ESTIMATING SUBSOIL RESISTANCE TO NITRATE LEACHING FROM EASILY MEASURABLE PEDOLOGICAL PROPERTIES[1]

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SUMMARY

Leaching of nitrate (NO_3^-) can increase the groundwater concentration of this anion and reduce the agronomical effectiveness of nitrogen fertilizers. The main soil property inversely related to NO_3^- leaching is the anion exchange capacity (AEC), whose determination is however too time-consuming for being carried out in soil testing laboratories. For this reason, this study evaluated if more easily measurable soil properties could be used to estimate the resistance of subsoils to NO_3^- leaching. Samples from the subsurface layer (20-40 cm) of 24 representative soils of São Paulo State were characterized for particle-size distribution and for chemical and electrochemical properties. The subsoil content of adsorbed NO_3^- was calculated from the difference between the NO_3^- contents extracted with 1 mol L^{-1} KCl and with water; furthermore, NO_3^- leaching was studied in miscible displacement experiments. The results of both adsorption and leaching experiments were consistent with the well-known role exerted by AEC on the nitrate behavior in weathered soils. Multiple regression analysis indicated that in subsoils with (*i*) low values of remaining phosphorus (Prem), (*ii*) low soil pH values measured in water (pH H_2O), and (*iii*) high pH values measured in 1 moL L^{-1} KCl (pH KCl), the amounts of surface positive charges tend to be greater. For this reason, NO_3^- leaching tends to be slower in these subsoils, even under saturated flow condition.

Index terms: anion exchange capacity, remaining phosphorus, retardation factor.

RESUMO: *ESTIMATIVA DA RESISTÊNCIA DE SUBSOLOS À LIXIVIAÇÃO DE NITRATO A PARTIR DE PROPRIEDADES PEDOLÓGICAS DE FÁCIL DETERMINAÇÃO*

A lixiviação de nitrato (NO$_3^-$) pode aumentar a concentração desse ânion no lençol freático e reduzir a eficiência agronômica dos fertilizantes nitrogenados. A capacidade de troca aniônica (CTA) é a principal propriedade do solo inversamente relacionada à lixiviação de nitrato; todavia a morosidade associada à quantificação da CTA inviabiliza sua determinação em laboratórios dedicados à avaliação da fertilidade do solo. Por essa razão, a presente pesquisa foi conduzida com o objetivo de avaliar se atributos pedológicos mais facilmente determináveis poderiam ser utilizados para estimar resistência de subsolos à lixiviação de NO$_3^-$. Amostras coletadas na camada subsuperficial (20-40 cm) de 24 solos representativos do Estado de São Paulo foram caracterizadas quanto à granulometria e a alguns atributos químicos e eletroquímicos. O teor de NO$_3^-$ adsorvido foi calculado a partir da diferença entre seus teores extraídos com solução de KCl 1 mol L^{-1} e com água; adicionalmente, a lixiviação de NO$_3^-$ foi estudada por meio de experimentos de deslocamento miscível. Os resultados foram concordantes com a conhecida importância da CTA tanto para a adsorção quanto para o retardamento da lixiviação de NO$_3^-$ em subsolos intemperizados . Por meio de análise de regressão linear múltipla foi possível observar que subsolos que apresentam (i) baixos valores de fósforo remanescente (Prem), (ii) baixos valores de pH determinados em água (pH H$_2$O) e (iii) altos valores de pH determinados em solução de KCl 1 mol L^{-1} (pH KCl) tendem a apresentar quantidades mais elevadas de cargas positivas. Por essa razão, a lixiviação de NO$_3^-$ tende a ser mais lenta nesses subsolos mesmo sob condição de fluxo saturado.

Termos de indexação: capacidade de troca aniônica, fósforo remanescente, fator de retardamento.

