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Correlation of Cationic Indices with Clay Dispersion Degree of Two Soils from Brazil Fertilized with Chicken Manure

Thadeu Rodrigues de Melo[1*], Wesley Machado[1] and João Tavares Filho[1]

[1]*Department of Agriculture, State University of Londrina, Londrina, Brazil.*

Authors' contributions

This work was carried out in collaboration between all authors. Author TRM designed the study, wrote the protocol, wrote the first draft of the manuscript and managed the literature searches. Authors TRM, WM and JTF managed the laboratorial analyses of the study, the experimental process and the statistical analyses. All authors read and approved the final manuscript.

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ABSTRACT

Aims: The aim of this work was to evaluate ESR (Exchangeable Sodium Ratio), $MCAR_{ex}$ (Monovalent Cation Adsorption Ratio) and $CROSS_{ex}$ (Cation Ratio of Soil Structural Stability) as indices, using exchangeable cations in calculations, to predict clay dispersion behavior in two soils with chicken manure application.
Study Design: Pots were completely randomized, with 10 replications per treatment.
Place and Duration of Study: A Red Latosol and a Red-Yellow Ultisol from Brazil were sampled. Pots were conducted in a greenhouse in Londrina - Paraná during 90 days.
Methodology: Chicken manure doses (0, 4, 8, 16 and 32Mg ha^{-1}) were applied and mixed with the soils. After 90 days of irrigation, samples were analyzed for Ca^{2+}_{ex}, Mg^{2+}_{ex}, K^{+}_{ex}, Na^{+}_{ex}, organic matter, pH_{water}, $pH_{KCl\ (1N)}$ and water dispersible clay. Clay dispersion degree, point of zero charge, ΔpH, ESR, $MCAR_{EX}$ and $CROSS_{EX}$ were calculated. ANOVA was calculated and the better-fit regression equation was shown.

**Corresponding author: E-mail: thadeurodrigues@yahoo.com.br;*

Results: No accurate relationship was found between ESR, $MCAR_{EX}$ or $CROSS_{EX}$ with clay dispersion degree.
Conclusion: ESP, $MCAR_{ex}$ and $CROSS_{ex}$ did not have enough correlation with clay dispersion of studied soils. More information about soil net charge, organic matter, Fe and Al (hydr) oxides are needed to a high scope index of soil structural stability.

Keywords: Flocculation; point of zero charge; organic fertilization; soil physics; soil fertility.

1. INTRODUCTION

Chicken meat production is expanding in Brazil since 1960 [1]. South region has received more investments and became Brazil's biggest producer [2]. Nowadays, Brazil is the biggest exporter and the third producer of chicken meat in the world and Paraná is the state with highest production [3]. In 2012, Brazil had over 1 billion heads of roosters, pullets, chickens and chicks [4]. Brazilian production of chicken manure goes around 1.35kg $chicken^{-1}$ [5]. Therefore, chicken manure inappropriate destination can cause many environmental problems due to the high produced volume and nutrients concentration. Many farmers use this residue as an organic fertilizer believing its use improves soil chemical and physical attributes. However, they do not evaluate the effect of their practices on soil physical changes. Moreover, little is known about the effects of chicken manure on physical and physicochemical properties of Brazilian soils.

Chicken manure produced in Brazil has a high concentration of monovalent cations, mainly K^+ and Na^+ [5,6]. These cations can expand diffuse double layer and disperse clays [7]. This effect is more important when soil has a lack of tri and/or divalent cations. Chicken manure also changes soil pH, commonly rising it [8,9]. The point of zero charge (pH_{PZC}) of Brazilian soils is usually smaller than pH_{Water}, therefore, an increase in pH_{Water} enhances net negative charge and clay dispersion tends to increase as well.

Water dispersible clay is a very important physical parameter of soils. It correlates with aggregation, porosity, density, soil erodibility [10], hydraulic conductivity [11,12] and pollutants transport [13].

Net charge is the most important factor in clay dispersion [14]. For soils with pH-dependent charges, the net charge is according to the difference between pH_{water} and point of zero charge (pH_{PZC}). ΔpH can be used to access soil net charge [15-18]. Some parameters that affect electrical double layers thickness such as ion valence and electrolyte concentration affect clay dispersion as well [14]. The increase in cations concentration or valence compresses electrical double layer, reducing particles' repulsive forces [19]. Fe and Al (hydr) oxides are efficient flocculant agents. Amorphous forms of Fe are more efficient causing flocculation than crystalline forms [20,21]. Organic matter polymers can bind clays and reduce their dispersion or favor it when polymer coats theparticles [22]. Multivalent cations can attach anionic organic polymers into the surface of the colloids and bind them [22]. Therefore, the dispersion of soil clays will depend on the balance between net charge, ions and organic polymers in the medium.

Sodium adsorption ratio (SAR) is used to evaluate the quality of irrigation water [23,24], but it is also used as a soil index [25,26] that correlates with clay dispersion and structural stability [23]. High values of SAR are associated with high clay dispersion, small structural stability and soil physical degradation [27,28].

In order to quantify the effect of K^+ and NH_4^+ as well, Smiles and Smith [29] proposed the monovalent cation adsorption ratio (MCAR) index. K^+ and NH_4^+ must be included because they can expand electrical double layer and be important to soils' structural stability.

