


Division - Soil Use and Management | Commission - Soil and Water Management and Conservation

# Impacts of Pig Slurry Applied to Two Different Soils on Nutrient Transport by Runoff

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**ABSTRACT:** Runoff in agricultural areas with intensive application of pig slurry can transport significant amounts of nutrients. This study evaluates the effects of different pig slurry (PS) application rates (0, 50, 100, and 200 m<sup>3</sup> ha<sup>-1</sup>) on nutrient loss through runoff during soybean cultivation under no-tillage. It was conducted at two sites in southern Brazil, one on an Alfisol (27° 43' south and 50° 3' west) and one on an Inceptisol (27° 47' south and 50° 18' west). The PS was applied to the soil once at the beginning of the soybean cycle. Each plot was 11 m long in the direction of the slope and 3.5 m wide. To induce runoff, artificial rainfall was applied in four different tests (T1, T2, T3, T4), with an intensity of 65 mm h<sup>-1</sup> for 90 minutes. The first test was performed one day after PS application, while the other tests were performed throughout the soybean cycle. During each test, runoff samples were collected at 10-min intervals after the beginning of runoff. The runoff amount and the NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, P, and K<sup>+</sup> concentrations in the runoff were measured. In T1, nutrient transport from the Alfisol and the Inceptisol increased with increasing PS doses. In some cases, this effect was still noticeable in T2 and T3, but not in the last test (T4). The transported amounts of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, P, and K<sup>+</sup> decreased as the period between PS application and simulated rainfall increased. Regardless of the soil and the treatment, NO<sub>3</sub><sup>-</sup> was transported in the greatest quantities, followed by K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and P.

**Keywords:** organic fertilization, artificial rainfall, nutrient loss.

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## INTRODUCTION

In the south of Brazil, pig farming, mostly under a confinement regime, is an important economic activity. The intense production and the generation of a large volume of residues in small family farms, sometimes concentrated in a limited area, have led to significant environmental problems (Basso et al., 2017). In the state of Santa Catarina, 47,000 m<sup>3</sup> day<sup>-1</sup> of pig slurry (PS) are produced (ABCS, 2014).

Pig slurry is applied to the soil as an organic fertilizer, replacing or supplementing the recommended mineral fertilization (Carvalho et al., 2014). Up to the first half of 2014, the maximum permitted amount of organic fertilizers applied to crops was 50 m<sup>3</sup> ha<sup>-1</sup> yr<sup>-1</sup>, but in the second half of 2014, Normative Instruction No. 11 was modified and, from then, the application of organic fertilizers to the soil has been following the agronomic recommendations as outlined in the Fertilization and Liming Manual (CQFS-RS/SC, 2004), with application rates determined according to soil analysis, the nutritional needs of the crop to be fertilized, nutrient contents, and the agronomic efficiency index of nutrients for each type of organic fertilizer (Fatma, 2014). However, due to the difficulties in the supervision by the environmental agency and the lack of incentives to farmers, the rules for the application of organic fertilizers are rarely followed, with significant risks for soil, water, and air quality.

Water contamination due to the application of PS to a soil can be caused by the transport of nutrients such as nitrogen (N), phosphorus (P), potassium (K), copper (Cu), zinc (Zn), and others contained in PS by runoff and drainage from the soil profile (Dal Bosco, 2007). The nutrients can either be adsorbed to the solid particles (mineral and organic) in the soil or dissolved in the runoff water (Barrows and Kilmer, 1963). Their concentrations in the runoff water varies with rainfall (Barrows and Kilmer, 1963), soil type, and concentration in the soil (Seganfredo et al., 1997; Silva et al., 2012), but also with the agricultural management practices employed, such as the cropping system, the soil preparation method, and the frequency and form of the application of fertilizers and correctives (Barrows and Kilmer, 1963; Seganfredo et al., 1997; Guadagnin et al., 2005; Gilles et al., 2009). Nutrients from organic fertilizers such as PS are more easily transported by runoff due to their lower density when compared to mineral fertilizers (Barrows and Kilmer, 1963). Moreover, the superficial application of PS or fertilizers without incorporation into the soil also facilitates nutrient transport by runoff (Cassol et al., 2002). Among the nutrients present in PS, N, P, and K usually occur in higher levels; of these, N and P pose an imminent risk of water pollution (Basso et al., 2005; Assmann et al., 2007).

Nitrate (NO<sub>3</sub><sup>-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>) are the two inorganic forms of N used by plants. While nitrate is mainly maintained in solution and most readily available for plant absorption, ammonium ions are mostly kept in the cation exchange complexes in the soil (Schoonover and Crim, 2015).

Since N deficiencies in crops are widespread and can lead to low crop yields, N fertilizers are often applied excessively. As a result, substantial losses of N may occur through ammonia volatilization or, since it is extremely mobile, nitrate leaching from the soil profile. In addition, excess N in a soil can lead to incomplete denitrification, resulting in the release of nitrous oxide into the atmosphere (Basso, 2003; Schoonover and Crim, 2015).

Nitrogen losses can be potentiated when PS is applied to soybean crops. Due to the biological N fixation, the soybean extracts less N from the soil, and consequently, the unnecessary application of N via PS results in the leaching of NO<sub>3</sub><sup>-</sup> into the soil profile (Owens et al., 2000; Caovilla et al., 2005). According to these authors, N losses can be minimized by crop rotation, for example, corn cultivation in sequence, which extracts

large amounts of N from the soil. Moreover, this makes the addition of nitrogen fertilizer in corn crops unnecessary.

The excess of  $\text{NO}_3^-$  in drinking water is a concern for several reasons. Most importantly, it can cause the blue-baby syndrome in newborns (Boink and Speijers, 2001), but in addition, when  $\text{NO}_3^-$  is converted into nitrosamines and nitrosamides in the human body, it becomes a potential carcinogen. It can also lead to poor congenital formations, mainly in the central nervous system (Ward et al., 2005).

