Micronutrient dynamics in black oat and maize supplied with dacite rock powder and dairy sludge on a tropical soil

Dinámica de micronutrientes en avena negra y maíz alimentados con polvo de roca dacítica y lodos lácteos en un suelo tropical

Dinâmica de micronutrientes em aveia preta e milho adubados com pó de rocha dacítica e lodo de laticínio em solo tropical.

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Abstract
Rock powders and organic by-products are increasingly considered as alternative nutrient sources in sustainable cropping systems, yet their effects on micronutrient supply and potential toxicity remain poorly documented. This greenhouse study evaluated the micronutrient dimension of a fertilization strategy based on dacite rock powder and dairy sludge previously shown to improve soil chemistry and macronutrient supply for black oat and maize. A Typic Hapludox soil received ten treatments combining liming, mineral fertilizers, dacite rock powder, and dairy sludge at increasing doses. Black oat and maize were grown sequentially in the same pots for 70 days each. Post-harvest soil samples were analyzed for extractable copper (Cu), manganese (Mn), and zinc (Zn), and leaf and root tissues were analyzed for Cu, Mn, and Zn concentrations. Micronutrient uptake was estimated by combining tissue concentrations with dry matter production. Mixtures of dacite rock powder and dairy sludge increased leaf and root biomass of both crops, with maize leaf dry matter exceeding that of the mineral fertilizer treatment at the highest mixed dose. Soil Cu, Mn, and Zn remained within ranges typical of weathered tropical soils, and leaf concentrations of all three micronutrients stayed within accepted sufficiency ranges, with no indication of toxicity. In maize, mixed treatments corrected a latent Cu deficiency observed in limed control plants, increasing leaf Cu concentrations from values near 2–3 mg kg^{-1} to approximately 7–9 mg kg^{-1}. Total Cu, Mn, and Zn uptake per plant increased with higher by-product doses, despite decreases in some tissue concentrations at the highest biomass levels, indicating a nutrient dilution effect rather than emerging deficiency. Root Mn concentrations increased more strongly than leaf Mn, especially in maize, suggesting root retention as a tolerance mechanism that limited excessive Mn accumulation in shoots. Overall, the combined use of dacite rock powder and dairy sludge supported macronutrient and micronutrient supply to black oat and maize without creating detectable toxicological constraints under the conditions tested.

Keywords: dacite rock powder, dairy sludge, micronutrients, copper, manganese, zinc, nutrient dilution, root retention, black oat, maize.

Resumen
Los polvos de roca y los subproductos orgánicos se consideran cada vez más como fuentes alternativas de nutrientes en los sistemas de cultivo sostenibles, pero sus efectos en el suministro de micronutrientes y su posible toxicidad siguen estando mal documentados. Este estudio en invernadero evaluó la dimensión de micronutrientes de una estrategia de fertilización basada en polvo de roca dacítica y lodos lácteos que previamente habían demostrado mejorar la química del suelo y el suministro de macronutrientes para la avena negra y el maíz. Un suelo típico Hapludox recibió diez tratamientos que combinaban encalado, fertilizantes minerales, polvo de roca dacítica y lodos lácteos en dosis crecientes. La avena negra y el maíz se cultivaron secuencialmente en las mismas macetas durante 70 días cada uno. Se analizaron muestras de suelo poscosecha para determinar cobre (Cu), manganeso (Mn) y zinc (Zn) extraíbles, y se analizaron los tejidos de las hojas y las raíces para determinar las concentraciones de Cu, Mn y Zn. La absorción de micronutrientes se estimó combinando las concentraciones en los tejidos con la producción de materia seca. Las mezclas de polvo de roca dacita y lodos lácteos aumentaron la biomasa de hojas y raíces de ambos cultivos, con la materia seca de las hojas de maíz excediendo la del tratamiento de fertilizante mineral en la dosis mixta más alta. El Cu, Mn y Zn del suelo se mantuvieron dentro de los rangos típicos de los suelos tropicales meteorizados, y las concentraciones foliares de los tres micronutrientes se mantuvieron dentro de los rangos de suficiencia aceptados, sin indicación de toxicidad. En el maíz, los tratamientos mixtos corrigieron una deficiencia latente de Cu observada en las plantas de control encaladas, aumentando las concentraciones foliares de Cu de valores cercanos a 2-3 mg kg^{-1} a aproximadamente 7-9 mg kg^{-1}. La absorción total de Cu, Mn y Zn por planta aumentó con dosis más altas de subproductos, a pesar de las disminuciones en algunas concentraciones tisulares en los niveles más altos de biomasa, lo que indica un efecto de dilución de nutrientes en lugar de una deficiencia emergente. Las concentraciones de Mn en las raíces aumentaron más fuertemente que las de Mn en las hojas, especialmente en el maíz, lo que sugiere la retención radicular como un mecanismo de tolerancia que limitó la acumulación excesiva de Mn en los brotes. En general, el uso combinado de polvo de roca de dacita y lodos lácteos favoreció el suministro de macronutrientes y micronutrientes a la avena negra y al maíz sin crear restricciones toxicológicas detectables en las condiciones probadas.

Palabras clave: Polvo de roca de dacita, lodos lácteos, micronutrientes, cobre, manganeso, zinc, dilución de nutrientes, retención de raíces, avena negra, maíz.

Resumo
Pós de rocha e subprodutos orgânicos são cada vez mais considerados como fontes alternativas de nutrientes em sistemas de cultivo sustentáveis, porém seus efeitos no fornecimento de micronutrientes e sua potencial toxicidade ainda são pouco documentados. Este estudo em casa de vegetação avaliou a dimensão dos micronutrientes em uma estratégia de fertilização baseada em pó de rocha dacítica e lodo de laticínios, previamente demonstrada como eficaz na melhoria da química do solo e no fornecimento de macronutrientes para aveia-preta e milho. Um solo Hapludox típico recebeu dez tratamentos combinando calagem, fertilizantes minerais, pó de rocha dacítica e lodo de laticínios em doses crescentes. Aveia-preta e milho foram cultivados sequencialmente nos mesmos vasos por 70 dias cada. Amostras de solo pós-colheita foram analisadas quanto ao teor de cobre (Cu), manganês (Mn) e zinco (Zn) extraíveis, e tecidos foliares e radiculares foram analisados quanto às concentrações de Cu, Mn e Zn. A absorção de micronutrientes foi estimada pela combinação das concentrações nos tecidos com a produção de matéria seca. Misturas de pó de rocha dacítica e lodo de laticínios aumentaram a biomassa foliar e radicular de ambas as culturas, com a matéria seca foliar do milho superando a do tratamento com fertilizante mineral na maior dose da mistura. As concentrações de Cu, Mn e Zn no solo permaneceram dentro dos limites típicos de solos tropicais intemperizados, e as concentrações foliares dos três micronutrientes permaneceram dentro dos limites de suficiência aceitáveis, sem indicação de toxicidade. No milho, os tratamentos mistos corrigiram uma deficiência latente de Cu observada nas plantas controle tratadas com cal, aumentando as concentrações foliares de Cu de valores próximos a 2–3 mg kg^{-1} para aproximadamente 7–9 mg kg^{-1}. A absorção total de Cu, Mn e Zn por planta aumentou com doses mais elevadas do subproduto, apesar da diminuição em algumas concentrações teciduais nos níveis mais altos de biomassa, indicando um efeito de diluição de nutrientes em vez do surgimento de deficiência. As concentrações de Mn nas raízes aumentaram mais acentuadamente do que nas folhas, especialmente no milho, sugerindo a retenção radicular como um mecanismo de tolerância que limitou o acúmulo excessivo de Mn na parte aérea. De modo geral, o uso combinado de pó de rocha dacítica e lodo de laticínio promoveu o fornecimento de macro e micronutrientes para aveia-preta e milho sem criar restrições toxicológicas detectáveis nas condições testadas.