Considering the major soil cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) have different dispersant or flocculant capacity, Marchuk and Rengasamy [30] proposed the use of cation ratio of soil structural stability (CROSS) index, based on Smiles and Smith equation. This index considers these differences through constant relationships between the flocculant powers of cations related to Na^+. Their relatives flocculant capacities are 1; 1.8; 27 and 45 for Na^+, K^+, Mg^{2+} and Ca^{2+}, respectively and are obtained by the flocculating power equation [30]. It means that a solution of Na^+ must be 45 times more concentrated than a Ca^{2+} solution to induce a similar quantity of flocculation.

Higher indices values are associated with an increase in clay dispersion. All the indices cited above consider monovalent cations always disperse and bivalent cations always flocculate the soil, but experimental observations can show contradictions, such as Mg^{2+} causing clay dispersion increment if compared to Ca^{2+} [12]. The indices cited above use the equilibrium cations at 1:5 soil:water ratio in calculations. In Brazil, farmers commonly have only soil exchangeable cations in routine soil analysis.

Due to the high amount of chicken manure produced in Paraná State, its high monovalent cations concentration and the lack of soil physical analyses at commercial farms, indices based on accessible attributes, such as exchangeable cations, which correlates with clay dispersion, are of great practical interest. These indices can guide soil fertilizers management to improve chemical and physical attributes.

Exchangeable cations can be used in the calculations by multiplying SAR with Gapon's constant. The index calculated with exchangeable cations is known as ESR (Exchangeable Sodium Ratio) [31]. A similar transformation was done for MCAR and CROSS, obtaining MCARex and CROSSex (formulas are shown in section 2.3).

The hypothesis is that clay dispersion will increase with dosages due to the increase in pH_{Water} and monovalent cations concentration. We also hypothesized the increase in clay dispersion will correlate with ESR, $MCAR_{ex}$ and $CROSS_{ex}$.

The goal of this work is to correlate clay dispersion with three indices, using exchangeable cation in calculations, to evaluate their potential use as physical quality indices for two important Brazilian soilsclassesmixed with chicken manure.

2. METHODOLOGY

2.1 Soils and Manure Collecting

Two soils were collected. The Red Latosol (RL) was situated under native rainforest, in Londrina city and the Red-Yellow Ultisol (RYU) was under pasture, in Jaguapitã city, both in Parana state. Soils were collected at the 0-20cm layer, air-driedand sieved (2 mm).

The chicken manure was collected from a commercial aviary in Londrina city after six flocks of chickens. Producers deposited wood shavings in the ground to reduce ammonia volatilization. Wood shavings plus chicken's excreta constitute the chicken manure. The average chicken density used in the aviary was 12 chickens m^{-2} and the fattening time of each flock was 46 days.

2.2 Soils and Manure Characterization

Soils and chicken manure were characterized (Table 1 and 2, respectively) before their use in the experiment. Soil chemical analyses were done according to [32] and the physical ones according to [33]. Chicken manure was characterized without sieving and sieving at 2 mm. The methodology used to access chicken manure nitrogen content was semi-micro Kjeldahl, with sulfuric acid titration [34]. C and N in chicken manure are shown in dry matter basis. pH_{CaCl2} was done in a 1:2.5 ratio (*v:v*).

2.3 Experiment and Soil Analyses

The experiment was conducted in pots filled with 1 dm^{-3} of soil, mixed with not composted and not sieved chicken manure of wood shavings. The doses applied were equivalent to 0, 4, 8, 16 and 32 Mg of dry matter ha^{-1} (*m:v*), considering 0,20 m of incorporation. The pots were irrigated three times a weekwith distilled water. Water content was maintained at 80% of saturation humidity for RL and 60% for RYU, by weight difference. After 90 days, soils were removed from pots, air-dried, sieved (2 mm) and analyzed.

According to [32], exchangeable basic cations (Ca^{2+}_{ex}, Mg^{2+}_{ex}, K^{+}_{ex}, Na^{+}_{ex}), potential acidity (H + Al), pH_{Water}, $pH_{KCl\ (1N)}$ and soil organic matter content (SOM) were evaluated. Ca^{2+} and Mg^{2+} were extracted with a KCl (1 N) solution. Ca^{2+} and Ca^{2+}+Mg^{2+} were titrated by EDTA. $Mg^{2+}$was calculated by difference.

Table 1. Characterization of Red Latosol (RL) and Red-Yellow Ultisol (RYU)

Soil	$H+Al^{3+}$ [a]	Ca^{2+}_{ex}	Mg^{2+}_{ex}	K^{+}_{ex}	Na^{+}_{ex}	Al^{3+}_{ex}	CEC [b] $pH_{7,00}$	P [c]	V [d]	pH $_{H2O}$	OM [e]	Clay	Silt	Sand
		---------------------------- cmolc dm^{-3}				------------------------------		mg dm^{-3}	- % -		----------------- g kg^{-1}		------------------	
RL	4.28	10.41	2.04	0.37	0.12	0.035	17.1	7.1	74.97	5.38	21.4	681.3	213.3	105.4
RYU	3.18	1.84	0.49	0.34	0.11	0.000	6.94	2.3	54.20	6.00	5.4	107.1	29.6	863.3

[a] Potential acidity; [b] Cation exchange capacity; [c] Phosphorous – Mehlich-1; [d] Basic cations saturation; [e] Organic matter

