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Phosphorus and aluminium mobilisation in ferralsols: effects of local sediment amendments, liming and straw application in a lab study

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Phosphorus (P) activation is a major challenge for agriculture on tropical soils like Ferralsols in East Africa, mainly due to soil acidity and high mobility of aluminium (Al). Strategies such as local sediment amendments and liming have shown potential to improve P availability in these soils. In this study, we performed three incubation experiments of soil slurries under laboratory conditions to investigate the temporal mobilisation of silicon (Si), iron (Fe), Al, and P by local sediment amendments. The three incubation experiments consisted of soil slurries with the following treatments: (i) solely two local sediment amendments (from Baringo and Nakuru) over 28 days; (ii) additional 0.15% liming treatment over 61 days; and (iii) straw addition under anoxic conditions over 80 days. We found that Fe reduction by straw addition increased P concentration in the soil solution by a factor of ten, independent of the sediment material. However, the effects of liming and sediment additions on P mobilisation were short-termed, characterised by an initial rapid release of P followed by a quick re-adsorption, precipitation or uptake of available P by soil microbes. Nevertheless, liming and sediment additions could have an indirect effect on P availability, as reduced Al reactivity-resulting from Si addition and potential Al-Si binding, as well as from the increase in pH-can lead to decreased P fixation.

KEYWORDS

phosphorus, aluminium, ferralsols, element mobilisation, liming, SROAS

1 Introduction

Food security remains a pressing issue in many parts of tropical Africa, where soil acidification and limited nutrient availability contribute to low crop yields (Du et al., 2020). About 29% of the soils in tropical Africa are classified as acidic, and in Kenya, acidic soils account for approximately 13% of agricultural land, primarily in the western region (Pandey et al., 1994; Kanyanjua et al., 2002). Soils prevalent in this region are among others Ferralsols. These soils are intensely weathered and are characterized by desilification, well-drained and acidic pH down to pH = 4-5 (Soil Survey Staff, 1999). The long-term weathering leads to the dissolution of easily soluble minerals and the subsequent

leaching of silicon (Si) and base cations such as potassium (K⁺), calcium (Ca2+), and magnesium (Mg2+) (von Uexküll and Mutert, 1995). These cations are replaced on the mineral surfaces by hydrogen (H⁺) and aluminium (Al³⁺) ions, reducing the availability of essential nutrients and increasing the availability of aluminium (von Uexküll and Mutert, 1995; Agegnehu et al., 2021). The good drainage of the soil promotes aerobic conditions, resulting in the formation of stable iron oxides, hydroxides and oxyhydroxides, primarily haematite (Fe₂O₃) and goethite (FeO(OH), (hereinafter referred to as iron oxides; Klamt and van Reeuwijk, 1993). The acidic pH leads to increasing protonation at the surface hydroxyl groups of Fe and Al oxides, resulting in a higher positive surface charge (Liu et al., 2013; Li et al., 2019). This, in turn, enhances the binding of negatively charged phosphate ions through electrostatic adsorption and ligand exchange (Kovács et al., 2020; Nkoh et al., 2021). The high surface area and charge density of Fe and Al oxides facilitates effective adsorption of phosphate ions via electrostatic interactions (Xu et al., 2007; Liu et al., 2013). While electrostatic adsorption is reversible, prolonged contact time may lead to ligand exchange, where the phosphate ion replaces a hydroxyl group (-OH) on the mineral surface, creating more stable bonds (Vissenberg et al., 2000; Nkoh et al., 2021). As a result, Ferralsols can have a relatively high total P content, but very little is mobile or accessible to plants (Hengl et al., 2017; Du et al., 2020). This issue of P fixation in Ferralsols has long been recognized and frequently discussed in scientific literature (Kellogg, 1956; Russel et al., 1974; Sanchez and Uehara, 1980; Ayodele and Agboola, 1981).

Scherwietes et al. (2024) have shown in a field experiment that the addition of certain local sediments lead to an increase in the pH value, P availability and therefore to an increase in the yield of barley in western Kenya. The extent of these positive effects strongly depends on the material and the amount added. However, the underlying mechanisms are not clearly understood yet (Scherwietes et al., 2024). The two sediments used by Scherwietes et al. (2024) are materials that originate from the rift zone of the African Rift Valley and are therefore presumably volcanically influenced and high in Si content (Scherwietes et al., 2024). Studies by Schaller et al. (2019); Schaller et al. (2022) showed that amending amorphous Si (ASi) to soil increases soil P mobility and plant availability. Through the weathering of amorphous silica (ASi), both monomeric and polymeric forms of silicic acid are released into the soil solution (Schaller et al., 2019; Schaller et al., 2022). Both forms can adsorb to mineral surfaces and compete with phosphorus for binding sites, potentially even displacing it from iron oxide surfaces, with polymeric silicic acid showing a stronger affinity than the monomeric form. (Dietzel, 2002; Schaller et al., 2021). However, beside its ability to increase the P mobilisation, silicic acid in soil solution may additionally decrease the bioavailability of Al by promoting the formation of short-range ordered aluminosilicates (SROAS, Exley et al., 2019; Lenhardt et al., 2021).