INTRODUCTION

Nitrate (NO$_3^-$) is the most oxidized nitrogen form in non-flooded soils which can be taken up by plants or transported into subtranen aquifers after intense rainfall or irrigation. This leaching can increase NO$_3^-$ concentrations to > 10 mg L^{-1} N in the groundwater, making it unsuitable for drinking (Brasil, 2001). Although Addiscott & Benjamin (2004) pointed out that there is no scientific evidence of nitrate-related damages to human health, the main concerns with regard to this anion are associated with its apparent involvement in the development of stomach cancer in adults and of methemoglobinemia in newborns (Addiscott, 2006).

Besides not giving rise to any insoluble products, nitrate, unlike anions such as sulfate and fluoride, occurs as non-complexed or "free" negatively charged ion (NO$_3^-$) in the soil solution. Therefore, the electrostatic adsorption by the surface positive charges of soil minerals plays an essential role in retarding NO$_3^-$ leaching (Ji, 1997; Dynia & Camargo, 1999; Alcântara & Camargo, 2010; Harmand et al., 2010). However, along with the amount of soil positive surface charges, other factors such as aquifer depth, local rainfall, rate and frequency of N fertilization, N uptake efficiency of crops, irrigation management and soil properties (e.g., porosity, texture and mineralogy) must be taken into consideration to assess the risk of groundwater contamination by NO$_3^-$ (Resende, 2002).

Liming and fertilization are essential for crops on tropical soils, but both practices favor NO$_3^-$ leaching. Dynia & Camargo (1999) verified that liming and phosphate fertilization reduced NO$_3^-$ adsorption in the plowed layer of a Brazilian Ferralsol. Similarly, Alcântara & Camargo (2010) observed that applications of carbonate, phosphate and sulfate favored NO$_3^-$ leaching in an electropositive Ferrasol. The effect of liming to reduce NO$_3^-$ adsorption results from the increase in the net negative surface charge that occurs in variable charge soils after the pH rises; on the other hand, the depletion of NO$_3^-$ adsorption sites caused by the presence of other anions, e.g., phosphate and sulfate, can be ascribed to the greater preference of the positive surface charges for those anions than for NO$_3^-$. Harmand et al. (2010) observed that the NO$_3^-$ adsorption by an Acrisol in Costa Rica was greater in deeper layers in agreement with the progressive increase in the net positive surface charge that was also observed from the soil surface to a depth of 180 cm.

Although the soil content of clay-size particles is usually positively correlated with NO$_3^-$ adsorption, this straightforward relationship is not always observed due to mineralogical differences among soils. To evaluate the NO$_3^-$ fate in soil, it would therefore be useful to consider soil properties that are not only faster to measure but also consistently correlated with the soil mineralogical composition and with its amount of positive surface charges. In this context, a potential

choice could be the so-called remaining phosphorus (Prem) (Bache & Williams, 1971), which is the P concentration that remains in solution after shaking 2.5 g of soil with 25 mL of 0.01 $CaCl_2$ mol L^{-1} containing 60 mg L^{-1} P for 1 h (Alvarez V. et al., 2000). Experimental observations indicated that non-allophanic kaolinitic soils usually have high Prem values, which decrease when the soil becomes richer in gibbsite and iron oxides. In general, minerals such as gibbsite and goethite are more abundant in highly weathered soils; since these minerals have surface – OH groups that can be protonated and high values of point zero charge (PZC), the number of positive surface charges tends to be higher in gibbsite- and goethite-rich soils even at moderate acidity. It can therefore be concluded that soils with low Prem values can adsorb greater amounts of anions through both inner- and outer-sphere complexations. The advantage of using Prem as anion-adsorption index can be ascribed to its simpler and faster determination and to its greater dependence on soil mineralogy than on soil texture (Alves & Lavorenti, 2004).

