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Incorporation of retorted oil shale in Brazilian agricultural soil: An assessment of impacts after successive applications

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ABSTRACT

Brazilian soils have unequivocal role on global food security. Production in these lands is subjected to multiple and successive inputs with variable composition, and the introduction of new products must be carefully validated to ensure environmental safety. The pyrobituminous oil shale from Irati geological formation is the most important Brazilian oil shale reserve, and its pyrolysis process yields a solid by-product known as retorted oil shale. Among alternative retorted oil shale reuses we hypothesize that it is safe and can either be used as raw material for agricultural inputs production or disposed in the soil without causing degradation. The aim of this work was to evaluate the soil contamination propensity after six cumulative applications of increasing retorted oil shale doses on an Arenic Rhodic Acrisol under no-tillage. The treatments were composed of four doses of retorted oil shale (0, 0.75, 1.5 and 3 Mg ha^{-1}) all with mineral fertilization, added annually from 2009 to 2014. In November 2015, disturbed and structure preserved soil samples were collected in 0.00–0.05, 0.05–0.10 and 0.10–0.20 m soil layers to determine the total content of trace elements (copper, zinc, nickel, chromium, barium, arsenic, lead and mercury), available macronutrients (calcium, magnesium, potassium, phosphorus and sulphur), macro and microaggregates, mean weight diameter of aggregates, bulk density, total porosity, macroporosity, microporosity and available water capacity. Retorted oil shale is environmentally safe for agricultural purposes when applied on soil surface or incorporated in the arable layer. In the medium term (6-yrs) cumulative doses of retorted oil shale up to 18 Mg ha^{-1} (annual dose of 3 Mg ha^{-1}) did not increase potentially toxic elements levels in a sandy soil under no-tillage system, except for copper at 0.00–0.05 m topsoil layer as well as soil physical attributes and available macronutrients levels were not affected. Policies should require robust field studies to validate new waste-derived products, to ensure food safety and maintain soil quality.

1. Introduction

Soils from Brazil dedicated to food production has unequivocal role on global food security. In 2018, the country participated with 45% of all world soybeans export, 44% of sugar, 33% of chicken, 20% of cattle and 9% of pork meat, as well as relevant stakes in corn grains and other food products (USDA, 2019a, 2019b; 2019c). This status was forged by recent growing of Brazilian agricultural competitiveness, thanks to favourable edaphoclimatic conditions and to the adoption of specific high-tech solutions.

One of them are the correction of nutritional deficiencies, inherent to old and well-weathered soils. But Brazilian farmers relies essentially on imported high-soluble fertilizers, which accounted for 83% of all used in the country in 2017 (AMA BRASIL, 2018). Heavy and repeated applications of fertilizers are therefore

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required, and new soil amendments have been introduced so well, as alternative to recovery or maintain soil fertility and ensure satisfactory agricultural production (Manning, 2018). Nevertheless, some inputs may cause deleterious effects to the environment. As examples, Chaney (2012) mentions the use of high Cd superphosphate in Australia which caused significant increase in wheat and potato Cd levels, and suggested that risk from long-term accumulation of phosphate fertilizer Cd (and other sources) must be controlled. De Conti et al. (2016) reported accumulation of Cu and Zn soil contents after successive pig slurry applications, while Casali et al. (2008) warned that successive applications of cupric fungicides in grapevine areas from Southern Brazil can increase total Cu concentration in soil profile.

Some products may be naturally rich in trace elements, or contaminated, what should be carefully evaluated and, in some cases, prevent its commercial availability to avoid toxic elements in agriculture and food chains. Most countries have their own policies to avoid use of contaminated products in agriculture, but each country has its specific rules, and exported goods may be subjected to unforeseen barriers and consequences. Along with heavy metals, other soil quality attributes can be affected by soil amendments, causing negative effects to the environment and crops performance (Ogbodo, 2013). These problems raised many questions about how better control and management of soil amendments could prevent future problems. Usually, regulatory agencies regulate new products for agricultural use to assure adequate levels of nutrients and heavy metals. However, this evaluation is restricted to the product itself and the investigation of the extent of its effects on the environment in the long-term is rarely performed. Better quality control and management of soil amendments could prevent future problems and certainly an insightful pre-analysis of new products would reduce risks to the environment and food safety.

Researches on waste reuse from mining activities in Brazil (Korchagin et al., 2019; Ramos et al., 2017), in Europe (Mohammed et al., 2014), in China and India (Basak et al., 2017; Li et al., 2016) addressed alternative nutrient sources to slower the nutrient-release. Despite this, possible negative effects may not have been thoroughly evaluated. Taken this into consideration, we proposed in this study an evaluation of soil contamination propensity by release of trace elements and soil quality depreciation when cumulative doses of a new amendment are applied on an Arenic Rhodic Acrisol, managed under no-tillage with grain crops sequence in a medium-term experiment. This type of study can be used to access soil side-effects caused by any type of soil inputs. The evaluated amendment was retorted oil shale (ROS), whose agronomic efficiency and potential applications were properly documented previously (Santos et al., 2017; Giacomini, 2017; Giacomini, 2017), therefore, its wide use in agriculture are potentially high. The ROS is a solid by-product of the oil, natural gas, and sulphur extraction from oil shale and represents 80–90% of the feedstock weight (around 5.000 tons per day) (Petrobras, 2019; Pimentel et al., 2010). ROS is obtained from a pyrolysis process that involve the shale heating in a controlled environment, where the complex kerogen network structure is broken down (Nicolini et al., 2011; Ribas et al., 2017). Concerning contaminants, in particular the residual contents of phenolic compounds and polycyclic aromatic hydrocarbons in ROS, previous studies showed that these organic compounds are unharmful, being easily degraded in the soil (Nicolini et al., 2011; Dolatto, 2015; Colimo, 2017).

