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**The potential of local sediments to improve barley yield by increasing  
phosphorus availability and decrease aluminium toxicity in Kenya**

**DISSERTATION**

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"I declare: I have completed the submitted dissertation independently and without unauthorized outside help and only with the help that I have indicated in the dissertation. All text passages taken literally or analogously from published works and all information based on verbal information are marked as such. In the research conducted by me and mentioned in the dissertation, I have complied with the principles of good scientific practice as laid down in the "Statutes of the Justus Liebig University Giessen for Safeguarding Good Scientific Practice"."

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## List of abbreviations

<b>Al</b>	Aluminium
<b>Al(OH)<sub>3</sub></b>	Gibbsite
<b>As</b>	Arsenic
<b>ASi</b>	Amorphous Silicon
<b>BaCl<sub>2</sub></b>	Barium chloride
<b>Ca</b>	Calcium
<b>CaCl<sub>2</sub></b>	Calcium chloride
<b>CaO</b>	Calcium oxide
<b>Ca(OH)<sub>2</sub></b>	Calcium hydroxide
<b>Cd</b>	Cadmium
<b>CEC</b>	Cation exchange capacity
<b>DAP</b>	Diammonium phosphate
<b>EARS</b>	East African Rift System
<b>EC</b>	Electrical conductivity
<b>Fe</b>	Iron
<b>Fe<sub>2</sub>O<sub>3</sub></b>	Hematite
<b>FeO(OH)</b>	Goethite
<b>g</b>	Gram
<b>H</b>	Hydrogen
<b>H<sub>2</sub>O</b>	Water
<b>H<sub>2</sub>O<sub>2</sub></b>	Hydrogen peroxide
<b>H<sub>2</sub>PO<sub>4</sub><sup>-</sup></b>	Dihydrogen phosphate ion
<b>ha</b>	Hectares
<b>HNO<sub>3</sub></b>	Nitric acid
<b>ICP-OES</b>	Inductively coupled plasma – optical emission spectrometry
<b>K</b>	Potassium
<b>kg</b>	Kilogram
<b>l</b>	Liter
<b>m</b>	Meter
<b>M</b>	Mole
<b>Ma</b>	Million years ago

<b>mg</b>	Milligram
<b>Mg</b>	Magnesium
<b>ml</b>	Milliliter
<b>mm</b>	Millimeter
<b>Mn</b>	Manganese
<b>N</b>	Nitrogen
<b>Na</b>	Sodium
<b>Na<sub>2</sub>CO<sub>3</sub></b>	Sodium carbonate
<b>NPK</b>	Nitrogen-Phosphorus-Potassium fertiliser
<b>OA</b>	Organic acid
<b>P</b>	Phosphorus
<b>PCA</b>	Principal component analysis
<b>Pb</b>	Lead
<b>PP</b>	Polypropylene
<b>TOC</b>	Total organic carbon
<b>EDX</b>	Energy dispersive X-Ray analysis
<b>Si</b>	Silicon
<b>SiO<sub>2</sub></b>	Silicon dioxide
<b>SEM</b>	Scanning electron microscope
<b>SROAS</b>	Short-range ordered aluminosilicates
<b>t</b>	Metric ton
<b>Vol. %</b>	Volume percentage
<b>Wt. %</b>	Weight percentage
<b>XRF</b>	X-Ray fluorescence analysis
<b>XRD</b>	X-Ray diffraction



## Summary

Ferralsol is one of the most widespread soil types in East Africa and is intensively used for agriculture. At the same time, it presents major challenges to farmers due to its strong weathering, low pH, and associated aluminium (Al) toxicity and phosphorus (P) fixation. These deficiencies are often addressed through the use of large quantities of mineral fertilisers, which are costly and can increase soil acidification over time.

This thesis investigates, from a biogeochemical perspective, a potentially more sustainable alternative: the use of locally available, volcanically influenced sediments from the Kenyan Rift Valley to improve soil fertility of Ferralsols. Due to their generally high pH, silicon (Si) content, and enrichment with essential nutrients (e.g. P), these materials could help reducing fertiliser demands, reduce Al toxicity, improve P availability, and increase crop yields. Two sediments (from Baringo and Nakuru in the Kenyan Rift Valley) were tested in field experiments in Eldoret, western Kenya.