Table 2. Chicken manure characterization

Sieve	pH $CaCl_2$	Water Content	C [b] total	N [c] total	C/N [d]
mm		-- %	--		
-------[a]	7,3	17,53	28,34	2,89	9,81
< 2	7,8	21,47	22,55	4,53	4,98

[a]Not sieved; [b] Carbon; [c] Nitrogen; [d] Carbon/Nitrogen ratio

Phosphorous, K^+ and Na^+were extracted with MEHLICH-1. Soil total organic carbon was oxidized with potassium dichromate through Walkley-Black methodology and soil organic matter content was calculated by multiplying total organic carbon with "van Bernmelen factor" of 1.724. Potential acidity (H+Al) was estimated with pH_{SMP} methodology. All pH evaluations were made in a 1:2,5 (*v*:*v*) proportion. Point of zero charge (pH_{PZC}) [35], ΔpH, ESR, $MCAR_{ex}$ and $CROSS_{ex}$ indices were calculated according to the following formulas:

$$pH_{PZC} = 2pH_{KCl(1N)} - pH_{Water} \tag{1}$$

$$\Delta pH = pH_{KCl(1N)} - pH_{Water} \tag{2}$$

$$ESR = \frac{Na^+_{ex}}{Ca^{2+}_{ex} + Mg^{2+}_{ex}} \tag{3}$$

$$MCAR_{ex} = \frac{Na^+_{ex} + K^+_{ex}}{Ca^{2+}_{ex} + Mg^{2+}_{ex}} \tag{4}$$

$$CROSS_{ex} = \frac{Na^+_{ex} + 0.56K^+_{ex}}{Ca^{2+}_{ex} + 0.6Mg^{2+}_{ex}} \tag{5}$$

Where: Na^+_{ex}, K^+_{ex}, Mg^{2+}_{ex} and Ca^{2+}_{ex} means exchangeable Sodium, Potassium, Magnesium and Calcium, respectively.

Water dispersible clay content was obtained by pipette method after adequate sedimentation time according to Stokes' law [33]. 20g of soil and 0.1L of distilled water were added in bottles and mixed in an orbital horizontal agitator at 200 rpm. After 1 hours the bottles' content was put in 1L beakers and then filled with distilled water [36]. This methodology was chosen due its smaller mechanical dispersion potential, if compared with the used in Brazil [37]. Beakers' content was mixed during 30 s and pipetted after 4h to 0.05m depth. Total clay analysis was done the same way as dispersed clay, except by the addition of 0.010L of NaOH (1N) before agitation. Clay dispersion degree (CDD), in g kg^{-1}, was obtained by the formula below.

$$CDD\ (g\ kg^{-1}) = \frac{(1000\ Dispersible\ clay)}{Total\ clay} \tag{6}$$

2.4 Experiment Design and Statistical Analyses

Each treatment had ten replications, with pots randomly disposed. Data normality and variance homogeneity were evaluated by Shapiro Wilk [38] and Hartley [39] methodologies, respectively. Data normality and variance homogeneity are ANOVA's requirements. If these parameters were adequate, ANOVA was calculated and, in case of sufficient small *P*-value of "F", the better-fit regression equations were shown. All analysis, except Hartley's which was done by hand, were done using the software SISVAR [40].

As all indices (ESR, $MCAR_{ex}$ and $CROSS_{ex}$) had variance heterogeneity, we decided to avoid data transformation, which would complicate their interpretation. Therefore, ANOVA and regression equations were not calculated and only average values and standard deviation bars are shown.

Spearman's correlation coefficients and their significance for population extrapolation were calculated as well.

3. RESULTS AND DISCUSSION

$K^+$is the prevalent monovalent cation in Brazilian chicken manures [5,6]. Monovalent cations, K^+_{ex} and Na^+_{ex}, had the same angular coefficient for both soils, with three times more K^+_{ex} than Na^+_{ex} (Fig. 1, Fig. 2 and Table 3). K^+_{ex} became more important than Mg^{2+}_{ex} in RYU (Fig. 2) due to the small cation exchange capacity (Table 1). The difference of K^+_{ex} over Na^+_{ex} in chicken manure is quantified only by $CROSS_{ex}$ index, which considers these two cations and their flocculant power differences. $MCAR_{ex}$ considers K^+ and Na^+ as well, but does not differentiate them. Therefore, monovalent cation type does not change $MCAR_{ex}$ value.

As an increment of monovalent over bivalent cations was observed for both soils, all indices increased too (Fig. 3 and Fig. 4). The increment of indices indicates an expansion in electrical double layer thickness [41], enhancing repulsive forces and favoring dispersion. Reports in literature shows direct association between monovalent cations increment, over bivalent ones, and clay dispersion [27,42].

Although the indices increased with chicken manure dosages, clay dispersion degree did not change in both soils (Fig. 5). Small Spearman correlations between the indices and clay dispersion degree for both soils and negative coefficients for RL suggest other factors are influencing clay dispersion behavior (Table 4). Therefore, the evaluation of these cations is not enough to predict clay dispersion degree influenced by chicken manure application in the studied soils.

