The use of retorted oil shale as urea coating does not modify chemical parameters of free-drained soil solution

O uso de ureia recoberta com xisto retortado não modifica os parâmetros químicos da solução do solo lixiviada

El uso de lutita retortada en el recubrimiento de urea no cambia los parámetros químicos de la solución del suelo lixiviada

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Abstract
The objective of this work was to investigate the possible contamination of soil solution with chemical elements present in the composition of retorted oil shale (ROS) when used together with nitrogen fertilization as urea. The experiment was conducted in a silvopastoral system with an experimental design of randomized blocks, with subdivided plots. The main treatments consisted of spatial arrangements of trees, while the split plots constituted the broadcast application of urea (U) and urea covered with ROS (U+ROS). Regardless of the spacing of the trees, the use of U + ROS implied no significant effect on the chemical parameters of the soil solution leached at 40 cm of soil depth. The heavy metals Cd, As, Al and Pb, the most hazardous trace elements present in ROS, were not even detected in soil solution, in none sampling event. Such results are mainly attributed to their low contents in ROS. Our results evidenced that, even with large and cumulative rates of ROS application, the potential for contamination of water table with ROS-derived trace elements is negligible in the soil and climate conditions of the present study. Thus, the use of ROS together with nitrogen fertilization has a potential in the use in agriculture, increasing the efficiency of nitrogen fertilization without causing environmental impacts.
Keywords: Nitrogen fertilization; Heavy metals; Soil contamination.

Resumo
O objetivo deste trabalho foi investigar a possível contaminação da solução do solo com elementos químicos presentes na composição do xisto retortado (XR) quando utilizado juntamente com a fertilização nitrogenada em um sistema silvipastoril. O experimento foi conduzido em um sistema silvipastoril com delineamento experimental de blocos ao acaso, com parcelas subdivididas. Os tratamentos principais consistiram em arranjos espaciais das árvores,

enquanto a subdivisão das parcelas constituiu na aplicação superficial de ureia (U) e ureia recoberta com XR (U+XR). Independentemente do espaçamento das árvores, o uso do XR junto com a ureia (U + XR) não houve efeito significativo nos parâmetros químicos da solução do solo lixiviada a 40 cm de profundidade. Os metais pesados Cd, As, Al e Pb, os os elementos mais perigosos presentes no XR, nem sequer foram detectados na solução do solo, em nenhum evento de amostragem. Tais resultados são atribuídos principalmente a seus baixos índices no XR. Nossos resultados evidenciaram que, mesmo com grandes e cumulativas taxas de aplicação de XR, o potencial de contaminação do lençol freático com elementos derivados do XR é insignificante nas condições climáticas do solo e do presente estudo. Dessa forma, o uso do XR juntamente com a adubação nitrogenada apresenta um potencial no uso na agricultura, aumentando a eficiência da adubação nitrogenada sem causar impactos ambientais.
Palavras-chave: Fertilização nitrogenada; Metais pesados; Contaminação do solo.

Resumen
El objetivo de este trabajo fue investigar la posible contaminación de la solución del suelo con elementos químicos presentes en la composición de la lutita retortada (LR) cuando se la añade a la fertilización nitrogenada en un sistema silvopastoril. El experimento se llevó a cabo en un sistema silvopastoril con un diseño de bloques completos al azar, con parcelas divididas. Los tratamientos principales consistieron en arreglos espaciales de los árboles, mientras que la subdivisión de las parcelas consistió en la aplicación superficial de urea (U) y urea recubierta con LR (U+LR). Independientemente del espaciamiento entre árboles, el uso de LR junto con urea (U + LR) no tuvo un efecto significativo en los parámetros químicos de la solución del suelo lixiviada a 40 cm de profundidad. Los metales pesados, Cd, As, Al y Pb, los elementos más peligrosos presentes en LR, ni siquiera fueron detectados en la solución del suelo en ningún evento de muestreo. Dichos resultados se atribuyen principalmente a sus bajos índices en LR. Nuestros resultados mostraron que, incluso con tasas de aplicación de LR grandes y acumulativas, el potencial de contaminación del agua subterránea con elementos derivados de LR es despreciable en las condiciones climáticas del suelo y del presente estudio. Por lo tanto, el uso de R junto con la fertilización nitrogenada presenta un potencial para su uso en la agricultura, aumentando la eficiencia de la fertilización nitrogenada sin causar impactos ambientales.
Palabras clave: Fertilización nitrogenada; Metales pesados; Contaminación del suelo.

