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AVALIAÇÃO DA POTENCIALIDADE DE DUAS ROCHAS VULCÂNICAS DO ESTADO DO RIO GRANDE DO SUL COMO REMINERALIZADOR DE SOLOS EM CULTIVO DE AVEIA PRETA, MILHO E EUCALIPTO

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Tese submetida ao Programa de Pós-graduação em Engenharia de Minas, Metalúrgica e Materiais da Universidade Federal do Rio Grande do Sul, como requisito parcial à obtenção do título de Doutor em Engenharia.

Orientador: Dr. Ivo André Homrich Schneider
Coorientadora: Profa. Dra. Claudete Gindri Ramos

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Esta Tese foi analisada e julgado adequado para a obtenção do título de Doutor em Engenharia e aprovado em sua forma final pelo Orientador e pela Banca Examinadora designada pelo Programa de Pós Graduação em Engenharia de Minas, Metalúrgica e Materiais da Universidade Federal do Rio Grande do Sul.

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RESUMO

Os métodos de remineralização incluem a aplicação de pó de rocha. Neste contexto, a presente tese investigou o uso de duas fontes de pó de rocha (andesito e dacito), incluindo estudos de caracterização dos materiais, ensaios cinéticos de liberação de nutrientes e elementos potencialmente tóxicos e cultivos agronômicos. A rocha dacito é proveniente de uma mineradora localizada no Distrito Mineiro do município de Nova Prata, no estado do Rio Grande do Sul, Brasil. O andesito é oriundo de uma mineradora localizada no município de Estância Velha, no mesmo estado. Para a caracterização das amostras, foi realizada a descrição petrográfica, distribuição granulométrica, identificação das fases mineralógicas, composição química elementar e geoquímica. Nos estudos cinéticos, os pós de rocha foram expostos, por um período de até 5760 h, a água Milli-Q em faixa de pH entre 7,4 e 8,8, em solução aquosa de ácido cítrico 0,1 mol L^{-1} na faixa de pH entre 2,1 e 3,3 e em solução aquosa de ácido acético 0,5 mol L^{-1} na faixa de pH entre 5,0 e 5,8. Os resultados mostraram, para ambas as rochas, bom índices de dissolução dos elementos Ca, Si, Mg, Fe, Al e K com a seguinte sequência: solução de ácido cítrico > ácido acético > água pura. A aveia preta (*Avena strigosa*) e, na sequência, o milho (*Zea mays*) foram cultivados em casa de vegetação em vasos com solo agrícola natural, tratado com o pó de rocha de dacito e com esse pó de rocha misturado com lodo de laticínios. Esse experimento foi realizado para determinar liberação de macronutrientes no solo, e nutrir as duas cultivares. Houve um acréscimo significativo ($p < 0,05$) em todos os parâmetros analisados em uma dose de 7.251 kg ha^{-1} de pó de rocha e 20.594 kg ha^{-1} de lodo de laticínio. Em comparação com o controle, ambas as safras cresceram melhor em altura e massa seca. Um aumento linear significativo ($p<0,01$) em Ca, K, Mg e P foram observadas nas folhas de aveia preta e milho onde foi realizado a aplicação das doses mais altas de misturas dos subprodutos. Os elementos potencialmente tóxicos em ambos os subprodutos foram irrelevantes, sugerindo que a mistura de pó de rocha dacito junto com lodo de laticínio pode ser um fonte potencial de Ca, K, Mg e P na agricultura sem representar risco de contaminação para o ambiente. Em paralelo, conduziu-se um experimento de cultivo agronômico a campo com duração de nove meses com a rocha andesito para avaliar o desempenho de eucalipto (*Eucalyptus saligna* Smith) cultivado em um argissolo. Foram utilizadas quatro doses diferentes (tratamento Tl = controle, tratamento T2 = fertilizante de nitrogênio, fósforo e potássio 100%, tratamento, T3 = pó de rocha 100% e tratamento T4 = pó de rocha 50% e fertilizante de nitrogênio, fósforo e potássio 50%). Constaram-se que os tratamentos T2 e T4 apresentaram o melhor desenvolvimento, situações onde o nível de K e P no solo foram maiores. Pode-se concluir que a utilização dos minerais das rochas dacito e andesito são uma alternativa para reduzir a utilização de fertilizantes altamente solúveis, reduzindo os possiveis impactos ambientais e aumentando a produtividade agrícola. Além disso, os estudos desenvolvidos contribuem para uma agricultura de tecnologia agrícola mais limpa e regenerativa e auxiliam na gestão dos resíduos no setor mineral.

Palavras-chave: rochas vulcânicas, pó de rocha, resíduo de mineração, agricultura orgânica, lodo de laticínio, dissolução mineral, andesito, dacito.

ABSTRACT

Remineralization methods include the application of rock dust. In this context, this thesis investigated the use of two sources of rock dust (andesite and dacite), including material characterization studies, kinetic tests for the release of nutrients and potentially toxic elements and agronomic crops. The dacite rock comes from a mining company located in the Mining District of the municipality of Nova Prata, in the state of Rio Grande do Sul, Brazil. The andesite comes from a mining company located in the municipality of Estância Velha, in the same state. To characterize the samples, petrographic description, particle size distribution, identification of mineralogical phases, elementary chemical and geochemical composition were carried out. In kinetic studies, the rock powders were exposed, for a period of up to 5760 h, to Milli-Q water in a pH range between 7.4 and 8.8, in an aqueous solution of citric acid 0.1 mol L^{-1} in the pH range between 2.1 and 3.3 and 0.5 mol L^{-1} aqueous acetic acid solution in the pH range between 5.0 and 5.8. The results showed, for both rocks, good dissolution rates for the elements Ca, Si, Mg, Fe, Al and K with the following sequence: citric acid solution > acetic acid > pure water. Black oats (Avena strigosa) and, subsequently, corn (Zea mays) were grown in a greenhouse in pots with natural agricultural soil, treated with dacite rock powder and this rock powder mixed with dairy sludge . This experiment was conducted to determine the release of macronutrients in the soil, and nourish the two cultivars. There was a significant increase ($p < 0.05$) was observed in all parameters analyzed at a dose of 7,251 kg ha^{-1} of rock dust and 20,594 kg ha^{-1} of dairy sludge. Compared to the control, both crops grew better in height and dry mass. A significant linear increase ($p<0.01$) in Ca, K, Mg and P were observed in black oat and corn leaves where the highest doses of mixtures of by-products were applied. The potentially toxic elements in both by-products were irrelevant, suggesting that the mixture of dacite rock powder together with dairy sludge can be a potential source of Ca, K, Mg and P in agriculture without posing a risk of contamination to the environment. In parallel, an agronomic field cultivation experiment lasting nine months was conducted with andesite rock to evaluate the performance of eucalyptus (Eucalyptus saligna Smith) grown in an argisol. Four different doses were used (treatment Tl = control, treatment T2 = 100% nitrogen, phosphorus and potassium fertilizer, treatment T3 = 100% rock dust and treatment T4 = 50% rock dust and nitrogen, phosphorus and potassium fertilizer 50%). It was found that treatments T2 and T4 showed the best development, situations where the level of K and P in the soil were higher. It can be concluded that the use of minerals from dacite and andesite rocks is an alternative to reduce the use of highly soluble fertilizers, reducing possible environmental impacts and increasing agricultural productivity. Furthermore, the studies developed contribute to cleaner and more regenerative agricultural technology and assist in waste management in the mineral sector.

Keywords: volcanic rocks, rock dust, mining residue, organic agriculture, dairy sludge, mineral dissolution, andesite, dacite.

SUMÁRIO

1 INTRODUÇÃO

Devido a alta divesificação e o potencial geológico, juntamente com grandes investimentos em infraestrutura e tecnologia, o Brasil ocupa uma posição relevante no cenário da mineração (BURBANO et al., 2022). Contudo, somos um dos maiores importadores e consumidores de fertilizantes na agricultura. (PHILIPP et al., 2022). Neste contexto, fontes alternativas a fertilização tradicional são, portanto, necessárias (KORCHAGIN et al., 2019).

Em 2019 o Brasil importou 24 milhões de toneladas de fertilizantes químicos. A maior quantidade foi de cloreto de potássio, com um volume de cerca de 4,9 milhões de toneladas (GLOBALFERT, 2020). Em 2020 foram consumidos 36,2 milhões de toneladas de fertilizantes no Brasil, sendo que desse total 80% são importados (AMA BRASIL, 2022). Além dos valores de transporte ser elevados, os custos de produção agrícola com fertilizantes químicos utilizados na agricultura correspondem a 40% (DOUGLAS et al., 2012, DOUGLAS et al., 2014).

Desta maneira, está sendo visto com prioridade o uso e destino dos resíduos sólidos gerados (aqui denominados subprodutos), oriundos de atividades industriais, dentre as quais podemos destacar a mineração e a indústrias de laticínios. A utilização de resíduos da mineração, com a consequente agregação de valor, resulta em uma abordagem relevante para a construção de alternativas sustentáveis para a preservação do meio ambiente (MANHÃES e HOLANDA, 2008).

O pó de rocha em muitas pedreiras era considerado um resíduo. Porém, esse material tem potencial para melhorar a fertilidade do solo, pois pode conter diversos minerais benéficos. Desta forma, o pó de rocha pode se tornar uma fonte de diminuição dos custos agrícolas (BURBANO et al., 2022).

Grande parte das regiões brasileiras são contempladas com reservas de rochas silicáticas ricas em P, Ca e Mg (RAMOS et al., 2015). Desta forma, diversos estudos demonstraram que se pode alcançar uma economia nos custos de produção em 50% com o uso remineralizadores de origem mineral (MELO et al., 2012). Uma das vantagens é a liberação lenta e contínua dos nutrientes (DOUGLAS et al., 2013, RAMOS et al., 2015). Mesmo quanto aplicados em uma alta dosagem, não oferece riscos de contaminação dos solos, uma vez que fornece os nutrientes que a planta de forma gradual (BURBANO et al., 2022).

As rochas vulcânicas silicáticas formadas na Serra Geral da Bacia do Paraná possuem ampla distribuição pelos estados da região Sul, e em partes das regiões Sudeste e Centro-Oeste, do Brasil. Esse fato, aliado ao seu uso na forma de agregados para a construção civil, as torna, muitas vezes, disponíveis na forma de finos de britagem em locais próximos aos polos agrícolas das regiões acima mencionadas. Por esta razão, o uso de pós de rochas vulcânicas, derivadas da formação Serra Geral, embora ainda sem o devido registro no Ministério da Agricultura, Pecuária e Abastecimento (MAPA), têm sido usados para a remineralização de solos, em especial no âmbito da agricultura familiar do Rio Grande do Sul, Santa Catarina e Paraná (KNAPIK, 1987; ALMEIDA e SILVA, 2009).

No processo de extração e adequação granulométrica das rochas, em geral, são geradas quantidades consideráveis de materiais na forma de partículas finas (DALMORA et al., 2016). No Brasil, a destinação final dos materiais tem sido, quase sempre, a disposição inadequada em áreas de descarte das minerações, resultando em impactos ambientais que podem comprometer o ecossistema (SIMSEK et al., 2005).

A denominação rochagem refere-se à utilização do pó de uma rocha, mais comumente as rochas silicatadas, em atividades agropecuárias. O processo parte do pressuposto em que as rochas podem fornecer a demanda química necessárias às culturas por meio da disponibilização balanceada dos minerais ao solo (RAMOS et al., 2015). Nas regiões de clima tropical ou subtropical, onde há períodos de chuvas intensas, os nutrientes minerais, derivados de fontes solúveis ou sintéticas, são rapidamente lixiviados, resultando em um aumento de custos de reposição dos fertilizantes a cada safra. Porém, de maneira diversa, os remineralizadores, no caso o pó de rocha, possibilitam que os nutrientes permaneçam mais tempo reagindo no solo, uma vez que são menos solúveis, garantindo, assim, a disponibilidade dos nutrientes essenciais para o desenvolvimento vegetal por mais tempo (THEODORO; ALMEIDA, 2013).

O processo de obtenção do pó é estritamente feito de forma física, procedendo-se apenas, quando necessário, a moagem da rocha “in natura”. Como referido, a rochagem possibilita o reaproveitamento de rejeitos de pedreiras e de outras atividades de mineração, o que promove a diminuição dos custos no processo de obtenção do insumo e geração de novos produtos. Apesar de ser uma prática antiga, os pós de rochas silicatadas foram incluídos apenas em 2013 na legislação brasileira dos fertilizantes, pela lei n° 12.890/2013 (BRASIL, 2013), que alterou a Lei nº 6.894 de 16.12.1980, tornando os em remineralizadores de solos, regulamentados como insumo agrícola em 2016 (BRASIL, 2016). O uso dos remineralizadores está em crescimento, sendo que no ano de 2021 foram utilizados em pelo menos em 5 milhões de hectares (ANUÁRIO ESTATÍSTICO, 2021).

Recentes pesquisas demonstram seus efeitos como uma possível fonte de elementos para nutrição (SORATTO et al., 2021ab; CONCEIÇÃO et al., 2022; CRUSCIOL et al., 2022) e para a efetiva utilização do fósforo (SANTOS et al., 2021; BUSATO et al., 2022; CONCEIÇÃO et al., 2022).

Os remineralizadores são definidos como minerais derivados de rochas silicáticas que passaram apenas por processos de cominuição, com o objetivo de melhorar as características químicas, físicas e biológicas de solos agrícolas. Esta definição de remineralizadores estabelecida pela Lei nº 12.890, de 10.12.2013 (BRASIL, 2013), que alterou a Lei no 6.894 de 16.12.1980 (BRASIL, 1980).

A Lei nº 12.890 foi regulamentada pela Instrução Normativa nº 5 de 10.03.2016 e publicada pelo Ministério da Agricultura, Pecuária e Abastecimento (MAPA) (BRASIL, 2016). Nesta Instrução normativa ficaram definidos os critérios para registro e fiscalização destes materiais, em função de cinco características geoquímicas, mineralógicas e agronômicas (BRASIL 2016):

a) soma de bases (SB) (CaO + MgO + K2O) no mínimo 9%;

b) teor mínimo de K_2O total de 1%;

c) conteúdo máximo de 25% de quartzo (sílica livre);

d) concentrações máximas de elementos potencialmente tóxicos: arsênio (As) < 15 mg/kg; cádmio (Cd) < 10 mg/kg; mercúrio (Hg) < 0,1 mg/kg; chumbo (Pb) < 200 mg/kg;

e) teste agronômico que comprove a eficiência do material em modificar as propriedades de fertilidade do solo e o desenvolvimento de plantas.

A Instrução Normativa nº 5 de 2016 determina ainda que deve ser declarado o pH de abrasão do pó de rocha e que a granulometria seja estabelecida entre as três classes: farelado, pó ou “filler” (BRASIL, 2016).

Diversos autores têm apontado que estas rochas podem ser utilizadas no manejo da fertilidade do solo, como ocorre com as cinzas vulcânicas (MINASNY et al., 2021) e sedimentos glaciais (GUNNARSEN et al., 2019). Estudo realizado por Crusciol et al. (2022) constatou que a utilização de agrominerais silicáticos potássicos, compostos principalmente por feldspatos potássicos, simulando a mesma forma como acontece em ambientes vulcânicos, possuem similar eficiência agronômica ao cloreto de potássio (KCl). Sendo assim, imitar a natureza é uma estratégia a ser seguida em relação aos processos de remineralização dos solos agricultáveis.

Além dos remineralizadores, outra fonte alternativa de fertilizante são os de origem orgânica. O aumento da população mundial cresceu significativamente. Diante deste fato, há a necessidade de se produzir mais alimentos, acarretando mudanças sobre o meio ambiente. A indústria alimentícia, em seu processo de fabricação, gera subprodutos e resíduos com altos teores de matéria orgânica e que necessitam uma devida destinação (CHENG, 2007).

No caso da indústria de laticínios, o Brasil produzia 5,2 milhões de toneladas de leite em 1974, passando para 35,5 milhões de toneladas em 2021. Esse aumento de produtividade se deve muito a pesquisas desenvolvidas no setor (EMBRAPA, 2022). O Brasil é considerado o 5° maior produtor de leite (FAO, 2019), representando 4,22% da produção mundial. O estado de Minas gerais em 2021 alcançou 24,7% da produção de leite seguido pelo estado do Paraná com 14,0%, Rio Grande do Sul 13,4%, Santa Catarina 11,7%, São Paulo 10,2%, Goiás 9,7%, Bahia 2,4%, Rondônia 2,3%, Rio de Janeiro 1,9% e Mato Grosso 1,8%, sendo esses os 10 estados com maior produtividade leiteira (EMBRAPA, 2022).

Efluentes líquidos, emissões atmosféricas e resíduos sólidos são os principais resíduos da indústria de laticínios (VILLA et al., 2007). Para cada litro de leite beneficiado são gerado 2,5 L de efluente. Os efluentes são gerados principalmente da limpeza e lavagem dos equipamentos e tubulações. Resíduos sólidos são gerados nos sistemas de tratamento de efluentes, especialmente, sobrenadantes da flotação e lodo biológico (FEAM e FIEMG, 2014).

A agroindústria brasileira é muito diversificada. Nessa tese foram consideradas diversas cultivares, entre as quais aveia preta, milho e eucalipto.

A aveia preta compõe uma das espécies essenciais de gramíneas para a formação de palhadas, destinadas a cobertura do solo (MELO et al., 2011) anteriormente a implantação da cultura de verão (RIQUETTI et al., 2012). Emprega-se principalmente nos Estados da Região Sul do Brasil, Sudoeste de São Paulo e Sul de Mato Grosso do Sul (CAIRES e MILLA, 2016). A principal razão por sua grande utilização é a facilidade em encontrar sementes e o fácil cultivo. Entre os benefícios estão a rusticidade, a capacidade de perfilhamento da planta, a resistência a infestação de pragas e doenças, e o rápido crescimento inicial que propicia a cobertura imediata do solo e a melhora da estrutura do solo através do sistema radicular (SILVA et al., 2009). Também propicia uma alta produção de massa seca da parte aérea com a decomposição longa e a ciclagem de nutrientes (CARVALHO et al., 2013; WUTKE et al., 2014). Desta forma, a aveia preta produz mais de seis toneladas de biomassa por hectare, sendo capaz de promover cobertura do solo, auxiliando o controle de plantas espontâneas (SILVA et al., 2009).

A cultura do milho integra uma das espécies agrícolas de grande importância no cenário mundial por ser uma fonte de alimento com custo baixo e com elevado valor energético, sendo visto como uma espécie vital para a humanidade. O milho pode ser utilizado para atender o mercado na produção de ração animal, sendo este o seu principal emprego. Entretanto, cerca de

15% da produção mundial de milho é destinada para nutrição humana. O milho encontra também emprego como matéria-prima em distintos segmentos e artigos (MORO e FRITSCHE-NETO, 2015).

No Brasil, o total da área destinada a árvores plantadas chegou a 9,93 milhões de hectares. Em particular, a produtividade do eucalipto alcançou seu melhor nível desde 2014, atingindo a 38,9 m³/ha/ano em 2021, utilizado principalmente na produção de madeira e celulose. O pinus, por sua parte, totalizou 29,7 m³/ha/ ano. Esses números maiores são maiores que as médias globais e constatam que, os investimentos em conhecimento e tecnologia no Brasil, são impulsionadores de uma produção florestal moderna. Neste mesmo ano foram certificados 7,37 milhões de hectares, o que representa um avanço de 8,3% em relação ao ano anterior (IBÁ, 2021).

Sendo assim, a aplicação de pós de rocha na agricultura deve ser considerada uma alternativa para remineralizar solos empobrecidos em nutrientes. A prática requer caracterização mineralógica, química e avaliação de seu desempenho agronômico (KORCHAGIN et al., 2019). Essa abordagem contribui tanto para solucionar os problemas ambientais associados à mineração de rochas quanto para criar uma alternativa mais limpa para a fertilização do solo em prol do desenvolvimento sustentável.

