CHEMICAL CHANGES IN AN OXISOL TREATED WITH PYROLIGNEOUS ACID

Alterações químicas em um latossolo tratado com extrato pirolenhoso

Aluísio Hideki Togoro[1], Juliana Aparecida dos Santos da Silva[1], Jairo Osvaldo Cazetta[2]

ABSTRACT

The use of pyroligneous acid (PA), a by-product of charcoal production, is an ancient practice applied in agriculture to control soil and plant pests and diseases. However, little is known about the chemical alterations that this product may cause on treated soil. Thus, the present work aimed to evaluate the effect of PA concentrations on soil ions movement and to verify possible soil chemical properties changes. Detachable columns were filled with Oxisol, submitted to application of 5 PA concentrations (0, 1, 2, 4, 8% v/v), followed by water infiltration in an amount corresponding to 1.5 times the soil total pore volume, and evaluated the soil of four depths (0-10, 10-20, 20-30, 30-40cm) and the leachate. The use of pyroligneous acid in concentrations up to 2 % (v/v) induces only slight decrease of k, Mg, basis saturation and total cation exchange capacity, in the 0-20 cm soil layer. The application of 4 % (v/v) and 8 % (v/v) pyroligneous acid induces severe increase on the potential acidity, and the decrease on the pH, basis saturation, total cation exchange capacity, and Ca concentration, in the layer of 0-20 cm soil. The P and K concentration reduces in the 0-20 cm soil layer by increasing from 1% to 8% the concentration of pyroligneous acid solution applied on soil surface. By increasing the PA concentration applied on the soil, there is increase of acidity, organic matter, P, K, Ca, and Mg, and decrease of sulfate in the leachate.

Index terms: Soil fertility, leaching, wood vinegar.

RESUMO

O uso do extrato pirolenhoso (PA), um produto obtido pela condensação dos gases oriundos da fabricação de carvão vegetal, é uma prática antiga aplicada na agricultura para controlar as pragas e doenças do solo e das plantas. Entretanto, pouco se sabe sobre as alterações químicas que esse produto pode causar no solo tratado. Assim, este trabalho teve o objetivo de estudar o efeito da aplicação de PA na movimentação de íons no perfil do solo e alterações nas suas propriedades químicas. Colunas desmontáveis foram preenchidas com Latossolo e submetidas à aplicação de 5 concentrações de PA (0, 1, 2, 4 e 8 % v/v), seguidas de infiltração com água equivalente a 1,5 vezes o volume dos poros e, posteriormente, analisado o solo de 4 profundidades (0-10, 10-20, 20-30, 30-40 cm), bem como o lixiviado. Verificou-se que a aplicação de 4 %(v/v) e 8 %(v/v) de PA induz aumento na acidez potencial, bem como diminuição do pH, da saturação de bases, da capacidade total de troca de cations e da concentração de Ca na camada de 0-20 cm do solo. A concentração de P e K reduz na camada de 0-20 cm à medida que se aumenta de 1% a 8% a concentração de PA aplicado no solo. Ao aumentar a concentração de PA aplicado ao solo, também ocorre o aumento da acidez, de matéria orgânica, P, K, Ca e Mg, e redução de sulfato no lixiviado.

Termos para indexação: Fertilidade do solo, lixiviação, vinagre de madeira.

INTRODUCTION

Due to the increasing global concern with environmental risks of soil and water contamination, resulting from the use of synthetic agricultural supplies, has being bolstered the industrial production, use and commerce of pyroligneous acid (PA), which has being preconized to plant and soil treatments (Alves et al, 2007; Steiner et al., 2008; Chalermsan; Peerapan, 2009; Schnitzer et al., 2010; Zulkarami et al., 2011; Pedro et al. 2012; Rheinheimer et al., 2012), besides other uses (Tiilikkala et al., 2010; Dariot et al., 2013).

Considering that PA is very acid, mainly due to the presence of acetic acid, and that contain a series of other organic substances (Souza et al., 2012), it is possible that it may have an effect of displacement of ions from the soil exchange complex (Jones, 1998; Andrade et al., 2003). This would have the advantage of improve some nutrient availability, but the disadvantage of increase the displacement and possible leaching of substances through soil profile. Therefore, studies on the impact of the use of this kind of product are of great agricultural and environmental importance,

---

[1] Universidade Estadual Paulista/UNESP – Jaboticabal – SP – Brasil

[2] Universidade Estadual Paulista/UNESP – Departamento de Tecnologia – Via de Acesso Prof. Paulo Donato Castellane – s/n – 14884900 – Jaboticabal – SP – Brasil – cazetta@fcav.unesp.br

Received in september 18, 2013 and approved in november 14, 2013

and absolutely necessary to support the correct and safe application of chemicals (synthetic or alternative agricultural supplies) on the soil (Raimundo et al., 2009; Vasconcelos et al., 2013). However, there is no scientific information about the influence of PA on soil chemical properties, fertility, ion movement in the soil profile and leaching.