1. Introduction

Oil shale is a sedimentary rock that presents itself in the forms of bitumen and querogen, organic complexes that when at high temperature and pressure (pyrolysis or retort process) produce oil, gas, sulfur, clay and complex organic structures (Nicolini et al. 2011). The U.S. holds the world's largest shale reserves, while in Estonia such reserves are most exploited, where 80% of power generation comes from shale pyrolysis (Omar & Rasha, 2018). Brazil has the world's second largest shale reserve and stands out as the most advanced technology holder for commercial use of oil shale resources (Pimentel et al. 2006). The retorted oil shale (ROS) comes from the process of extracting oil and gas (retorting). ROS presents some chemical and physical attributes that, added to its low cost, turns itself an interesting option for being used as soil conditioner for agriculture (Nicolini et al. 2011). It is composed by elements such as Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, S, Sb, Se, Si, Sr, Ti, Zn, Cl and SO_4, which concentration varies according to the locality of the mine, composition of the kergenical, quantity of elements in the Matrix rock and the process of extraction (Orupõld et al. 2008; Nicolini et al. 2011).

Nitrogen (N) is considered the most widely used nutrient in agriculture, being consumed worldwide 107.6 Tg N yr^{-1} (Lu & Tian, 2017), where the main source is urea, due to its best cost-benefit ratio (FAO, 2018). However, urea has a low efficiency of use by plants due to the different pathways of N losses (Mira et al. 2017). One of the main loss occurs by volatilization of ammonia - NH_3 (Cantarella et al. 2008; IPCC, 2014). In order to diminish such losses, efficient and cheap alternatives are mandatory, as inhibitors and coating technologies.

Because of its chemical and physical characteristics, ROS has a potential for being a coating technology and diminish losses of NH_3 volatilization from urea. The main characteristics are the adsorbent characteristic on the surface of its particles (Pimentel et al., 2006); the presence of micronutrients, mainly Cu and B, increasing urease inhibition (Benini et al. 2004; Stafanato et al. 2013); the presence of sulfur and pyrite (Ribas et al. 2017), causing a decrease in the pH around the urea granules covered by the ROS (Montalti et al. 1991; Albuquerque JR. et al. 2004); and the increase in the porosity of the ROS during the pyrolysis process, which can physically retain NH_3 due to the increase in its specific area (Ribas et al. 2017).

However, in the chemical composition of ROS, trace elements can indicate a potential pollutant from this residue, whose vertical transfer could imply in surface water and groundwater contamination/pollution by the leaching process, but few is known about such potential.

Pereira & Vitti (2004) and Santos et al. (2017) evaluated the release of metals from ROS and reported that its use did not modify the soil concentrations of toxic metal ions, pointing out the low concentration of the respective trace elements in the ROS, and, in general, the presence of ROS did not contribute to leaching and bioavailability of trace elements, maintaining these elements below threshold levels according to current legislation. However, there is still a need for further information on the leaching of chemical elements present in ROS, mainly considering the employment of ROS in a large quantity, as the continuous use in coated urea for many years.

This study aimed to analyze the potential for groundwater contamination by chemical elements present in the composition of the retorted oil shale when used together with nitrogen fertilization in a silvopastoral system, using free drainage lysimeters for soil solution sampling in undisturbed soil.

2. Methodology

The field experiment was conducted in the municipality of São Gabriel, Rio Grande do Sul state, south of Brazil (30°20'59"S and 54°15'82"W). The biome of the region is characterized as Pampa and the local climate is subtropical with hot summers and cold winters, classified as CFa according to the Köeppen classification system. The average annual temperature is 19 °C, with a maximum of 40 °C in the summer and a minimum of -3°C in winter and with an average annual precipitation of 1400 mm.

The study area has been used for about 30 years as native grassland for forage. In 2012, a silvopastoral system (SSP) was implemented, with the introduction of the native leguminous tree species *Parapiptadenia rigida* (Benth.) Brenan (red angico) on the native vegetation. The experimental design was randomized blocks with split-plots, with three replicates. In the main plots (30 x 36 m), the treatments consisted of: NG: Native grassland; NG + PR$_4$: Native grassland + *P. rigida* with spatial arrangement of 2 x 4 m; and NG+ PR$_6$: Native grassland + *P. rigida* with spatial arrangement of double lines 6 x (2 x 2) m. The split plots consisted of mineral nitrogen fertilization using urea (U) and ROS-coated urea (U + ROS).