1.1 OBJETIVOS

Neste contexto, o objetivo geral desta pesquisa foi investigar dois tipos de rochas vulcânicas oriundos da formação Serra Geral, especificamente um dacito e um andesito, como agentes mineralizadores de solo.

Os objetivos específicos foram:

a) caracterizar os remineralizadores a ser utilizados nos experimentos em termos químicos, físicos, mineralógicos e agrônomicos;

b) avaliar a potencialidade dos remineralizadores para disponibilização de macro e micronutrientes, por meio de ensaios de lixiviação em água e em solução ácidas;

c) estudar o efeito sinérgico da adubação realizada com pó de rocha e lodo de estação de tratamento de efluentes do setor de laticínios na fertilidade do solo e no crescimento de aveia preta e milho;

d) estudar, de forma comparativa, a aplicação do pó de rocha, adubação convencional e o efeito da aplicação de pó de rocha com adubação convencional na fertilidade do solo e cultivo de *Eucalyptus saligna* Smith.

1.2 INTEGRAÇÃO DOS ARTIGOS CIENTÍFICOS

A pesquisa desenvolvida nesta tese está alinhada com as àreas de Tecnologia Agronômica também com a Tecnologia Mineral. É necessário compreender os processos envolvidos na disponibilização de nutrientes, fertilidade agronômica e elementos potencialmente tóxicos, por meio de testes de lixiviação em soluções aquosas contendo pó de rochas vulcânicas e em experimentos agronômicos.

Em vista disso três artigos foram produzidos visando os seguintes avanços:

1) Entender os processos geoquímicos de alteração dos minerais das rochas e liberação de elementos devido à aplicação de soluções extratoras, da composição mineralógica e granulometria dos pós de rochas;

2) Acrescentar ao conceito de agricultura orgânica a utilização de produtos minerais *in natura*, justificando cientificamente as quantidades e qualidades que incorporam ao solo;

3) Comprovar a hipótese de que o uso dos resíduos oriundos da extração e beneficiamento de rochas vulcânicas é uma alternativa viável para reduzir o consumo de fertilizantes solúveis;

4) Transmitir o conhecimento adquirido aos setores de mineração de rochas vulcânicas, indústrias de laticínios e agrícola, a partir da remineralização de solos, que é uma técnica viável, para os pequenos, médios e grandes agricultores que terão a oportunidade de ser beneficiados em fertilidade de solos e aumento da produtividade, com redução de custos expressivos.

O artigo “Understanding the mobility of potential nutrients in rock mining by- products: An opportunity for more sustainable agriculture and mining”, publicado no periódico Science of the Total Environment, traz a caracterização química, física e mineralógica das rochas dacito e andesito bem como os resultados de um experimento de liberação cinética em água e na presença de ácidos fracos. O objetivo desse atigo foi ter um melhor entendimento nas taxas de dissolução através da cinética de lixiviação para determinar adequadamente a capacidade de suprimento de nutrientes das rochas aos solos, podendo ser otimizada a sua eficiência como fertilizante, para reduzir o uso de fertilizantes solúveis e desenvolver diretrizes para o descarte seguro e adequado de subprodutos e reduzir a poluição ambiental.

O artigo “Sustainable release of macronutrients to black oat and maize crops from organically-altered dacito rock powder”, publicado no periódico Natural Resources Research, teve como objetivo avaliar o subproduto inorgânico (pó de rocha dacito) e o subproduto orgânico (lodo de leite) misturado com solo tropical como fertilizante para a produção de aveia preta e milho.

No artigo "Application of andesite rock as a clean source of fertilizer for eucalyptus crop: Evidence of sustainability", publicado no periódico Journal of Cleaner Production, foi realizada uma caracterização química e mineralógica detalhada de uma amostra de pó de rocha classificada como andesito vesicular no cultivo do *Eucalyptus saligna* Smith (ESS). O objetivo do trabalho foi determinar os efeitos de quatro tratamentos agronômicos, envolvendo o controle, adubação convencional, pó de rocha, e a mistura de ambos, na disponibilidade do P e K no solo e no desenvolvimento do eucalipto na cidade Triunfo no estado do Rio Grande do Sul.

UNDERSTANDING THE MOBILITY OF POTENTIAL NUTRIENTS IN ROCK MINING BY- PRODUCTS: AN OPPORTUNITY FOR MORE SUSTAINABLE AGRICULTURE AND MINING

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2 UNDERSTANDING THE MOBILITY OF POTENTIAL NUTRIENTS IN ROCK MINING BY-PRODUCTS: AN OPPORTUNITY FOR MORE SUSTAINABLE AGRICULTURE AND MINING

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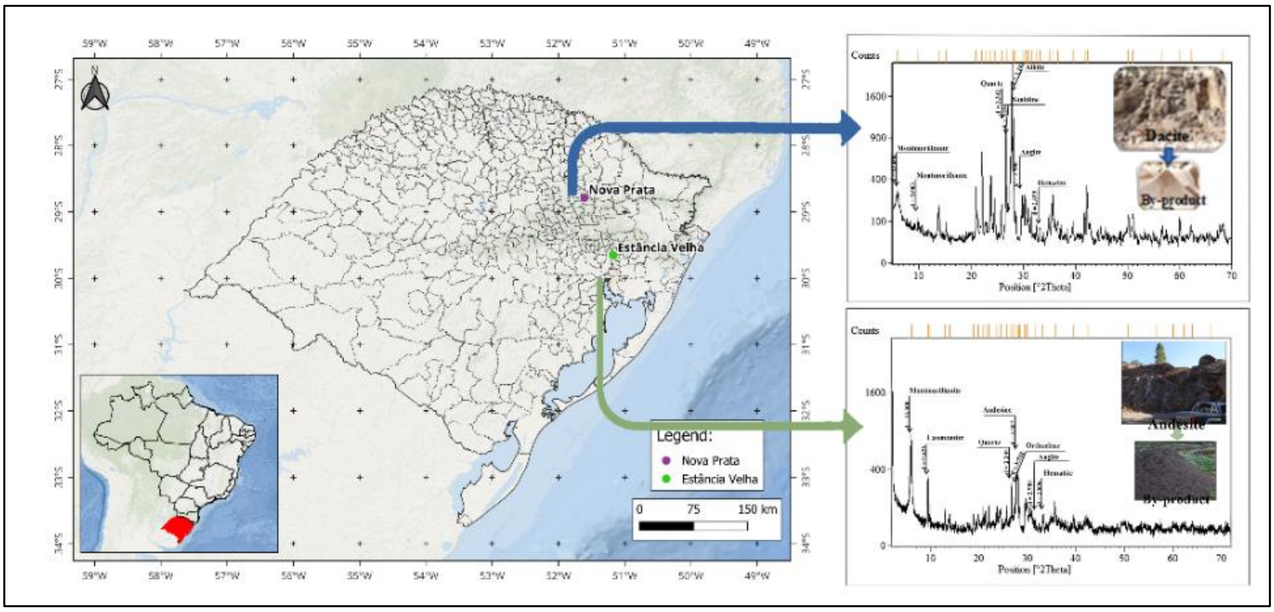
H I G H L I G H T S

• The dissolution experiments of by-products were performed with different extraction solutions.
• Volcanic rock by-product as a source of multi-nutrients.
• Three mathematical models were used to describe and estimate the behavior of multi-nutrients release from by- products.

GRAPHICAL ABSTRACT



ABSTRACT

The increase in demand for highly soluble fertilizers brings a global sustainability concern. Alternative sources for traditional fertilization are therefore needed. Rock powder use has been proposed as an alternative approach to soil remineralization. However, research on the agricultural potential of minerals and rocks as alternative sources of nutrients is limited to changes in soil chemical attributes or effects on crop yield. In this work, we report an experimental study addressing the dissolution of two silicate rock-derived powders (andesite and dacite) that were produced during mining activities in Southern Brazil. The rock powders were exposed to Milli-Q water at pH (7.4–8.8) range, in solutions of 0.1 mol L^{-1} citric acid at pH range 2.1–3.3, and Milli-Q water acidified with 0.5 mol l^{-1} acetic acid (pH 5–5.8), in a continuous mechanical rotatory shaker at room temperature. Dissolution kinetics were determined as a function of reaction times at 24 to 5760 h, and solution pH. Based on this kinetics, dissolution rates were determined for the individual powders and compared to expected values for aluminosilicates. Based on this comparison, it was shown that the application of andesite and dacite rock-derived powder to replace high soluble fertilizers is feasible due to high dissolution rates of their minerals. The average andesite dissolution rates in Milli-Q water, in citric acid solution, and in Milli-Q water acidified with acetic acid were 2.1×10^{-5}, 1.92×10^{-1} and 6.3×10^{-4} mmol cm^{-2} s^{-1}, respectively for Ca, being 183%, 22.6%, and 69.2% higher than for the dacite rock. This make andesite rock a potential substitute for carbonate-based liming. In contrast, the average dacite dissolution rates in Milli-Q water, in citric acid solution, and in Milli-Q water acidified with acetic acid were 1.05×10^{-5}, 7.22×10^{-5}, and 3.72×10^{-5} mmol cm^{-2} s^{-1}, respectively for K, being 72.0%, 61.4%, and 73.6% higher than the andesite rock. This highlights its potential use as a K source for agriculture to replace highly soluble K-fertilizers.

Keywords: Mineral dissolution; Silicate rocks; Andesite; Dacite; Multi-nutrients source; Sustainable agriculture; Dissolution kinetics.

2.1 INTRODUCTION

For a society increasingly aware of the degree of systemic disturbances caused by the increasing demand for several consumer products and by intensification in the exploitation of natural resources, particularly as in agriculture, alternative sources to traditional fertilization, are therefore needed (KORCHAGIN et al., 2019).

The use of rock powders as an alternative of soil fertilizer is a very old practice to increase soil nutrient content and crop productivity, particularly for tropical soils (Silva, 2016; Manning and Theodoro, 2018). This practice can be applied in many countries by exploiting local geological sources (MANNING and THEODORO, 2018).

Investigations into the agricultural potential of minerals and rocks as alternative sources of mainly K have been oriented by the fertility notion prevailing in agrarian sciences, restricting itself to the evaluation of changes in the soil chemical attributes or in the productivity of crops, without considering the factors associated with release kinetics and to the effects of weathering on the alteration of by-product minerals. Among the nutrients that that may be supplied by volcanic rock powders, K has been the most widely studied to determine whether it can become immediately available in soils at rates significant for crops.

According to Manning (2018), determine the dynamics of mineral nutrient release from rocks and understanding the processes of weathering and alteration of minerals, is critical to neutralize soil acidity in mined areas, for the remediation of contaminated areas, or as a nutrient source for agricultural crops, by the rock-derived powders application.

Mineral dissolution rates can be influenced by the presence of organic ligands, as such ligands may bind metal cations in solution, or may form complexes on the mineral surface that enhance dissolution rates. The dissolution effects are strongly dependent on ligand, mineral species, and on pH (VAN NOORT et al., 2018).

Several studies on K release kinetics were carried out with rock dust in dilute salt solutions, low molecular weight organic acids (citric and oxalic) and cation exchange resins (SILVA et al., 2013; MEIRA et al., 2014). These acids were also used as extractors in the K and Mg release kinetics by Silva (2016), and in the evaluation of the solubility of minerals of volcanic rock by Ramos et al. (2015). There is concern about the real effectiveness of these materials with the low solubility of rock minerals being the major limiting factor. Knowledge of dissolution kinetics is required to properly determine the nutrient supply capacity of rocks to soils; optimize its efficiency as a fertilizer to reduce the use of soluble fertilizers and develop guidelines for the safe and proper disposal of by-products, and reduce environmental pollution (NISHANTH and BISWAS, 2008).

In Southern Brazil, tonnes of rock powder are produced in different quarries (KORCHAGIN et al., 2019). Little research has been done on the kinetics of Al, Ca, Fe, K, Mg, Na and Si release from silicate rock-derived powders intended for agricultural use.

To study the applicability of andesite and dacite rock-derived by- products, leaching tests have been carried out. These by-products have been dissolved over a period of 24 to 5760 h, in Milli-Q water at pH (7.4–8.8) range, in solutions of 0.1 mol L^{-1} citric acid at pH (2.1–3.3) range, and Milli-Q water acidified with 0.5 mol L^{-1} acetic acid at pH (5–5.8) range, under stirred continuous on a mechanical rotatory shaker, at room temperature. These conditions were chosen to approximate natural weathering conditions, including the potential to form concentration gradients in the liquid phase, and limiting particle collisions that may abrade leached or precipitated layers. According to Hochella and Banfield (1995), such leached or precipitated layers may form on the particles during weathering in agricultural fields. During the experiment, the solutions pH was measured to observe the effects of different solution in the elements release and mineral dissolution rates. After the experiment, the concentrations of Al, Ca, Fe, K, Mg, Na and Si were used to calculate element release rates through the fluid flow rate, the specific surface area and mass of the solid used in the experiment (GUDBRANDSSON et al., 2011). The Information of this study are fundamental for ensuring safe and efficient use of silicate rock- derived by-products as soil fertilizer.

2.2 MATERIAL AND METHODS

2.2.1 By-product samples

Twenty kilograms of each by-product powder with particle sizes below 5.0 mm for chemical characterization and kinetic release experiment were used in this investigation. Vesicular andesite and dacite rocks, respectively, were from Estancia Velha, and Nova Prata, both of Rio Grande do Sul state, Southern Brazil (Figure 1).

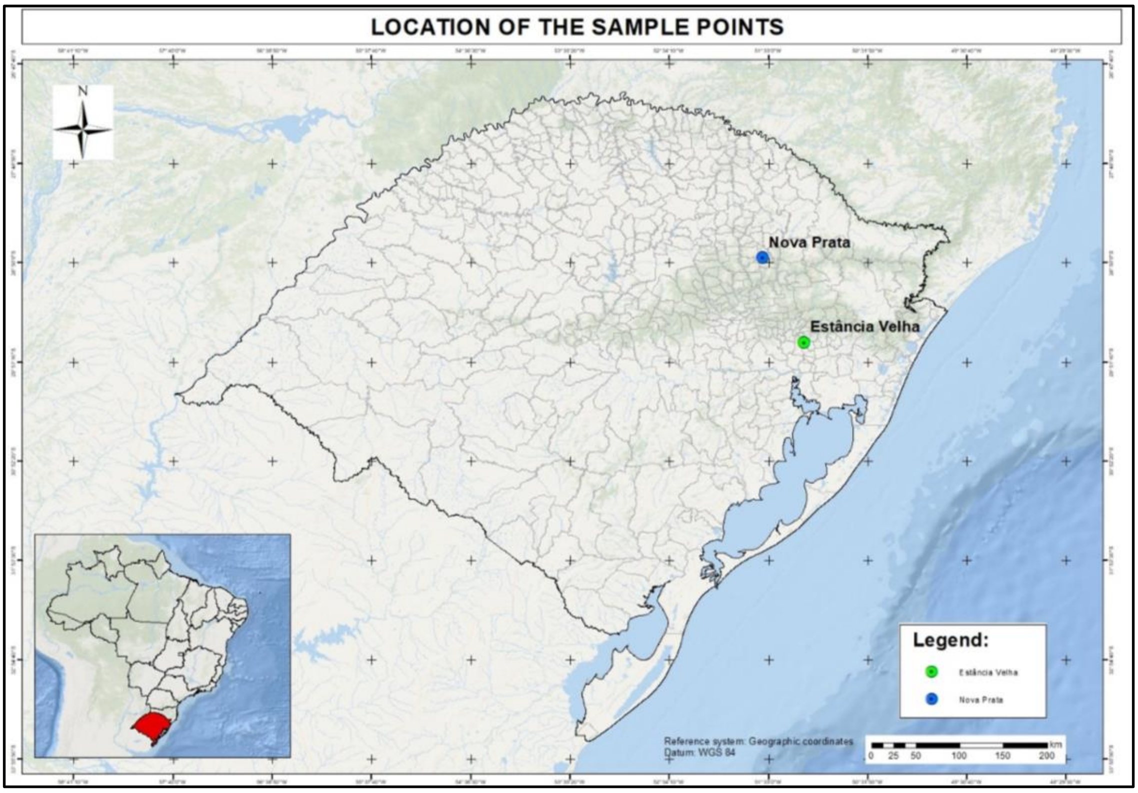


Figure 1. Studied area.

The study region is recognized for the large volume generated (52,400 m^3 annually) of mining tailings (TOSCAN et al., 2007). According to Nardy et al. (2008) in the Serra Geral Group the dominant volcanic rocks are basalt, basaltic andesite and andesite, followed by riodacite and little rhyolite, composed of 30 to 50% of plagioclase, 20 to 35% of augite and pigeonite and 5 to 15% of opaque minerals.

2.2.2 By-products particle size distribution

The granulometry of the by-products has great influence in nutrients release, because the smaller the grain size, the larger the surface area exposed to exogenous conditions (Ramos et al., 2017). The particle size distribution of the particles was determined by using laser diffraction equipment (CILASTM1064).

The specific surface areas of andesite and dacite were determined by an N2 adsorption Brunauer–Emmett–Teller method (BET, Shimadzu, Micromeritics FlowSorb II 2300).

2.2.3 By-products mineralogy

The mineralogical phases of the by-products were determined by X-ray diffraction (XRD) in a Philips X-ray diffractometer, according to Ramos et al. (2019).

2.2.4 By-products chemical composition

The determination of the chemical composition of major elements (in % of oxides weight) of the by-product samples was performed by X-ray fluorescence (XRF). Quantitative analysis was performed using the lithium tetraborate fused powder sample technique, with calibration curve from rock patterns. X-ray fluorescence technique was employed to determine the chemical composition of the by-products. This analysis was performed in compliance with Ramos et al. (2019).

2.2.5 Mineral dissolution and procedures

Dissolution experiments were carried out in in a continuous shaken mechanical system for 5760 h in a plastic vial, hermetically sealed, at room temperature (25 ± 1 °C). Table 1 shows the dissolution experimental conditions.

Table 1. Methods and procedures to extract and determine multi-nutrients release from solid to liquid phase.

Extractor solutions	pH	Concentrations	Amount of bay - products	Amount of solution	Shaking	Methods
		(mol L^{-1}	(g)	(L)	(rpm)	
Milli-Q water (W)	7,05	-	250	2,5	30	BSEN (2002)[a]
Cítrico acid (CA)	1,87	0,1	250	2,5	150	Teixeira et al. (2015)
W + acétic acid (AA)	5,00	0.5 acétic acid	100	2,0	30	Etim na Onianwa (2013)

In experiment with mildly acidified water by acetic acid (AA), the solutions pH was adjusted at 5 ± 0.2 by addition of 10 mL of 0.5 mol L^{-1} acetic acid solution, every seven days. An amount of 20 mL of each solution was collected at 24, 48, 72, 96, 168, 336, 504, 720, 1440, 2160, 2880, 3600, 4320, 5040, and 5760 h and filtered. Before aliquots collect, the pH of the extraction solutions was measured in DM-2P Digimed pH-meter, to verify the relationships between this parameter with the mineral dissolution rates. After each collect was made the replacement of the solutions and the by-products remaining in the filters for vials. These experiments were performed in laboratory conditions with three replicates. The concentrations of multi-elements released in each solution were quantified by ICP-AES.

The Al, Ca, Fe, K, Mg, Na, and Si concentrations, were used to calculate element release rates (ri,j) using the dissolution equation (GUDBRANDSSON et al., 2011):

$$\text{Ri, j} = \frac{\text{CiFR}}{\text{Ajm}} \tag{1}$$

where ci represents the concentration of the element in the outlet fluid, FR designates the fluid flow rate, Aj and m refer to the specific surface area and mass of the solid, respectively.