The movement of substances in the soil profile and possible leaching depends on several factors, among them the concentration of ions and other substances in the soil solution, soil adsorption capacity, pH (Qafoku et al., 2000), type of charge exchange complex, and porosity (Shiptalo et al., 2000; Casagrande et al., 2003). Also, ion movement and leaching occurrence is promoted in the conditions of intense rain, or under excess of irrigation, and water infiltration in the soil (Padilla et al., 1999). Such conditions are very common in areas with soil subjected to frequent tillage, fertilization and irrigation as those used for horticultural purposes. Also, the soils under the horticulture activity often require treatment to prevent or control pests and diseases, where the use of pyroligneous acid have been preconized, still without enough knowledge to be done in a safe way.

Although the study on the behavior of substances in intact soils should be ideally developed under real field conditions, the research under such situation is very difficult, is subjected to several environmental variables, besides expensive (Melo e Curi, 2012; Vasconcelos et al., 2013). Moreover, horticultural soils usually are very disturbed due to the intense cultivation. Thus, soil columns are considered as a good tool and alternative for measuring substances transport in disturbed soil samples, migration and leaching through porous medium, under controlled conditions (Shackelford, 1995; Qafoku et al., 2000).

Taking into account the aforementioned, it was idealized this work with the objective of study the movement of ions in the soil profile, the changes on soil fertility, and the possible leaching in a horticultural soil treated with pyroligneous acid, followed by water infiltration.

MATERIAL AND METHODS

This work was carried out at the Technology Department of the Faculty of Agriculture and Animal Sciences (FCAV/UNESP), Jaboticabal, SP, Brazil.

The assay consisted in a split-plot experiment, with a factorial 5x4 combination, meaning five main treatments (application of PA at 0, 1, 2, 4 and 8% v/v on the top of soil columns), and four soil layers (depths) of evaluation as secondary treatments (layers of 0-10, 10-20, 20-30 and 30-40 cm). These 20 treatments were developed with three replications, totaling 60 experimental units.

Each main treatment consisted of a column with 40 cm height and 15 cm diameter, made by four PVC (polyvinyl chloride) rings (10 cm high) superimposed. The rings were attached to each other with silicone glue, complemented by fixing externally with a 4.5 cm wide adhesive tape. The column internal wall was coated with a layer of sand fixed by using PVC glue, to avoid water preferential movement. To prevent soil loss from the column, an additional PVC ring was placed on the column top. Also, a perforated plate, and a polyethylene fabric was placed in the bottom of the column to soil support and avoid soil loss. After filled with soil, the column was mounted on a funnel connected to a liachate collecting bottle by a PVC tube.

The soil used to fill up the columns was a clayey Oxisol composed by 226 g kg^{-1} sand, 223 g kg^{-1} silt, and 551 g kg^{-1} clay, determined by following indications of Embrapa (1997). The original soil fertility (determined according to RAIJ et al., 2001) characteristics were: pH 5.5 ($CaCl_2$), 17 g dm^{-3} organic matter (OM), 132 mg dm^{-3} P (resin), 3 $mmol_c$ dm^{-3} K, 37 $mmol_c$ dm^{-3} Ca, 22 $mmol_c$ dm^{-3} Mg, 20 $mmol_c$ dm^{-3} H+Al, 82 $mmol_c$ dm^{-3} total ion change capacity (T), 76% Basis saturation (BS), 0.2 mg dm^{-3} B, 11 mg dm^{-3} Cu, 10 mg dm^{-3} Fe, 18 mg dm^{-3} Mn, 2 mg dm^{-3} Zn, 2 mg dm^{-3} S-SO_4^{2-}.

The soil was air dried, sieved (2 mm) and transferred to columns. Each column was filled up to 40 cm (corresponding to 7.068 dm^3). For a uniform filling, the columns were lightly compacted by letting them fall vertically from a 5 cm height, for three times.

The total columns pore volume (3.954 dm^3) was calculated from the total soil porosity (55.94%) and from columns volume (7.068 dm^3). The total porosity was obtained using the particle density (2.86 g cm^{-3}) and soil density (1.26 g cm^{-3}), following indications of Embrapa (1997).

The PA used was the PiroQualis® (AGRISA Ltda: Candido Mota-SP), produced from *eucalyptus* wood, which chemical characteristics were: pH 2.9; 21.04 g dm^{-3} Organic matter; 0.04 g dm^{-3} N; 0.6 mg dm^{-3} P; 11.5 mg dm^{-3} Ca; 25.0 mg dm^{-3} Mg; 5.4 mg dm^{-3} S; 343.2 mg dm^{-3} Fe; 1.1 mg dm^{-3} Mn; 2.7 mg dm^{-3} Zn; < 0.1 mg dm^{-3} K; mg dm^{-3} Cu. The pH was determined by potentiometry, OM by titration, and N by Kjeldhal methods in the original solution. After complete nitric-perchloric acid digestion, P was determined by vanadate-molibdate spectrometry, S by turbidity, and other elements by atomic absorption spectrometry (Embrapa, 2009).