The soil of the site is classified as Umbric Rhodic Acrisol according to FAO classification (IUSS, 2016) or ArgissoloVermelho Distrófico latossólico to the Brazilian system of soil classification (Embrapa, 2014). Mean slope is <2% in the field site. In the beginning of this study (2012), the soil layers 0-10 and 10-20 cm presented contents of total organic carbon (TOC) of 22 and 7 g kg^{-1} and total nitrogen (TN) of 2 and 3g kg^{-1}, respectively. In relation to physical attributes, the soil has mean clay contents of 216, 304 and 438 g Kg^{-1} for the layers 0-20, 20-40 and 40-60, respectively. A well defined Bt horizon is present, starting at 40cm depth. Total porosity of the soil in the 0-5 cm layer is 0.50 m^{3}m^{-3}, possessing 0.11 m^{3}m^{-3} of macropores and 0.39 m^{3}m^{-3} of micropores. In the 0-40 cm layer, the mean total porosity is 0.45 m^{3}m^{-3}, with 0.08 m^{3}m^{-3} of macropores and 0.36 m^{3}m^{-3} of micropores.

Nitrogen fertilization occurred in December 2016, August 2017, December 2017 and August 2018. In each season, a rate of 100 kg of N ha^{-1} was broadcasted in both treatments, applied on soil surface. This dose was established based on the official recommendation for natural pastures (CQFS-RS/SC, 2016). Moreover, in the U + ROS treatment, a rate of 300 kg ha^{-1} of powdered retorted shale was broadcasted twice, in December 2016 and December 2017, immediately after the application of the U + ROS in order to simulate the accumulated effect of successive applications of ROS. Therefore, the 600 kg of extra ROS applied in the soil of the experiment is equivalent to a cumulative application of about 80 years of fertilization (two applications of 100 kg N ha^{-1} yr^{-1}), since about 4 kg of ROS is employed for pelletizing 100 kg of urea.

The ROS used in the present study was originated from the Oil Shale Industrialization Unit of Petrobras S/A located in São Mateus do Sul, Paraná state, Brazil. According to its chemical characteristics, ROS has a pH of 4.6 and the following content of elements, in % (w/w): SiO_2: 52.6; Al_2O_3: 11.6; Fe_2O_3: 7.5; S: 3.3; K_2O: 2.5; CaO: 26.0; MgO: 1.7; Na_2O: 1.4; P_2O_5: 0.3; and MnO: 0.040. In smaller concentrations (mg kg^{-1}), ROS had: Zn: 127.0; Cu: 61.2; Co: 21.1; Mo: 9.9; Se: 2.3; Pb: 27.5; As: 30.6; Cd: 0.5; Hg: 0.2; Ni: 22.5 and Ba: 414.5. The pelletization of urea with ROS was performed with aligel ligand, presenting 48.2% N and pH 8.1 in the final product, while the percentage of N and the pH only of urea was 49.8 and 8.6, respectively.

The soil solution was sampled through free drainage lysimeters (zero tension) already installed at the site of the experiment. They were placed in 2013, following Basso et al (2005), and each lysimeter measures 60x40cm. Each subplot (fertilized with U and U + ROS) has two lysimeters, totaling 36 lysimeters. The upper part of the lysimeters is 40 cm deep in the soil, which consists of the transition between A and the Bt horizons. The lysimeters were installed laterally after opening trenches, so that the soil above the lysimeter was kept with undisturbed structure.

Two events of soil solution sampling were carried out after each of the fertilizations of December 2016 and December 2017. Samplings were performed shortly after natural precipitation events that generated a leachate solution (at least 24h after the end of the precipitation). Following Dec. 2016 fertilization, samplings were performed in January and in March 2017 (43 and 121 days after fertilization, respectively), while after the fertilization of Dec. 2017 the samplings were carried out in March and in July 2018 (109 and 210 days, respectively, after application). No other soil solution sampling was performed in the interval between fertilization and the second soil solution sampling event after each fertilization.