Considering that ROS would be applied extensively and in considerable amounts in agricultural soils dedicated for food production, possible impacts on soil quality and food contamination must be accounted for. The objective of the present study was to evaluate the soil contamination risk after cumulative applications of retorted oil shale and sequential cropping in an Arenic Rhodic Acrisol conducted under no-tillage system.

2. Material and methods

2.1. Retorted oil shale characterization

The oil shale is extracted by the Industrialization Unit of Petrobras S/A through open mining from the Irati geological formation in São Mateus do Sul, Parana State, South Brazil, being available in two rock layers with high oil grade, between 20 and 40 m depth. The ROS used in the field experiment was obtained after temperature stabilization, from piles stored recently in the mine cave. The collected material was submitted to crushing, milling and sieving so that the used granulometry was $100\% < 0.3$ mm. The ROS was sampled for geochemical characterization and stored in protection bags (polipropilene) at room temperature for annual applications in the field experiment. The geochemical analyses from ROS sample were carried out at AcmeLabs - Analytical Laboratories Ltd, Vancouver, Canada (Table 1). The mineralogical analyses show that main minerals present are quartz, pyrite, plagioclase feldspar, gypsum, and mixed-layer clay minerals such as illite (Pimentel et al., 2010; Ribas et al., 2017).

2.2. Study site and experimental design

The field experiment was carried out in the experimental area at Federal University of Santa Maria (29°45′S, 53°42′W), south of Brazil, from 2009 to 2014. Aiming to perform the ROS environmental monitoring it was chosen an area with edaphoclimatic conditions of both agricultural and environmental interest such as sandy soil, and average annual precipitation of 1,769 mm.

The soil was classified as an Arenic Rhodic Acrisol (IUSS - World Reference Base for Soil Resources, 2014) which presented at 0.00–0.10 m layer low pH (5.4) and organic matter content (18 g kg^{-1}); medium phosphorus and high potassium available contents (31 and 105 mg dm^{-3} respectively), medium magnesium and calcium contents (1.2 and 3.3 cmol$_c$ dm^{-3} respectively) and potential acidity (H + Al) of 2.3 cmol$_c$ dm^{-3} (Doumer et al., 2011).

The experimental design was a randomized complete block with four replications of 25 m^2 (5×5 m). In the plots, annual applications of nitrogen, phosphorus and potassium, using urea, triple superphosphate and potassium chloride, respectively, were carried out aiming to cultivate black bean (*Phaseolus vulgaris*) in the summer and wheat (*Triticum* spp.) in the winter. ROS doses of 0, 0.75, 1.5 and 3.0 Mg ha^{-1} were annually applied in the area, and at the end of the experimental period (6 years) the soil presented cumulative doses from 4.5 to 18 Mg ha^{-1} (Table 2). In 2009 the ROS was applied on the soil surface followed by incorporation by tillage, preceding the black bean sowing. From 2010 to 2014, applications of ROS doses were

Table 1
Geochemical analysis of retorted oil shale used in the experimental area.

Elements	%	Elements	mg kg^{-1}	Elements	mg kg^{-1}
Total Solids	86.8	Phosphorus	1,547	Arsenic	12.6
Oils and Greases	0.37	Potassium	2,746	Barium	82.4
		Calcium	11,325	Cadmium	<1.15
		Magnesium	2,146	Lead	18.3
		Sulphur	840	Chromium	<5.18
		Sodium	1,675	Mercury	<0.12
		Boron	76	Selenium	1.73
		Zinc	32.2		
		Copper	36.9		
		Cobalt	6.71		
		Manganese	95.5		
		Iron	25,000		

Table 2
Treatments and cumulative doses of retorted oil shale and fertilizer applied in an Arenic Rhodic Acrisol from 2009 to 2014.

Treatment	ROS ($Mg\ ha^{-1}\ year^{-1}$)	Cumulative doses of ROS[a] ($Mg\ ha^{-1}$)					
		2009	2010	2011	2012	2013	2014
T1 - 0 + NPK[b]	0	0	0	0	0	0	0
T2 – 0.75 + NPK	0.75	0.75	1.5	2.25	3	3.75	4.5
T3 – 1.5 + NPK	1.5	1.5	3	4.5	6	7.5	9
T4 - 3 + NPK	3	3	6	9	12	15	18
T5 – 0	0	0	0	0	0	0	0

[a] Accumulated ROS from previous applications.
[b] Annual basic fertilization: 100 kg $ha^{-1}$of nitrogen (N), 120 kg $ha^{-1}$of phosphorus (P_2O_5) and 90 kg $ha^{-1}$of potassium (K_2O); T1: Fertilizer Control (without ROS + basic fertilizer); T2: Annual application ROS of 0.75 Mg ha^{-1} + basic fertilizer; T3: Annual application ROS of 1.5 Mg ha^{-1} + basic fertilizer; T4: Annual application ROS of 3 Mg ha^{-1}+ basic fertilizer; T5: Absolute Control (without ROS + without basic fertilizer).

carried out at the time of wheat sowing, in the soil surface, since the soil management system was converted into no-tillage.