Palavras-chave: Pó de rocha dacítica, lodo de laticínios, micronutrientes, cobre, manganês, zinco, diluição de nutrientes, retenção de raízes, aveia preta, milho.

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1. Introduction

Intensive crop production systems rely heavily on soluble mineral fertilizers, yet there is growing interest in alternative nutrient sources that can sustain yields while reducing environmental impacts and dependence on nonrenewable inputs. Finely ground silicate rocks, or rock dusts, have been proposed as soil remineralizers that gradually supply macronutrients and micronutrients and improve soil properties, particularly in highly weathered tropical soils (Harley & Gilkes, 2000; Morales-Aranibar, 2022; Ramos et al., 2021). Recent reviews and case studies have shown that basaltic and dacitic rock powders can enhance soil fertility and crop productivity when their mineralogy is suitable and their application is tailored to local conditions (Nguyen et al., 2024; Richardson, 2024; Toscani & Campos, 2017; Viana et al., 2021). At the same time, the use of rock dust as part of enhanced weathering strategies has been linked to potential co-benefits for soil biological and physical functions and long-term carbon sequestration, which has attracted attention in the context of climate change mitigation (Xavier et al., 2024; Fang et al., 2023).

Organic by-products such as sewage and industrial sludges represent another large stream of materials with potential agronomic use. These materials often contain high amounts of nitrogen, phosphorus, and organic carbon and can improve soil structure and biological activity, but their use is constrained by concerns about contaminants, particularly heavy metals (Rocha et al., 2025; Burke et al., 2023; Saha et al., 2017). Studies from different regions have reported that sewage sludge application can increase soil metal contents and alter their speciation, yet have also shown that, when contaminant levels are monitored and application rates are managed, sludge can be safely used to supply nutrients and organic matter to agricultural soils (Janaszek & Kowalik, 2023; McBride & Cherney, 2004). Combining rock powders with organic amendments such as sludges has been proposed to stabilize nutrients, enhance weathering, and recycle industrial by-products within agricultural systems (Nguyen et al., 2024; Viana et al., 2021). These synergistic effects are generally attributed to a combination of mineral dissolution, organic complexation of metal cations, and stimulation of microbial activity in the rhizosphere, processes that can collectively enhance micronutrient availability from rock-derived minerals (Ribeiro et al., 2020; Fang et al., 2023).

Biological processes play a central role in the weathering of silicate minerals and the mobilization of nutrients from rock dust. Mineral-weathering bacteria and other rhizosphere microorganisms can produce organic acids, chelating ligands, and biofilms that lower pH at mineral surfaces, disrupt passivating layers, and enhance the dissolution of nutrient-bearing phases (Ribeiro et al., 2020; Fang et al., 2023). Co-application of silicate rock powders with humic-like substances or organic materials has been shown to increase nutrient uptake and plant growth in weathered tropical soils, likely through a combination of chemical complexation, improved soil physical conditions, and stimulation of microbial activity (Busato et al., 2022; Toscani & Campos, 2017). These interactions suggest that combining rock powders with organic by-products such as dairy sludge could improve the agronomic performance of rock-based fertilizers by increasing the availability of both macro- and micronutrients.

Adequate supply of the micronutrients copper (Cu), manganese (Mn), and zinc (Zn) is essential for cereal growth, enzyme function, and grain nutritional quality, yet both deficiencies and toxicities of these elements are common under certain soil and management conditions (Leite et al., 2006; Agarwala et al., 1995; Millaleo et al., 2010). Critical leaf levels for Cu and Mn in cereals have been established from long-term field and pot experiments, and deficiencies have been associated with yield losses in maize and other crops, especially following liming of acidic soils that reduces metal availability (Davis & Beckett, 1978; Franck & Finck, 1980; Kirchmann & Eskilsson, 2010). Zinc deficiency has also been widely documented in cereal systems, and both low and excessive Zn inputs can impact growth and grain quality (Teklić et al., 2013; Gupta & Kalra, 2006). Foliar and soil applications of Cu, Zn, and Mn can correct deficiencies and improve yield and grain quality in wheat and other cereals when doses and timing are appropriate (Stępień & Wojtkowiak, 2016; Ray et al., 2024).

At the same time, increases in biomass driven by improved nutrition or elevated atmospheric CO_2 often lead to decreases in nutrient concentrations in plant tissues, a phenomenon referred to as nutrient dilution (Broberg et al., 2017; Riedell, 2010). Recent work on nitrogen use efficiency and nutrient dynamics in cereals has highlighted the importance of distinguishing between dilution and true deficiency, emphasizing that total nutrient uptake and tissue mass need to be considered alongside concentrations when assessing plant nutritional status (Grzebisz & Biber, 2024; Kumar et al., 2024). This distinction is particularly important for micronutrients such as Cu, Mn, and Zn, where moderate reductions in concentration at high yield may not indicate an inadequate supply but could still have implications for the nutritional quality of cereal grains consumed by humans (Teklić et al., 2013; Ray et al., 2024).

Plants possess sophisticated mechanisms to regulate Mn uptake, distribution, and detoxification, which influence how they respond to both deficiency and excess. Mn is taken up by roots through specific transporters and subsequently partitioned among cell walls, cytosol, and vacuoles, with the balance controlled by transporter proteins and subcellular sequestration processes (Pittman, 2005; Millaleo et al., 2010; Alejandro et al., 2020). In maize, the tonoplast-localized transporter ZmNRAMP2 has been shown to mediate root-to-shoot translocation of Mn, and mutants lacking this transporter retain more Mn in roots but suffer from reduced shoot Mn and impaired growth under Mn-limiting conditions (Guo et al., 2022). Broader reviews of Mn handling in plants have emphasized that root retention, vacuolar compartmentation, and cell wall sequestration are key tolerance mechanisms that can prevent excess Mn from reaching sensitive shoot tissues while maintaining sufficient Mn for metabolic functions (Alejandro et al., 2020; Meier et al., 2025). These processes imply that increases in total Mn supply do not necessarily translate into proportional increases in shoot Mn concentrations or toxicity symptoms.

Building on this body of work, a previous greenhouse study evaluated the agronomic potential of blending dacite rock powder with dairy sludge on the same Typic Hapludox soil used here and reported improved soil pH, reduced aluminum saturation, enhanced macronutrient availability, and increased dry matter production of black oat and maize (Ramos et al., 2021). That study also showed that concentrations of potentially toxic elements such as As, Cd, Cr, Hg, and Pb in the by-products were below regulatory limits and did not pose an apparent contamination risk. However, the earlier work focused on macronutrients and did not explicitly assess how the combined by-products affected the status of Cu, Mn, and Zn in soil and plant tissues, nor did it investigate the potential for nutrient dilution or toxicological constraints related to these micronutrients.

This research addresses this gap by re-examining the same experimental system with specific emphasis on the micronutrient dimension. The objectives were to determine whether mixtures of dacite rock powder and dairy sludge provide sufficient Cu, Mn, and Zn to support black oat and maize nutrition on an acidic, nutrient-poor tropical soil; to assess whether high doses of these by-products lead to potentially toxic accumulations of Cu, Mn, or Zn in soil or plant tissues; and to explore whether observed changes in tissue concentrations represent true deficiency, toxicity, or nutrient dilution associated with increased biomass. By integrating concentration, biomass, and calculated uptake data and interpreting them in light of current understanding of rock weathering, micronutrient dynamics, and Mn homeostasis (Harley & Gilkes, 2000; Ribeiro et al., 2020; Alejandro et al., 2020; Guo et al., 2022), this work seeks to clarify the micronutrient and toxicological implications of using dacite rock powder and dairy sludge as a combined fertilization strategy. In doing so, it contributes to the broader discussion on how rock-based and organic amendments can be integrated into sustainable nutrient management approaches that support crop productivity, micronutrient security, and environmentally sound reuse of industrial by-products.