Immediately after collecting the soil solution, pH and electrical conductivity (EC) of the samples were determined, using a pH meter (TEC 5, Tecnall) and an Electrical Conductivity meter (470, Jenway), according to Tedesco et al. (1995).

Dissolved organic carbon (DOC) contents of the soil solution were determined by colorimetry in light spectrophotometer (2000UV, BEL Photonic) after oxidation by potassium dichromate (Nelson & Sommers, 1996). Phosphorus (P) contents were determined by colorimetry in light spectrophotometer (2000uv, BEL Photonic,) according to Murphy & Riley (1962). Ammonium (NH_4) and nitrate (NO_3) contents of the soil solution were performed by Kjeldahl distillation, while sodium (Na) and potassium (K) contents were evaluated in Flame photometer (1382, TKS Technologies), according to Tedesco (1995).

An aliquot of each soil solution sample taken after the first fertilization was analyzed for total contents of Al, Cd, Pb, Ca, Cu, Fe, Mg, Mn and Zn by inductively coupled plasma atomic emission spectrometry (ICP-AES Perkin Elmer, Akron, Ohio, USA). During the second fertilization, the determination of total levels of Al, Ca, Cu, Fe, Mg, Mn and Zn was performed by microwave plasma atomic emission spectrometry (MP AES 4200, Aligen) and the total contents of As, Cd and Pb by atomic emission spectrometry by inductively coupled plasma (ICP-AES Perkin Elmer, Akron, Ohio, USA).

The pH buffering capacity (pHBC) of U and U+ROS samples was determined by pH titration curves after adding acid and alkali at known concentrations. For this, 20g aliquots of U and U+ROS (7 replicates) were arranged in snap-cap bottles. In one of the replicates, 40 ml of distilled water was added. In the remaining six replications, HCl and NaOH solutions were added at different concentrations (3.9, 8.6 and 17.5 mmol L^{-1} and 3.9, 8.4 and 17.8 mmol L^{-1}, respectively). After stirring with glass stick, snap-cap bottles were hermetically closed and waited for 24 hours to perform pH readings. From the results, pHBC was estimated considering the amount of acid or base (converted to cmol H^+) that is required to change the pH of one kg of soil in one unit. The estimated buffering power refers to the range of pH 4 to 6, where the titration curve approaches a straight (Helyar & Porter, 1989).

The results were subjected to analysis of variance (Anova) in a split-plot randomized block design (tree arrangements were considered as the main treatments, while the presence of ROS-coated urea was the split plot), and the means of the treatments were compared by the Tukey test at a 10% probability level, using the Sisvar software.

3. Results and Discussion

There was no significant effect of trees spacing and the addition of ROS on the chemical parameters of the soil solution leached at 40 cm depth of the soil (Tables 1, 2, 3 and 4).

In the first fertilization event, the concentrations of Al, As, Cd, Pb were lower than the limits of quantification of the methods (Table 1), during the two soil solution samplings, for all treatments. Therefore, their contents fell below the guiding values of current legislation, CONAMA Resolution 420/09 and CETESB Decree 195/2005, which provides on reference values for soils and groundwater, demonstrating the non-contamination of the soil solution with these elements traced in the presence of ROS. The concentrations of these heavy metals were also below the values stipulated by NBR 1004:2004, a standard that classifies solid waste as to their potential risks to the environment and public health and stipulates maximum concentration limits in extracts obtained in a waste leaching test.

Table 1 - Concentrations of cations in the solution of the leached soil in a silvopastoral system with application of retorted oil shale during the first fertilization. (December 2016).

