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Selected rock powders as sources of nutrients for soil fertilization and maize-wheat grain production in southern Brazil

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Abstract

The current study evaluated alternative sources of nutrients to improve the soil fertility status and yield of maize-wheat succession in Southern Brazil. The treatments were: T1: no fertilization; T2: liming with dolomitic marble; T3: alternative liming (AL) with limestone interbedded with shale; T4: AL + 50% P - with Arad natural phosphate (P-ANP) + 50% P – triple superphosphate (P-TSP); T5: AL + 100% P-ANP; T6: AL + 100% P-ANP + 100% K-rich monzogranite; T7: AL + 100% P-ANP + 100% N (50% N from tung pressed cake (N-TPC) + 50% N-urea); T8: AL + 100% P-ANP + 100% K-rich monzogranite + 100% N (50% N-TPC + 50% N-Urea) + 100% S; T9: AL + regional average rate of NPK (5-20-20) formulation. Except for T7 and T8, all treatments received the full recommended rate of N through Urea. Immediate and residual effects were evaluated over 2.5 years (90, 360 and 900 days) on soil fertility and maize - wheat yield. The limestone interbedded with shale released Ca, Mg and corrected soil acidity similarly to dolomitic marble. The fertilization strategies used in T4, T7 and T8 presented the highest cumulative productivities while T3 (U$ = 1223), T9 (U$ = 1174) and T4 (U$ = 1122) resulted in higher profits than the other evaluated fertilization strategies. The limestone interbedded with shale (T3), alone or combined with 50% of P-ANP + 50% of P – TSP (T4) provided the best economical and technical results, highlighting the potential of selected alternative regional sources for soil fertility improvement and plant-nutrients supply.

Introduction

Soil fertility correction and proper plant nutrition are key factors for crop performance in modern agriculture. Intensive crop production in agroecosystems is strongly dependent on a limited list of highly concentrated nutrient sources, generally available in the form of soluble fertilizers, the exploration and manufacture of which is dominated by a few countries and companies. Brazil, according to ANDA (2021), imported about 85% of the total used fertilizers in 2021, where 88%, 64% and 95% refers to soluble sources of N (mainly urea and ammonium sulphate), P_2O_5 (mainly monoammonium phosphate) and K_2O (mainly potassium chloride) respectively, demonstrating the dependency of the Brazilian agriculture on foreign nutrient sources. Therefore, new strategies are required to provide alternatives against the high costs, logistic concerns, foreign dependence and restricted access of small farmers to these products, in addition to the lower risks of nutrient losses and environment contamination (van Straaten, 2007; Fageria *et al.*, 2010; Silva *et al.*, 2012; Ciceri *et al.*, 2017; Swoboda *et al.*, 2022).

Agrominerals, defined as rocks with the ability to restore soil fertility status and supply significant contents of plant-available nutrients, have been evaluated and used in a regional scale, in combination with organic sources to compose alternative fertilization strategies (van Straaten, 2007). Several rock types are naturally enriched in nutrients present in the mineral structure. Therefore, to meet the requirements of the crops in soils, the release rate is challenging. In this way, the validation of regionally available raw materials that provide nutrients and organic compounds efficiently and safely, is fundamental for the sustainable development of countries like Brazil, whose agriculture plays a crucial role in the economy and food security.

Acidity is one of the main chemical limitations to crop productivity in tropical soils, and soil fertility is strongly dependent on pH correction. The corrective measure of liming affects food production across tropical soils in Asia, Africa and Latin America. In particular, grain crops are severely limited in uncorrected soils (Behera and Shukla, 2015). Tropical well drained soils are known for their high acidity and aluminium toxicity, as well as deficiency in essential macronutrients (Fageria and Nascente, 2014). Therefore, acidity correction is the first step for the success of farming in well-weathered soils.

The best way to overcome soil acidity is to lime the soil with calcium and/or magnesium carbonates (calcite and dolomite), whereby the minerals react with hydrogen released by the soil water as well as carbon dioxide and aluminium in the form of hydroxide, mitigating Al toxicity in plants (Goulding, 2016). Liming also provides negative charges and increases the potassium and phosphorus availability to plants, although the magnitude of this depends on the limestone composition and soil nutrient stocks (Meriño-Gergichevich *et al.*, 2010; Mendes *et al.*, 2015). Dolomitic marble is the main liming material used in Southern Brazil, extracted from metamorphic dolomitic rocks (Philipp *et al.*, 2016), and its recommendation has been based on its effectiveness of pH correction (neutralization power) and its reactivity (particle size). However, there is a growing demand for the use of regionally available liming materials such as by-products of the pyrobituminous shale exploration, a sedimentary rock from the Irati Formation (Holanda *et al.*, 2018), mainly the interbedded limestone layers. This material contains secondary macronutrients (calcium, magnesium and sulphur) and micronutrients that might be used for plant nutrition, in addition to the capacity to neutralize soil acidity (Mangrich *et al.*, 2001).

Apart from using conventional fertilizers, the correction of soil nutritional deficiencies can also be achieved with the application of finely ground rock types such as natural phosphates, gypsum, mafic and ultramafic rocks (Silva *et al.*, 2012; Rafael *et al.*, 2017). In recent years, the silicate rocks, mainly those found in the form of fine residues from the grinding processes in quarries, have attracted more attention. With the advantage of being abundant and regionally available, these resources have been reused as sources for plant nutrients and reduce the external dependence, in particular K, Ca and Mg bearing rocks (Brazil. Ministry of Agriculture, Livestock and Food Supply, 2016; Swoboda *et al.*, 2022). In addition, these resources can be used to increase the cation exchangeable capacity (Anda *et al.*, 2015) and water holding capacity of sandy soils (Kahnt *et al.*, 1986). Nevertheless, several of them are not efficient or present potentially toxic elements in harmful levels. Therefore, the results of applying finely ground rocks on tropical soils largely depend on their chemical and mineralogical composition, on soil deficiencies and specific crop requirements (van Straaten, 2017).

Several nutrients present in rocks might be used to reduce soil deficiencies and match crop requirements. Silicate rocks containing K-bearing minerals and K-rich rocks such as phonolite and nepheline syenite (Nogueira *et al.*, 2021; Soratto *et al.*, 2021), glauconite bearing rocks (Safatle *et al.*, 2020), biotite (Basak, 2019; Pramanik *et al.*, 2019) are available at a regional scale, and various studies have shown the successful use of selected rocks in agriculture. Despite this, these materials cannot provide for all plant requirements, needing the combination with other nutrient sources. Common plant nutrient resources, such as P-bearing minerals (natural phosphates), and agroindustry wastes (e.g., organic cakes) can be used in association with such agrominerals to develop a fertilization strategy for annual crops, as an alternative to conventional fertilizers, while contributing for the circular economy and the sustainable recycling of waste that is available at a regional scale.

Thus, the purpose of the current study was to evaluate the effectiveness of different fertilization strategies, based on selected agrominerals and agro-industrial wastes, on soil chemical quality, grain productivity and profitability of the maize-wheat succession in southern Brazil.

Materials and methods

Study site

The experimental site was installed and conducted at the Lowland Experimental Station (Embrapa Clima Temperado), Capão do Leão (52°26'W, 31°49'S, 16 m a.s.l.), Rio Grande do Sul State, Brazil. According to the Köppen classification, the climate of the region is humid subtropical (*Cfa*) (Alvares *et al.*, 2013), with an average annual temperature of 17°C and average annual rainfall of 1400 mm. The soil of the site selected for the current study was classified as a Planosol (IUSS, 2014), and presented a low fertility status in the arable layer (0.0–0.2 m): low clay content (<200 g/kg), low organic matter content (<25 g/kg), low water pH (<5.0), low base saturation (<50%) and high aluminium saturation (>20%), medium concentrations of available calcium (2.0–4.0 $cmol_c$/l) and magnesium (0.5–1.0 $cmol_c$/l), low extractable potassium (21–40 mg/l) and phosphorus (3.1–6.0 mg/l) content and high available sulphur (>5 mg/l), zinc (>0.5 mg/l), copper (>0.4 mg/l) and boron (>0.3 mg/l) contents. The data of soil analysis are presented in Table 1 and interpreted based on the Committee on Soil Chemistry and Fertility CQFS (2016) of Rio Grande Sul and Santa Catarina States, Brazil.

Nutrient sources

Rocks with potential to correct soil acidity and nutritional deficiencies of P and K were selected for the current work. The geochemical characterization is presented as a supplementary material while the mineralogical composition is presented in Table 2. Called agrominerals, these rocks were evaluated as resources of macronutrients to improve soil fertility status and to cultivate the maize-wheat succession for grain production, in comparison to the average rate of conventional NPK (5-20-20) formulation.