2.3. Soil sampling, chemical and physical analysis

In November 2015, 60 disturbed and aggregate soil samples were collected in 0.00–0.05, 0.05–0.10 and 0.10–0.20 m layers (5 treatments x 4 blocks × 3 soil layers). Disturbed samples were submitted to analyses of: trace elements: copper, zinc, nickel, chromium, barium, arsenic, lead and mercury, by acid digestion (aqua regia) followed by quantification in ICP-MS realized by AcmeLabs; available nutrients: calcium, magnesium, potassium, phosphorus and sulphur; organic matter (OM), soil pH and cation exchange capacity ($CEC_{pH7.0}$), all performed using the methodology described in Teixeira et al. (2017). In addition, aggregate samples were employed to determine the distribution of water-stable aggregates in six size classes (C1 = 9.52–4.76 mm; C2 = 4.75–2.00 mm; C3 = 1.99–1.00 mm; C4 = 0.99–0.25 mm; C5 = 0.24–0.105 mm and C6<0.105 mm) by wet sieving. Macroaggregates (%) were considered as C1+C2 (stable aggregates with sizes greater than 2 mm) while microaggregates (%) as the sum of C3, C4, C5 and C6 (with sizes lower than 2 mm). The mean weight diameter (MWD) of aggregates were calculated according to Kemper and Rosenau (1986).

In the same layers were collected 180 undisturbed soil samples (5 treatments x 4 blocks × 3 soil layers x 3 repetitions) to determine in the laboratory the bulk density (BD), macroporosity (Ma), microporosity (Mi), total porosity (TP) and available water capacity (AWC). Unless BD, all were obtained from soil water retention curves (SWRC), which were determined by considering the matric potentials of 1 and 6 kPa (tension table), 10, 33 and 100 kPa (Richards pressure chamber) (Klute, 1986) and greater than 300 kPa (WP4c psychrometer, DEVICES, 2015). The experimental SWRC data were adjusted according to Van Genuchten (1980). The adjusted data and van Genuchten's empirical parameters were used to calculate the field capacity (FC, $m^3\ m^{-3}$), considered from SWRC as the estimated value of volumetric water content in equilibrium at 10 kPa, while the permanent wilting point (PWP, $m^3\ m^{-3}$) as the estimated water content retained at 1,500 kPa. The available water capacity (AWC, $m^3\ m^{-3}$) was calculated by subtracting PWP from FC; Microporosity was considered as the volumetric soil water content in equilibrium at 6 kPa; total porosity was considered as the volumetric water content in equilibrium at soil saturated condition (0 kPa); macroporosity was obtained by subtracting Mi from TP; and bulk density was calculated by dividing the dry mass of each soil core by the internal volume of the sampling cylinder.

2.4. Statistical data analysis

The data set of each response variable was submitted to the analysis of variance (ANOVA). When ANOVA resulted in significant effects for at least one treatment by F test, means were compared by Tukey's test ($p < 0.05$). All data analysis was performed using the statistical software Sigmaplot (2004).

3. Results and discussion

As shown in the Fig. 1(a–f), independent of the soil layer, the levels of trace elements such as cooper, zinc, nickel, chromium, barium and arsenic were below the average quality reference values by soil groups for the natural contents in soils of the state of Rio Grande do Sul (Althaus et al., 2018) and to preventive values in soils stablished by Brazilian National Council of Environment (CONAMA Nr. 420/2009).

Although far below the reference values, the level of cooper at the topsoil (0.00–0.05 m), as shown in Fig. 1a, increased in the higher ROS dose of 18 Mg ha^{-1} (T4) in relation to 4.5 Mg ha^{-1} (T2) and to the treatments without ROS (T1 and T5). This result agrees with Al-Harahsheh et al. (2012), Santos (2015) and Al-Saqarat et al. (2017) which in desorption experiments showed that ROS is a good source of copper. However, the authors observed that also other elements such as zinc, chromium and/or macronutrients such as calcium and magnesium can be available. In our study, there was no significant difference between treatments and layers for zinc (Fig. 1b), nickel (Fig. 1c), chromium (Fig. 1d) and macronutrients such calcium, magnesium, potassium, phosphorus and sulphur (Table 3) although present in significant contents in its constitution (Table 1).

To date, ROS should not be considered as an environmental concern due to the results mentioned above in our study and due to the low level of lead and mercury (not shown in the Figure) observed in the cumulative doses of ROS (T2 to T4), which did not exceed 0.01 mg kg^{-1} for lead and ranged between 0.29 and 0.64 mg kg^{-1} for mercury at 0.20 m depth.

