

# Seasonal and depth effects on some parameters of a forest soil

## Efeitos sazonais e de profundidade sobre alguns parâmetros do solo de uma floresta

Luís Ramon Moreno Toni<sup>1</sup>; Henrique de Santana<sup>1</sup>;  
Cássia Thaís Bussamra Vieira Zaia<sup>2</sup>; Dimas Augusto Morozin Zaia<sup>13\*</sup>

### Abstract

The main goal of this paper is to study the effect of wet/dry season and the depth on several parameters of the forest soil. This work has shown that the concentration of  $\text{Al}^{3+}$  increases and that the concentration of exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and pHs (distilled water and  $\text{CaCl}_2$ ) decreases with the increase in depth and that these results are correlated. The concentrations of exchangeable cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and organic matter (OM) are affected by dry/wet season. Rain increases the solubility of organic carbon, thus decreasing OM and releasing exchangeable cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ). P (available) shows an increase in its concentration with an increase in depth. The low concentration of P (available) in the soil samples could be due to the low pH of the soils. The value of  $\text{pH}_{\text{pzc}}$  is influenced by exchangeable cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ), and the pHs ( $\text{CaCl}_2$  and distilled water) are higher than  $\text{pH}_{\text{pzc}}$ . This means that the net charge of these soils is negative. CEC and  $\text{CEC}_{\text{potencial}}$  decrease with the increase in depth in most soil samples. For mostly of the samples, the season (wet/dry) does not affect CEC,  $\text{CEC}_{\text{potencial}}$ ,  $\text{K}^+$ , or  $\text{Na}^+$ .

**Key words:** Soil. Forest. Exchangeable cations. Season. Soil horizons.

### Resumo

O principal objetivo deste trabalho é estudar o efeito da estação chuva/seca e a profundidade sobre diversos parâmetros do solo de floresta. Este trabalho mostrou que a concentração de  $\text{Al}^{3+}$  aumenta e que a concentração de cátions trocáveis ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) e pH (água destilada e  $\text{CaCl}_2$ ) diminuem com o aumento na profundidade e estes resultados são interdependentes. As concentrações de cátions trocáveis ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) e matéria orgânica (MO) são afetadas pela estação seca/chuva. Chuva aumenta a solubilidade de carbono orgânico, portanto diminui MO e libera cátions trocáveis ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ). P (trocável) mostra um aumento na sua concentração com um aumento na profundidade. A pequena concentração de P (trocável) nas amostras de solo pode ser devido ao baixo pH dos solos. O valor de  $\text{pH}_{\text{pzc}}$  é influenciado pelos cátions trocáveis ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ), e os pHs ( $\text{CaCl}_2$  e água destilada) são maiores do que  $\text{pH}_{\text{pzc}}$ . Isto significa que a carga destes solos é negativa. CTC e  $\text{CTC}_{\text{potencial}}$  diminuem com o aumento da profundidade para a maioria das amostras de solos. A estação (seco/chuva) não afeta CTC,  $\text{CTC}_{\text{potencial}}$ ,  $\text{K}^+$  ou  $\text{Na}^+$ , para a maioria das amostras.

**Palavras chave:** Solo. Floresta. Cátions trocáveis. Estação. Horizontes dos solos.

<sup>1</sup> Departamento de Química-CCE, Universidade Estadual de Londrina (UEL) – Londrina-Pr.

<sup>2</sup> Departamento de Ciências Fisiológicas-CCB, Universidade Estadual de Londrina (UEL) – Londrina-Pr.

<sup>3</sup> \* Corresponding author Dimas A. M. Zaia e-mail: damzaia@uel.br

## Introduction

The variation of concentration of exchangeable cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) in forest soils with depth has been reported by several authors (PRENZEL; SCHULTE-BISPING, 1995; NISSINEN; ILVESNIEMI; TANSKANEN, 1998; FERNANDES et al., 2002; CZEPINKA-KAMINSKA; KONECKA-BETLEY; JANOWSKA, 2003; DIJSTRA; FITZHUGH, 2003; ANNAN-AFFUL et al., 2004; ANNAN-AFFUL et al., 2004; YANAI et al., 2005). In general, they observed that the concentration of  $\text{Al}^{3+}$  increases with the increase in depth, while those of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  decrease. However, there are several explanations for these results such as acid rain, organic matter decomposition,  $\text{Al}^{3+}$  speciation in soils, soil pH, and ionic strength of ions in soils. For  $\text{Na}^+$  and  $\text{K}^+$ , there is not an agreement or an explanation for the variation of their concentrations in soils with depth in the literature. The seasonal variation of concentration of exchangeable cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) in forest soils has also been studied and in general variations of  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  are related to growing season (summer) and rain, while  $\text{Na}^+/\text{K}^+$  are not much influenced by seasonal variations (PHILLIPS; GREENWAY, 1998; CZEPINKA-KAMINSKA; KONECKA-BETLEY; JANOWSKA, 2003).

The variation of several forest soil parameters with depth and season (pH, organic matter/OM, available phosphorus/P-available, cation exchange capacities/CEC, potential cation exchange capacities/ $\text{CEC}_{\text{potential}}$ ) have also been studied by several authors (FERNANDES et al., 2002; CZEPINKA-KAMINSKA; KONECKA-BETLEY; JANOWSKA, 2003; DIJSTRA; FITZHUGH, 2003; ANNAN-AFFUL et al., 2004; CIOTTA et al., 2004; IGWE; ZAREI; STAHR, 2005; MURASHKINA; SOUTHARD; KOPTSIK, 2005). There is no agreement in the literature about the increase/decrease of pH with the increase in depth for forest soils and its cause (FERNANDES et al., 2002; CZEPINKA-KAMINSKA; KONECKA-BETLEY; JANOWSKA, 2003;

MURASHKINA; SOUTHARD; KOPTSIK, 2005). Czepinka-Kaminska, Konecka-Betley and Janowska (2003) and Dijkstra and Fitzhugh (2003) observed that pH is influenced by wet/dry seasonal variation. As expected, several authors observed a decrease in OM with an increase in depth, but there is not an explanation for the variation of OM with season (FERNANDES et al., 2002; DIJSTRA; FITZHUGH, 2003; ANNAN-AFFUL et al., 2004; CIOTTA et al., 2004; IGWE; ZAREI; STAHR, 2005; MURASHKINA; SOUTHARD; KOPTSIK, 2005). Fernandes et al. (2002) and Annan-Afful et al. (2004) found that P (available) decreased with an increase in depth. Several studies have shown that the variation of CEC and  $\text{CEC}_{\text{potential}}$  with depth and season are related to the variations of concentrations of exchangeable cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and OM. However, there is no agreement on the variation of CEC/ $\text{CEC}_{\text{potential}}$  with depth (ULREY et al., 1995; FERNANDES et al., 2002; CZEPINKA-KAMINSKA; KONECKA-BETLEY; JANOWSKA, 2003; ANNAN-AFFUL et al., 2004).

The present paper reports on the changes of several soil parameters ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , pH, P (total), P (available), OM,  $\text{pH}_{\text{pzc}}$ , CEC,  $\text{CEC}_{\text{potential}}$ ) with depth and season for samples collected at a forest reserve located on the campus of Universidade Estadual de Londrina, PR, Brazil.

## Materials and methods

### Materials

All reagents were of analytical grade.

### Soils

Soil samples weighing about 2.0 kg were collected in a forest reserve located on the campus of Universidade Estadual de Londrina, PR (Brazil) at two different points,  $P_0$  and  $P_2$ , (Figure 1) at the following depths 0-32 cm, 32-74 cm, 74-104 cm, 104-155 cm, 155-200 cm and 2-37 cm, 37-65 cm,

65-105 cm, 105-153 cm, 153-200 cm, respectively, in March and June 2004 and classified as haplorthox. X-ray analysis of the soil revealed the following clays: kaolinite, gibbsite, and vermiculite. Kaolinite

is the most concentrated (ROCHA; BARROS; GUIMARÃES, 1991). Soil samples were oven-dried at 40 °C for 24 h, crushed, and sieved with 2-mm mesh. De Santana et al. (2006) reviewed several aspects of the origin of this soil.