2.3 RESULTS AND DISCUSSION

2.3.1 By-product particle size characterization

The particle size distribution of the by-products, obtained by a sieving, is shown in Figure 2. The size distribution analysis showed that 100% of the particles of andesite had a minimum size of 500 µm and 50% had a minimum size of 31 µm. Dacite had 100% of the particle sizes below 500 µm and 50% below 99 µm. This lower size distribution of andesite may increase nutrients release. Priyono and Gilkes (2008) investigated the multi-nutrients dissolution kinetics of silicate rock with particle sizes below 0.25 mm and 0.15 mm in organic acid solution. The authors showed that the dissolution rate of cations increased with smaller particle size.

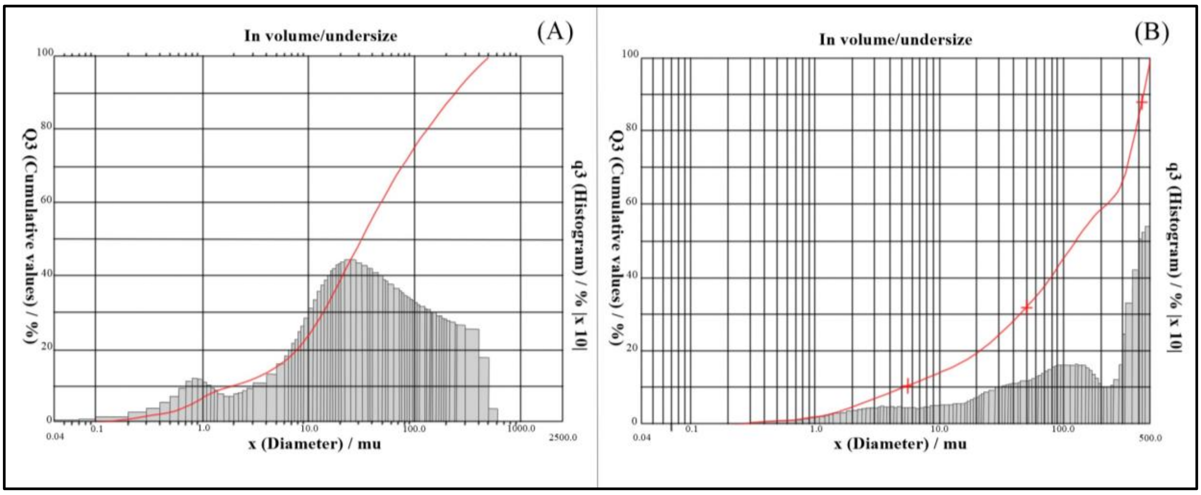


Figure 2. Granulometric distribution curves obtained by laser diffraction. (A): Andesite rock powder; (B) Dacite rock powder.

The specific surface area, as determined by BET method, was 10.05 m^{-2} g^{-1} for andesite and 4.90 m^{-2} g^{-1} for dacite. These results agree with those obtained by Nielsen and Fisk (2008) that measured the specific surface area of 13 samples of silicate rock taken from the sea using the BET method and showed a range of 0.3–52 m^{-2} g^{-1}.

2.3.2 Mineralogy

Table 2 shows the main mineral phases of the by-product samples, and the semi-quantitative approximation based on the intensity of the X-ray diffraction peaks (Figure 3).

The andesite rock mineralogical studies showed the high content of laumontite, a zeolite group mineral (Figure 3A), which is related to vesicles filling, which gives the rock an alkaline characteristic and high cation exchange capacity (MASTINU et al., 2019). This feature is fundamental to provide the exchange of nutrients between mineral particles and soil/water/roots (NUNES et al., 2014).

Table 2. Semiquantitative approximation (%) of the main mineral phases present in the andesite and dacite samples.

Mineral species	Chemical formulas	Mineral groups	Abundance (%)
Andesite			
Andesine	$(Na,Ca)(Si,Al)_4O_8$	Plagioclases	27.1
Laumontite	$Ca_4Al_8Si_{16}O_{48}.14H_2O$	Zeolite	12.9
Hematite	Fe_2O_3	Hematite	2.70
Orthoclase	$KAlSi_3O_8$	K-Feldspars	13.3
Quartz	SiO_2	Silica	5.40
Montmorillonite	$(Na,Ca)(Al,Mg)_2Si_4O_{10}(OH)_2.n(H_2O)$	Smectites	14.1
Augite	$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$	Pyroxenes	24.6
Total			100.1
Dacite			
Albite	$NaAlSi_3O_8$	Plagioclases	35.3
Hematite	Fe_2O_3	Hematite	1.00
Cristobalite	SiO_2	Silica	5.80
Quartz	SiO_2	Silica	12.4
Montmorillonite	$(Na,Ca)(Al,Mg)_2Si_4O_{10}(OH)_2.n(H_2O)$	Smectites	2.20
Sanidine	$(K,Na)(Si,Al)_4O_8$	K-Feldspars	28.6
Augite	$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$	Pyroxenes	14.7
Total			100.0

This shows great potential for by-products application as soil fertilizer (RAMOS et al., 2017). The presence of montmorillonite, with smaller proportion in dacite rock, and hematite shows the marked condition of weathering of the rocks (Figure 3A-B). Andesine occurs in andesite and albite in dacite, that are feldspar class minerals (Figure 3A-B). Andesine has a high proportion of calcium and sodium, and albite has a high sodium content in their structure. These minerals resistance to weathering is low (ALLEONI and MELO, 2009), with high potential for the release of calcium and sodium to medium. X-ray diffraction analysis show the occurrence of orthoclase in the andesite and sanidine in the dacite (Figure 3 A-B), that are minerals of K-feldspar group. Potassium is released when these minerals are slowly weathered (RAWAT et al., 2016). The pyroxenes such as diopside in andesite, and augite in dacite can release Mg, Fe, and Ca, and form new minerals. These results concur with Deer et al. (2013), that most common rock-forming minerals were plagioclases, pyroxenes, and feldspar. The susceptibility to weathering that the mineral phases present in the studied samples, are a good indication of the ability of multi- nutrients release to the soil.

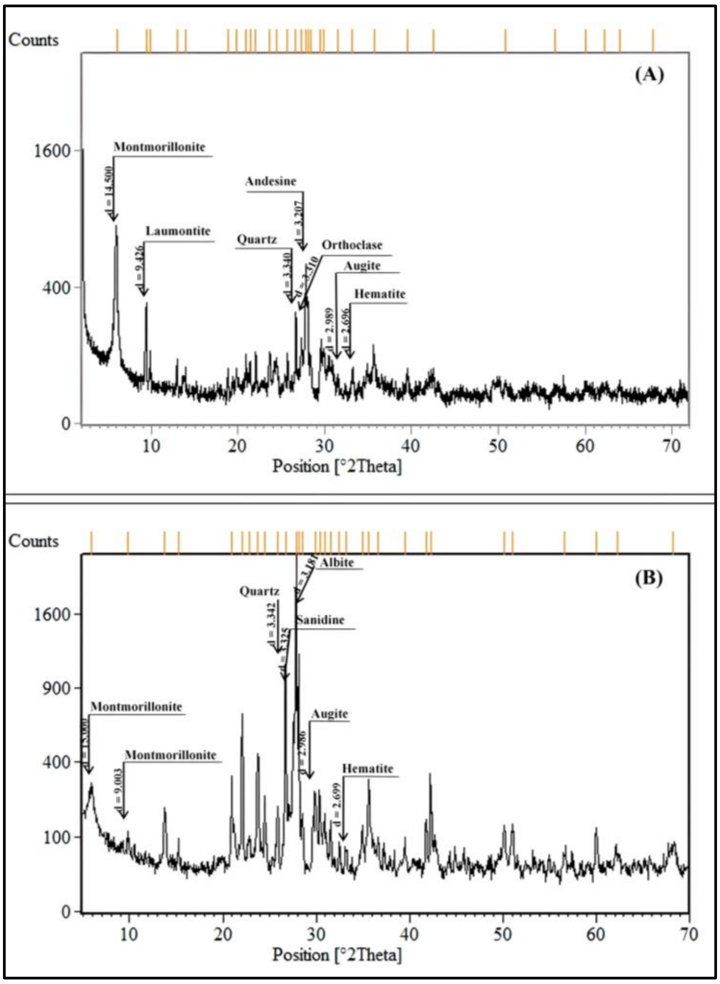


Figure 3. (A) X-ray diffractogram of andesite; (B) X-ray diffractogram of dacite.

2.3.3 By-products chemical composition

The chemical composition of the by-products, expressed as major and minor elements, allowed to classify the rocks as andesite (SZYMÁNSKI and SZKARADEK, 2018) and dacite (STRECKEISEN, 1976). According to the Total Alkali Silica (TAS) classification of andesite, it includes an average amount of silica (57% to 63%), more than basalt and less than dacite (GILL, 2010). Compared to each other, and as expected, andesite contains higher Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, Na_2O and MnO contents. In dacite the SiO_2 and K_2O contents are higher than in andesite (Table 3). Based on macronutrient K content, the dacite would be the most indicated as potassium fertilizer. Potassium is very necessary nutrient for enhance the productivity of many crops (CARVALHO et al., 2018). The andesite has higher levels of Mg and Ca, which are also important macronutrients to agriculture. These elements could be supplied from pyroxene alteration (BUCHS and HOWIE, 2016). The role of calcium is to regulate nutrient transport, and to support many enzyme functions (GILLIHAM et al., 2011). Magnesium is important to the photo- synthetic process (GUO et al., 2016). The P_2O_5 content of by-products are similar (Table 3), representing more than three times the P_2O_5 content of the Earth's crust average.

Table 3. Concentration of the major elements of by-products samples (%) expressed by respective oxides.

Oxides	Andesite	Dacite
	%	
SiO_2	57.1	67.1
TiO_2	1.17	0.92
Al_2O_3	14.1	12.6
Fe_2O_3	9.50	6.41
MnO	0.17	0.11
MgO	3.57	2.18
CaO	5.38	3.14
Na_2O	3.22	2.92
K_2O	2.49	3.79
P_2O_5	0.26	0.28
LOI	2.70	0.53
Total	99.7	99.9

[a] Loss on ignition.

Table 3 shows the concentration of the major and minor elements of by-products expressed by respective oxides. These results agree with those obtained by Ramos et al. (2019), which characterized a similar rock to those of this study and its application as soil remineralizer in black oat and maize crops.

According to Donatello et al. (2010) the P_2O_5 crustal average concentration is 1.18g kg^{-1} (0.1%). Phosphorus is essential to all life, including plants (VANCE et al., 2003). Silicon is essential to crop growth, although it is not regarded as an essential nutrient. According to Epstein (1999) Si-deficient plants have generally structurally weaker and more prone to growth, development and reproduction irregularity. Silicon is the only nutrient that is not harmful when over-absorbed. In addition, it helps to control pests and increase the productivity and quality of agricultural products (KEEPING, 2017; BEERLING et al., 2018).

An important concern when applying silicate rock-derived powders to agricultural soils is the potential toxic elements release, as these rocks can contain such elements in relatively high concentrations. Ramos et al. (2017, 2019), studied the nutrients release of silicate rock-derived powder and concluded that the rock has low concentrations of potential toxic elements, which do not represent an environmental risk.

2.3.4 Multi-elements release and their rates

The concentration of multi-elements released from andesite and dacite in extractant solutions, and the solutions pH values, as a function of reaction time are showed in supplementary material. Figure 4 shows the accumulated multi-nutrient concentrations released by the by-products at 24–5760 h.

The all multi-elements release from both by-products in Milli-Q water was very low (Figure 4); the accumulated release of Al (8.03 mmol kg^{-1}) and K (11.2 mmol kg^{-1}) from andesite at 5740 h was smaller than from dacite (12.2 mmol kg^{-1} of Al and 19 mmol kg^{-1} of K). Calcium, Na and Si cumulative released was similar from both by-products, around 60, 103 and 70 mmol kg^{-1}, respectively. The Mg and Fe (32.4 and 1.31 mmol kg^{-1}) accumulated release from andesite was significantly higher than from dacite (9.2 and 0.62 mmol kg^{-1}). This low release in water, suggests the precipitation of (Al, Ca, Fe, K, Mg, Na and Si)-bearing mineral (s) (SUGIMORI et al., 2009), that make up the andesite and dacite rocks. The low release of multi-elements from andesite and dacite rock powder in water, also can be explained by its high pH value, and its low ability to remove interlamellar cations from rock minerals (SILVA et al., 2013).

The most distinguished differences were observed in the accumulated release of Ca, Mg and Fe from andesite rock, and of Al, K, Na and Si from dacite rock, in citric acid solution (Figure 4); andesite rock released 3263 mmol kg^{-1} of Ca, 3687 mmol kg^{-1} of Mg and 1209 mmol kg^{-1} of Fe, while the dacite released 1523, 783 and 870 mmol kg^{-1}, respectively.

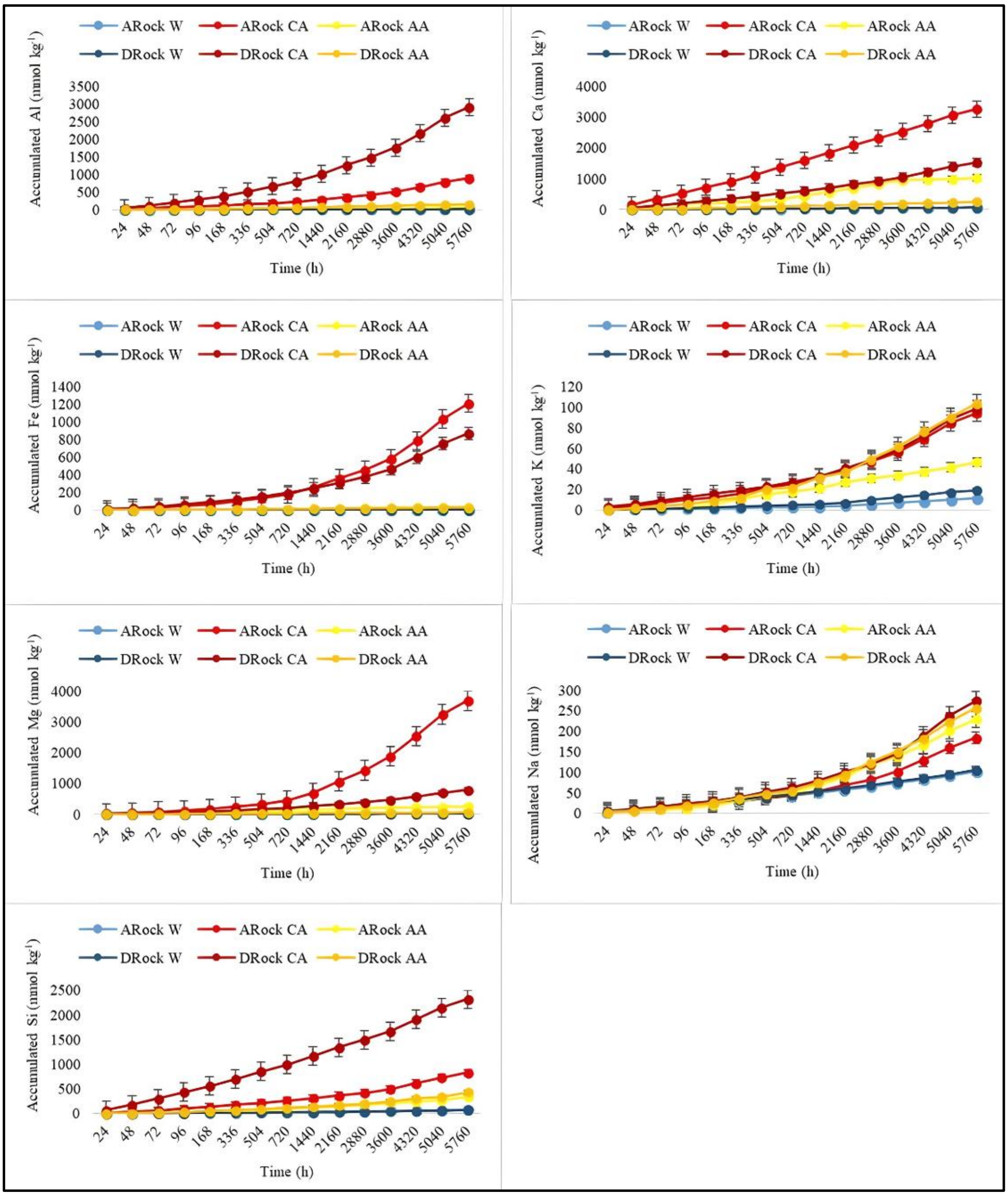


Figure 4. Accumulated amounts of A1, Mg, Si and Fe (mmol kg−1) released from biotite under different extractants solution, plotted against experimental time (h) at room temperature. Vertical bars (I) represent the standard error from three replications.

In andesite and dacite rock mineral dissolution in water acidified with acetic acid (Figure 4), the behavior of accumulate multi-elements release was like in Milli-Q water. There were a lot of differences in released amounts between Milli-Q water acidified with acetic acid, N100% above than Milli-Q water, and N100% below than citric acid solution. The dissolution rates (r) from andesite and dacite are shown as a function of time in (Figure 5), and as a function pH in (Figure 6), where the differences in the amounts of releases between extraction solutions are emphasized. All multi-elements release rates of both by-products decreased with increasing pH, and increased with decreasing pH (Figure 6), displaying a synclinal shaped pH dependence.

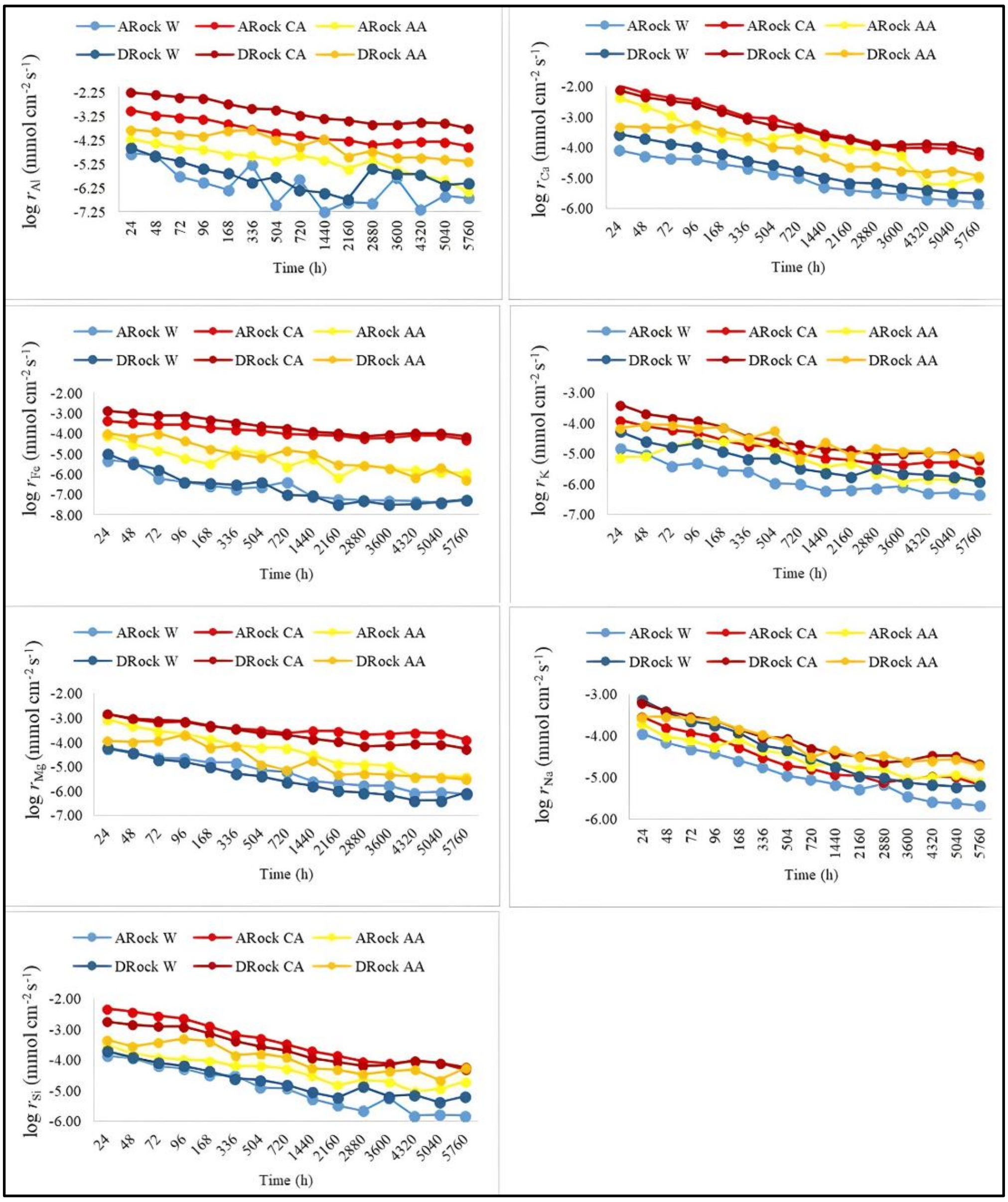


Figure 5. Multi-elements release rates from andesite and dacite as a function time.