Thus, both an increase in soil pH-resulting in reduced protonation - and an increase in Si concentration in the soil solution can contribute to enhanced P availability while simultaneously decreasing Al availability. Scherwietes et al. (2024) hypothesized that the pH increase resulting from adding local sediments is the primary factor driving the increase in P and the decrease in Al content in the soil. However, in a subsequent field experiment, they introduced a lime treatment to isolate the pH effects and found that the addition of Baringo sediment still resulted in the highest yield (Scherwietes et al., 2024; under review). This suggests that Si mobilisation from the sediment material may play a more significant role in improving plant productivity than previously assumed. To gain deeper insights into the underlying soil processes following local sediment amendments, laboratory experiments were conducted. Three incubation experiments were designed to monitor element dynamics (Si, P, Al, Fe) from soil/ sediment treatments over time. To examine the potential effect of Si on P availability and Al binding, an initial incubation experiment was performed with soil + sediment treatments, as well as an additional Si reference treatment with added pure ASi. In a second incubation experiment, a soil + lime treatment was added instead of the soil + ASi treatment to isolate the effect of pH on P availability and Al binding.

Although Ferralsols are generally well-aerated, temporary anoxic microsites can form during heavy rainfall events in the rainy season due to soil heterogeneity and the addition of organic material, as microorganisms consume oxygen while decomposing organic matter (Keiluweit et al., 2018; Lacroix et al., 2023). To investigate potential reductive dissolution of Fe minerals and the corresponding release of P in these microsites, a third incubation experiment was conducted under anoxic conditions with the addition of straw. We hypothesized that: (i) adding local sediments will increase P availability and decrease Al availability in the soil solution, with similar effects expected for the Si reference treatment, as Si influences P mobilisation and Al binding; (ii) the soil + lime treatment will result in a higher P release and lower Al mobility compared to the sediment and Si treatments, as the pH increase may be the primary driving factor; and (iii) P availability in the soil solution will increase through the reductive dissolution of Fe minerals, as Fe-bound P may be released under anoxic conditions.

2 Materials and methods

2.1 Sample materials

In November 2021, soil and sediment samples were collected in Kenya during hot and dry weather conditions. The soil samples were taken from an agricultural site in Kaptagat, located north of Eldoret in Uasin Gishu County, western Kenya (0.406667N, 35.21154E, Supplementary Figure S1), and hereafter referred to as the "Control" sample. The soils in the Eldoret region are predominantly Plinthic Ferralsols, characterized by low pH and high Fe content (Nyachiro and Briggs, 1987). Specifically, the untreated Control soil has a pH of 4.7, a cation exchange capacity (CEC) of 9.7 cmol⁺ kg⁻¹ of soil, and a total organic carbon (TOC) content of 2.6% (Scherwietes et al., 2024). The total Al content is 104 g kg⁻¹, with a plant-available Al content (CaCl₂-extractable) of 0.04 g kg⁻¹ (Scherwietes et al., 2024). A Feo/Fed oxalate/dithionite ratio of 0.04 indicated strong weathering, typical for older soils (Moody and Graham, 1995; Scherwietes et al., 2024). The elemental composition and composition of exchangeable cations of the soil are described in Scherwietes et al. (2024).

To assess and compare the effects of two local sediment materials on soil properties, sediment samples were taken from two sites within the East African Rift System (EARS). The first sediment, from Nakuru district south of Lake Nakuru (0.49726S, 36.091794E, Supplementary Figure S1), referred to as "Nakuru", consists of tuffs, diatomaceous silts, and superficial deposits (McCall, 1966). Scherwietes et al. (2024) described it as a mix of splintery/molten Si- and Al-rich particles of various sizes. The second sediment, taken from an area west of Lake Baringo (0.574643N, 35.984597E, Supplementary Figure S1) and hereafter called "Baringo," is a Ca-rich lacustrine sediment with an aggregated matrix (5–25 μ m) and attached fine particles (\leq 1–5 μ m) containing Al and Si (Hackman, 1987; Scherwietes et al., 2024). Only the Baringo sediment showed significant P enrichment (0.13%) and a high proportion of soluble Si (Scherwietes et al., 2024). Both sediments are alkaline, with the Baringo sediment having a pH of around 8.6 and the Nakuru sediment a pH of 9.4 (1:2.5 in water, Scherwietes et al., 2024). The elemental composition and the composition of exchangeable cations of the sediments are described in Scherwietes et al. (2024). According to Scherwietes et al. (2024), the sediment from Baringo was primarily composed of Si (21 wt%) and Ca (10.2 wt%), with additional enrichment in P (0.13 wt%) and Mg (3.24 wt%). In contrast, the sediment from Nakuru was dominated by Si (30.2 wt%) and Al (8.3 wt%), along with elevated levels of Na (4.46 wt%) and K (4.27 wt%). Their location within the rift valley suggests they may be influenced by volcanic tephra deposits (Tryon and McBrearty, 2006; Blegen et al., 2016).

Samples were collected using a small shovel, air-dried, transported to Germany in plastic bags, and then sieved to 2 mm in the laboratory.