In the first field experiment, the sediments were applied at two rates (1 vol.% and 3 vol.%) to a Ferralsol and compared to an untreated control (Chapter 2). Barley (*Hordeum vulgare* L., 'Hessekwa') was sown on all plots after sediment incorporation. The 3% Baringo treatment showed particularly strong effects: Soil pH increased from 4.7 to 7.0, P availability increased, and Al availability decreased significantly. This resulted in a yield increase of 1061%. Other treatments showed only moderate or no improvements. These results suggest that volcanically influenced sediments may be a promising, locally available, and natural option for improving the fertility of acidic soils, although effectiveness strongly depends on the specific sediment and application rate.

Since the underlying mechanisms could not be clearly distinguished in the first experiment, a second field experiment was conducted on the same experimental site the following year (Chapter 3). The effects of the sediments were compared to two globally established soil improvement methods: liming and straw return. New plots were established with liming, and half of each plot was amended with straw. Again, the 3% Baringo treatment resulted in a significant increase in soil pH, P availability, and yield, while liming showed similar but slightly lower effects. The untreated control produced no grain. These findings indicate that pH increase is a driving factor for the observed yield improvements. However, unlike liming, the 3% Baringo treatment also significantly increased Si availability, which may explain its better

performance. Neither in the other treatments (Baringo 1%, Nakuru 1%, and 3%) nor in the straw addition treatments were positive changes in nutrient availability or yields observed.

To better understand the effects of sediment additions on the mobilisation of Si, Al, P, and iron (Fe) in Ferralsol, three laboratory incubation experiments were conducted, using soil slurries from the Kenyan field site (Chapter 4). The incubations were carried out as follows: (i) sediment addition at two concentrations (1 wt.% and 5 wt.%) over 28 days; (ii) an additional treatment with 1 wt.% lime over 61 days; (iii) sediment and straw addition under anoxic conditions over 80 days. The results showed that both sediments and lime resulted in only short-term increases in P concentrations in the soil solution. It is assumed that the released P was quickly re-adsorbed or precipitated with other elements. Nevertheless, a long-term reduction in available Al concentrations was observed in all Baringo sediment and lime treatments. The third incubation experiment clearly demonstrated the strong influence of Fe minerals on P fixation in Ferralsol. Through the reductive dissolution of Fe(III) phases, P concentrations in the soil solution increased tenfold, independently of sediment addition.

The results of this thesis demonstrate that the use of local sediments, can have a high potential for more sustainable agriculture on acidic soils in Kenya.

## Zusammenfassung

Ferralsole zählen zu den am weitesten verbreiteten Bodentypen in Ostafrika und werden landwirtschaftlich intensiv genutzt. Gleichzeitig stellen Ferralsole durch ihre starke Verwitterung, den niedrigen pH-Wert sowie der damit verbundenen Aluminiumtoxizität (Al) und Phosphorfixierung (P) Landwirte vor große Herausforderungen. Häufig wird versucht, diese Defizite durch den Einsatz großer Mengen an Mineraldünger auszugleichen, was jedoch mit hohen Kosten und oftmals negativer Langzeitwirkung wie einer Förderung der Bodenversauerung einhergeht.

Diese Arbeit untersucht daher aus biogeochemischer Perspektive eine potenziell nachhaltigere Alternative: den Einsatz lokal verfügbarer, vulkanisch beeinflusster Sedimente aus dem kenianischen Rift Valley zur Verbesserung der Bodenfruchtbarkeit von Ferralsolen. Aufgrund ihres meist hohen pH-Werts, Siliziumgehalts (Si) und der Anreicherung mit essenziellen Nährstoffen (z.B. P) könnten diese Materialien dazu beitragen, den Düngerbedarf sowie die Al-toxizität zu senken, P-Verfügbarkeit zu erhöhen und so die Erträge zu steigern. Dafür wurden zwei Sedimente (aus Baringo und Nakuru im Kenianischen Rift Valley) in Feldversuchen in Eldoret (Westkenia) auf ihre Wirksamkeit untersucht.