Silicon release rates are important in silicate dissolution because Si is a network former and represent silicate dissolution rates. The release rate of Si of andesite at pH < 3.25 was faster by about 6% above than dacite (Figures 5-6). The faster Si release was also evident for dacite dissolution at pH <5.1, about 9% higher andesite. The release rates of Si from andesite and dacite rock, at pH <3.25 can be characterized by much faster rates by about two orders of magnitude than those at pH <5.1, and by similar rates for dissolution of both andesite and dacite (Figure 5A-B). These faster Si release rates can be attributed to the Si adsorption onto Fe^{3+} oxides/hydroxides surfaces (SIEVER and WOODFORD, 1979); precipitation of Si-bearing secondary minerals; inhibition of silicate dissolution by the formation of secondary precipitates or altered layers on mineral surfaces (MORRIS and FLETCHER, 1987); and direct dissolved oxygen (DO) interaction with silicate surfaces (OUYANG et al., 2003). Experiments at pH > 9 (in Milli-Q water) (Figure 6) have the lowest release rates and exhibit the greatest dispersion, possibly due to the effects of precipitation. These results confirm the observation of Sugimori et al. (2009), cited earlier in this study. Thus, Milli-Q water does not affect the dissolution rates of either andesite or dacite at pH 7.6–8.8.

The average rate constants for release of Na and Al from andesite (log r = −7.6 and −6.9 mol cm^{-2} s^{-1}) and dacite (log r = −7.1 and − 6.8 mol cm^{-2} s^{-1}) are about three order of magnitude fast than those reported by Declercq et al. (2013) for rhyolite dissolution at pH 2 and 25 °C. The rates constants reported for plagioclase are higher to those reported by Holdren and Speyer (1987) for dissolution of andesine at a pH of 3, which ranger from log r = −15.1 to −14.6 mol cm^{-2} s^{-1}. The variation of dissolution rates from dacite with pH was similar to that obtained by Hellmann (1994) for albite dissolution (−4.1 mol cm^{-2} s^{-1} at pH 5), and for K-Feldspar (−6.2 mol cm^{-2} s^{-1} at pH 5–8.6) from andesite and dacite (Figure 6). It's important to highlight, that the andesite and dacite dissolution rates in all extraction solutions were higher than the K-Feldspar dissolution rates (1.67 × 10–12 mol cm^{-2} s^{-1}at pH 5) reported by Bevan and Savage (1989). Andesite and dacite dissolution rates were like pyroxenes dissolution rates obtained by Sverdrup (1990) at pH < 6 (−7.3 mol cm^{-2} s^{-1}) (Figure 6).

White and Brantley (2003) reported experimental weathering rates that decreased constantly with time over at least six years. The authors showed that ongoing weathering will lead to a slowing down of mineral dissolution. It is notable that weathering rates based on natural systems are of 1 to 3 orders of magnitude less than those estimated in laboratory experiments (SVERDRUP, 1990). In contrast to this interpretation, in experiment conducted by Leonardos and Theodoro (1999) at the Água Limpa farm in Brasília, Brazil were used three forms of fertilization over 13 years in latosols (volcanic rock powder, NPK combined with volcanic rock powder, and NPK). According to the authors, the growth of the eucalyptus plants grown in the NPK-fertilized plot was rapid until the fourth year. After this period, tree growth decreased significantly as compared to the growth of plants treated only with rock dust, which grew linearly, although more slowly at the beginning.

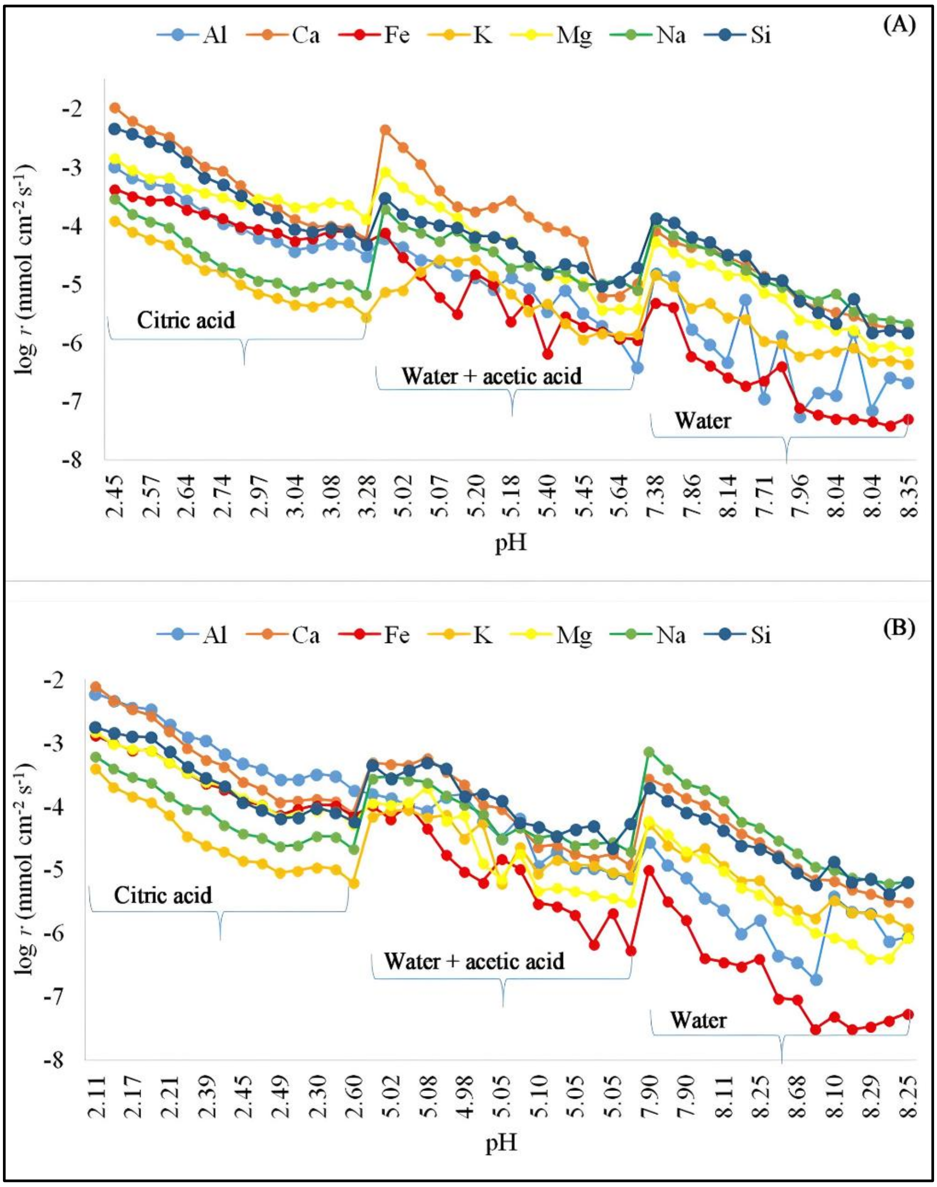


Figure 6. Multi-elements release rates from (A) andesite and (B) dacite versus solutions pH.

The weathering rates estimated in laboratory experiments of the present work, although they are upper to 1–3 orders of magnitude than those on natural systems are of great relevance for providing subsidies for better rock choice and adaptation of fertilization recommendations.

2.4 CONCLUSIONS

This work analyzed the kinetics rates of the releasing of multi- nutrients from two volcanic rock mining by-products to providing subsidies for better adaptation of fertilization recommendations. The agricultural use of by-products in tropical soils suggests replacing soluble fertilizers because there are primarily composed of aluminosilicates, whose nutritional properties significantly influence soil fertilization. The important elements, such as Ca, K, Mg, P, and Si, for agricultural production are also present in both by-products. However, several factors restrict the rock dust use as alternative source of nutrients for soil and are the main challenges of the technique. We can highlight the complex composition of the rocks; location of the deposits of these rocks in relation to the site of application; the presumed low-cost methods of milling; and the behavior of these rocks in the interaction with the environment where they will be applied.

The results of kinetics of multi-nutrients release of this study indicated that the by-products have potential to be used as a multi- nutrients fertilizer and liming. These results reinforce the importance of deepen researches related to rocks, which should be tested for use in varying conditions of soils, crops and agricultural systems in different regions of the world. This is justified by the fact that these rocks are abundant with wide distribution and variable in the earth.

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DECLARATION OF COMPETING INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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SUSTAINABLE RELEASE OF MACRONUTRIENTS TO BLACK OAT AND MAIZE CROPS FROM ORGANICALLY-ALTERED DACITE ROCK POWDER

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3 SUSTAINABLE RELEASE OF MACRONUTRIENTS TO BLACK OAT AND MAIZE CROPS FROM ORGANICALLY-ALTERED DACITE ROCK POWDER

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ABSTRACT

By-products from the dairy industry and mining activities represent a great environmental overload, which justify research for value-added reuse of these by-products (dairy sludge and dacite rock powder). Dairy sludge is generated at a rate of about 0.2–10 l per liter of processed milk, and dacite powder, from rock mining extraction and processing, is generated for about 52,400 m^3 per year in Nova Prata city, Southern Brazil. For both by-products, the compositions of calcium (Ca), magnesium (Mg), potassium (K) and phosphorous (P), arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb) were determined by using appropriate analytical techniques. A greenhouse experiment was conducted to determine release of macronutrients, such as Ca, K, Mg, and P, from by-products to support black oat (Avena strigosa) and maize nutrition. Twelve by-products doses were blended with a typic Hapludox soil and were applied to pots with five replications each. Black oat (first cultivation) and, sequentially, maize (second cultivation) were cultivated for 70 days each. Ameliorations in soil chemical attributes, leaf dry matter yield, and plant nutritional status were evaluated at the end of each cultivation. There was a significant ($p < 0.05$) increase in all parameters evaluated in a dose of 7251 kg ha^{-1} of dacite rock powder and 20,594 kg ha^{-1} of dairy sludge. Compared to the control treatments, both crops grew well better on all mixtures. The presence of potentially toxic elements in both by-products was irrelevant, indicating that effective blending of dacite rock powder along with dairy sludge could be a potential source of Ca, K, Mg, and P in agriculture without posing a risk of contamination to the environment.

keywords: Dairy sludge, Dacite rock powder, By-products, Soil fertilization.

3.1 INTRODUTION

The dairy industry requires large amounts of water for washing pipes, machinery, and floors, but the liquid residue of a dairy product originates mainly from the manufacturing process, generating a large volume of wastewater, about 0.2–10 l per liter of processed milk (Balannec et al. 2005). The high production and proper sludge disposal are problematic issues for the dairy industry (Bhadouria & Sai, 2011). The main negative impacts of these byproducts are not only the contamination of drinking water but also the harm to aquatic ecosystems, which can lead to death of fish and other animals, besides emitting unpleasant odors into the atmosphere and accumulation of waste (Qasim & Mane, 2013). In addition, sludge generated in the flotation treatment of the dairy industry, generally a source of N, could also contribute significant amounts of phosphorus (P), calcium (Ca), potassium (K), sodium (Na), magnesium (Mg), sulfur (S), zinc (Zn), and other important nutrients for crops (Qasim & Mane, 2013). In natura application of dairy sludge is suitable from the environmental outlook, and it shows a beneficial property in the recovery of degraded land. Sludge utilization favors plant yields and can reduce the use of highly soluble fertilizers (Oszust et al. 2015). The application of sludge produced by the dairy industry in agricultural soils is an attractive option for their reuse because several nutrients are provided and the physical attributes of the soil can be ameliorated (Frac et al. 2017). Several studies with these types of sludge demonstrated an increase in agricultural productivity (Macoon et al. 2002) and ameliorated soil fertility (Suárez et al., 2004). This is because plants can modify the pH values of the rhizosphere, but they also exude organic acids and other strategies, increasing solubilization of insoluble compounds, which can increase nutrient availability (De Conti et al. 2019).

The main negative aspect of the use of dairy sludge is the low K content (López-Mosquera et al. 2002). Still, the dairy sludge is very rich in organic material, so it is expected that it has high bioactivity. This characteristic may be advantageous for blending with another less bioactive by-product, but with a larger nutrient diversity, such as dacite rock dust (Ferrari et al. 2019). The association of high biological activity materials, such as dairy industry sludge, with rocks may influence the process of alteration of rock minerals (Stranghoener et al. 2018). According to Anjanadevi et al. (2016), the release of rock nutrients can be hastened by blending the rocks with organic by-products, thereby promoting mineral dissolution by biological process.

Given the complex nature of rock minerals, appropriate analytical procedures need to be defined to satisfactorily characterize the composition and bioavailability of existing rock elements, as crop responses may be associated not only with K from rocks, but also with synergistic factors and effects arising from its composition (Ramos et al. 2017).

Rock minerals and industrial minerals typically do not generate environmental impacts such as acid drainage and environmental contamination. The survey carried out by Toscan et al. (2007) revealed that in 2005, an amount of approximately 52,400 m^3 of rock mining by-product was generated in Nova Prata, Rio Grande do Sul, Brazil. As they are sometimes found in more populated areas or near cities, the mining industry faces the challenges of avoiding landscape damage and properly disposing the processing tailings. In addition, they compete for physical space with the community in their surroundings, due to the opportunity cost of using the areas (Lins, 2008).

In Brazil, volcanic rocks present good potential as a source of K. According to Santos et al. (2016), the rock powder addition can be an effective K fertilizer for cultivation of eucalyptus, maize, and grass. Rock powder has been reported as a soil remineralizer and a source of plant nutrients in several countries such as Australia and India (Basak, 2019; Basak et al. 2020), Brazil (Dalmora et al. 2020; Ramos et al. 2019), and the UK (Manning, 2018; Mohammed et al. 2014). Theodoro and Leonardos (2006) showed that the rock powder application blended with organic by-product achieved better productivity crop yields than the application of just rock powder. The combined application of dacite rock powder with dairy sludge can be a promising approach because insoluble nutrients in mineral rocks can be made available by the action of organic acids produced during organic-matter decomposition (Basak et al. 2017). These point to the possibility of converting by-products with environmental contamination potential to inputs to be used in agriculture. This may be an alternative means of combating the waste problems of the dairy and rock mining industries. It is necessary to conduct more research to verify the fertilizing property of these by-products compared to high-solubility fertilizers. It is also relevant that their use as agricultural input is properly planned to maximize benefit of their qualities and minimize the potential environmental risks.

A relevant factor that makes the use of dairy sludge and rock mining by-products attractive in agriculture is the abundance of elements such as nitrogen (N), Mg, Ca, and P. However, it is extremely relevant to monitor the soils that receive these materials to detect possible long-term accumulation of harmful elements (Cavallaro et al. 1993; López-Mosquera et al. 2000). López-Mosquera et al. (2000) showed that the application of sludge from the dairy industry to acidic soils did not accumulate potentially toxic elements (PTEs) during the experimental period of four years.

In a previous study, Ramos et al. (2019) performed a detailed granulometric, petrographic, chemical, and mineralogical characterization of the dacite rock powder and its potential use as soil remineralizer in the growth of black oat (Avena strigosa) and, sequentially, maize crops. The use of dacite rock powder and dairy sludge by-products is still an unexplored research field. The aims of this present work were to assess the inorganic by-product (dacite rock powder) and the organic by-product (dairy sludge) blended with tropical soil as fertilizer to determine the ideal proportions of these three components for the production of black oat and maize. It is possible to state that the present study stands out for its contribution to the mitigation of by-product production, since it is the first study to reuse these by-products as soil fertilizer.

3.2 MATERIALS AND METHODS

3.2.1 Samples of Dacite Rock Powder, Dairy Sludge, Soil, and Seeds

Fifty kilograms of dacite rock powder passing an ASTM Series #10 sieve, 2 mm fraction, was supplied by the Sindicato da Indústria de Extração de Pedreiras quarry, Nova Prata city, Rio Grande do Sul state (RS), Brazil. The dairy sludge was obtained from the dairy industry of Nova Petrópolis city, RS, Brazil. An amount of 200 l of dairy sludge was collected in 20-l capacity plastic containers directly from maturation ponds, after having undergone maturation for 7 days. A 5-l portion of the dairy sludge sample was oven-dried at 40 ^oC until reaching constant weight and sent for chemical composition analysis.

The typic Hapludox soil (USDA, 1999) was collected from the region of Nova Santa Rita, RS, at depths of 0–20 cm (A-horizon), in an amount weighing 800 kg. This material was air-dried, homogenized, sieved, and quartered. For soil fertility analysis and granulometric distribution, an amount of approximately 1 kg of soil was used. Soil fertility analysis was performed according to Donagema et al. (2011), before and after plants harvesting. Table 1 shows the results of soil fertility analyses.

Black oat is a grass recommended for fall-winter green manure and successfully used in the rotation and/or succession of soybean, bean, and sunflower crops. Black oat cultivation ‘‘breaks’’ the cycle of pests, diseases, and nematodes and reduces weed infestation, as well as producing ‘‘mulch’’ for direct planting of grains and vegetables. It is also an excellent fall-winter forage and can be eaten by sheep, goat, and cattle in direct grazing, hay, and silage (Velazco, 2013). Maize, the most important commercial plant originating in the Americas, is a highly polypic species, with about 300 breeds and thousands of varieties. Its culture is widely spread around the world, featuring specific races and varieties adapted to different ecological conditions (Fornasieri Filho, 2007).

Table 1. Attributes of the typic Hapludox soil collected from the top 0–20 cm layer and used in the experiment.

Atributes	Unit	Soil
pH in H_2O		5.2
H + Al	$cmol_c$ dm^{-3}	3.5
CEC*		4.0
Al exchangeable	extractor KCl 1 mol l^{-1}	0.3
Ca exchangeable	extractor KCl 1 mol l^{-1}	2.6
Mg exchangeable	extractor KCl 1 mol l^{-1}	0.7
Saturação %		
Al		7.8
Base		49
Clay		21
Organic matter		1.6
P available	extractor Mehlich-1	62
K	extractor Mehlich-1	62

*Cation exchange capacity

3.2.2 Analytical procedures

A detailed procedure, including thin-section petrographic description, mineralogical characterization, and chemical analysis, in percentage weight of oxides, of the dacite rock powder, was performed by Ramos et al. (2019). X-ray diffraction (XRD), and X-ray fluorescence (XRF) techniques, were used by the authors.

A combination of HNO_3, HCl, $HClO_4$, and HF acids, in accordance with García-Delgado et al. (2012), was used for dairy sludge and dacite rock powder sample digestions before quantification by inductively coupled plasma–mass spectrometry (ICP–MS) of the PTEs such as arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), and selenium (Se). Calcium, K, Mg, and P were determined by using inductively coupled plasma–atomic emission spectrometry (ICP–AES).

