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Energy and enviromental adavtagees of using leather fertilizer

In Brazil, the tanning industry generates large quantities of waste. This country occupies a significant position as a producer of hide - especially bovine leather. The solid residue is often discarded in the environment without treatment, implying environmental problems and energy waste. Typically, control and industrial solid-waste management in the country are characterized by a lack of the studies on the subject, the quantity and quality of waste generated, along with the lack of compatible units of final treatment and disposal in some regions. The leather is tanned with chromium salts. This process aims at obtaining a better finishing, increasing the resistance to wear and corrosion. Tanning hides with chromium (III) salts makes them more flexible and soft. Thus, this study aims to verify a mathematical model of the behaviour of potential nitrogen mineralization and the behaviour of chromium (III) salt in soils after applications of fertilizer made of hydrolysate bovine leather. The mathematical model will be applied according to the data obtained, and after application of established methodology.

Keywords: Leather Left-overs; The Behaviour of Chromium (III) Salt; Mathematical Model.

Vantagens energéticas e ambientais do uso de adubo em couro

No Brasil, a indústria de curtimento gera grandes quantidades de resíduos. Este país ocupa uma posição significativa como produtor de pele - especialmente couro bovino. Os resíduos sólidos são muitas vezes descartados no ambiente sem tratamento, o que implica problemas ambientais e desperdício de energia. Normalmente, o controle e o gerenciamento industrial de resíduos sólidos no país são caracterizados pela falta de estudos sobre o assunto, quantidade e qualidade dos resíduos gerados, além da falta de unidades compatíveis de tratamento final e descarte em algumas regiões. O couro é bronzeado com sais de crómio. Este processo visa obter um melhor acabamento, aumentando a resistência ao desgaste e à corrosão. O bronzeamento com os sais de cromo (III) os torna mais flexíveis e macios. Assim, este estudo pretende verificar um modelo matemático do comportamento da mineralização de nitrogênio potencial e do comportamento do sal de cromo (III) em solos após aplicação de fertilizante feito de hidrolisado de couro bovino. O modelo matemático será aplicado de acordo com os dados obtidos, e após a aplicação da metodologia estabelecida.

Palavras-chave: Esfregas de Couro; O Comportamento do Sal de Cromo (III); Modelo Matemático.

Topic: **Consumo e Meio Ambiente**

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INTRODUÇÃO

Brazil has a significant position as a producer of animal hide, especially bovine leather, which verifies the generation of a large volume of industrial waste (ABQTIC, 1996). The leather usually is tanned with chromium salts. This process vies to obtain resilience and a better finishing. Tanning hides with chromium (III) salts provides soft, flexible leather that can be tainted in a variety of colors. Other chemicals used for tanning are tannins (derived from vegetable matter), aluminum salts and zirconium salts (ABQTIC, 1996).

Tanning is only the process that turns hide into leather, what really happens is a modification of the properties of the proteins, causing changes on the dilatation and on the bonds between groups of the dermic structure (HERNANDEZ, 1995). The result is the increased stability of the collagen system, less dilatation and increase of the retraction temperature, thus the leather becomes resistant to enzymes and to the action of microorganisms. Due to the great variety of types of leather, it's easy to assume there is a myriad of different tanning methods, however the most used by the industry is the chromium (III) salts tanning because it offers elasticity and better management (BARROS et al., 2001). The control and management of solid industrial waste in Brazil are usually characterized by the lack in specialized studies, by the quantity and quality of the residue produced – that is cause of concern to process of degradation of the environment, and by the lack of waste-treatment units capable of dealing with the volume of residue produced in some regions. The result is the inadequate disposal of the residue on the environment; this also implies wasting of energy and potential environmental problems (SCHNEIDER, et al., 2000).