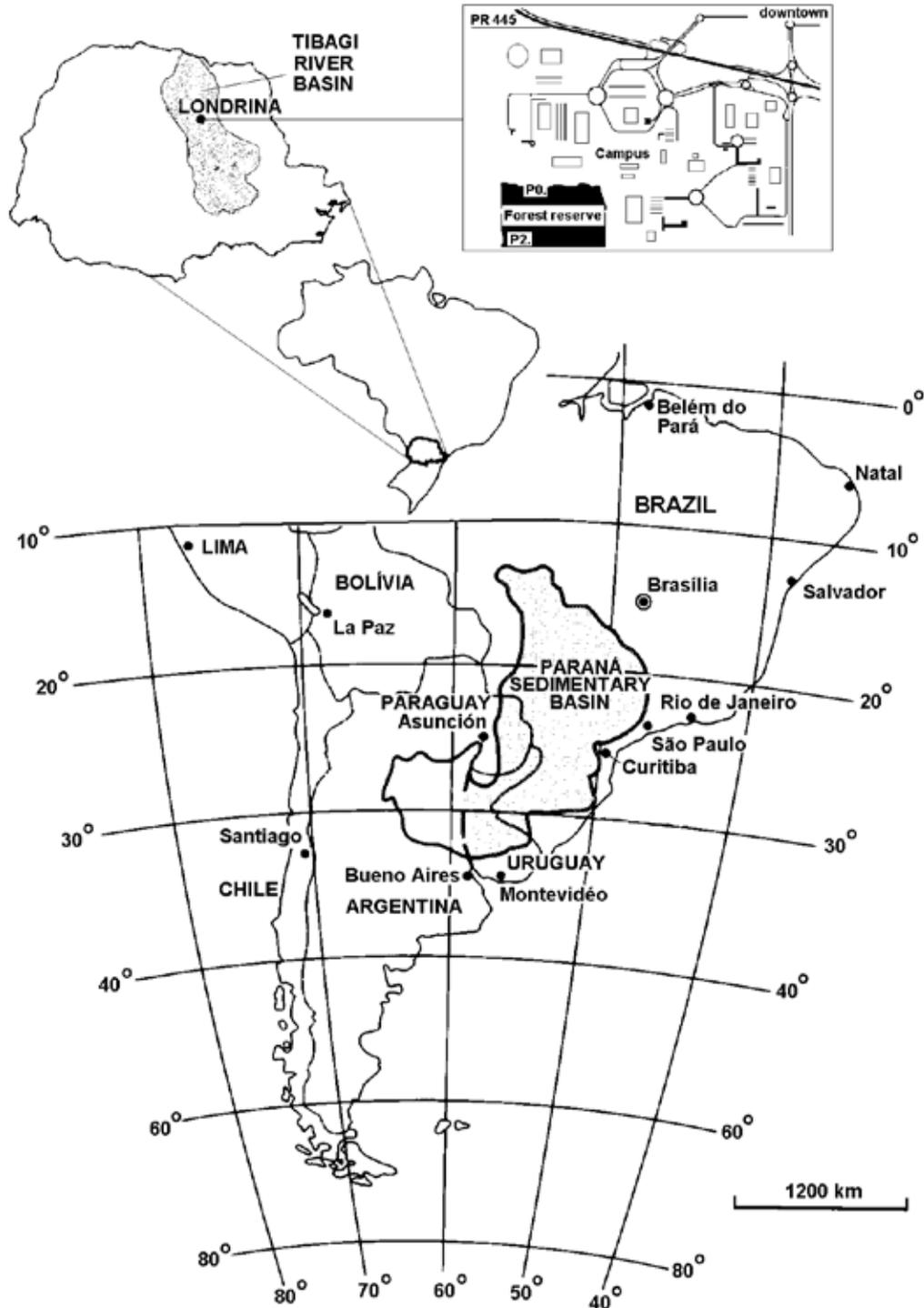


Figure 1. Location of the forest reserve on Universidade Estadual de Londrina

## Methods

### Soil Characterization (tables 1, 2, 3, and 4)

Exchangeable cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ), pH in distilled water and  $0.010 \text{ mol L}^{-1}$  of  $\text{CaCl}_2$ , total and available phosphorus (P (total), P (available), organic matter (OM), and cation exchange capacities (CEC and  $\text{CEC}_{\text{potential}}$ ) were determined for all soil samples by the standard methods described by Instituto Agrônomo do Paraná (1992) and Empresa Brasileira de Pesquisa Agropecuária (1997). The point of zero charge ( $\text{pH}_{\text{pzc}}$ ) was determined using the equation  $\text{pH}_{\text{pzc}} = 2\text{pH KCl-}1.0 \text{ mol L}^{-1} - \text{pH H}_2\text{O-distilled water}$  (UEHARA 1979).

### Statistical analysis

Comparisons between means were assessed using Student's t-test, ANOVA, and Student-Newman-Kleus test (S.N.K. test) at a significance level of  $p < 0.05$ .

## Results and discussion

Table 1 shows the analysis of exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and the soil acidity ( $\text{Al}^{3+}$ ) in  $1.0 \text{ mol L}^{-1}$  KCl of soils of a forest reserve located in Universidade Estadual de Londrina, PR. An increase in the concentration the soil acidity  $\text{Al}^{3+}$  (S.N.K. test  $p < 0.05$ ) and a decrease in the concentrations of

exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (S.N.K. test  $p < 0.05$ ) with an increase in depth were observed for most soil samples (table 1). Nissinen, Ilvesniemi and Tasnskanen (1998), Dijkstra and Fitzhugh (2003) and Yanai et al. (2005) studied soils from a boreal forest, a mixed hardwood forest in Connecticut, and a hardwood forest in New Hampshire, respectively. These authors also observed an increase in the concentration of the soil acidity  $\text{Al}^{3+}$  and a decrease in the concentrations of exchangeable cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) with an increase in depth. According to Yanai et al. (2005), these results could not be attributed to the decrease in pH due to acid rain and the consequent replacement of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with  $\text{Al}^{3+}$ , because forest floor horizons are difficult to distinguish repeatably and accurately in the field. Furthermore, variation in sampling depth contributes to a high variance, which makes it difficult to detect small changes in forest floor properties. However, Dijkstra and Fitzhugh (2003) attributed the increase in  $\text{Al}^{3+}$  concentration with depth to the release of  $\text{Al}^{3+}$  after TOC (total organic C) decomposition. Using batch reactor experiments, Guibaud and Ayele (2000) studied the effect of pH and ionic strength on the release of  $\text{Al}^{3+}$  by several horizons of three different forested soils. For moderately acid pH, the concentration of released  $\text{Al}^{3+}$  appeared to be related to the buffer value of the horizon, whereas for very acid pH, besides the release of the soil acidity  $\text{Al}^{3+}$ , it was observed that a part of the  $\text{Al}^{3+}$  in the soil crystal structure particles was released.

**Table 1.** Concentration of exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and the soil acidity ( $\text{Al}^{3+}$ ) in soil samples from forest reserve located on the Universidade Estadual de Londrina campus.