Im ersten Feldversuch wurden die beiden Sedimente in zwei Ausbringungsraten (1 Vol.-% und 3 Vol.-%) auf einem Ferralsol in Eldoret ausgebracht und mit einer unbehandelten Kontrolle verglichen (Kapitel 2). Nach der Einarbeitung wurde auf allen Flächen Gerste (*Hordeum vulgare* L., ‚Hessekwa‘) ausgesät. Besonders die Behandlung mit 3 % Baringo zeigte starke Effekte: Der pH-Wert stieg von 4,7 auf 7,0, die P-Verfügbarkeit nahm zu und die Al-Verfügbarkeit sank deutlich. Dies führte zu einer Ertragssteigerung von 1061 %. Die anderen Behandlungen zeigten nur moderate oder keine Verbesserungen. Die Ergebnisse deuten darauf hin, dass vulkanisch beeinflusste Sedimente eine vielversprechende, lokal verfügbare und natürliche Möglichkeit zur Verbesserung der Fruchtbarkeit saurer Böden darstellen könnten. Die Wirkung ist jedoch stark von dem jeweiligen Sediment und der Ausbringungsmenge abhängig.

Da im ersten Versuch die genauen Wirkmechanismen nicht klar getrennt werden konnten, wurde im Folgejahr ein zweiter Feldversuch durchgeführt (Kapitel 3). Hierbei wurden die Sedimentwirkungen mit zwei etablierten Bodenverbesserungsmaßnahmen verglichen: Kalkung und Strohzugabe. Dafür wurden auf derselben Versuchsfläche neue Parzellen mit einer Kalkzugabe etabliert und jede Parzelle wurde halbseitig mit einer Strohzugabe kombiniert.

Auch in diesem Versuch führte Baringo 3 % zu einer signifikanten Erhöhung des pH-Werts, der P-Verfügbarkeit und des Ertrags. Die Kalkung zeigte ähnliche Effekte, allerdings mit einem etwas geringeren Ertrag. Die unbehandelte Kontrolle brachte keinen Kornertrag hervor. Diese Ergebnisse sprechen dafür, dass der pH-Wert ein zentraler Treiber für die beobachteten Ertragssteigerungen ist. Allerdings konnte Baringo 3 % im Gegensatz zur Kalkung auch die Si-Verfügbarkeit deutlich erhöhen, was ein möglicher Grund für die nochmals besseren Resultate dieser Behandlung sein könnte. Bei den anderen Varianten (Baringo 1 %, Nakuru 1 % und Nakuru 3 %) konnten hingegen keine signifikanten Veränderungen in der Nährstoffverfügbarkeit oder den Erträgen festgestellt werden. Auch die Zugabe von organischem Material in Form von Stroh zeigte keinen positiven Effekt im Vergleich zur Kontrolle.

Um die Effekte der Sedimentzugaben auf die Mobilisierung von Si, Al, P und Eisen (Fe) im Ferralsol besser zu verstehen, wurden im Labor drei ergänzende Inkubationsversuche durchgeführt (Kapitel 4). Als Ausgangsmaterial dienten Bodenschlämme des kenianischen Versuchsfeldes. Die Inkubationen wurden wie folgt durchgeführt: (i) Zugabe der Sedimente in zwei Konzentrationen (1 Gew.-% und 5 Gew.-%) über 28 Tage; (ii) Zusätzliche Variante mit 1 Gew.-% Kalkung über 61 Tage; (iii) Sediment- und Strohzugabe unter anoxischen Bedingungen über einen Zeitraum von 80 Tagen. Die Ergebnisse zeigten, dass sowohl die Sedimente als auch die Kalkung nur kurzfristig zu erhöhten P-Konzentrationen in der Bodenlösung führten. Es ist anzunehmen, dass das freigesetzte P rasch wieder adsorbiert oder mit anderen Elementen ausgefällt wurde. Dennoch konnte in allen Varianten mit Baringo-Sediment sowie in der Kalkbehandlung eine langfristige Reduktion der verfügbaren Al-Konzentration beobachtet werden. Im dritten Inkubationsversuch wurde deutlich, wie stark die P-Fixierung im Ferralsol durch Fe-Minerale beeinflusst wird. Durch die reduktive Auflösung der Fe(III)-Phasen konnte die P-Konzentration in der Bodenlösung unabhängig von der Sedimentzugabe um das Zehnfache gesteigert werden.