Due to the difficulty in obtaining appropriate locations for, and the costs of a landfill site, the usage of leather burr and left-overs on the soil for agriculture is becoming one of the most viable solutions. Is som cases the usage of these residues can be recommended for their corrective and fertilizing value, another positive aspect is the fact that these residues carry elements that are essential to the growth of plants, such as nitrogen, phosphorus, calcium, magnesium and sulfur.

The aim is to evaluate the behavior of nitrogen on sandy and clayey soils, present in Brazil, to the usage of fertilizer made from hydrolyzed bovine leather. Studying the behavior of the mineralized nitrogen on the soil after the application of the leather-fertilizer and the potential of nitrogen mineralization on each soils, by means of a first order mathematical model (STANFORD et al., 1972).

TOOLS AND METHODS

For this experiment were used two types of soil, the raw-samples were collected horizontally of the surface and of 5cm of depth. One raw-sample came from a site dedicated to the production of bananas, on the side of the Jacinto Machado (SC) road (29 º 04'24,73'' S e 49 º 48'05,38'' W), and is classified as clayey – Red Nitosol, of basaltic origin. The other raw-sample was collected at the city of Praia Grande-SC (29 º 03'41.11'' S e 49º47'31.79'' W), of soil classified as a sandy - quartzarenic Neosol, good for the cultivation of manioc.

After the collection, the raw-samples were crumbled, dried on open-air, sifted (2mm sieve) and divided in 12 (twelve) portions each. These portions were divided in fractions of 200g (dry matter) that were packed into propylene flasks of approximately 178 cm^3. The fractions were irrigated with water twice a week for one year. This incubation period took place at a laboratory of the University of Bologna (UNIBO), under environment temperature and humidity.

The experiment was designed to be randomized in factor of 3 by 2 by 4, which corresponds to 3 measures of soil, two measures of leather fertilizer (powder and pellets), repeated four times. The fractions of each soil composed a total of 24 samples.

The treatments consisted in the usage of a control sample for one type of leather fertilizer with particle size of ≥ 2mm in 4 measures of soil, to a base of 14% of nitrogen (Dose 0 = 0 control sample, Dose 1 = 143mg of fertilizer for 100mg of soil, Dose 2 = 714mg of fertilizer for 500mg of soil and Dose 3 = 1430mg of fertilizer for 1000mg of soil). The leather fertilizer with particle size of more than 2mm was compared to a base of 13,3% of nitrogen (Dose 0 = 0 control sample, Dose 1 = 150mg of fertilizer for 100mg of soil, Dose 2 = 750mg of fertilizer for 500mg of soil and Dose 3 = 1500mg of fertilizer for 1000mg of soil). All samples were done in triplicates.

For a comparison to the Brazillian soils were used three types of soil in two different depts from three different sites in the city of Pistoia, in Tuscany – Italy. The raw-samples were collected from sites at farms that have been treated with the leather fertilizer for over thirty years, and sites from the same farms where the soil never received any fertilizer at all. At the Nanni farm, 0-30 and > 30cm of depth from Mr. Franco Alessandro's seed-plot, in San Pierino Casa al Vesgovo; at the Nicolai farm, 0-50 and > 50cm of depth from Mr. Nicolai Giogioa's seed-plot, in Quarrata; at Buong farm, 0-30 and >30 cm of depth from Mr. Buongiovanni's seed-plot. In Badia a Pacciana.

The control samples from the Nanni farm were of 20cm of depth, from Buongiovanni's were of 15cm of depth and the control sample from the Nicolai farm was collected from 50cm of depth. The experiment was designed to be random, however, the different depths of soil were chosen because of the different types of crops. At Pistoia, the leather fertilizer is most used in seed-plots and for seedlings of ornamental plants, the fertilizer is applied on the soil' surface. The amount used by property is, on average, 1000 to 1600kg by acre per year.