The monzogranite is geologically classified as a typical intrusive plutonic acid rock (more than 66% total SiO_2) belonging to the Pelotas Batholith (Philipp *et al.*, 2016). The minerals present in monzogranite with potential agronomic interest are mafic (biotite, hornblende and amphibole), plagioclase and altered K-feldspar (Table 2). After being mined in a quarry in Pelotas,

Table 1. Soil chemical attributes at 0.0 to 0.2 m of a Planosol before the implementation of the experiment (Embrapa Clima Temperado, Pelotas/RS)

pH	Base saturation	Al	Ca	Mg	K	P	S	Mn	Cu	Zn	B
	------- % -------		--- $cmol_c$/l ---				---------------------- mg/l --------------------------				
4.9	40.3	20.3	2.3	0.7	57	11.4	11.4	16.6	0.9	0.6	0.3

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Table 2. Mineralogy description of the agrominerals used as nutrient alternative sources

Rock powders (Agrominerals)	Mineralogy	Reference
Limestone interbedded with shale	Quartz, plagioclase (albite), pyrite, illite, smectite, kaolinite, chlorite, calcite, dolomite and analcime	Ribas *et al.* (2017) Holanda *et al.* (2018)
Monzogranite	Quartz, K-feldspar, plagioclase and mafic minerals (biotite, amphibole and hornblende)	Grecco *et al.* (2017)
Arad natural phosphate	Francolite, calcite, calcareous microfossils (foraminifera), clays (detrital kaolinite), chert, secondary gypsum, halite	Gill and Shiloni (1994)

RS State, Brazil, the monzogranite is crushed to produce gravel-size stones for civil construction purposes. During the crushing process, a ground material regarded as a residue of the grinding process was sampled, finely ground and sieved to obtain the desired particle size of 100% <0.3 mm.

The limestone interbedded with shale (limestone shale) is a sequence of sedimentary rock layers belonging to the Irati formation, Paraná (PR) Basin. The limestone occurs as interbedded layers between two main oil shale layers (Ribas *et al.*, 2017). While the oil shale layers are mechanically mined by Petrobras-SIX in São Mateus do Sul, PR, Brazil, several layers of limestone shale are regarded either as a mining residue or stock piled as a co-product, mostly destined for regional road paving material in rural areas. Samples of the limestone shale were manually selected from stock piles, finely ground and sieved to obtain the desired particle size of 100% <0.3 mm.

The dolomitic marble is a commercial product conventionally mined in open pit mines located in the Passo Feio Metamorphic Complex (Gomes *et al.*, 2020) located in Caçapava do Sul, RS State, Brazil. The rock is explored for agricultural and civil construction purposes. The finely ground dolomitic marble is a typical liming material for soil acidity correction, available with the particle size of 95% <0.3 mm.

Due to the limited availability of P-bearing agrominerals in southern Brazil, the Arad natural phosphate – ANP, a sedimentary reactive rock phosphate imported from Arad, Israel and regionally sold as natural phosphate product for agriculture was selected for the current study.

Limestone shale, Arad natural phosphate and monzogranite rocks were submitted to geochemical analysis (Acme Labs, Vancouver, Canada) after total digestion in aqua regia (supplementary material). Moreover, samples of the monzogranite were also submitted to Brazilian Geological Survey, CPRM-Porto Alegre for petrographic analysis. The elemental sulphur (powder) and the NPK fertilizer (granules of 5-20-20 formulation), available as commercial fertilizers, were purchased on the local market.

The tung pressed cake is a co-product from the tung oil agroindustry. Fruits of tung (*Vernicia fordii*) trees, harvested in Fagundes Varela, RS State, Brazil were pressed by extrusion to extract the oil, remaining the tung pressed cake (crumbs), which is packed and sold as an organic fertilizer (N source) in the local market. Figure 1 shows the different origins of the selected regional sources of nutrients, while the total concentrations of macronutrients of mineral and organic sources are presented in Table 3.

Multiannual field experiment

Considering that it is not possible to supply all nutrient requirements to correct soil deficiencies and grain crops demand without the combination of a group of nutrient sources, a multiannual field experiment was designed in the way that the nutrient sources were 'additively' combined to evaluate their associated effects on soil fertility status and crop response. Therefore, each treatment was considered as a fertilization strategy.

A field experiment was installed and conducted in a randomized complete block design using 36 plots of 50 m^2 (5 × 10 m), with nine treatments (fertilization strategies) and four replications. Three sampling times (90, 360 and 900 days (d) after application of treatments) were performed to evaluate the effects of nutrient sources on soil chemical attributes, therefore representing long effects in the soil over 2.5 years. Types, loads of nutrients and application rates of liming materials plus nutrient sources are presented in Table 4. The treatments were as follows: T1 - control (without liming nor fertilization); T2 - conventional liming material (marble); T3 - alternative liming material – AL (limestone interbedded with shale); T4 - AL + 50% of P recommendation through Arad natural phosphate (ANP, sedimentary) + 50% of P recommendation with soluble phosphate; T5 - AL + 100% of P via ANP; T6 - AL + 100% of P via ANP + 100% of K recommendation through monzogranite; T7 - AL + 100% of P via ANP + 100% of N (50% N recommendation through tung pressed cake (TPC, organic source) + 50% N-urea); T8 - AL + 100% of P via ANP + 100% of K recommendation through monzogranite + 100% of N (50% via TPC + 50% N-urea) + 100% of S recommendation; T9 - AL + average regional rate of NPK (5-20-20) formulation. Unless for T7 and T8, all treatments received the full recommended rate of N through Urea.

Recommendations of CQFS (2016), with reference to the soil chemical analysis (Table 1) guided the choice of application rates of nutrients. While the liming dose for all treatments was calculated to achieve the desired pH of 6.0, the dose of P (via Arad Natural Phosphate) and K (monzogranite) of T4 to T8 was calculated to correct soil levels (rise up from low to medium level) plus the recommended dose for maize crop maintenance (170 kg/ha N, 195 kg/ha P_2O_5 and 155 kg/ha K_2O), while for the NPK rate of T9 (300 kg/ha of NPK 5-20-20 formulation) were considered as the regional average rate for maize crop maintenance. All nutrient sources were thoroughly distributed on the soil surface, then incorporated into the arable soil layer (0.0–0.20 m) before planting by a chisel plough pulled by a tractor, except T9 (NPK), which was applied in the planting row by a no-tillage seeder pulled by a tractor.

The grain yield of two successive crops was used to evaluate the immediate (1st crop) and residual (2nd crop) effects on crop performance. The 1st cropping season was maize (cultivar Pioneer 30B39), planted with a no-tillage seeder in early-December 2011, with a plant density of 60 000 plants/ha. The 2nd crop was wheat (cultivar Embrapa BRS 327), planted

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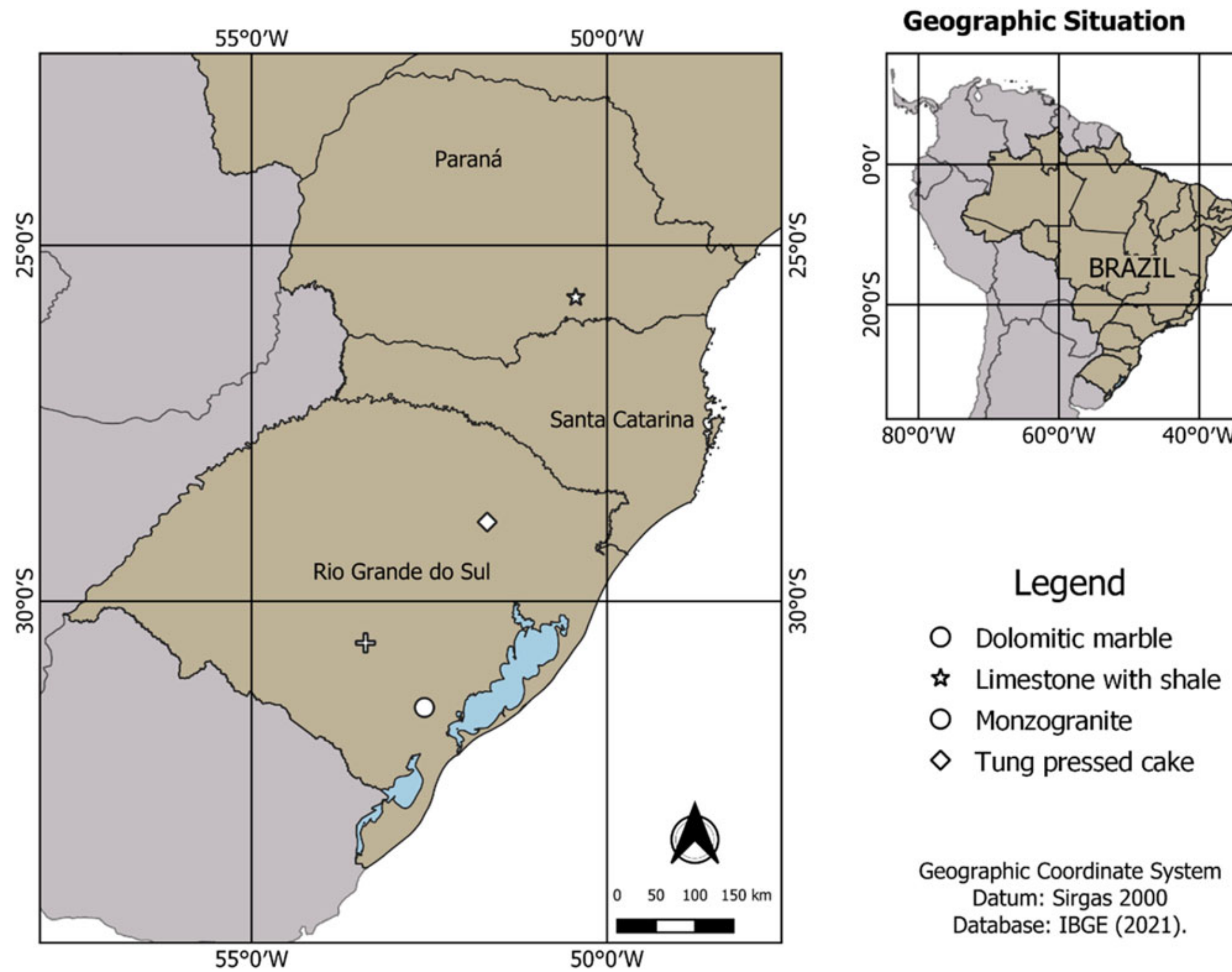