Trat.	N-NH$_4$	Na	K	Al	Ca	Mg	Zn	Fe	Mn	As	Cd	Pb
	-- mg L^{-1} --									----------- µg L^{-1}--------		
1st leachate sampling (43 days after fertilization)												
NG	2.327 ns	1.023 ns	1.33 sn	< 2.0	37.525 ns	2.457 ns	0.397 ns	0.120 ns	0.619 ns	< 5.0	< 0.14	<6.2
NG+PR$_4$	2.493	1.371	2.243	< 2.0	40.781	3.517	0.398	0.138	0.596	< 5.0	< 0.14	<6.2
NG+PR$_6$	2.736	1.492	1.923	< 2.0	47.017	4.988	0.396	0.171	0.652	< 5.0	< 0.14	<6.2
U	2.524	1.274	1.798	< 2.0	42.061	3.670	0.395	0.158	0.659	< 5.0	< 0.14	< 6.2
U+ROS	2.514	1.316	1.864	< 2.0	41.488	3.638	0.399	0.128	0.587	< 5.0	< 0.14	< 6.2
2nd leachate sampling (121 days after fertilization)												
NG	2.265 ns	0.461 ns	1.572 ns	< 2.0	43.407 ns	1.875 ns	0.402 ns	0.086 ns	0.581 ns	< 5.0	< 0.14	< 6.2
NG+PR$_4$	2.527	0.494	2.713	< 2.0	55.307	2.975	0.402	0.077	0.563	< 5.0	< 0.14	< 6.2
NG+PR$_6$	2.594	0.217	2.704	< 2.0	50.054	2.857	0.398	0.081	0.562	< 5.0	< 0.14	< 6.2
U	2.466	0.441	2.044	< 2.0	53.644	2.577	0.402	0.080	0.575	< 5.0	< 0.14	< 6.2
U+ ROS	2.487	0.334	2.692	< 2.0	46.665	2.673	0.399	0.082	0.561	< 5.0	< 0.14	< 6.2

Effect of the planting of *Parapiptadenia rigida* in two spatial distributions. NG: Native grassland; NG+PR$_4$: Native grassland + *P. rigida* with spatial arrangement of 2 x 4 m; and NG+PR$_6$: Native grassland + *P. rigida* with spatial arrangement of double lines 6 x (2 x 2) m; effect of forage mineral fertilization with urea (U) and with urea covered with retorted shale (U+ROS). ns: no significant difference by tukey test ($P < 0.10$) between means. (n=3). Fonte: Autores.

Following the second fertilization event, the concentrations of Al, Cd, As and Pb were also below the limits of detection (Table 2). However, it is important to note that the minimal detection level was different from the analysis of the first event. In the second event of fertilization, whose analysis were performed in less sensitive equipment, the detection level for As and Pb were < 20 µg L^{-1} (Table 2), while their reference values for contamination are 10 µg L^{-1} according to CONAMA Resolution 420/09. However, concentrations remain within the reference values of NBR 10004:2004, which are 1000 µg L^{-1} for As and Pb.

Table 2 - Concentrations of cations in the solution of the leached soil in a silvopastoral system with application of retorted oil shale during the second fertilization (December 2017).

Trat.	N-NH$_4$	Na	K	Al	Ca	Mg	Zn	Fe	Mn	As	Cd	Pb
	-- mg L^{-1} --									----------- µg L^{-1}-------		
	1st leachate sampling (109 days after fertilization)											
NG	1.105 ns	1.490 ns	3.083 ns	< 0.100	15.839	1.764 ns	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0
NG+PR$_4$	0.758	1.168	3.455	< 0.100	16.547	2.445	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0
NG+PR$_6$	0.685	1.344	3.876	< 0.100	17.467	2.224	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0
U	1.276	1.387	2.843	< 0.100	15.076	1.874	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0
U+ROS	0.560	1.110	3.773	< 0.100	16.206	2.164	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0
	2nd leachate sampling (210 days after fertilization)											
NG	0.831	1.272	2.008	< 0.100	12.098	1.676	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0
NG+PR$_4$	0.420	2.501	4.159	< 0.100	24.977	3.786	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0
NG+PR$_6$	0.455	1.756	2.632	< 0.100	24.431	2.759	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0
U	0.580	1.549	2.734	< 0.100	16.544	2.390	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0
U+ROS	0.485	1.863	2.912	< 0.100	21.185	2.690	< 0.075	< 0.075	< 0.009	< 20.0	< 2.0	< 20.0

Effect of the planting of *Parapiptadenia rigida* in two spatial distributions. NG: Native grassland; NG+PR$_4$: Native grassland + *P. rigida* with spatial arrangement of 2 x 4 m; and NG+PR$_6$: Native grassland + *P. rigida* with spatial arrangement of double lines 6 x (2 x 2) m; effect of forage mineral fertilization with urea (U) and with urea covered with retorted shale (U+ROS);. ns: no significant difference by tukey test (P <0.10) between means. (n=3). Fonte: Autores.