The farms chosen for sampling use the leather fertilizer consistently, up to twice a year, once in the spring and once in autumn. The total amounts of nitrogen and carbon in the leather fertilizer and in Brazilian soil were measured by elemental analysis after removing the inorganic carbon with acid. The samples of crumbled, dry soil weighed into silver capsules (of about 10mg each) were placed on appropriate wells on a cast iron plate. The inorganic carbon was removed by adding 1 – 2 drops of a solution of 1:1 HCl (hydrochloric acid) until the effervescence was over. The iron plate was then heated to 80 ºC on a hot plate, until the samples were dry. Once cooled, the cups were sealed and analyzed by the elemental CHNS-O. (mod. EA1110, Thermo-Finnigan).

The incremental samples were subjected to dry combustion: the flue gases in a helium stream through two quartz tubes containing the metal catalysts. The first tube, also known as oxidation or combustion tube (which operates at a 1020 °C), contains chromium oxide, ensuring complete oxidation of carbon to CO2 oxide and cobalt, which holds silver halogens and compounds sulfur. The second reduction tube (650 °C), containing reduced copper enables the reduction of nitrogen oxides into molecular nitrogen.

The output tubing reduces the loss of helium gas and the end result comprises of only CO2, H2O and N2. The latter is formed by a anhydrone (anhydrous magnesium perchlorate), while N2 and CO2 were separated by passage through the gas chromatography column and quantified by a thermal conductivity detector (TCD).

The total amount of nitrogen also needed to be measured, it was done by Kjeldahl method: 2,5g of soil were weighed and placed in cylindrical glass container with 300ml of Kjeldahl; 11ml of sulfuric acid (H2SO4) at 96% were slowly added and then 3,5g of potassium sulfate (K2SO4) along with 3,5mg of selenium were also added to mineralize organic matter. The glass was heated with a special cooker for 30 minutes and when it fogged up a glass funnel was used to eliminate the organic matter, leaving behind only the minerals, i.e. when the contents of the glass became completely white. To ensure all the organic matter was gone the contents of the glass were boiled for about 15 minutes. Water was added until the volume came to 250ml and to help drop the temperature, then it was left to decant. The nitrogen levels were then done in a Kjeldahl apparatus – VAPODEST.

The extraction of mineralized nitrogen from Brazilian soils was obtained weighing 2,5g of pre-prepared soil, i.e. soil that was treated with the leather fertilizer, in plastic vials, with 25ml of potassium chloride (KCl) 2M shaken intermittently for one hour. After this period, it was allowed to sit for the decantation of the solid matter, filtered on Whatman paper 42 and then stored into plastic vials at 4 ºC. The incubation period of de soils was of 0, 30, 60, 90 and 200 days, during which the humidity of the soil was maintained at 60 % of water holding capacity. The moisture of the soil was maintained at 13.25% in sandy soil and 19.4 % in clayey soil, the amount of deionized water used was calculated through weighing. The amount of mineralized nitrogen was measured read in the autoanalyzer device.

RESULTS AND DISCUSSION

The carbon and nitrogen were analyzed in leather fertilizer (Table 1) and in Brazilian soils (Table 2). It was observed that the analysis results of the leather fertilizer (Table 1) indicate that the total nitrogen concentration is on average 133.3 g / kg, or 13.33 %. The amount of carbon present in the fertilizer and is 381.8 g / kg, or 38 %.

By Italian law the C / N ratio should not exceed 4 %, because the greater the amount of carbon less the amount of free nitrogen for the plants. The ratio between carbon and nitrogen in the fertilizer is 2.9 for powder and 2.8 for pellets. Malavolta et al. (2000) claims that some organic substances are relatively poor in nitrogen. On this matter one can say that it is not the case, since the analysis of the samples show that the elements mentioned have balanced ratio. In this case the carbon to nitrogen ratio (C/N) is 3/1 on average, as said by Ciavatta (2006), when adding leather fertilizer to the soil. The C/N ratio is typically of 3 to 5.

Table 1: Results of the total amount of nitrogen and of organic carbon of the leather fertilizer.