Figure 1. Location of the regional sources of nutrients in Southern Brazil.

in early June 2012 with a plant density of 300 000 plants/ha. For corn, 170 kg/ha of N was applied for all treatments, divided into two applications of urea (50% base plus 50% covering), unless for T7 and T8, where 50% base of N was applied through TPC (85 N kg/ha) at implantation. For wheat, 170 kg/ha was applied again, for all treatments through urea, divided into two applications.

Table 3. Total concentrations of N, P_2O_5, K_2O, CaO, MgO and S of mineral and organic sources

	Total content (%)					
Nutrient Sources	N	P_2O_5	K_2O	CaO	MgO	S
Dolomitic marble (RPAN = 60.8%)				20.9	15.8	
Limestone shale (RPAN = 60%)		0.2	0.6	20.5	13.6	1.1
Monzogranite		0.1	4.3*	2.4	1.0	
Arad natural phosphate (ANP)		33.9**	0.2	54.0	0.2	1.1
Tung pressed cake	2.5	0.6	3.6	0.3	0.4	
NPK – conventional soluble fertilizer	5.0	20.0	20.0	7.0		4.0
Triple superphosphate (TSP)		41.0		9.8		
Elemental sulphur						99.0
Urea	45					

*Calculation of the application rate considered that 50% of the added K_2O can be available for the first two cropping cycles. RPAN: Relative Power of Acidity Neutralization.
**Total content. For the calculation of ANP rate, the soluble content in 2% citric acid solution (13.93% P_2O_5) was considered.

Table 4. Type, doses at implementation and total loads of mineral and organic sources of macro and micronutrients applied in each treatment along the maize plus wheat cultivation seasons

	T1	T2	T3	T4	T5	T6	T7	T8	T9
Sources of nutrients					------------------------------ Mg/ha ------------------------------				
Dolomitic marble	-	3.2	-	-	-	-	-	-	-
Limestone shale	-	-	3.2	3.2	3.2	3.2	3.2	3.2	3.2
Arad natural phosphate	-	-	-	0.7	1.4	1.4	1.4	1.4	-
Triple superphosphate	-	-	-	0.238	-	-	-	-	-
Monzogranite	-	-	-	-	-	7.2	-	7.2	-
Tung pressed cake	-	-	-	-	-	-	3.4	3.4	-
Elemental sulphur	-	-	-	-	-	-	-	0.03	-
NPK formulation (05-20-20)	-	-	-	-	-	-	-	-	0.3
Urea	0.378	0.378	0.378	0.378	0.378	0.378	0.189	0.189	0.344
Macronutrients					------------------------------ kg/ha ------------------------------				
N	340.0	340.0	340.0	340.0	340.0	340.0	340.0	340.0	340.0
P_2O_5			6.4	341.2	481.0	488.2	501.4	508.6	66.4
K_2O			19.2	20.6	22.0	331.6	144.4	454.0	79.2
CaO		656.0	656.0	1057.3	1412.0	1584.8	1422.2	1595.0	677.0
MgO		505.6	435.2	436.6	438.0	510.0	451.6	523.6	435.2
S			35.2	42.9	50.6	50.6	50.6	80.3	47.2
Micronutrients					------------------------------ kg/ha ------------------------------				
Mn	-	0.99	8.43	8.43	8.43	12.33	8.52	12.42	8.43
Cu	-	0.02	0.05	0.06	0.07	0.13	0.10	0.16	0.07
Zn	-	0.04	0.06	0.34	0.63	1.00	0.75	1.11	0.11
B	-	-	-	-	-	-	0.07	0.07	-

The profit (P) of each fertilization strategy was calculated as: P = (grain yield × price of the products) - (sum of the costs of all nutrient sources). The effects of nutrient sources on the soil chemical parameters with time were evaluated in a longer run, through 900 days (2.5 years). In this way, three soil samplings from the topsoil layer (0.0–0.2 m), collected at the 90, 360 and 900 days after treatment application, respectively, were collected for chemical analyses. The following soil chemical attributes were evaluated according to the methodologies described in Tedesco *et al.* (1995): soil pH (in water); available P and exchangeable K extracted with HCl 0.05 mol/l + H_2SO_4 0.0125 mol/l solution (Mehlich-1); exchangeable Ca, Mg, Mn and Al extracted with KCl 1 mol/l solution; available S content ($S\text{-}SO_4$), evaluated through colorimetry after extraction with $Ca(H_2PO_4)_2$; available B extracted with hot water (55 ± 3°C); available Cu and Zn extracted with Mehlich-1 solution.

The original data were evaluated, including the presence of outliers, and subjected to statistical analysis of variance. The effects of treatments (fertilization strategies), sampling times (90, 360 and 900 days after application) and the interaction of both were analysed. When the effects were significant (F test, $P < 0.05$), the means were compared by Tukey's test ($P < 0.05$). All data and statistical analyses were performed using Machado & Conceição (2003) and Sigmaplot (2004) software.

Results

Effect of fertilization strategies with regional sources of nutrients on soil chemical attributes

The fertilization strategies significantly affected the main soil chemical attributes in the 0.0–0.2 m soil layer (Table 5). All soil macronutrients (P, K, Ca, Mg and S), pH, Al and base saturation (Fig. 2), Mn and Zn contents were influenced by at least one of the treatments that combine alternative nutrient sources. Considering fertilization, Cu and B contents were not affected, while for the soil sampling time, only Mn did not vary significantly over the three sampling dates. Meanwhile, for P and S contents, significant effects were observed for the interaction of fertilization × season (Figs 3(a) and (d)).

Considering the effects of agrominerals on soil pH, as expected, liming the soil (T2-T9) significantly increased the pH compared to the control; (T1), specifically the treatments T3-T9 with limestone shale (sedimentary rock), similar to treatment T2 – dolomitic marble (metamorphic rock) (Fig. 2(a)). On the other hand, it is important to note that at 90 d after liming, none of treatments achieved the desired pH of 6.0. The soil pH was increased and sustained until 360 d but reverted back significantly 900 days after application of treatments (Fig. 2(b)). A very similar behaviour to soil pH was observed for base saturation (Fig. 2(c)). Despite the significant effect of liming, the rates and

Table 5. Analysis of variance of the experimental treatment factors: (a) fertilization (T1 to T9); (b) sampling season of soil chemical attributes (90 × 360 × 900 d after fertilization)

Source of experimental variation	Soil attributes											
	pH	Base saturation (%)	Al^{3+} saturation (%)	P	K	Ca	Mg	S	Mn	Cu	Zn	B
Fertilization	**	**	**	**	*	**	**	**	**	NS	**	NS
Season	**	**	**	**	**	**	**	**	NS	**	**	**
Fertilization × season	NS	NS	NS	*	NS	NS	NS	**	NS	NS	NS	NS

Test F: *significant at $P < 0.05$; **significant at $P < 0.01$; NS not significant at $P < 0.05$ nor at $P < 0.01$.

nutrient sources applied in all treatments were insufficient to reach the desired pH of 6.0, although a quite satisfactory level of base saturation (51–70%) was achieved, as recommended by Pavinato *et al.* (2017) for the maize-wheat succession. The combination of limestone shale with Arad natural phosphate, tung pressed cake and monzogranite (treatment T8) promoted a higher mean pH and base saturation compared to other treatments (5.6 and 62%, respectively). However, the differences between fertilized treatments were not significant except for the difference between T7 and T8. The base saturation was also affected by the time (Fig. 2(d)), showing lower mean values than recommended by Pavinato *et al.* (2017) at 900 d after application of the treatments.