| Sample         | Depth (cm) | Exchangeable cations and the soil acidity ( $\text{cmol kg}^{-1}$ ) |                              |                            |                              |                          |                              |
|----------------|------------|---|------------------------------|----------------------------|------------------------------|--------------------------|------------------------------|
|                |            | $\text{Al}^{3+\psi}$  |                              | $\text{Ca}^{2+\psi}$       |                              | $\text{Mg}^{2+\psi}$     |                              |
| P*             | Depth (cm) | M   | J                            | M                          | J                            | M                        | J                            |
| P <sub>0</sub> | 0-32       | 0.99±0.01 <sup>a,c,0</sup>  | 0.59±0.02 <sup>c,d,e,0</sup> | 2.30±0.01 <sup>a</sup>     | 2.65±0.15 <sup>a</sup>       | 1.75±0.05 <sup>a,0</sup> | 3.95±0.05 <sup>a,0</sup>     |
| P <sub>0</sub> | 32-74      | 1.46±0.03 <sup>b,d</sup>  | 1.33±0.01 <sup>b,c</sup>     | 1.70±0.10 <sup>b,c,0</sup> | 0.80±0.10 <sup>b,0</sup>     | 0.90±0.50                | 2.30±0.10 <sup>b,c</sup>     |
| P <sub>0</sub> | 74-104     | 1.50±0.01 <sup>b,d,0</sup>  | 1.17±0.01 <sup>b,d,f,0</sup> | 1.10±0.01 <sup>b,d,0</sup> | 0.70±0.01 <sup>b,0</sup>     | 0.65±0.25                | 1.45±0.05 <sup>b,d,f</sup>   |
| P <sub>0</sub> | 104-155    | 1.69±0.04 <sup>a</sup>  | 1.48±0.03 <sup>a</sup>       | 1.10±0.10 <sup>b,d,0</sup> | 0.50±0.01 <sup>b,0</sup>     | 0.15±0.15 <sup>b,0</sup> | 1.60±0.10 <sup>b,d,f,0</sup> |
| P <sub>0</sub> | 155-200    | 1.48±0.03 <sup>b,d,0</sup>  | 1.22±0.01 <sup>b,d,f,0</sup> | 1.00±0.10 <sup>b,d</sup>   | 0.60±0.01 <sup>b</sup>       | 0.55±0.05 <sup>0</sup>   | 1.15±0.05 <sup>b,d,e,0</sup> |
| P <sub>2</sub> | 2-37       | 0.06±0.01 <sup>b,d</sup>  | 0.01±0.01 <sup>b,d</sup>     | 8.40±0.10 <sup>a,0</sup>   | 9.10±0.10 <sup>a,0</sup>     | 1.65±0.35                | 2.55±0.05 <sup>b,c</sup>     |
| P <sub>2</sub> | 37-65      | 0.06±0.01 <sup>b,d</sup>  | 0.01±0.01 <sup>b,d</sup>     | 6.35±0.25 <sup>a</sup>     | 6.10±0.10 <sup>b,c</sup>     | 1.50±0.10                | 2.00±0.20 <sup>b,d,e</sup>   |
| P <sub>2</sub> | 65-105     | 0.10±0.01 <sup>b,d</sup>  | 0.05±0.01 <sup>b,d</sup>     | 3.80±0.10 <sup>a,0</sup>   | 3.05±0.05 <sup>b,d,f,0</sup> | 2.80±0.40                | 3.45±0.05 <sup>a</sup>       |
| P <sub>2</sub> | 105-153    | 0.35±0.03 <sup>b,c,0</sup>  | 0.22±0.01 <sup>c,0</sup>     | 2.60±0.10 <sup>a</sup>     | 2.80±0.01 <sup>b,d,f</sup>   | 2.45±0.05 <sup>0</sup>   | 1.45±0.05 <sup>b,d,f,0</sup> |
| P <sub>2</sub> | 153-200    | 0.43±0.01 <sup>a,0</sup>  | 0.24±0.01 <sup>a,0</sup>     | 1.60±0.10 <sup>a</sup>     | 1.95±0.05 <sup>b,d,e</sup>   | 1.95±0.25                | 1.65±0.15 <sup>b,d</sup>     |

\*P=soil sampling points, M=March, J=June,  $\psi$ exchangeable cations in KCl 1.0 mol L<sup>-1</sup>. All the results are the means of two analyses. The results are presented as mean±S.E.M. SNK test (p<0.05) For  $\text{Al}^{3+}$ : P<sub>0</sub>M ANOVA (F=93.51, P=0.000), SNK test a/b and c/d; P<sub>0</sub>J ANOVA (F=359.28, P=0.000) SNK test a/b, c/d and e/f; P<sub>2</sub>M ANOVA (F=119.81, P=0.000) SNK test a/b and c/d; P<sub>2</sub>J ANOVA (F=131.30, P=0.000) SNK test a/b and c/d. For  $\text{Ca}^{2+}$ : P<sub>0</sub>M ANOVA (F=50.99, P=0.000) SNK test a/b and c/d; P<sub>0</sub>J ANOVA (F=123.86, P=0.000) SNK test a/b; P<sub>2</sub>M ANOVA (F=420.22, P=0.000) SNK test a/a; P<sub>2</sub>J ANOVA (F=1751.25, P=0.000) SNK test a/b, c/d and e/f. For  $\text{Mg}^{2+}$ : P<sub>0</sub>M ANOVA (F=5.22, P=0.049) SNK test a/b; P<sub>0</sub>J ANOVA (F=228.95, P=0.000) SNK test a/b, c/d and e/f; P<sub>2</sub>M ANOVA (F=4.17, P=0.075); P<sub>2</sub>J ANOVA (F=46.21, P=0.000) SNK test a/b, c/d and e/f. It was also used the Student's test to compare March (M) and June (J) results for each depth, <sup>0</sup>(p<0.05).

They also observed that ionic strength had an effect on the release of  $\text{Al}^{3+}$ , which depended on the speciation of  $\text{Al}^{3+}$  in the soils. Fernandes et al. (2002) studied a tropical forest soil (two depths: 0-10 cm and 10-20 cm) and observed: 1) an increase in the concentration of  $\text{Al}^{3+}$  with depth, 2) the concentrations of  $\text{Ca}^{2+}$  did not change and 3)  $\text{Mg}^{2+}$  decreased. Prenzel and Schulte-Bisping (1995) studied more than 2,000 soil samples from German forests. They showed that exchangeable cations changed with decreasing pH mainly due to the displacement of  $\text{Ca}^{2+}$  by  $\text{Al}^{3+}$ . It should be pointed out that we also observed a decrease in pH with depth for the soils studied here (S.N.K. test p < 0.05) (table 2).

Table 1 also shows an analysis of exchangeable cations and the soil acidity, of soil samples collected at two different times: March and June 2004. In general, we observed a decrease in the concentration of the cations in the samples collected in June when compared to those of samples collected in March (Student's t-test p < 0.05). It should be pointed out that March (summer) is wet season (95.2 mm rain) and June (fall) is the dry season (45.0 mm rain) (SIMEPAR INSTITUTO TECNOLÓGICO, 2005). Phillips and Greenway (1998) studied the effect of waterlogging and subsequent drying on several soil parameters. They found that waterlogging increased the concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , due to the increased solubility of organic carbon. In

fact, the effect was larger in the soil with higher organic carbon content. For soils of the Kampinoski National Park, Poland, Czepinska-Kaminska, Konecka-Betley e Janowska (2003) showed that the highest concentrations of cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) were obtained in the middle of the growing season (July, summer) and it lasted until September, when it dropped down to the initial value in May one year later. We observed a decrease in OM (Student's t-test  $p < 0.05$ ) in March when compared to the values obtained in June (table 3). These results could be due to the wet and growing season (March). Rain could have increased the solubility of organic carbon, thus decreasing OM (table 3) and releasing exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and the soil acidity ( $\text{Al}^{3+}$ ) (table 1).

Table 2 shows the analysis of exchangeable cations,  $\text{K}^+$  and  $\text{Na}^+$  in  $0.05 \text{ mol L}^{-1}$  HCl, and pHs ( $0.01 \text{ mol L}^{-1}$   $\text{CaCl}_2$  and distilled water) of soil samples. For  $\text{P}_0$ ,  $\text{K}^+$  decreased with depth (S.N.K. test  $p < 0.05$ ). On the other hand,  $\text{K}^+$  increased with depth for  $\text{P}_2$  (S.N.K. test  $p < 0.05$ ) (table 2). However, with one exception ( $\text{P}_0$ , June),  $\text{Na}^+$  did not vary with depth (table 2). Annan-Afful et al. (2004) also observed a decrease in  $\text{K}^+$  with depth and that  $\text{Na}^+$  did not change in soils of the Ashanti Region, Ghana forest. However, according to Czepinska-Kaminska, Konecka-Betley e Janowska (2003), soil samples from the Kampinoski National Park, Poland showed that  $\text{K}^+$  and  $\text{Na}^+$  were almost completely depleted below the first soil horizon. In contrast, Fernandes et al. (2002) did not observe changes in  $\text{Na}^+$  and  $\text{K}^+$  concentrations with depth (0-10 cm and 10-20 cm). There is no agreement in the literature about variations of  $\text{Na}^+$  and  $\text{K}^+$  in soils with depth. However it should be pointed out these soils are very different from each other thus some conclusions should be very carefully.

The pHs (distilled water and  $\text{CaCl}_2$ ) of soil samples decreased with the increase in depth (S.N.K. test  $p <$

$0.05$ ) (table 2). As described above, the decrease in pH could be due to the displacement of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  by  $\text{Al}^{3+}$  (PRENZEL; SCHULTE-BISPING, 1995; GUIBAUD; AYELE, 2000). However, Fernandes et al. (2002) did not observe changes in pH with the increase in depth, while Dijkstra and Fitzhugh (2003) and Czepinska-Kaminska, Konecka-Betley e Janowska (2003) observed that pH did not change for some forest soils and increased with the increase in depth for others. Murashkina, Southard e Koptsik (2005) studied northwestern Russia taiga soils and found an increase in pH with increase in depth. They attributed this pH increase to the increase in the concentration of carbonates. Therefore, there is no agreement about the increase/decrease in pH with the increase in depth for forest soils or its cause in the literature.