Considering that: (*i*) the minerals gibbsite, hematite, and goethite are the main anion adsorbents in non-allophanic tropical soils and that their contents increase as these soils weather; (*ii*) both the point of zero charge (PZC) and soil pH values influence the sign and amount of electrical charges in the soil mineral surfaces; and (*iii*) that the higher amounts of negative surface charges and of anions such as carbonate, phosphate and sulfate usually found in the soil suface (0-20 cm) disfavor nitrate adsorption, it can be assumed that acidic subsoils with greater oxide amounts and, for this reason, low Prem values, are able to adsorb more NO_3^- than acidic subsoils richer in kaolinite. In this context, the purpose of this study was to evaluate the potential of Prem together with soil pH values measured in water (pH H_2O) and in 1 mol L^{-1} KCl (pH KCl) for predictions related to the delay of NO_3^- leaching from subsurface layers of Ferralsols and Acrisols.

MATERIAL AND METHODS

Soils

Twenty four samples were taken from the subsoil (20-40 cm) of Ferralsols and Acrisols at different locations in São Paulo State, air-dried, ground and passed through a 2-mm sieve. The soil contents of oxidizable carbon and clay-size particles were evaluated using the the Walkley-Black and the pipette method, respectively, whereas the soil particle density was determined through the pycnometer procedure (Embrapa, 1997). (Embrapa, 1997). The Si, Fe and Al contents associated to secondary minerals were determined after boiling the soil samples in 9 mol L^{-1} H_2SO_4 at a solid/solution ratio of 1:20 (Embrapa, 1997);

from the results, the weathering indices Ki (SiO_2/Al_2O_3, mol mol^{-1}) and Kr [SiO_2/(Al_2O_3 + Fe_2O_3), mol mol^{-1}] were calculated. Oxalate-extractable Fe and Al (Fe_o and Al_o) contents were also determined according to Buurman et al. (1996).

The soil pH values were measured in water (pH H_2O), 0.01 mol L^{-1} $CaCl_2$ (pH $CaCl_2$) and 1 mol L^{-1} KCl (pH KCl) at a solid/liquid ratio of 1:2.5 (Embrapa, 1997). Remaining phosphorus (Prem) was determined as proposed by Alvarez V. et al. (2000), by shaking 2.5 g of soil with 25 mL of 0.01 mol L^{-1} $CaCl_2$, containing 60 mg L^{-1} P for 1 h, and analyzing the filtered solutions for P by the blue molybdenum method of Murphy & Riley (1962).

The cation and anion exchange capacities (CEC and AEC) were determined by saturating the soils with the ions Ca^{2+} and Cl^- through successive shakings and centrifugations of 2 g of soil with 20 mL of unbuffered 0.01 mol L^{-1} $CaCl_2$ in 50-mL centrifuge tubes. When the Ca^{2+} and Cl^- concentrations in the supernatants reached 0.02 mol_c L^{-1}, the ions were desorbed in two extractions with 15 mL of 0.5 mol L^{-1} $MgSO_4$. Both extracts were combined in flasks filled to the 50-mL mark with the extractant and analyzed for Ca^{2+} by atomic absorption spectrophotometry and for Cl^- by colorimetry (Florence & Farrar, 1971). The soil CEC and AEC values were calculated, respectively, from the respective amounts of Ca^{2+} and Cl^- determined after subtraction of the contributions of these ions in the entrapped solutions; whose volumes were calculated as the difference between the masses of the tubes containing the soils weighed before the first application of the saturated solution and after the last centrifugation and discarding of the supernatant.

Nitrate adsorption and leaching

To assess NO_3^- adsorption, 2.5 g of air-dried and sieved ($\phi \leq 2$ mm) soil and 25 mL of 1 mol L^{-1} KCl were transferred to 50-mL centrifuge tubes that were shaken for 2 h and centrifuged. The supernatants were analyzed for NO_3^- according to Yang et al. (1998). The same procedure was repeated using water as extractant. The adsorbed nitrate was considered equal to the difference between the KCl- and H_2O-extractable NO_3^- soil contents (Ryan et al., 2001).