Die Ergebnisse dieser Arbeit zeigen, dass die Verwendung lokaler Sedimente, ein hohes Potenzial für eine nachhaltigere Landwirtschaft auf sauren Böden in Kenia haben kann.

## Chapter 1: Introduction

### *Overview of the geology in Kenya*

The geology of Kenya is characterized by a complex system, which can be broadly divided into three different geological provinces: the Nyanza Craton in western Kenya, the Mozambique Orogenic Belt of central and eastern Kenya and the East-African Rift System (EARS) that runs north-south through central Kenya (Mooney and Christensen, 1994). The Nyanza Craton is considered tectonically stable and consists of Archean metamorphic rocks like a variety of gneisses and granitoids, dated to 2550 to 2300 million years ago (Ma, Mosley, 1993; Mooney and Christensen, 1994). The Mozambique Belt lies to the east and south of the Nyanza Craton and was formed during the Pan-African orogeny in the Neoproterozoic era (Mosley, 1993). This period of tectonic activity, marked by faulting, folding and metamorphism, began around 850 Ma (Mosley, 1993). The metamorphism reached greenstone and amphibolite-grade and granitoids were deposited as dikes and sills (Mooney and Christensen, 1994). From Mesozoic to early Cenozoic, there was very low tectonic activity on the Nyanza Craton or the Mozambique Belt, allowing the bedrock to be eroded to a near-flat plain (Baker et al., 1972). This ended with the formation of the EARS in the early Cenozoic around 30 Ma (Chorowicz, 2005). Divergent plate tectonics opened a rift valley running north-south through central Kenya and led to a variety of late Pliocene and Quaternary volcanic activities in the rift region, which were predominantly basaltic and trachytic (Baker et al., 1972; Chorowicz, 2005). These volcanic rocks were deposited in the region and covered it with around 144,000 km<sup>3</sup> of volcanic material (Williams, 1972). Additionally, numerous lake and basin landscapes were formed in the course of rifting and volcanic activity (Chorowicz, 2005). These landscapes were filled with lacustrine and fluvial deposits through sedimentation (Chorowicz, 2005). The occurrence of volcanic eruptions in the last few hundred years indicate that the Kenyan Rift is still active (Mooney and Christensen, 1994).

The presence of very old and tectonically mostly stable structures such as the Nyanza Craton on the one hand and the relatively recent formation of the Rift Valley with ongoing volcanic activity and volcanic ash deposition on the other hand has resulted in a wide variety of different soil types in Kenya. Some of the common soil types occurring in Kenya are Ferralsols, Nitisols and Andosols (Sombroek et al., 1980). Andosols are very young soils, developed from weathering of glass-rich volcanic tephra like volcanic ash, tuff and pumice in humid tropical climate (FAO, 2014). Therefore, Andosols in Kenya are mainly found in the Rift Valley within

the volcanic highlands, characterized by high precipitation and input of fresh volcanic tephra (Sombroek et al., 1980; FAO, 2014). Nitisols are also found in the area of the Rift Valley in the volcanic highlands, but also in its surroundings (Sombroek et al., 1980). This soil type is characterized as older and more weathered, which has developed from intermediate to basic parent rock (in Kenya mostly volcanic basalt and trachyte; FAO, 2014). However, Nitisols may be rejuvenated by the addition of volcanic ash (FAO, 2014). Andosols and Nitisols have good physical properties (e.g. water holding capacity, stable structure, porosity) and a good chemical fertility, making them some of the most agriculturally productive soils in the tropics (FAO, 2014). Nevertheless, the prevalence of these soils in Kenya is lower than the occurrence of very old and highly weathered soils such as Ferralsols. In contrast to Andosols and Nitisols, Ferralsols tend to occur in the geologically mostly stable and old regions of Kenya (Sombroek et al., 1980; FAO, 2014). Ferralsols are usually formed in flat or hilly terrain, and there is usually no evidence of recent deposits in the profile (FAO, 2014). High average annual temperatures and precipitation in the sub-humid to humid tropics and old landscapes without active tectonics provide the deep and long-time chemical weathering of primary minerals, the dissolution of silicic acid and the leaching of base cations (Zech et al., 2014). This results in acidic soils with limited essential nutrients for plant growth, meaning they have a low natural potential for productive agriculture. Nevertheless, due to the high prevalence of Ferralsols, many Kenyan farmers are dealing with the challenges that these soils pose to agriculture.