Importantly, low Al^{3+} saturation levels were observed in all of the treatments involving limestone shale (T3-T9) in relation to T1 (Fig. 2(e)), the same effect was observed with conventional liming (T2 - dolomitic marble). Again, similar to what was observed with pH and base saturation, the behaviour of Al^{3+} saturation values along the time (Fig. 2(f)) denote a limited persistence of liming effects at 2.5 years after application of treatments.

In general, the Al^{3+} saturation should be lower than 10% (CQFS, 2016) to maximize agricultural effectiveness, as presented by treatments T2 to T9. As expected, the control plot lacking corrective addition (T1) showed an Al^{3+} saturation much higher than this critical limit since the beginning of the experiment. In this sense, lower Ca and Mg contents were observed in the control treatment during the evaluations, mainly at 900 d, when both nutrients fell below the critical content (Ca < 2.0 $cmol_c$/l and Mg < 0.5 $cmol_c$/l) for grain crops (CQFS, 2016). In contrast to this, the treatments with limestone shale (T3 to T9) as well as with dolomitic marble (T2), provided significant increases in Ca and Mg contents when compared to the initial characterization (T1), raising the Ca content (2–4 $cmol_c$/l) up into the medium availability range (Fig. 4(a)) and the Mg content (>1$cmol_c$ /l) up into the high availability range (CQFS, 2016), even after maize-wheat succession (Fig. 4(c)). At 900 days, Ca and Mg contents dropped back down in all fertilization strategies (T2 to T9), possibly due to the loss of nutrients from crop grain harvests and intense leaching of cations promoted by high cumulative rainfalls, helped by the limited capacity of the soil to retain cations, evidenced by the small clay content in the topsoil layer (160 g/kg).

Considering the soil's K content, both fertilization strategies and time after application of treatments had significant influence on the soil's K concentration (Table 5). The fertilization strategy T8 (limestone interbedded with shale + ANP + monzogranite + N (TPC and urea) + S) resulted in a higher value (0.09 $cmol_c$/l) than the control treatment T1 (0.07 $cmol_c$/l) (Fig. 3(b)). However, it should be noted that all values remained at low (0.08–0.15 $cmol_c$/l) and very low (≤0.079 $cmol_c$/l) availability ranges, independent of the period. This result shows that the monzogranite rock powder (311.7 kg/ha K_2O via 7.2 Mg/ha) combined with TPC, and a possible solubilizing increase by S, provided at least part of the K crop demand. However, it was not effective enough to increase the readily available soil content of K (extractable by Mehlich-1) above the sufficiency level (>0.23 $cmol_c$/l) during the period of the experiment. It should be noted that the treatment with the average rate of NPK formulation (T9) also did not increase significantly the available soil content of K, probably because a lower amount of K was applied in T9 as compared to those with the monzogranite combined with TPC.

The soil's extractable phosphorus content (P Mehlich-1) showed significant differences for the treatments (T1-T9), and for sampling time (90, 360 and 900 d after application) there was a significant interaction between treatments × sampling time (Table 5). Considering the fertilization strategies in the first sampling period, T6 (liming + ANP + monzogranite) differed from those treatments without P input (T1, T2 and T3), while the others with P through ANP (T4, T5, T7, T8) and with the NPK formulation (T9), the latter with P through soluble form, remained equal to each other and to those without P input (T1, T2 and T3). For the 2nd sampling time (360 d), those treatments with ANP (T4 – with ½ part of P via TSP, T5, T6 and T8) showed higher P concentrations, remaining between 60 to 76 mg/l of P. The treatments without P sources (T1, T2 and T3) and with soluble source (T9) remained at the same P level (≤12.93 mg/l of P). For the 3rd sampling time (900 d), all treatments remained at the same level, ranging from 4.1 to 29.9 mg/l (Fig. 3(a)).

When ANP was combined with limestone shale (T5 and T6), and plus TSP (T4), the P content extracted by Mehlich-1 remained in the high to very high availability ranges from 90 to 360 d, but dropped to the medium range at 900 d. On other hand, when the ANP was combined with tung pressed cake, the extractable phosphorus level moved from the medium to the low availability range from 90 to 900 d in the T7 treatment, and from high to low availability from 90 to 900 d in T8. Finally, for the T9 treatment, where the limestone shale was combined with soluble NPK, the extractable P content in the soil remained low to very low throughout the experiment.

The available S content in soil was significantly affected by fertilization (T1-T9), and by the sampling time (90 × 360 × 900 d) there was a significant interaction fertilization × sampling time. The S soil content was classified in the high availability class (10–20 mg/l) before starting the experiment. After 90 d, treatment T8 presented the highest S level (22.1 mg/l), followed by treatment T4 and T9, all these contrasting with the lower levels of S observed for treatments T1, T2, T3 and T7. The addition of 0.03 Mg/ha of

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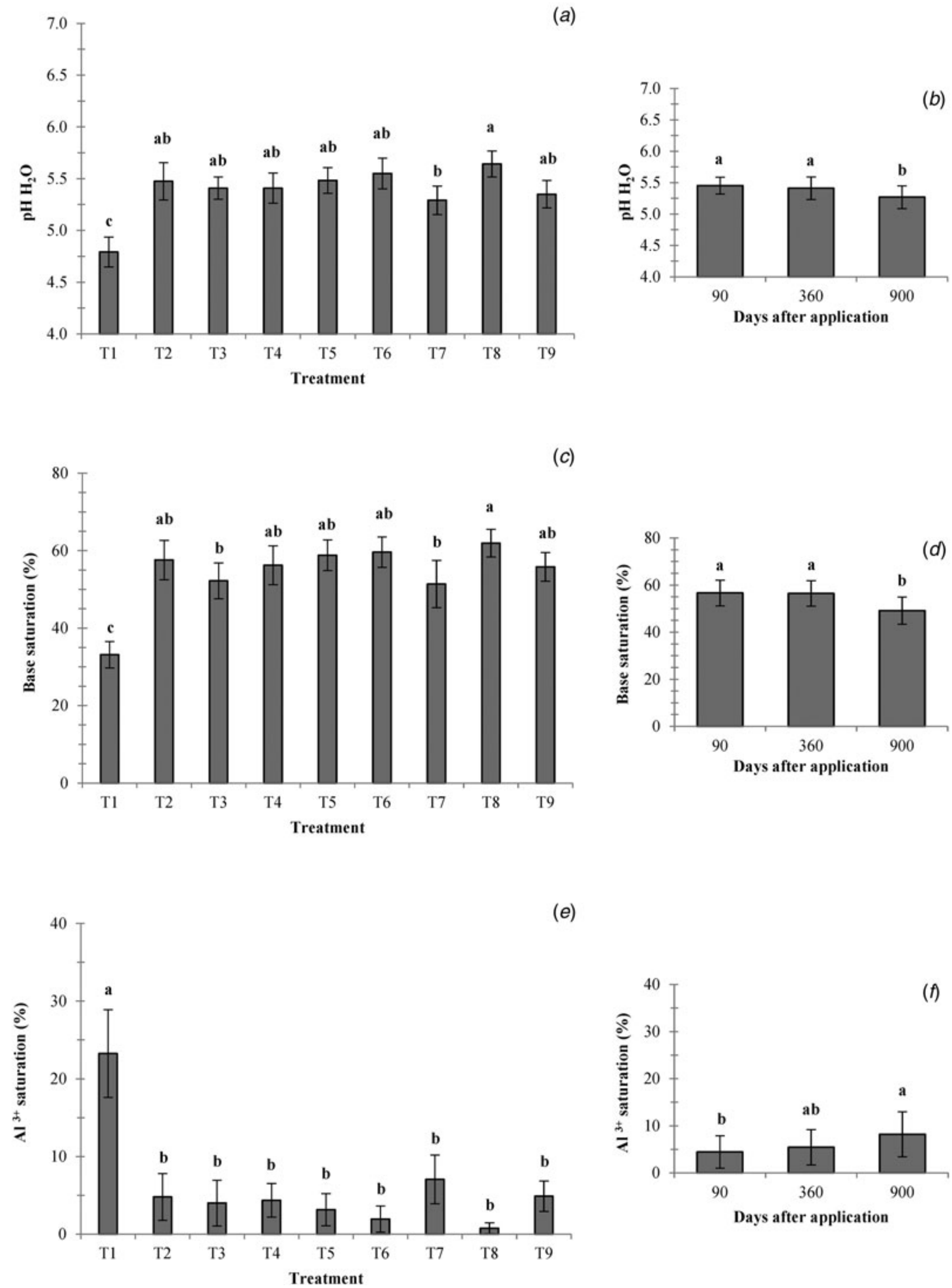