Soil pH was measured in soil–water (1:1) suspension. Soil P and K were extracted according to the Mehlich 1 method, and exchangeable Ca and Mg were extracted with 1 mol l^{-1} KCl and were all analyzed by ICP–AES.

3.2.3 Experimental site and preparation

In 2013, two-pot experiments were conducted in a plastic greenhouse, located at Environmental Research Center of La Salle University in Nova Santa Rita, RS. Different soil mixtures were studied in 12 dm^3 pots. The treatments in Table 2 were defined according to the Brazilian Society of Soil Science (SBCS 2004).

3.2.4 Experimental design

In experiment 1, black oat was cultivated on increasing doses of dacite rock powder in experimental soil and on increasing doses of the mixtures of dacite rock powder and dairy sludge in experimental soil. Five replicates of each treatment were performed, resulting in 60 pots. Nine seeds of black oat were planted in pots containing 10 dm^3 of soil; these were the only three plants grown for 70 days. The black oats were harvested, and the fresh matter was dried at 40 °C until it reached a constant weight, weighed, and milled for analysis of the dry matter. Soil samples were collected of all for chemical and physical analyses in an amount of 500 cm^3 from each pot at depths of 0–20 cm. The chemical analyses were performed on composite soil samples representing all replicate pots of each treatments.

In experiment 2, the remaining soil samples were homogenized, sieved in a 4-mm mesh sieve, and put in the same pots. Nine seeds of maize were planted, and only three plants were grown for 70 days. The maize was harvested on January 30, 2014, and fresh matter and soil samples were treated as a described above for black oat.

The effect on soil amelioration, growth, and dry matter production of black oat, of increasing doses of dacite rock powder blended or not with dairy sludge in soil was compared with each other and between the control treatments (Table 2). These experiments allow the comparison of the fertilization efficiency of the dacite rock powder and the dacite rock powder blended with dairy sludge and their application for the fertilization of black oat and maize. In addition, to evaluate the immediate and residual effects of the by-products, all results were evaluated statistically by using of Tukey test at a significance level of 5% ($p < 0.05$) using the statistical software SAS Enterprise Guide 6.1.

Table 2. Treatments applied to the soil

Treatments	*DL	Dacite	KCl	Sludge	**TSP	K_2O		CaO		MgO		P_2O_5	
	($kgha^{-1}$)	($kgha^{-1}$)	($kgha^{-1}$)	($kgha^{-1}$)	($kgha^{-1}$)	Dacite ($kgha^{-1}$)	Sludge ($kgha^{-1}$)	Dacite ($kgha^{-1}$)	Sludge ($kgha^{-1}$)	Dacite ($kgha^{-1}$)	Sludge ($kgha^{-1}$)	Dacite ($kgha^{-1}$)	Sludge ($kgha^{-1}$)
PK-Absolute control	3300	0	0	0	0	0	0	0	0	0	0	0	0
P-Standard control	3300	0	0	0	238	0	0	0	0	0	0	0	0
K-Control	3300	0	100	0	0	0	0	0	0	0	0	0	0
PK-Standard control	3300	0	100	0	238	0	0	0	0	0	0	0	0
R906	3300	906	0	0	238	30	0	32	0	21	0	2	0
R1813	3300	1813	0	0	238	60	0	65	0	41	0	5	0
R3625	3300	3625	0	0	238	120	0	129	0	82	0	9	0
R7251	3300	7251	0	0	238	240	0	258	0	165	0	19	0
R906 + S2574	3300	906	0	2574	0	30	1.3	32	15	21	2.5	2	50
R1818 + S5149	3300	1813	0	5149	0	60	2.6	65	30	41	5	5	100
R3625 + S10297	3300	3625	0	10.297	0	120	5.2	129	60	82	10	9	200
R7251 + S20594	3300	7251	0	20.594	0	240	10.4	258	120	165	20	19	400

* Dolomitic limestone (DL) with total neutralization relative power (TNRP) of 72%; **Triple superphosphate TSP

3.3 RESULTS AND DISCUSSION

3.3.1 Chemical composition of dacite rock powder and dairy sludge

The chemical compositions of the dacite rock powder and the dairy sludge, determined by ICP– MS and ICP–AES, as well as the limits of allowed PTEs in sewage sludge (SS), for application in agricultural soils, by legislations of Brazil (2006), European Union (EU, 1986), and USA (USEPA, 1999), are presented in (Table 3).

The data in Table 3 show that Ca, K, and Mg concentrations in the dacite rock powder were higher than in the dairy sludge. The function of Ca is to control nutrient transport, and to assist various enzymatic functions of plants (White & Broadley, 2003). Potassium is an essential nutrient for plant development, which acts on activation of enzymes in the formation of organic substances, in the synthesis of protein and starch, and in regulation of respiration and photosynthesis (Rawat et al. 2016). Magnesium promotes the activation of enzymes in photosynthesis, supplies adenosine triphosphate as an energy source, and is involved in the transport of photosynthates between the plant organs (Kwano et al. 2017). In contrast, the P content in the dairy sludge was higher than in the dacite rock powder. Phosphorus is fundamental for all forms of life (Vance et al. 2003). The levels of PTEs in the dairy sludge were below the levels permitted for sewage sludge by all studied legislations (Table 3). The results concur with the studies of López-Mosquera et al. (2002), who reported similar concentrations of elements in dairy sludge of Spain.

In Brazil, there is a legislation with well-defined specifications for the use of rock powder in soil fertilization. These include the maximum permitted limits for PTEs, which are 15, 10, 0.1, and 200 ppm for As, Cd, Hg, and Pb, respectively (Brazil, 2016). According to (Table 3), the levels of PTEs in the dacite rock powder were below the limits allowed for its application in Brazilian agricultural soil. According to Tikariha and Sahu (2014), dairy sludge, in addition to low PTE content, has high levels of easily degradable carbon, which can avoid the loss of soil nutrients and promote the increase in agricultural production. This indicates that there will be no risk of environmental contamination or to human health due to the application of both byproducts to soil.

Table 3. Chemical compositions of dacite rock powder and dairy sludge samples

Elements	Sludge (mg kg^{-1})	Dacite (mgkg^{-1})	Brazil(2006) SS limit (mg kg^{-1})	USEPA (1999) SS limit (mg kg^{-1})	E.U (1986) SS limit (mgkg^{-1})
Ca	4790	16,919	–	–	–
K	1019	15,713	–	–	–
Mg	640	5210	–	–	–
P	8370	705	–	–	–
As	< 0.60	3.0	41.0	75.0	–
Cd	< 0.10	0.08	39.0	85.0	40.0
Cr	< 0.02	7.0	1000	3000	1000
Hg	< 0.10	< 0.01	17.0	57.0	25.0
Pb	7.78	18.7	300	840	1200
Se	0.53	0.08	100	100	–

3.3.2 Improvement in soil chemical attributes

Figure 1 shows that after application of the treatments, soil chemical attributes such as pH and Al saturation were altered significantly by the application of R3625 + S10297 and R7251 + S20594 mixtures ($p < 0.05$) when analyzed at 70 days after incorporation into the soil. In control treatments, there were an increase in Al saturation and reduction in soil pH (Figure 1) at 140 days after treatments.

Acid soils limit plant growth in many parts of the world. According to Goulding (2016), soil acidity occurs due to a set of factors, including deficit of macronutrients such as Ca, K, Mg, N, P, and of the micronutrient molybdenum (Mo) besides toxicity by hydrogen, Al, and manganese (Mn). Acidity can reduce nitrogen fixation in the soil, making it susceptible to erosion and compaction. The use of by-products with potential to soil pH increase is essential for agricultural production. This interpretation is reinforced by results presented in (Figure 1), which proved that the blended by-products have potential to increase soil pH in the short term (140 days).

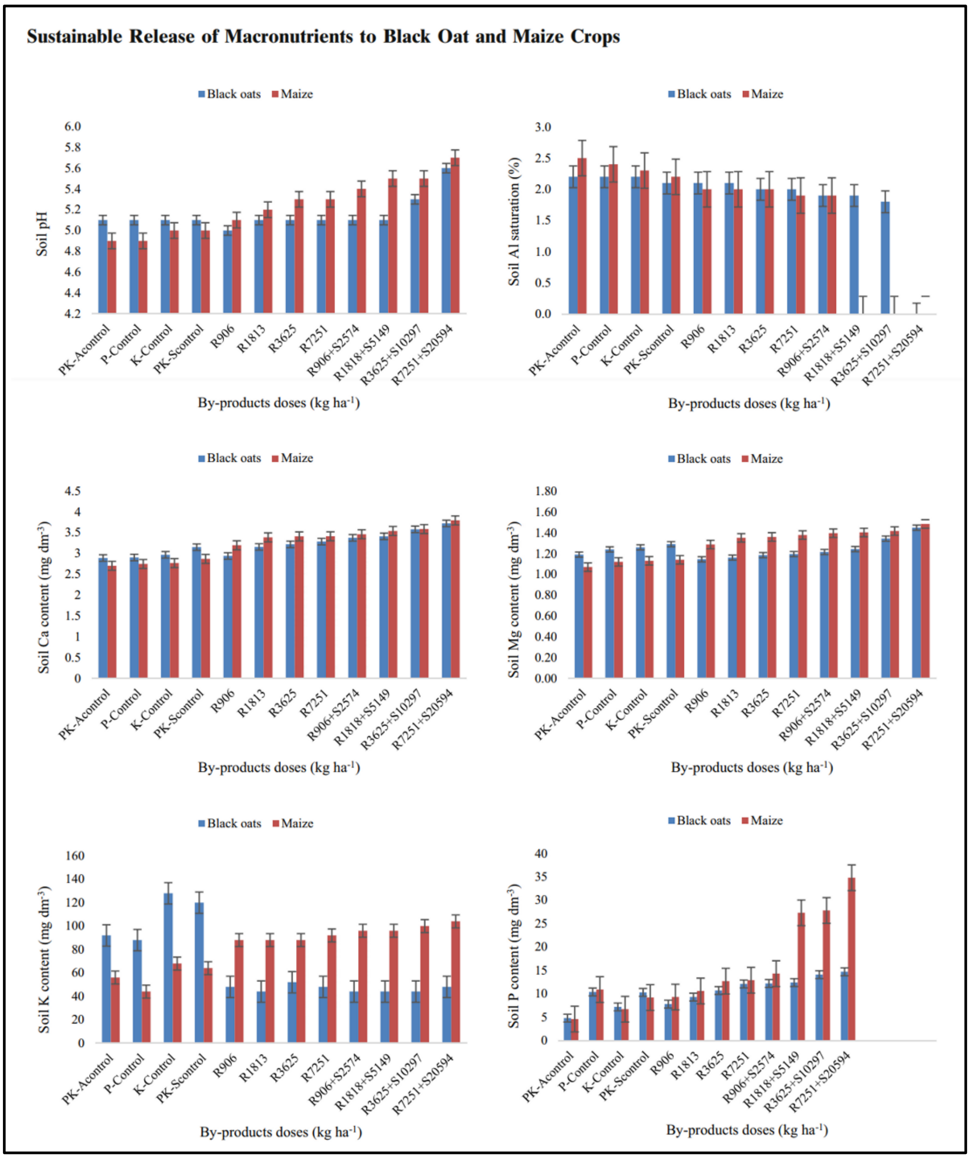

Figure 1. Soil chemical attributes after addition of different mixtures of dacite rock power (R) and dairy sluge (S). Vertical bars (1) represent standard errors from replications.

Considering the technique proposed in the two experiments, it can be inferred that they presented an equal or greater performance than soluble fertilization with P and K (P-Standard control, KControl, and PK-Standard control) (Figure 1). In soils without added dairy sludge, all chemical attributes were significantly lower than in mixtures of dairy sludge and dacite rock powder ($p< 0.01$). However, the dacite rock powder alone elevated all fertility parameters in the soils to levels higher than the control treatments at 140 days (Figure 1).

Figure 1 shows that the application of the by-products, besides raising pH and reducing Al saturation, increased the levels of exchangeable Ca and Mg in the soil, especially after the maize cultivation. In treatments with mixed dacite rock powder and by-products, the concentrations of these nutrients increased linearly, whereas they decreased in all control treatments. This can be explained by the fact that the dacite rock powder has high Ca and Mg contents, which are constituent elements of the mineral augite ((Ca,Na) (Mg,Fe,Al,Ti) $(Si,Al)_2O_6$), and when mixed with the dairy sludge and the soil, was able to release Ca and Mg, indicating that the by-products have immediate release potential of these nutrients. After maize harvesting, the levels of readily available K and P were significantly higher in soils with by-products mixtures than with the dacite rock powder alone ($p< 0.05$), and increasing doses of dacite rock powder and dairy sludge readily provided increased K and P levels ($p< 0.01$) (Figure 1). According to Moura et al. (2016), the availability of K in the soil in most tropical plantation areas is very low, but it is not as low as it occurs with P. All control treatments presented lower K and P contents in the soil compared to the other treatments. This indicates that dairy sludge contributed little to K concentrations in soils, in agreement with Hue and Ranjith (1994) and Suárez et al. (2004) that dairy sludge has low K content.

A relevant agronomic indicator of fertilizer efficiency is the solubility of K. High-solubility fertilizers are readily available to plants and can cause an increase in soil K level beyond the recommended range (Santos et al. 2016). Thus, a gradual release, such as what occurs with dacite rock powder, would be advantageous because K concentrations in the soils increased after both crops cultivation, evidencing the residual effect of dacite rock powder (Figure 1). The gradual release may be an advantage also when used for organic agriculture (van Straaten, 2016). Solubilization of nonexchangeable K can occur by changing the pH value, but also by exudation of organic acids in the rhizosphere (Volf et al. 2018). The ability of roots to reduce the concentration of K in the soil solution accelerates the weathering of the mineral sanidine (K(AlSi3O8)) present in dacite rock powder, increasing its capacity to supply K to plants. The ability of black oat to reach maximum growth (Figure 2) with lower K supply (Figure 1) can be due to their less requirement for this nutrient compared to maize. Basak et al. (2020) showed that volcanic rock by-products can supply K and essential micronutrients such as Cu, Fe, Mn, and Zn when blended with organic materials. They considered volcanic rock to be a potential source of K as well as micronutrients to supply plants requirement without any contamination risk by PTEs.

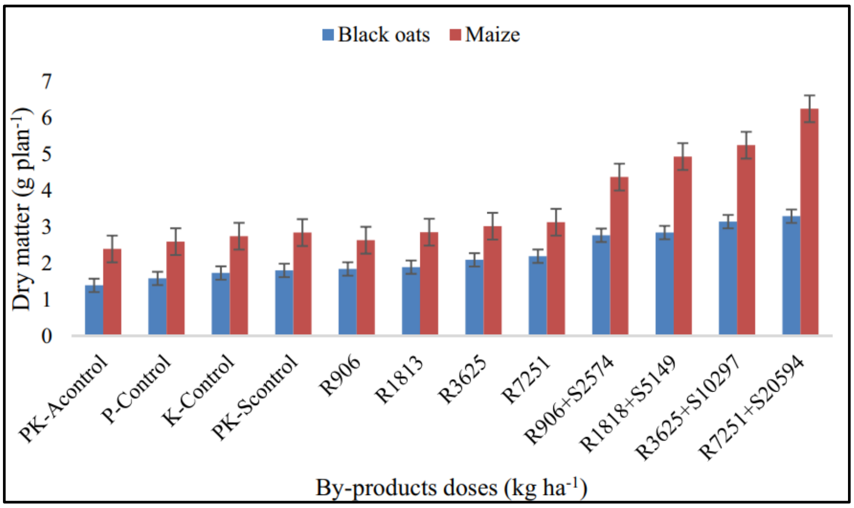

Figure 2. Effect of different mixtures of dacite rock powder (R) and dairy sludge (S) on dry matter production of black oats and maize. Vertical bars (I) represent standard errors from five replications.

Tropical soils typically have low concentrations of available P and high P-fixation potential, especially when soluble fertilizers are applied (Withers et al. 2018). This interpretation placed P, together with N, as the main limiting nutrients of Brazilian agricultural production (Fageria, 2009). Rosling et al. (2007) reported that P occurs as apatite needles in rock matrix. When apatites weather, which favors its dissolution, it releases P into the soil (Spohn et al. 2020). The soil pH is the variable that most affects the availability of P in the soil; a pH of 5.7 (Figure 1) promoted higher availability of P in the soil solution and higher uptake by black oat and maize grown in the treatment R7251 + S20594 (Table 4). This result agrees with Fageria (2009) that most agricultural plants do best in soil with pH of around 6.0.

A synergistic effect was observed between the concentration of Mg in the soil (Figure 1) and the absorption of P by maize leaves (Table 4), because Mg acted as a P loader. Control treatments (with P and K fertilizer) were lower than those obtained in the mixtures of dacite rock powder and by-products after the two crops (Table 4). This is because there was a reduction in P availability due to soil acidification. This result even on soils with high phosphate fixation can be attributed to the readily available P present in abundance in the dairy sludge (McLaughlin & Champion, 1987; Sommers & Sutton, 1980). Several authors (e.g., Furrer et al. 1984; Gupta & Hani, 1979; Haraldsen & Pedersen, 2003) observed that the release of P by sewage sludge is greater than or similar to that of soluble fertilizers, as was observed in this study. The gradual increases in available P content in the soils with dacite rock powder, and by-products mixtures (Figure 1) demonstrate that such sources are adequate for succession of crops, especially in tropical soil that has potential for P to be lost by leaching.

3.3.3 Effects of treatments on nutrients uptake by leaves of black oat and maize

In experiments 1 and 2, black oat and maize crops responded significantly ($p< 0.01$) to increasing amounts of by-product mixtures compared to boosted levels of dacite rock powder and PK fertilizer (control treatments) (Table 4). The difference in growth responses may be explained by oxidative processes (mineralization) of organic matter in the dairy sludge over dacite rock minerals (Turek et al. 2019), releasing their nutrients more rapidly into the soil.

The levels of Ca and K uptake were much higher than the sufficiency limits for leaves of both crops in all treatments with dacite rock powder and dairy sludge mixtures (Table 4). Magnesium was higher only in maize leaves in the treatments R1818 + S5149, R3625 + S10297 and R7251 + S20594. In the other treatments, the levels of this nutrient remained within the range of sufficiency.

Table 4 shows that in maize leaves, P suitability levels were achieved in all dacite rock powder doses and in all mixtures of by-products. In black oat leaves, only in R7251 + S20594 mixture did the P levels reach the appropriate range. Regarding the effect of dacite rock powder doses only on nutrient uptake by plant leaves, the results of this study are consistent with those obtained by Ramos et al. (2019). They suggested that dacite rock powder may be a source of Ca, K, Mg, and P and can replace high-solubility fertilizers.

Table 4. Nutrient concentrations in leaves of black oats and maize, and levels of adequacy sufficiency according to Pauletti (2004).