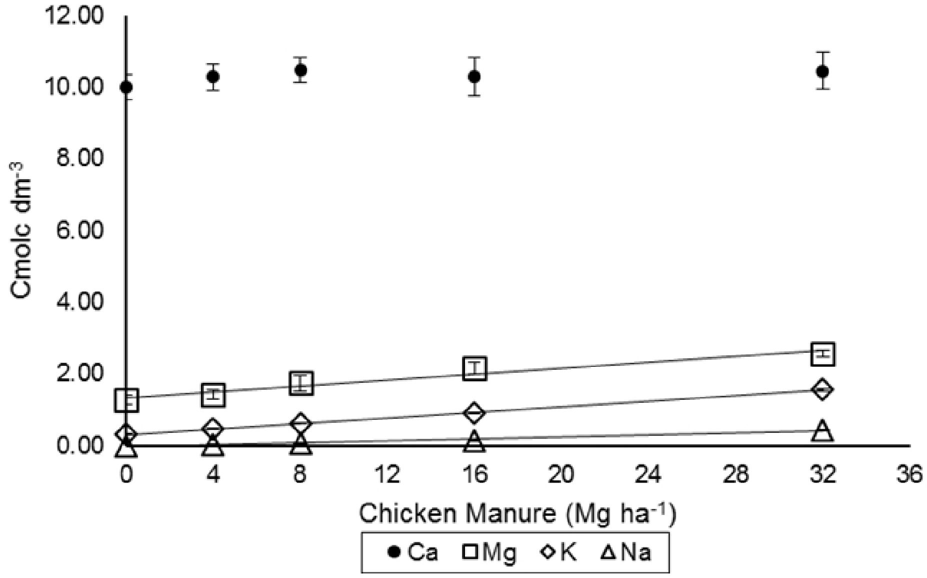

Fig. 1. Exchangeable cations in Red Latosol (RL) in function of chicken manure doses
No equation was adjusted for Calcium because of ANOVA's high P-value
Standard error bars are shown
ANOVA's and regression's parameters are shown in Table 3

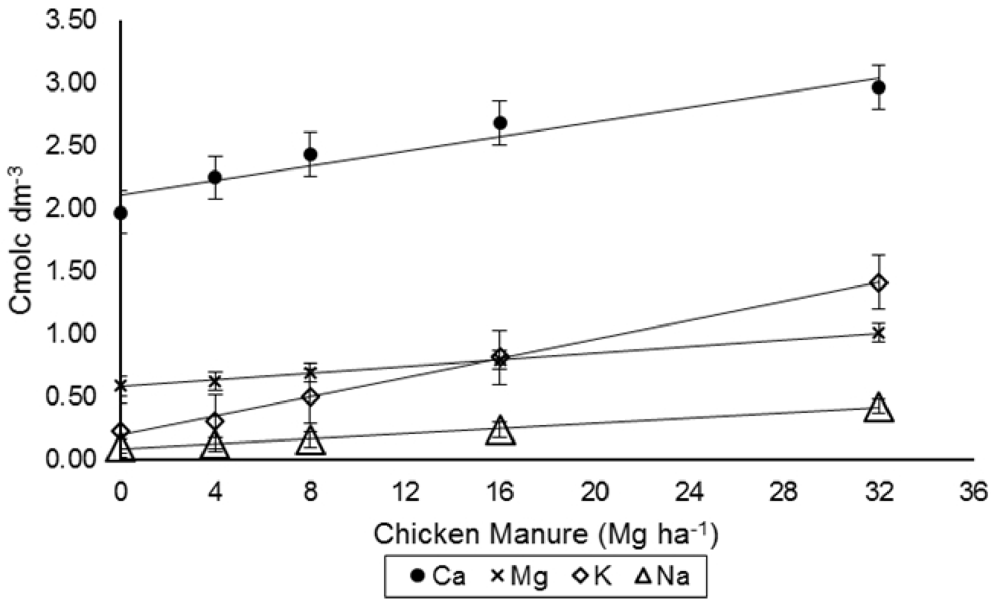

Fig. 2. Exchangeable cations in Red-Yellow Ultisol (RYU) in function of chicken manure doses
Standard error bars are shown, ANOVA's and regression's parameters are shown in Table 3

Table 3. *P*-values from ANOVA and regression (Regr.), r² and better-fit equations (Y =) for cations content due to chicken manure application in Red Latosol (RL) and Red-Yellow Ultisol (RYU)

	Red Latosol				Red-Yellow Ultisol			
	ANOVA	Regr.			ANOVA	Regr.		
	P-value	*P*-value	r^2	Y =	*P*-value	*P*-value	r^2	Y =
Ca_{ex}	.5859	-----------	.3835	10.303[a]	<.001	<.001	.9232	0.29169x+2.11018
Mg_{ex}	<.001	<.001	.9533	0.040906x+1.34213	<.001	<.001	.9989	0.01339x+0.58375
K_{ex}	<.001	<.001	.9989	0.038709x+0.31093	<.001	<.001	.9966	0.03793x+0.20003
Na_{ex}	<.001	.0103	.9752	0.013013x -0.02255	<.001	<.001	.9908	0.01024x+0.09015

[a]*Considered as a constant because of ANOVA's high P-value, the value is an average of all doses of chicken manure*

Table 4. Spearman's correlation coefficients and coefficients' significance (*P*-value) between clay dispersion degree and ESR, $MCAR_{ex}$, $CROSS_{ex}$ and ΔpH for Red Latosol (RL) and Red-Yellow Ultisol (RYU)

Soil	Indices			ΔpH
	ESR	$MCAR_{ex}$	$CROSS_{ex}$	
RL	-0.135	-0.116	-0.121	-0.056
P-value	.400	.469	.449	.726
RYU	0.165	0.023	0.061	-0.001
P-value	.254	.874	.676	.995