The solutions were applied, according to the respective treatments, on the soil surface, in an amount equivalent to 80% of the total pore volume calculated. In order to simulate irrigation or rain, and guarantee percolation to make possible the collection and analyze the leachate, deionized water was applied on the top of the soil column in an amount corresponding to 1.5 times the total pore volume, 24 hours after treatments application.

The leachate volume, pH and electrical conductivity of the added and drained liquid (leachate) were measured, and then submitted to chemical analysis (Embrapa, 2009), after filtration through Whatman n.1 filter paper, in order to determine organic matter (OM), P, K, Ca, Mg and S-SO_4^{-2}.

After stopping the water percolation, the columns were disassembled and the soil from each depth (ring) was removed, and subjected to chemical (fertility) analysis according to Raij et al. (2001).

Data were subjected to variance analysis by F test. Regression analysis was used to study the PA concentrations effects on variables determined in the leachate, and the Tukey test (5%) was carried out to compare means among soil depths and PA concentrations. Statistical analysis was developed by using the software Agrostat (Barbosa; Maldonado Junior, 2010).

RESULTS AND DISCUSSION

Gradual decrease in soil pH due to increasing PA concentrations was observed in the 0-20 cm depth in the 4% and 8% PA treatment, while in the soil layers of 20-30 cm and 30-40 cm pH remained similar to that before treatments (Table 1). From 0 to 40 cm depth, a total variation of 1.1 unit of pH was detected in the

Table 1 – Means of pH, and concentrations of Organic Mater (OM) expressed as (g dm^{-3}), phosphorous (P) and Sulfur (S-SO_4^{-2}) expressed as (mg dm^{-3}), in soil layers (depths) after application of solutions with growing concentrations (% v/v) of pyroligneous acid on soil column top, and water infiltration 24 hours after treatments imposition.

Variables	Depths	0% (Control)	1 %(v/v)	2 %(v/v)	4 %(v/v)	8 %(v/v)	F	VC (%)
pH	0-10 cm	5.7 aA	5.7 aA	5.7 aA	5.0 bB	4.8 cC	97.62 **	1.32
	10-20 cm	5.7 aA	5.8 aA	5.8 aA	5.7 aA	5.3 bB	21.78 **	
	20-30 cm	5.7 aA	5.8 aA	5.8 aA	5.8 aA	5.7 aA	1.32 ^{ns}	
	30-40 cm	5.7 aA	5.7 aA	5.8 aA	5.9 aA	5.9 aA	3.18 ^{ns}	
	F	0.08 ^{ns}	0.89 ^{ns}	1.91^{ns}	39.46 **	64.28 **		
OM	0-10 cm	17 aA	18 aA	19 aA	18 aA	19 aA	1.64 ^{ns}	4.56
	10-20 cm	18 aA	19 aA	19 aA	19 aA	19 aA	0.33 ^{ns}	
	20-30 cm	18 aA	17 aA	19 aA	19 aA	19 aA	2.95 ^{ns}	
	30-40 cm	18 aA	18 aA	18 aA	19 aA	19 aA	0.94 ^{ns}	
	F	0.74 ^{ns}	2.03 ^{ns}	1.41 ^{ns}	0.31 ^{ns}	0.16 ^{ns}		
P	0-10 cm	132 aA	125 aA	123 aAB	111 bBC	107 cC	10.25 **	4.4
	10-20 cm	131 aA	130 aAB	130 aAB	127 aAB	117 bC	3.09*	
	20-30 cm	127 aA	129 aA	131 aA	128 aA	129 aA	0.15 ^{ns}	
	30-40 cm	133 aA	126 aA	128 aA	125 aA	134 aA	1.77 ^{ns}	
	F	0.31 ^{ns}	0.54 ^{ns}	0.38 ^{ns}	3.37 *	8.34 **		
S-SO_4^{-2}	0-10 cm	2 aA	2 aA	2 aA	2 aA	1 aA	1.03 ^{ns}	10.4
	10-20 cm	2 aA	2 aA	3 aA	1 aA	1 aA	3.85 ^{ns}	
	20-30 cm	2 aA	1 aA	2 aA	2 aA	1 aA	0.60 ^{ns}	
	30-40 cm	3 aA	3 aA	4 aA	3 aA	1 aA	8.40 ^{ns}	
	F	2.58 ^{ns}	4.21 ^{ns}	6.00 ^{ns}	7.64 ^{ns}	0.21 ^{ns}		

Results of ANOVAs, with the F test (F) significance, are shown: ** $P<0.01$, * $P<0.05$, ns $P>0.05$; VC (%) = Variation coefficient; For each variable data, means followed by same letter do not differ by Tukey test at P=0.05 (uppercase letters compares means within lines, and lowercase letters within columns).

treatment of 8% PA. The decrease of soil pH in top layers is attributed to the acidity of pyroligneous extract (Souza et al., 2012), and the leaching of bases to other layers (Table 2) may have contributed to soil acidity increasing (Raij, 2011).