### *Challenges for agriculture on Ferralsols*

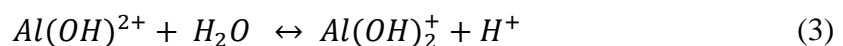
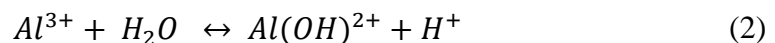
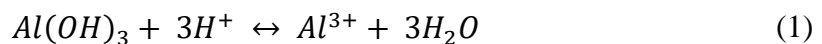
#### *Physical and chemical properties of Ferralsols*

The physical properties of Ferralsols are good for productive agriculture (FAO, 2014). They are characterized by a stable soil structure with friable aggregates, numerous macropores and a great soil depth with diffuse horizon boundaries (FAO, 2014; Kögel-Knabner and Amelung, 2014). These properties make these soils less susceptible to erosion, promote a good water and air permeability and allow deep rooting for plants. However, the chemical fertility of Ferralsols is poor, due to the intense and deep weathering (FAO, 2014). This results in an accumulation of stable residual minerals, such as quartz, and secondary minerals, predominantly iron (Fe)- and Al-oxides and kaolinite. The more easily weathered primary minerals and ferromagnesian minerals, as well as the more resistant feldspars, are completely dissolved (Kögel-Knabner and Amelung, 2014). Consequently, silicon (Si) as well as base cations, such as potassium ( $K^+$ ), calcium ( $Ca^{2+}$ ) and magnesium ( $Mg^{2+}$ ) are leached from the soil (von Uexküll and Mutert, 1995). The cation exchange sites on the mineral surfaces become increasingly occupied by

hydrogen ( $H^+$ ) and aluminium ( $Al^{3+}$ ) ions, leading to the characteristically low pH values of 4 – 5 in Ferralsols (Kögel-Knabner and Amelung, 2014). This process of intense weathering is also known as ferralinitisation (Kögel-Knabner and Amelung, 2014). The mineralogy of Ferralsols is dominated by low-activity clay (mostly kaolinit) and stable Fe and Al oxides, hydroxides and oxyhydroxides, primarily goethite [ $FeO(OH)$ ], hematite ( $Fe_2O_3$ ) and gibbsite [ $Al(OH)_3$ ] in varying amounts (Klamt and van Reeuwijk, 1993; Kögel-Knabner and Amelung, 2014). The high prevalence of these minerals promotes a very low cation exchange capacity (CEC), which limits the availability of essential nutrients for plants (Klamt and van Reeuwijk, 1993).

#### *Aluminium toxicity due to low soil pH*

Soil acidity is one of the key challenges agriculture is facing in Kenya. Around 13% (7.5 million ha) of Kenya's soils are considered acidic, including Ferralsols with pH values between 4 and 5 (Kanyanjua et al., 2002). Under these conditions, Al becomes more soluble, and its toxicity to plants increases, as its solubility strongly depends on the pH (von Uexküll and Mutert, 1995). When the pH drops below 5.5, Al hydroxide [ $Al(OH)_3$ ] gradually begins to dissolve, releasing  $Al^{3+}$  ions into the soil solution (Equation 1; Bojórquez-Quintal et al., 2017; Li and Johnson, 2016). These ions are highly mobile and phytotoxic (Sade et al., 2016). Once released,  $Al^{3+}$  can displace base cations from exchange sites at mineral surfaces, thereby increasing the proportion of exchangeable Al in the soil (Bojórquez-Quintal et al., 2017). In contact with water, however,  $Al^{3+}$  may hydrolyse to form hydroxyl complexes such as  $Al(OH)^{2+}$  and  $Al(OH)_2^+$ , which are less mobile and less phytotoxic (Li and Johnson, 2016; Bojórquez-Quintal et al., 2017). However, this hydrolysis process releases  $H^+$  ions, which further lower the soil pH and results in further dissolution of  $Al(OH)_3$  and release of  $Al^{3+}$  (Equations 2–3; Li and Johnson, 2016). This creates a self-reinforcing cycle: as the pH drops, Al solubility, and therefore toxicity, increases. Ferralsols additionally have a low CEC, due to their mineral composition dominated by low-activity clays like kaolinite and stable Fe- and Al-oxides (e.g., goethite, hematite, and gibbsite; Klamt and van Reeuwijk, 1993). This limits their ability to buffer pH changes, intensifying the processes of soil acidification and Al toxicity even faster (Havlin, 2013).