Leather Fertilizer	*Nitrogen (%)*	*Nitrogen Average (%)*	*Nitrogen Error*	*Carbon (%)*	*Carbon Average (%)*	*Carbono Error*
Cuoio Grao	13,453	13,333	0,308	39,478	38,182	0,982
Cuoio Grao	13,195			37,657		
Cuoio Grao	13,045			37,973		
Cuoio Grao	13,815			38,822		
Cuoio Grao	13,157			36,979		
Cuoio Polvere	14,548	14,055	0,400	40,293	39,791	0,511
Cuoio Polvere	14,191			40,132		
Cuoio Polvere	13,952			39,029		
Cuoio Polvere	13,454			39,537		
Cuoio Polvere	14,129			39,965		

Source: Paola Gioacchini - UNIBO, 2011.

The analysis results of Brazilian soil described in Table 2 indicate that the total amount of nitrogen in sandy soil is, is on average, 1.87 g / kg and in clayey soil is, on average, 1.44 g / kg. The amount of carbon is present in the sandy soil is 20.6 g / kg and in the clayey soil is 8.76 g / kg.

Table 2: Results of the total amount of nitrogen and of organic carbon in sandy and clayey Brazilian soils.

Solos	*Nitrogen (%)*	*Carbon (%)*	*Carbon Average (g/kg)*	*Nitrogênio Average (g/kg)*	*C/N*
Sandy	0,183	1,926	20,6	1,87	11,0
	0,192	2,077	37,657		
	0,187	2,179	37,973		
Clayey	0,129	0,882	8,76	1,44	6,1
	0,149	0,871			
	0,153	0,874			

Source: Paola Gioacchini - UNIBO, 2011.

The Italian soil that presented the highest total amount of carbono, by Kjeldahl method, came from Nicolai Farm, at 0-50cm of depth, with 8,74g/kg, followed by the soil from Nanni Farm, at 0-30 cm of depth, with 7,32g/kg. At Nanni Farm analysis show 6,46g/kg at depths greater than 30cm, at Nicolai Farm it shows 5,87g/kg at depths greater than 50cm, at Buong the results are 6,70g/kg at 0-30 and 6,14g/kg at more than 30cm. It is noticed that the greater the depth the smaller the total amount of carbon is. This shows that the effects of the use of the leather fertilizer show more results closer to the surface, at 0-30cm of depth (Table 3). To calculate the total amount of organic carbono the equation used wwas the following (E-q. 1)

$$C = \frac{3}{2} \cdot \frac{(B - A)}{1000} \cdot \frac{MFe_{ii}}{6} \cdot \frac{200}{20} \cdot 12 \cdot \frac{1000}{m} \qquad Eq. 1$$

Where:
C = the amount of organic carbon in g/kg.
3/2 = the molar proportion of redox (2 moles of potassium bichromate reacted with 3 moles of carbon).
B= the volume of sulfated iron (II) solution used on the titulation of the reagente blank, in milliliters.
A= the volume of sulfated iron (II) solution used on the titulation of the sample, in milliliters.
200 ml/20 ml= ratio
$MFe_{(II)}$= Effective molarity of the sulfated iron (II) solution
12= Carbon’s atomic weigh in g/mole
m= Final mass of the soil sample, in grams

The Kjeldahl method was used on Tuscan soil to see if there were differences among the other methods, because it has become a reference method for the determination of total nitrogen. The method consists of a complete digestion of the samples in concentrated sulfuric acid with catalysts such as salts of potassium sulfate and selenium at high temperature. The soil that showed the highest total nitrogen was in Nicolai Farm, depth of 0-50 cm with 0.96 g/kg, followed Nanni Farm in the 0-30 cm depth with 0.89 g / kg. In Nanni farm in depth greater than 30 cm analysis showed 0.70 g / kg; Nicolai Farm in depth > 50 with 0.64 g / kg; Buong 0-30 cm depth with 0.77 g / kg and greater than 30 cm with 0.67 g / kg (Table 3). To calculate the results the following equation was used:

$$NTK = \frac{14 \cdot \Delta \cdot N}{P} \qquad \text{Eq. 2}$$

where

N= Titulation read by the Kjeldahl aparatus

P= weigh of the soil in grams

The difference between the titulation (N) and the control sample= Δ

Table 3: Total of organic carbon and nitrogent and C/N ratio of Tuscan soil.

