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Distribution of different forms of acidity in some lateritic soils of Purulia district of West Bengal

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Abstract
Twenty four acid soil samples collected from six blocks of Purulia district representing part of red and lateritic belt of West Bengal and Alfisols soil order were analysed to characterise their nature of acidity and their relationship with soil properties. The mean values of total acidity (TA), hydrolytic acidity (HA) and exchange acidity (EA) were 1.91, 1.53 and 0.38 cmol (p^+) kg^{-1} which were ranged from 1.35-2.59, 1.20-1.94 and 0.15-0.65 cmol (p^+) kg^{-1} respectively. On an average, the contribution of electrostatically bound aluminium (Al^{3+}) and hydrogen (H^+) to exchange acidity varied from 60.0-80.0 and 20.0-40.0 per cent with the mean values of 70.42 and 29.58 per cent respectively. The different types of acidity were significantly and positively correlated with organic C, clay content and CEC of soil but negatively correlated with soil reaction (pHw and pHca). They also showed significant positive correlations with each other.

Keywords: Red and lateritic soil, Alfisols, forms of acidity, soil properties

Introduction
In India acid soils cover about 49 million hectares i.e., approximately 34% of cropped land (Maji *et al.*, 2012) [8]. The soils having pH less than 6.5 occupy approximately 90 million hectares of the total geographical area of India and around 25 million hectares of arable land in India was strongly acidic soils (pH < 5.5) (Sharma and Sarkar, 2005) [14]. Around 2.2 million hectares of West Bengal is under acid soil which is disseminated from foot-hill soils of North (Entisols) red and laterite soils of West (Alfisols) and coastal acid sulfate soils of south (Chand and Mandal, 2000) [3]. Soil acidity is one of the major soil problems which reduces the growth and yield of crops in vast areas of the world (Shainberg *et al.*, 1989) [13]. In red and lateritic zone of West Bengal, India, soil acidity poses a serious problem for crop production. Exchangeable hydrogen (H^+) and aluminium (Al^{3+}), oxides of iron (Fe) and Al, dominant clay minerals and organic matter are the key factors of forming acid soil (Panda *et al.*, 2009) [10]. Plant growth and productivity in acid soil is significantly restricted as these soils are less fertile (Bhat *et al.*, 2010) [1]. The proportion of different forms of acidities in such acid soils determines their nutrient holding capacities and lime requirement values. Knowledge of forms of acidity, therefore, helps in the management of acid soils. The objective of the study was to determine: (i) the different forms of acidity, (ii) interrelationship between various forms of acidity and selected soil properties.

Materials and Methods
Description of the sampling sites
Soil sampling was done from six blocks of Purulia district (Purulia I, Purulia II, Hura, Puncha, Manbazar I and Manbazar II) which represents a part of the red and lateritic belt of West Bengal. Purulia, the westernmost district of the Indian state of West Bengal and a part of Chotanagpur plateau, is located between 23º 42′ 00″ North and 22º 42′ 35″ South latitude and 86º 54′ 37″ East and 85º 49′ 25″ West longitude occupying an area of 6259 square kilometres. It is traversed by the Tropic of Cancer. These red and lateritic soil were developed in Chotanagpur Plateau having undulating topography. The mean annual precipitation of Purulia is varied from 1100 to 1500 mm and the relative humidity becomes high (~ 75-85%) but it drops down during hot season. Temperatures may be as low as 7 °C during cold winter season and 46 °C during hot summer. Kangsabati, Kumari, Dwarakeswar, Subarnarekha and Damodar are the dominant rivers of the district.

The soil fertility status is also very low. The soil is light and porous in nature with low organic matter, low available P, low micronutrients like zinc and boron contents and low water holding capacity.

Soil sampling and analysis
Twenty four soil samples were collected (0-0.20 m depth) during May 2017 from Purulia I, Purulia II, Hura, Puncha, Manbazar I and Manbazar II blocks of Purulia district representing part of the red and lateritic zone of West Bengal, India and also representing soil order of Alfisols. After collection they were air-dried, powdered and sieved (2 mm). The pH in soil water suspension i.e., pH_w (1:2.5::soil:water), pH in soil $CaCl_2$ suspension i.e., pH_{ca} (1:2.5::soil:0.1M $CaCl_2$ solution), oxidizable organic carbon (OC) (Walkley and Black, 1934) [16], clay content (hydrometer method) and various types of acidity like total acidity, exchange acidity, hydrolytic acidity, and electrostatically bound H^+ (EBH^+) and Al^{3+} ($EBAl^{3+}$) of the processed soil samples were estimated. Total acidity and exchange acidity of the soils were determined by extracting the soils with 1.0 M sodium acetate (pH 8.2) (Kappen, 1934) [5] and 1.0 M KCl (McLean *et al.*, 1965) [9] respectively and subsequently titrating with standard NaOH using phenolphthalein as an indicator. Electrostatically bound Al ($EBAl^{3+}$) was estimated in 1.0 M KCl extract by titrating with 0.1 N hydrogen chloride (HCl) after adding sodium fluoride (NaF). Electrostatically bound H^+ (EBH^+) was calculated simply by calculating the difference between exchange acidity and $EBAl^{3+}$. Hydrolytic acidity was calculated taking the difference between total acidity and exchange acidity (Peech *et al.*, 1962) [11].