2.2 Mobilisation experiments

Mobilisation experiments were conducted to observe the dissolution of P, Si, Fe and Al in the soil solution over time in different scenarios as detailed below. Four replicates of each treatment were prepared for all mobilisation experiments. All incubation experiments were conducted until a steady state was reached. Physical parameters such as pH (SenTix 41, WTW, Weilheim, Germany), electrical conductivity (EC; TetraCon 325, WTW, Weilheim, Germany) and redox potential (SenTix ORP-T 900, WTW, Weilheim, Germany) were measured using a WTW pH/ Cond 3,320 m (WTW, Weilheim, Germany). Elemental analyses of the samples were carried out using inductively coupled plasma optical emission spectroscopy (ICP-OES; iCAP 6300 DUO, ThermoFisher Scientific Inc., Walham, Massachusetts. United States of America).

2.2.1 Effect of local sediment amendment on element mobilisation

To monitor the mobilisation of P, Si, Fe and Al in soil solution over time, 50 g of soil sample were weighed into 250 mL polypropylene (PP) bottles and mixed with 1 wt% or 5 wt% of the respective sediment. For comparison, a separate batch of soil sample was also incubated with 1% ASi (Aerosil300, Evonik, Hanau-Wolfgang, Germany) instead of sediment material (hereafter referred as Aerosil treatment). After the addition of 150 mL deionised water, the soil slurries were shaken for 4 weeks at room temperature (KS 501 D, Janke and Kunkel IKA Labortechnik, Staufen, Germany). Subsamples were taken after 12 h, 24 h, 48 h, 96 h, 1 week and 4 weeks by centrifuging 15 mL of soil slurry from each bottle at 3,200 g for 5 min (Centrifuge 5,804, Eppendorf AG, Hamburg, Germany). The supernatant from each subsample was then filtered through 0.2 µm membrane filters.

2.2.2 pH effect on element mobilisation after liming

In a second incubation experiment, a lime treatment was added instead of the Aerosil treatment. For this experiment, three sediment treatments (1 wt% Baringo, 3 wt% Baringo, 3 wt% Nakuru) and one lime treatment (1 wt% CaO) were mixed with 50 g of soil sample into 250 mL polypropylene (PP) bottles. Additionally, samples containing only sediment material were included as reference treatments. 200 mL of deionized water was added to each sample, which was then sealed and shaken for 61 days (KS 501 D, Janke and Kunkel IKA Labortechnik, Staufen, Germany). Subsamples were collected at 12 h, 24 h, 48 h, 96 h, 1 week, 2 weeks, 4 weeks, and 8 weeks. To collect the subsamples, 15 mL of the soil slurry was centrifuged at 3,200 g for 5 min and the supernatant was filtered through 0.2 µm membrane (Centrifuge 5,804, Eppendorf AG, Hamburg, Germany). The pH and EC were measured for each subsample. To maintain a pH above 5.5 in the lime treatment, small amounts of lime (CaO) were added as necessary throughout the incubation period, based on real-time pH monitoring.

2.2.3 Fe dissolution under reducing conditions

A third incubation experiment was performed under reducing conditions with the addition of organic straw material. In this setup, 50 g of soil sample was weighed into 250 mL PP bottles and mixed with 1 wt% of the respective sediment material (or Aerosil300, Evonik, Hanau-Wolfgang, Germany) and 3 wt% dried and ground wheat straw. A reference treatment without straw was also carried out to assess the impact of organic matter addition. In a vinyl anaerobic chamber (Coy Laboratory Products, Michigan, United States of America), 200 mL of deionized water was added to each sample, which was then sealed and shaken for 80 days (KS 501 D, Janke and Kunkel IKA Labortechnik, Staufen, Germany). Subsamples of 15 mL were collected on days 3, 10, 17, 31, and 80 under anaerobic conditions. These subsamples were centrifuged at 3,200 g for 5 min and filtered through 0.2 µm membrane filters (Centrifuge 5,804, Eppendorf AG, Hamburg, Germany). Each subsample's pH, redox potential, and EC were measured inside the anaerobic chamber to maintain consistent anaerobic conditions.

2.2.4 Oxalate/dithionite extractable Fe, Al, Si and P

Oxalate- and dithionite-extractable Fe, Al, Si and P of the control soil were determined with ammonium oxalate and sodium dithionite in order to determine the proportion of very stable (oxalate extractable) and less stable (dithionite extractable) minerals and the corresponding bound P quantities. The ammonium oxalate extraction was conducted following the method described by Schwertmann (1964). 0.5 g of dried soil was mixed with 30 mL of 0.2 M ammonium oxalate solution in centrifuge tubes and the pH was adjusted with oxalic acid to



pH 3.0. The samples were shaken at room temperature and in darkness for 4 h and subsequently centrifuged at 10,000 g for 10 min (Centrifuge 5,804, Eppendorf AG, Hamburg, Germany). The supernatants were filtered through 0.45 µm membrane filters and analysed for Fe, Al, Si and P. The sodium dithionite extraction was conducted following the method described by Mehra and Jackson (2013). Dried soil sample (0.5 g) was weighed into centrifuge tubes and 40 mL of 0.3 M sodium citrate and 1 M sodium bicarbonate was added. After heating to 80 C in a water bath, 1 g of sodium dithionite was added. The suspension was shaken gently for 15 min and centrifuged at 10,000 g for 10 min (Centrifuge 5,804, Eppendorf AG, Hamburg, Germany). After filtering through 0.45 µm membrane filter, it was analysed for Fe, Al, Si and P. All elemental concentrations of ammonium oxalate extraction and sodium dithionite extraction were determined using ICP-OES (iCAP 6300 DUO, ThermoFisher Scientific Inc., Walham, Massachusetts, United States of America).