Soils	Total organic Carbon(g/kg C)	Total Nitrogen (g/kg N)	C/N
Nanni 0-30	7,23	0,89	8,12
Nanni >30	6,46	0,7	9,23
Control sample Nanni	12,77	0,81	15,8
Nicolai 0-50	8,74	0,96	9,1
Nicolai >50	5,87	0,64	9,17
Control Sample Nicolai	8,93	1,04	8,59
Buong 0-30	6,70	0,77	8,7
Buong >30	6,14	0,67	9,16
Control Sample Buong	11,77	0,85	13,9

Source: Luciano Cavani, 2011.

After the variance analysis, Tukey tests were used in Duncan and t-test (P <0.05) for comparing the average values of N mineralized in soil, forming groups in accordance with the least significant difference indicated by tests. Values followed the same letter and are not significantly different at P = 0.05 (t LSD test Bonferroni adjusted version); code Meaning: "*", 0.05; "**", 0.01; "***", 0.001; LSD = no significant difference. In sandy soil the fertilizer pellets and powder are not significantly different. In the clayey soil the fertilizer particle size also didn’t have significant difference.

To study the process of mineralized nitrogen in samples of clay and sandy soils of Brazil following doses were applied: G1 / P1 100 mg N kg -1 ds; G2 / P2 = 300 kg mg of N - 1ds; G3 / P3 N = 1000 mg kg -1 ds. They were incubated for 0, 30, 60, 90 and 200 days. The polyethylene bottles were placed at room temperature. Every three days the moisture was measured and returned to the initial amount of water by means of a pipette, dropper (PE), thereby depositing the water without modifying the structure and the accommodation of the samples within the vials. Each treatment was carried out with three replications, totaling 24 bottles for each soil (sandy and clayey).

At the beginning and the end of each incubation period the amount of mineral N was measured in each sample, through the extraction of nitrate and ammonium with 2M KCl. The ammonia nitrogen (N-NH4) and nitric nitrogen (N-NO3) in sandy and clayey soils during the first 30 days after application of the leather fertilizer are shown in Figure 1. In clayey soil the N- NH4 increases after ninety days. However, in sandy soil N- NH4 decreases in the period of thirty days. The nitric nitrogen (N-NO3) in sandy soil, during the period of sixty days, increased and after this period there was a decrease. However, in clayey soil it there was a linear increase of nitric nitrogen (N-NO3) in all drawings.

The data on accumulation of NO3 and NH4 in sandy and clayey soils was adjusted with AGROGEL. As shown on Figure 1, DAA means days after the addition of nitrogen; control is the control of soil, i.e., soil untreated; G = granular (pellets); P = powder; G1 / P1 100 mg kg -1 C ds; G2 / P2 = 300 kg mg of N - 1ds; G3 / P3 = 1000 mg kg- 1 N DS.