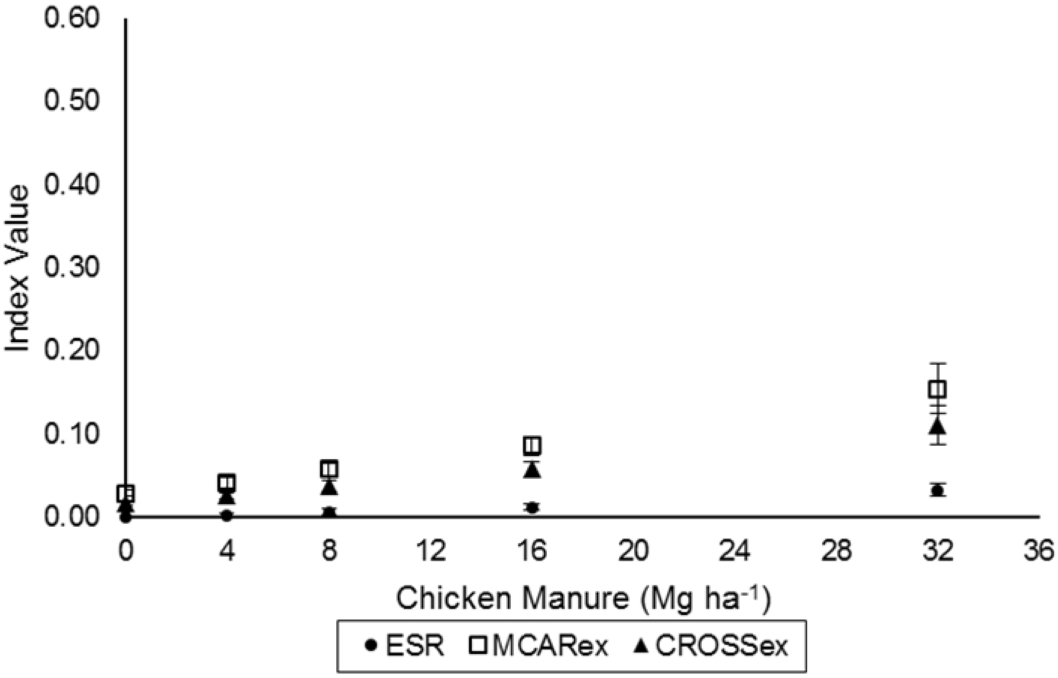

Fig. 3. ESR, $MCAR_{ex}$ and $CROSS_{ex}$ indices due to chicken manure dosages in Red Latosol (RL)

ANOVA and regressions were not calculated due to variance heterogeneity and to avoid indices transformation Standard deviation bars are shown

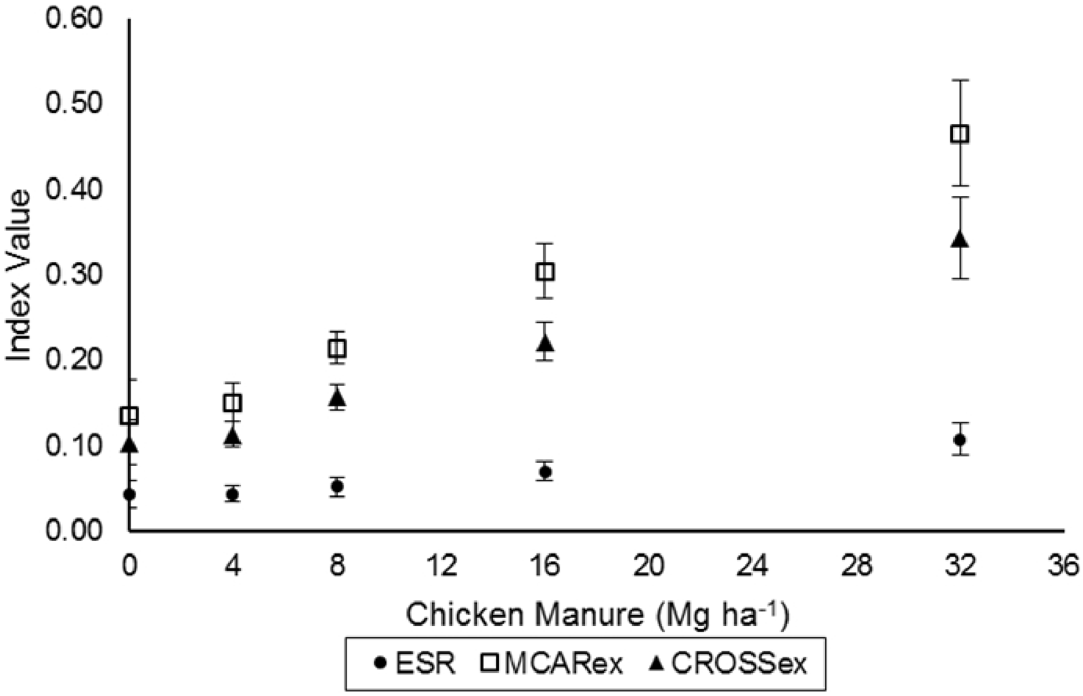

Fig. 4. ESR, $MCAR_{ex}$ and $CROSS_{ex}$ indices due chicken manure dosages in Red-Yellow Ultisol (RYU)