Leaching experiments were carried out in pre-weighed PVC tubes (internal diameter 5 cm) with a fine stainless steel screen, lined with geotextile (bidim®) attached to the bottom. After being packed with 20 cm of air-dried sieved ($\phi \leq 2$ mm) soil and "weighed, each PVC tube was vertically immersed from its bottom in 13,5 cm of deionized (DI) water for 24 h;" afterwards, the column was hold in a support and DI water was dripped for more 24 h to give rise to a 1-cm liquid layer on the soil surface, which was kept with a lateral drain. When the flow became constant in the soil column, the water was replaced by an aqueous dripping solution containing 50 mg L^{-1}

KNO_3 and 25-mL effluent fractions were collected in the column bottom until their nitrate concentrations become equal to 50 mg L^{-1}. The C/C_0 ratios, calculated from the nitrate concentrations of the effluent (C) and influent solutions (C_0, 50 mg L^{-1}) were submitted with their respective cumulative numbers of pore volume to the software Disp (Borges Jr. & Ferreira, 2006) for the calculation of the nitrate retardation factor from the numerical solution of the onedimensional convective-dispersive ion transport equation proposed by van Genuchten & Wierenga (1986):

$$R \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \qquad (1)$$

where R is the retardation factor, C_r is the ion concentration in the soil solution (mg L^{-1}), t is the time (min), D is the dispersive-diffusive coefficient (m^2 min^{-1}), x is the distance from soil surface (m), and v is the flow velocity (m min^{-1}).

The total volume occupied by pores in each soil column was calculated by multiplying the soil volume (392.7 cm^3) by the soil porosity, which in turn was calculated as 1 - (ρ_b - ρ_p), where ρ_b is the soil bulk density calculated as the ratio of soil weight by the soil volume in the PVC tube, and ρ_p is the soil particle density.

Statistical analyses

The experimental results were subjected to simple linear correlation and to multiple regression analyses using the Statistical Analysis System - SAS version 9.1 (SAS, 1994).

RESULTS AND DISCUSSION

Soil characterization

The classification, localization and the evaluated properties of the studied subsoils (Table 1), show that most of them were clayey (clay > 350 g kg^{-1}) and acidic (pH $CaCl_2$ < 5.5) (Embrapa, 2006). The sample from Adamantina (soil 24) was the least weathered (Ki = 3.9; Kr = 3.2) whereas the sample from Jardinópolis (soil 1) was the most weathered one (Ki = 0.1; Kr = 0); these conclusions were based on the fact that the 9 mol L^{-1} H_2SO_4 digestion dissolves all soil minerals but quartz. Therefore, the richer in oxides such as gibbsite, hematite, and goethite the soil is, the lesser will be its Ki and Kr values; on the other hand, for soils richer in minerals such as vermiculite, illite, and kaolinite the greater Si contents determined after the sulfuric digestion give rise to higher Ki and Kr values (Embrapa, 2006). Considering the Kr values as an approximate criterion to discriminate kaolinitic (Kr > 0.75) from oxidic (Kr < 0.75) tropical soils (Embrapa, 2006), it

can be inferred that kaolinite was the most abundant mineral in the clay and silt fractions in 16 of the 24 subsoils. The Fe and Al contents extracted with the ammonium oxalate solution ranged from 0 (soil 24) to 8 g kg^{-1} (soil 2) for Fe and from 1 (soils 13, 20, 21, 22, 23, and 24) to 7 g kg^{-1} (soil 2) for Al. The Prem values varied from 0 (soils 3 and 7) to 54.3 mg L^{-1} (soil 21) with a mean value of 19.9 mg L^{-1} and were inversely correlated with the soil contents of Fe-H_2SO_4 (r = -0.70**), Al-H_2SO_4 (r = -0.93**), Fe_o (r = -0.56**), and Al_o (r = -0.88**), and positively correlated with the weathering indexes Ki (r = 0.71**) and Kr (r = 0.66**). These correlations indicate that Prem can be a suitable estimator of the soil content of Fe and Al oxides. An example of the dependence of Prem on the soil mineralogy can be observed in the soils 1 and 9, which had equal contents of clay-size particles (381 g kg^{-1}) but quite different Prem values (2.4 and 18.1 mg L^{-1}, the lower value in the more oxidic soil). Furthermore, the coefficient of variation of the Prem values among the studied samples was high (84 %); this indicates a great capacity of discriminating the subsoils according to the Fe and Al oxide contents.