Concentrations of Mn and Zn in the leachate solution in the collections of the two fertilizations were not increased by the application of ROS, presenting values lower than those determined by CONAMA Resolution 420/09 and CETESB Decree 195/2005 in the treatments of plots and subplots (Tables 1 and 2).

The concentrations of the other cations analyzed (NH_4, Na, K, Ca, Mg and Fe) in the leached soil solution presented very similar values between the treatments of the plots and subplots (Tables 1 and 2). Therefore, in addition to the absence of effect from ROS on heavy metals in soil solution, ROS does not affect the concentration of nutrients in general, even if applied at relatively large rate (or in accumulated applications). Therefore, the observed concentrations of the elements should come from the soil itself. Another important fact is that the observed concentrations of other possibly toxic elements (Mn, Zn, NO_3) were also lower than those stipulated by current legislation.

Putting all the results together, our study demonstrates the potential of ROS for being employed as coating of urea without damaging the water table conditions. Obviously, these results are valid for this type of soil, which has a certain amount of clay (Loamy soil) and organic matter, that is, a not so low adsorption capacity. On the other hand, a large amount of macropores and continuity of these pores throughout the profile are expected, given by the high root density of the forage of the native field and the fauna of the local soil, which would favor a water percolation. Even so, vertical transfer of metals to lysimeters was not detected, which is a very favorable point for the use of ROS without risks to the environment.

The volume of leached solution in the first collection performed in the two fertilizations decreased by around 40% due to the presence of the arboreal component compared to T1 (Native grassland), and the presence of ROS in the treatments did not affect the leached volume. In the second collection, leached volumes were smaller and quite homogeneous among treatments, both during the first fertilization and in the second fertilization (Table 3 and 4).

Table 3 - Volume, values of electrical conductivity (EC) and pH, dissolved organic carbon (DOC), phosphorus (P) and nitrate (NO_3^-) concentration of leached soil solution in a Silvipastoral System with retorted oil shale application during the first fertilization (December 2016).

Treatment	Volume ($m^3 ha^{-1}$)	EC (mS)	pH	DOC (Kg C ha^{-1})	P (mg L^{-1})	N-NO3 (mg L^{-1})
----------------------------------- 1st COLLECTION ------------------------------------						
NG	1000.0 ns	0.181 ns	6.38 ns	1.427 ns	0.002 ns	1.917 ns
NG+PR4	625.0	0.251	7.00	0.474	0.003	2.026
GN+PR6	541.6	0.261	6.66	1.321	0.013	2.396
U	583.3 ns	0.244 ns	6.64 ns	0.519 ns	0.009 ns	2.123 ns
U+ROS	625.0	0.218	6.71	1.629	0.003	2.103
----------------------------------- 2nd COLLECTION ------------------------------------						
NG	208.3 ns	0.232 ns	6.27 ns	0.248 ns	0.000 ns	1.860 ns
NG+PR4	166.6	0.295	6.54	0.254	0.188	2.035
NG+PR6	195.8	0.281	6.50	0.249	0.089	2.376
U	208.3 ns	0.264 ns	6.47 ns	0.224 ns	0.059 ns	2.061 ns
U+ROS	204.1	0.281	6.42	0.279	0.139	2.145

Effect of the planting of *Parapiptadenia rigida* in two spatial distributions. NG: Native grassland; NG+PR4: Native grassland + *P. rigida* with spatial arrangement of 2 x 4 m; and NG+PR6: Native grassland + *P. rigida* with spatial arrangement of double lines 6 x (2 x 2) m; effect of forage mineral fertilization with urea (U) and with urea covered with retorted shale (U+ROS). ns: no significant difference by tukey test (P <0.10) between means. (n=3). Fonte: Autores.

Table 4 - Volume, values of electrical conductivity (EC) and pH, dissolved organic carbon (DOC), phosphorus (P) and nitrate (NO_3^-) concentration of leachate soil solution in a silvopastoral system with retorted oil shale application during second fertilization (December 2017).