2. Materials and methods

2.1. Experimental site and soil

The experiment was conducted in a plastic greenhouse at the Environmental Research Center of La Salle University in Nova Santa Rita, Rio Grande do Sul, Brazil, using the same pots, soil, and treatments previously described for the evaluation of macronutrient release from dacite rock powder and dairy sludge in black oat and maize (Ramos et al., 2021). The soil was a Typic Hapludox collected from the 0–20 cm layer of an agricultural field near Nova Santa Rita. According to the original soil test report, the soil contained 21% clay, had a pH in water of 5.2, and low available phosphorus and potassium, with 6.2 mg dm^{-3} P and 62 mg dm^{-3} K. 0.3 cmolc dm^{-3} exchangeable aluminum, 2.6 cmolc dm^{-3} calcium, 0.7 cmolc dm^{-3} magnesium, 2.9 mg dm^{-3} copper, 3.9 mg dm^{-3} zinc, and 48 mg dm^{-3} manganese, and the effective cation exchange capacity was 7.04 cmolc dm^{-3}, with 50% base saturation. These properties characterize a moderately acidic, nutrient-poor tropical soil that is typical for the region and responsive to liming and fertilization.

2.2. Treatments and experimental design

The study used ten treatments (T1–T10) that combined liming, soluble fertilizers, dacite rock powder, and dairy sludge, following the fertilization plan originally designed for the macronutrient study (Ramos et al., 2021). Dolomitic limestone with a relative neutralizing value of 72.6% was applied at 2200 kg ha^{-1} to all treatments and mixed thoroughly with the soil before potting. Potassium and phosphorus rates were defined according to local recommendations for black oat and maize, and were supplied by mineral fertilizers, dacite rock powder, and dairy sludge in different proportions (Table 1).

Table 1. Treatments T1–T10 with liming, mineral fertilizer, dacite rock powder, and dairy sludge rates (kg ha^{-1}).

Treatment	Description	Limestone	Rock powder	Dairy sludge	Total K2O	Total P2O5
T1	Mineral fertilizer control	2200			0	0
T2	Mineral fertilizer control	2200			60	100
T3	Rock powder + dairy sludge	2200	906	2574	30	50
T4	Rock powder + dairy sludge	2200	1818	5148	60	100
T5	Rock powder + dairy sludge	2200	3625	10297	120	200
T6	Rock powder + dairy sludge	2200	7250	20594	240	400
T7	Rock powder	2200	906		30	100
T8	Rock powder	2200	1812		60	100
T9	Rock powder	2200	3625		120	100
T10	Rock powder	2200	7250		240	100

The treatments included two controls receiving only mineral fertilizers, four treatments receiving mixtures of dacite rock powder and dairy sludge at increasing doses, and four treatments receiving dacite rock powder without dairy sludge at corresponding rock doses. The target field-equivalent rates of dacite rock powder in these treatments were approximately 906, 1818, 3625, and 7251 kg ha^{-1}, and the corresponding dairy sludge rates in the mixed treatments were approximately 2574, 5149, 10297, and 20594 kg ha^{-1}. The detailed fertilization plan, including equivalent rates of K_2O and P_2O_5, and the conversion to grams per 12-kg pot, is provided in Table 1.

For each treatment, soil was weighed into 12 dm^3 pots corresponding to approximately 12 kg of dry soil, thoroughly mixed with the assigned amendments, and incubated to allow initial reactions between the soil, dacite rock powder, and dairy sludge. The greenhouse experiment followed a completely randomized design with five replicate pots per treatment in the original study (Ramos et al., 2021). In this work, the number of replicate samples available for each response variable depended on the analytical subset: for dry matter yield, three replicate plants per treatment were available, whereas for tissue micronutrient concentrations, two composite samples per treatment were analyzed. These replication levels are explicitly considered in statistical analysis.

2.3. Crop management and sampling

Black oat (*Avena strigosa*) was grown as the first crop and maize (*Zea mays L.*) as the second crop, sequentially in the same pots, following the original macronutrient experiment (Ramos et al., 2021). For each crop, nine seeds were sown per pot and later thinned to three plants per pot. Crops were grown for 70 days under greenhouse conditions with regular irrigation to maintain soil moisture near field capacity, and no additional fertilization was applied during the growth period.

At harvest, shoots were cut at the soil surface, separated into leaves and stems as necessary, and oven-dried at 40 °C until constant weight. Roots were carefully removed from the soil, washed free of adhering soil particles with deionized water, and oven-dried at 40 °C to constant weight. Dry leaves and roots was recorded for each pot as grams per plant, using the mean dry mass of the three plants. After the black oat harvest, the soil from each pot was homogenized, passed through a 4-mm sieve, and returned to the same pot for the subsequent maize crop. At the end of the maize cycle, the same procedures for plant harvest, tissue separation, washing, and drying were followed.

Composite soil samples were collected from each treatment and crop after harvest by combining subsamples from the replicate pots. For each crop, the composite samples were used to determine post-harvest soil concentrations of copper (Cu), manganese (Mn), and zinc (Zn).

2.4. Chemical analysis

This study focused on micronutrient status in soil, leaves, and roots, using analytical data generated in parallel with the macronutrient experiment. For each treatment and crop, post-harvest soil samples were analyzed for extractable Cu, Mn, and Zn, expressed as mg dm^{-3}. Leaf and root tissues of black oat and maize were analyzed for Cu, Mn, and Zn concentrations, expressed as mg kg-1 on a dry mass basis. Analytical procedures followed standard soil fertility and plant nutrition methods routinely used in tropical agronomy laboratories and were the same as those used to characterize the original experiment (Ramos et al., 2021). In brief, soil samples were dried and sieved, micronutrients were extracted with an acid extractant suitable for assessing available Cu, Mn, and Zn in weathered tropical soils, and the elements were determined by optical emission spectrometry. Plant samples were ground to a fine powder, digested in an acid mixture, and the same spectrometric technique quantified Cu, Mn, and Zn. Quality control included the use of laboratory reference materials and internal standards.

2.5. Calculation of micronutrient uptake

For each treatment and crop, micronutrient uptake by leaves and roots was calculated by combining tissue concentrations with dry matter data. For a given element and organ, uptake per plant was calculated as U = C × DM, where U is the uptake in milligrams per plant, C is the tissue concentration in milligrams per kilogram, and DM is the dry mass in kilograms per plant. Dry mass data were obtained for three replicate plants per treatment, and tissue concentrations were available for two composite samples per treatment. To estimate uptake, the mean concentration for each treatment and organ was multiplied by the mean dry mass for that treatment. This approach allows a distinction between changes in concentration due to biomass accumulation and those associated with altered elemental uptake.

2.6. Statistical analysis

Data were analyzed using one-way analysis of variance (ANOVA) to evaluate the effect of treatments on plant dry matter, micronutrient concentrations in leaves and roots, and total micronutrient uptake. The experimental design was completely randomized. Before analysis, assumptions of normality and homogeneity of variance were assessed. When the ANOVA indicated significant differences among treatments ($p < 0.05$), means were compared using Tukey's Honest Significant Difference (HSD) post-hoc test. All statistical computations were performed using standard Python libraries for scientific computing. Results are presented as means ± standard deviation (SD), and letters indicate significant differences among treatments.