In addition to being an excellent source of N for plants, PS is a significant source of P and K (Assmann et al., 2007). Most of the natural P in a soil is derived from mineral weathering and the decomposition of organic matter. However, the contents of plant-available P are generally very low in soils, since most of the P is insoluble (Schoonover and Crim, 2015). Unlike  $\text{NO}_3^-$ , which is mobile in the soil profile, P readily binds to soil minerals and is therefore often transported with sediments in runoff (Klein and Agne, 2012). However, transport of P through the soil profile into groundwater can also occur when large amounts are applied to the soil surface several times in succession (Basso et al., 2005).

Potassium, considered a mobile element, is susceptible to leaching; however, its dynamics is determined, in part, by the exchange of ions and the adsorption by clays (Oren et al., 2004). Environmentally, K is not considered a potential contaminant, and there are no regulations that indicate a threshold value of K in water bodies.

The quality standard of water bodies in Brazil is established by Resolution Conama 357 (Conama, 2005). For freshwater bodies of class 1, class 2, and class 3, Conama 357 states a limit of  $10 \text{ mg L}^{-1}$  for  $\text{NO}_3^-$ . For total ammonium nitrogen, the threshold, besides varying with the class and type of flow (lentic, intermediate, or lotic), depends on the pH of the water. For P, the limit varies according to the class and flow type of the water body. The most restrictive values are  $3.7 \text{ mg L}^{-1}$  for total ammonium nitrogen and  $0.02 \text{ mg L}^{-1}$  for P.

An excess of N and P in water triggers the widely investigated eutrophication phenomenon (Smith and Schindler, 2009; Bachmann et al., 2013; Fontana et al., 2014; Smith et al., 2014; Andrietti et al., 2016; Grilo et al., 2016; Wiegand et al., 2016).

In the literature, there are numerous studies on the effect of PS application on nutrient losses from a field. Studies focused on comparisons between the application of PS, which is an organic fertilizer, and mineral fertilizer (Bertol et al., 2005, 2010; Santos et al., 2015; Tomer et al., 2016), evaluations of different rates and amounts of PS applied (Ceretta et al., 2005, 2010; Mecabo Júnior et al., 2014; Sacomori et al., 2016), comparisons of PS application with different organic sources, such as aviary manure (Oliveira et al., 2015) or bovine manure (Lourenzi et al., 2014), evaluations of different time intervals between the application of PS and the occurrence of the first rain event (Smith et al., 2007; Flynn et al., 2013), comparisons of the PS application method, with or without incorporation into the soil (Allen and Mallarino, 2008), or the application of PS in different management systems (Pineiro et al., 2016).

However, there is a lack of studies evaluating the loss of nutrients after the application of PS as a crop develops; in addition, studies carried out in large field plots, such as those used in the present study ( $38.5 \text{ m}^2$ ), are scarce. Most studies have been performed using plots of only  $1 \text{ m}^2$  and are therefore not very representative. Hence, the objective of this study was to evaluate the effects of different PS application rates on nutrient loss through runoff during the development of a soybean crop under no-tillage on large plots considered to be representative of field conditions. To induce runoff, the plots were irrigated.

## MATERIALS AND METHODS

### Site description

The study was conducted during the spring/summer 2013/2014 in two experimental areas, one near the city of São José do Cerrito and the other near the city of Lages, both located in the state of Santa Catarina, Brazil. The coordinates of the São José do Cerrito site are 27° 43' south and 50° 31' west, at an approximate elevation of 800 m. The soil is a *Nitossolo Bruno aluminoférrico húmico* (Santos et al., 2013), an Alfisol (Soil Survey Staff, 2014), with 280 g kg<sup>-1</sup> of sand, 100 g kg<sup>-1</sup> of silt, and 620 g kg<sup>-1</sup> of clay (Barbosa et al., 2012) and with a clayey texture (USDA, 2017). The experimental area of Lages is located at 27° 47' south and 50° 18' west at an approximate elevation of 900 m. The soil is a *Cambissolo Húmico aluminico léptico* (Santos et al., 2013), an Inceptisol (Soil Survey Staff, 2014), with 196 g kg<sup>-1</sup> of sand, 412 g kg<sup>-1</sup> of silt, and 392 g kg<sup>-1</sup> of clay (Ramos et al., 2014) and with a silty clay loam texture (USDA, 2017).

According to the classification of Köppen system, the climate in both areas is of type Cfb: subtropical, humid, rainy, with fresh summers. Mean annual rainfall ranges between 1,450 to 1,650 mm (Inmet, 1992).

In each site, eight plots were constructed; each plot was 11 m long and 3.5 m wide, with a total area of 38.5 m<sup>2</sup>, as recommended by Embrapa (1975). Thus, the useful area at each site was 308 m<sup>2</sup>. The longest side of each plot was arranged in the direction of the slope of the terrain. The mean slope of the terrain in *Nitossolo* (Alfisol) and *Cambissolo* (Inceptisol) was 0.140 and 0.135 mm<sup>-1</sup>, respectively. To hydraulically isolate the sides and the upper ends of each plot, galvanized metal sheets with a height of 0.2 m were used, which were buried in the soil at a depth of 0.1 m. In addition, in each plot, at the lower end, a collection system was installed to concentrate the runoff. This system was composed of a galvanized metal trough coupled to a 6-m long PVC pipe.

### Treatments and experimental design

The experimental design was completely randomized, and four treatments with two replicates were evaluated at each site. Therefore, each site had eight plots, and each plot covered an area of 38.5 m<sup>2</sup>. The treatments consisted of four amounts of PS (0, 50, 100, and 200 m<sup>3</sup> ha<sup>-1</sup> yr<sup>-1</sup>), applied to the soil surface in a soybean crop (*Glycine max*). The amounts were based on Fatma's Normative Instruction No. 11 (Fatma, 2000), which, at the time our experiments were initiated (2013), established 50 m<sup>3</sup> ha<sup>-1</sup> yr<sup>-1</sup> as the maximum rate of PS which could be applied to crops. Our intention was to test this rate, as well as double and quadruple rates, because the majority of farmers did not respect this 50 m<sup>3</sup> ha<sup>-1</sup> yr<sup>-1</sup> limit.

The work at São José do Cerrito (*Nitossolo* - Alfisol) started at the end of the autumn/winter 2013 cropping season, after research conducted by Mecabo Júnior et al. (2014) on a turnip crop (*Raphanus raphanistrum*). At the end of its growth, the turnip crop was cut and left on the soil to serve as mulch. Soybeans were sown as the follow-up crop.