The oxidizable carbon (OC) contents in the subsoils ranged from 2.3 g kg^{-1} for the Haplic Acrisol of Votuporanga (soil 21) to 24.4 g kg^{-1} for the Rhodic Ferralsol of Miguelópolis (soil 2), with a mean value of 10.6 g kg^{-1}. No correlation was observed between the OC contents and the values of cation and the anion exchange capacities (CEC and AEC). On the other hand, the CEC values were directly correlated with the soil pH measured in water (r = 0.55**) and in 0.01 mol L^{-1} $CaCl_2$ (r = 0.47*).

The subsoil AEC ranged from 0.13 (soil 5) to 1.05 $cmol_c$ kg^{-1} (soil 3), with a mean value of 0.35 $cmol_c$ kg^{-1}, and was correlated with Prem (r = -0.63**) and with the contents of clay (r = 0.49**), Fe-H_2SO_4 r = 0.44**), Al-H_2SO_4 (r = 0.63**) and Al_o (r = 0.42**). No correlation was observed between AEC and the soil pH measured in water, 0.01 mol L^{-1} $CaCl_2$ or 1 mol L^{-1} KCl.

The multiple regression of AEC with Prem, pH KCl and pH H_2O (Table 2) showed that these variables explained 52 % of the AEC variation among the studied soils. According to Neter et al. (1990), when the predictor variables of a multiple regression model are correlated to each other, multi-collinearity is said to exist. In this case, the following problems can occur: (*i*) parameter estimates may not be significant, despite the existence of a definite statistical relationship, and (*ii*) a parameter estimate may have a sign different from the expected. Multi-collinearity can be detected by calculating the variance inflation factors (VIF), which measure the inflation of the variances for the regression coefficients above the expected if there is no correlation among the predictor variables; a VIF value >10 indicates the presence of strong multi-collinearity. The calculated VIF values (Table 2) indicated absence of multi-collinearity among the predictor variables, so that the signs of their

Table 1. Classification, localization and selected properties of the studied soils