2.3 Statistics

All statistical analyses were performed using R (Version 4.3.2; R Core Team, 2023) within RStudio (Version 2024.04.1 + 748). Treatment effects on element mobilisation were assessed using analysis of variance (ANOVA) on the mean values per replicate across all time points using the package *stats* (R Core Team, 2023), followed by Tukey's HSD *post hoc* test using the emmeans package (Lenth, 2024) for pairwise comparisons and multcompView (Graves et al., 2019) to generate compact letter displays for group differences. Principal Component Analysis (PCA) was performed using the *prcomp()* function from the *stats* package (R Core Team, 2023). Variables were standardised (z-transformed) prior to analysis to account for differences in scale. For the oxalate and dithionite extraction data, paired t-tests (*stats*) were applied to assess statistical differences between extraction methods. Visualisation of all results was done using *ggplot2* package (Wickham, 2024).

3 Results

3.1 Element mobilisation after local sediment amendment

In the first incubation experiment, Aerosil300 was added as an additional treatment. Reference treatments were conducted using either sediment material or Aerosil300 with water only. The reference materials and soil/sediment treatments were analysed separately.

The addition of 1% Aerosil increased Si concentrations in the soil solution compared to the control (p < 0.001, Tukey; Figure 1). In contrast, both Baringo treatments (1% and 5%) reduced Si concentrations (p < 0.001 for both, Tukey). Nakuru 1% showed no significant effect on Si mobilization (p = 1.000, Tukey). Aluminium concentrations decreased under the Aerosil 1% treatment (p < 0.001, Tukey), as well as under both Baringo treatments (1%: p < 0.001; 5%: p = 0.001, Tukey). The Nakuru 1% treatment had no significant effect



on Al mobilisation (p = 0.994, Tukey). Only Aerosil 1% decreased Fe concentrations (p < 0.001, Tukey). All other treatments showed no significant difference from the control (p > 0.05, Tukey), although a

slight, non-significant increase in Fe was observed for both Baringo treatments. Phosphorus release increased only in the Baringo 5% treatment (p < 0.001, Tukey). All other treatments showed no

significant differences (p > 0.05, Tukey). Soil pH increased in Baringo 1% (5.3 \pm 0.02) and Baringo 5% (6.5 \pm 0.06) compared to the control (4.7 \pm 0.07; p < 0.005 for both, Tukey). No significant pH change was observed for Nakuru 1% (4.8 \pm 0.07; p = 0.946, Tukey) or Aerosil 1% (4.7 \pm 0.06; p = 0.695, Tukey). The PCA revealed a negative correlation between Si and P, suggesting that samples with low Si tend to have higher P concentrations (Supplementary Figure S2).

In the reference materials, Aerosil released the highest amount of Si into solution (all p < 0.001 vs. other materials, Tukey; Supplementary Figure S3). No significant difference in Si release was observed between the 1% and 5% concentrations of Baringo or Nakuru sediment. The 5% Nakuru reference released the highest amounts of Fe (p < 0.001, Tukey) and Al (p = 0.035 vs. Baringo 5%; p < 0.001 vs. others, Tukey). Baringo 5% released more Fe and Al than Baringo 1% (Fe: p = 0.024; Al: p < 0.003, Tukey) and Aerosil 1% (p < 0.001 for both, Tukey), and more Al than Nakuru 1% (p < 0.001, Tukey). No significant differences in Fe and Al release were found among Nakuru 1%, Baringo 1%, and Aerosil 1% (p > 0.05, Tukey). The highest P release occurred in the Baringo 5% reference (p < 0.001 vs. all except Nakuru 5%; p = 0.035 vs. Nakuru 5%, Tukey). Both Nakuru 5% and Baringo 1% released more P than Nakuru 1% and Aerosil 1% (p < 0.001, Tukey), but did not differ significantly from each other (p = 0.153, Tukey). The lowest P release was observed in Nakuru 1% and Aerosil 1%.

3.2 Effect of lime on element mobilisation

In the second incubation experiment, lime was included as an additional treatment. Reference treatments were conducted using only the sediment materials or lime mixed with water. Reference and soil/sediment treatments were analysed separately.