Table 2 also shows an analysis of exchangeable cations ( $\text{K}^+$ ,  $\text{Na}^+$ ) in HCl  $0.05 \text{ mol L}^{-1}$  and pHs ( $\text{CaCl}_2$   $0.01 \text{ mol L}^{-1}$  and distilled water) of soil samples collected at two different times (March and June 2004). For exchangeable cations ( $\text{K}^+$ ,  $\text{Na}^+$ ), we observed an increase in the concentration of  $\text{K}^+$  in the  $\text{P}_0$  sample (0-32 cm) collected in June compared to that collected in March (Student's t-test  $p < 0.05$ ). For all the other samples, the concentration of exchangeable cations did not change (Student's t-test  $p > 0.05$ ) (table 2). These results show that  $\text{K}^+$  and  $\text{Na}^+$  are not as much influenced by seasonal variation (wet/dry seasons) as other exchangeable cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) (table 1). Czepinska-Kaminska, Konecka-Betley e Janowska (2003) also observed that the concentration of  $\text{Na}^+$  did not change with seasonal variation for forest soils; however, they observed that  $\text{K}^+$  did not change for one sample and that two other samples showed an increase. In contrast, Phillips and Greenway (1998) showed that one of the effects of waterlogging is an increase in  $\text{Na}^+$  and  $\text{K}^+$ .

**Table 2.** Concentration of exchangeable cations and pH in CaCl<sub>2</sub> and distilled water in soil samples from forest reserve located on Universidade Estadual de Londrina campus

| Sample         | Depth (cm) | Exchangeable cations (cmol kg <sup>-1</sup> ) |                              |                              |                          | pH (CaCl <sub>2</sub> ) <sup>#</sup> |                          | pH (H <sub>2</sub> O)        |                              |
|----------------|------------|---|------------------------------|------------------------------|--------------------------|--------------------------------------|--------------------------|------------------------------|------------------------------|
|                |            | K <sup>+</sup> <sup>φ</sup>                   |                              | Na <sup>+</sup> <sup>φ</sup> |                          | M                                    | J                        | M                            | J                            |
| P <sub>0</sub> | 0-32       | 0.015±0.001 <sup>a,φ</sup>                    | 0.028±0.001 <sup>a,φ</sup>   | 0.008±0.001                  | 0.014±0.001 <sup>a</sup> | 4.18±0.02 <sup>a,φ</sup>             | 4.37±0.03 <sup>a,φ</sup> | 5.19±0.01 <sup>b,φ</sup>     | 4.82±0.01 <sup>a,φ</sup>     |
| P <sub>0</sub> | 32-74      | 0.006±0.001 <sup>b</sup>                      | 0.011±0.001 <sup>b,d,f</sup> | 0.003±0.001                  | 0.007±0.001 <sup>b</sup> | 4.05±0.01 <sup>b,d</sup>             | 4.03±0.01 <sup>b,d</sup> | 5.21±0.01 <sup>b,φ</sup>     | 4.52±0.01 <sup>b,d,f,φ</sup> |
| P <sub>0</sub> | 74-104     | 0.008±0.001 <sup>b</sup>                      | 0.011±0.001 <sup>b,d,f</sup> | 0.003±0.001                  | 0.008±0.001 <sup>b</sup> | 4.05±0.01 <sup>b,d</sup>             | 4.07±0.01 <sup>b,d</sup> | 5.19±0.01 <sup>b,φ</sup>     | 4.54±0.02 <sup>b,d,f,φ</sup> |
| P <sub>0</sub> | 104-155    | 0.004±0.001 <sup>b</sup>                      | 0.005±0.001 <sup>b,c</sup>   | 0.003±0.001                  | 0.007±0.001 <sup>b</sup> | 4.05±0.01 <sup>b,d</sup>             | 4.08±0.01 <sup>b,d</sup> | 4.81±0.02 <sup>a,φ</sup>     | 4.41±0.01 <sup>b,d,e,φ</sup> |
| P <sub>0</sub> | 155-200    | 0.006±0.001 <sup>b</sup>                      | 0.006±0.001 <sup>b,c</sup>   | 0.003±0.001                  | 0.007±0.001 <sup>b</sup> | 4.13±0.01 <sup>b,c</sup>             | 4.16±0.01 <sup>b,c</sup> | 5.16±0.01 <sup>b,φ</sup>     | 4.67±0.02 <sup>b,c,φ</sup>   |
| P <sub>2</sub> | 2-37       | 0.009±0.001 <sup>b,d,e</sup>                  | 0.009±0.001 <sup>b,d</sup>   | 0.005±0.001                  | 0.008±0.001              | 5.96±0.02 <sup>a,φ</sup>             | 6.60±0.01 <sup>a,φ</sup> | 6.56±0.01 <sup>a,φ</sup>     | 7.19±0.01 <sup>a,φ</sup>     |
| P <sub>2</sub> | 37-65      | 0.006±0.001 <sup>b,c</sup>                    | 0.012±0.001 <sup>b,d</sup>   | 0.007±0.001                  | 0.007±0.001              | 6.08±0.01 <sup>a,φ</sup>             | 6.56±0.01 <sup>a,φ</sup> | 6.46±0.01 <sup>b,d,f,φ</sup> | 7.03±0.01 <sup>b,c,φ</sup>   |
| P <sub>2</sub> | 65-105     | 0.014±0.001 <sup>b,d,f</sup>                  | 0.009±0.001 <sup>b,d</sup>   | 0.007±0.001                  | 0.007±0.001              | 6.41±0.01 <sup>a,φ</sup>             | 6.29±0.01 <sup>a,φ</sup> | 6.46±0.01 <sup>b,d,f,φ</sup> | 6.72±0.01 <sup>b,d,e,φ</sup> |
| P <sub>2</sub> | 105-153    | 0.012±0.001 <sup>b,d</sup>                    | 0.017±0.001 <sup>b,c</sup>   | 0.003±0.001                  | 0.005±0.001              | 4.88±0.01 <sup>a,φ</sup>             | 4.95±0.01 <sup>a,φ</sup> | 5.71±0.01 <sup>b,c,φ</sup>   | 5.27±0.02 <sup>b,d,f,φ</sup> |
| P <sub>2</sub> | 153-200    | 0.029±0.001 <sup>a</sup>                      | 0.034±0.001 <sup>a</sup>     | 0.005±0.001                  | 0.008±0.001              | 4.53±0.01 <sup>a,φ</sup>             | 4.81±0.01 <sup>a,φ</sup> | 5.55±0.01 <sup>b,d,e,φ</sup> | 5.30±0.01 <sup>b,d,f,φ</sup> |

\*P=soil sampling points, M=March, J=June, <sup>φ</sup>exchangeable cations in HCl 0.05 mol L<sup>-1</sup>, <sup>#</sup>0.01 mol L<sup>-1</sup> of CaCl<sub>2</sub>. All the results are the means of two analyses. The results are presented as mean±S.E.M. SNK test (p<0.05) For K<sup>+</sup>: P<sub>0</sub>M ANOVA (F=18.20, P=0.003), SNK test a/b; P<sub>0</sub>J ANOVA (F=85.70, P=0.000) SNK test a/b, c/d and e/f; P<sub>2</sub>M ANOVA (F=79.50, P=0.000) SNK test a/b, c/d and e/f; P<sub>2</sub>J ANOVA (F=109.70, P=0.000) SNK test a/b and c/d. For Na<sup>+</sup>: P<sub>0</sub>M ANOVA (F=5.00, P=0.054); P<sub>0</sub>J ANOVA (F=9.30, P=0.015) SNK test A/B; P<sub>2</sub>M ANOVA (F=2.00, P=0.144); P<sub>2</sub>J ANOVA (F=1.50, P=0.329). For pH CaCl<sub>2</sub>: P<sub>0</sub>M ANOVA (F=22.63, P=0.002), SNK test A/B and C/D; P<sub>0</sub>J ANOVA (F=71.04, P=0.000) SNK test A/B and C/D; P<sub>2</sub>M ANOVA (F=4180.44, P=0.000) SNK test A/A; P<sub>2</sub>J ANOVA (F=7878.70, P=0.000) SNK test A/A. For pH (H<sub>2</sub>O) P<sub>0</sub>M ANOVA (F=180.13, P=0.003), SNK test A/B; P<sub>0</sub>J ANOVA (F=12.59, P=0.000) SNK test A/B, C/D and E/F; P<sub>2</sub>M ANOVA (F=2284.70, P=0.000) SNK test A/B, C/D and E/F; P<sub>2</sub>J ANOVA (F=5566.06, P=0.000) SNK test A/B, C/D and E/F. It was also used the Student's test to compare March (M) and June (J) results for each depth, <sup>φ</sup>(p<0.05).