The primary effect of Al toxicity is the inhibition of root growth and limiting the development of root systems and their functions (Foy et al., 1965; Kochian et al., 2004). As a result, plants show reduced uptake of both water and essential nutrients (Foy et al., 1965; Kochian et al., 2004). At elevated concentrations and under conditions of high bioavailability, aluminium can also be absorbed by plants and accumulate in plant tissue, which can lead to significant declines in the yield of agricultural crops (Cocker et al., 1998a; Lal and Singh, 1998).

#### *Phosphate fixation on Fe and Al oxides*

In addition to soil acidity, the specific mineralogical composition of Ferralsols causes a second major challenge to agriculture on these highly weathered tropical soils, which is the strong fixation of phosphate by Fe and Al oxides. Due to prolonged weathering, Ferralsols are enriched in stable Fe and Al oxides such as hematite, goethite, and gibbsite (Klamt and van Reeuwijk, 1993; Kögel-Knabner and Amelung, 2014). These minerals are responsible for a high phosphorus (P) binding in Kenyan acid soils (Agegnehu and Sommer, 2000). The P binding is ranging from moderate (100 – 400 mg kg<sup>-1</sup> soil) in western Kenya to high (<400 mg kg<sup>-1</sup> soil) in acid soils in the highlands east of the Rift Valley (Buresh et al., 1997; Kisinyo et al., 2014). With acidic conditions, the surface hydroxyl groups of the abovenamed oxides become increasingly protonated, resulting in a higher positive surface charge (Liu et al., 2013; Li et al., 2019b). This enhances the retention of negatively charged phosphate species such as H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, which dominates with low pH, 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 facilitate strong interactions with phosphate ions (Xu et al., 2007; Liu et al., 2013). While electrostatic adsorption is relatively weak and reversible, extended contact can lead to ligand exchange, in which the phosphate ion replaces a hydroxyl group (–OH) on the mineral surface, forming more stable bonds (Vissenberg et al., 2000; Nkoh et al., 2021). As a consequence, Ferralsols often contain substantial amounts of total P, but very little remains soluble and available to plants (Hengl et al., 2017; Du et al., 2020). This phenomenon of P fixation has long been recognised as a major limitation in Ferralsol fertility and is well documented in the scientific literature (Kellogg, 1956; Russel et al., 1974; Sanchez and Uehara, 1980; Ayodele and Agboola, 1981).

### ***Methods to improve fertility of Ferralsols***

#### *Phosphorus fertilisation with mineral fertilisers*

Phosphorus is one of the most important plant nutrients and is essential for key physiological processes such as root development and fruit formation (Raghothama, 2005; Shen et al., 2011).

In many parts of East Africa, however, P deficiency occurs due to a high nutrient depletion rate and the prevalence of soils with high P adsorption capacity, such as Ferralsols (Sanchez et al., 1997; Smaling et al., 1997; Bationo et al., 2012). Therefore, P is often the yield-limiting nutrient, as high crop yields may not be achieved without sufficient supply (Nziguheba et al., 2002; Bationo et al., 2012). Kisinyo et al. (2014) revealed that application rates of 26 to 52 kg P ha<sup>-1</sup> in acidic soils in Kenya resulted in P recovery rate of only 9.6 to 13.5 %, which is largely due to direct fixation by soil minerals. As a result, high amounts of soluble P fertilisers are required to achieve sufficient yields (Bationo et al., 2012). While commercial farms may be able to afford these inputs, most smallholders face significant challenges due to high prices and limited access (Minde et al., 2008; Bekunda et al., 2010).