Treatment	Volume (m³ ha⁻¹)	EC (mS)	pH	DOC (Kg C ha⁻¹)	P (mg L⁻¹)	N-NO₃ (mg L⁻¹)
		-- 1st COLLECTION --				
NG	323.86 ns	0.051 ns	7.33 ns	0.455 ns	0.075 ns	1.155 ns
NG+PR₄	200.17	0.051	7.37	0.163	0.054	0.946
NG+PR₆	174.62	0.053	7.51	0.109	0.042	0.735
U	208.45 ns	0.054 ns	6.99 ns	0.266 ns	0.081 ns	1.276 ns
U+ROS	242.90	0.044	7.41	0.244	0.030	0.560
		-- 2nd COLLECTION --				
NG	320.26 ns	0.132 ns	6.40 ns	0.523 ns	0.157 ns	0.797 ns
NG+PR₄	222.91	0.194	6.65	0.310	0.046	0.506
NG+PR₆	222.06	0.206	6.98	0.338	0.047	0.718
U	241.20 ns	0.170 ns	6.40 ns	0.369 ns	0.085 ns	0.671 ns
U+ROS	251.73	0.148	6.40	0.494	0.054	0.524

Effect of the planting of *Parapiptadenia rigida* in two spatial distributions. NG: Native grassland; NG+PR₄: Native grassland + *P. rigida* with spatial arrangement of 2 x 4 m; and NG+PR₆: Native grassland + *P. rigida* with spatial arrangement of double lines 6 x (2 x 2) m; effect of forage mineral fertilization with urea (U) and with urea covered with retorted shale (U+ROS). ns: no significant difference by tukey test (P <0.10) between means. (n=3). Fonte: Autores.

The electrical conductivity (EC) measure of the soil solution is indicative of the increase or decrease in the content of salts dissolved in soils (EMBRAPA, 2014). The EC in soil solution collections obtained similar values in fertilization with U and U+ROS and planting spacing. Our results corroborates those reported by Santos et al. (2017) in soil extracts where successive doses of retort shale were applied under field conditions, in which they did not observe changes in EC and inferred that although with higher levels of some elements in ROS, the quantities released were not enough to cause a change in EC values.

Although in general there is no significant effect of the treatments, the pH of soil solution under native field tended to be lower than in the solution of soils with red angico. This trend was consistent in the two collections of the two fertilization events. The presence of ROS, on the other hand, did not affect the pH of the drained solutions (difference less than 0.1 pH unit on average between U and U+ROS).

Soil pH in urea treatment was 5.75 and pH of the soil of treatment with ROS was 5.68, with no significant difference between them. It is worth remembering that, to estimate the cumulative effect of ROS being added to the soil, 300 kg ha⁻¹ of ROS were applied that theoretically would favor acidification of the soil and solution. The absence of effect on soil pH was also verified by Pereira and Vitti (2004), who evaluated the alteration in the characteristics of two São Paulo soils in the presence of up to 12 t ha⁻¹ ROS.

The analysis of pH buffering capacity (pHBC) in urea and urea covered by retorted shale showed that the presence of ROS had a marked effect on pH buffering during the alkalinization process (Graph 1), which, theoretically, would keep the pH around the urea granule lower, prevailing the formation of NH₄ over NH₃, and thus decreasing N losses by volatilization.

Graph 1: Titration curves for determining pH buffer capacity (pHBC). U (urea); U+ROS (urea + retorted oil shale).
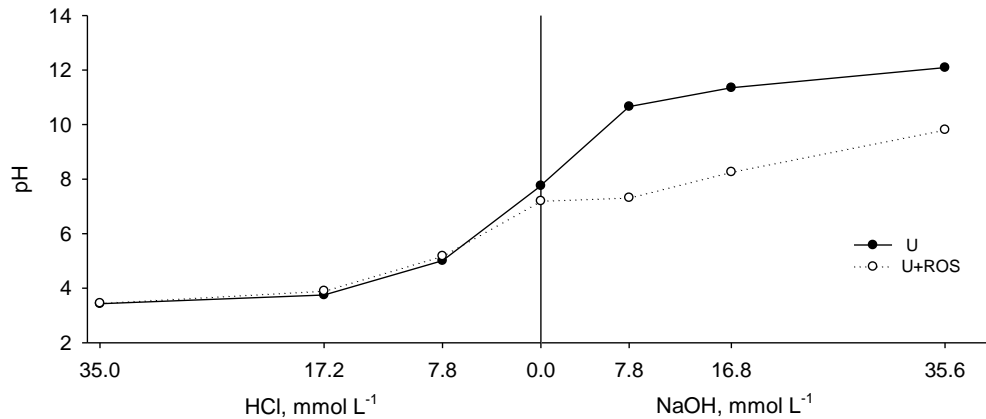
Fonte: Autores.