The concentration of organic matter in all PA treatments and all studied soil layers remained similar (P>0.05) to control treatment (Table 1). Although it seems that sulfate ($S\text{-}SO_4^{-2}$) data in top layers tended to be lower in 4% an 8% PA treatments, probably due to low original concentrations and relatively high data coefficient of variance (10.4 %), no difference could be confirmed (Table 1).

No significant (P>0.05) differences were observed for P content in the soil profile treated with PA concentration from 0 (control) to 2% v/v. However, there was decrease in the 0-10 cm layer of soil treated with 4% PA. Also, a decrease was detected in the top layers (0-10 cm and 10-20 cm) and an increase in the lower studied layers of the soil subjected to application of 8% PA (Table 1).

Soils with high clay, iron-oxides and aluminum-oxides content are favorable for the adsorption of phosphorus (Basso et al., 2005). Thus, in the clayey Oxisol used in this research, a poor movement of P was expected in the control treatment when carried out water infiltration. However, the changes clearly observed in the treatment 8% PA indicates that P was withdrawn from the top and moved to other soil layers (Table 1). This may have occurred, once was already shown that increasing the concentration of organic acids (molar ratio between organic acid and P) induces reduction in the phosphate adsorption by the soil by competition between organic acids and the P for the clay adsorption sites (Andrade et al., 2003; Guppy et al., 2005). Another hypothesis is that organic acids may cause the dissolution of Fe and Al structure of crystalline or poorly crystallized minerals, and form complexes with soluble metal cations in the soil, reducing the surface for phosphate adsorption in the soil (Jones, 1998; Andrade et al., 2003; Guppy et al., 2005). This hypothesis of the dissolution of part of Fe and Al oxides, caused by the relatively high acid concentrations in PA 4% and 8%, should be considered because the oxides dissolution would induce important disturbance in the clay surface, what could explain also the alterations in the total cation exchange capacity (T), mainly observed in the top layers of the treated soil (Table 2), what is very uncommon under regular conditions.

There was decrease in the K, Ca and Mg concentration in the 0-20 cm layer when was increased PA concentration. However, no difference was observed for K and Mg in the 30-40 cm layer and Ca in the 20-30 cm layer (Table 2).

The movement of Ca in the soil profile was not significant in treatments with PA concentrations of 1% and 2%, and Mg in PA 1%. Also, no difference was observed for the control treatment. Therefore, it is clear that the PA application, especially in higher concentrations (4 and 8%), was responsible for decrease these nutrients concentration on soil superficial layers (Table 2).

An important factor that have contributed to cations leaching was the raising the soil acidity due to the application of PA, what occurred especially in the superficial layer (0-20 cm), where there was a greater decrease in K, Ca and Mg concentrations (Table 2). This affirmative is supported by the reports of Raij (2011), on that all source of acidity induces losses of cations by soil leaching. This supposition is also reinforced by the observations that the values of basis saturation (BS%) tended to follow the same trend observed for the soil pH variations (Table 1 and 2). Such relationships observed between pH and BS(%) were expected, since BS(%) express part of the total cation exchange capacity (T) occupied by Ca, Mg and K, instead of H+Al (RAIJ, 2011).

Significant (P <0.01) increase was observed for soil potential acidity (H+Al) due to the PA treatment (Table 2). The application of 4 and 8% PA resulted in higher soil potential acidity (H+Al) at 0-10 and 10-20 cm (Table 2).

On treatment in which 8% PA was applied, the average values of H+Al have reduced from 39.33 to 19.33 $mmol_c\ dm^{-3}$ by varying from 0 to 40 cm depths, and a parallel reduction was obtained for pH and BS(%). Also, an increase was observed for H+Al in 0-10 and 10-20 cm (Table 2). This suggests that the acidity (H+) coming from PA applications, induced a displacement of exchangeable bases and, consequently, leaded to losses of these bases during water percolation.

Besides soil, the leachate (percolate) was also determined and chemical analyzed. The average volume recovered (5.76 dm^3) corresponded to 96% of the total amount applied on column top, and difference (P>0.05) was observed among treatments, for leachate volumes.

Values of leachate pH ranged from 7.15 to 6.08 showing a linear decrease by increasing PA concentration (Figure 1A). This decrease was expected once PA contains high acid concentration (SOUZA et al., 2012). However, comparing continuous line with dotted line of figure 1A, it was found that the leachates pH were much higher than those of added solutions, what can be explained by either dilution (from the water applied on the column top, simulating irrigation, to observe possible leaching), and organic acids absorption by the soil.