Treatments*	Black oats				Maize			
	Ca	Mg	K	P	Ca	Mg	K	P
	Adequacy sufficiency (g kg^{-1})							
	2.5–5.0	1.5–5.0	15.0–30.0	2.0–5.0	2.0–8.0	2.0–5.0	17.0–35.0	2.0–4.0
PK-Acontrol	4.80	2.57	25.2	1.46	7.03	3.95	30.4	1.63
P-Control	4.98	2.70	28.4	1.33	7.94	4.87	30.4	1.56
K-Control	4.35	2.58	30.3	1.36	6.59	4.17	27.9	1.26
PK-Scontrol	4.07	2.48	32.1	1.43	7.47	4.84	33.4	1.63
R906	5.66	2.66	30.8	1.73	8.66	4.41	46.6	2.33
R1813	5.91	2.73	31.1	1.89	8.90	4.97	53.4	2.16
R3625	5.83	2.59	28.8	1.79	9.52	4.84	56.3	2.73
R7251	5.27	2.51	30.2	1.79	8.89	4.55	48.7	2.06
R906 + S2574	5.93	2.46	35.5	1.46	10.7	4.49	40.5	2.43
R1818 + S5149	6.30	2.67	37.3	1.56	11	5.65	45.1	2.13
R3625 + S10297	6.97	2.67	38.3	1.73	12.70	5.89	44.8	2.09
R7251 + S20594	6.58	2.51	39.5	2.46	13.38	6.87	46.2	3.73

*R represents dacite rock powder, and S dairy sludge

3.3.4 Effects of treatments on growth of black oat and maize

The dry matter production of black oat and maize leaves increased significantly in soils treated with dairy sludge and dacite rock powder (Figure 2). The highest effect was observed with the highest dose of the combined by-products in relation to all treatments, including those that received soluble fertilizer, in which increases of more 100% were recorded for black oat and maize. These results agree with those obtained by Ramos et al. (2019), who concluded that the use of dacite rock powder increased the production of black oat and maize crops. The dry matter production of black oat and maize increased linearly with the addition rate of dacite rock powder and with by-products mixtures (Figure 2). Haraldsen and Pedersen (2003) also used different mixtures of soil, soluble fertilizer (NPK), sewage sludge, and crushed rock to evaluate the growth of ryegrass. They showed that the best blend for ryegrass was rock powder, soil, and sewage sludge.

According to Li et al. (2019), total yield is the most important factor to be considered when evaluating plant growth in response to applied fertilizers. Figure 3 shows the responses to treatments in nutrients accumulation by leaves of the crops. A significant linear increase ($p < 0.01$) in Ca, K, Mg, and P accumulation in black oat leaves was observed in higher doses of by-product mixtures (Figure 3).

Table 4 shows that the maize extracted the maximum possible amount of Ca, K, Mg, and P from the soil, resulting in higher concentrations of these nutrients in all treatments with dacite rock powder and dairy sludge mixtures. As seen in (Figure 3), this is evident when comparing the treatments that received the by-products mixed with the control and with dacite rock powder only, demonstrating the high reactivity of the dairy sludge. This shows the importance of the organic source as a multielement nutrient supplier, and it can be stated that the release of its nutrients is as fast as for high-solubility fertilizers. This interpretation is reinforced by the work of Theodoro and Leonardos (2014) who used basalt, kamafugite, carbonate schist, and biotite gneiss, mixed or not with an organic source. They verified that P, K, Ca, and Mg availability increased in soil with rock powder treatments, as compared to control treatments, at one year after application. Increases in pH and cation exchange capacity were observed in soils treated with rock powder, mixed or not with an organic source. That study also suggested that the solubility of minerals in rock powder and the release of their nutrients increase over time, due the interaction of minerals with organic acids produced by roots in the soil. It is evident that the solubility of minerals differs, and the addition of organic matter is advised in order to increase nutrient release by mineral breakdown (van Straaten, 2013).

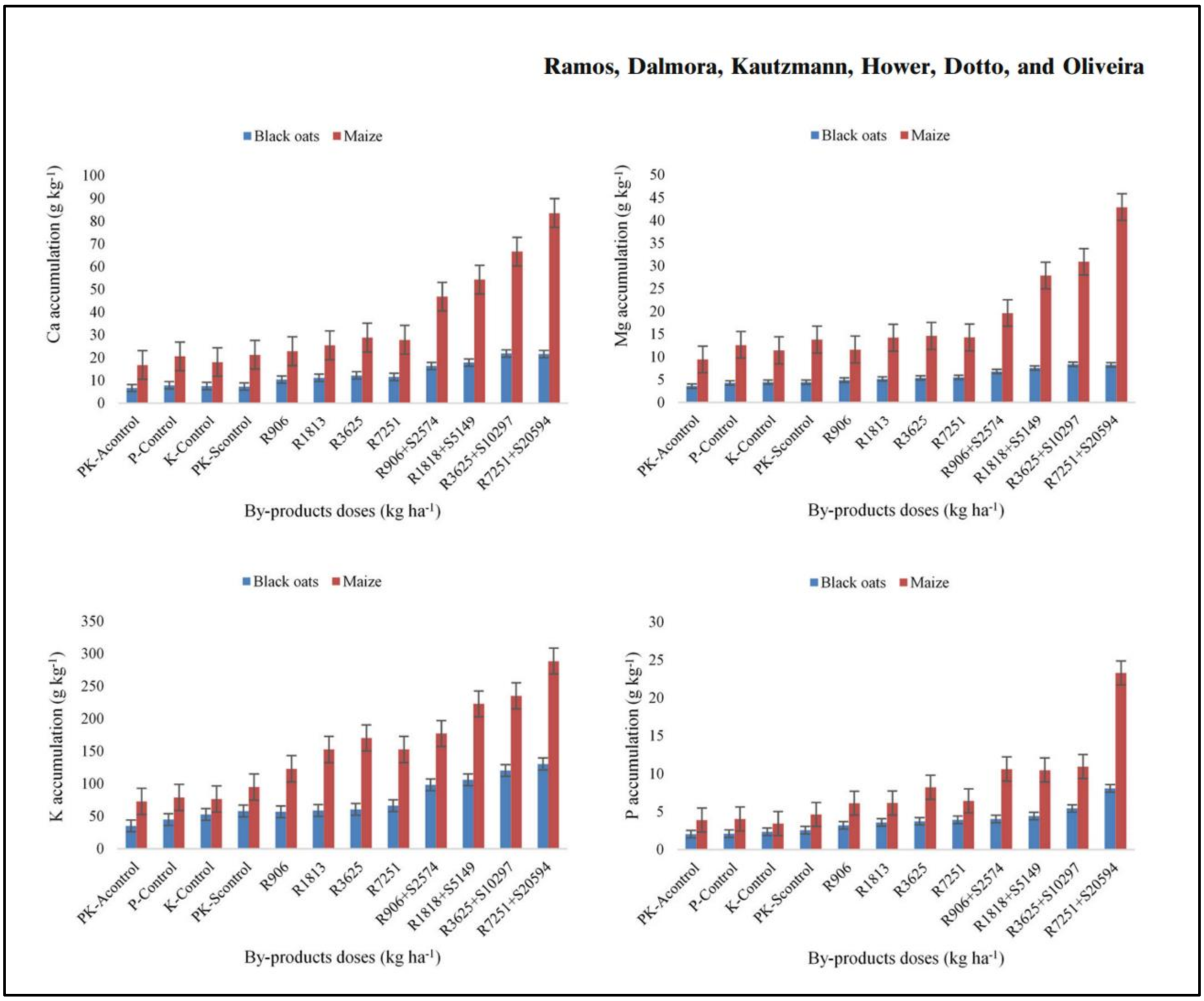

Figure 3. Calcium, K, Mg, and P cumulative absorption in leaves of black oats and maize grown in soil after addition of different mixtures of dacite rock powder (R) and dairy sludge(S). Vertical bars (I) represent standard errors from five replications.

There are few studies on plant cultivation in soil containing blended rock powder and dairy sludge. Haraldsen and Pedersen (2003) showed that sewage sludge addition to soil, in suitable quantity, can yield positive results on ryegrass growth. The gap in the literature about tropical soil fertilization with dairy sludge and dacite rock powder blend hindered the comparison between the results of this study with previously published research. According to the results of this study, the by-products blended can be used to replace high soluble fertilizers as they demonstrated enhanced effects in soil fertility, dry matter production, and nutrients uptake by black oat and maize leaves.

3.4 CONCLUSIONS

The results obtained in this study showed the potential use of the two combined by-products as a source of Ca, K, Mg, and P. The by-product mixtures contributed to the amelioration of nutrient concentrations in leaves of crops and in soil attributes. The by-product mixtures may provide an alternative to the use of soluble fertilizers at suitable dosages and times, especially for acid soils. In addition, the R7251 + S20594 treatment, which consisted of 7251 kg ha^{-1} dacite rock powder and 20,594 kg ha^{-1} dairy sludge mixtures produced with typic Hapludox soil, was responsible for the better black oat and maize development, showing that the dairy industry sludge has high reactivity and can be used to increase the solubility of rock minerals. Thus, the methodology used will be promising and feasible for application to small- and medium-sized farmers, who can benefit in terms of productivity.

The by-products of rock mining and the dairy industry can be considered for significant reduction of environmental hazards and the high costs of final disposal. This study opens perspectives for future research into the use of combined by-products in soil-building processes. Moreover, microbiological and maturity analyses applied to by-products were not performed here, but they can provide vital information for understanding how bioactivity favors the transformation of potentially polluting byproducts in nutrients source for agriculture. To apply by-products to improve poor soils in nutrient, it will be important to select suitable rocks and organic matter according to climatic–edaphic conditions as well as to specific requirements of each crops. The use of different by-products in agriculture can solve a stranglehold on industrial activity, both mining and food, decreasing the risk of environmental pollution. Soil remineralization on a large scale using byproducts is needed to address environmental mismanagement, which causes soil loss much faster than can be regenerated naturally. In addition, this innovative technique will contribute to increased carbon storage in soils and forests.

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APPLICATION OF ANDESITE ROCK AS A CLEAN SOURCE OF FERTILIZER FOR EUCALYPTUS CROP: EVIDENCE OF SUSTAINABILITY

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4 APPLICATION OF ANDESITE ROCK AS A CLEAN SOURCE OF FERTILIZER FOR EUCALYPTUS CROP: EVIDENCE OF SUSTAINABILITY

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ABSTRACT

Global demineralization of agricultural soils due to unsustainable use of highly soluble fertilizers and intensive exploitation is an issue of increasing concern. Methods of remineralization include the application of volcanic rock by-product, such as vesicular andesite on mineral-deficient fields. The present work analyzed the petrography, mineralogy, and chemistry of volcanic rock by-product (vesicular andesite rock), as well as on-field experiment with eucalyptus. The petrographic description was performed on a polished thin section by optical microscopy. The mineralogical phases were identified with X-ray diffraction. The by-product chemical composition was determined by X-ray fluorescence and inductively coupled plasma mass spectrometry for potentially toxic elements. Additional chemical compositions were analyzed using a scanning electron microscope equipped with a dispersive X-ray detector. A nine-month field experiment was carried out to evaluate the agronomic performance of *Eucalyptus Saligna* Smith cultivated in an Ultisol. Four different doses (treatment Tl = control, treatment T2 = nitrogen, phosphorous, and potassium fertilizer 100%, treatment T3 = by-product 100%, and treatment T4 = by-product 50% and nitrogen, phosphorous and potassium fertilizer 50%), were applied on soil. Responses to treatments were evaluated from height and diameter at breast height at three, six, and nine months after eucalyptus planting. The total phosphorous and potassium content in soil was measured at three and six months after eucalyptus planting. The results showed that the by-product is composed of plagioclase, potassium feldspar, zeolite, smectite, and opaque minerals with apatite as an accessory mineral. The primary oxides found in by-product via X-ray fluorescence were silicon, aluminum, iron, calcium, sodium and with lower concentration, the potassium and phosphorus. In all evaluated parameters, it was verified that T2 and T4 treatments significantly enhanced the available soil phosphorous, and the eucalyptus height, with maximum gains (79% and 62% of phosphorous, and 20% and 23% of height) at nine months after eucalyptus plantation. The maximum gains of eucalyptus diameter at breast height were similar (23% and 24%) at six months after plantation. Soil available potassium was significantly enhanced in T3, T4 and T2 treatments at nine months after planting, with maximum gains of 71%, 55% and 53%. The work indicated an improvement in the phosphorus and potassium levels in soils, and in eucalyptus crop growth by adding by-product, being a partial nitrogen, phosphorous and potassium fertilizer substitution strategy.The use of these geological materials is presented as an alternative to increase agricultural productivity and reduce the environmental impacts caused by excessive use of highly soluble fertilizers.

Keywords: By-product of rock mining; Soil remineralizer; Sustainable silviculture

4.1 INTRODUCTION

Eucalyptus is one of the most common and economically important forest species that have been established in many areas of the world due to their fast growth and profitability (Goded et al., 2019). Most of these areas are tropical and have a low fertility soil, often poor and acidic, with very low phosphorus (P) and potassium (K) contents (RABEL et al., 2018).These nutrients are needed by eucalyptus to obtain high productivity (GORNÇALVES et al., 2008). For this reason, the highly soluble fertilizers have been applied to guarantee an adequate nutrient supply for crops (KORCHAGIN et al., 2019).

The commonly used fertilizers for eucalyptus are ammonium sulphate ($(NH_4)_2S0_4$), potassium chloride (KCI), and single super-phosphate (SSP). Nitrogen (N), P, and K from sources such as $(NH_4)_2S0_4$, SSP, and KCl are highly soluble and can be rapidly lost through leaching (MANNING, 2010). Most N fertilizers cause the soil to acidify, significantly affecting soil biota and plant nutrient availability (HUANG et al., 2017). The main threat of soluble fertilizers is the pollution of surface water during the first months after its application and planting (GORNÇALVES et al., 2013).

It is evident that measures need to be taken to decrease soil demineralization and highly soluble fertilizers consumption (KORCHAGIN et al., 2019). One of the measures taken was to add crushed rocks to maintain soil fertility and to support crop production (MANNING and THEODORA, 2018).

Several studies demonstrated positive results from the use of rock dust as soil remineralizers, such as: a single application can be effective for up to four or five years

(MACHADO et al., 2016); the P, K, calcium (Ca), and magnesium (Mg) levels have been increasing over time and the productivity is similar to or higher than soluble fertilization (THEODORA et al., 2013); and low availability of potentially toxic elements (PTEs) and aluminum (Al) (RAMOS et al., 2017); lower risk of contamination or eutrophication of water sources because the crushed rock has a gradual solubility, contrary to highly soluble fertilizers. This is a relevant issue where continuous application of fertilizers, especially single superphosphate, has resulted in cadmium (Cd) toxicity in soils throughout the world (GREGER et al., 2016).

Other advantages are a widespread availability of volcanic rocks in the Earth's surface (GILL, 2010); and the volcanic rock mining by-product use as a soil remineralizer do not need chemical processing, that is, can be used as it is mined (*in natura*) (SILVA et al., 2013). There is a notorious production of by-products from the volcanic rock mining in southern Brazil (DALMORA et al., 2016). These by-products are accumulated alongside different quarries, ultimately needing an environmentally appropriate final disposal (KORCHAGIN et al., 2019).

By-products application in agriculture should be considered as an alternate to remineralize nutrient-depleted soils, and for reducing the environmental risk of this material that requires mineralogical and chemical characterization and an evaluation of their agronomic performance (KORCHAGIN et al., 2019). This approach contributes both to solving environmental issues associated with rock mining and to create a cleaner alternative for soil fertilization.

Basalt by-products from quarries in South Brazil are well known as soil remineralizers (NUNES et al., 2014), but not yet the vesicular andesite by-product. It is of great relevance to conduct research on the agronomic performance of these rocks.

In Brazil, soil remineralizers have been developed, and Brazilian federal law n° 12890 (BRAZIL, 2013) allows these to be used for crop nutrition, with specifications clearly defined by appropriate regulation (BRAZIL, 2016). Soil remineralizers are all mineral materials that have only size reduction and size classification by mechanical processes and that change the soil fertility indices by addition of macro and micronutrients for crops and improve the physical or physicochemical properties or the biological activity of soils (Brazil, 2013). This approach provides a model for all countries to explore local geological sources and reduce the use on of high solubility fertilizers (MANNING and THEODORA, 2018).

In this study, the relationship between petrographic, mineralogic, and geochemical characteristics of one by-product (andesite vesicular) from a quarry in Estancia Velha city and the effects of four agronomic treatments in the availability of P and K to soil and in the growth of the Eucalyptus Saligna Smith clonal in Triunfo city, Southern Brazil were discussed.

This work seeks to bring awareness on the impact of mining activity, the unsustainable consumption of highly soluble fertilizer (NPK) and provide information on eucalyptus fertilization practices in subtropical regions with the use of volcanic rock mining by-products.

4.2 MATERIAL AND METHODS

4.2.1 Soil, by-product, and seedlings samples

Soil samples were collected at depths of 0-20cm from several points of the experimental site, before remineralization treatments application. The samples were composited from 45 sub-samplings.

Ten of vesicular andesite rock powder (by-product) with particle sizes below 2.8mm (for chemical characterization and soil application) and ten kg of bedrock (for petrographic description and chemical composition by scanning electron microscope) were supplied by the lncopel lndustria e Comercio de Pedras Ltda of the Estância Velha district.

The clonal Eucalyptus saligna Smith (ESS) seedlings were purchased from Metalurgica e Viveiro DACKO, located in the municipality of Herval Grande, Rio Grande do Sul, Brazil. The seedlings had an average size of 30 cm. This species was chosen because it is resistant to frost, its rapid growth, and high homogeneity in the field (DELGADO-MATAS and PUKKALA, 2011).

4.3 ANALYTICAL METHODS

4.3.1 Petrography

Petrographic thin section observations were made to identify the andesite vesicular mineral phases. The sample was analyzed on optical microscope (Model Eclipse 50i POL, Nikon, Japan) under natural (NL) and polarized reflected light (PL).

4.3.2. Mineralogy

X-ray diffraction (XRD) technique was employed to characterize the mineralogical composition of the by-product using a Philips X-ray diffractometer (Model X'PertMPD, Philips, Amsterdam), equipped with a curved graphite monochromator and fixed copper anode, operating at 40 kV and 40 mA. The angle range analyzed was from 5 to 75°. The step size used was 5°/ 1 s. Cu Ka. radiation (1.54184 Å), Ka.1 (1.54056 Å), Ka.2 (1.54439 Å), and K (1.39222 Å). The mineral identification from XRD data was done using the X'pert High Score Software, version 2.0a (2.0.1).

4.3.3 Chemical composition analysis

4.3.4 By-product

Chemical analyses of the by-product were performed in triplicate, after manual milling using a porcelain mortar and pestle to obtain particles less than 0.074 mm. Chemical composition in percentage weight of oxides was determined by X-ray fluorescence (XRF) (Model MagiX (DY1583), Panalytical, Amsterdam) after digestion of 2 g of the sample by total fusion with lithium tetraborate in an automatic machine (Silva et al., 2011).

The by-product sample was digested with four acids (hydrochloric, nitric, hydrofluoric, and perchloric) in a microwave for 1 h (Querol et al., 1997) to determine a PTEs composition. The analysis was performed at the Institute of Environmental Assessment and Water Research (Spain) by inductively coupled plasma-mass spectroscopy (ICP-MS).

The mineral compositions of the by-product were investigated on a polished thin section using a scanning electron microscope (SEM) (Model EVO MA 10, Zeiss, Germany), equipped with an energy-dispersive X-ray spectrometer (EDS). The mineral identifications were made based on morphology and grain composition using back-scattered electron mode.

4.3.5 Soil

Soil samples were subjected to chemical extraction by Mehlich (1984). The P and k content were determined by inductively coupled plasma-optical emission spectrometer (ICP-OES). These analyses were performed before treatments applications to determine the amount of inputs to be applied in agronomic treatments, and after three and six months of eucalyptus plantation to verify the agronomic efficiency of the treatments. The experimental soil was classified as Ultisol (USoil) according to the United States Department of Agriculture soil classification (USDA, 1999), with 44.5% of clay in A horizon. Briefly, the USoil presented concentrations of 3.1 $mg1^{-1}$ of P and 37 $mg1^{-1}$ of k. This indicated a poor soil and practically without reserve of these nutrients, according to the SBCS (2004).

4.3.6 Experimental site and preparation

This work started in September 2015 in an experimental site of 0.41 ha at Triunfo (485.959 S; 6,722,047 W, South America n Datum 1969) (Figure 1) in the state of Rio Grande do Sul, Brazil. The Triunfo site was characterized by a gentle slope.