3. Results and discussions

3.1. Nutrient removal assessment

Application of dacite rock powder and dairy sludge altered soil Cu, Mn, and Zn concentrations only moderately compared with the mineral fertilizer controls (Table 2). After black oat, extractable soil Cu ranged from 3.09 to 3.87 mg dm^{-3}, Mn from 65.2 to 124.4 mg dm^{-3}, and Zn from 4.99 to 5.74 mg dm^{-3}. Similar ranges were observed after maize, with soil Cu between 2.19 and 3.95 mg dm-3, Mn between 61.7 and 87.3 mg dm^{-3}, and Zn between 4.53 and 5.39 mg dm^{-3}. In both crops, soils receiving mixtures of dacite rock powder and dairy sludge showed slightly higher mean Mn and Zn concentrations than soils receiving dacite rock powder alone or mineral fertilizers, whereas Cu showed little consistent change among treatments. No treatment generated extractable Cu, Mn, or Zn levels outside the range typically considered agronomically acceptable for weathered tropical soils.

Table 2. Post-harvest extractable soil Cu, Mn, and Zn concentrations (mg dm^{-3}) after black oat and maize cultivation.

Treatment	Cu after oat	Mn after oat	Zn after oat	Cu after maize	Mn after maize	Zn after maize
T1	3.54	82.64	5.70	3.02	64.01	5.06
T2	3.66	124.43	5.62	3.14	87.3	4.58
T3	3.39	100.1	4.99	3.95	78.1	5.26
T4	3.47	116.8	5.24	3.43	76.8	5.19
T5	3.87	73.3	5.45	3.63	66.2	5.18
T6	3.09	65.2	5.74	3.49	61.7	5.39
T7	3.47	77.2	5.28	3.33	68.3	5.07
T8	3.67	73.0	5.60	2.69	65.0	4.53
T9	3.67	65.2	5.55	3.40	71.5	5.08
T10	3.42	79.2	5.41	2.19	76.8	4.92

Treatment group comparisons indicated that the highest mixed dose of dacite rock powder plus dairy sludge (T6) produced somewhat elevated Mn in soil relative to the absolute control, but this increase remained within the variability observed among intermediate doses. The rock-only treatments (T7–T10) produced small changes in soil Mn and Zn compared with the controls, consistent with the slow dissolution expected for silicate rock powders. Across both crops, there was no indication of progressive accumulation of Cu, Mn, or Zn in soil with increasing doses of dacite rock powder and dairy sludge.

3.2. Dry matter production of black oat and maize

Dry production of black oat and maize leaves and roots responded positively to the by-product treatments (Figure 1). In black oat, leaf dry mass increased significantly from 1.41 ± 0.02 g $plant^{-1}$ in the absolute control (T1) to 2.54 ± 0.04 g $plant^{-1}$ at the highest mixed dose (T6). Root dry mass showed a similar pattern, with T6 producing greater root mass (1.95 g) compared to the control (0.57 g).

Maize responded even more strongly: leaf dry mass increased from 3.41 ± 0.05 g plant^{-1} in the control (T1) to 4.80 ± 0.07 g plant^{-1} in the highest mixed treatment (T6), significantly outperforming the mineral fertilizer treatment (T2, 3.85 g plant^{-1}). Root dry mass in maize increased from 1.49 g plant^{-1} in T1 to 2.45 g plant^{-1} in T6. Rock-only treatments (T7–T10) generally produced intermediate yields, lower than the mixed treatments but often higher than the absolute control. These treatment effects on leaf and root dry matter are summarized in Table 2.

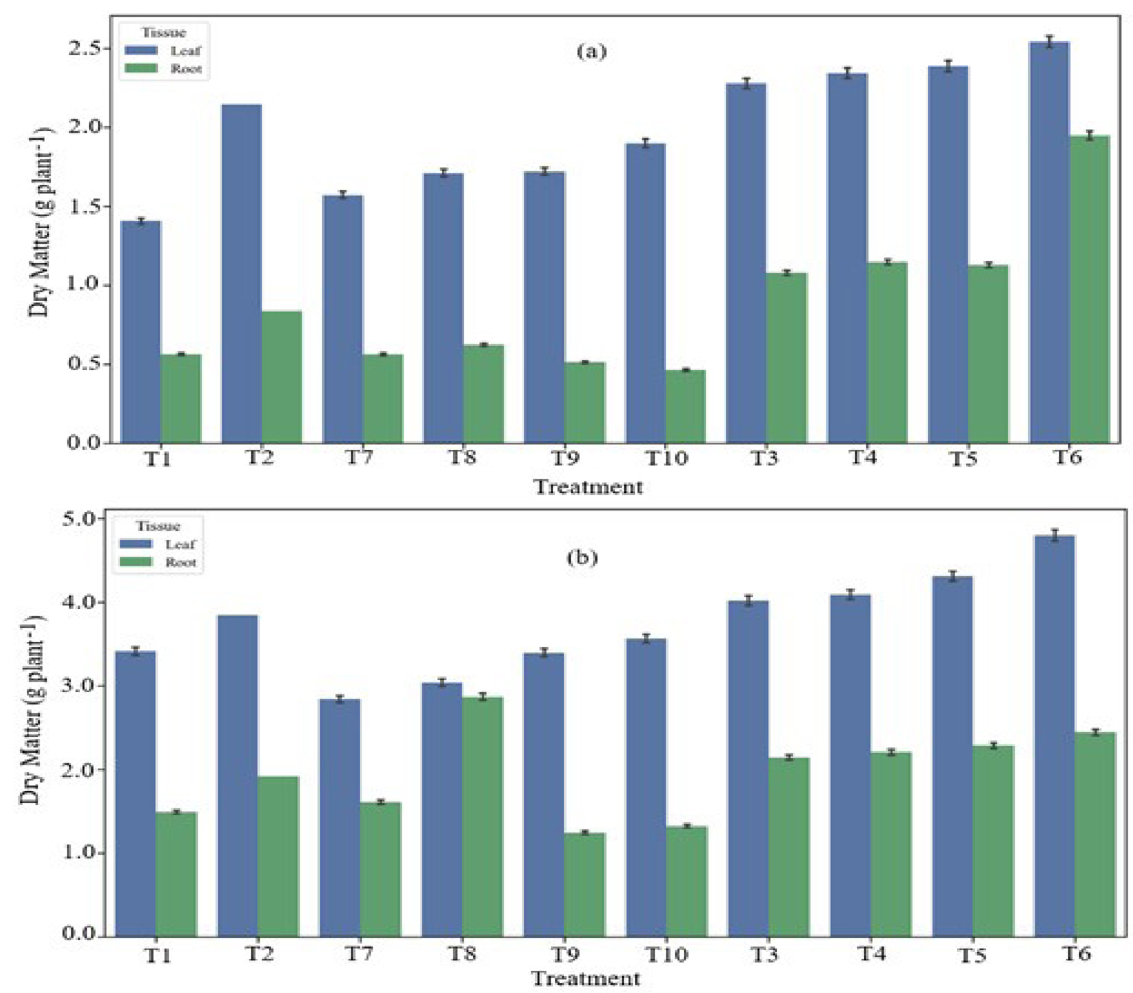

Figure 1. Leaf and root dry matter of black oat and maize as affected by treatments T1–T10. (a) Black Oat; (b) Maize.

3.3. Micronutrient concentrations in leaves and roots

In black oat leaves, Cu concentrations were highest in the control (T1, 13.0 mg kg^{-1}) and rock-only treatments, but decreased significantly in the mixed treatments, reaching 8.2 mg kg^{-} in T6 (Table 3). However, these values remained well within sufficiency ranges. In contrast, maize showed a clear correction of Cu deficiency: the control (T1) plants had severely low Cu (2.49 ± 0.20 mg kg^{-1}), while the high-dose mixed treatment (T6) restored levels to 8.76 ± 0.94 mg kg^{-1}, significantly higher than both the control and the mineral fertilizer (T2, 6.26 mg kg^{-1}).