Among the soil/sediment treatments, all combinations differed significantly in pH (p < 0.001, Tukey), except the control and Nakuru 3% (p = 0.089, Tukey; Figure 2). Baringo 1%, lime, and Baringo 3% increased pH, with Baringo 3% showing the highest value (6.1 ± 0.08 ; p < 0.001, Tukey). A similar trend was observed for EC. The control and Nakuru 3% exhibited lower EC values than Baringo 1% (p < 0.001 and p = 0.019, Tukey), Baringo 3%, and lime (both p < 0.001, Tukey). The highest EC was observed in the Baringo 3% treatment (313 µS cm⁻¹; p < 0.001, Tukey). Element release followed a similar pattern for Fe and Al. Lime increased Fe and Al concentrations in the soil solution compared to all other treatments. Differences were significant when compared to the control (Fe: p < 0.001; Al: p =0.007, Tukey), Baringo 1% (Fe: p = 0.042; Al: p = 0.026, Tukey), Baringo 3% (Fe: p = 0.047; Al: p = 0.024, Tukey), and Nakuru 3% (Fe: p = 0.009; Al: p = 0.034, Tukey). No other treatment combinations showed significant differences in Fe or Al concentrations (p > 0.05, Tukey). Across all treatments, Fe and Al concentrations declined sharply after an initial peak in the first 2 weeks. Phosphorus dissolution followed the same general pattern. Baringo 3% increased P concentrations compared to the control (p < 0.001, Tukey), Nakuru 3% (p = 0.001, Tukey), and Baringo 1% (p = 0.006, Tukey). However, it did not differ significantly from the lime treatment (p = 0.186, Tukey). PCA did not reveal any clear correlations between the measured variables in the second experiment (Supplementary Figure S4).

The pH of the reference materials was considerably higher than that of the soil/sediment treatments (Supplementary Figure S5). The Baringo 3% reference reached the highest pH (9.2 \pm 0.5), although differences among references were not statistically significant (p = 0.288, ANOVA). In contrast, all reference treatments differed significantly in EC (p < 0.001, Tukey), with Baringo 3% showing the highest and Nakuru 3% the lowest values. Si dissolution varied significantly among references (p < 0.001 for all comparisons, Tukey). The Baringo 3% reference released the most Si, whereas Nakuru 3% released the least. Regarding Fe and Al, the Nakuru 3% reference showed the highest concentrations, releasing significantly more of both elements than either Baringo reference (p < 0.001 for both Fe and Al, Tukey). The Baringo 1% and 3% references did not differ from each other (Fe: p = 0.786; Al: p = 0.209, Tukey). Phosphorus release was also affected by material and concentration. Baringo 3% released more P than both Baringo 1% (p < 0.001, Tukey) and Nakuru 3% (p = 0.035, Tukey). No significant difference was observed between Baringo 1% and Nakuru 3%.

3.3 Effect of Fe dissolution on element mobilisation

In the third incubation experiment, pH increased over time in all treatments under reducing conditions (Figure 3). The fastest and strongest increase in pH was observed for Baringo 1%, reaching 5.7 ± 0.06 after 10 days and 6.4 ± 0.02 after 82 days. A statistically difference in pH was only found between Aerosil 1% and Baringo 1%, with Baringo 1% showing a higher value (p = 0.049, Tukey). Redox potential was highest in the reference treatment (-64 mV), which differed significantly from all other treatments (p < 0.001, Tukey). The lowest redox potential occurred in Baringo 1% (-169 mV). No significant differences were observed among the treatments with straw addition (control, Baringo 1%, Nakuru 1%, Aerosil 1%; p > 0.05, Tukey). Electrical conductivity followed a similar trend. Among the straw-amended treatments, only Baringo 1% exhibited significantly higher EC compared to Nakuru 1% (p < 0.05, Tukey); all other comparisons were not significant. PCA did not reveal any clear correlations between the measured variables in the third experiment (Supplementary Figure S6).

Regarding element concentrations, the reference treatment released significantly less Al but significantly more Fe than all other treatments (both p < 0.001, Tukey). All other treatments did not differ significantly in Fe and Al concentrations (p > 0.05, Tukey). For Si, the control and Nakuru 1% treatments showed lower concentrations in the soil solution than both to the reference (p = 0.033 and p = 0.028, Tukey) and Aerosil 1% (p = 0.001; p < 0.001, Tukey). Baringo 1% did not differ significantly from any other treatment in terms of Si release. No significant differences in P concentrations were found between treatments (p > 0.05, Tukey), except for Aerosil 1%, which was released more P than the reference treatment (p = 0.036, Tukey).

3.4 Oxalate/dithionite extractable elements in ferralsol

An oxalate/dithionite extraction revealed that the proportion of Fe extractable with dithionite in the control soil was higher (Fe_{dith} = 62.516 ± 0.846 g kg-1, p < 0.001, t = -179.31, df = 3, t-Test) than that



FIGURE 3

The physical parameters pH, redox potential and electrical conductivity and the release of Fe, Al, Si and P of each treatment under reducing conditions. The treatments were mixed with water and shaken for 81 days. The red dotted lines show the pH threshold of 5.5 and the threshold of redox potential at -120 mV. Error bars indicate standard deviation. Significant differences in the mean of all measurements between all treatments are represented by different letters, common letters indicate no significant difference (p < 0.05).