Only P<sub>0</sub> (0-32 cm) showed an increase in pH (CaCl<sub>2</sub>) when dry (June) and wet (March) season samples were compared. For P<sub>2</sub> [pH (CaCl<sub>2</sub>)], all samples, except one (P<sub>2</sub>, 65-105 cm), had an increase in pH (Student's t-test, p < 0.05) (table 2). Again, comparing June and March results, pH (distilled water) decreased for all depths for P<sub>0</sub> and for the two last ones for P<sub>2</sub>. Because of the soluble salts (NaCl, NaSO<sub>4</sub>, etc), the pH measured in distilled water is more susceptible to seasonal variation than the pH measured in CaCl<sub>2</sub> (table 2). Therefore, the pH measured in CaCl<sub>2</sub> is more reliable than that measured in distilled water (LUCHESE; FAVERO; LENZI, 2002). Phillips and Greenway (1998) observed an increase in pH due to waterlogging, which could be attributed to the release of Ca<sup>2+</sup> and Mg<sup>2+</sup>. Dijkstra and Fitzhugh (2003) and Czepinska,

Konecka-Betley e Janowska (2003) also observed an increase in pH for some samples collected in spring (wet season) when compared to those collected in fall (dry season). These results are similar to those we obtained for pH measured in distilled water (table 2). Czepinska, Konecka-Betley e Janowska (2003) measured pH in distilled water, but Dijkstra and Fitzhugh (2003) did not add this information to their paper. Therefore, these pH results could be due to the interference of soluble salts (NaCl, NaSO<sub>4</sub>, etc).

Table 3 shows analyses of total phosphorus, P (total), available phosphorus, P (available), and organic matter, OM. The P (total) concentration of most soil samples did not change with the increase in depth. In contrast, the P (available) concentration increased with the increase in depth (S.N.K. test p

< 0.05) (table 3). However, Fernandes et al. (2002) and Annan-Afful et al. (2004) observed a decrease in P (available) with an increase in depth. The concentrations of P (available) in the soils studied here ranged from 0.08 to 1.00 mg kg<sup>-1</sup> and are lower than those obtained by other authors (0.77-2.72 mg kg<sup>-1</sup>) (FERNANDES et al., 2002; ANNAN-AFFUL

et al., 2004; ANNAN-AFFUL et al.; 2004). This lower concentration of P (available) in our soil samples could be due to the low pH of the soils (table 2), because phosphate is more adsorbed by Al<sup>3+</sup> in soils at acidic pHs and Brazilian soils are rich in Fe<sup>3+</sup>, which also adsorbs phosphate (GUILHERME et al, 2000; LUCHESE; FAVERO; LENZI, 2002).

**Table 3.** Concentration of phosphorus (total), phosphorus (available), and OM in soil samples from forest reserve located on Universidade Estadual de Londrina campus

| Sample         |             | P (total)*<br>P <sub>2</sub> O <sub>5</sub> (g kg <sup>-1</sup> ) |                          | P (available) **<br>P <sub>2</sub> O <sub>5</sub> (mg kg <sup>-1</sup> ) |                              | OM (g kg <sup>-1</sup> )# |                               |
|----------------|-------------|---|--------------------------|--|------------------------------|---------------------------|-------------------------------|
| P*             | Depths (cm) | M   | J                        | M  | J                            | M                         | J                             |
| P <sub>0</sub> | 0-32        | 0.94±0.04 <sup>B</sup>  | 0.88±0.01 <sup>B</sup>   | 0.08±0.03 <sup>A,ϑ</sup>   | 0.30±0.01 <sup>B,E,ϑ</sup>   | 23.74±0.12 <sup>A,ϑ</sup> | 26.61±0.04 <sup>A,ϑ</sup>     |
| P <sub>0</sub> | 32-74       | 0.89±0.01 <sup>B</sup>  | 0.87±0.01 <sup>B</sup>   | 0.25±0.01 <sup>B,D,E,ϑ</sup>   | 0.39±0.01 <sup>B,D,F,ϑ</sup> | 15.36±0.05 <sup>A,ϑ</sup> | 16.11±0.12 <sup>A,ϑ</sup>     |
| P <sub>0</sub> | 74-104      | 1.03±0.01 <sup>A,ϑ</sup>  | 0.87±0.01 <sup>B,ϑ</sup> | 0.19±0.01 <sup>B,C,ϑ</sup>   | 0.28±0.01 <sup>B,C,ϑ</sup>   | 11.62±0.02 <sup>A,ϑ</sup> | 14.14±0.06 <sup>A,ϑ</sup>     |
| P <sub>0</sub> | 104-155     | 0.86±0.01 <sup>B</sup>  | 0.81±0.01 <sup>A</sup>   | 0.48±0.01 <sup>B,D,F</sup>   | 0.41±0.02 <sup>B,D,F</sup>   | 10.81±0.01 <sup>A,ϑ</sup> | 15.54±0.03 <sup>A,ϑ</sup>     |
| P <sub>0</sub> | 155-200     | 0.93±0.01 <sup>B,ϑ</sup>  | 0.84±0.01 <sup>ϑ</sup>   | 0.49±0.01 <sup>B,D,F</sup>   | 0.52±0.03 <sup>A</sup>       | 6.16±0.01 <sup>A,ϑ</sup>  | 11.02±0.03 <sup>A,ϑ</sup>     |
| P <sub>2</sub> | 2-37        | 0.74±0.01 <sup>A</sup>  | 0.78±0.01 <sup>B</sup>   | 0.35±0.03 <sup>B,E</sup>   | 0.33±0.01 <sup>B,D,E</sup>   | 24.55±0.05 <sup>A,ϑ</sup> | 22.77±0.04 <sup>A,ϑ</sup>     |
| P <sub>2</sub> | 37-65       | 0.82±0.01 <sup>B</sup>  | 0.80±0.01 <sup>B</sup>   | 0.41±0.04 <sup>B,C,ϑ</sup>   | 0.82±0.01 <sup>B,C,ϑ</sup>   | 17.88±0.03 <sup>A,ϑ</sup> | 14.03±0.10 <sup>B,C,E,ϑ</sup> |
| P <sub>2</sub> | 65-105      | 0.77±0.01   | 0.82±0.01 <sup>B</sup>   | 0.85±0.02 <sup>B,D,F,ϑ</sup>   | 0.11±0.01 <sup>B,D,F,ϑ</sup> | 8.69±0.01 <sup>A</sup>    | 8.88±0.13 <sup>B,D,F</sup>    |
| P <sub>2</sub> | 105-153     | 0.83±0.02 <sup>B</sup>  | 0.79±0.01 <sup>B</sup>   | 0.94±0.02 <sup>B,D,F</sup>   | 1.00±0.03 <sup>A</sup>       | 6.36±0.01 <sup>A,ϑ</sup>  | 9.09±0.04 <sup>B,D,F,ϑ</sup>  |
| P <sub>2</sub> | 153-200     | 0.78±0.01 <sup>ϑ</sup>  | 0.89±0.01 <sup>A,ϑ</sup> | 0.67±0.01 <sup>A</sup>   | 0.76±0.05 <sup>B,D,F</sup>   | 5.35±0.01 <sup>A,ϑ</sup>  | 8.26±0.01 <sup>B,D,ϑ</sup>    |

