nutrients like NO_3^-, PO_4^{3-}, SO_4^{2-}, etc. Further, the lower magnitude of charge potential in these soils also enhances their ability for coagulation, flocculation, and better aggregate formation. These samples can therefore be considered structurally more stable.

Incubation study with different fertilizer management practices on soils resulted that the treatment consisting of RDF for NPK fertilizers (T2) rendered the highest values of PZC components which had direct bearing with availability of primary nutrients (Table 9). Highest amount of secondary nutrients in soil, conversely, corresponded to application of lime/gypsum in treatment T4 (Table 10), which supplied the primary nutrients were at optimum level. Higher PZC values indicated less difference between solution pH and PZC that reduced the CEC under treatment T2 leading to greater chances of nutrient losses through leaching. Thus, of all the treatments, treatment T4 comprising of FYM + NPK +

lime/gypsum can be considered as the best treatment regulating soil PZC and nutrient availability in soil.

Table 9. Interaction effect on the availability of primary nutrients in treated soil samples under incubation

Treatment Combination	Av. N 15 DAT	Av. N 30 DAT	Av. P_2O_5 15 DAT	Av. P_2O_5 30 DAT	Av. K_2O 15 DAT	Av. K_2O 30 DAT
Black Soil (Vertisol)						
OS1T1	363.78	342.09	11.87	8.94	281.03	255.77
OS1T2	521.94	472.33	18.41	16.51	375.81	370.99
OS1T3	492.32	413.61	16.89	15.06	339.82	309.69
OS1T4	446.78	403.60	14.81	11.63	352.19	341.47
Laterite Soil (Alfisol)						
OS2T1	283.34	225.79	21.31	18.03	251.57	23.74
OS2T2	487.08	424.70	38.55	33.92	372.22	345.83
OS2T3	452.74	373.60	35.81	36.93	307.20	266.43
OS2T4	323.60	288.51	29.22	26.70	337.62	324.39
Red Soil (Alfisol)						
OS3T1	301.06	224.56	15.84	12.71	260.35	245.98
OS3T2	512.08	464.83	27.33	25.91	380.82	341.39
OS3T3	461.27	440.45	26.45	28.02	337.63	272.71
OS3T4	338.67	300.70	22.63	24.72	3358.91	310.53
Interaction Effect						
S.Em (±)	2.25	2.16	0.12	0.12	2.55	4.16
LSD (0.05)	6.58	6.31	0.36	0.34	7.45	12.14
Alluvial Soil (Entisol)						
AS1T1	376.32	288.51	14.65	12.92	233.04	189.71
AS1T2	492.89	368.00	27.51	24.88	311.04	288.04
AS1T3	431.56	411.09	23.04	25.63	277.02	252.66
AS1T4	388.86	322.75	22.37	20.75	303.66	274.02
Alluvial Soil (Inceptisol)						
AS2T1	290.88	251.54	29.20	25.67	184.80	177.76
AS2T2	489.57	381.58	50.31	48.29	249.17	226.61
AS2T3	424.77	337.45	46.72	45.03	206.58	180.15
AS2T4	325.97	312.88	44.59	45.44	228.42	200.85
Alluvial Soil (Alfisol)						
AS3T1	341.58	245.79	22.59	20.05	181.50	170.30
AS3T2	472.42	392.45	32.67	28.40	279.11	252.50
AS3T3	432.04	338.69	29.47	27.23	205.68	192.92
AS3T4	361.23	313.25	25.08	27.66	232.65	221.08
Interaction Effect						
S.Em (±)	2.99	3.91	0.163	0.15	1.90	2.12
LSD (0.05)	8.74	11.43	0.47	0.45	5.55	6.19

Table 10. Interaction effect on the availability of secondary nutrients in treated soil samples under incubation

Treatment Combination	**Ex. Ca^{2+}**		**Ex. Mg^{2+}**		**Av. S**	
	15 DAT	**30 DAT**	**15 DAT**	**30 DAT**	**15 DAT**	**30 DAT**
Black Soil (Vertisol)						
OS1T1	11.40	12.40	2.50	3.50	42.33	36.19
OS1T2	10.90	13.40	2.25	3.90	48.91	39.40
OS1T3	11.70	13.30	2.65	4.10	46.80	40.41
OS1T4	16.81	20.42	3.02	4.57	57.82	44.94
Laterite Soil (Alfisol)						
OS2T1	0.71	0.85	0.55	1.20	32.04	26.93
OS2T2	1.35	1.60	1.05	2.15	36.72	31.49
OS2T3	1.00	0.95	1.10	1.60	33.69	30.22
OS2T4	3.72	4.64	1.68	2.49	35.81	32.97
Red Soil (Alfisol)						
OS3T1	0.55	0.95	1.05	1.96	34.26	32.00
OS3T2	1.15	1.37	0.90	0.88	44.18	37.40
OS3T3	0.95	1.75	1.65	1.60	41.72	35.09
OS3T4	3.46	4.21	1.87	1.72	42.61	36.76
Interaction Effect						
S.Em (±)	0.04	0.04	0.01	0.01	0.20	0.17
LSD (0.05)	0.10	0.13	0.02	0.04	0.60	0.50
Alluvial Soil (Entisol)						
AS1T1	0.25	0.45	0.20	0.15	74.03	72.88
AS1T2	0.65	0.55	0.26	0.22	77.30	75.77
AS1T3	1.10	0.65	0.35	0.28	79.30	78.53
AS1T4	2.43	3.05	0.83	1.43	84.27	81.93
Alluvial Soil (Inceptisol)						
AS2T1	2.15	2.25	1.80	1.85	51.33	47.65
AS2T2	2.20	2.40	1.95	2.00	55.02	54.84
AS2T3	2.95	2.30	2.15	1.95	53.75	50.27
AS2T4	6.23	7.89	3.18	2.73	57.38	54.11
Alluvial Soil (Alfisol)						
AS3T1	1.59	1.74	1.66	1.68	66.30	63.15
AS3T2	3.03	3.48	1.79	2.08	68.59	66.36
AS3T3	2.74	2.91	1.93	2.22	65.91	64.20
AS3T4	5.67	6.02	2.94	3.14	70.57	67.44
Interaction Effect						
S.Em (±)	0.01	0.02	0.01	0.01	0.33	0.32
LSD (0.05)	0.04	0.05	0.02	0.03	0.97	0.94

4. CONCLUSION

Since the studied soils contained a mixture of permanent and variable charged components as ascertained by differences in PZSE and PZNC values, they can be considered ideal for amendment through different fertilizer management practices. The PZC components were significantly influenced by physico-chemical factors like clay and organic carbon content, free sesquioxides, exchangeable calcium and available phosphorus in the soils. Due to the greater difference between the soil solution pH and PZC values in soils with high clay and organic matter content like Vertisol (black soil) and Entisol (alluvial soil), the exchange and availability of cationic nutrients (N-NH_4^+, K^+, Ca^{2+}, Mg^{2+}) get enhanced due to higher CEC while that of anionic nutrients like nitrate, phosphate, and sulphate gets affected. Therefore, the pH of these soils must be regulated for better availability of anionic nutrients. The highly weathered soil samples like alluvial soil, red soil and laterite soils of Alfisol order due to their smaller difference between soil solution pH and PZC values, and thus exhibiting optimal CEC over a narrow pH range, favour better availability of anionic nutrients (NO_3^-, PO_4^{3-}, SO_4^{2-}) and simultaneously require frequent fertilizer application along with organic manures for enhanced retention of nutrients, their mobility, and availability in soil.

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