Element	Al _{ox} [g kg ⁻¹]	Fe _{ox} [g kg⁻¹]	P _{ox} [g kg⁻¹]	Si _{ox} [g kg⁻¹]	Al _{dith} [g kg ⁻¹]	Fe _{dith} [g kg⁻¹]	P _{dith} [g kg⁻¹]	Si _{dith} [g kg⁻¹]
C1	4.021	2.110	0.136	0.273	8.208	61.595	0.540	0.857
C2	4.848	2.794	0.183	0.352	8.347	62.060	0.563	0.880
C3	4.789	2.831	0.180	0.351	8.381	62.937	0.568	0.838
C4	4.686	2.723	0.175	0.331	8.410	63.473	0.570	0.850
Control (mean)	4.586 ±0.383	2.615 ±0.339	0.169 ±0.022	0.327 ±0.037	8.336 ±0.089	62.516 ±0.846	0.560 ±0.014	0.856 ±0.018

TABLE 1 Oxalate and dithionite extractable Al, Fe, P and Si in g kg⁻¹ of the control soil. C1-C4 are four repetitions of the extraction, the mean and standard deviation is shown in the last row.

extractable with oxalate (Fe_{ox} = 2.615 ± 0.339 g kg-1, Table 1). Similarly, dithionite extraction released more P ($P_{ox} = 0.169 \pm$ 0.022 g kg-1, $P_{dith} = 0.560 \pm 0.014$ g kg-1; p < 0.001, t = -78.76, df = 3, t-Test), more Si (Si_{\rm ox} = 0.327 \pm 0.037 g kg-1, Si_{\rm dith} = 0.856 \pm 0.018 g kg-1; *p* < 0.001, *t* = -26.25, *df* = 3, t-Test) and more Al (Al_{ox} = 4.586 ± 0.383 g kg-1, Al_{dith} = 8.336 ± 0.089 g kg-1; p < 0.001, t =-24.53, df = 3, t-Test) compared to oxalate extraction. To accurately determine the proportion of Fe, Al, Si, and P that is extractable solely by dithionite, the element content extracted by oxalate must be subtracted from the content extracted by dithionite. This calculation isolates the fraction uniquely dissolved by dithionite. The results indicate that the solely dithionite-extractable fractions of Fe $(\text{Fe}_{\text{dith-ox}} = 59.901 \pm 0.668 \text{ g kg-1}, p < 0.001, t = -179.64, df = 3,$ t-Test), P (P_{dith-ox} = 0.392 ± 0.01 g kg-1, p < 0.001, t = -14.35, df = 3, t-Test) and Si (Si_{dith-ox} = 0.530 ± 0.04 g kg-1, p = 0.012, t = -5.368, df = 3, t-Test) are higher than those extracted by oxalate. In contrast, no significant differences were observed between the oxalate- and the solely dithionite-extractable fractions of Al (Al_{dith-ox} = $3.750 \pm$ 0.306 g kg-1, p = 0.093, t = 2.432, df = 3, t-Test).

4 Discussion

4.1 Comparable findings in incubation experiments and field experiment

This study investigated the processes contributing to the improvement of barley growth and yield after the addition of two sediments (Nakuru and Baringo) to a Ferralsol from Eldoret, Western Kenya. The results are in agreement with those of Scherwietes et al. (2024) who reported that the addition of Baringo sediments significantly increased soil available phosphorus (P) and improved P uptake and accumulation in plant tissues. In our study, an increase in the P concentration in the soil solution was also observed in the first two incubation trials (both with an application rate of 3%) due to the addition of Baringo sediments. In addition, the 2024 field trial showed a reduction in available aluminium (Al) in the soil after treatment with Baringo sediment, and a significantly lower Al concentration in the soil solution was observed in the first incubation trial of this study. In contrast, the mobilisation of elements after the addition of Nakuru sediment in the present

incubation experiments did not show any major differences compared to the control. This agrees with the results of Scherwietes et al. (2024), where the effects of adding Nakuru sediment were also significantly lower than those of Baringo sediment.

4.2 Silicon potentially reduces Al mobility but has no effect on P dissolution

The results of the first incubation experiment indicate a relationship between the soluble Si in the Baringo sediment (or Aerosil respectively) and the Al in the soil. Scherwietes et al. (2024) found a high proportion of ASi in the Baringo sediment. Amorphous Si is more soluble than the crystalline Si, which is the predominant form of Si in the Nakuru sediment (Belton et al., 2012; Scherwietes et al., 2024). However, the Si concentration in the soil solution was higher in the control and the Nakuru treatment than in the Baringo treatments. This might be due to the interaction of the silicic acid released by the Baringo sediments with Al and Fe oxides of the soil. The main mechanisms of these interactions are electrostatic adsorption and surface complexation between Si and the surface of Al and Fe oxides, changing its electrochemical properties, reactivity and stability (Elisa et al., 2016). With Al, Si can form complexes like aluminosilicate compounds. These may precipitate and reduce Al dissolution into the soil solution (Tubana and Heckman, 2015; Schaller et al., 2021). Lenhardt et al. (2021) demonstrated that certain conditions could also lead to the formation of SROAS. These include specific Si/Al ratios and the pH value (Lenhardt et al., 2021). Even if the bulk soil solution does not meet the ideal conditions described by Lenhardt et al. (2021), SROAS can still form. Microsites at particle surfaces may provide suitable conditions for their formation. The decreased Si concentration and Al concentration in the soil solution in the Baringo treatments indicates that these interactions between Si and Al likely took place in this study. This is also in line with the strongest decrease in Al concentration in the soil solution with the Aerosil treatment. Aerosil300, being almost pure ASi, released a substantial amount of Si into the soil solution. This is also observed in the Aerosil reference treatment (Supplementary Figure S3). The released Si can readily adsorb onto Al oxides or form aluminosilicates, thereby reducing the Al concentration in the