These results are far below from the investigation limits, stablished for agricultural soils where applications of wastes are allowed (CONAMA Nr. 420/2009), which is 180 and 12 mg kg^{-1}, respectively. In addition, the Fig. 1(e and f) showed that the higher ROS dose (18 Mg ha^{-1}) was unable to increase the soil content of barium and arsenic. These results are in agreement with those from Santos et al. (2017) and Loeck (2018) which observed that the ROS can be used as a soil conditioner in agriculture without adding harmful elements to the environment.

About others chemical attributes, in the medium term (6-yrs) it was also verified that accumulated doses of ROS did not promote significant alterations in soil OM, pH, $CEC_{pH7.0}$ and available contents of macronutrients (Table 3) as mentioned above.

The soil OM presented content below 2.5% in all treatments and layers, considered as a low level in Brazilian soils according to CQFS (2016). As a sandy soil, consequently the low OM content reflected

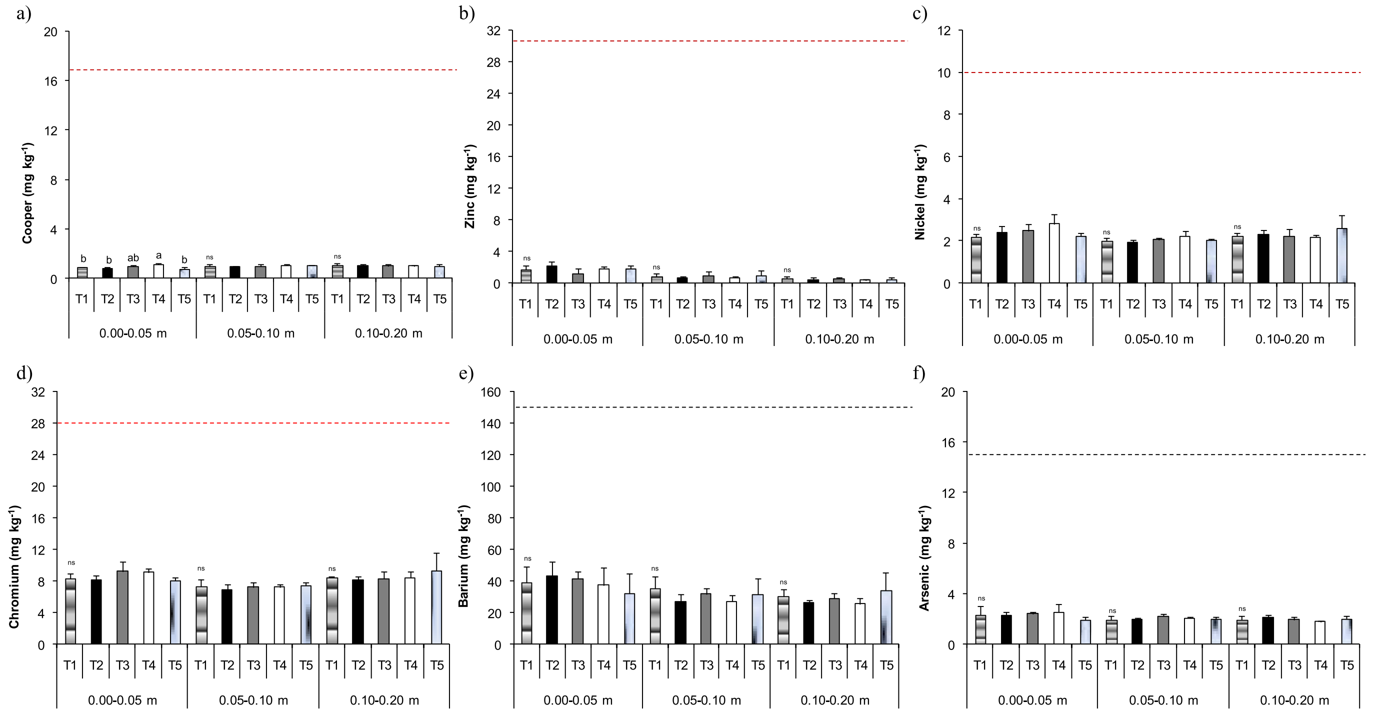

Fig. 1. Mean values of cooper (a), zinc (b), nickel (c), chromium (d), barium (e) and arsenic (f) content of an Arenic Rhodic Acrisol under no-tillage submitted to cumulative doses of retorted oil shale for 6 years. T1: Fertilizer Control (without ROS + basic fertilizer); T2: Annual application ROS of 0.75 Mg ha^{-1} + basic fertilizer; T3: Annual application ROS of 1.5 Mg ha^{-1} + basic fertilizer; T4: Annual application ROS of 3 Mg ha^{-1} + basic fertilizer; T5: Absolute Control (without ROS + without basic fertilizer). Values followed by the same letter in the column are not significantly different by the Tukey test ($p < 0.05$). ns: not significant. Red dashed line: Average quality reference values, in the 90th percentile, by soil groups for the natural metals contents in soils of the state of Rio Grande do Sul (Brazil). Black dashed line: Preventive values in soils stablished by Brazilian National Council of Environment (CONAMA Nr. 420/2009). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3
Mean values of organic matter (OM), pH, CEC potential (CTC$_{pH7.0}$), calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P) and sulphur (S) content of an Arenic Rhodic Acrisol under no-tillage and submitted to cumulative doses of retorted oil shale for 6 years.