Another problem is the type of P fertilisers commonly used on Ferralsols. The most widespread forms are diammonium phosphate (DAP) and compound NPK fertilisers (Nziguheba et al., 2016). Both may contain ammonium, which is converted to nitrate through nitrification, releasing H<sup>+</sup> in the process (Salvator et al., 2019; Wang et al., 2021). This contributes to further acidification of already acidic soils, especially with long-term use (Salvator et al., 2019; Wang et al., 2021).

#### *Liming to increase soil pH*

Another method of improving the fertility of Ferralsols is the application of lime materials rich in Ca<sup>2+</sup> and/or Mg<sup>2+</sup> (Fageria and Baligar, 2008). Ferralsols are characterized by a low pH, resulting in high Al toxicity and a strong phosphate adsorption capacity (Klamt and van Reeuwijk, 1993). Liming can effectively address these challenges by neutralizing excess H<sup>+</sup> ions, thereby increasing the pH (Wang et al., 2021). As the pH increases above 5.5, the toxic Al<sup>3+</sup> changes into the less soluble solid Al(OH)<sub>3</sub> (Bolan et al., 2003). This reduces the concentration of toxic Al<sup>3+</sup> in the soil solution, decreasing Al toxicity (Bolan et al., 2003; Bojórquez-Quintal et al., 2017). At the same time, the increased pH causes the deprotonation of Fe and Al oxides, reducing their positive surface charge (Fageria and Baligar, 2008). This can decrease the electrostatic adsorption of negatively charged phosphate species, such as H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, resulting in less phosphate fixation and higher P availability (Fageria and Baligar, 2008). In addition, lime directly provides Ca<sup>2+</sup> and Mg<sup>2+</sup> to the soil, which are important nutrients that are rarely present in Ferralsols due to long-term weathering (Fageria and Nascente, 2014; Li et al., 2019a). These nutrients can displace acid-forming cations, such as H<sup>+</sup> and Al<sup>3+</sup>, from clay mineral and oxide exchange sites, thereby increasing base saturation (Fageria and Baligar, 2008). Several studies have demonstrated the positive effects of liming

on acidic soils in Kenya, including reducing Al toxicity, increasing soil pH, and improving the availability of Ca, Mg, N and P (Kanyanjua et al., 2002; Li et al., 2019a). Liming, especially in combination with small amounts of mineral fertiliser, has a clearly positive effect on the yield of various crops (Kisinyo et al., 2014).

Still, despite the well-documented scientific benefits, lime is rarely used in Kenyan agricultural practices due to several factors. First, it is only available from a few agrochemical dealers, which limits access, especially in rural areas (Kisinyo et al., 2014). Second, the application process is labour-intensive due to the lack of suitable machinery. This makes it difficult for many smallholders to use lime because they do not have the financial resources for additional labour (Kisinyo et al., 2014). Additionally, there is a significant knowledge gap regarding the benefits of lime, which results in low overall demand (Kisinyo et al., 2014).

### ***Local sediments as a sustainable solution?***

#### *Local sediments with volcanic influence*

A new, sustainable method of improving the fertility of Ferralsols in Kenya could be adding local sediments from the Rift Valley to the soil. The EARS region is characterized by a high incidence of recent volcanic activity (Chorowicz, 2005; Blegen et al., 2016). Volcanism in this region is represented by alkaline basaltic-trachytic magmas (Tryon and McBrearty, 2006; Blegen et al., 2016). Large volcanoes in particular, including Menengai in the Pleistocene, have released large quantities of pyroclastic material over large areas of the EARS (Blegen et al., 2016). This material has been deposited and may have altered the physicochemical properties of the initial sediments. Natural processes such as wind transport, water erosion and ash fall might have mixed volcanic materials into existing lacustrine and terrestrial sedimentary soils (Pyle, 1999; Blegen et al., 2016). The content of base-forming cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ) in the volcanic materials could have increased the pH of the existing sediments (Tryon and McBrearty, 2006; Blegen et al., 2016). Additionally, pyroclastic deposits of basaltic-trachytic composition contain relatively high concentrations of elements including Si, Ca, Na and P, which may also have been increasingly introduced into the sediments of the Rift Valley (Tryon and McBrearty, 2006; Blegen et al., 2016). Using these sediments as soil amendments for agriculture on Ferralsols could have some beneficial effects on soil fertility.