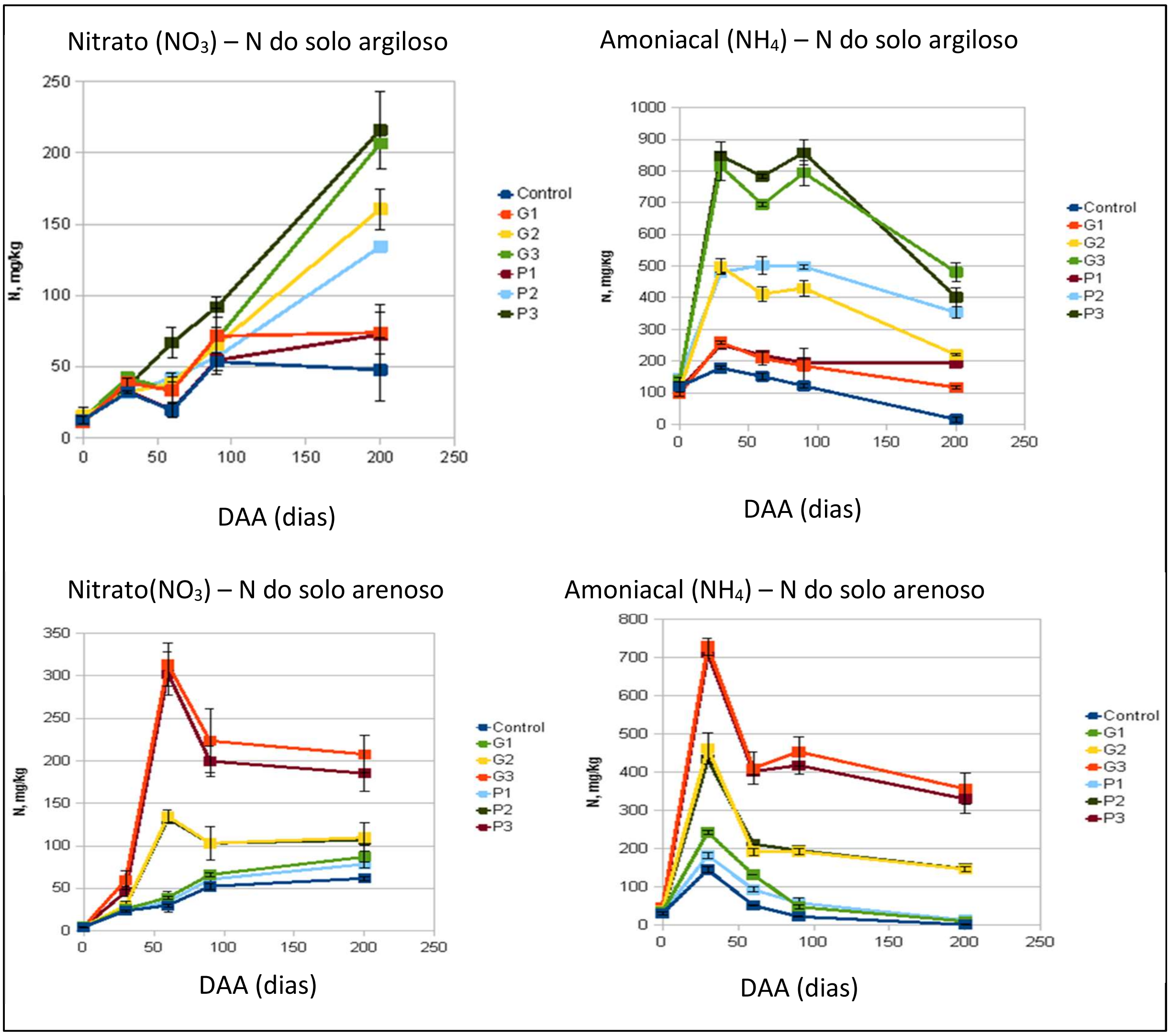

Figure 1: Inorganic nitrogen sandy and clay soils nos Brazil for the period of 200 days.

From the results of mineralized nitrogen the mineralization potential of nitrogen (N0) values of were calculated of each soil by means of the negative first order exponential model (SMITH et al., 1972). The data was adjusted with AGROGEL to estimate the nonlinear parameters. Nitrogen mineralization kinetics were applied in the two Brazilian soils; sandy and clay, which were incubated in polyethylene flasks during time interval (dt) of 0, 30, 60, 90 and 200 days. At the end of each period the samples were processed in the Autoanalyzer. The variation of the potentially mineralized nitrogen is expressed in terms of a kinetic constant of mineralization (k) , as described by the expression :