\*P=soil sampling points, M=March, J=June, \*Total phosphorus in H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O 1:1; \*\*Available phosphorus in HCl 0.05 mol L<sup>-1</sup> and H<sub>2</sub>SO<sub>4</sub> 0.0125 mol L<sup>-1</sup>, #organic matter (OM) from dichromate oxidation; All the results are the means of two analyses. The results are presented as mean±S.E.M. SNK test (p < 0.05) For P (total): P<sub>0</sub>M ANOVA (F=10.38, P=0.012), SNK test A/B; P<sub>0</sub>J ANOVA (F=8.30, P=0.020) SNK test A/B; P<sub>2</sub>M ANOVA (F=8.56, P=0.018) SNK test A/B; P<sub>2</sub>J ANOVA (F=19.30, P=0.003) SNK test A/B. For P (available): P<sub>0</sub>M ANOVA (F=126.42, P=0.000), SNK test A/B, C/D and E/F; P<sub>0</sub>J ANOVA (F=28.91, P=0.001) SNK test A/B, C/D and E/F; P<sub>2</sub>M ANOVA (F=99.97, P=0.000) SNK test A/B, C/D and E/F; P<sub>2</sub>J ANOVA (F=184.77, P=0.000) SNK test A/B, C/D and E/F. For OM: P<sub>0</sub>M ANOVA (F=12354.01, P=0.000), SNK test A/A; P<sub>0</sub>J ANOVA (F=8102.60, P=0.000) SNK test A/A; P<sub>2</sub>M ANOVA (F=93737.61, P=0.000) SNK test A/A; P<sub>2</sub>J ANOVA (F=6227.97, P=0.000) SNK test A/B, C/D and E/F. It was also used the Student's test to compare March (M) and June (J) results for each depth. <sup>ϑ</sup>(p < 0.05).

The analysis of OM shown (table 3) shows that it decreased with the increase in depth (S.N.K. test p < 0.05) as expected since the addition of OM to forest soils is mainly due to fallen leaves and branches on the first horizon. Several other authors also observed a decrease in OM/total carbon/total nitrogen with an increase in depth (FERNANDES et al., 2002;

DIJKSTRA; FITZHUGH, 2003; ANNAN-AFFUL et al., 2004; CIOTTA et al., 2004; IGWE; ZAREI; STAHR, 2005).

The concentration of P (total) in the soil samples collected at P<sub>0</sub> and P<sub>2</sub> in March (wet season) and June (dry season) changed only at the depths of

74-104/155-200 and 153-200 cm, respectively (Student's t-test  $p < 0.05$ ) (table 3). For  $P_0$ , the values of P (total) were larger in March than in June while for  $P_2$  the opposite was observed. For  $P_0$  at depths 0-32/32-74/74-104 cm and  $P_2$  at depth 37-65 cm, the concentration of P (available) in the soil samples collected in June increased when compared to those of samples collected in March and distinctly from that obtained for  $P_2$  at depth 65-105 cm (Student's t-test  $p < 0.05$ ) (table 3).

Among all  $P_0$  and  $P_2$  soil samples collected at depths of 105-153 and 153-200 cm, OM increased for the ones collected in June (dry season) when compared to those collected in March (wet season) (Student's t-test  $p < 0.05$ ) (table 3). Therefore, rain may have increased the solubility of organic carbon, thus decreasing OM. However, the opposite was observed for  $P_2$  samples at depths 2-37 and 37-65 cm (Student's t-test  $p < 0.05$ ) (table 3). Dijkstra and Fitzhugh (2003) observed a decrease in TOC in some soil samples collected in spring when compared to those collected in fall, but the opposite was also obtained. Therefore, there is no simple explanation for the variation of OM with season.

Table 4 shows  $pH_{pzc}$ , CEC, and  $CEC_{potential}$  of soil samples. The  $pH_{pzc}$  of  $P_0$  samples (table 4) are close to the  $pH_{pzc}$  of kaolinite (2.7-4.1, depending on the measurement method), which is the most common clay in this soil (PARKS, 1967; ROCHA; BARROS; GUIMARÃES, 1991; APPEL et al., 2003). However, the  $pH_{pzc}$  of  $P_2$  samples (table 4) are higher than the  $pH_{pzc}$  of kaolinite (2.7-4.1). This effect could be due to the high concentrations of exchangeable cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ) in  $P_2$  samples

when compared to those of  $P_0$  (tables 1, 2). Alleoni et al. (2003) and De Santana et al. (2006) also observed that exchangeable cations have an effect on the increase of  $pH_{pzc}$ . The pHs measured in  $CaCl_2$  as well as in distilled water (table 2) are higher than  $pH_{pzc}$  (table 4), which means that the net charge in those soils is negative. For  $P_0$ ,  $pH_{pzc}$  increased with an increase in depth in contrast with what occurs with  $P_2$  samples (S.N.K. test  $p < 0.05$ ) (table 4). For  $P_0$ , the increase in  $pH_{pzc}$  with an increase in depth could be due to an increase in the concentration of  $Al^{3+}$ , which is higher than that at  $P_2$  (table 1). Arias, Barral e Diaz-Fierros (1995) also observed that  $Al^{3+}$  has an effect on the increase of  $pH_{pzc}$ . On the other hand, the decrease in the  $pH_{pzc}$  of  $P_2$  could be due to the decrease in the concentration of exchangeable cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ) (table 1). The same result was obtained by Van Raij and Peech (1972).

For most soil samples, CEC and  $CEC_{potential}$  decreased with the increase in depth (S.N.K. test  $p < 0.05$ ) (table 4). This was expected because exchangeable cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ) (table 1) and OM (table 3) also decreased with an increase in depth and CEC and  $CEC_{potential}$  are related to their variations. Several other authors who studied forest soils also observed a decrease in CEC/ $CEC_{potential}$  with an increase in depth (ULREY et al., 1995; OLSSON; BENGTTSSON; LUNDKVIST, 1996; CZEPINSKA-KAMINSKA; KONECKA-BETLEY; JANOIWSAKA, 2003; ANNAN-AFFUL et al., 2004). However, Fernandes et al. (2002) studied a tropical forest soil (two depths: 0-10 cm and 10-20 cm) and observed that  $CEC_{potential}$  remained constant.

**Table 4.**  $\text{pH}_{\text{pzc}}$ , CEC and  $\text{CEC}_{\text{potential}}$  values of soil samples from the forest reserve located on the Universidade Estadual de Londrina campus.