solution. While both the Baringo and Aerosil treatments effectively reduced Al levels in the soil solution, only the Baringo treatment was able to maintain these reduced levels over time. This maintained effect was probably due to the increase in pH associated with the Baringo sediment, which stabilised Al by preventing its redissolution (Bojórquez-Quintal et al., 2017). In contrast, Aerosil had no effect on pH, allowing Al to redissolve over time. However, the Baringo sediment also releases additional Al into the soil solution, as observed in the Baringo reference treatment (Supplementary Figure S3). The additional Al release is likely to result in a less substantial reduction in Al concentration in the soil solution compared to the Aerosil treatment (Scherwietes et al., 2024). In addition to reacting with Al, Si can also adsorb onto the protonated surfaces of Fe oxides in Ferralsols, such as hematite and goethite (Dietzel, 2002). Uncharged mono- and polysilicic acids are deprotonating at the positively charged surfaces of these oxides, stabilising them and preventing further dissolution processes (Sigg and Stumm, 1981; Nguyen and Picardal, 2016; Nguyen et al., 2017). However, only the Aerosil treatment probably provided an excess of Si sufficient to allow Si adsorption on the protonated surfaces of Fe oxides. Despite the potential for Si to adsorb onto Al (or with Aerosil also Fe) oxide surfaces-where it might compete with negatively charged P at binding sites-no significant increase in P mobilisation was observed in this study (Pérez et al., 2014; Schaller et al., 2024). An increase in P concentration in the soil solution was detected only in the 5% Baringo treatment, but only at the beginning of the observation period. This initial rise in P concentration likely resulted from P released by the dissolution of the Baringo sediment itself, as observed in the Baringo reference treatment (Supplementary Figure S3). The rapid decline in P concentration in this treatment suggests that P was adsorbed to mineral surfaces again quickly. The lack of sustained P mobility may be due to several factors: P could be too strongly adsorbed to the Al or Fe oxide surfaces for Si to effectively displace it, or it may be occluded within the mineral matrix, making it inaccessible for exchange. Additionally, any dissolved P could be rapidly adsorbed again and thus immobilised, possibly also through the formation of aluminosilicates or SROAS.

4.3 Short-time effect on P mobilisation by liming

To investigate the effects of lime on P mobilisation in the studied soil, an additional lime treatment was conducted. The pH in this treatment was adjusted to above 5.5, comparable to the pH range observed in the Baringo 3% treatment. The control, Baringo 1% and Nakuru 3% treatments had pH below 5.5. A pH value above 5.5 promotes the transformation of Al into less mobile forms such as $Al(OH)_2^+$ or $Al(OH)_3$ (Russel et al., 1974; Agegnehu and Sommer, 2000; Bojórquez-Quintal et al., 2017). Such transformation may have occurred in this study, as the Al concentration in the soil solution at the end of the experiment was lowest in both the lime and the Baringo 3% treatments. However, both treatments showed a significant increase in Al concentration in the soil solution at the beginning of the experiment. In the lime treatment, the effect may be due to an uneven distribution of lime particles initially. Larger particles dissolve more slowly than smaller ones. In certain areas on the surface of these larger particles, the pH can be much higher than in the surrounding solution. This localised high pH can lead to Al mobilisation, which usually begins at a pH of around 7.5 (Schaller et al., 2021). However, over time, the larger lime particles will dissolve completely. This prevents further aluminium mobilisation. The initial increase in Al in the Baringo 3% treatment may be explained by the dissolution of Al content from the sediment itself (Scherwietes et al., 2024). Both the lime and the Baringo 3% treatments showed a strong release of P to the soil solution only at the beginning of the experiment, with levels quickly decreasing and remaining low in the long term. In the case of the Baringo 3% treatment, the initial P release might be due to the dissolution of the sediment material (Scherwietes et al., 2024). For the lime treatment, the initial increase in P could have been linked to the dissolution of Al from the particle surface due to liming, which may have released P originally adsorbed to Al oxides (Sanchez and Uehara, 1980). After neutralizing the pH in the bulk solution to above 5.5, Al likely transformed into less mobile forms like Al(OH)₂⁺ or Al(OH)₃, leading to re-adsorption of the released P (Bojórquez-Quintal et al., 2017). By the end of the second incubation experiment, the Al concentration in the soil solution was very low in the lime and Baringo 3% treatments, suggesting that Al availability had been depleted. It can be hypothesized that a subsequent P addition after liming or Baringo 3% treatment would have a more pronounced effect on P availability, as the low Al levels would limit its ability to bind and immobilize the added P.