Table 2 – Means ($mmol_c$ dm^{-3}) of K, Ca, Mg, potential acidity (H+Al), Total Cations Exchange Capacity (T), and Basis Saturation (%) in different soil layers (depths), after application of solutions with growing concentrations (% v/v) of pyroligneous acid on soil column top, and water infiltration 24 hours after treatments imposition.

Variables	Depths	Pyroligneous acid concentration					F	VC (%)
		0%(Control)	1 %(v/v)	2 %(v/v)	4 %(v/v)	8 %(v/v)		
K	0-10 cm	2.6 bA	2.0 cAB	1.8 bB	0.9 cC	1.1 cC	18.97 **	10.34
	10-20 cm	3.1 baA	2.8 bcA	2.6 aAB	2.0 bBC	1.8 cC	13.10 **	
	20-30 cm	3.3 baA	3.1 abA	3.1 aA	2.8 aA	2.7 bA	2.51 ^{ns}	
	30-40 cm	3.4 aA	3.5 aA	3.5 aA	3.4 aA	3.7 aA	0.47 ^{ns}	
	F	3.54 *	13.02 **	13.09 **	31.99 **	35.19 **		
Ca	0-10 cm	40 aA	39 aA	38 aA	27 bB	22 cC	97.62 **	3.81
	10-20 cm	40 aA	41aA	40 aA	39 aA	32 bB	20.55 **	
	20-30 cm	41 aA	40 aA	41 aA	41 aA	40 aA	0.81 ^{ns}	
	30-40 cm	41 aA	40 aA	40 aA	42 aA	43 aA	2.55 ^{ns}	
	F	0.08 ^{ns}	0.54 ^{ns}	1.20 ^{ns}	36.88 **	72.25 **		
Mg	0-10 cm	22 aA	21 aAB	19 bB	9 cC	6 dC	129.94 **	5.64
	10-20 cm	21 aA	21 aA	21 aA	19 bA	12 cB	38.51 **	
	20-30 cm	21 aA	21 aA	21 aA	21 aA	19 bB	7.75 *	
	30-40 cm	21 aA	22 aA	22 aA	22 aA	22 aA	0.79 ^{ns}	
	F	0.98 ^{ns}	0.32 ^{ns}	7.28 **	163.69 **	210.41 **		
H+Al	0-10 cm	23 aB	21 aB	23 aB	38 aA	39 aA	80.83 **	7.08
	10-20 cm	23 aBC	24 aBC	21 aC	25 bBC	32 bA	18.46 **	
	20-30 cm	23 aA	21 aA	20 aA	23 bA	23 cA	1.88 ^{ns}	
	30-40 cm	22 aA	22 aA	21 aA	21 bA	19 cA	1.10 ^{ns}	
	F	0.25 ^{ns}	0.90 ^{ns}	0.94 ^{ns}	32.71 **	46.11 **		
BS	0-10 cm	68 aA	66 aA	66 bA	43 cB	34 dC	166.07 **	3.29
	10-20 cm	68 aA	68 aA	69 abA	65 bA	53 cB	29.52 **	
	20-30 cm	68 aAB	67 aAB	70 aA	70 aAB	65 bB	4.54 **	
	30-40 cm	67 aB	67 aB	72 aAB	72 aAB	75 aA	7.22 **	
	F	0.18 ^{ns}	0.26 ^{ns}	5.69 **	143.16 **	248.02 **		
T	0-10 cm	95 aA	93 aAB	90 aBC	86 bC	87 bC	17.91 **	1.73
	10-20 cm	95 aAB	97 aA	93 aB	91 aC	87 bD	17.67 **	
	20-30 cm	96 aA	96 aA	92 aB	93 aAB	94 aAB	3.91 *	
	30-40 cm	97 aA	97 aA	93 aAB	94 aAB	93 aB	4.94 **	
	F	0.89 ^{ns}	3.00 ^{ns}	2.36 ^{ns}	12.97 **	16.44 **		

Results of ANOVAs, with the F test (F) significance, are shown: ** $P<0.01$, * $P<0.05$, ns $P>0.05$; VC (%) = Variation coefficient; For each variable data, means followed by same letter do not differ by Tukey test at P=0.05 (uppercase letters compares means within lines, and lowercase letters within columns).