Soil	Classification[1]	Localization	C[2]	Clay[3]	SiO_2[4]	Fe_2O_3[4]	Al_2O_3[4]	Ki[5]	Kr[5]	Fe_o[6]	Al_o[6]	Prem[7]	pH[8] CaCl$_2$	KCl	H$_2$O	CEC[9]	AEC[9]
				—	—	g kg^{-1}	—			— g kg^{-1} —		mg L^{-1}				— cmol$_c$kg^{-1} —	
1	Xanthic Ferralsol	Jardinópolis	15.1	381	8	300	276	0.1	0.0	3	6	2.4	4.6	4.9	5.0	0.65	0.66
2	Rhodic Ferralsol	Miguelópolis	24.4	407	93	246	288	0.5	0.4	8	7	9.7	4.7	4.5	5.3	2.64	0.22
3	Xanthic Ferralsol	Guaíra	6.2	438	126	189	292	0.7	0.5	3	5	0.0	5.9	6.2	5.7	1.46	1.05
4	Xanthic Ferralsol	São Pedro	22.1	350	68	64	148	0.8	0.6	2	5	20.0	4.4	4.2	6.2	1.88	0.23
5	Rhodic Ferralsol	Ribeirão Preto	9.3	397	89	139	150	1.0	0.6	3	3	20.3	7.3	7.4	7.8	6.13	0.13
6	Xanthic Ferralsol	Itirapina	6.6	319	68	39	153	0.8	0.7	1	2	29.3	4.7	4.6	5.4	0.97	0.19
7	Xanthic Ferralsol	Espírito Santo do Pinhal	6.6	559	147	96	309	0.8	0.7	1	4	0.0	5.4	5.9	5.0	0.56	1.04
8	Rhodic Ferralsol	Cordeirópolis	12.8	549	160	189	254	1.1	0.7	3	5	3.6	4.6	4.5	5.1	1.55	0.58
9	Rhodic Ferralsol	Guaíra	16.7	381	105	107	170	1.1	0.8	4	4	18.1	3.9	3.9	4.6	1.31	0.43
10	Rhodic Ferralsol	Leme	10.5	491	169	193	259	1.1	0.8	3	3	5.0	5.3	5.2	5.9	2.04	0.35
11	Rhodic Ferralsol	Luis Antônio	10.9	442	177	261	220	1.4	0.8	4	4	8.1	4.0	4.0	4.5	2.14	0.41
12	Xanthic Ferralsol	Piracicaba	3.9	299	89	43	141	1.1	0.9	2	4	16.9	3.9	4.0	4.3	1.65	0.19
13	Haplic Acrisol	Vera Cruz	4.3	208	64	21	93	1.2	1.0	1	1	35.9	4.1	4.1	4.4	0.75	0.20
14	Haplic Acrisol	Capão Bonito	7.8	365	135	54	175	1.3	1.1	2	3	19.2	4.4	4.2	6.4	2.70	0.24
15	Haplic Acrisol	Monte Alegre do Sul	19.0	489	177	82	216	1.4	1.1	3	5	11.0	4.5	4.3	5.1	4.15	0.23
16	Haplic Acrisol	Mococa	9.7	462	194	104	226	1.5	1.1	2	3	22.8	5.4	5.2	5.9	2.28	0.23
17	Haplic Acrisol	Itapetininga	12.0	575	186	54	242	1.3	1.2	1	5	2.3	4.2	4.0	4.9	3.32	0.48
18	Haplic Acrisol	Mococa	12.0	442	203	104	234	1.5	1.2	2	3	21.9	5.8	5.6	6.3	5.18	0.21
19	Rhodic Ferralsol	Tatuí	14.4	628	269	175	284	1.6	1.2	5	6	2.8	4.1	4.0	4.6	2.95	0.41
20	Haplic Acrisol	Monte Alegre do Sul	11.6	262	130	64	133	1.7	1.3	2	1	35.6	5.0	4.8	5.5	3.47	0.24
21	Haplic Acrisol	Votuporanga	2.3	101	36	25	25	2.5	1.5	1	1	54.3	5.5	5.3	4.6	1.66	0.19
22	Haplic Acrisol	Andradina	5.0	149	60	32	42	2.4	1.7	1	1	52.8	5.6	5.4	6.2	2.05	0.22
23	Haplic Acrisol	Adamantina	6.2	150	77	32	48	2.7	1.9	1	1	39.1	5.2	4.9	5.4	1.98	0.18
24	Haplic Acrisol	Adamantina	3.9	94	40	7	17	3.9	3.2	0	1	45.3	4.2	3.9	6.0	1.18	0.20

[1] FAO (2006). [2]Oxidizable carbon (Embrapa, 1997). [3]Pipette method (Embrapa, 1997). [4]Soil contents of Si, Al and Fe extracted by boiling 9 mol L^{-1} H_2SO_4 expressed as their respective oxides (Embrapa, 1997). [5]Weathering indexes given by Ki = 1.7 SiO_2/Al_2O_3 and Kr = 1.7 SiO_2/(0.63 Fe_2O_3 + Al_2O_3). [6]Soil contents of oxalate-extractable Fe and Al. [7]Remaining phosphorus (Alvarez V. et al., 2000). [8]pH measured in 0.01 mol L^{-1} $CaCl_2$ (pH $CaCl_2$), water (pH H_2O), and 1 mol L^{-1} KCl (pH KCl) (Embrapa, 1997). [9]Cation exchange capacity and anion exchange capacity.