Treat	OM	pH	CEC$_{pH7.0}$	Ca	Mg	K	P	S
	%		cmolc dm^{-3}	cmolckg^{-1}		mg kg^{-1}		
0.00-0.05 m								
T1	2.13 ± 0.54^{ns}	5.63 ± 0.25^{ns}	7.55 ± 0.66^{ns}	2.99 ± 0.86^{ns}	0.80 ± 0.18^{ns}	96.0 ± 9.80^{ns}	47.30 ± 4.08^{ns}	12.80 ± 4.8^{ns}
T2	2.38 ± 0.49	5.55 ± 0.19	8.48 ± 0.81	3.04 ± 0.61	0.82 ± 0.18	93.0 ± 6.00	54.10 ± 16.35	11.88 ± 4.15
T3	1.88 ± 0.32	5.53 ± 0.40	8.00 ± 1.16	3.05 ± 0.74	0.76 ± 0.20	100.0 ± 24.22	62.05 ± 47.59	13.45 ± 3.82
T4	2.08 ± 0.41	5.03 ± 0.24	7.88 ± 0.98	2.21 ± 1.07	0.54 ± 0.26	100.0 ± 16.65	59.58 ± 13.80	11.73 ± 4.76
T5	1.90 ± 0.14	5.58 ± 0.49	7.53 ± 0.62	2.70 ± 0.96	0.88 ± 0.26	100.0 ± 35.33	19.25 ± 12.68	13.23 ± 5.60
Mean	**2.07**	**5.46**	**7.89**	**2.80**	**0.76**	**97.80**	**48.46**	**12.62**
0.05-0.10 m								
T1	1.38 ± 0.29^{ns}	5.30 ± 0.40^{ns}	6.78 ± 0.51^{ns}	1.91 ± 0.68^{ns}	0.69 ± 0.30^{ns}	68.0 ± 10.33 ^{ns}	25.55 ± 6.63^{ns}	10.35 ± 2.70^{ns}
T2	1.30 ± 0.34	5.00 ± 0.27	7.45 ± 1.54	1.53 ± 0.54	0.55 ± 0.20	53.0 ± 11.49	31.93 ± 26.24	11.88 ± 4.36
T3	1.40 ± 0.16	5.35 ± 0.59	8.15 ± 1.39	2.11 ± 0.96	0.68 ± 0.39	64.0 ± 10.83	21.70 ± 10.99	11.08 ± 4.09
T4	1.28 ± 0.42	5.05 ± 0.41	7.10 ± 1.26	1.63 ± 0.49	0.48 ± 0.12	64.0 ± 11.31	28.13 ± 6.37	11.18 ± 3.35
T5	1.38 ± 0.19	5.10 ± 0.59	7.83 ± 1.00	1.57 ± 1.09	0.59 ± 0.29	53.0 ± 20.49	13.05 ± 6.58	12.68 ± 4.46
Mean	**1.35**	**5.16**	**7.46**	**1.75**	**0.60**	**60.40**	**24.07**	**11.43**
0.10-0.20 m								
T1	1.10 ± 0.24^{ns}	5.15 ± 0.17^{ns}	7.18 ± 0.95^{ns}	1.43 ± 0.54^{ns}	0.58 ± 0.16^{ns}	56.0 ± 16.33^{ns}	18.10 ± 10.63^{ns}	12.35 ± 4.69^{ns}
T2	1.08 ± 0.10	4.93 ± 0.25	8.35 ± 2.98	1.31 ± 0.68	0.54 ± 0.30	51.0 ± 9.45	16.93 ± 14.03	10.85 ± 3.35
T3	1.13 ± 0.10	5.55 ± 0.93	8.00 ± 0.96	2.34 ± 1.23	0.83 ± 0.56	62.0 ± 15.49	15.28 ± 9.71	11.43 ± 4.29
T4	1.00 ± 0.22	4.95 ± 0.19	6.68 ± 1.10	1.21 ± 0.47	0.41 ± 0.16	59.0 ± 10.00	22.20 ± 11.21	10.80 ± 3.27
T5	1.08 ± 0.15	5.05 ± 0.47	8.75 ± 2.41	1.28 ± 0.79	0.49 ± 0.28	38.0 ± 14.79	15.55 ± 9.70	11.18 ± 3.58
Mean	**1.08**	**5.13**	**7.79**	**1.51**	**0.57**	**53.20**	**17.61**	**11.32**

T1: Fertilizer Control (without ROS + basic fertilizer); T2: Annual application ROS of 0.75 Mg ha^{-1} + basic fertilizer; T3: Annual application ROS of 1.5 Mg ha^{-1} + basic fertilizer; T4: Annual application ROS of 3 Mg ha^{-1} + basic fertilizer; T5: Absolute Control (without ROS + without basic fertilizer). Values followed by the same letter in the column are not significantly different by the Tukey test ($p < 0.05$). ns: not significant.