| Sample         |             | $\text{pH}_{\text{pzc}}^{\Phi}$ |                              | CEC ( $\text{cmol kg}^{-1}$ ) |                              |   |                              |
|----------------|-------------|---------------------------------|------------------------------|-------------------------------|------------------------------|---|------------------------------|
|                |             |                                 |                              | $\text{CEC}^{\Theta}$         |                              | $\text{CEC}_{\text{potential}}^{\beta}$ |                              |
| P*             | Depths (cm) | M                               | J                            | M                             | J                            | M                                       | J                            |
| P <sub>0</sub> | 0-32        | 3.22±0.01 <sup>B,D,E,Θ</sup>    | 3.68±0.01 <sup>A,Θ</sup>     | 5.06±0.04 <sup>A,Θ</sup>      | 7.21±0.12 <sup>A,Θ</sup>     | 12.21±0.09 <sup>A,Θ</sup>               | 13.81±0.22 <sup>A,Θ</sup>    |
| P <sub>0</sub> | 32-74       | 3.11±0.01 <sup>B,D,F,Θ</sup>    | 3.55±0.01 <sup>A,Θ</sup>     | 4.07±0.38 <sup>B</sup>        | 4.45±0.19 <sup>B,C</sup>     | 10.87±0.48 <sup>B,C</sup>               | 10.65±0.19 <sup>B,C</sup>    |
| P <sub>0</sub> | 74-104      | 3.13±0.01 <sup>B,D,F,Θ</sup>    | 3.77±0.01 <sup>A,Θ</sup>     | 3.27±0.25 <sup>B</sup>        | 3.34±0.05 <sup>B,D</sup>     | 9.47±0.25 <sup>B,D</sup>                | 9.29±0.01 <sup>B,D,F</sup>   |
| P <sub>0</sub> | 104-155     | 3.59±0.01 <sup>A,Θ</sup>        | 4.00±0.01 <sup>A,Θ</sup>     | 2.95±0.01 <sup>B,Θ</sup>      | 3.59±0.13 <sup>B,D,E,Θ</sup> | 10.20±0.04 <sup>B</sup>                 | 10.29±0.23 <sup>B,E</sup>    |
| P <sub>0</sub> | 155-200     | 3.53±0.01 <sup>B,C,Θ</sup>      | 4.05±0.01 <sup>A,Θ</sup>     | 3.04±0.18 <sup>B</sup>        | 2.98±0.04 <sup>B,D,F</sup>   | 9.44±0.08 <sup>B,D,Θ</sup>              | 8.73±0.11 <sup>B,D,F,Θ</sup> |
| P <sub>2</sub> | 2-37        | 5.05±0.01 <sup>A</sup>          | 5.15±0.03 <sup>A</sup>       | 10.12±0.26 <sup>A,Θ</sup>     | 11.68±0.15 <sup>A,Θ</sup>    | 13.07±0.11 <sup>A</sup>                 | 13.03±0.10 <sup>A</sup>      |
| P <sub>2</sub> | 37-65       | 5.10±0.01 <sup>A,Θ</sup>        | 4.96±0.01 <sup>B,C,Θ</sup>   | 7.92±0.35 <sup>A</sup>        | 8.13±0.10 <sup>A</sup>       | 10.02±0.45 <sup>B,C</sup>               | 9.68±0.05 <sup>B,C</sup>     |
| P <sub>2</sub> | 65-105      | 5.33±0.01 <sup>A,Θ</sup>        | 4.85±0.01 <sup>B,D,E,Θ</sup> | 6.72±0.40 <sup>A</sup>        | 6.57±0.11 <sup>A</sup>       | 8.22±0.40 <sup>B,D</sup>                | 8.52±0.26 <sup>B,D,F</sup>   |
| P <sub>2</sub> | 105-153     | 3.69±0.01 <sup>A,Θ</sup>        | 4.16±0.01 <sup>B,D,F,Θ</sup> | 5.42±0.12 <sup>A,Θ</sup>      | 4.49±0.05 <sup>A,Θ</sup>     | 9.57±0.07 <sup>B,Θ</sup>                | 8.24±0.10 <sup>B,D,F,Θ</sup> |
| P <sub>2</sub> | 153-200     | 3.53±0.02 <sup>A,Θ</sup>        | 4.15±0.01 <sup>B,D,F,Θ</sup> | 4.01±0.16 <sup>A</sup>        | 3.88±0.10 <sup>A</sup>       | 8.91±0.26 <sup>B,Θ</sup>                | 7.08±0.20 <sup>B,D,E,Θ</sup> |

\*P=soil sampling points, M=March, J=June,  $\Phi$ point of zero charge ( $\text{pH}_{\text{pzc}}$ ) using the equation  $\text{pH}_{\text{pzc}} = 2\text{pH KCl} - 1.0 \text{ mol L}^{-1} - \text{pH H}_2\text{O}$ -distilled water (Uehara 1979);  $\Theta$ cation exchange capacities (CEC) were calculated by the sum up the exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ) in KCl 1.0 mol L<sup>-1</sup> and  $\text{K}^+/\text{Na}^+$  in HCl 0.05 mol L<sup>-1</sup>;  $\beta$ potential cation exchange capacities ( $\text{CEC}_{\text{potential}}$ ) were calculated by the sum of CEC and the potential extractable acidity ( $\text{Al}^{3+} + \text{H}^+$ ) using 0.5 mol L<sup>-1</sup> Ca(Oac)<sub>2</sub>. All the results are the means of two analyses. The results are presented as mean±S.E.M. SNK test (p<0.05) For  $\text{pH}_{\text{pzc}}$ : P<sub>0</sub>M ANOVA (F=517.80, P=0.000), SNK test A/B, C/D and E/F; P<sub>0</sub>J ANOVA (F=449.50, P=0.000) SNK test A/A; P<sub>2</sub>M ANOVA (F=4594.80, P=0.000) SNK test A/A; P<sub>2</sub>J ANOVA (F=842.42, P=0.000) SNK test A/B, C/D and E/F. For CEC: P<sub>0</sub>M ANOVA (F=16.43, P=0.004), SNK test A/B; P<sub>0</sub>J ANOVA (F=203.81, P=0.000) SNK test A/B, C/D and E/F; P<sub>2</sub>M ANOVA (F=70.38, P=0.000) SNK test A/A; P<sub>2</sub>J ANOVA (F=862.22, P=0.000) SNK test A/A. For  $\text{CEC}_{\text{potential}}$ : P<sub>0</sub>M ANOVA (F=21.51, P=0.002), SNK test A/B and C/D; P<sub>0</sub>J ANOVA (F=130.39, P=0.000) SNK test A/B, C/D and E/F; P<sub>2</sub>M ANOVA (F=39.02, P=0.000) SNK test A/B and C/D; P<sub>2</sub>J ANOVA (F=199.05, P=0.000) SNK test A/B, C/D and E/F. For each depth, it was also used the Student's test to compare March (M) and June (J) results,  $\Theta$ (p<0.05).

For all P<sub>0</sub> and P<sub>2</sub> samples at depths 105-153 and 153-200 cm, the  $\text{pH}_{\text{pzc}}$  of the samples collected in June (dry season) was higher than those of samples collected in March (wet season) (Student's t-test p < 0.05) (table 4). The reverse was obtained for P<sub>2</sub> samples at depths 37-65 and 65-105 cm (Student's t-test p < 0.05) and for depth 2-37 cm; it remained constant (Student's t-test p > 0.05) (table 4). In this case, it is not easy to find out which components affect  $\text{pH}_{\text{pzc}}$ .

For most P<sub>0</sub> and P<sub>2</sub> samples, the wet/dry season did not affect either CEC or  $\text{CEC}_{\text{potential}}$  (Student's t-test p > 0.05) (table 4). CEC showed an increase for P<sub>0</sub> (0-32, 104-155 cm) and P<sub>2</sub> (2-37 cm) samples collected in June (dry season) when compared to those collected in March (wet season) (Student's t-test p < 0.05) (table 4). In contrast, the  $\text{CEC}_{\text{potential}}$  of P<sub>0</sub> (155-200 cm) and P<sub>2</sub> (105-153, 153-200 cm) samples collected in June decreased when compared to those of samples collected in March (Student's

t-test  $p < 0.05$ ) (table 4). Czepinska-Kaminska, Konecka-Betley e Janowska (2003) observed an increase in CEC for two samples collected in July (wet season) and that of one sample did no change. Thus, in this case, it is not easy to find out which components affect CEC and  $CEC_{potential}$  either.

## Conclusion

In summary, this work has shown that the concentration of  $Al^{3+}$  increases with the increase in depth and those of exchangeable cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ) decrease with the increase in depth, and that this could related to the decrease in pH with depth.

The concentrations of the cations ( $Al^{3+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) are affected by dry/wet season. We observed a decrease in concentration of exchangeable cations in the samples collected in June (dry season) when compared to those of samples collected in March (wet season). Rain may have increased the solubility of organic carbon, thus decreasing OM and releasing cations ( $Al^{3+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ).

The concentration of the exchangeable cation  $Na^+$  did not change with depth. For  $P_0$ , the concentration of  $K^+$  decreased with depth while for  $P_2$  it increased. There is no agreement in the literature about variations of  $Na^+$  and  $K^+$  in soils with depth.

The pHs (distilled water and  $CaCl_2$ ) of the soil samples decreased with the increase in depth, possibly due to the displacement of  $Ca^{2+}$  and  $Mg^{2+}$  by  $Al^{3+}$ .

The concentration of P (total) did not change with the increase in depth. P (available) showed an increase in concentration with an increase in depth. The low concentration of P (available) in soil samples could be due to the low pH of these soils, because phosphate is more adsorbed by  $Al^{3+}$  and  $Fe^{3+}$  at acidic pHs.

The seasonal variation results (wet/dry season) of P (total) and P (available) are not consistent with any explanation.

As expected, the concentration of OM decreased with the increase in depth.

Most soil samples collected in June (dry season) showed an increase in OM when compared to the values of those collected in March (wet season). Rain may have increased the solubility of organic carbon, thus decreasing OM.

The value of  $pH_{pzc}$  is influenced by the concentrations of exchangeable cations ( $Al^{3+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ), and the pHs measured in  $CaCl_2$  and distilled water are higher than  $pH_{pzc}$ , which means that the soil net charge is negative.

The results of seasonal variation (wet/dry) of  $pH_{pzc}$  are not consistent with any explanation.

For most of the soil samples, CEC and  $CEC_{potential}$  decreased with an increase in depth. This was expected because exchangeable cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ) and OM also decreased with an increase in depth, and CEC and  $CEC_{potential}$  are related to their variations.