The preparation of the experimental area at Lages (*Cambissolo* - Inceptisol) started at the end of the autumn/winter harvest of 2012, after an experiment conducted by Ramos et al. (2014) had ended. From this moment on, the soil did not experience any type of management. As a result, spontaneous plant development occurred, predominantly Papuan grass (*Brachiaria plantaginea*). In April 2013, this cover was cut and removed from the plots. Afterwards, all plots were plowed twice with three discs on different days, once in the direction of the slope and once against the direction of the slope. Subsequently, in July 2013, black oats were planted manually in all plots. At the end of

their growth cycle, they were cut and left on the ground to serve as mulch. Afterwards, soybeans were sown.

In both experimental areas, the soybeans (*Glycine max*, cultivar Brasmax Força RR) were sown in November 2013 with a manual planter. The line spacing was 0.5 m, with seven lines per plot. During the soybean cycle, herbicide, insecticide, and fungicide were applied. On the *Nitossolo* - Alfisol, there was turnip residue, while on the *Cambissolo* - Inceptisol, there was black oat residue on the soil surface.

### Pig slurry application

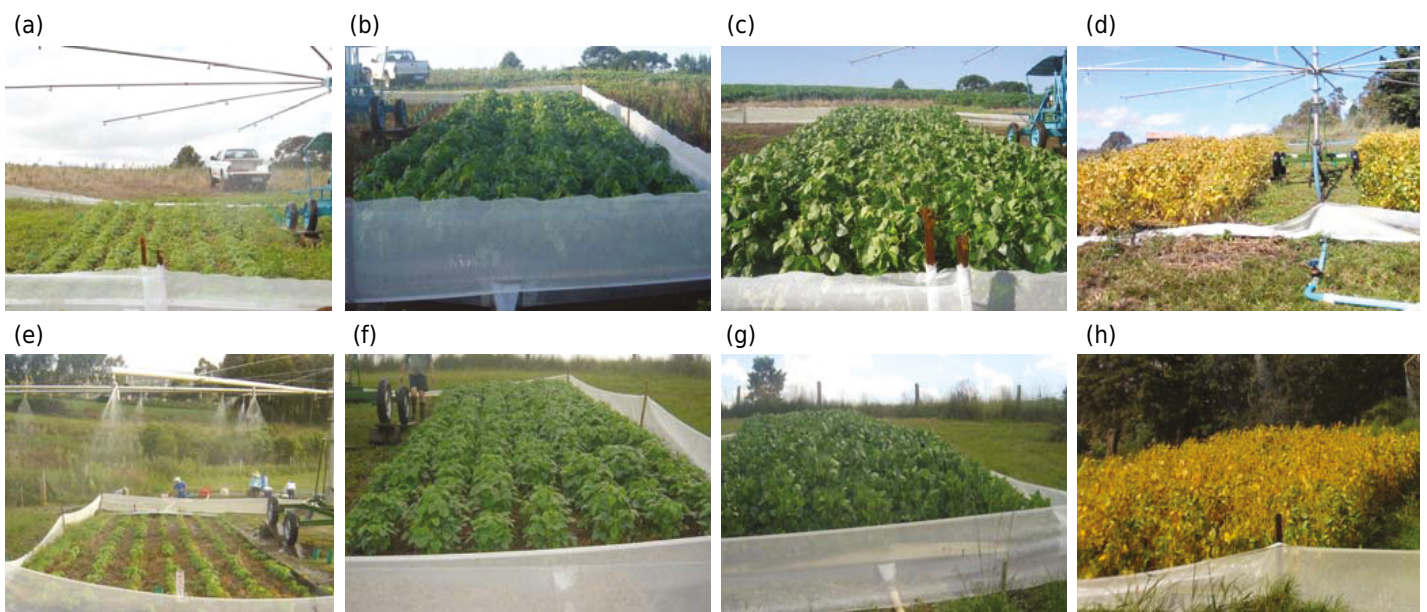
Pig slurry was applied to the soil surface on each plot once, soon after soybean germination and one day before the first simulated rainfall test. The PS was applied manually with the aid of watering cans and consisted of a mixture of feces, urine, water, and other residues from cleaning the pig facilities. Prior to use, it was stored in stabilization ponds.

Prior to this experiment, previous crops on the two experimental sites had already received applications of PS at the same rates used in this work. That is, the experiment was already outlined, and the same parcel that received  $50 \text{ m}^3 \text{ ha}^{-1} \text{ yr}^{-1}$  at the first time received the same rate at the subsequent applications. This logic was also repeated in the other plots, which received 0, 100, and  $200 \text{ m}^3 \text{ ha}^{-1} \text{ yr}^{-1}$  of PS for both sites. On *Nitossolo*, the PS had already been applied once on the black oats, once on the corn, and once on the forage turnip, while on the *Cambissolo*, the PS had already been applied once on the black oat cultivation. Thus, with the application of PS on soybean, the *Nitossolo* received PS four times and the *Cambissolo* two times.

### Simulated rain tests and rain simulators

In each treatment, four artificial rainfall events were applied, each at a constant rate of  $65 \text{ mm h}^{-1}$  and for a duration of 90 minutes. The intensity of  $65 \text{ mm h}^{-1}$  follows the recommendations by Wischmeier and Smith (1978).

On both soils (*Nitossolo* and *Cambissolo*), the first rainfall test (T1) was performed one day after the application of PS, and the subsequent rainfall tests were performed 20, 40, and 110 days after PS application (T2, T3, and T4, respectively). The soybean crop at the time of each rainfall test is shown in figure 1.



**Figure 1.** Pictures of the soybean crop at the time of the four rainfall applications on the *Nitossolo* - Alfisol and the *Cambissolo* - Inceptisol. *Nitossolo*: a = T1, b = T2, c = T3, and d = T4; *Cambissolo*: e = T1, f = T2, g = T3, and h = T4.

Between each simulated rainfall test, natural rainfall events occurred. Ten days before the T1 test, 42 mm of natural rain precipitated; between tests T1 and T2, 72 mm of natural rain precipitated; between T2 and T3, 125 mm; and between T3 and T4, 345 mm of natural rainfall occurred.