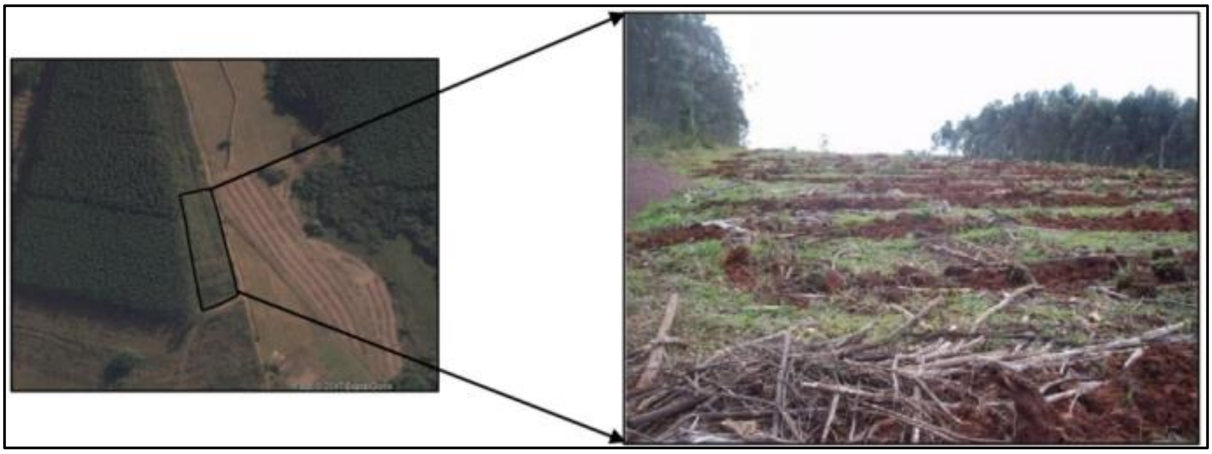

Figure 1. Experimental overview. Source. Google Earth, 2015.

Based on fertilization practices used in the region, treatments were defined to increase P (from 3.1 to 12 mg 1^{-1}) and k (from 37 to 60 mg l^{-1}) according to the Brazilian Society of Soil Science (SBCS 2004). The agronomic treatments were added on the soil surface, 30 d before planting of eucalyptus seedlings (Table 1).

Table 1. Doses of limestone (DL), SSP and by-product applied in field experiment.

Treatments	DL kg/ha^{-1}	By-product kg/ha^{-1}	KNO_3 kg/ha^{-1}	SSP kg/ha^{-1}
T1-Control	0	0	0	0
T2- NPK fertilizer	6.000	0	230	660
T3- By-product	0	6.600	0	0
T4- By-product 50% and NPK 50%	3.000	3.300	115	333

4.3.7 Experimental design

The experiment was conducted side by side with four agronomic treatments replicated three times (Figure 2). Plots were composed of three rows of 3 m wide with 14 plants per row; space between rows was of 2 m and 3 m between plants in the row. Six plants of the central rows were measured for height (H) and diameter at breast height (DBH). A visual inspection was conducted each week for one month in order to detect and replace dead seedlings. Treatments response was evaluated by H and DBH at three, six, and nine months after eucalyptus planting. Soil samples were taken at depths of 0-20 cm on the central rows of every treatment (each sample composed by ten sub-samplings). Treatments response was evaluated by total P and K in soil after three and nine months after eucalyptus planting.

All data were submitted to analyses variance by the Least Significant Difference (LSD) test at a significance level of 5% ($p < 0.05$) using the statistical software SAS Enterprise Guide 6.1.

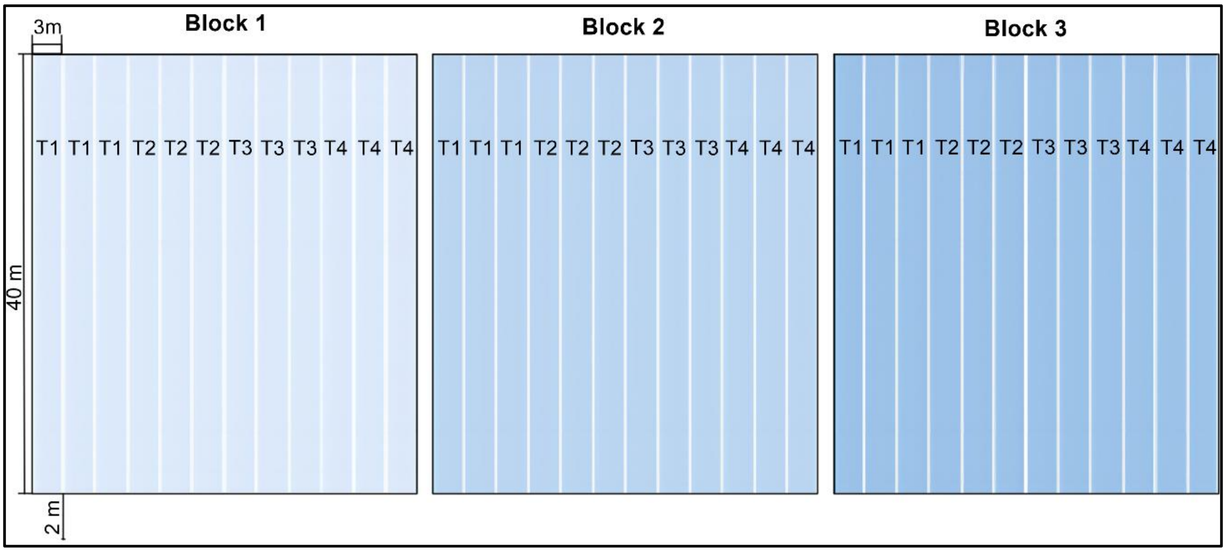

Figure 2. Treatments distribution

4.4 RESULTS AND DISCUSSION

4.4.1 Petrography

Optical microscope observations revealed that the andesite has an intermediate composition between basalt and granite featuring a microcrystalline to glassy matrix with a microporphyritic texture of granulation less than 1mm (Figure 3A and B). Plagioclase micro-phenocrysts, comprising less than 30% of the volume of the rock, appear isolated or glomerophyritic (Figure 3A). Vesicles surrounded by zeolites were obse1ved (Figure 3C and D). The minerals identified in the matrix were plagioclase, opaque minerals, and laumontite zeolite with apatite as an accessory mineral. Opaque minerals appear associated with the interstitial mesostasis and occur as dendritic and cruciform crystals (Figure 3B). Apatite crystals have needle shapes up to 0.05 mm and are associated with the interstitial-domain. The microphenocrysts of plagioclase and zeolite are of 1.2 and 8 mm. The interstitial domains of andesite are weakly anisotropic indicating partial devitrification, oxidation is frequent where the matrix is replaced by iron hydroxide. The occurrence of all these minerals that are susceptible to weathering is a good indication that the vesicular andesite rock by-product can release macronutrients and micronutrients into the soil.

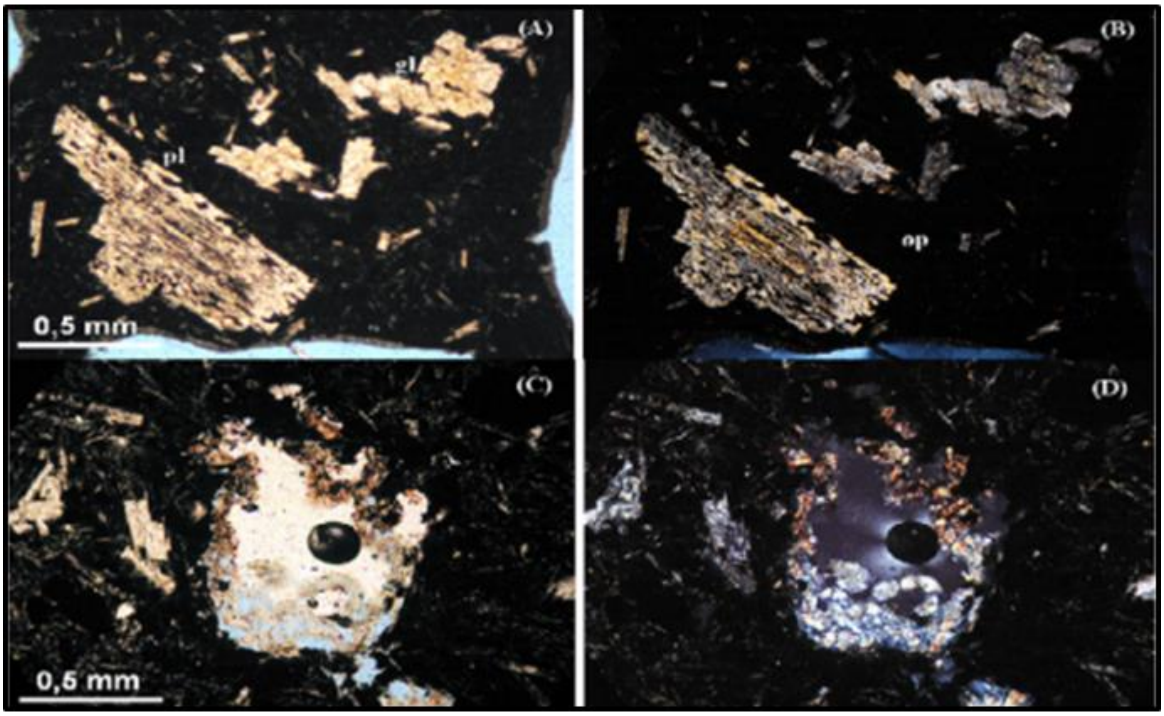

Figure 3. Petrographical images of by-product. (A) plagioclase microphenocrysts isolated (pl) or glomerophyritic (gl) (NL): (B) opaque minerals (PL): (C) vesicles surrounded by laumontite zeolite (NL): (D) vesicles surrounded by laumontite zeolite (PL).

4.4.2 Mineralogy

The XRD pattern of the by-product is shown in (Figure 4). It can be seen that the main three peaks correspond to quartz ($Si0_2$). Andesine ($(Na,Ca)(Si,Al)_4 0_8$). And montmorillonite-chlorite ($(Na,Ca\ )_{0,3}(Al,Mg)_2Si_4O_{10}(0H)2{\bullet}n(H_20)$). It was also possible to detect orthoclase ($KAISi_3O_8$). laumontite ($CaAl_2Si_4O_{12}{\bullet}4(H_20)$), enstatite ($Mg_2Si_2O_6$) and hematite ($Fe_20_3$). This corresponds to minerals most common volcanic rock-forming minerals (DEER et al., 2013).

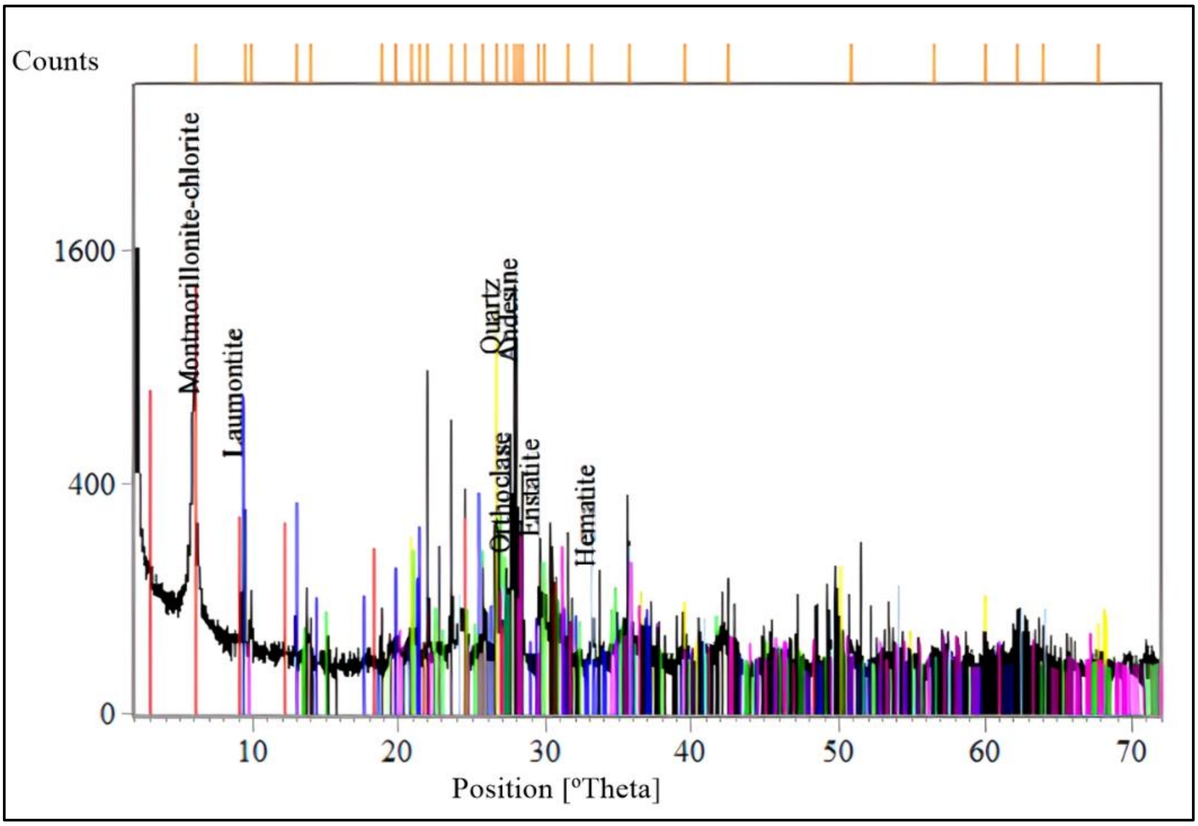

Figure 4. X-ray diffractogram from by-product sample.

Smectites (montmorillonite-chlorite mixed layer) are important in soils due to their high cation exchange capacity (HUGGETT, 2015). This indicates a possible ability to change cations into soil suspensions.

Scanning electron microscope/EDS analysis confirm the occurrence of orthoclase in the by-product (Figure 5A). Orthoclase, a K-feldspar, when added to soil can release K more easily due to the action of weathering (MANNING et al., 2017). Potassium is very necessary nutrient for enhance the productivity of many crops (CARVALHO et al., 2018).

Figure 5B shows that the apatite makes up the by-product sample.

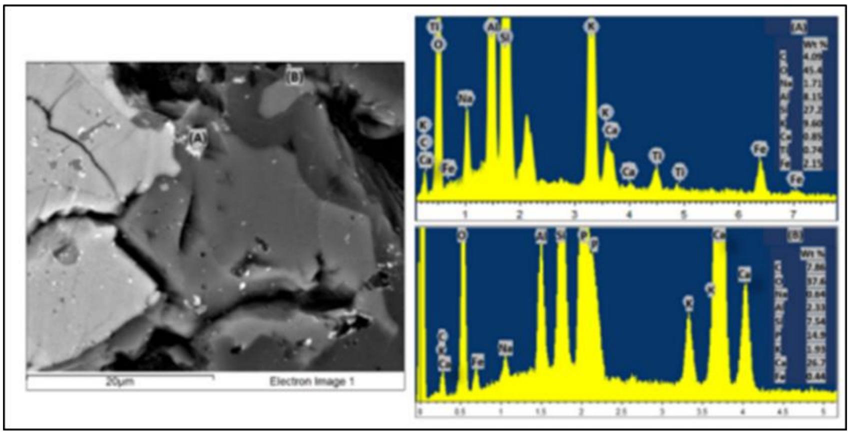

Figure 5. SEM image of apatite and orthoclase detected in the by-product. (A) EDS spectrum of orthoclase: (B) EDS spectrum of apatite.

Apatite is an accessory phosphate mineral that occurs in almost all igneous rocks and is known to be partially resistant to weathering (PICCOLI and CANDELA, 2002), with slow dissolution and P release. This interpretation is contradictory to studies of Ramos et al. (2015), which showed recovery up to 93% of the P in leaching tests using similar rock powder to this study. This fact indicates that the P may be of great potential in aiding several processes of plant growth through remineralization.

The by-product is mainly composed of aluminosilicates, which mean that besides of its application as a fertilizer, it also could be used in ceramic production. This is a relevant possibility to study in a future work, since the predominance of these components suggests the fabrication, for example, refractory materials (SANCHEZ-PENA et al., 2018).

The agricultural use of by-product in tropical soils suggest replacing soluble fertilizers because the aluminosilicates have nutritional properties significantly influence soil fertilization (TUBANA et al., 2016).

4.4.3 Chemical composition

According to Table 2, the by-product is primarily composed of $Si0_2$ along with a high presence of other silicates. These results concur with those obtained by Nunes et al. (2014), who characterized four similar rocks and their application as a soil remineralizer.

Silicon is essential to crop growth, although it is not regarded as an essential nutrient. According to Epstein (1999) Si-deficient plants have generally structurally weaker and more prone to growth, development and reproduction irregularity. Silicon is the only nutrient that is not harmful when over-absorbed. In addition, it helps to control pests and increase the productivity and quality of agricultural products (KEEPING, 2017; BEERLING et al., 2018).

Aluminum oxide (Al_20_3) was another compound noted to has significant concentration in by-product analyzed. Although the by-product particles contained important fractions of Al, a low release of this element is expected to the soil. Aluminum is very stable within the crystalline structure of the by-product particles; this is very important because Al may be toxic to the plants. The toxicity by Al dissolution is not considered to be an environmental concern. This interpretation was proven by the investigations of Ramos et al. (2019), who studied the potential use of volcanic rock powder as soil remineralizer in black oats and, sequentially maize crops. These authors showed ameliorations in soil attributes, like high levels of Ca K and P and low levels of exchangeable Al and Al saturation.

Table 2**.** Chemical composition in percentage weight of oxides of the by-product sample.

Oxides	Andesite
SiO_2	57,1
TiO_2	1,17
Al_2O_3	14,1
Fe_2O_3	9,5
MnO	0,17
MgO	3,57
CaO	5,38
Na_2O	3,22
K_2O	2,49
P_2O_5	0,26
LOI[a]	2,7
Total	99,7

[a] Loss on ignition

In terms of potential (based on content) for the macronutrient K, the by-product could be proposed as a soil remineralizer according to the Brazilian normative instruction n°05 (BRAZIL, 2016). The by-product presents the sum of chemical compounds (CaO + MgO + K_20) higher than 9% and K_20 content is higher than 1%, in compliance with the Brazilian normative instruction n° 05 (Brazil, 2016). From these results, the criteria for a remineralizer are satisfied by the by-product studied here. This is a positive characteristic that represents good potential for agricultural use, especially in nutrient-poor soil such as USoil. The average P concentration of the Earth's upper crust is approximately 0.1% P_20_5 (CORDELL and WHITE, 2011). According to Table 2, the P_20_5 content of the by-product is almost three-times above the crustal average. This result may be attributed to the occurrence of apatite, identified by optical microscopy and by SEM/ EDS (Figure 5B), in the by-product. Apatite is the most abundant phosphate mineral, accounting for more than 95% of all P in the Earth's crust and is found as an accessory mineral in volcanic rocks (PTACEK, 2016). Phosphorous and K are important nutrients to obtain high productivity in several crops, for example, in tropical soils (CARVALHO et al., 2018).

In the characterization of rocks destined for the remineralization of soils, it is important to quantify major elements, as well as PTEs, which may be necessary and beneficial to plant physiology, but cannot extrapolate the limits established by environmental legislations.

The limits maximum of PTEs in soil remineralizers allowed by Brazilian normative instruction n°05 (BRAZIL, 2016) are 15 ppm arsenic (As), 10 ppm cadmium (Cd), 0.1 ppm mercury (Hg), and 200 ppm lead (Pb).The results of analysis by lCP-MS demonstrates that the by-product sample has low concentrations of PTEs <1 ppm As, 0.6 ppm Cd, 0.01 ppm Hg, and 15.6 ppm Pb, which do not represent an environmental risk Table 3.

Table 3. Chemical composition results obtained by ICP-MS of the by-product sample.