4.4 Dissolution of Fe oxides increases P availability

The third incubation experiment indicates a strong increase in P mobilisation due to reductive dissolution of Fe oxides under reducing conditions. The redox potential was lower in treatments with organic matter (all with mean of < -150 mV) compared to the reference treatment without organic matter (mean of -63 mV). A lower redox potential and the presence of organic material may facilitate the reductive dissolution of Fe oxides through both abioticchemical and biotic-microbial pathways (Xiu et al., 2021). Specifically, Fe oxides act as electron acceptors during the microbial oxidation of organic matter by bacteria (Bonneville et al., 2004). Consequently, treatments containing organic matter showed a lower redox potential compared to the reference without organic material, where less organic matter was available for oxidation. Through electron acceptance, Fe(III) oxides such as ferrihydrite, goethite, or hematite can be reduced, forming Fe²⁺ (Bonneville et al., 2004). However, the susceptibility of various Fe oxides to reduction differs significantly as crystallinity plays a significant role in their reductive dissolution (Lovley and Phillips, 1986; Larsen and Postma, 2001; Bonneville et al., 2004). The more crystalline the Fe(III) phase is, the less susceptible it is to reduction (Lovley and Phillips, 1986). Highly crystalline Fe oxides, in particular hematite, have a more stable structure that resists reduction compared to less crystalline forms like ferrihydrite (Lovley and Phillips, 1986). In this study, an increase in Fe mobilisation was observed across all treatments, with significantly higher Fe dissolution in the treatments that included organic matter, likely due to the microbial and abiotic reduction processes (Bonneville et al., 2004). The same pattern was observed for EC, which additionally indicates a strong reductive dissolution of soil and sediment minerals. However, the reductive dissolution of Fe can also impact the availability of other nutrients, such as P (Lovley and Phillips, 1986). Phosphorous availability may increase since it is often adsorbed onto Fe oxide surfaces and can be released into the soil solution during their reduction (Lovley and Phillips, 1986).

In this study no significant differences in P mobilisation were observed between all treatments, including the reference without organic matter addition. However, in the third incubation experiment, P concentrations in the soil solution were about ten times higher in all treatments compared to the first and second experiments. This suggests that reductive dissolution of Fe may have occurred across all treatments. As a result, P that was previously strongly adsorbed or occluded in mineral matrices could have been mobilised. Despite higher Fe dissolution in treatments with organic amendments, no corresponding increase in P concentration was observed. One explanation is that the added organic matter likely stimulated microbial activity, leading to increased microbial biomass (Liang et al., 2017). These microbes may have taken up the mobilised P for growth and metabolism, reducing its presence in the soil solution (White and Metcalf, 2007). Alternatively, the released P could have been re-adsorbed onto newly formed Fe compounds or precipitated as insoluble minerals with other elements (Pérez et al., 2014). Both processes would reduce P availability in the soil solution again.

However, it is likely that only the weakly crystalline Fe(III) oxides like ferrihydrite were dissolved, as these phases are reduced already at less negative redox potentials (Gorski et al., 2016). An oxalate/dithionite extraction conducted in this study revealed that the studied soil contains a significantly higher proportion of dithionite-extractable Fe compared to oxalate-extractable Fe. While oxalate is only able to dissolve low crystalline Fe(III) phases such as ferrihydrite or short-ranged ordered Fe(III) phases, dithionite is able to dissolve also high crystalline Fe(III) phases such as goethite or hematite (Schwertmann, 1964). Consequently, the findings indicate a greater proportion of highly crystalline Fe(III) phases in the studied soil relative to the more readily reducible ferrihydrite or amorphous Fe(III) phases. This prevalence of highly crystalline Fe suggests that much of the P in the soil still remains immobilised under the tested conditions.

5 Conclusion

This study explored the effects of adding local sediments to Ferralsols from western Kenya through three laboratory incubation experiments on element mobilisation, aiming to understand the associated soil processes. Results showed that most P in the studied soil was strongly adsorbed to highly crystalline iron oxides such as goethite and hematite, with smaller amounts associated with less crystalline phases like ferrihydrite and amorphous Fe. The dissolution of these less crystalline phases under anoxic conditions significantly increased P availability in the soil solution by a factor of 10. Unfortunately, such anoxic conditions only occur very rarely in Ferralsols. Ferralsols are actually very porous, well drained and have good air circulation, which may allow oxygen to enter the soil system, preventing the formation of reducing conditions. Nevertheless, during heavy rainfall events in the rainy season, temporary anoxic microsites can form due to soil heterogeneity and the presence of organic matter and thus lead to reduction of Fe minerals. However, the addition of local sediments may also have a potentially positive effect on P availability. Although the laboratory tests showed that a direct effect on P mobilisation occurs mainly through an increase in pH (as seen with liming) and a potential addition of P from the sediment material itself, the addition of Si may also have an indirect effect on P mobilisation. Both liming and the addition of pure ASi effectively reduced the availability of Al in the soil solution, thereby lowering its capacity to adsorb P and render it unavailable. This suggests that P fertilisation following treatment with the local sediment from Baringo, or after liming, could result in significantly greater benefits than fertilisation without such pre-treatment. Consequently, pre-treatment of agricultural land with Baringo sediment or lime has the potential to substantially reduce the need for mineral P fertilizers. However, the specific sediment material and its application rate are critical factors in determining effectiveness. For instance, the sediment material from Nakuru studied here did not exhibit similar effects on soil pH, Si availability, or P mobilisation as the sediment material from Baringo. This highlights the importance of selecting appropriate sediment types tailored to the specific soil conditions to optimize agricultural benefits.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

ES: Visualization, Formal Analysis, Data curation, Writing – review and editing, Methodology, Writing – original draft. MS: Writing – review and editing, Methodology. JohS: Writing – review and editing. TB: Writing – review and editing. JorS: Supervision, Writing – review and editing, Conceptualization, Funding acquisition.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Generative AI statement

The author(s) declare that no Generative AI was used in the creation of this manuscript.

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Supplementary material

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