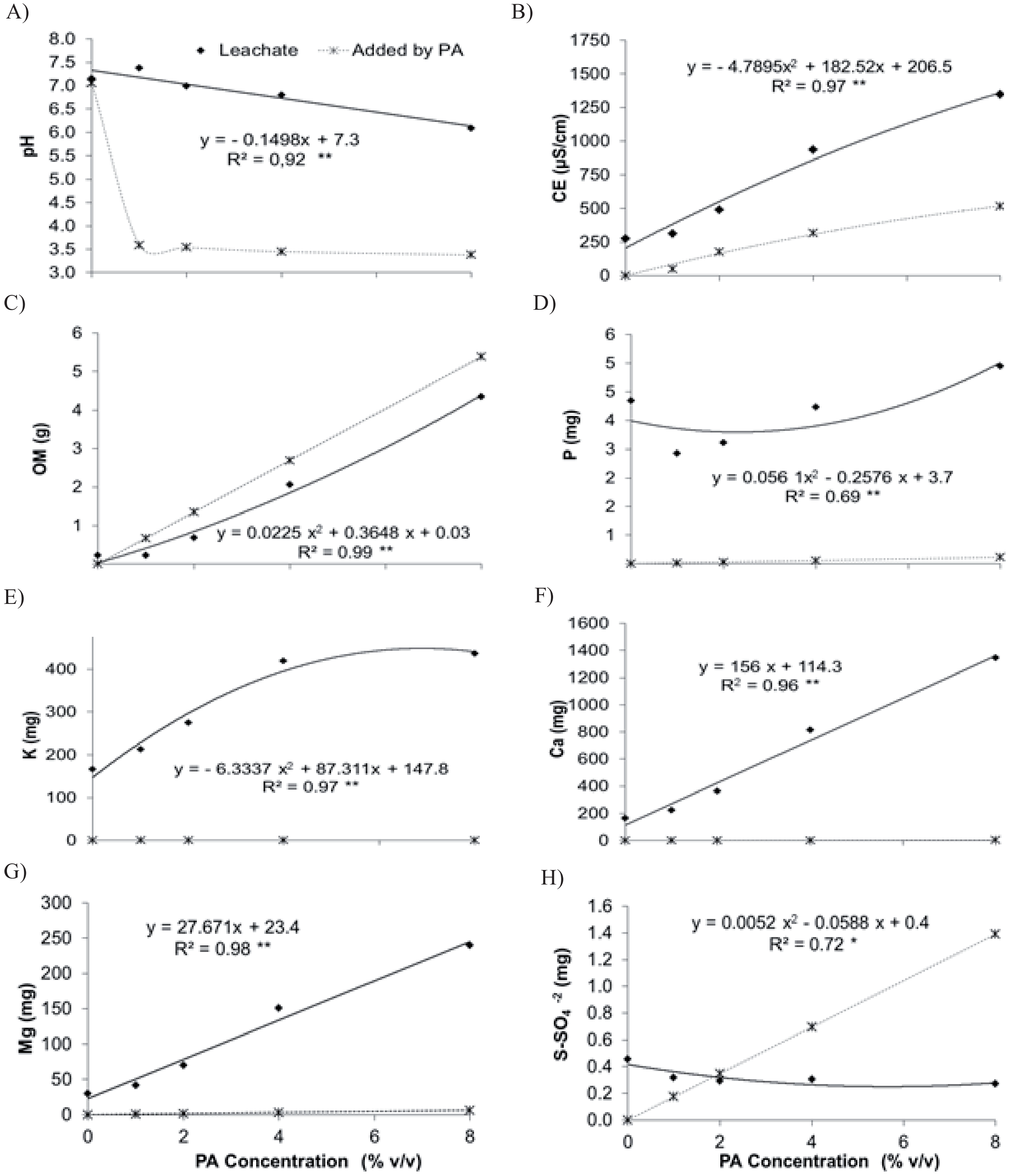

Figure 1 – Means of pH, Electrical Conductivity (CE), and amount of Organic Matter (OM), P, Ca, Mg, and S-SO_4^{-2} determined in the leachate (continuous lines). Dotted lines correspond to values of PA solutions (for pH and CE), and the input coming from the added PA solutions (for OM, P, Ca, Mg and S-SO_4^{-2}), after application of solutions with growing concentrations (%v/v) of pyroligneous acid (PA) on soil column top, and water infiltration 24 hours after treatments imposition. Results of ANOVAs, with the F test significance to R^2 (determination coefficient), are shown: ** P<0.01; * P<0.05. Jaboticabal, UNESP, 2012.

The electrical conductivity (EC) represents the concentration of electrolytes in the solution (AMARAL et al., 2004), and a significant ($P < 0.05$) increase in EC averages was observed by the increasing on PA concentration in the leachate (Figure 1B). Once the EC of PA solutions applied on the soil were much lower than the leachate EC (Figure 1B, comparing the continuous line with dotted line), it is clear that the increase in the leachate EC was due to ions coming from the soil.

There was increase of OM values in the leachate, as function of increasing PA concentration applied on the soil (Figure 1C, continuous line), what was lower than the amount applied in the soil top considering the applied volumes of PA, and its OM content (Figure 1C, dotted line). If dividing the amount of OM in the leachate of the treatment 8% PA (4.38 g) by the leachate volume (5.76 dm^3), it is obtained the concentration of 0.76 g dm^3 OM in the leachate. Considering that the original 8 %(v/v) PA contained 1.68 g dm^3 (8% of 21 g dm^3 in the original PA), it is possible to verify that great part (about 54%) of the OM added by way of PA was absorbed by the soil, what also occurred in about the same extension for the other treatments. Probably the OM leached was compensated by the input coming from PA addition, what may help to explain why soil OM concentration remained unaltered (Table 1).