ANOVA and regressions were not calculated due variance heterogeneity and to avoid indices transformation, Standard deviation bars are shown

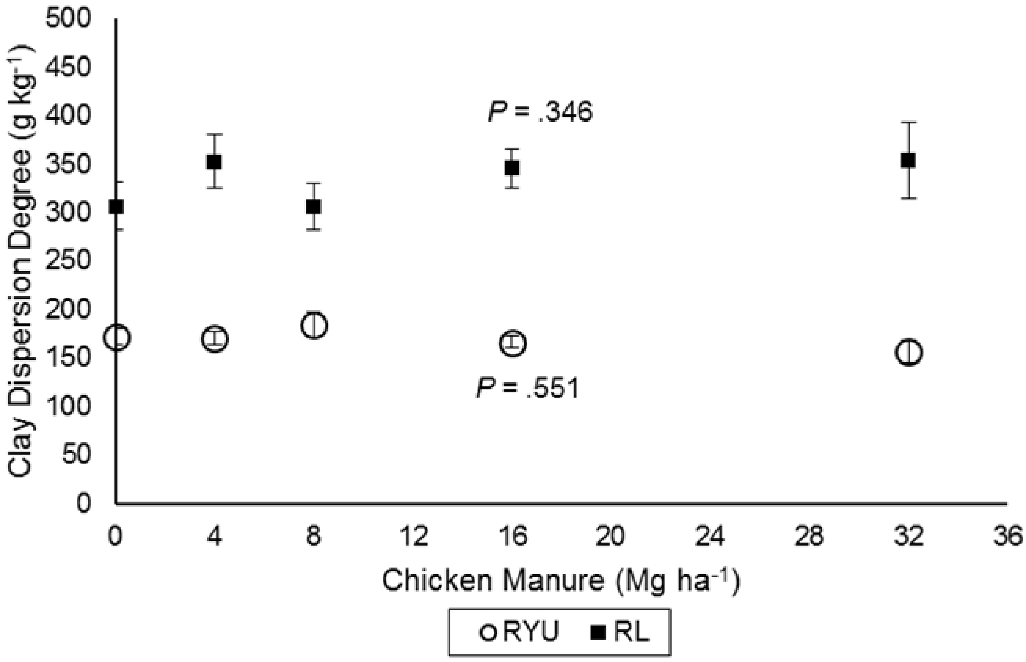

Fig. 5. Clay dispersion degree in Red Latosol (RL) and Red-Yellow Ultisol (RYU) according to chicken manure doses

No equation was adjusted for both soils because of ANOVA's high P-value, Standard error bars are shown

For RL, no change was found in ΔpH, which is related with particles' net charge (Fig. 6). Considering that for variable charge soils, the net charge depends on the distance between pH_{PZC} and pH_{Water}, the high buffering capacity of this soil can explain the lack of alterations in ΔpH. High buffering capacity originates from high clay and organic matter content (Table 1). pH_{Water} increased more sharply in RYU than in RL (Figs. 7 and 8) due to buffering capacity differences.

In RYU, the approximation between pH_{Water} and pH_{PZC} at higher doses (Fig. 8) is the reason for ΔpH changes. Considering net charge is the major factor controlling clay dispersion [14] and that in RYU it is approaching zero (Fig. 6), a reduction of clay dispersion degree was expected due to changes in electric double layers repulsion forces [43].

In a similar experiment with sewage sludge, [16] found a high relation between water dispersible clay content and ΔpH values in a very clayey soil (r^2 = 0.94) and a moderate relation with a medium texture soil were found (r^2 = 0.64). These soils were collected from the same cities of the ones used in this experiment.

In RYU, ΔpH changes probably did not reduce clay dispersion due to the high increment of monovalent cations (Fig. 2). Changes in ΔpH, tending to flocculation, are being counterbalanced by K^+_{ex} and Na^+_{ex} increment, tending to dispersion and as result, clay dispersion degree is stable and no correlation was found between ΔpH and clay dispersion degree (Table 4).

Chicken manure changes pH_{Water} as the result of many processes [8]. High content of basic cations is the main cause of acidity reduction, but other reactions can influence pH changes, as shown in [9].

Organic matter can affect clay dispersion too. Organic polymers can bind and join particles or repulse them by "coating" [22]. In RL, organic matter content did not change (Fig. 9). Considering organic matter changed in RYU (Fig. 9), it can be affecting clay dispersion as well.

Hydrophobicity can occur in some organic matter compounds [44] and affect particles structural stability on weathered soils [45]. Unfortunately, as no organic matter specific characterization was done, the effect of a specific group of organic compounds in clay dispersion degree could not be evaluated.