Leaf Mn concentrations in maize decreased from 93.9 mg kg^{-1} in the control to 74.0 mg kg^{-1} in T6, suggesting a dilution effect or reduced availability due to pH changes, but remained sufficient. Root Mn concentrations were notably higher than leaf concentrations in both crops (e.g., Maize T6: Root 247.7 vs Leaf 74.0 mg kg^{-1}), indicating effective root retention. Zinc concentrations in maize leaves were lower in the mixed treatments compared to the control, but remained adequate (>20 mg kg^{-1}). The distribution of Cu, Mn, and Zn between leaves and roots is shown in Table 3.

Table 3. Micronutrient concentrations (mg kg^{-1}) in leaves and roots of black oat and maize.

Treatment	Oat leaf Cu	Oat leaf Mn	Oat leaf Zn	Oat root Cu	Oat root Mn	Oat root Zn	Maize leaf Cu	Maize leaf Mn	Maize leaf Zn	Maize root Cu	Maize root Mn	Maize root Zn
T1	12.97	82.73	66.58	15.89	93.14	72.39	2.49	93.87	63.14	16.05	170.99	30.90
T2	13.62	91.89	63.94	20.96	112.47	82.28	6.26	92.31	34.74	14.40	121.93	42.87
T3	11.78	87.84	73.74	26.30	118.67	78.97	6.79	81.37	34.33	17.94	149.24	45.39
T4	11.66	67.37	76.11	20.39	135.09	39.39	6.28	64.42	30.21	17.49	148.31	40.10
T5	7.64	48.60	74.15	10.57	178.33	65.74	7.79	65.81	33.80	27.59	225.52	42.65
T6	8.22	54.49	71.35	13.36	207.58	64.05	8.76	74.01	42.44	24.54	247.67	53.97
T7	15.04	93.71	71.29	13.87	93.29	74.51	6.77	86.66	68.24	16.64	160.65	40.42
T8	12.53	76.09	67.70	12.56	83.27	70.82	7.96	69.09	32.82	22.62	119.19	36.36
T9	11.59	79.28	61.83	15.74	92.31	84.05	7.82	88.81	29.26	17.75	125.20	43.44
T10	9.76	64.19	74.24	14.74	112.02	81.23	5.34	86.43	55.28	17.38	137.88	36.81

3.4. Micronutrient uptake and dilution effects

Total micronutrient uptake (leaf and root) generally increased with the application of dacite rock powder and dairy sludge, driven by the biomass gains. For maize, total Cu uptake increased more than threefold from T1 (0.032 mg plant^{-1}) to T6 (0.102 mg plant^{-1}), confirming that the increased biomass was supported by enhanced Cu acquisition (Table 4).

Plots of leaf Cu concentration versus leaf dry matter (Figure 2) revealed distinct patterns: for Black Oat, a negative trend indicated a dilution effect (higher biomass, lower concentration). However, for Maize Cu, the trend was positive across the mixed treatments, confirming that the amendment supplied sufficient Cu to not only maintain but also increase tissue concentrations despite the rapid growth.

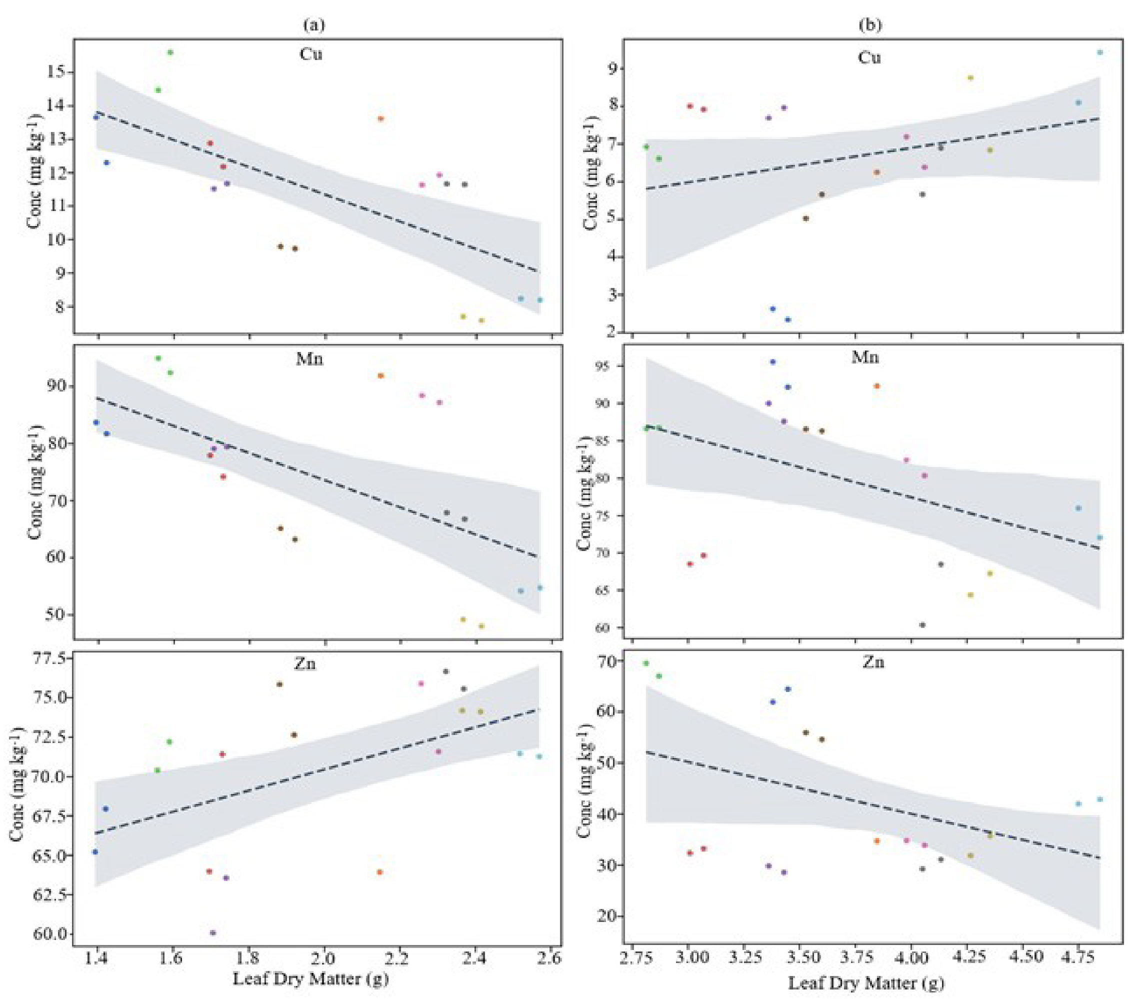

Figure 2. Leaf and root dry matter of black oat and maize as affected by treatments T1–T10. Nutrient Dilution Effect: (a) Black Oat; (b) Maize.

Table 4. Total calculated micronutrient uptake (mg plant^{-1}) for black oat and maize (leaf and root).