low (<7.5 cmol$_c$ dm^{-3}) and medium values (not higher than 8.75 cmol$_c$ dm^{-3}) of CEC$_{pH7.0}$ in all layers and treatments (Table 3), evidencing that accumulated ROS doses from 4.5 to 18 Mg ha^{-1} were not sufficient to increase soil CEC$_{pH7.0}$, even though ROS present carbon content of around 6%, 2:1 minerals in its constitution and substantial CEC$_{pH7.0}$ (Doumer et al., 2016; Saif et al., 2017;

Ribas et al., 2017). The non-effect on soil chemical properties in the medium-term was somehow expected since annual carbon input by ROS application was no more than 250 kg ha^{-1} in the higher dose (T4). This behaviour converges with Leão et al. (2014), who also did not observe changes neither in the soil OM nor in the particulate and mineral carbon fractions after ROS cumulative addition of 15 Mg ha^{-1} in the same soil type as the present study.

Concerning to soil pH, in general it was verified that values were below 5.5 in all layers and treatments (Table 3), inadequate level for grain crops under no-tillage system in southern Brazil (CQFS, 2016), indicating that ROS was not able to influence soil pH, although its relevant concentration of calcium carbonate (Ribas et al., 2017). This was also observed by Gonçalves (2016) at 2-year experiment (December 2011) in the same experimental area. The author attributed the result to the low carbonate concentration when compared to common liming sources, and low reactivity of the silicates present in ROS.

In relation to macronutrients, considering soil nutrient availability ranges established by CQFS (2016), calcium content in the topsoil can be considered in medium level (2.21–3.05 cmol$_c$ kg^{-1}), while below to 0.05 m depth it is in the low range, from 1.21 to 2.34 cmol$_c$ kg^{-1}. About magnesium, in all layers most of treatments remained between 0.5 and 1.0 cmol$_c$ kg^{-1}, considered as medium availability class. For potassium, it was verified contents classed as high availability at 0.00–0.05 m layer, as medium to high in the 0.05–0.10 m layer, and as medium to low in the 0.10–0.20 m layer. After 6-year experiment, available contents of calcium, magnesium and potassium were not increased with the accumulated doses of ROS as well as did not differed from control treatments (Table 3). Therefore, the amount of nutrients provided by ROS is low yet, and may not have significant influence in the soil fertility status.

No significant differences between ROS (T2 to T4) and the control treatments (T1 and T5) were demonstrated by phosphorus and sulphur available contents, similarly as observed for the other macronutrients (Table 3). However, as well as verified for potassium, high levels of phosphorus were observed in the topsoil of those treatments that received NPK application; the underneath layers showed medium to low phosphorus levels. Sulphur levels higher than 10 mg kg^{-1}, which is considered adequate to leguminous crops were observed in all treatments and layers. It may be due to a positive effect from NPK fertilization or by the soil natural capability to provide this nutrient. On the other hand, in a previous study at the same edaphoclimatic conditions, Osorio Filho (2006) showed that sulphur atmospheric deposition by rainwater is also an important source of this nutrient as it is around of 3.2 kg ha^{-1} year^{-1}.

The BD values in the topsoil are smaller (between 1.40 and 1.48 Mg m^{-3}) than in underlying layers (1.58–1.73 Mg m^{-3}), with significant differences among accumulated doses of ROS only at 0.10–0.20 m layer, where the T2 (4.5 Mg ha^{-1}) presented higher BD than T3 (9 Mg ha^{-1}). However, both did not differ from the treatment without ROS (T1) and absolute control (T5), evidencing that ROS should not be the main factor of BD changes (Table 4). Similar behaviour was observed regarding TP and Ma values, which presented a tendency of superiority in the 0.00–0.05 m layer (between 0.39 and 0.43 m^3 m^{-3} and 0.11–0.17 m^3 m^{-3}, respectively) in relation to subsurface layers, below to 0.05 m (between 0.29 and 0.35 m^3 m^{-3} and 0.03–0.11 m^3 m^{-3}, respectively). In both attributes, T2 showed significantly lower TP and Ma than T4 (cumulative dose of 18 Mg ha^{-1}) at 0.05–0.10 and 0.10–0.20 m layers (Table 4). Again, both did not differ from 0 Mg ROS ha^{-1} (T1) and absolute control (T5) treatments.