Considering the PA chemical composition and the amounts added in each treatment, it was calculated the total input of P, K, Ca, Mg and S coming from PA. It was found that, except for S, the PA contributions were negligible (dotted lines of Figure 1).

It was observed only a slight amount of P leached, and small variations among treatments (Figure 1D). Low values of P in the leachate were also observed by Luchese et al. (2008), what was attributed to the strong phosphate sorption on clays typically found in the oxisols like this one used in this research. In spite of the low P leaching, it was verified a tendency of elevation of values by increasing PA concentration (Figure 1D). Under regular soil conditions, higher P adsorption was expected by pH decrease (CASAGRANDE et al., 2003) and, consequently, lower P leaching. The opposite tendency observed in this work (Figure 1D) suggests that PA concentrations above 4% should have induced soil chemical changes different from those usually observed in varying pH by using carbonates application. The higher the PA concentration applied, the higher was the amount of K, Ca and Mg in the leachate (Figures 1E, 1F, 1G). This shows that PA induces the downward movement of cations through the soil. Thus, the application of high concentrations of PA, and subsequent irrigation may lead to nutrient loss from top to soil layers deeper than 40 cm (Table 2).

Taking into account the total values in the leachate at the treatment with PA 8%, the Ca was the nutrient with higher loss (1362 mg per column), followed by K (441 mg per column) and Mg (244 mg per column). Computing the total amount available (detected by fertility analysis as mmolc dm^{-3}, and converting to mg dm^{-3}, and mg per column) in the soil, each column contained 5240 mg Ca, 1187 mg Mg, and 827 mg K. Discounting the (negligible) input coming from the 3.2 dm^3 8% PA (2.8 mg Ca, 6.4 mg Mg, and 0 mg K), the amount of Ca, Mg, and K found in the leachate corresponded to 26%, 20% and 53%, respectively, of these ions in the soil. Although K was in lower concentration in the soil, it moved to the percolate in greater proportion compared to Ca and Mg. This probably occurred due to lower K capacity to form complexes, when compared to Ca and Mg, and in the free ion form it is easier to be dragged by infiltration solution.

Although no difference was confirmed in the soil, the amount of leached sulfate tended to decrease with PA concentration (Figure 1H, continuous line), although increasing sulfate input occurred by PA additions (Figure 1H, dotted line). This result is in accordance with previous report (CASAGRANDE et al., 2003) showing that sulfate adsorption in the soil tended to be increased by reducing the pH value and, thus, a lower sulfate leaching was expected.

CONCLUSIONS

The use of pyroligneous acid in concentrations up to 2% (v/v) induces only slight decrease of k, Mg, basis saturation and total cation exchange capacity, in the 0-20 cm soil layer.

The application of 4%(v/v) and 8% (v/v) pyroligneous acid induces severe increase in the potential acidity, and the decrease the pH, basis saturation, total cation exchange capacity, and Ca concentration, in the layer of 0-20 cm soil.

The P and K concentration reduces in the 0-20 cm soil layer by increasing from 1% to 8% the concentration of pyroligneous acid solution applied on soil surface.

By increasing the PA concentration applied on the soil, there is increase of acidity, organic matter, P, K, Ca, and Mg, and decrease of sulfate in the leachate.

ACKNOWLEDGEMENT

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for the financial support (Scholarship to the first author, Proc. FAPESP n. 2010/04015-4).

REFERENCES

ALVES, M. et al. Ação de diferentes preparações de extrato pirolenhoso sobre *Brevipalpus phoenicis* (GEIJSKES). **Revista Brasileira Fruticultura**, 29(2):382-385, 2007.

AMARAL, A.S.; ANGHINONI, I.; DESCHAMPS, F.C. Resíduos de plantas de cobertura e mobilidade dos produtos da dissolução do calcário aplicado na superfície do solo. **Revista Brasileira de Ciência do Solo**, 28(1):115-123, 2004.

ANDRADE, F. V. et. al. Adição de ácidos orgânicos e húmicos em Latossolos e adsorção de fosfato. **Revista Brasileira de Ciência do Solo**, 27(6):1003-1011, 2003.

BARBOSA, J.C.; MALDONADO JUNIOR, W. **Agrostat – Sistema para análises estatísticas de ensaios agronômicos. Versão 1.0**. Jaboticabal: Departamento de Ciências Exatas, 2010.

BASSO, C. J. et.al. Dejeto líquido de suínos: II-perdas de nitrogênio e fósforo por percolação no solo sob plantio direto. **Ciência Rural**, 35(6):1305-1312, 2005.