This decrease in pH around the urea granules covered by ROS may be related to the presence of sulfur and pyrite in its constitution (Ribas et. al., 2017), which in turn release H^+ ions (Montalti et al. 1991; Albuquerque Jr. et al. 2004). The fact that the ROS buffered the increase in pH in the titration curves and, at the same time, did not imply changes in soil pH and leached solution, strengthens the potential of using this co-product as a viable technology to reduce N losses by volatilization of NH_3.

During the first fertilization, DOC contents in solution presented higher levels than those found in the second collection, which may have been favored by the higher volumes of leached solution. However, they remained low in both collections and did not present significant differences in the presence of ROS and in the different spacing of angico-red planting. Such behavior is indicative that the presence of ROS did not affect mineralization rates and the dissolution of labile C present in the soil.

The P concentrations in the leached solution did not present significant differences between treatments with U or U+ROS and between the treatments of the plots, keeping their concentrations low in the collections of the two fertilizations performed and evidencing that the contents found in the solution does not prove the application of ROS in the soil (Table 3 and 4). In Brazil, CONAMA Resolution 357/05 establishes critical P levels for surface waters of 0.020 - 0.025; 0.030 - 0.050 and 0.050 - 0.075 mg L^{-1} for water classes 1, 2, 3, respectively. In other countries the literature indicates that concentrations between 0.01-0.02 mg L^{-1} (Klein & Agne, 2012) can already cause eutrophication, even though such concentration is below the minimum required by plants. Thus, the P contents found in this study, although low, deserve to be looked carefully in order to avoid future environmental problems.

Although excess P in the environment causes several negative impacts, with special reference to water quality, Brazilian legislation does not recognize P as soil contaminant and CONAMA Resolution 420/09, which deals with groundwater quality, does not establish critical values for the presence of P, because, as well as nitrate, P mobility in soil is very small, and therefore percolation losses in agricultural soil are considered negligible (Klein & Agne, 2012).

The NO_3 concentrations remained low in the collections of the two fertilizations in all analyzed treatments, and the presence of ROS and different red angico planting spacings did not generate significant increments of NO_3 in soil solution. The highest values found were 2.39 mg L^{-1} of NO_3, in the $NG+PR_6$ treatment of the plots, during the first collection of the first fertilization, 76% less than determines CONAMA Resolution N°. 420 and CETESB Decree 195/2005, which provides on the guiding values for soils and groundwater. Thus, even at the highest concentration found, there was negligible risk of contamination of the water table by nitrate. The red angico is a legume, which presents biological nitrogen fixation (BNF)

interesting for the laying forage; considering that there was no increase in mineral N in the solution, N cycling seems to be very close, with few losses – in other words, the transfer of the mineralized N of the tissues of the angico seems to be reused quickly by the forage constantly absorption. During the first fertilization, leaching collections occurred 43 and 121 days after application of 100 kg N ha^{-1}. There were losses of 54 and 44 (U and U+ROS) kg N ha^{-1} via volatilization before the first leaching event (data not demonstrated in this article). The remaining N was probably immobilized by microbial tissue, absorbed by plants and adsorbed by the soil (NH_4 and NO_3 contents), as concentrations in leachate soil solution was low. In addition, the large density of roots from the trees and grassland forages must have implied an extraordinary N absorption capacity. In this case, a single application of 100 kg N ha^{-1} does not pose a major threat to contamination of underground watercourses by NO_3. The addition of ROS to urea increased the NH_4 content in the soil (data not published yet), but this did not mean an increase in leached NO_3. Thus, the use of ROS together with N fertilization has a potential in the use in agriculture, increasing the efficiency of N fertilization without causing impacts to the water table, even if large rates of ROS are applied.

4. Conclusion

The application of ROS as urea pelletizer does not contribute to increase the concentration of the chemical pollutants in soil leachate, suggesting a negligible potential for contaminating the water table.

Although the concentration of heavy metals in the ROS is low, evaluations regarding the potential for vertical transfers as leachates in extremely sandy soils are required in future researches.

Acknowledgments

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