The rains were applied with rainfall simulators with rotating arms. On the *Nitossolo*, a Swanson-type simulator was used, in which the arms are driven by an engine (Swanson, 1965). A buoyancy-type simulator, developed by Bertol et al. (2012), where the movement of the arms occurs due to the water pressure, was used in the experiment conducted on the *Cambissolo*.

Both simulators have 10 arms, with each arm being 7.5 m long and with three sprinklers (type S.S.CO. VEEJET 80/100) mounted on it (Meyer and McCune, 1958). The sprinklers were installed at 2.5 m above ground level and simultaneously wetted the area of two plots. In the experiment on the *Nitossolo*, the water was pumped from a nearby river, while in the experiment on the *Cambissolo*, water was obtained from a lake.

The parameters  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , P,  $\text{K}^+$ , and pH were determined in the waters used in the simulated rainfall events, with the following results:  $\text{NO}_3^- = 0.030 \text{ mg L}^{-1}$ ;  $\text{NH}_4^+ = <0.001 \text{ mg L}^{-1}$ ;  $\text{P} = <0.001 \text{ mg L}^{-1}$ ;  $\text{K}^+ = 0.034 \text{ mg L}^{-1}$  in the river water and  $\text{NO}_3^- = 0.014 \text{ mg L}^{-1}$ ;  $\text{NH}_4^+ = <0.001 \text{ mg L}^{-1}$ ;  $\text{P} = <0.001 \text{ mg L}^{-1}$ ;  $\text{K}^+ = 0.042 \text{ mg L}^{-1}$  in the lake water. The pH was 6.9 for the river and 6.6 for the lake water.

### Sampling and analysis of the runoff water

During the simulated rainfall, the flow was measured at intervals of 10 minutes. For this, a graduated bucket was used to measure the volume and a stopwatch to mark the time, and the runoff rate was calculated accordingly (Cogo, 1981). In addition, subsamples were collected in 0.25-L vessels for the determination of nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), phosphorus (P), and potassium ions ( $\text{K}^+$ ).

Immediately after collection, the samples for the nutrient analyses were placed in an icebox, transported to the laboratory, and stored at temperatures between -1 and -4 °C until the analyses. The samples were then thawed and directly analyzed for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{K}^+$ , using an ion exchange chromatograph (Dionex, model ICS-90) and following the standards outlined in the Usepa Method 300.0 (Pfaff, 1993) and the Usepa Method 300.1 (Hautman and Munch, 1997). To determine P, the method of Murphy and Riley (1962) was used. After thawing, the samples were filtered through a 0.45- $\mu\text{m}$  cellulose ester membrane and then analyzed with a molecular absorption spectrophotometer (Model Spekol, Analytik Jena). According to these procedures, the species of P analyzed was dissolved reactive phosphorus.

### Analysis of the PS

In the PS, the same nutrients were analyzed as in the runoff water ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , P, and  $\text{K}^+$ ), plus pH and dry matter content (DM). The pH was determined with a potentiometer, while DM was evaluated by weighing the samples and drying them in an oven at 105 °C until constant weight.

For the determination of the nutrients in the PS, the solid and liquid phases were separated. The liquid phase was then analyzed via ion exchange chromatography, while for the solid phase, it was first necessary to perform a digestion and extraction process for the desired cations and anions. For the cations, digestion followed the Usepa 3051A method (Usepa, 2007), while for the extraction of the anions, the methodology elaborated by Stanic et al. (2011) was adopted. The characteristics of the PS are presented in table 1.

### Data analysis

The mean concentration and the mean of the total mass of the nutrients were weighted in relation to the runoff volume. For the *Nitossolo*, the nutrient contents and masses were

**Table 1.** Characterization of the pig slurry (PS) applied to the *Nitossolo* and the *Cambissolo*

| Property   | <i>Nitossolo</i> - Alfisol | <i>Cambissolo</i> - Inceptisol |
|--|----------------------------|--------------------------------|
| pH   | 6.40                       | 7.00                           |
| DM (%)   | 0.35                       | 0.38                           |
| NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> ) | 14,871                     | 11,912                         |
| NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> ) | 21                         | 32                             |
| P (mg L <sup>-1</sup> )                            | 1,345                      | 5,466                          |
| K <sup>+</sup> (mg L <sup>-1</sup> )               | 18,617                     | 26,206                         |

DM = dry mass. The pH was determined with a potentiometer, while DM was evaluated by weighing the samples and drying them in an oven at 105 °C until constant weight. For the determination of the nutrients in the PS, the liquid phase was analyzed via ion exchange chromatography and for the solid phase, it was necessary to perform a digestion process: Usepa 3051A method (Usepa, 2007) and a extraction process: methodology elaborated by Stanisic et al. (2011).

weighted in relation to the following runoff volumes: 34, 8, 3, and 19 mm, respectively, for T1, T2, T3, and T4. For the *Cambissolo*, the flow volumes adopted for the weighting were 34, 18, 5, and 11 mm, respectively, for T1, T2, T3, and T4. The data for total nutrient mass in the runoff were subjected to analysis of variance, and the means, when different between treatments, were compared with Tukey's test for 5 % significance, using the software package ASSISTAT 7.7 (Silva and Azevedo, 2016).