Table 2. Results of the multiple regression analysis relating the anion exchange capacity (AEC) to remaining phosphorus (Prem), soil pH measured in water (pH H_2O), and soil pH measured in 1 mol L^{-1} KCl (pH KCl)

Parameter	Estimate	Standard error	t value	prob>t	VIF[1]
a_0	0.57062	0.25264	2.26	0.0352	0.00
a_1	-0.00850	0.00223	-3.82	0.0011	1.04
a_2	-0.14204	0.05744	-2.47	0.0225	1.67
a_3	0.15083	0.05353	2.82	0.0106	1.63

AEC = a_0 + a_1 Prem + a_2 pH H_2O + a_3 pH KCl; F-value = 9.32; prob>F = 0.0005; R^2 = 0.52; n=24. [1] VIF: variance inflation factor.

coefficients are in real agreement with their expected individual effects on AEC. The negative signs of Prem and pH H_2O show that the AEC increases as both decrease, i.e., the AEC increases as the soil becomes oxide-richer (low Prem) and more acidic (low pH H_2O) since both situations increase the number of protonated hydroxyl surface groups (-OH + H^+ → OH_2^+); furthermore, the AEC increases as the soil pH KCl values become higher, which can be ascribed to the positive correlation observed between the point of zero charge and the pH KCl values of Ferralsols and Acrisols with low contents of exchangeable Al and organic matter (Alves & Lavorenti, 2005). Therefore, despite the low value calculated for the determination coefficient (R^2) of the regression model, which could be improved by increasing the experimental dataset used for the fitting (Cagliari et al., 2011), the obtained

equation was able to indicate the expected individual effects of the predictor variables on AEC. This model allows estimations, for instance, of different AEC values for soils with different mineralogies and similar pH H_2O values or for soils with different mineralogies and similar clay contents.

Nitrate adsorption and leaching

The subsoil content of adsorbed NO_3^- ranged from 0 (soil 11) to 58.7 mg kg^{-1} (soil 7) with a mean value of 10.2 mg kg^{-1} (Table 3) and was not correlated with the soil clay content, pH KCl, and pH H_2O. On the other hand, it was inversely correlated with Prem ($r= -0.42*$) and directly correlated with AEC ($r = 0.71**$). The multiple regression of adsorbed NO_3^- against Prem, pH H_2O, and pH KCl was not statistically significant (F-value = 2.07, $p > F = 0.1371$).

The nitrate breakthrough curves for the studied soils were between those drawn for the Haplic Acrisol of Monte Alegre do Sul (soil 20) and for Xanthic Ferrasol from Guaíra (soil 3) (Figure 1), which had, respectively, the least and the highest nitrate retardation factors (RNO_3^-) (Table 3). The mean RNO_3^- value (0.93) indicated weak NO_3^- retention by the subsoil samples and was about 15 times lower than the value obtained in similar breakthrough experiments for phosphate in Brazilian Ferralsols (Oliveira et al., 2004). This agrees with the weaker outer-sphere and the stronger inner-sphere surface complexations responsible for the respective retentions of NO_3^- and phosphate in variable charge soils (Ji, 1997; Zhang & Yu, 1997). The anion exchange capacity was the only evaluated soil property that correlated with the NO_3^- retardation factor ($r = 0.70**$), in close agreement with the electrostatic nature of NO_3^- adsorption.
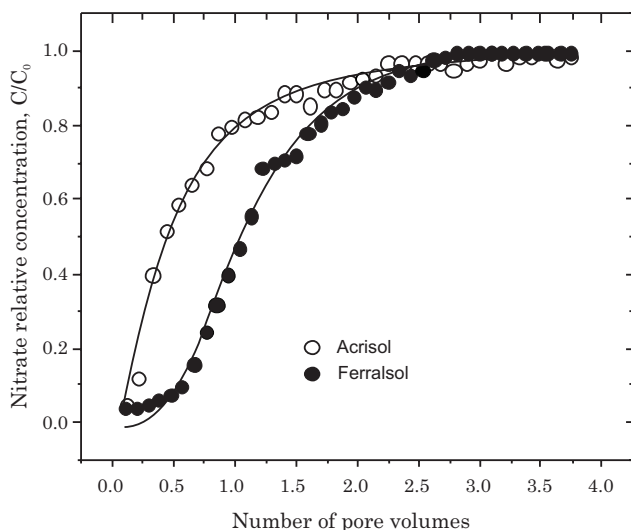
Table 3. Soil contents and retardation factors of nitrate in the studied soils