PTEs	By-product mg Kg^{-1}/ppm
As	<1
Cd	0,6
Cr	30,8
Cu	42,5
Hg	0,01
Pb	15,6
Zn	112,6

As the Brazilian normative instruction n° 05 is restricted to PTEs such as As, Cd, Hg, and Pb, the PTEs maximum values allowed by Brazilian National Environmental Council (Brazil, 2009) in Resolution n° 420, were used to protect the soil quality. The maximum levels allowed by Brazil (2009) are 35 mg kg^{-1} As, 3 mg kg^{-1} Cd, 150 mg kg^{-1} chromium (Cr), 200 mg kg^{-1} copper (Cu), 12 mg kg^{-1} Hg, 180 mg kg^{-1} Pb, and 300 mg kg^{-1} zinc (Zn).

This interpretation agrees with Hartmann et al. (2015) that the use of rock by-products as a soil remineralizer can be a safe alternative for their reuse.

Table 3 shows that the PTEs concentration of by-product it is well below the limits established by Brazilian normative instruction n° 05 (BRAZIL, 2016) and Resolution n° 420 (Brazil, 2009). Similar results were obtained by Ramos et al. (2017) with a by-product from the same region of this study. These authors carried out leaching tests in five acid solutions and concluded that very low levels of potentially toxic elements were made available to extraction solutions. These results indicate that the addition of by-product to the soil will not cause toxicity risks to plants or to the environment.

4.4.4 Potassium and phosphorus availability to the USoil

Figure 6 shows the average K concentrations in soils after three and nine months of eucalyptus planting. After nine months, the soil K content of T3 treatment (100% by-product) was significantly higher ($p = 0.002$) than all other treatments. In T4 treatment (50% by-product and 50% NPK) the average K concentration ins soil was significantly higher ($p = 0.02$) than in T2 treatment (100% NPK). T2 treatment did not reach the adequacy level of 60 $mg1^{-1}$ for eucalyptus cultivation (SBCS, 2004). In contrast, treatments with by-product (T3 and T4) provided K content above than 60 $mg1^{-1}$.The high content of K in T3 treatment was exclusively due to the presence of orthoclase. This mineral has 14.05% of K in it is composition and was detected in by-product via XRD analysis (Figure 4). The by-product 6600 kg ha^{-1} dose has the potential to totally replace soluble K fertilizers. Similar results were obtained by Ramos et al. (2019), who investigated the plant availability of Ca, Mg, K and P in dacite rock by-product by growing black oats and maize for 70 deach, with different by-product doses. The authors showed that the K supplied by by-product was available to the plants.

Figure 7 shows the average P concentrations in soils after three and nine months of eucalyptus planting. Tropical soils usually have low concentrations of available P and high potential for fixation of P applied by using soluble fertilizers (SCHUTZ et al., 2018). This context places P, along with N, as one of the most limiting nutrients in crop production in Brazil (WITHERS et al., 2018). In clayey soils, as in the present study, the critical level, i.e. sufficiency level, of P for eucalyptus production is 9 mg dm-3 (SBCS, 2004). The eucalyptus clones are nutritionally more demanding and are more subject to deficiency of this nutrient. Unlike K, it was found that after nine months, fertilization with 100% by-product (T3) provided lower soil P values than T2 and T4 treatments. The latter presented levels of P in the soil above the critical level for the development of the plants (Figure 7). The T4 treatment with combined fertilization with by-product and NPK presented higher P contents than all other treatments (Figure 7). This fact suggests that the addition of NPK favored the weathering of apatite, with 18.43% P, thus releasing the P faster in the soil.

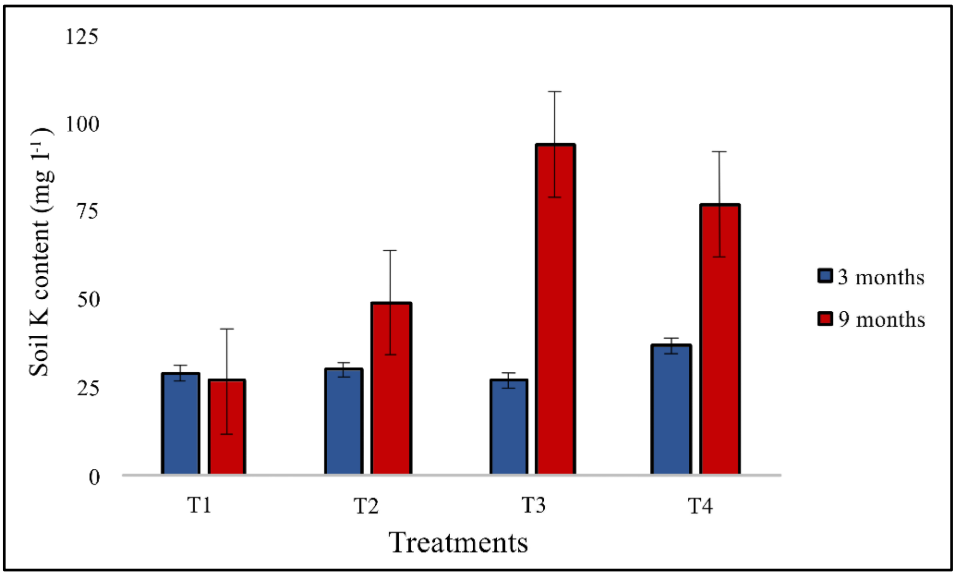

Figure 6. Treatment effects on the K content in soils after three and nine months of ESS planting.

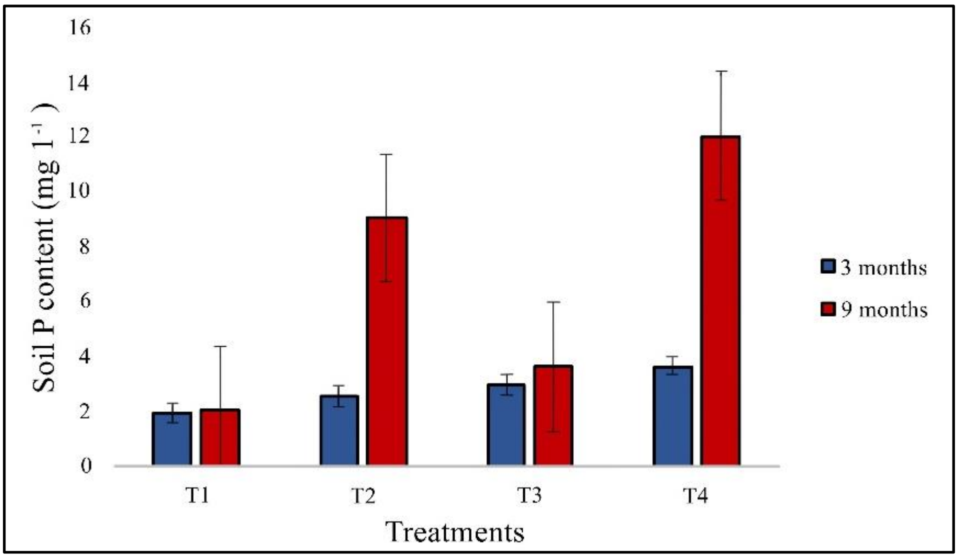

Figure 7. Treatment effects on the P content in soils after three and nine months of ESS planting

The results of the T3 treatment were superior to those obtained by Toscani and Campos (2017). They applied 300 t ha^{-1} of basalt powder composed of 1.15% K_20 and 0.379% P_20_5. The concentrations of experimental soil were of 74 mg dm^{-3} of K and 5.9 mg dm^{-3} of P. After twelve months of common bean planting, the soil K content was 35 mg dm^{-3} and P was 1.7 mg dm^{-3}.

The by-product combined with NPK added in T4 treatment proved to be a promising alternative source for the supply of P in the studied soil. The T4 treatment have potential to partially replace P fertilizers.

Despite low P release observed in T3 treatment compared to highly soluble fertilizers in T4 treatment, results using by-products as a soil remineralizer are promising (Nunes et al., 2014; Ramos et al., 2017). According to Beerling et al. (2018), the by-products of rock mining (considered an environmental problem) could supply the demand for highly soluble fertilizers and provide sub-sidies to farmers to use the technique globally.

The results obtained in this study conform to those of Theodoro et al. (2010) that rocks can provide nutrients that are important for crops. The by-product of this study presented notable reactivity in soils of treatments T3-T4.

4.4.5 Eucalyptus saligna Smith growth

In this experiment, there was no substitution of ESS seedlings because all of them survived. Size responses in terms of DBH and H of ESS at three, six, and nine months after planting are shown in (Figure 8A and B).

During the all evaluations, the highest DHB and H were observed in T4 and T2 treatments. Trees in the T3 treatment were similar in H and DBH to the control treatment that received no fertilization. The same behavior was noted in the T2 and T4 treatments (Figure 8A and B).

At nine months, the response of H in T4 treatment was significantly higher than all treatments ($p < 0.05$). There was a H gain of 45% and DBH of 42% compared to control (Figure 8A and B). Height and DHB responses to all treatments were directly proportional to tree age (Figure 8A and B).

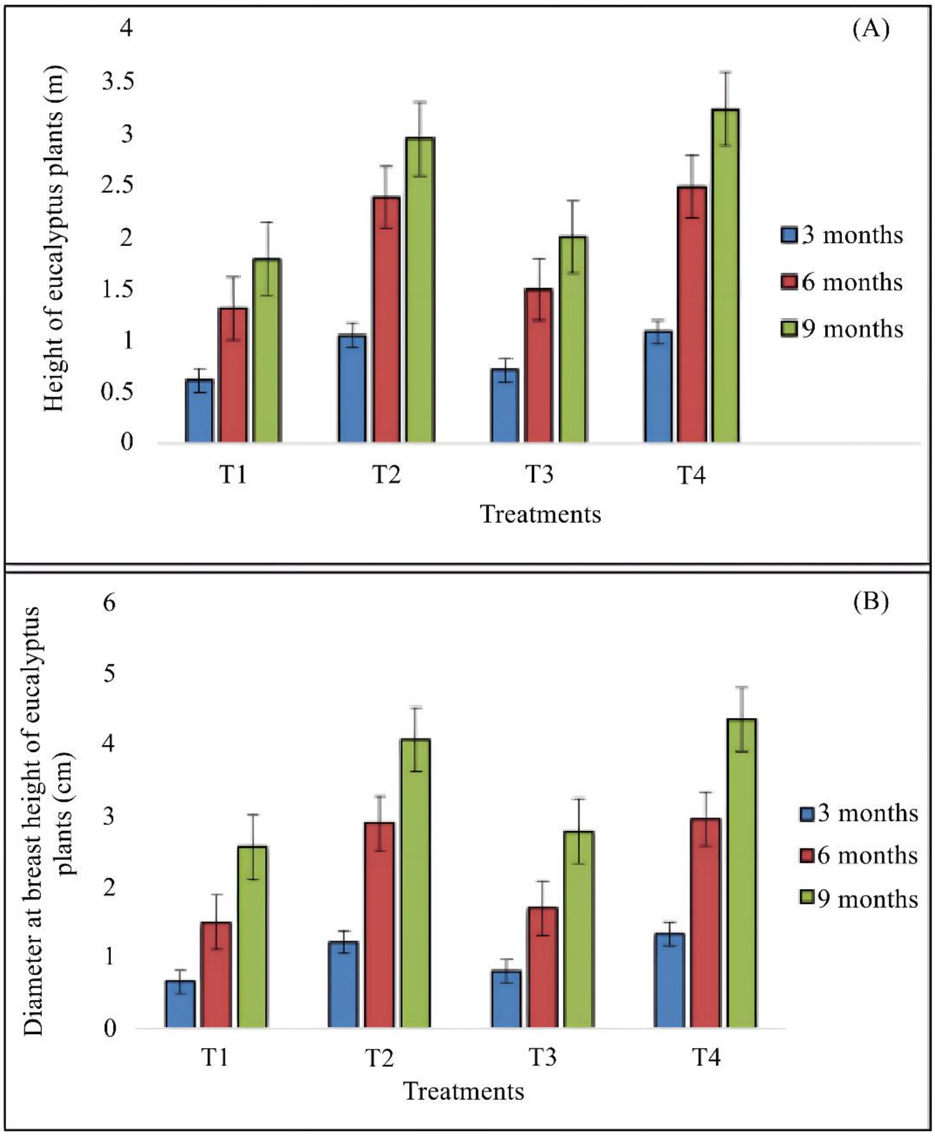

Figure 8. Treatment effects. (A) on the height and (B) on diameter at breast height of eucalyptus plants

Similar results to those of this study were found only in an experiment conducted by Leonardos and Theodora (1999) at the Agua Limpa farm in Brasilia, Brazil. These authors used three forms of fertilization over 13 years in latosols (volcanic rock powder, NPK combined with volcanic rock powder, and NPK). According to the authors, the growth of the eucalyptus plants grown in the NPK- fertilized plot was rapiduntil the fourth year. After this period, tree growth decreased significantly as compared to the growth of plants treated only with rock dust, which grew linearly, although more slowly at the beginning.

In this study, the development of ESS plants grown in USoil treated with combined doses of by-product and NPK (T4) was initially favored since the NPK acted as a catalyzer and the subsequent growth may be maintained by the released nutrients from by-product minerals.

4.5 CONCLUSIONS

This study indicated that by-product of vesicular andesite rock contains macronutrients such as Ca, K, Mg, and P, jointly with micronutrients like Cu and Zn. The low potentially toxic elements concentrations from by-product do not represent environmental risk what shows a good potential to be used as a soil remineralizer. The amount of K release in soil was significantly higher in T3 treatment with by-product dose of 100% suggesting that the mineral powder could act as an immediate release K source, being to a potential total substitute of soluble K fertilizer.

The amount of P release in soil, and DHB and H measures of the eucalyptus plants were significantly higher in soil mixture with doses of 50% by-product and 50% NPK (T4 treatment). This suggest that the vesicular andesite by-product can be a partial substitute of soluble P fertilizer.

A further understanding of the underlying biogeochemical processes is needed so that mineral materials and conditions can be modified to achieve desired agronomic effectiveness. Further sub-sequent evaluations of K and P in soils, DHB and H measures of the eucalyptus plants at long-term are needed to assess the quantitative K and P supply behaviors of the rock mineral powder in order to support sustainable agricultural production.

The use of vesicular andesite powder as a soil remineralizer in agriculture may be suitable for solving the problem of by-products deposited outside the mines and to decrease the consumption of highly soluble fertilizers.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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5 CONCLUSÕES

Conforme os resultados alcançados neste estudo, entende-se que o pó de rocha vulcânica pode ser utilizado como fonte de macro e micronutrientes para o solo, uma vez que apresenta na sua composição diversos minerais silicatados, como ortoclásio, piroxênios, plagioclásios e minerais de ferro magnesianos naturalmente alteráveis. Os ensaios de lixiviação em meio ácido evidenciaram uma desaceleração da liberação dos elementos/nutrientes para a solução extratora.

Os atributos de transformação a longo prazo e natural das rochas as deixam interessantes para a aplicação como remineralizares. A oxidação dos ortoclásio e piroxênios, assim como os argilominerais que completam as fraturas e vênulas e que ocorrem inclusive na matriz, apontam para a potencialidade de desestabilização (troca e/ou modificação) dessas fases minerais, com consecutivo acréscimo do potencial de liberação de cátions, dessa forma, podendo colaborar com a remineralização dos solos. Devido a isso, muitas são as vantagens agronômicas em se fazer o uso de resíduos de rochas vulcânicas como fertilizantes, como por exemplo: a) baixa liberação através da lixiviação dos macro e micronutrientes em água, tornando, assim, baixas as perdas por lixiviação; b) grande solubilidade dos minerais em solução de ácidos fracos, como os presentes nas soluções do solo, em liberação a longo prazo e eficiente dos mesmos para as culturas cultivadas.

A liberação cinética de dois pós de rocha de silicato (andesita e dacito), foi avaliada em um período que variou de 24 horas até 5760 horas, expostos à água Milli-Q em faixa de pH de 7,4 a 8,8, em soluções de ácido cítrico 0,1 mol L^{-1} na faixa de pH de 2,1 a 3,3 e água Milli-Q acidificada com 0,5 mol l^{-1} de ácido acético na faixa de pH de 5 a 5,8. Com base na comparação de dados, verificou-se que a aplicação de pó derivado da rocha andesito e dacito pode ser viável e substituir parcialmente fertilizantes altamente solúveis devido às altas taxas de dissolução de seus minerais. A taxa de dissolução média do andesito em água Milli-Q, com solução de ácido cítrico e em água Milli-Q acidificada com ácido acético foram $2,1 \times 10^{-5}$, $1,92 \times 10^{-1}$ e $6,3 \times 10^{-4}$mmol cm^{-2} s^{-1}, respectivamente para Ca, sendo 183%, 22,6% e 69,2% maior que a rocha dacito. Isso torna a rocha de andesito um potencial substituto para a calagem à base de carbonato. Em contraste, as taxas médias de dissolução de dacito em água Milli-Q, em solução de ácido cítrico e em água Milli-Q acidificada com ácido acético ficaram de $1,05 \times 10^{-5}$, $7,22 \times 10^{-5}$ e $3,72 \times 10^{-5}$ mmol cm^{-2} s^{-1}, nesta ordem para K, sendo 72,0%, 61,4% e 73,6% superiores que a rocha andesítica. Isso destaca seu potencial de uso como fonte de K para a agricultura e pode ser utilizada na substituição de fertilizantes de K altamente solúveis.

Todos os pós de rocha utilizados nos experimentos atenderam os índices estabelecidos de soma de bases, teor de K_2O e os conteúdos de elementos potencialmente tóxicos (As, Cd, Hg e Pb) estabelecidos pela Instrução Normativa nº 05 de 2016 do Ministério da Agricultura Pecuária e Abastecimento (MAPA) para registro como produto Remineralizador de Solos.

Para os estudos de misturas da rocha dacito com lodo de laticínio em cultivos de aveia preta e milho, esses podem fornecer uma alternativa para a substituição do uso de fertilizantes solúveis, especialmente para solos ácidos. Houve um incremento significativo de ($p <0,05$) em todos os parâmetros analisados, na dose de 7.251 kg ha^{-1} de pó de rocha dacito e 20.594 kg ha^{-1} de lodo de laticínio. Em comparação com os tratamentos controle, ambas as safras se desenvolveram muito melhor em relação a massa seca de todas as misturas, indicando que a incorporação do lodo de laticínio com o pó de rocha dacito traz um resultado eficaz e pode ser um fonte potencial de Ca, K, Mg e P na agricultura, além de baixar os índices de saturação de Al, sem representar risco de contaminação para o ambiente.

Os valores médios de qualidade da fertilidade do cultivo de eucalipto para os quatro tratamentos, com três repetições, demonstraram que houve diferenças entre os tratamentos. A quantidade de liberação de K no solo foi significativamente maior no tratamento T3, com dose de 100% do andesito, indicando que o pó rocha atua como fonte K, podendo vir a ser um potencial substituto parcial do fertilizante K solúvel. A quantidade de P liberado no solo e as medidas de DAP e H das plantas de eucalipto foram significativamente mais elevadas no solo com doses de 50% andesito e 50% NPK (T4).

O estudo sobre metodologias e modos aplicação do pó de rocha ou remineralizadores, ainda carece de esforços e pesquisas para se ter um melhor entendimento dos mecanismos de disponibilidade dos nutrientes e suas características tecnológicas.

6 SUGESTÕES PARA TRABALHOS FUTUROS

- Testar diferentes espécies vegetais;
- Avaliar a microbiologia do solo presentes na rizosfera;
- Testar inoculação de microrganismo;
- Análise de transformações do carbono orgânico e matéria orgânica;
- Realizar cultivos de longo prazo, densidade de lenho e nível de clorofila;
- Testar diferentes fontes de matéria orgânica;
- Fazer experimento utilizando plantas que produzam frutas (Citros, tomates cereja e pimentão, por exemplo), avaliando assim o uso de pó de rocha em plantas que necessitam de maior tempo de crescimento e possuem necessidades nutricionais diferentes.

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