CASAGRANDE, J.C. et. al. Adsorção de fosfato e sulfato em solos com cargas elétricas variáveis. **Revista Brasileira de Ciência do Solo**, 27(1), p.51-59, 2003.

CHALERMSAN, Y.; PEERAPAN, S. Wood vinegar: by-product from rural charcoal kiln and its role in plant protection. **Asian Journal of Food Agro-Industry**, 21(special issue):189-195, 2009.

DARIOT, D.; MOURA, A.B.D.; MARTINS, I.P.D. Vegetable charcoal and pyroligneous acid: Technological, economical and legal aspects of its production and commerce. **Journal of Technological management & Innovation**, 8(special issue, ALTECH):310-320, 2013.

EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA - EMBRAPA. Centro Nacional de Pesquisas de Solos. **Manual de métodos de análises de solos**. 2 ed., Rio de Janeiro: EMBRAPA, 1997. 212p.

EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA - Embrapa. Embrapa Informação Tecnológica. **Manual de análises químicas de solos, plantas e fertilizantes**. 2.ed., Brasília: EMBRAPA, 2009. 627p.

GUPPY, C.N. et. al. Competitive sorption reactions between phosphorus and organic matter in soil: a review. **Australian Journal of Soil Research**, 43(2):189-202, 2005.

JONES, D. L. Organic acids in the rhizosphere – a critical review. **Plant and soil**, 205(1):25-44, 1998.

LUCHESE, A.V.; COSTA, A.C.S.; SOUZA JÚNIOR, I.G.S. Lixiviação de íons após a aplicação de resíduos orgânicos de uma indústria farmoquímica. **Revista Brasileira de Engenharia Agrícola e Ambiental**, 12(2):189-199, 2008.

MELLO, C.R.; CURI, N. Hydropedology. **Ciência e Agrotecnologia**, 36(2):137-146, 2012.

PADILLA, I.Y.; JIM YEH, T.C.; CONKLIN, M.H. The effect of water content on solute transport in unsaturated porous media. **Water Resources Research**, 35(11):3303-3313, 1999.

PEDRO, E.S. et.al. Produtos de diferentes grupos químicos no controle da mancha branca do milho. **Semina: Ciências Agrárias**, 33(1):2981-2984, 2012.

QAFOKU, N.P.; SUMNER, M.E.; RADCLIFFE, D.E. Anion transport in columns of variable charge sub soils: nitrate and chloride. **Journal of Environmental Qualality**, 29(2):484-493, 2000.

RAIJ, B. V. et. al. **Análise química para avaliação de fertilidade de solos tropicais**, Campinas: Instituto Agronômico, 2001, 285p.

RAIJ, B. Van. **Fertilidade do solo e manejo de nutrientes**. 1.ed., Piracicaba: International Plant Nutrition Institute, 2011, 420 p.

RAYMUNDO, E.R. et. al. Transporte de Atrazina en un Andosol y un Vertisol de México**. Interciencia**, 34(5):330-337, 2009.

REINHEIMER, A.R. et.al. Produtos fitossanitários alternativos no controle da mosca-branca (Bemisia tuberculata) (Maatile-Ferrero), na mandioca. **Semina: Ciências Agrárias**, 33(4):1419-1426, 2012.

SCHNITZER, J.A.; et al. Substratos e extrato pirolenhoso no cultivo de orquídeas brasileiras *Cattleya intermedia* (John Lindley) e *Miltonia clowesii* (John Lindley) (Orchidaceae). **Acta Scientiarum Agronomy**, 32:139-143, 2010.

SHACKELFORD, C.D. Cumulative mass approach for column testing. **Journal of Geotechnical Engineering**, 121(10):696-703, 1995.

SHIPTALO, M.J.; DICK, W.A.; EDWARDS, W.M. Conservation tillage and macropore factors that affect water movement and the fate of chemicals. **Soil & Tillage Research**, 53:167-183, 2000.

SOUZA, J.B.G.; RÉ-POPPI, N.; RAPOSO, L. Characterization of pyroligneous acid used in agriculture by gas chromatography-mass spectrometry. **Journal of Brazilian Chemical Society**, 23(4):610-617, 2012.

STEEINER, C. et. al. Charcoal and smoke extract stimulate the soil microbial community in a highly weathered xanthic Ferralsol. **Pedobiologia**, 51(5-6):359-366, 2008.

TIILIKKALA, K. et. al. History and use of wood pyrolysis liquids as biocide and plant protection product. **The open agriculture journal**, 4(special issue 2):111-118, 2010.

VASCONCELOS, F.C.W. et. al. Macro simultor (version 5.0) for predicting atrazine herbicide behaviour in brazilian latossols. **Ciência e Agrotecnologia**, 37(3):211-220, 2013.

ZULKARAMI, B. et. al. Effect of pyroligneous acid on growth, yield and quality improvement of rockmelon in soilless culture. **Australian Journal of Crop Science**, 5(12):1508-1514, 2011.