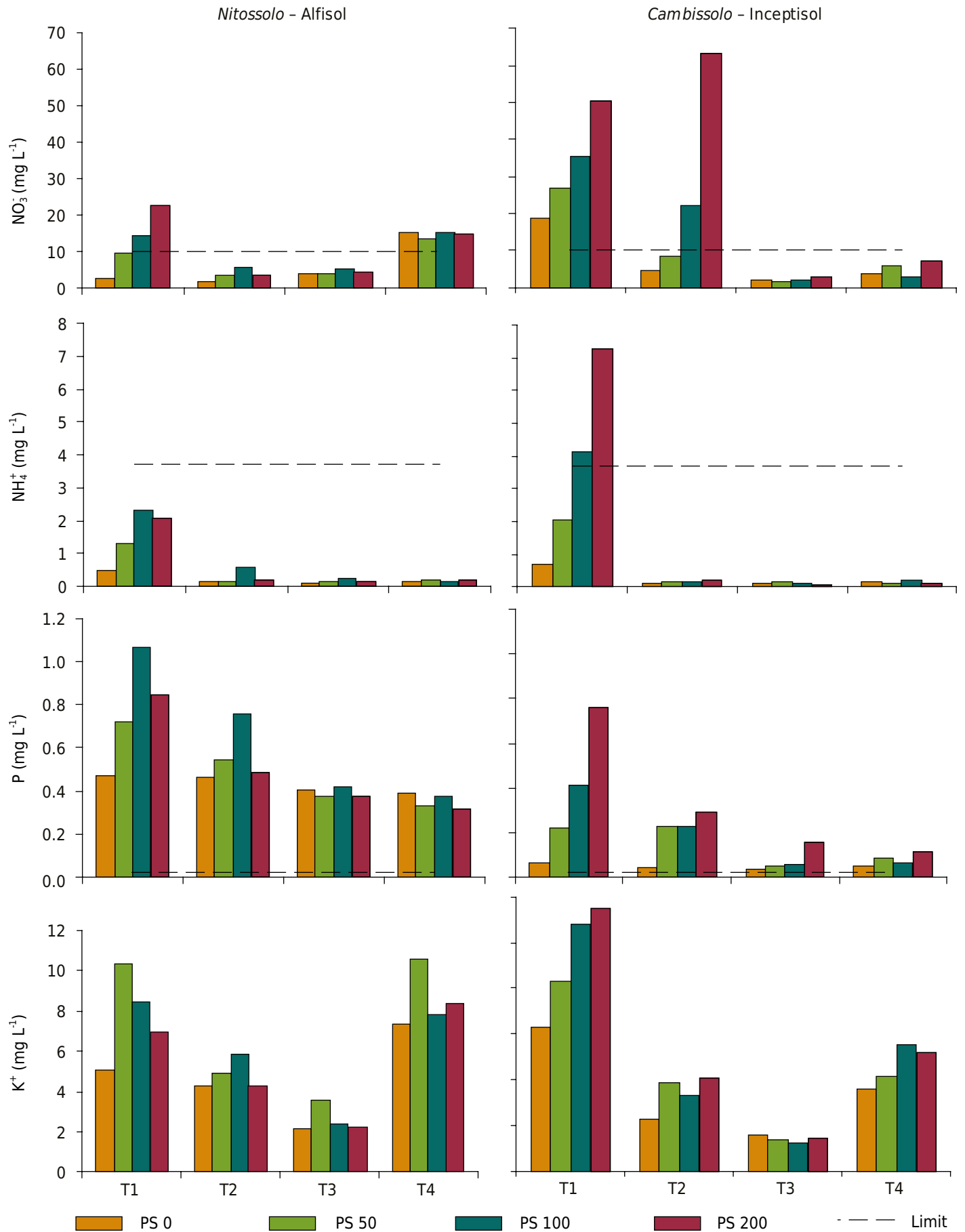
## RESULTS AND DISCUSSION

The nutrient concentrations in the runoff from the *Nitossolo* and *Cambissolo* plots after simulated rainfall are displayed in figure 2. The total nutrient mass in the runoff is shown in table 2.

During the first rainfall test (T1) on the *Nitossolo* (Figure 2), the concentrations of all nutrients in the runoff from the treatments which had received PS were above those of the treatment which had not received PS. In general, in the second rainfall test (T2), the nutrient concentrations in all treatments became similar, and after the third (T3) and fourth test (T4), it was no longer possible to perceive a difference in nutrient concentrations in the runoff due to the different rates of PS applied. Similarly, in the *Cambissolo* treatments, the nutrient concentrations in the runoff from T1 were also higher in the treatments which had received PS than in those without PS (Figure 2). This effect was still visible in T2, but the different amounts of PS applied practically no longer affected the nutrient concentrations in the runoff from T3 and T4.

For both *Nitossolo* and *Cambissolo*, T1 showed a clear difference in nutrient concentrations in the runoff between the treatments which had received PS and that which had not. Also, the concentrations generally increased with the amount of PS applied. In the subsequent rainfall tests (T2, T3, and T4) the concentrations began to decrease and equalize, and the different PS application rates had no impacts because a part of the nutrients applied by the PS was absorbed by the crop and the other part was lost during the events of natural rainfall and simulated rainfall. This behavior is also verified by table 2, which shows the total nutrient mass transported by the runoff in each treatment during the four simulated rainfall tests.

Both the mean concentration (Figure 2) and the total mass (Table 2) of all nutrients in the runoff from all treatments of both soils were higher in T1, with a tendency to decrease in the subsequent tests (T2 and T3) to increase in the last test (T4). The increase in mean concentration and total mass in the last test (T4) occurred for practically all nutrients in almost all treatments. This can be explained by the decomposition of the oat and turnip residue from the previous cultivation and, mainly, by the decomposition of soybean leaves from the current crop. Almost certainly, the mineralization of organic matter due to the decomposition of this material contributed to this increase in both soils. A similar



**Figure 2.** Influences of pig slurry (PS) application rate (0, 50, 100, and 200 m<sup>3</sup> ha<sup>-1</sup>) on the mean concentrations of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, P, and K<sup>+</sup> in runoff water from four simulated rainfall tests (T1, T2, T3, and T4) carried out during soybean cultivation on a *Nitossolo* and a *Cambissolo*. The line refers to the limit established for each nutrient by resolution 357 of Conama (2005).