Treatment	Oat leaf Cu uptake	Oat leaf Mn uptake	Oat leaf Zn uptake	Oat root Cu uptake	Oat root Mn uptake	Oat root Zn uptake	Maize leaf Cu uptake	Maize leaf Mn uptake	Maize leaf Zn uptake	Maize root Cu uptake	Maize root Mn uptake	Maize root Zn uptake
T1	0.020	0.115	0.093	0.009	0.052	0.040	0.008	0.317	0.213	0.024	0.253	0.046
T2	0.030	0.192	0.134	0.018	0.092	0.068	0.023	0.347	0.130	0.027	0.228	0.080
T3	0.026	0.200	0.168	0.028	0.128	0.085	0.027	0.327	0.138	0.038	0.320	0.098
T4	0.028	0.162	0.184	0.024	0.159	0.046	0.026	0.271	0.127	0.039	0.337	0.091
T5	0.018	0.115	0.176	0.012	0.202	0.074	0.033	0.282	0.142	0.063	0.516	0.098
T6	0.023	0.156	0.205	0.029	0.457	0.141	0.047	0.401	0.229	0.067	0.684	0.149
T7	0.024	0.150	0.114	0.008	0.054	0.043	0.019	0.251	0.198	0.027	0.264	0.066
T8	0.022	0.133	0.119	0.008	0.053	0.045	0.025	0.215	0.102	0.066	0.350	0.107
T9	0.021	0.140	0.109	0.008	0.049	0.044	0.027	0.310	0.102	0.023	0.160	0.056
T10	0.019	0.127	0.147	0.007	0.054	0.039	0.019	0.322	0.206	0.024	0.191	0.051

3.5. Comparison of mixed and rock-only treatments

Comparisons between treatments with dacite rock powder plus dairy sludge and those with dacite rock powder alone at matching rock doses indicated that the presence of dairy sludge enhanced both biomass production and micronutrient uptake. At the highest rock dose (T6 vs T10), the mixed treatment produced 35% more maize leaf biomass (4.80 g vs 3.56 g) and more than doubled the total Cu uptake (0.102 vs 0.042 mg plant^{-1}). This pattern suggests that the organic amendments not only provided direct nutrients but also facilitated the weathering or retention of rock-derived minerals. These differences in total Cu, Mn, and Zn uptake among treatments are summarized in Figure 3.

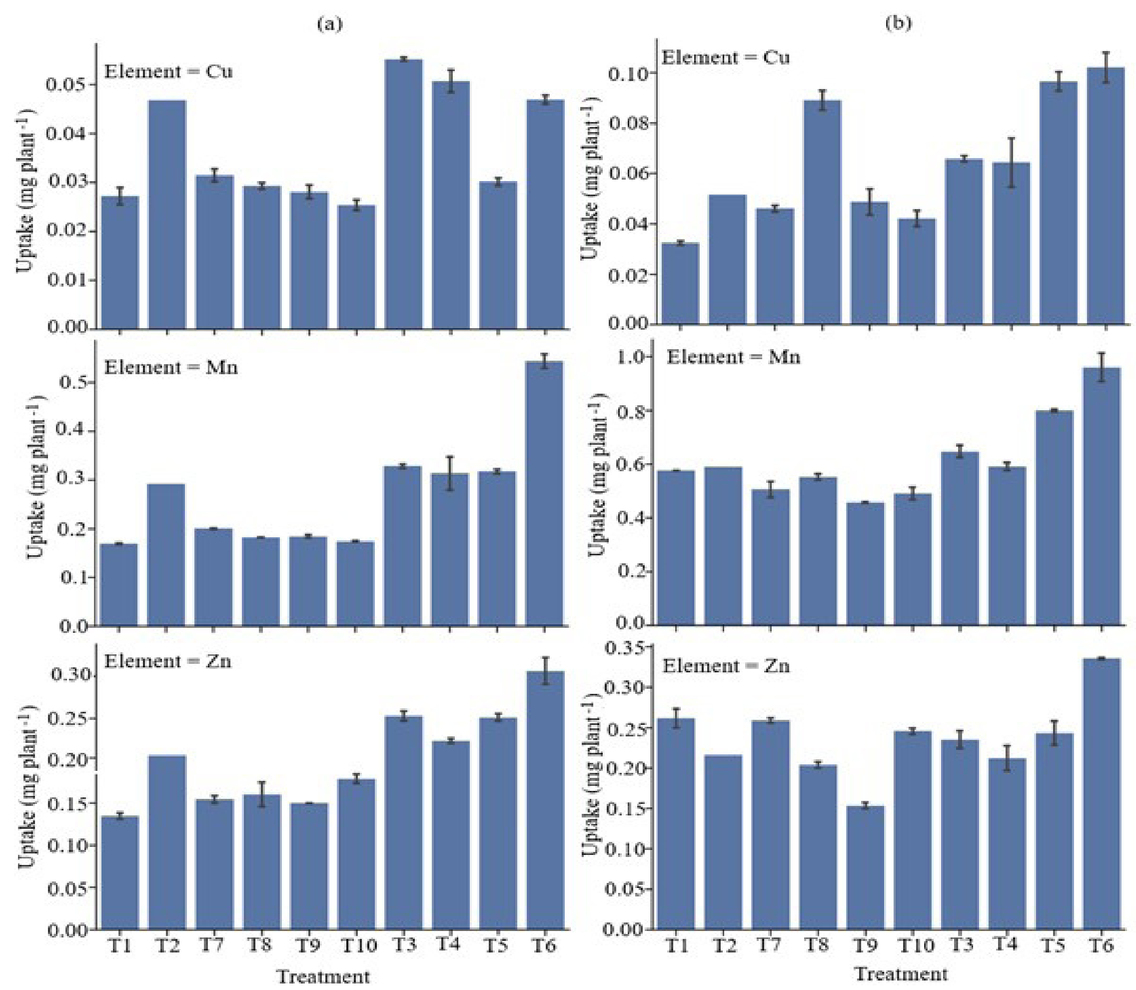

Figure 3. Total Cu, Mn, and Zn uptake (leaf and root) of black oat and maize for treatments T1–T10. Total micronutrient uptake: (a) Brack Oat, (b) Maize.

4. Discussion

The present study evaluated whether a previously tested combination of dacite rock powder and dairy sludge that was shown to supply macronutrients to black oat and maize (Ramos et al., 2021) also provided adequate amounts of the micronutrients Cu, Mn, and Zn without creating toxic conditions in soil or plant tissues. The results showed that the mixtures of dacite rock powder and dairy sludge increased leaf and root dry matter of both crops, particularly maize (Figure 1), while maintaining soil and tissue Cu, Mn, and Zn concentrations within widely accepted sufficiency ranges for cereals (Table 2). Micronutrient uptake per plant increased with increasing doses of the mixtures despite some decreases in tissue concentrations at the highest biomass levels, indicating that the system did not induce micronutrient deficiency, but rather nutrient dilution associated with enhanced growth.

4.1. Micronutrient sufficiency and correction of Cu deficiency

Leaf Cu, Mn, and Zn concentrations in black oat and maize across treatments were generally consistent with published sufficiency ranges for cereals (Table 3). Critical leaf levels for Cu and Mn in maize have been reported in the low single-digit to low double-digit mg kg^{-1} range, with deficiency occurring below approximately 5 mg kg^{-1} Cu and 20–30 mg kg^{-1} Mn, and adequate Zn typically above about 20–25 mg kg^{-1} (Davis & Beckett, 1978; Franck, & Finck, 1980; Leite et al., 2006). The control maize plants exhibited leaf Cu concentrations near the lower end of this range, consistent with previous observations that liming of acidic soils can exacerbate Cu and Mn deficiencies and depress cereal yields if micronutrients are not supplied (Kirchmann & Eskilsson, 2010). In contrast, the mixtures of dacite rock powder and dairy sludge elevated maize leaf Cu into a range of 7–9 mg kg^{-1} while increasing biomass (Table 3), which suggests that the combined by-products corrected a latent Cu deficiency that was present in the fertilized but rock-free control treatments.