Figure 2. Effect of different fertilization strategies (T1–T9) on soil pH, base saturation and aluminium saturation of the arable soil (0.0–0.2 m): independently of the sampling time (*(a)*, *(c)* and *(e)*); and independently of the fertilization strategy at 90, 360 and 900 d after application of treatments (*(b)*, *(d)* and *(f)*). Boxes with the same low case letter are not significantly different by the Tukey test ($P < 0.05$). ns: not significant. Vertical bars represent the standard deviation of each treatment mean ($n = 12$) and days after application ($n = 36$).

elemental sulphur in treatment T8 was the most probable reason of the increase in available S contents in this treatment T8, although this effect was quite temporary, because for the 2nd and 3rd sampling time, no significant differences between treatments were observed. Considering the effect of the sampling time, the S content dropped significantly over time in treatments T4, T8 and 9 from the 1st to 2nd and 3rd soil samplings, back to similar levels observed in T1 and before the start of the experiment.

For the evaluated micronutrients, all of them were initially classified in the high availability range before the start of the experiment (Table 1). During the experiment, while Mn and Zn contents were significantly affected by treatments (Table 5), Cu and B were not. Furthermore, the sampling time affected the levels of Cu, Zn and B. A higher Mn mean value was observed in treatment T1 compared to treatments T2 and T8 (Fig. 4(e)). Conversely, no effect of sampling time was observed for Mn,

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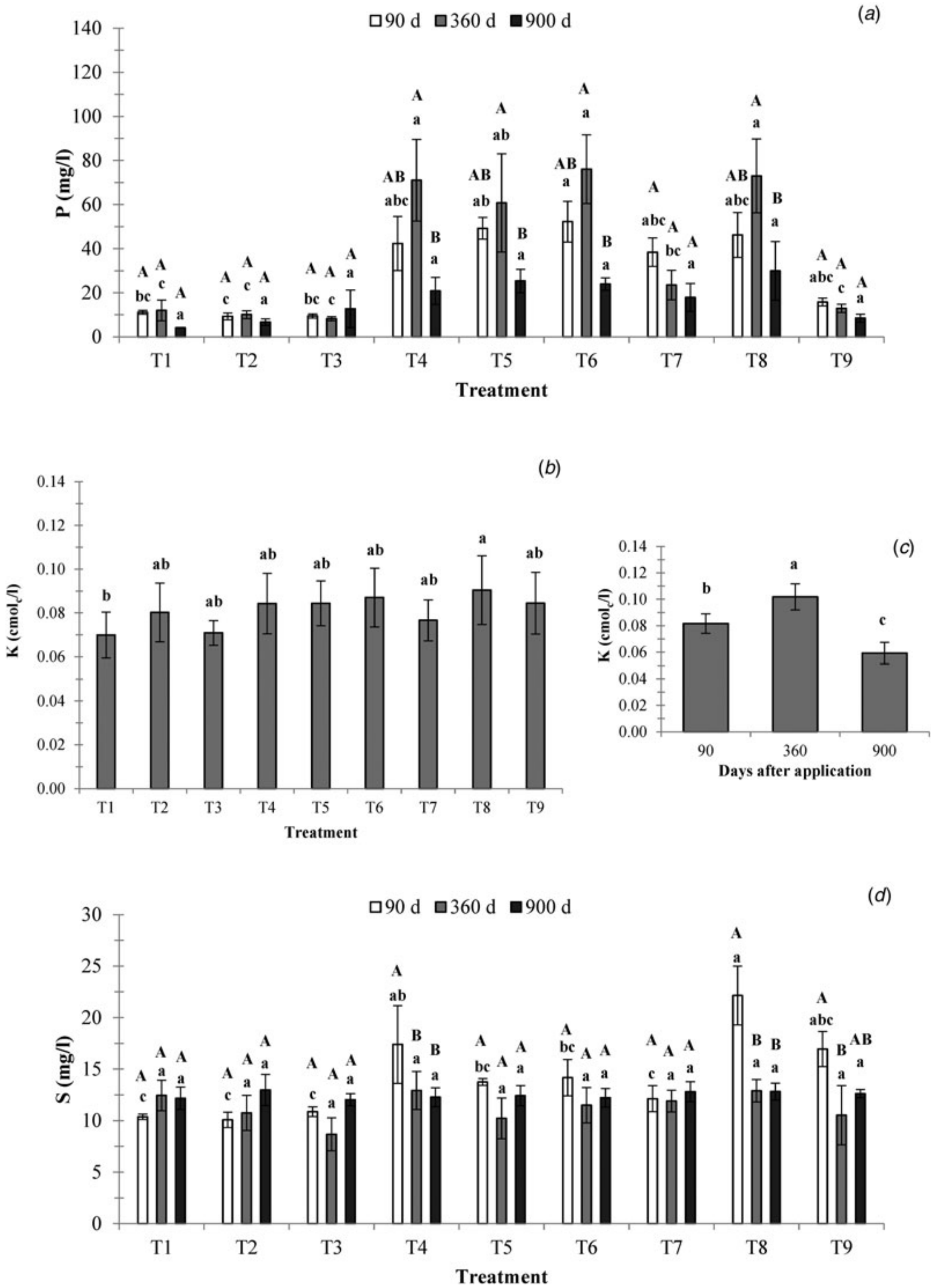

Figure 3. Effect of different fertilization strategies (T1–T9) on extractable phosphorus and potassium (Mehlich-1), and available sulphur of the arable soil (0.0-0.2 m): interaction between fertilization strategies (T1–T9) and sampling time for phosphorus *(a)* and sulphur *(d)*; independently of the sampling time for potassium *(b)*; and independently of the fertilization strategy for potassium *(c)* at 90, 360 and 900 d after fertilization.
For P and S, treatments with the same low case letters are not significantly different by the Tukey test ($P < 0.05$). Within each fertilization strategy (T1–T9), means with the same upper-case letters do not differ significantly by the Tukey test ($P < 0.05$). The vertical bars represent the standard deviation. For P and S: each treatment mean ($n = 4$). For K: each treatment mean ($n = 12$), for days after application ($n = 36$).

and mean values of all treatments remained stable, between 12.88 to 13.84 mg/l (Fig. 4(f)).

Effect of fertilization strategies on crop yield

Different fertilization strategies significantly affected crop yield for both maize and wheat grain (Table 6). The maize yield was significantly higher in treatments T7 (4884 kg/ha), T8 (4877 kg/ha) and T4 (4835 kg/ha) in relation to T5 (3171 kg/ha), T2 (3021 kg/ha), T1 (2932 kg/ha) and T6 (2881 kg/ha). Important to note is that the maize yield in T7, T8 and T4 treatments was close to the regional average (4807 kg/ha) observed in 2012.