**Table 2.** Influence of pig slurry (PS) application rates (0, 50, 100, and 200 m<sup>3</sup> ha<sup>-1</sup>) on the means of the total mass ± standard deviation of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, P, and K<sup>+</sup> in runoff water from four simulated rainfall tests (T1, T2, T3, and T4) carried out during soybean cultivation on a *Nitossolo* - Alfisol and a *Cambissolo* - Inceptisol. In addition, for each nutrient, we evaluated the total mass applied via PS and carried by the runoff, as well as the percentage loss in relation to the amount applied (%)

| Treatment   | Total applied | T1                           | T2              | T3              | T4              | Total carried | %     |
|---|---------------|------------------------------|-----------------|-----------------|-----------------|---------------|-------|
| <i>Nitossolo</i> - Alfisol                          |               |                              |                 |                 |                 |               |       |
| NO <sub>3</sub> <sup>-</sup> (kg ha <sup>-1</sup> ) |               |                              |                 |                 |                 |               |       |
| PS 0  | 0.00          | 0.82 ± 0.15 a <sup>(1)</sup> | 0.13 ± 0.03 a   | 0.12 ± 0.04 a   | 2.86 ± 0.27 a   | 3.93          | 0.0   |
| PS 50   | 2.76          | 3.15 ± 2.36 a                | 0.30 ± 0.05 a   | 0.12 ± 0.02 a   | 2.53 ± 0.28 a   | 6.10          | 100.0 |
| PS 100  | 5.52          | 4.78 ± 1.12 a                | 0.45 ± 0.31 a   | 0.15 ± 0.01 a   | 2.92 ± 0.37 a   | 8.29          | 100.0 |
| PS 200  | 11.04         | 7.70 ± 7.48 a                | 0.31 ± 0.14 a   | 0.13 ± 0.06 a   | 2.86 ± 0.08 a   | 11.01         | 99.7  |
| NH <sub>4</sub> <sup>+</sup> (kg ha <sup>-1</sup> ) |               |                              |                 |                 |                 |               |       |
| PS 0  | 0.00          | 0.154 ± 0.033 a              | 0.012 ± 0.006 a | 0.003 ± 0.002 a | 0.028 ± 0.012 a | 0.20          | 0.0   |
| PS 50   | 1.04          | 0.442 ± 0.015 a              | 0.009 ± 0.003 a | 0.004 ± 0.001 a | 0.033 ± 0.015 a | 0.49          | 47.1  |
| PS 100  | 2.07          | 0.779 ± 0.367 a              | 0.047 ± 0.044 a | 0.006 ± 0.001 a | 0.024 ± 0.009 a | 0.86          | 41.3  |
| PS 200  | 4.15          | 0.714 ± 0.209 a              | 0.015 ± 0.001 a | 0.004 ± 0.001 a | 0.034 ± 0.027 a | 0.77          | 18.5  |
| P (kg ha <sup>-1</sup> )                            |               |                              |                 |                 |                 |               |       |
| PS 0  | 0.00          | 0.158 ± 0.016 b              | 0.039 ± 0.013 a | 0.012 ± 0.002 a | 0.075 ± 0.017 a | 0.28          | 0.0   |
| PS 50   | 1.70          | 0.243 ± 0.050 bc             | 0.045 ± 0.002 a | 0.011 ± 0.003 a | 0.062 ± 0.016 a | 0.36          | 21.2  |
| PS 100  | 3.41          | 0.362 ± 0.002 a              | 0.064 ± 0.006 a | 0.012 ± 0.001 a | 0.072 ± 0.029 a | 0.51          | 15.0  |
| PS 200  | 6.82          | 0.287 ± 0.024 ac             | 0.041 ± 0.005 a | 0.011 ± 0.003 a | 0.061 ± 0.016 a | 0.40          | 5.9   |
| K <sup>+</sup> (kg ha <sup>-1</sup> )               |               |                              |                 |                 |                 |               |       |
| PS 0  | 0.00          | 1.71 ± 0.26 a                | 0.35 ± 0.19 a   | 0.06 ± 0.01 a   | 1.40 ± 0.09 a   | 3.53          | 0.0   |
| PS 50   | 5.21          | 3.51 ± 0.37 a                | 0.41 ± 0.16 a   | 0.10 ± 0.01 a   | 2.02 ± 0.51 a   | 6.04          | 100.0 |
| PS 100  | 10.41         | 2.86 ± 0.55 a                | 0.49 ± 0.00 a   | 0.07 ± 0.01 a   | 1.49 ± 0.08 a   | 4.91          | 47.1  |
| PS 200  | 20.83         | 2.38 ± 0.79 a                | 0.36 ± 0.03 a   | 0.07 ± 0.01 a   | 1.61 ± 0.50 a   | 4.42          | 21.2  |
| <i>Cambissolo</i> - Inceptisol                      |               |                              |                 |                 |                 |               |       |
| NO <sub>3</sub> <sup>-</sup> (kg ha <sup>-1</sup> ) |               |                              |                 |                 |                 |               |       |
| PS 0  | 0.00          | 6.43 ± 1.74 b                | 0.90 ± 0.68 a   | 0.12 ± 0.02 a   | 0.44 ± 0.16 a   | 7.89          | 0.0   |
| PS 50   | 2.64          | 9.36 ± 3.88 ab               | 1.59 ± 0.04 a   | 0.09 ± 0.06 a   | 0.71 ± 0.30 a   | 11.76         | 100.0 |
| PS 100  | 5.28          | 12.21 ± 3.12 ab              | 4.03 ± 2.26 a   | 0.11 ± 0.03 a   | 0.36 ± 0.04 a   | 16.71         | 100.0 |
| PS 200  | 10.55         | 17.32 ± 0.55 a               | 11.45 ± 5.53 a  | 0.14 ± 0.00 a   | 0.80 ± 0.56 a   | 29.71         | 100.0 |
| NH <sub>4</sub> <sup>+</sup> (kg ha <sup>-1</sup> ) |               |                              |                 |                 |                 |               |       |
| PS 0  | 0.00          | 0.222 ± 0.089 c              | 0.019 ± 0.011 a | 0.003 ± 0.001 a | 0.014 ± 0.013 a | 0.26          | 0.0   |
| PS 50   | 1.58          | 0.690 ± 0.039 bc             | 0.026 ± 0.003 a | 0.006 ± 0.001 a | 0.011 ± 0.003 a | 0.73          | 46.2  |
| PS 100  | 3.17          | 1.416 ± 0.476 b              | 0.026 ± 0.001 a | 0.005 ± 0.002 a | 0.023 ± 0.016 a | 1.47          | 46.4  |
| PS 200  | 6.34          | 2.498 ± 0.115 a              | 0.033 ± 0.003 a | 0.004 ± 0.004 a | 0.013 ± 0.003 a | 2.55          | 40.2  |
| P (kg ha <sup>-1</sup> )                            |               |                              |                 |                 |                 |               |       |
| PS 0  | 0.00          | 0.021 ± 0.012 b              | 0.007 ± 0.001 a | 0.002 ± 0.001 a | 0.006 ± 0.001 a | 0.04          | 0.0   |
| PS 50   | 2.10          | 0.074 ± 0.009 ab             | 0.041 ± 0.043 a | 0.002 ± 0.000 a | 0.009 ± 0.006 a | 0.13          | 6.0   |
| PS 100  | 4.21          | 0.140 ± 0.107 ab             | 0.041 ± 0.040 a | 0.003 ± 0.001 a | 0.007 ± 0.000 a | 0.19          | 4.5   |
| PS 200  | 8.41          | 0.262 ± 0.031 a              | 0.052 ± 0.004 a | 0.008 ± 0.005 a | 0.013 ± 0.006 a | 0.34          | 4.0   |
| K <sup>+</sup> (kg ha <sup>-1</sup> )               |               |                              |                 |                 |                 |               |       |
| PS 0  | 0.00          | 2.16 ± 0.53 a                | 0.42 ± 0.02 a   | 0.08 ± 0.04 a   | 0.42 ± 0.02 a   | 3.08          | 0.0   |
| PS 50   | 9.29          | 2.87 ± 0.69 a                | 0.71 ± 0.11 a   | 0.07 ± 0.03 a   | 0.48 ± 0.06 a   | 4.13          | 44.5  |
| PS 100  | 18.58         | 3.71 ± 1.18 a                | 0.60 ± 0.26 a   | 0.07 ± 0.03 a   | 0.64 ± 0.13 a   | 5.02          | 27.0  |
| PS 200  | 37.17         | 3.96 ± 0.14 a                | 0.74 ± 0.31 a   | 0.07 ± 0.02 a   | 0.59 ± 0.22 a   | 5.36          | 14.4  |