The observed Cu responses agree with earlier work showing that Cu and Zn additions can influence growth and enzyme activities in maize and other cereals (Agarwala et al., 1995) and that residual Cu and Zn from fertilizers can continue to affect plant concentrations and yield in subsequent crops (Gupta & Kalra, 2006). In this experiment, no explicit Cu or Zn fertilizer was added beyond what was contained in the dacite rock powder and dairy sludge. The correction of low maize leaf Cu concentrations by the mixed treatments, therefore, indicates that the byproducts supplied sufficient Cu to overcome the sensitivity of the limed Typic Hapludox to Cu deficiency. This finding is relevant for nutrient management in highly weathered tropical soils, where liming is often necessary to reduce acidity but can inadvertently reduce the availability of certain micronutrients.

For black oat, leaf Cu, Mn, and Zn concentrations remained well within sufficient ranges across treatments, and increases in biomass were not associated with values near deficiency thresholds. Together with the maize results, this pattern indicates that the dacite rock powder and dairy sludge mixtures supported adequate micronutrient status in both crops and, in the case of maize Cu, improved the nutritional status relative to conventional mineral fertilization alone. At the same time, the maximum observed leaf concentrations of Cu, Mn, and Zn were far below values associated with toxicity in cereals, and concentrations in edible organs such as grain would be expected to remain within safe dietary limits reported for trace metals in cereal grains (Teklić et al., 2013).

4.2. Nutrient dilution versus deficiency under high biomass accumulation

The concentration data showed that in some treatments, especially those with the highest dose of dacite rock powder and dairy sludge, leaf Cu concentrations in black oat and, to a lesser extent, in maize decreased compared with intermediate doses, even though dry matter continued to increase (Figure 1). Similar patterns have been described in cereals under conditions of enhanced growth, where increased biomass leads to a dilution of nutrient concentrations without necessarily reducing total nutrient uptake (Broberg et al., 2017; Riedell, 2010). Recent analyses of nitrogen use efficiency and nutrient dynamics in cereals have emphasized that high yields can be accompanied by lower tissue nutrient concentrations unless fertilization is balanced, and that distinguishing between nutrient dilution and true deficiency requires consideration of both concentrations and total nutrient mass in plant tissues (Grzebisz & Biber, 2024; Kumar et al., 2024).

In this study, calculated uptake of Cu, Mn, and Zn per plant increased with increasing doses of the dacite rock powder and dairy sludge mixtures, even in treatments where leaf concentrations declined (Table 4). This was particularly evident for maize, where the highest mixed dose produced the greatest biomass and the highest total uptake of all three micronutrients (Table 4; Figure 2), while leaf Mn and Zn concentrations remained within relatively narrow ranges. These results support the interpretation that the observed decreases in some tissue concentrations at high biomass represent nutrient dilution rather than emerging deficiency. This distinction is important given concerns about "hidden hunger," where reductions in the concentration of micronutrients in staple crops may occur without visible deficiency symptoms (Ray et al., 2024). In the present system, dilution was accompanied by increased uptake and improved growth, suggesting that the agronomic and nutritional outcomes were positive within the tested range of doses.

4.3. Mechanisms of micronutrient supply from dacite rock powder and dairy sludge

The limited changes in soil extractable Cu, Mn, and Zn across treatments, combined with the enhanced biomass and tissue micronutrient status in the mixed treatments, suggest that the dacite rock powder and dairy sludge acted as a slowly dissolving source of micronutrients whose effectiveness was mediated by biological and geochemical processes. Previous work has shown that silicate rock powders can supply K, Ca, Mg, and Fe to soils but that their short-term effectiveness is constrained by low solubility and slow dissolution rates, which depend on mineralogy, grain size, and the chemical disequilibrium between soil solution and mineral surfaces (Harley & Gilkes, 2000; Morales-Aranibar, 2022; Ramos et al., 2021). Reviews of rock dust use in sustainable agriculture have emphasized that local rock composition, soil conditions, and crop type strongly influence the agronomic response to rock powders, and that micronized or porous materials may enhance nutrient release (Nguyen et al., 2024; Richardson, 2024).

The enhanced micronutrient availability observed in the mixed treatments likely results from the interaction of three complementary mechanisms. Mineral dissolution of dacitic rock powder provides a primary source of Cu, Mn, and Zn. Weathering of silicate minerals releases these elements gradually as the soil solution becomes chemically undersaturated with respect to mineral surfaces (Harley & Gilkes, 2000; Morales-Aranibar, 2022). The organic matter present in dairy sludge can form soluble complexes with metal cations, preventing their rapid precipitation or adsorption onto soil minerals and thereby increasing their persistence in plant-available forms. Organic ligands such as humic and fulvic acids are known to enhance micronutrient mobility and uptake by plants in highly weathered soils. Microbial activity stimulated by the organic amendment can accelerate mineral weathering processes through the production of organic acids, chelating compounds, and biofilms that promote dissolution of silicate minerals and mobilization of nutrient cations (Ribeiro et al., 2020; Fang et al., 2023). The combination of these mechanisms explains why treatments receiving both dacite rock powder and dairy sludge consistently produced higher biomass and micronutrient uptake than rock powder alone.

Biological processes in the rhizosphere and in organic amendments can accelerate mineral weathering and micronutrient release. Mineral weathering bacteria and other microorganisms can produce organic acids, chelating agents, and biofilms that enhance the dissolution of silicate minerals and the mobilization of nutrient cations (Ribeiro et al., 2020; Fang et al., 2023). Co-application of silicate rock powders with humic-like substances or organic materials has been reported to increase nutrient uptake and plant growth in weathered tropical soils, likely through a combination of chemical complexation, improved physical properties, and stimulation of microbial activity (Busato et al., 2022; Toscani & Campos, 2017). The dairy sludge supplied organic matter and nutrients, and its combination with dacite rock powder consistently produced greater biomass and micronutrient uptake than dacite alone at comparable rock doses (Figure

3). This pattern supports the view that organic amendments can enhance the agronomic value of rock powders by promoting their weathering and the availability of both macro- and micronutrients.

The relatively small increases in soil extractable Cu, Mn, and Zn in the mixed treatments compared with controls are consistent with the concept that much of the micronutrient supply from the byproducts was rapidly taken up by plants or retained in forms not captured by the applied soil extraction method. In addition, the increases in soil pH and exchangeable Ca and Mg previously reported for these treatments (Ramos et al., 2021) may have moderated the solubility and mobility of Mn and Zn, thereby limiting the risk of excessive accumulation in soil solution despite additional inputs from the dacite rock powder and dairy sludge.

4.4. Manganese handling and root retention as a tolerance mechanism

One of the key patterns in the present data was the tendency for Mn to accumulate more strongly in roots than in leaves, particularly in maize, where root Mn concentrations reached values near 260 mg kg^{-1} at the highest mixed dose, while leaf Mn remained in a narrower range (Table 3) that is not considered toxic for cereals. This distribution aligns with current understanding of Mn transport and homeostasis in plants, where controlled uptake at the root surface, sequestration in root cell walls and vacuoles, and regulated loading into the xylem are key mechanisms that enable plants to tolerate variable Mn supply (Alejandro et al., 2020; Millaleo et al., 2010; Pittman, 2005).

Recent work in maize identified a tonoplast-localized transporter, ZmNRAMP2, that mediates root-to-shoot translocation of Mn and showed that mutants lacking this transporter retain more Mn in roots, display lower shoot Mn, and exhibit reduced growth under Mn-limiting conditions (Guo et al., 2022). Other studies have described Mn hyperaccumulators and tolerant species that sequester Mn in root cell walls or vacuoles, thereby preventing excess Mn from reaching sensitive shoot tissues (Yang et al., 2019). In soybeans, mycorrhizal associations have been shown to increase Mn retention in roots and reduce translocation to shoots under high Mn supply, improving tolerance to Mn-rich conditions (Cardoso et al., 2003). The root–shoot Mn partitioning observed in the present experiment is consistent with these mechanisms, suggesting that maize and black oat were able to accommodate the additional Mn supplied by the dacite rock powder and dairy sludge by increasing root storage rather than allowing excessive accumulation in leaves.