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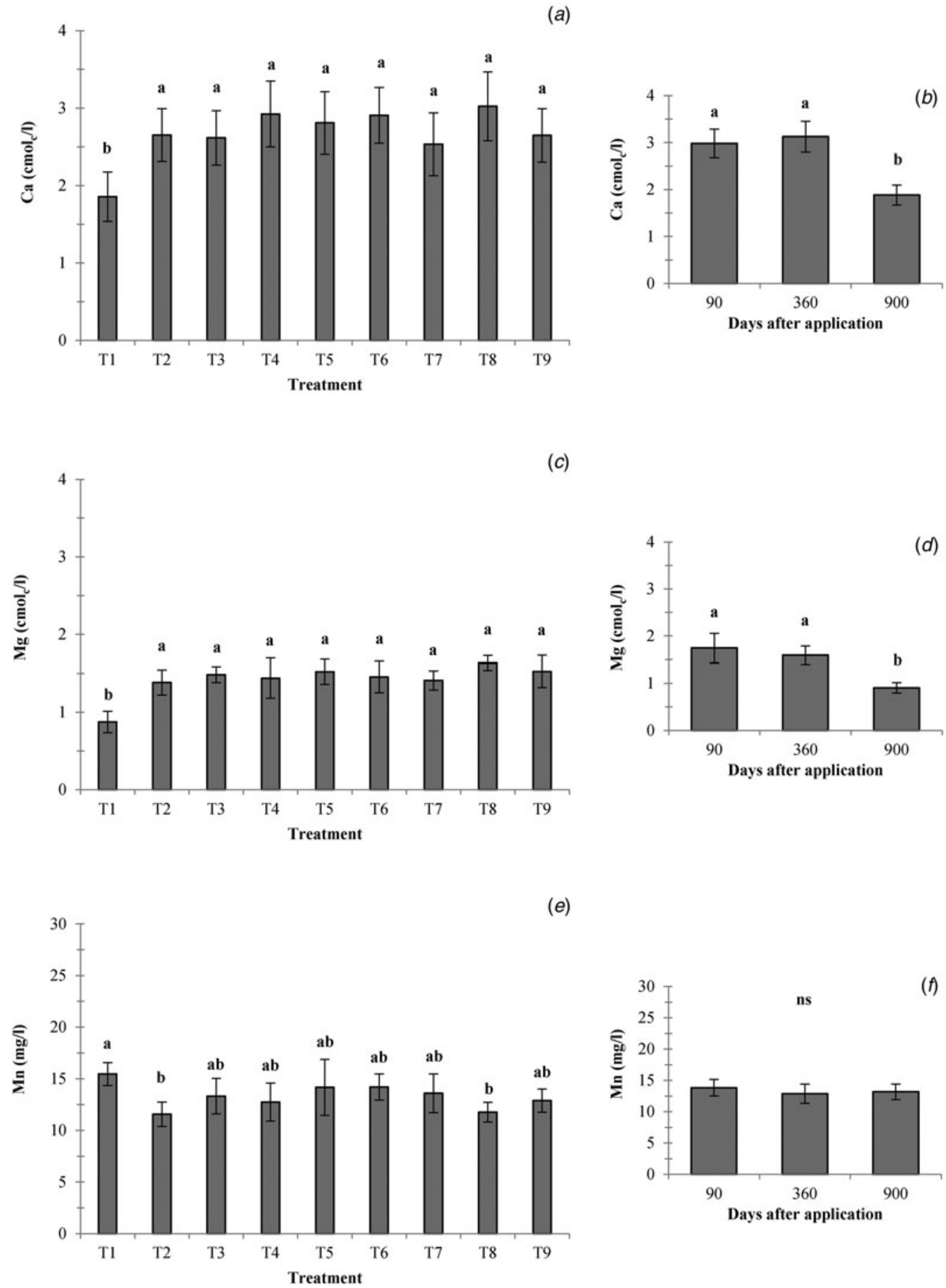

Figure 4. Effect of different fertilization strategies (T1–T9) on available calcium, magnesium and manganese of the arable soil (0.0–0.2 m): independently of the sampling time ((*a*), (*c*) and (*e*)); and independently of the fertilization strategy at 90, 360 and 900 d after application of treatments ((*b*), (*d*) and (*f*)).
Boxes with the same low case letter are not significantly different by the Tukey test ($P < 0.05$). ns: not significant. Vertical bars represent the standard deviation of each treatment mean ($n = 12$) and days after application ($n = 36$).

Regarding wheat yield, treatments T9 (1966 kg/ha), T7 (1954 kg/ha), T4 (1817 kg/ha), T8 (1810 kg/ha) and T6 (1803 kg/ha) were similar to the regional average yield (1942 kg/ha) while treatments T2, T3 and T5 were up to 20% lower (Table 6).

The cumulative yield demonstrates the performance of alternative fertilization strategies on maize, wheat and maize + wheat yields, compared to average rate of NPK formulation commonly used in southern Brazil, also confirming the benefits in a longer run (Table 6).

Discussion

The application of mineral and organic sources of nutrients improved the soil fertility status. As expected, Ca and Mg levels in the soil were improved by liming, thus affecting soil acidity-related variables such as pH, Al and base saturation.

The first stage of soil acidity neutralization occurs when carbonates are applied to acid soils, the dissolution in water produces

Table 6. Mean yield and standard errors of maize (main effect) and wheat (residual effect) grown in Planosol under different mineral and organic sources, differences in relation to mean yield of crops in Rio Grande do Sul State, Brazil (Δref) and the profit (P) of the fertilization strategies

Treatments	Maize yield kg/ha	Δref %	Wheat yield kg/ha	Δref %	Maize + wheat yield kg/ha	Δref %	Profit U$
T1	2932 ± 443b	−39	1303 ± 212b	−33	4235 ± 412c	−37	1001
T2	3021 ± 935b	−37	1543 ± 126ab	−21	4564 ± 904bc	−32	968
T3	3871 ± 717ab	−19	1629 ± 76ab	−16	5500 ± 711abc	−19	1223
T4	4835 ± 599a	1	1817 ± 108a	−6	6651 ± 648a	−1	1122
T5	3171 ± 603b	−34	1613 ± 228ab	−17	4784 ± 669bc	−29	631
T6	2881 ± 319b	−40	1803 ± 200a	−7	4684 ± 406bc	−31	327
T7	4884 ± 1,110a	2	1954 ± 262a	1	6837 ± 1,293a	1	798
T8	4877 ± 748a	1	1810 ± 161a	−7	6687 ± 878a	−1	478
T9	4205 ± 581ab	−13	1966 ± 283a	1	6171 ± 654ab	−9	1174
Regional yield	4807*		1942		6749		

T1, control; T2, conventional liming; T3, alternative liming; T4, alternative liming + 50% P natural phosphate + 50% P soluble triple phosphate; T5, alternative liming + 100% P natural phosphate; T6, alternative liming + 100% P natural phosphate + 100% K monzogranite; T7, alternative liming + 100% P natural phosphate + 100% N (50% organic source and 50% urea); T8, alternative liming + 100% P natural phosphate + 100% K monzogranite + 100% N (50% organic source and 50% urea) + 100% S; T9 - alternative liming + regional average rate (300 kg/ha) of NPK (5-20-20) formulation. Unless T7 and T8, all treatments received the full recommended rate of N-Urea. Values followed by the same letter in the column are not significantly different by the Tukey test ($P < 0.05$).
*of corn and wheat in Rio Grande do Sul State, Brazil (CONAB, 2018).

bicarbonate, which is much more reactive with the exchangeable and residual soil acidity (Fageria and Nascente, 2014; Brady and Weil, 2016). Consequently, Ca and Mg react with H^+, replacing it on the clay and organic matter exchange sites (Meriño-Gergichevich *et al.*, 2010; Fageria and Nascente, 2014).

In this way, the pH and the base saturation control soil fertility status and their dynamic is driven by the dolomite and calcite carbonate dissolution, present in marbles and in the limestone shale (Ribas *et al.*, 2017; Saif *et al.*, 2017). Carbonates undergo a congruent dissolution, meaning that there are no 'residues' (secondary minerals) after the full weathering, only the chemical elements are released. Conversely, an incongruent dissolution means that the result after weathering is the released elements plus secondary minerals in the soil (Crundwell, 2014). The rainfall amount is of primary importance for the speed of the liming reaction. From the time of lime application until the 1st soil sampling the rainfall was 348 mm (90 d), while the 2nd soil sampling took place when the cumulative rainfall was 1174 mm (360 d), reinforcing the effect of climatic factors on carbonate dissolution.

Besides the effects of precipitation, the particle-size distribution of rock powders plays a fundamental role in the dissolution rate. Rock powders containing carbonates and having liming effects are sold commercially with 95% of particles <0.3 mm, and therefore considered reactive within 90 d after incorporation in the arable soil layer. It is expected that the soil with limestone shale might have an equal or even higher carbonate dissolution rate than the dolomitic marble, probably due to differences in the nature of rock formation and/or texture. The limestone shale is a sedimentary rock, with less crystallized minerals, composed of microgranular grains of dolomite and calcite minerals, with rhombohedral structures and relatively equidimensional grains (Saif *et al.*, 2017). Therefore, in addition to the neutralization power and granulometry, petrographic analyses, characterization of the mineral composition, texture, particle-size distribution, and a description of the fine-grained structure of rocks can influence the corrective's choice.

Considering the liming sources, the limestone interbedded with shale, used individually or in association with other agrominerals containing CaO and MgO, is similar in increasing soil pH and decreasing the Al^{3+} saturation in relation to dolomitic marble (Fig. 2(e)). Other studies have shown the positive effects of limestone shale, corroborating the effectiveness of carbonates from the Irati Formation (Rodrigues *et al.*, 2021a, 2021b).