<sup>(1)</sup> Means followed by the same letters do not differ at the 5 % probability level according to the Tukey test. For NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and K<sup>+</sup>, was used an ion exchange chromatograph (Dionex, model ICS-90), following the standards outlined in the Usepa Method 300.0 (Pfaff, 1993) and the Usepa Method 300.1 (Hautman and Munch, 1997). To determine P (dissolved reactive phosphorus), the method of Murphy and Riley (1962) was used and the samples was analyzed with a molecular absorption spectrophotometer (Model Spekpol, Analytik Jena).

behavior has been observed by Mecabo Júnior et al. (2014). It is believed that the greatest effect was from the decomposition of soybean leaves, because significant leaf fall was observed only at the end of the crop cycle (Figure 1), whereas oat and turnip residues were already present at sowing. Another factor that may have influenced the increase in the total nutrient mass in the runoff from the T4 test is the fact that the runoff also increased in this test in all treatments from both soils compared to the previous test (T3).

Comparing the nutrient concentrations in the runoff from the *Nitossolo* and *Cambissolo* (Figure 2) with resolution 357 of Conama (2005), we observed that in the first rainfall test (T1), the  $\text{NO}_3^-$  concentrations in the runoff from the *Nitossolo* were higher than the limit of  $10 \text{ mg L}^{-1}$  in the two treatments which received PS, namely PS 100 and PS 200, and in all treatments of the T4 test. In the *Cambissolo*, the  $\text{NO}_3^-$  concentrations were above the limit in all treatments in the T1 test and in two treatments, PS 100 and PS 200, in the T2 test. Note that in the *Cambissolo*, the limit for  $\text{NO}_3^-$  was exceeded even in the treatment with the lowest PS application rate.

Concentrations of  $\text{NH}_4^+$  in the runoff did not exceed the maximum threshold of  $3.7 \text{ mg L}^{-1}$  (the most restrictive Conama value) in any treatment or rainfall test in the *Nitossolo* (Figure 2). For the *Cambissolo* (Figure 2), this limit was exceeded only in the first rainfall test in PS 100 and PS 200. In contrast, the P limit of  $0.02 \text{ mg L}^{-1}$  (the most restrictive Conama value) was exceeded in the runoff from all treatments in all simulated rainfall tests for both soils (Figure 2), but this behavior was more pronounced in the *Nitossolo*. This can be explained by the initial concentration of P in the soils, which was  $26 \text{ mg kg}^{-1}$  for the *Nitossolo* and  $12 \text{ mg kg}^{-1}$  for the *Cambissolo*, considered very high and medium/high, respectively, according to the Fertilization and Liming Manual (CQFS-RS/SC, 2004).

Hence, the application of PS as fertilizer increased the concentrations of the nutrients  $\text{NO}_3^-$  and P in the runoff from the *Nitossolo* and of the nutrients  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and P in the runoff from the *Cambissolo* (Figure 2) to the point where they exceeded the thresholds stated by the Brazilian legislation. This may result in the pollution of surface water receiving inflow containing these nutrients. The same consequence of the application of PS on the concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , P,  $\text{Zn}^{2+}$ , and  $\text{Cu}^{2+}$  in runoff from a *Oxisol* (*Latossolo*) was observed by Oliveira et al. (2015). In view of this, the application of PS as fertilizer to soils must be constantly monitored to reduce the environmental risks.

Nutrients losses in both soils are linked to chemical-physical properties. While, for example, in the PS 200 treatment (Figure 2), the concentrations of P in the *Nitossolo* runoff decreased over time (direction T1 > T4) from  $0.84$  to  $0.31 \text{ mg L}^{-1}$  (2.7 times lower), in the *Cambissolo* runoff, they decreased from  $0.76$  to  $0.11 \text{ mg L}^{-1}$  (6.9 times lower). This decrease is due to the lower clay content (39 %) of the *Cambissolo* and the lower Cation Exchange Capacity - CEC; according to the Manual of Fertilization and Liming (CQFS-RS/SC, 2004), its CEC is considered average. Thus, nutrients are more easily solubilized, while in the *Nitossolo*, the interaction of solute with clay, which is present at higher concentrations (62 %), impeding nutrient loss. Figure 2 and table 2 show this effect for other elements, such as for  $\text{NH}_4^+$  and  $\text{K}^+$ .