Improvements in the soil physical attributes was expected with ROS addition, especially for aggregation and microporosity. Retorted oil shale has high specific surface area, sorption capacity and porosity, features created during the kerogen losses from rock pores while the pyrolysis process performed at about 500 °C occurs (Saif et al., 2017; Ribas et al., 2017). Therefore, ROS could play a role as a binding agent and consequently enhances soil aggregation. In a previous study, Leão et al. (2014) observed a short-term effect of ROS on carbon retention when crop residues were added to the soil in association with the ROS by-product. According to Pimentel et al. (2006), ROS reactivity can be linked to the presence of 2:1 clay minerals, especially illite and montmorillonite, and silanoids, as well as hydroxylic and carboxylic functional groups. These properties could favour associations with soil organic compounds and minerals. However, this unexpected behaviour is probably due to the facts: 1. ROS porous spaces are mainly intra-particles, not uniform and disconnected (Tiwari et al., 2013); 2. Pyrolysis process results in small pores, mainly with diameters around 3 nm (Bai et al., 2012), which does not influence the microporosity nor the available water content; 3. Either the 6-year period with addition of ROS or the applied doses were not enough to show significant changes in Mi and AWC, since independent of the ROS dose added (T2 to T4), no significant differences neither trend were observed when compared to the treatment without application of ROS (T1) and absolute control (T5) in all evaluated soil layers (Table 4).

Thus, through the above it is estimated that the lowest BD, higher TP and Ma observed at 0.00–0.05 m depth in relation to the underlying layers is mostly due to no-till management employed in the experiment, where the crop biomass remained on the soil surface (Tormena et al., 2017) associated to root system crops (Calonego et al., 2017). This analysis converges with the aggregate size distribution data, because up to the 0.10 m depth, layer with higher root colonization (Reinert et al., 2008; Reichert et al., 2009), there was higher Macroag and MWD in relation to 0.10–0.20 m layer. For sandy soils, it is known that macroaggregation is almost entirely dependent on biological processes (Brady and Weill, 2016), and no-tillage system enables a regular labile carbon input, promoting the soil organic matter cycling, and acting as a binding agent between microaggregates to generate macroaggregates (Braida et al., 2011).

The high specific surface area and nanopores presented in ROS may prevent macro and micronutrient losses when combined to conventional NPK formulations, improving nutrient use efficiency in the long run. In Brazil, at present moment a number of researchers have demonstrated the potential of ROS in agriculture applications. In short time ROS has shown efficiency as an additive in pig slurry composting processes and in mixture with urea. In composting process, Giacomini (2017) demonstrated that ROS promoted nitrogen losses mitigation by reducing NH_3 volatilization in 36%, and methane emissions between 64 and 74%, without affecting nitrous oxide emissions. Ranzan (2014), in turn, evaluated the nitrogen fertilization efficiency influenced by application of urea with ROS in upland rice and observed higher content of N in rice leaves when ROS and urea mixture was applied. The author calls the attention for the potential of this by-product in increasing nitrogen use efficiency, usually low at Brazilian edaphoclimatic conditions. Additionally, in the short-term, the application of ROS to soil can also reduce CO_2 emissions without reducing the soil microbial biomass (Doumer et al., 2011) as well as increase carbon retention in the soil (Leão et al., 2014).

3.1. *Implications for theory and practice*

This work evaluated the contamination risk related to increasing and successive rates of ROS, a by-product that can be widespread in Brazilian soils in the near future, with implications to word food security, considering the global commercialization level of agricultural products yielded in this region. The soil monitoring with

Table 4
Mean values of bulk density (BD), total porosity (TP), macroporosity (Ma), microporosity (Mi), available water capacity (AWC), percentage of macroaggregates (Macroag) and microaggregates (Microag), and mean weight diameter of aggregates (MWD) of an Arenic Rhodic Acrisol under no-tillage and submitted to cumulative doses of retorted oil shale for 6 years.