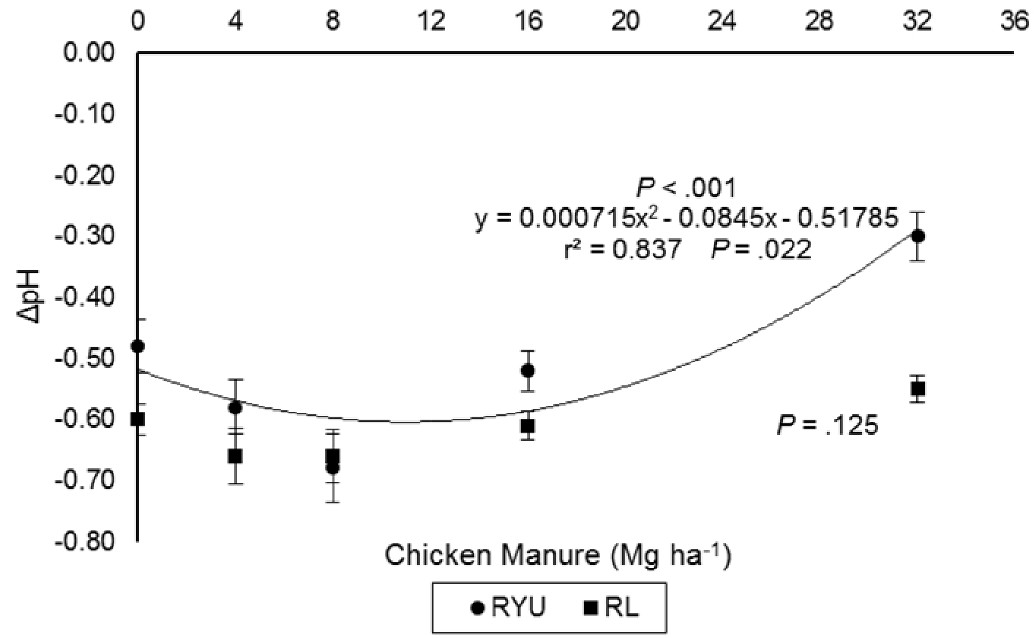

Fig. 6. ΔpH influenced by chicken manure doses in Red Latosol (RL) and Red-Yellow Ultisol (RYU)

For Red-Yellow Ultisol, the first P-value is from ANOVA and the second is from regression; No equation was adjusted for Red Latosol because of ANOVA's high P-value; Standard error bars are shown

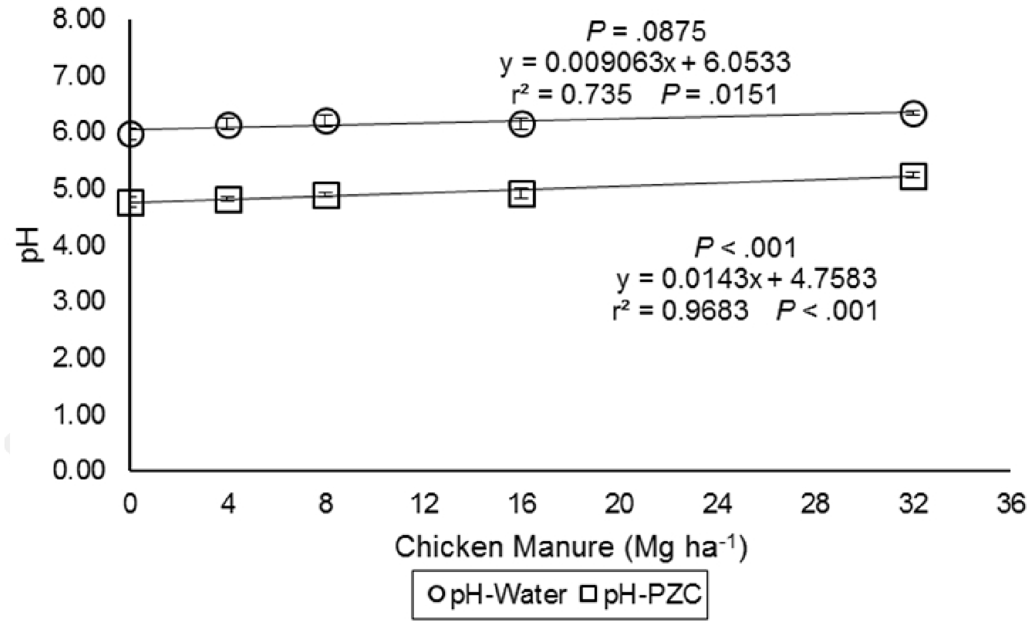

Fig. 7. Point of zero charge (pH_{PZC}) and pH_{Water} influenced by chicken manure doses in Red Latosol (RL)

The first P-value is from ANOVA and the second is from regression;Standard error bars are shown