d[Norg]dt=-k·Norg Eq.3

Applying in Eq.3 the definite integral to the first part of N0 to Norg and a time of zero to t on the second part, N0 being the amount of mineralized organic N at time zero, i.e., the mineralization potential of nitrogen, equation 3 becomes:

$$\int_{N_0}^{N_{org}} \frac{d[N_{org}]}{N_{org}} = \int_0^t -kdt$$

$$\int \frac{d[N_{org}]}{N_{org}} - \int \frac{d[N_0]}{N_0} = -K(\int \frac{d[t]}{[t]} - \int \frac{d[0]}{0})$$

$$\ln[N_{org}] - \ln N_0 = -kt + 0$$

$$\ln\left[\frac{N_{org}}{N_0}\right] = -kt$$

$$\frac{N_{org}}{N_0} = e^{-kt}$$

$$[N_{org}] = N_0 \cdot e^{-kt} \qquad Eq.4$$

Moreover, it is possible to calculate the potentially mineralized nitrogen [Nm] in the existing system, so the nitrogen balance can be written as follows:

$$[N_{org}] + [N_m] = N_0$$

Replacing organic nitrogen (Norg) by potentially mineralized nitrogen minus mineralized nitrogen, i.e. [Norg] = N0 - Nm in equation (Eq.4) it is obtained:

$$N_0 - N_m = N_0 * e^{-kt}$$
$$- N_m = - N_0 + N_0 * e^{-kt}$$
$$N_m = N_0 - N_0 * e^{-kt}$$

Then the evolution of the mineralized nitrogen in the soil can be calculated by Eq. 5:

$$[N_m] = N_0 * (1 – e^{-kt}) \qquad Eq. 5$$

This approach, in effect, serves to verify the inorganic nitrogen behavior after a time interval and comparing the accumulated values as a function of time. With this equation, it can be seen that the results of inorganic nitrogen after 200 days of incubation were not good, however, the means of nitrogen release are not clear. The value of the nitrogen mineralization potential was extrapolated, and is in agreement with the dose of nitrogen in data of the Italian soil.

CONCLUSION

The rate of mineralization in the soil with leather fertilizer was higher in the initial period, between 30 and 60 days of incubation. The mineralized nitrogen can be used as an availability rate, because the only way to store nitrogen in the soil is through the organic medium, being the most stable form for a long period, which slowly undergoes mineralization. In other forms, N is subject to volatilization, absorption by the plant and washing out of the zone permeated by the roots. Nitrogen contained in leather fertilizer is a very well accepted product in Italy. The benefits of using leather residues in the soil can match or exceed those achieved with the mineral fertilizer, especially in relation to productivity and cutting costs with fertilizers, especially nitrogenized fertilizers. It is not used in large quantity in relation urea, as urea with 46% of nitrogen costs 40 euros per 100 kilograms today, this means that it costs 0.8 euros per kilogram of urea while leather fertilizer with 12% nitrogen costs 30 euros per 100 kg, that means 2.5 euros per kilo. Although nitrogen is the most abundant nutrient of Earth's atmosphere (78% of Earth's atmosphere), is not included as a constituent of any terrestrial rock. Maybe it's for this reason it is the most expensive element of fertilizers, since it’s presence requires various chemical reactions, which require a lot of energy.

It is noted that the extractable chromium does not assist in nitrogen mineralization, since the organic matter in the leather fertilizer is relatively of easy to decomposition, which confirms that the organic matter contained in this fertilizer aids in the high fraction of nitrogen mineralization, adding a significant amount of total N.

It was observed that the results of inorganic nitrogen after 200 days of incubation in sandy and clayey soils from Brazil were not good, however, the means of nitrogen release are not clear. Through the equation of the negative exponential model of the first order (STANFORD et al., 1972), the amount of nitrogen mineralization potential was extrapolated, and is in good agreement with the dose of nitrogen and data on Italian soil.

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