Soil	Nitrate			$RNO_3^{-(4)}$
	$KCl^{(1)}$	$H_2O^{(2)}$	Adsorbed[3]	
		mg kg^{-1}		
1	62.1	53.6	8.5	1.02
2	63.0	38.8	24.2	0.84
3	148.6	117.0	31.6	1.19
4	39.7	26.3	13.4	0.94
5	97.0	96.4	0.6	0.76
6	13.9	9.1	4.8	0.79
7	185.9	127.2	58.7	1.15
8	26.4	14.3	12.1	1.13
9	24.7	24.0	0.8	0.94
10	28.1	26.3	1.8	0.96
11	19.0	19.0	0.0	1.15
12	31.4	29.7	1.7	0.98
13	55.5	55.3	0.1	0.97
14	34.7	13.7	21.0	0.92
15	34.7	25.1	9.6	0.77
16	33.9	30.2	3.6	0.73
17	31.4	10.9	20.5	0.92
18	82.9	81.6	1.3	0.85
19	30.6	29.7	0.9	0.94
20	35.5	25.1	10.4	0.70
21	59.6	57.6	2.0	1.02
22	27.2	22.3	5.0	0.90
23	27.2	18.8	8.4	0.91
24	38.0	33.1	4.9	0.95

[1] Soil content of 1-mol L^{-1} KCl-extractable nitrate. [2] Soil content of water-extractable nitrate. [3] Soil content of adsorbed nitrate [NO_3^- adsorved = NO_3^- KCl - NO_3^- H_2O (Ryan et al., 2001)]. [4] Nitrate retardation factor

For the soils 2, 5, 6, 15, 16, 18, and 20, the RNO_3^- values ranged from 0.70 to 0.85. It is probable that in these soils the NO_3^- ions were electrostatically repelled rather than attracted, which characterizes the so-called negative adsorption (Ji, 1997). The negative correlation ($r = -0.68**$) observed between RNO_3^- and the relative amount of negative surface charges, given by the ratio [CEC/(CEC + AEC)] x 100, indicates that RNO_3^- values tend to be low in soils where CEC is much higher than AEC. The RNO_3^- values lower than 0.85 were observed in those samples presenting [CEC/(CEC + AEC)] x 100 > 90 %, indicating that these subsoils are highly susceptible to NO_3^- leaching under extreme rainfall conditions.

Finally, subsoils values of Prem, pH KCl, and pH H_2O seem to be promising for the determination of appropriate amounts of nitric fertilizers for Ferralsols and Acrisols in order to minimize nitrate leaching.

Figure 1. Nitrate breakthrough curves of Acrisol samples from Monte Alegre do Sul (soil 20) and Ferralsol from Guaíra (soil 3).

The adequate use of those properties for the above purpose should be further studied considering other aspects that also affect the NO_3^- behavior in cultivated soils. Among them, it can be pointed out the changes in crop N demand according to the growth stage and gypsum application which, in turn, allows for deeper root growth in acidic subsoils.

CONCLUSIONS

1. The multiple regression model based on the subsoil properties Prem, pH KCl, and pH H_2O allows a reliable estimation of AEC values in the subsurface (20-40 cm) layer of Ferralsols and Acrisols.

2. Considering that AEC is the most important electrochemical soil property related to nitrate adsorption, the resistance of the subsurface layer (20-40 cm) of Ferralsols and Acrisols to nitrate leaching under saturated-flow condition can be estimated based on the subsoil properties Prem, pH KCl, and pH H_2O.

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