Statistical Analyses
Standard statistical methods using Windows-based SPSS (20.0) was used to calculate the range, mean and standard deviation of studied soil parameters along with types of soil acidity and to calculate the Pearson's correlation coefficient among the forms of acidities and also with different soil properties.

Results and Discussion
Soil characteristics
Some important characteristics of soils of the studied sites are presented in Table 1. All the studied soils were acidic in nature varied from 4.5-5.4 (pH_w) and 4.2-5.2 (pH_{ca}) with mean pH values of 4.98 (pH_w) and 4.65 (pH_{ca}) (Table 1). Lower values of pH_{ca} than pH_w in all the soil samples explained that the soils were negatively charged and with low base saturation. Oxidizable organic carbon content (ranging from 1.75-3.97 g kg^{-1} with mean of 3.06 g kg^{-1}) was low due to rapid oxidation of organic matter in the study area because of high temperature of 42-46^{0}C during peak summer months. The mean clay content of the studied soils was 21.14% having range of 15.52-28.56%. The mean CEC of the soils was 9.00 cmol (p^+) kg^{-1}.

Forms of soil acidity
Range and mean values of different forms of acidities of the studied soil are presented in Table 2. The total acidity (TA) of the soils was varied from 1.35 to 2.59 cmol (p^+) kg^{-1} (Table 2). Similarly, the hydrolytic acidity (HA) and exchange acidity (EA) were varied from 1.20 to 1.94 and 0.15 to 0.65 cmol (p^+) kg^{-1} with the average of 1.53 and 0.38 cmol (p^+) kg^{-1}. Exchange acidity (EA) contributes around 19.38 % to total acidity (TA) with range value of contribution of 11.11 to 25.10 %. Das *et al.*, (1991) [4] in red-lateritic and terai soils and Chand and Mandal (2000) [3] in Entisols, Alfisols and Inceptisols of West Bengal also reported such low contribution of EA to TA. Bhat *et al.* (2017) [2] reported similar low contribution (19.7%) of EA to TA and Kundu (2017) [7] also reported that EA contributed 22.67% of TA. However, the mean value of contribution of hydrolytic acidity (HA) to TA was 80.62 % ranged from 74.90 to 88.89%. McLean *et al.* (1965) [9] reported that "the exchange acidity (EA) includes the exchangeable H^+ and Al^{3+} held at the permanent charge sites of the soil exchange complex". The ranges of electrostatically bound aluminium and hydrogen ions were 0.09-0.44 and 0.06 -0.21 cmol (p^+) kg^{-1} having average of 0.27 and 0.11 cmol (p^+) kg^{-1} respectively. The electrostatically bound hydrogen (EBH^+) contributed 20.0 to 40.0% (mean 29.58%) to EA. Although electrostatically bound aluminium ($EBAl^{3+}$) contributed 60.0 to 80.0% (mean 70.42%) to EA. Bhat *et al.* (2017) [2] and Kundu (2017) [7] also detected that contribution of EBH^+ to EA was lower than the contribution of $EBAl^{3+}$ to EA in some acid soils of West Bengal.

Correlation study on forms of soil acidities and soil properties
Different types of acidity were significantly correlated with the estimated soil properties (Table 3). It was observed that pH_w was significantly and negatively correlated with TA (r = -0.989**), HA (r= -0.986**), EA (r= -0.983**), $EBAl^{3+}$ (r= -0.971**) and EBH^+ (r= -0.883**). Similarly, pH_{ca} was significantly and negatively correlated with TA (r = -0.960**), HA (r= -0.955**), EA (r= -0.958**), $EBAl^{3+}$ (r= -0.955**) and EBH^+ (r= -0.838**). Organic C content of soil was also significantly and positively correlated with TA (r = 0.822**), HA (r= 0.818**), EA (r= 0.819**), $EBAl^{3+}$ (r= 0.856**) and EBH^+ (r= 0.619**) indicating the role of soil humus as a source of soil acidity by dissociating H^+ at varying pH (Sarkar *et al.*, 1997) [12]. According to Keeney and Corey (1963) [6] the different functional groups of organic matter having H^+ ions influence the forms and magnitude of soil acidity. Correlation study also showed that different forms of acidity were significantly and positively correlated with each which indicates existence of a dynamic equilibrium amongst different forms of acidity (Table 4). This significant positive correlation amongst different forms of acidity also indicates that liming should be done to ameliorate not only the active acidity and/or exchangeable Al but also all other forms of acidities present in soils. Correlation study also showed that the proportion of EA to TA would increase with decrease in pHw and increase with increase in pHca (Table 4). The similar result was also observed for the proportion of HA to TA (Table 4). Correlation study also showed that the proportion of EA to TA would increase with increase in organic C, clay, CEC of soil and reverse was the relationship for the ratio of HA to TA with organic C, clay, CEC of soil. Bhat *et al.* (2017) [2] and Kundu (2017) [7] also discoursed similar type of relationships between soil properties and forms of acidity, and among different forms of soil acidity in their study.