The decrease of mean values of pH (Fig. 2(b)), base saturation (Fig. 2(d)), Ca and Mg (Fig. 4(b), (c) and (d)), and the increase in Al^{3+} saturation (Fig. 2(f)), over time have shown that soil acidity and related problems returned faster than expected, probably because of the limited liming effects. Acidification in the soil system may typically be accelerated by the reaction of N input sources like urea and TPC in the soil. Soil acidification by synthetic fertilizers and organic matter decomposition (Fageria and Nascente, 2014) mostly occurs due to the release of H^+ during the nitrification process (Brady and Weil, 2016). In Brazil, studies about the application of tung pressed cake, used as a substrate for vegetable production, showed a tendency to reduce the pH with increasing application rates (Watthier *et al.*, 2017), possibly by H^+ dissociation from carboxylic groups, by nitrate leaching or N releases in the soil profile (Burle *et al.*, 1997). In a tropical climate, the highly weathered soils become naturally acidified due to high rates of precipitation, the main H^+ introducer in the soil system (Brady and Weil, 2016), as well as a result of leaching of bases (Fageria and Nascente, 2014). Therefore, soils with low natural fertility like the one of the current study should be frequently monitored (e.g., every 2 years) to assure suitable pH conditions for grain crops.

Considering the use of agrominerals to supply K for soil correction and plant requirements, the finely ground monzogranite, formed by K-feldspar, plagioclase, biotite, amphibole and quartz (Vieira *et al.*, 2016; Ciceri *et al.*, 2017) needs to be improved before being considered an effective source of K. Usually, the more relevant part of the K supplied to plants might be supplied by the available K fraction of soil, while the remaining can be extracted from organic matter or other less available forms of mineral phases. According to Britzke *et al.* (2012), exchangeable and non-exchangeable K fractions might supply part of the K required for crop development in lowlands. Furthermore, several monocots such as elephant grass and corn have a stronger K extraction capacity because of the ability to release low molecular weight acids to break chemical bonds of silicates. Therefore, as proposed by Ciceri *et al.*, (2017), the assessment of crop performance in response to the application of an agromineral with K-feldspar should consider, in addition to the K_2O content, petrographic characteristics that reveal the K-mineral's texture and degree of mineral alteration in the rock. In this sense, weatherable minerals such as biotite and secondary clay minerals (celadonite, smectite, vermiculite) might be important K sources for plants.

The particle-size of the monzogranite used in the current study (100% of particles <0.3 mm) is fine and comparable to calcareous rocks, but might still be not fine enough to release most of K through mineral dissolution within one crop season. Several technologies might be employed to boost K-release in K-bearing agrominerals. These include ultrafine grinding that increase the proportion of particles <0.074 mm, which increased the K-release of a phonolite from Minas Gerais, Brazil (Nogueira *et al.*, 2021), hydrothermal treatment with sulphuric acid (Safatle *et al.*, 2020), incubation with organic acids and K-solubilizing microorganisms (Basak, 2019), co-composting (Basak, 2018), among others (Pramanik *et al.*, 2019, 2020). It is important to use materials that promote agronomic efficiency and keep the transport distances short. These technologies have potential as local solutions for the use of K-rich agrominerals to cultivate annual crops.

The use of 3.4 Mg/ha of tung pressed cake (Table 4) added around 122 kg/ha K_2O (Table 3) in treatments T7 and T8, totalling 144 and 454 kg/ha K_2O (total amounts), respectively, while 60 kg/ha of K_2O was added in treatment T9 via soluble form through KCl. In fact, for treatment T9 the amount of K_2O (60 kg/ha) applied as KCl was not previously designed to increase the K-level in the soil. Despite the addition of high amounts of K via tung pressed cake (plus monzogranite in T8), in T7 and T8, the available K levels were not significantly higher compared to those variants receiving less K. The same applies for T6, which only received monzogranite. The K release from tung pressed cake still remains to be studied. Also, regarding the monzogranite, although a significant effect was observed for available K in soil of T8 *v.* T1, the release rates from the various K bearing minerals, K feldspar, biotite, need to be studied.

It is important to note that K is commonly considered as highly susceptible to leaching in sandy soils (Rosolem *et al.*, 2010). The soil of the study has only 160 g/kg clay, thus, if large rates of soluble K_2O are applied, this element can be easily leached out from the topsoil after heavy rainfalls. High K_2O rates can also induce a reduction in Ca, Mg and S uptake, like observed in upland rice by Filho *et al.* (2017). Therefore, this characteristic limits the application of high rates of highly soluble K sources close to root systems, highlighting the importance to find and develop slowly dissolving K sources.

Considering the P content, the treatments without natural or reactive phosphorus sources (treatments T1, T2 and T3) remained in the low to very low range of soil P availability (CQFS, 2016), independent of the period. Considering that the P content in the initial soil characterization was classified in the low availability class (Table 1), these results were expected for these treatments. Even with the increase of soil pH in the T2 and T3 treatments, and for treatment T9, there was no increase in soil P availability, mostly because the P inputs were negligible for T2 and T3, while for T9, although being almost all through a soluble form, the amount of P_2O_5 was only 66.4 of P_2O_5 (Table 4). In addition, the sandy property of the soil (160 g/kg) implies low P stocks, and the nutrient extraction by the crop probably explains the negligible change in the P levels. Considering the amount of nutrients as presented in Table 3 and the loads in Table 4, the ANP provided up to 475 kg/ha of P_2O_5 to the soil (total content), explaining the most part of soil P content changes over time. It is very important to note that Mehlich-1 extraction overestimates soil P available contents after natural phosphate application (Bortolon *et al.*, 2009), and usually plants do not access all this P content. In this way, although the effect of the application of natural phosphate (ANP) on available P in the soil is remarkable (Fig. 3(a)), its effects on crop performance is less evident, as presented by the results on grain yield obtained in the present study (Table 6). It is also important to note that when ANP and TPC (T7 and T8) where combined, the P levels in the soil where reduced. This might have happened because of the higher yields observed in the treatments with this combination, exporting higher P amounts than other treatments.

The available soil Zn content was especially favoured by the T6, T8, T7 and T5 treatments in relation to T2 (Table 4). These results show that the combination of limestone interbedded with shale, and mainly ANP and monzogranite might have played an important role in supplying the available Zn content, despite that Zn is already naturally present in the soil (Zn values in the T1 treatment were at the same level as all other treatments). Considering the sampling times, the Zn contents dropped significantly from 1st (0.99 mg/l at 90 d) to 2nd (0.68 mg/l at 360 d) sampling, demonstrating the impact of plant extraction and soil losses/fixation of Zn after two cropping seasons. Therefore, special attention should be paid to this element after two cropping seasons. In relation to available contents of Cu and B, the treatments did not differ significantly during the evaluated period, but both were affected by the sampling time: Cu mean contents dropped from 0.79 mg/l to 0.43 mg/l while for B contents increased from 0.23 mg/l to 0.42 mg/l from the 1st to 3rd sampling time, respectively (Fig. 5(d) and (f)). These patterns might be highly affected by soil pH because the availability of such micronutrients is usually controlled by this soil chemical property.

The changes in soil nutrient status and chemical properties clearly show the technical effectiveness of selected nutrient sources, with special emphasis on finely ground rock powders, in improving the available contents of major nutrients in the soil exchangeable complex. The limestone interbedded with shale was comparable to conventional liming to increase the soil pH, as well as to increase Ca and Mg contents in the soil. The Arad natural phosphate, although not produced in the region, displayed its already well-known capacity to increase P in the soil. However, its effect on yield was limited (see Table 6, T5 and T6). Treatment T8, which combined monzogranite and TPC, was the only one that raised the available soil K content significantly. In contrast, T6, which also received much higher amounts of K than the other treatments (but only via monzogranite, without TPC), did not show a significant increase in available soil K. Thus, the main origin of K supply (monzogranite or TPC) could not be clearly stated in the present study. In this context, considering agronomic and environmental aspects, the combination of the selected regional sources, mainly the limestone