From an agronomic and food safety perspective, this pattern is favorable because it implies that high doses of the byproducts did not lead to harmful Mn concentrations in leaves or, by extension, grains, while the plants maintained adequate Mn for metabolic functions. It also indicates that evaluating only soil Mn or total plant Mn would not capture the physiological regulation of Mn distribution, underscoring the value of measuring both root and shoot tissues when assessing potential micronutrient toxicity.

4.5. Dairy sludge reuse, heavy metals, and environmental risk

The dairy sludge used in this study originated from a dairy processing plant and had previously been shown to contain low concentrations of potentially toxic elements such as As, Cd, Cr, Hg, and Pb, well below regulatory limits for agricultural use (Ramos et al., 2021). The additional assessment of Cu, Mn, and Zn in soil and plant tissues in this work provides further evidence that, under the tested conditions, blending this sludge with dacite rock powder did not generate problematic accumulations of heavy metals or micronutrients. These findings are consistent with broader reviews and case studies indicating that sewage and industrial sludges can be used as fertilizers when contaminant concentrations are controlled and application rates are managed, but that careful risk assessment is required due to the variability in sludge composition and the potential for long-term buildup of metals (Rocha et al., 2025; Burke et al., 2023; Saha et al., 2017).

Studies from different regions have reported that repeated sludge applications can increase soil concentrations of certain metals and alter their speciation, with implications for plant uptake and environmental mobility (Janaszek & Kowalik, 2023; McBride & Cherney, 2004). However, they also show that the magnitude and significance of these effects depend on the initial sludge composition, soil properties, application rates, and crop species. The absence of strong increases in soil Cu, Mn, and Zn and the maintenance of plant tissue concentrations within agronomically acceptable ranges (Table 2) suggest that, at least in the short term and at the tested doses, dairy sludge of the studied quality can be used in combination with rock powder without compromising soil or plant health. Long-term experiments and field-scale monitoring would be required to confirm that these favorable conditions are maintained under repeated applications and in different environmental settings.

4.6. Contributions to sustainable development goals

The reuse of mining and dairy industry byproducts as soil amendments is closely aligned with several United Nations Sustainable Development Goals (SDGs). By demonstrating that dacite rock powder and dairy sludge can jointly supply both macro- and micronutrients to cereal crops without causing detectable toxicity, this study contributes to SDG 2

(Zero Hunger) by supporting strategies to maintain crop productivity and micronutrient density in staple crops. The correction of latent Cu deficiency in maize and the maintenance of adequate Mn and Zn status (Table 4; Figures 2 and 3) illustrate how integrated nutrient management can help address micronutrient malnutrition in food systems (Ray et al., 2024; Teklić et al., 2013).

At the same time, diverting dairy sludge and rock fines from waste streams to agricultural use supports SDG 12 (Responsible Consumption and Production) by closing nutrient loops and reducing the burden of waste disposal on landfills and water bodies (Rocha et al., 2025; Saha et al., 2017). The use of silicate rock powders has been proposed as a means to enhance soil health, sequester carbon through enhanced weathering, and mitigate climate change, which links this approach to SDG 13 (Climate Action) and SDG 15 (Life on Land) by improving soil biological, physical, and geochemical fertility (Xavier et al., 2024; Richardson, 2024). Although this research did not quantify greenhouse gas fluxes or carbon sequestration, the positive effects on soil fertility and plant growth indicate that the tested by-product mixtures can be integrated into broader sustainable nutrient management strategies that contribute to multiple SDGs.

4.7. Limitations and future research

Several limitations of this study should be acknowledged when interpreting the findings. First, the experiment was conducted under greenhouse conditions with two consecutive crops in pots, which may not fully capture the spatial and temporal complexity of field environments. Second, the number of analytical replicates for tissue micronutrient concentrations was small, limiting the statistical power for detecting differences among treatments and precluding a detailed analysis of treatment–environment interactions. As a result, the emphasis was placed on consistent patterns in biomass, concentrations, and calculated uptake across treatment groups rather than on formal hypothesis testing.

Third, the assessment of micronutrients focused on Cu, Mn, and Zn, which are particularly relevant for cereal nutrition and potential toxicity in the studied system, but did not include other elements such as Fe, Ni, or Mo. In addition, only vegetative tissues were analyzed; grain micronutrient concentrations and yield components were not measured and should be evaluated in future work to better understand the implications for human nutrition. Finally, the study considered a single combination of dacite rock powder and dairy sludge from specific sources, and the results may not be directly transferable to other rock types, sludge compositions, or soil and climate conditions.

Future research should therefore include multi-year field trials that track soil and plant micronutrient dynamics under repeated applications of rock powder and dairy sludge, including grain yield and micronutrient concentrations, and that quantify potential changes in the speciation and mobility of heavy metals. Studies that couple agronomic measurements with molecular and physiological analyses of micronutrient transporters, such as NRAMP family members involved in Mn homeostasis (Guo et al., 2022; Alejandro et al., 2020), could clarify how different crops regulate micronutrient uptake and partitioning under rock-based fertilization. Comparative experiments with other organic amendments and rock types, as well as life-cycle assessments of environmental impacts, would further position the use of dacite rock powder and dairy sludge within integrated strategies for sustainable nutrient management and soil remineralization.

5. Conclusions

This study evaluated the micronutrient implications of a fertilization strategy based on dacite rock powder combined with dairy sludge in a tropical soil cultivated with black oat and maize. The combined amendments significantly increased biomass production in both crops. In black oat, leaf dry matter increased from 1.39 to 2.87 g $plant^{-1}$, while maize leaf dry matter increased from 3.38 to 5.41 g $plant^{-1}$, indicating a strong agronomic response to the mixed treatments.

The application of dacite rock powder and dairy sludge also corrected a latent Cu deficiency in maize. Leaf Cu concentrations increased from 2.49 to 8.76 mg kg^{-1}, reaching agronomically adequate levels without inducing micronutrient toxicity. At the same time, extractable soil micronutrient concentrations remained within typical ranges for weathered tropical soils, with Cu ranging from 3.09–3.87 mg dm^{-3} after black oat and 2.19–3.95 mg dm^{-3} after maize, Mn from 65.2–124.4 and 61.7–87.3 mg dm^{-3}, and Zn from 4.99–5.74 and 4.53–5.39 mg dm^{-3}, respectively.

Micronutrient uptake increased with increasing doses of the by-product mixtures. In maize, total Cu uptake increased from 0.032 to 0.102 mg $plant^{-1}$, while Mn accumulation in roots reached up to 247.7 mg kg^{-1}, suggesting effective physiological regulation that limited excessive Mn translocation to shoots. Reductions in some tissue concentrations at high biomass levels were therefore attributed to a nutrient dilution effect rather than micronutrient deficiency.

The results indicate that the combined application of dacite rock powder and dairy sludge represents a promising multi-nutrient fertilization strategy for acidic tropical soils, enhancing crop growth and micronutrient supply without evidence of short-term micronutrient accumulation or toxicity. Future research should validate these findings under multi-year field conditions and assess long-term soil micronutrient dynamics and crop yield responses.

Conflict of Interest

The authors declare that they have no conflict of interest.

Declaration of competing interests

The authors affirm that there are no conflicts of interest to disclose.

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