Table 1: Physico-chemical properties of the experimental soils

Locations	Sample No.	pHw (1:2.5)	pHca (1:2.5)	Organic C (%)	Clay (%)	CEC [cmol(p$^+$)kg^{-1}]
Purulia I	S1	4.9	4.6	3.87	15.86	9.05
	S2	5.0	4.6	3.20	20.23	8.10
	S3	5.3	4.9	1.95	16.52	7.59
	S4	5.1	4.8	2.80	17.12	8.12
Purulia II	S5	4.8	4.5	3.97	25.64	9.12
	S6	5.3	4.9	1.95	16.89	8.56
	S7	4.5	4.2	3.64	26.52	10.34
	S8	5.0	4.6	3.15	21.02	9.56
Hura	S9	5.0	4.7	3.55	22.68	9.45
	S10	4.8	4.5	3.92	25.18	9.56
	S11	5.3	4.9	1.75	16.52	7.12
	S12	4.6	4.3	3.54	25.23	10.12
Puncha	S13	4.8	4.5	3.96	25.85	9.52
	S14	5.1	4.7	2.70	21.25	9.28
	S15	4.5	4.2	3.25	28.56	10.45
	S16	5.4	5.2	2.40	15.52	9.49
Manbazar I	S17	5.1	4.7	2.30	19.12	7.21
	S18	5.4	5.2	2.20	17.52	8.72
	S19	4.8	4.5	3.35	22.12	9.52
	S20	4.8	4.4	3.40	25.35	9.85
Manbazar II	S21	4.6	4.3	3.85	26.23	10.25
	S22	5.1	4.7	3.05	17.86	8.54
	S23	5.0	4.7	3.70	19.96	9.60
	S24	5.3	5.0	1.95	18.56	6.89
Range		4.5-5.4	4.2-5.2	1.75-3.97	15.52-28.56	6.89-10.45
Mean		4.98	4.65	3.06	21.14	9.00
SD		0.28	0.28	0.74	4.06	1.04