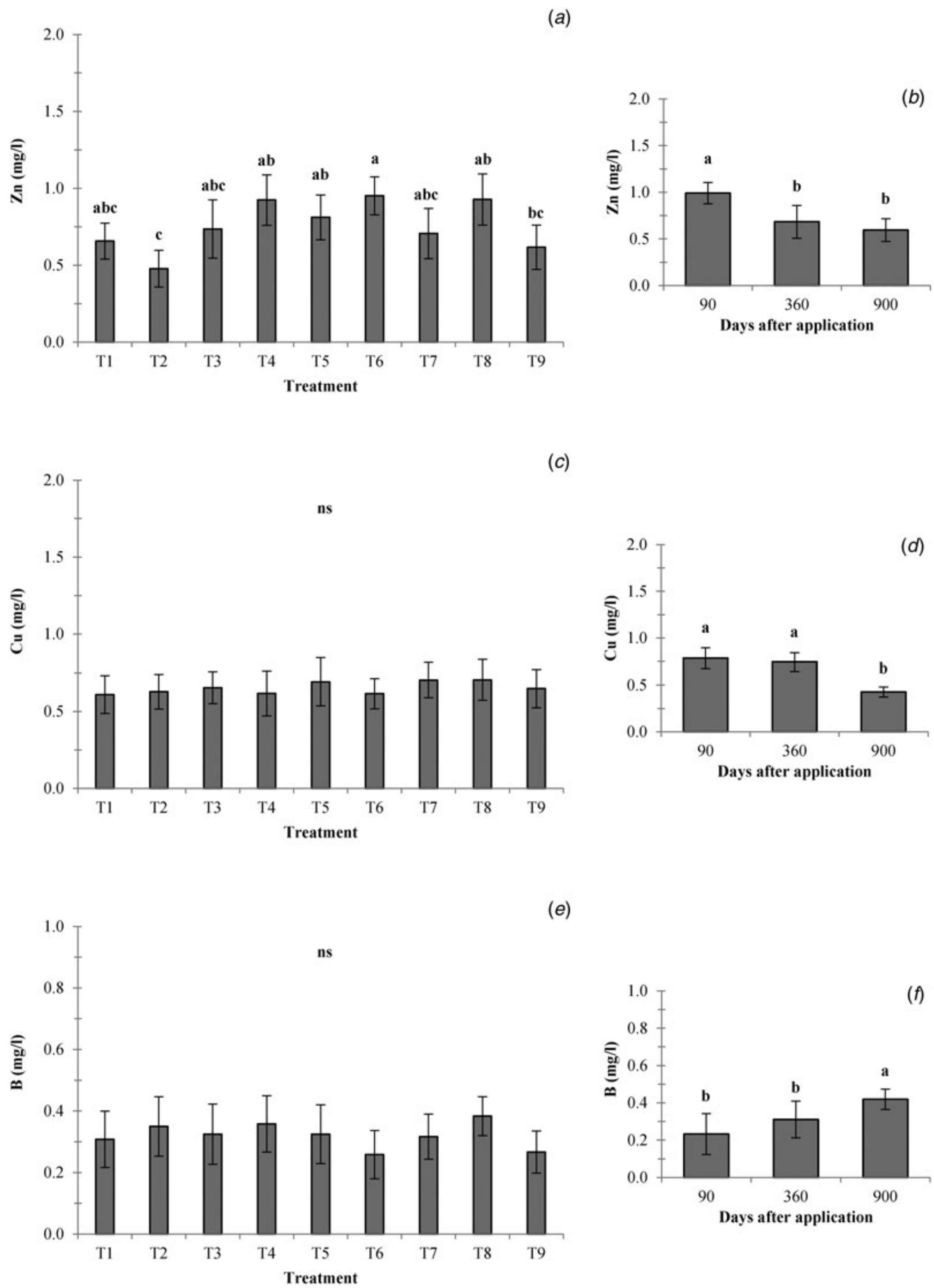

Figure 5. Influence of different fertilization strategies (T1–T9) on available zinc, copper and boron of the topsoil (0.0–0.2 m): independently of the sampling time ((*a*), (*c*) and (*e*)); and independently of the fertilization strategy at 90, 360 and 900 d after application of treatments ((*b*), (*d*) and (*f*)).
Boxes with the same low case letter are not significantly different by the Tukey test ($P < 0.05$). ns: not significant. Vertical bars represent the standard deviation of each treatment mean ($n = 12$) and days after application ($n = 36$).

interbedded with shale and the ANP, can be used as alternative sources of nutrients, keeping the available soil nutrients within affordable levels.

The results of maize grain yield (1st crop cycle) presented by some of the tested fertilization strategies in comparison to the average rate of NPK formulation demonstrate the technical viability of using regional sources as an alternative way to provide nutrients for annual cropping systems. The low maize yield observed in T1 was expected because of the low natural soil nutrient levels, without receiving any acidity corrective nor NPK as base fertilization. The maize yield in the T2 treatment remained 37% lower than the regional mean, even with the addition of dolomitic marble. The concomitant application of limestone interbedded with shale and ANP (T5) and monzogranite (T6)

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highlight the negative effect verified in yield when applying liming materials and rock phosphate powders together right before sowing, which probably resulted in limited intake of P by plants. Thus, the combined application of liming material and rock phosphate did not contribute to increase yields for T5 and T6 (Table 6). At slightly acid to neutral pH levels, immobilization of soluble P by Ca may occur, forming calcium phosphates. Additionally, P immobilization by Fe and Al oxides is well-known in highly weathered soils. On the other hand, this negative result can be compensated by applying at least a part of the recommended phosphate through soluble P forms, like as used in treatment T4.

In the case of treatments T5 and T6, the P release pattern of ANP strongly influenced maize yield. The high P content observed in treatments with ANP at 90 d (Fig. 3(a)) is partially explained by the Mehlich-1 extraction method, which uses an acidic extractive solution, dissolving the calcium phosphate particles that had not yet completely dissolved in the soil, thus overestimating the P availability for plants. On the other hand, the phosphate ions are released concomitantly with calcium from liming. This causes precipitation as dicalcium phosphate and, consequently, transformed into more stable, unavailable forms of P to plants, such as octo-calcium phosphate and hydroxyapatite, yielding a drastic reduction of P in soil solution. Similar results were observed by Shen *et al.* (2011) in a calcareous soil.

With regard to wheat productivity, the results show the importance of the residual effect of alternative fertilization strategies. Liming plus ANP and TPC (T7) and soluble S (T8), or liming plus ANP, where ANP was partially substituted by highly soluble forms of phosphorus (T4) could sustain a 2nd crop cycle in a similar way than NPK. This was probably due the high load of nutrients (Table 4) applied through these fertilization strategies (T7 and T8). Apart from the higher applied nutrient loads, the higher yield observed in T7 and T8 when compared to T5 and T6 can be partially explained by the acidifying effect of elemental Sulphur and the attenuation of P immobilization promoted by TPC. While the elemental Sulphur helps to dissolve P from ANP, a smoothing effect of TPC (as an organic material) could be the responsible of a reduction in P immobilization by Fe and Al oxides, and even by Ca.

For the monzogranite (treatments T6 and T8), the most probable process of K release is by the incongruent dissolution of silicates over time (Garcia *et al.*, 2020). The weathering of K-bearing silicate minerals from monzogranite (biotite, K-feldspar) can also result in other benefits for sandy soils, by generating negative permanent charges which may increase the cation exchange (Santos *et al.*, 2021), and increase water holding capacity (Mastella *et al.*, 2022; Mazahar and Umar, 2022). Rhizosphere processes and biological activity, which may further enhance mineral dissolution through H-ions release and complexing of organic compounds that react with mineral surfaces (Shen *et al.*, 2011), as well as isomorphic substitution, are the main ways to generate negative charges by agrominerals in agricultural soils.

Looking at the cumulative yield, the limestone interbedded with shale was at least equal to or even more efficient than the dolomitic marble for reducing soil acidity, releasing Ca and Mg and improving crop yield. However, the combination of liming through limestone shale and P - ANP (treatment T5 and T6) restricted the crop yield, therefore, their concomitant application must be avoided. This can be achieved by using a part of P application through conventional TSP, as to observed in treatment T4. The performance of maize plus wheat yield of T3 (U$ = 1223) resulted in a slightly higher profit (+ 4.2%) than T9 (U$ = 1174). Evidently, the profit of annual crops largely depends on the sum of costs of all nutrient sources, including transportation and application (not considered here), thus, it is essential provide for the farmers new, efficient and low-cost nutrient sources, in a regional scale. In this sense, the limestone interbedded with shale, alone (T3) or combined with 50% of P-ANP + 50% of P – TSP (T4) and the average regional rate of NPK fertilization (T9) provided the best economical and technical results, highlighting the potential of selected regionally available resources (rock powders) to perform soil fertilization strategies as an alternative or complement to conventional fertilization.

Conclusions

The limestone shale was agronomically effective by releasing Ca and Mg, and correcting soil acidity similarly to dolomitic marble, with marked improvement on maize and wheat yields. The best profits were reached when limestone shale was used alone or combined with 50% P-natural phosphate plus 50% P-triple superphosphate.

The agronomic efficiency (grain yield) of maize and wheat promoted by T4, T7 and T8 was comparable to the average regional rate of NPK (5-20-20) fertilization (T9), highlighting the technical viability of low grade and less soluble agrominerals as alternative nutrient sources. On other hand, when considering the resulted profit, only T3 and T4 where comparable to the conventional NPK formulation.

The results of the present study highlight the strategy of using lower grade and less soluble agrominerals, considering the available resources as alternative nutrient sources. This new strategy should be accompanied by a shift of recommending fertilization sources and rates, from a single crop to a production system-driven solution.

Supplementary material. The supplementary material for this article can be found at https://doi.org/10.1017/S002185962300062X.

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Ethical standards. Not applicable.

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