## Acknowledgements

This research has been supported by grants from capes/PROAP, Fundação Araucária (number 2421), and CNPq (473076/2004).

## References

- ALLEONI, L. R. F.; ZAMBROSI, F. C. B.; MOREIRA, S. G.; PROCHOW, L. I.; PAULETTI, V. Liming an electrochemical attributes of an oxisol under no tillage. *Scientia Agrícola*, Piracicaba, v. 60, n. 1, p. 119-123, 2003.
- ANNAN-AFFUL, E.; IWASHIMA, N.; OTOO, E.; OWUSU-SEYERE, E.; ASUBONTENG, K. O.; KAMIDOHZONO, A.; MASUNAGA, T.; WAKATSUKI, T. Land use dynamics and nutrient characteristics of soils and plants along topo-sequences in inland valley watersheds Ashanti Region, Ghana. *Soil Science and Plant Nutrition*, Tokyo, v. 50, n. 5, p. 633-647. 2004.
- ANNAN-AFFUL, E.; IWASHIMA, N.; OTOO, E.; ASUBONTENG, K. O.; KUBOTA, D.; KAMIDOHZONO, A.; MASUNAGA, T.; WAKATSUKI,

- T. Nutrient and bulk density characteristics of soil profiles in six land use systems along topo-sequences in inland valley watersheds of Ashanti Region. Ghana. *Soil Science and Plant Nutrition*, Tokyo, v. 50, n. 5, p. 649-664, 2004.
- APPEL, C.; MA, L. Q.; RHUE, R. D.; KENNELLEY, E. Point of zero charge determination in soils and minerals via traditional methods and detection of electroacoustic mobility. *Geoderma*, Amsterdam, v. 113, n. 1, p. 77-93, 2003.
- ARIAS, M.; BARRAL, M. T.; DIAZ-FIERROS, F. Effects of iron and aluminum oxides on the colloidal and surface properties of kaolin. *Clays and Clay Minerals*, New York, v. 43, n. 4, p. 406-416, 1995.
- CIOTTA, M. N.; BAYER, C.; ERNANI, P. R.; FONTOURA, S. M. V.; WOBETO, C.; ALBUQUERQUE, J. A. Liming management and its effect on acidity components of an oxisol under no tillage. *Revista Brasileira de Ciência do Solo*, Campinas, v. 28, n. 2, p. 317-326, 2004.
- CZEPINSKA-KAMINSKA, D.; KONECKA-BETLEY, K.; JANOWSKA, E. The dynamics of exchangeable cations in the environment of soils at Kampinoski National Park. *Chemosphere*, Oxford, v. 52, n. 3, p. 581-584, 2003.
- DE SANTANA, H.; TONI, R. M.; BENETOLI, L. L. O. B.; ZAIA, C. T. B. V.; ROSA JUNIOR, M.; ZAIA, D. A. M. Effect in glyphosate adsorption on clays and soils heated and characterization by FT-IR spectroscopy. *Geoderma*, Amsterdam, v. 136, n. 3/4, p. 738-750, 2006.
- DIJKSTRA, F. A.; FITZHUGH, R. D. Aluminum solubility and mobility in relation to organic carbon in surface soils affected by six tree species of the northeastern United States. *Geoderma*, Amsterdam, v. 114, n. 1/2, p. 33-47, 2003.
- EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA – EMBRAPA. *Manual de métodos de análises de solo*. 2. ed. Rio de Janeiro: EMBRAPA, 1997.
- FERNANDES, S. A. P.; BERNOUX, M.; CERRI, C. C.; FEIGL, B. J.; PICCOLO, M. C. Seasonal variation of soil chemical properties and CO<sub>2</sub> and CH<sub>4</sub> fluxes in unfertilized and P-fertilized pastures in an utisol of Brazilian Amazon. *Geoderma*, Amsterdam, v. 107, n. 3/4, p. 227-241, 2002.
- GUIBAUD, G.; AYELE, J. pH and ionic strength effect on release of aluminum by limousin acidic brown earth soils-Impact on natural water pollution. *Environmental Technology*, London, v. 21, n. 13, p. 257-269, 2000.
- GUILHERME, L. R. G.; CURI, N.; SILVA, M. L. N.; RENO, N. B.; MACHADO, R. A. F. Phosphorus adsorption in lowland soils from Minas Gerais state, Brazil. *Revista Brasileira de Ciências do Solo*, Campinas, v. 24, n. 1, p. 27-34, 2000.
- IGWE, C. A.; ZAREI, M.; STAHR, K. Mineral and elemental distribution in soils formed on the river Niger floodplain, eastern Nigeria. *Australian Journal of Soil Research*, Melbourne, v. 43, n. 2, p. 147-158, 2005.
- INSTITUTO AGRONÔMICO DO PARANÁ – IAPAR. *Manual de análise química de solo e controle de qualidade*. Londrina: IAPAR, 1992.
- LUCHESE, E. B.; FAVERO, L. O. B.; LENZI, E. *Fundamentos da Química do Solo*. 2. ed. Rio de Janeiro: Freitas Bastos Editora, 2002.
- MURASHKINA, M.; SOUTHARD, R. J.; KOPTSIK, G. N. Soil landscape relationships in the taiga of northwestern Russia highlight the differences in the U. S. and Russian soil classification systems. *Soil Science*, Baltimore, v. 170, n. 6, p. 469-480, 2005.
- NISSINEN, A.; ILVESNIEMI, H.; TANSKANEN, N. Apparent cation-exchange equilibria in podzolic forest soils. *European Journal of Soil Science*, Oxford, v. 49, n. 12, p. 121-132, 1998.
- OLSSON, B. A.; BENGTSSON, J.; LUNDKVIST, H. Effect of different harvest intensities on the pools of exchangeable cations in coniferous forest soils. *Forest and Ecology Management*, Amsterdam, v. 84, n. 1/3, p. 135-147, 1996.
- PARKS, G. A. Aqueous surface chemistry of oxides and complex oxide minerals. Iso-electric point and zero point of charge In: STUMM, W. (Ed.) *Equilibrium concepts in natural water systems*. Washington: Advanced in Chemistry series, 1967. n. 67, p. 121-160.
- PHILLIPS, I. R.; GREENWAY, M. Changes in water-soluble and exchangeable ions, cation exchangeable capacity, and phosphorus (max) in soils under alternating waterlogged and drying conditions. *Communication Soil Science and Plant*, New York, v. 29, n. 1/2, p. 51-65, 1998.
- PRENZEL, J.; SCHULTE-BISPING, H. Some chemical parameter relations in a population of German forest soils. *Geoderma*, Amsterdam, v. 64, n. 3/4, p. 309-326, 1995.
- ROCHA, G. C.; BARROS, O. N. F.; GUIMARÃES, M. F. Spatial distribution and characteristics of the soils occurring at campus of the Universidade Estadual de Londrina, Paraná, Brazil. *Semina*, Londrina, v. 12, p. 25-37, 1991.

- SIMEPAR INSTITUTO TECNOLÓGICO – SIMEPAR. *Withdrawn World Wide Web in April*. 2005. Disposable in: <http://www.simepar.br/index.html>. Access in: 10 Jun. 2008.
- UEHARA, G. Mineral-chemical properties of oxisols. In: INTERNATIONAL SOIL CLASSIFICATION WORKSHOP, 2.; 1979, Bangkok. *Proceedings...* Bangkok: Soil Survey Division-Land Development Department, 1979. p 45-60.
- ULREY, A. L.; GRAHAM, R. C.; CHADWICK, O. A.; WOOD, H. B. Decade-scale changes of soil carbon, nitrogen and exchangeable cations under chaparral and pine. *Geoderma*, Amsterdam, v. 65, n. 1/2, p. 121-134, 1995.
- VAN RAIJ, B.; PEECH, M. Electrochemical Properties of Some Oxisols and Alfisols of the Tropics. *Soil Society of America Journal*, Madison, v. 36, n. 4, p. 587-593, 1972.
- YANAI, R. D.; PHILLIPS, R. P.; ARTHUR, M. A.; SICCAMA, T. G.; HANE, E. N. Spatial and temporal variation in calcium and aluminum in northern hardwood forest floors. *Water and Air Pollution*, London, v. 160, n. 1/4, p. 109-118, 2005.