Table 2: Different forms of acidity [cmol (p$^+$) kg^{-1}] of the studied soils

Locations	Sample No.	TA	HA	EA	EBAl^{3+}	EBH$^+$	% EBAl^{3+} of EA	% EBH$^+$ of EA	EA/TA	HA/TA	EBAl^{3+}/EA	EBH$^+$/EA
		[cmol (p$^+$) kg^{-1}]										
Purulia I	S1	2.04	1.58	0.46	0.34	0.12	73.91	26.09	0.23	0.77	0.74	0.26
	S2	1.91	1.51	0.40	0.31	0.09	77.50	22.50	0.21	0.79	0.78	0.23
	S3	1.51	1.26	0.25	0.15	0.10	60.00	40.00	0.17	0.83	0.60	0.40
	S4	1.68	1.37	0.31	0.21	0.10	67.74	32.26	0.18	0.82	0.68	0.32
Purulia II	S5	2.14	1.65	0.49	0.35	0.14	71.43	28.57	0.23	0.77	0.71	0.29
	S6	1.48	1.26	0.22	0.15	0.07	68.18	31.82	0.15	0.85	0.68	0.32
	S7	2.44	1.83	0.61	0.41	0.20	67.21	32.79	0.25	0.75	0.67	0.33
	S8	1.91	1.52	0.39	0.25	0.14	64.10	35.90	0.20	0.80	0.64	0.36
Hura	S9	1.98	1.56	0.42	0.29	0.13	69.05	30.95	0.21	0.79	0.69	0.31
	S10	2.14	1.66	0.48	0.38	0.10	79.17	20.83	0.22	0.78	0.79	0.21
	S11	1.44	1.24	0.20	0.14	0.06	70.00	30.00	0.14	0.86	0.70	0.30
	S12	2.34	1.79	0.55	0.39	0.16	70.91	29.09	0.24	0.76	0.71	0.29
Puncha	S13	2.19	1.70	0.49	0.36	0.13	73.47	26.53	0.22	0.78	0.73	0.27
	S14	1.76	1.44	0.32	0.24	0.08	75.00	25.00	0.18	0.82	0.75	0.25
	S15	2.59	1.94	0.65	0.44	0.21	67.69	32.31	0.25	0.75	0.68	0.32
	S16	1.35	1.20	0.15	0.09	0.06	60.00	40.00	0.11	0.89	0.60	0.40
Manbazar I	S17	1.76	1.45	0.31	0.22	0.09	70.97	29.03	0.18	0.82	0.71	0.29
	S18	1.50	1.29	0.21	0.14	0.07	66.67	33.33	0.14	0.86	0.67	0.33
	S19	2.08	1.65	0.43	0.31	0.12	72.09	27.91	0.21	0.79	0.72	0.28
	S20	2.19	1.71	0.48	0.37	0.11	77.08	22.92	0.22	0.78	0.77	0.23
Manbazar II	S21	2.42	1.85	0.57	0.41	0.16	71.93	28.07	0.24	0.76	0.72	0.28
	S22	1.76	1.46	0.30	0.24	0.06	80.00	20.00	0.17	0.83	0.80	0.20
	S23	1.84	1.51	0.33	0.24	0.09	72.73	27.27	0.18	0.82	0.73	0.27
	S24	1.47	1.28	0.19	0.12	0.07	63.16	36.84	0.13	0.87	0.63	0.37
Range		1.35-2.59	1.20-1.94	0.15-0.65	0.09-0.44	0.06-0.21	60.0-80.0	20.0-40.0	0.11-0.25	0.75-0.89	0.60-0.80	0.20-0.40
Mean		1.91	1.53	0.38	0.27	0.11	70.42	29.58	0.19	0.81	0.70	0.30
SD		0.35	0.21	0.14	0.11	0.04	5.41	5.41	0.04	0.04	0.05	0.05

TA=Total acidity, HA= Hydrolytic acidity, EA= Exchange acidity, EBAl^{3+} and EBH$^+$= Electrostatically bound aluminium and hydrogen respectively

Table 3: Simple Pearson correlation coefficient (r) values between different soil properties with different forms and their proportions of soil acidity

Variables	pHw	pHca	Organic C	Clay	CEC
Total acidity (TA)	-0.989**	-0.960**	0.822**	0.900**	0.753**
Hydrolytic acidity (HA)	-0.986**	-0.955**	0.818**	0.907**	0.760**
Exchange acidity (EA)	-0.983**	-0.958**	0.819**	0.881**	0.734**
$EBAl^{3+}$	-0.971**	-0.955**	0.856**	0.870**	0.715**
EBH^{+}	-0.883**	-0.838**	0.619**	0.794**	0.684**
EA/TA	-0.947**	-0.944**	0.842**	0.823**	0.669**
HA/TA	0.947**	0.944**	-0.842**	-0.823**	-0.669**
$EBAl^{3+}$/EA	-0.379	-0.445*	0.527**	0.309	0.189
EBH^{+}/EA	0.379	0.445*	-0.527**	-0.309	-0.189

* and ** indicate correlation is significant at the 0.05 and 0.01 level (two tailed); $EBAl^{3+}$, EBH^{+} represent electrostatically bound aluminium and hydrogen respectively.

Table 4: Simple Pearson correlation coefficient (r) values among different forms of soil acidity

Variables	Total acidity	Hydrolytic acidity	Exchange acidity	$EBAl^{3+}$	EBH^{+}
Total acidity	1.000				
Hydrolytic acidity	0.997**	1.000			
Exchange acidity	0.994**	0.983**	1.000		
$EBAl^{3+}$	0.984**	0.977**	0.985**	1.000	
EBH^{+}	0.887**	0.870**	0.904**	0.818**	1.000

* and ** indicate correlation is significant at the 0.05 and 0.01level (two tailed); $EBAl^{3+}$, EBH^{+} represent electrostatically bound aluminium and hydrogen respectively.

Conclusions

The different forms of acidity like total acidity (TA), hydrolytic acidity (HA) and exchange acidity (EA) was varied in the studied acidic Alfisols of Purulia district of red and lateritic belt of West Bengal. Contributions of HA and EA to TA and that of $EBAl^{3+}$ and EBH^{+} to EA was also varied widely. Studied forms of soil acidity showed significant positive correlations with organic C, clay content and CEC and but negative correlations with pHw and pHca. Again, there was significant positive correlations among different types of soil acidity.

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