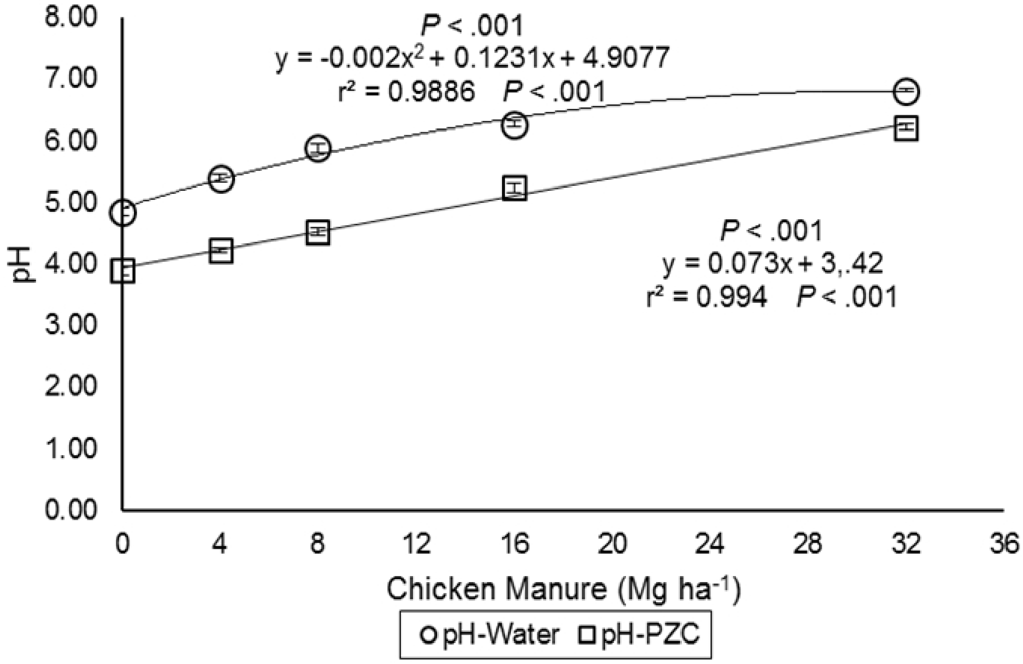

Fig. 8. Point of zero charge (pH_{PZC}) and pH_{Water} influenced by chicken manure doses in Red-Yellow Ultisol

The first P-value is from ANOVA and the second is from regression
Standard error bars are shown

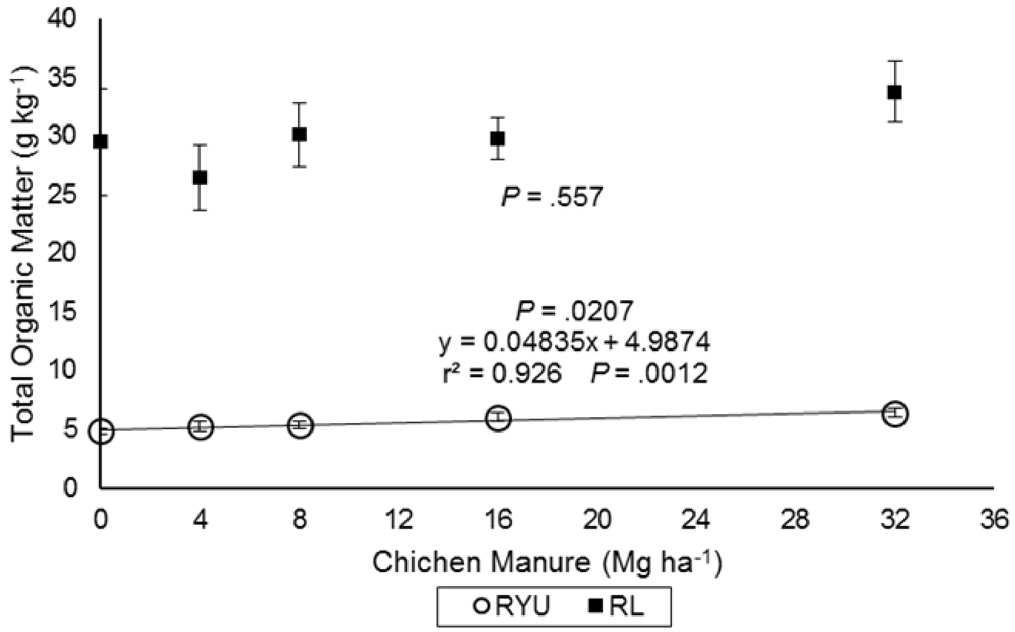

Fig. 9. Organic matter in Red Latosol (RL) and Red-Yellow Ultisol (RYU) according to chicken manure doses

For Red-Yellow Ultisol, the first P-value is from ANOVA and the second is from regression, No equation was adjusted for Red Latosol because of ANOVA's high P-value, Standard error bars are shown

In literature, chicken manure effects on physical attributes of Brazilian soils are divergent. Testing doses of chicken manure in an Oxisol under pasture, at field conditions, [6] found flocculation effects after 60 and 210 days from application. The authors proposed that grass root growth, causing soil particles approximation and exudate liberation, was responsible for soil flocculation.

[46], after 3 years of chicken manure application in a Brazilian Red Latosol, using two doses: 4.750 and 5.312kg ha^{-1}, did not find statistical difference in water dispersible clay content when compared with the areas without chicken manure. According to [47], not composted chicken manure caused degradation in soil's physical attributes when compared with composted chicken manure and mineral fertilizers.

Fe and Al (hydr) oxides also affects soil particles' stability [20]. Amorphous Fe are more efficient than crystalline forms to flocculate soil particles [21]. Anyway, for the studied soils, organic matter, Fe and Al (hydr) oxides specific analyses are necessary for establishing high scope indices for water dispersible clay in Brazilian soils.

4. CONCLUSION

A greenhouse experiment was done to exclude plant factors, such as root growth and exudate liberations, to evaluate the applicability of ESR, $MCAR_{ex}$ and $CROSS_{ex}$ for two important soil classes of Paraná state. Increasing doses of chicken manure did not cause clay dispersion increment in the studied soils, as expected. The indices had small correlation with clay dispersion. This behavior implies that attributes related to soil net charge, organic matter, Fe and Al (hydr) oxides must be considered as well to increase the scope of indices to predict clay dispersion degree behavior.

More studies are needed with different soil classes to validate the results of this experiment and, if confirmed, new indices can be proposed and tested in greenhouse and field conditions. The use of high correlation indices can be useful to guide the use of organic and inorganic fertilizers, once farmers do not evaluate clay dispersion in their farms. This way, fertilizers management can focus on soil chemical and physical quality.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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