The  $\text{NO}_3^-$  does not follow the same general trend presented for the other elements because nitrogen can be lost to the soil by various processes such as adsorption and fixation of ammonia, immobilization by microorganisms, mineralization, nitrification, erosion, volatilization, water losses, leaching (Sengik et al., 2001), absorption by plants (Shen et al., 2003), and adsorption to the sediment (Yano et al., 2000; Søvik and Syversen, 2008). Plants, with the exception of legumes and other groups that fix molecular nitrogen ( $\text{N}_2$ ) in symbiosis with microorganisms, absorb mineral nitrogen mainly in the nitric ( $\text{NO}_3^-$ ) and ammonia ( $\text{NH}_4^+$ ) forms, whereas in the soil, the organic form predominates, implying the transformation of organic N to mineral N through heterotrophic microorganisms (Séguy et al., 2001). This explains, for example, that in the PS 200 treatment (Figure 2), the  $\text{NH}_4^+$  of T1 to T4 showed a decay rate of  $2.10$  to  $0.18 \text{ mg L}^{-1}$  (11.66 times lower) for the *Nitossolo* and from  $7.27$  to  $0.11 \text{ mg L}^{-1}$  (66.09 times lower) for the *Cambissolo*.

The *Cambissolo* showed a loss pattern higher than that of the *Nitossolo*, regardless of the applied dose, except for PS 0, where we observed oscillations caused by the incorporation of nutrients by the leguminous plants. Regardless of the soil and the treatment, the nutrient with the highest mean concentration in and with the highest total mass transported by the runoff was  $\text{NO}_3^-$ , followed by  $\text{K}^+$ ,  $\text{NH}_4^+$ , and P (Figure 2 and Table 2). This differs from the results of Ceretta et al. (2010) with 12 applications of PS on an Alfisol (*Planossolo*) between 2002 and 2007; the authors observed that the  $\text{K}^+$  transport via runoff was higher than that of P, which in turn was higher than that of N.

Considering the nutrient mass lost in the runoff in each rainfall test (Table 2), for the *Nitossolo*, a statistical difference only appeared between treatments in the T1 test for the nutrient P. In the *Cambissolo*, also only in the T1 test, the treatments were statistically different for all nutrients except K.

Based on our results, an effect of the different PS application rates on the masses of the studied nutrients was significant only in the first rainfall test (T1), performed only 15 hours after PS application. This implies that intense rainfall soon after the application of PS without its incorporation into the soil increases the risk of nutrient loss by runoff, which has also been concluded by Allen and Mallarino (2008). Smith et al. (2007) found that, when applied to the surface of a pasture, PS posed a higher risk to water quality when rainfall occurred one day after the application compared to mineral fertilizer or chicken litter applied at the same rate. As time elapsed between the application of PS and the simulated rainfall, the risk of N and P loss through runoff decreased. European legislation stipulates that chemical or organic fertilizers are not allowed to be applied to the soil if heavy rainfall is anticipated within 48 hours after application (SI, 2014). When testing this and two other, smaller time intervals (48, 24, and 12 hours), Flynn et al. (2013) confirmed that a safe time interval between the application of PS and the first rain event must not be less than 48 hours to limit the transport of P and sediments by runoff.

Regarding the amount of nutrients lost in relation to those applied via PS (Table 2), in general, 100 % of the  $\text{NO}_3^-$  applied were lost in all treatments for both soils. These losses can be explained by the low N demand by the soybean crop due to biological N fixation and by the high mobility of  $\text{NO}_3^-$ . The lost amounts of the other nutrients in both soils were less than 50 % of the amount applied via PS. Among these, the nutrient lost at a lower percentage was P (less than 21 % in the *Nitossolo* and less than 6 % in the *Cambissolo*), which is explained by its low mobility in the soil. In this sense, it can be said that the amounts of nutrients lost by the surface flow in relation to the amounts applied via PS are considerable, especially for  $\text{NO}_3^-$ .

In light of our results, with respect to the mean nutrient concentrations and the total mass of nutrients in the runoff from both the *Nitossolo* and the *Cambissolo*, there was a definite effect of PS on water quality in the first rainfall test (T1). In some cases, this effect was still noticeable after T2 and T3. After T4, no effect of the rate of PS application was noticed. After T1, the mean concentration and total mass of all nutrients evaluated in the runoff increased with increasing PS application rates. This corroborates the observations by Ceretta et al. (2005), who found that concentrations of mineral nitrogen and available phosphorus in runoff were directly related to the PS applications of 0, 20, 40, and  $80 \text{ m}^3 \text{ ha}^{-1}$ . Similarly, Ceretta et al. (2010) observed that an increase in the amount of PS added (0, 20, 40, and  $80 \text{ m}^3 \text{ ha}^{-1}$ ) increased the losses of N, P, and K by surface runoff.

## CONCLUSIONS

The transport of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , P, and  $\text{K}^+$  by runoff from a *Nitossolo* - Alfisol and *Cambissolo* - Inceptisol increased with increasing amounts of PS applied to the soil in the first simulated rainfall test (T1), which was carried out soon after PS application.

In some cases, an effect of the amount of PS applied on the nutrient transport by runoff was still noticeable in subsequent simulated rainfalls (T2 and T3), but not any more in the last simulated rainfall event (T4).

The transported amounts of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , P, and  $\text{K}^+$ , originating from the PS, decreased with an increasing period between PS application and the simulated rainfall events.

Regardless of the soil and the treatment,  $\text{NO}_3^-$  was transported by runoff in the greatest quantities, followed by  $\text{K}^+$ ,  $\text{NH}_4^+$ , and P.

The *Cambissolo* - Inceptisol showed a higher nutrient loss pattern than the *Nitossolo* - Alfisol, regardless of the applied dose, except for PS 0, for which we observed oscillations caused by the incorporation of nutrients by the leguminous plants.

The amount of nutrients lost via surface flow in relation to that applied via PS is considerable, especially for  $\text{NO}_3^-$ .

According to the nutrient concentrations in the runoff evaluated for the *Nitossolo* - Alfisol and the *Cambissolo* - Inceptisol, it is unclear whether the PS doses applied in this study result in significant environmental problems. For such an evaluation, it is also necessary to consider the drained flow and the lateral flow, as the runoff represents only a small part of the water flow in the soil. In addition, the water samples from the runoff contains suspended solids at concentrations different from those found in water bodies, usually assessed for comparison purposes with the environmental resolution.

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