Treat	BD	TP	Ma	Mi	AWC	Macroag	Microag	MWD
	Mg m^{-3}	m^3 m^{-}				%		mm
	0.00-0.05 m							
T1	1.41 ± 0.14^{ns}	0.42 ± 0.05^{ns}	0.14 ± 0.05^{ns}	0.29 ± 0.01 a	0.17 ± 0.04^{ns}	69.09 ± 3.97^{ns}	30.91 ± 3.97^{ns}	2.50 ± 0.31^{ns}
T2	1.44 ± 0.12	0.39 ± 0.04	0.11 ± 0.04	0.28 ± 0.01 ab	0.19 ± 0.01	72.76 ± 6.72	27.24 ± 6.72	2.39 ± 0.60
T3	1.40 ± 0.04	0.42 ± 0.02	0.16 ± 0.04	0.26 ± 0.02 ab	0.17 ± 0.04	70.05 ± 2.99	29.95 ± 2.99	2.40 ± 0.42
T4	1.48 ± 0.09	0.43 ± 0.02	0.17 ± 0.03	0.26 ± 0.02 ab	0.16 ± 0.02	69.91 ± 5.53	30.09 ± 5.53	2.34 ± 0.38
T5	1.45 ± 0.10	0.41 ± 0.03	0.16 ± 0.05	0.25 ± 0.02 b	0.17 ± 0.01	73.49 ± 5.84	26.51 ± 5.84	2.49 ± 0.11
Mean	**1.43**	**41.51**	**14.85**	**26.66**	**0.17**	**71.06**	**28.94**	**2.42**
	0.05-0.10 m							
T1	1.65 ± 0.04^{ns}	0.33 ± 0.03 ab	0.06 ± 0.02 ab	0.27 ± 0.02 a	0.19 ± 0.01^{ns}	71.39 ± 4.99^{ns}	28.61 ± 4.99^{ns}	2.49 ± 0.40^{ns}
T2	1.72 ± 0.04	0.29 ± 0.01 b	0.03 ± 0.01b	0.25 ± 0.01 ab	0.19 ± 0.01	65.55 ± 4.91	34.45 ± 4.91	1.88 ± 0.47
T3	1.58 ± 0.05	0.34 ± 0.02 ab	0.10 ± 0.03 ab	0.25 ± 0.02 ab	0.18 ± 0.02	71.80 ± 3.44	28.20 ± 3.44	2.21 ± 0.31
T4	1.65 ± 0.05	0.35 ± 0.01 a	0.11 ± 0.01 a	0.25 ± 0.02 ab	0.17 ± 0.01	67.26 ± 8.94	32.51 ± 8.91	2.05 ± 0.82
T5	1.68 ± 0.09	0.32 ± 0.01 ab	0.08 ± 0.02 ab	0.24 ± 0.01 b	0.16 ± 0.01	74.34 ± 5.86	25.66 ± 5.86	2.23 ± 0.59
Mean	**1.66**	**32.70**	**7.63**	**25.08**	**0.18**	**70.07**	**29.89**	**2.17**
	0.10-0.20 m							
T1	1.64 ± 0.07 ab	0.33 ± 2.59 ab	0.06 ± 0.01b	0.26 ± 0.02^{ns}	0.18 ± 0.01^{ns}	67.04 ± 6.75^{ns}	33.06 ± 6.60^{ns}	1.73 ± 0.72^{ns}
T2	1.73 ± 0.05 a	0.29 ± 1.48 b	0.05 ± 0.01 b	0.25 ± 0.01	0.17 ± 0.02	62.81 ± 4.12	37.19 ± 4.12	0.98 ± 0.37
T3	1.60 ± 0.06 b	0.33 ± 1.86 ab	0.09 ± 0.02 ab	0.24 ± 0.01	0.17 ± 0.00	65.09 ± 5.78	34.91 ± 5.78	1.33 ± 0.56
T4	1.66 ± 0.05 ab	0.34 ± 1.98 a	0.11 ± 0.03 a	0.23 ± 0.01	0.15 ± 0.02	64.70 ± 1.78	35.30 ± 1.78	1.32 ± 0.29
T5	1.68 ± 0.03 ab	0.31 ± 1.08 ab	0.07 ± 0.02 ab	0.24 ± 0.01	0.16 ± 0.01	66.25 ± 5.77	33.75 ± 5.77	1.27 ± 0.31
Mean	**1.66**	**32.13**	**7.73**	**24.40**	**0.17**	**65.18**	**34.84**	**1.33**

T1: Fertilizer Control (without ROS + basic fertilizer); T2: Annual application ROS of 0.75 Mg ha^{-1} + basic fertilizer; T3: Annual application ROS of 1.5 Mg ha^{-1} + basic fertilizer; T4: Annual application ROS of 3 Mg ha^{-1} + basic fertilizer; T5: Absolute Control (without ROS + without basic fertilizer). Values followed by the same letter in the column are not significantly different by the Tukey test ($p < 0.05$). ns: not significant.

ROS application after high rates in the medium to long run allowed us to fulfil one of the three requirements that any agricultural product should meets: environmental safety, food safety and agronomic efficiency. Theoretically, ROS is still considered as a waste for the industrial sector. Nevertheless, the abovementioned applications (composting additive, coated urea, absorbent) combined with the absence of contamination risk supported by the findings of this and other researches related to environmental security allows to recommend ROS as a raw material for agricultural applications. In practice, considering the scenario of increasing use of wastes in agriculture, if all new agricultural products developed from wastes shall be studied at this level, soils, water and food contamination would be strongly prevented.

4. Conclusions

The present work combined a set of steps (product preparation, long-term field experiment, soil sampling, laboratory and data analyses) to evaluate and validate one agricultural product to guarantee its environmental safety. By assessing possible side-effects in soil and solutes after cumulative retorted oil shale rates, this study has demonstrated that ROS is environmentally safe for agricultural purposes when applied on the soil surface, or incorporated within the arable layer. After 6-yrs of cumulative doses of retorted oil shale up to 18 Mg ha^{-1} (annual rate of 3 Mg ha^{-1}), levels of potentially toxic elements were not increased in a sandy soil under no-tillage system, except for copper at 0.00–0.05 m topsoil layer. Nevertheless, this is of minor consequences by the fact that copper is a micronutrient for mostly crops within the observed interval. Thus, studies of this nature normally don't consider the possible impacts of agricultural products on soil physical attributes. Soil amendments are of great importance for agriculture: waste destination, sustainable use of sandy soils, clean and safe production. In this context, again the retorted oil shale has not significantly changed soil physical attributes and nutrients levels.

Finally, it is strongly recommended that present and new policies should include robust field studies in the list of requirements to validate new waste-derived products to ensure food safety and maintain soil quality. Considering the potential impacts, without considering the medium to long-term studies with sequential applications in soils, a wide set of crops and foods could be harmed if no systematic studies like this were properly performed.

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Appendix A. Supplementary data

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