#### *Increase in pH*

One potential benefit of adding local, volcanically influenced sediments to Ferralsols for agriculture could be an increase in soil pH. The presence of alkaline, basaltic-trachytic

pyroclastic material in many sediments in the Rift Valley likely contributes to increased pH levels. Similar to the effects observed with liming, the high concentrations of base-forming cations such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  from the sediment materials may result in a pH increase in acidic Ferralsols after the application. This process can reduce Al toxicity by decreasing the prevalence of  $\text{Al}^{3+}$  ions, and decreasing P fixation by deprotonation of Fe and Al oxide surfaces. These beneficial effects may increase nutrient availability for plants.

#### *Silicon and phosphorus*

The tuffs and tephra of recent volcanoes in the Kenyan Rift Valley have silica ( $\text{SiO}_2$ ) contents of around 50–70% (Tryon and McBrearty, 2006; Blegen et al., 2016). The weathering of these silicate-rich pyroclastic materials releases silicic acid, which plays an important role in plant physiology (Katz et al., 2021; Schaller et al., 2021). Depending on Si concentration and soil solution pH, silicic acid can be present in soil solution in either monomeric or polymeric form (Schaller et al., 2021). Both forms can adsorb onto mineral surfaces and compete with other anions, such as phosphates, for adsorption sites (Dietzel, 2002; Schaller et al., 2021). Several studies have found that Si can displace phosphate ions from Fe oxide surfaces, thereby increasing P availability in the soil (Taylor, 1995; Weng et al., 2012; Schaller et al., 2019; Uhuegbue et al., 2024). In addition, Schaller et al. (2019; 2022) found that fertilisation with amorphous Si (ASi) can promote the reductive dissolution of Fe mineral phases, which can mobilize P that was previously adsorbed or occluded in Fe oxides. Due to the presumably high Si content of volcanically influenced Rift Valley sediments, adding them to desilicified Ferralsols could potentially increase the concentration of available Si in soils toward plants. Combined with the sorption and solubility processes mentioned before, this could enhance the availability of essential nutrients such as P and consequently promote plant growth.

#### *Silicon and aluminium*

In addition to the mobilisation of P, an additional supply of Si from Rift Valley sediments may also contribute to reducing Al toxicity in Ferralsols. Silicon does not only adsorb onto surfaces of Fe oxides but also interacts with Al oxides through electrostatic adsorption and surface complexation (Elisa et al., 2016). These interactions can alter the electrochemical properties of Al oxides, including their stability and surface reactivity (Elisa et al., 2016). Several studies have demonstrated that Si and Al can co-precipitate as aluminosilicate compounds, thereby reducing the bioavailable  $\text{Al}^{3+}$  (Pačes, 1978; Tubana and Heckman, 2015; Exley et al., 2019; Schaller et al., 2021). Lenhardt et al. (2021) revealed that under specific conditions (certain Al/Si ratio and pH levels), there is also a possible formation of short-range ordered

aluminosilicates (SROAS). These are poorly crystalline Al-Si phases and could further reduce soluble Al concentrations. Numerous studies have shown that this Si-induced reduction in Al toxicity has positive effects on various important crop species like barley (*Hordeum vulgare* L.; Hammond et al., 1995), millet (*Sorghum bicolor* L.; Hodson and Sangster, 1993), wheat (*Triticum aestivum* L.; Cocker et al., 1998b) and maize (*Zea mays* L.; Corrales et al., 1997).

### ***Outline of this thesis***

Volcanic ash is known to improve soil fertility. However, little is known about the effects of sediments influenced by volcanic ash on acidic soils, such as Ferralsols, even though these sediments are abundant in the Kenyan Rift Valley.

This study examined how two different volcanic ash rich sediments from Kenyan Rift Valley affect the agricultural productivity of barley (*Hordeum vulgare* L., 'Hessekwa'). After exploring suitable sediments and a planting site, a field experiment was conducted in Eldoret, western Kenya. Two application rates of the sediments were tested to analyse their influence on the availability of Al, Si, P, and Fe in the soil and on the barley yield.

The experiment was based on the following hypotheses:

- i) The addition of sediment improves the P availability and reduces the potentially toxic Al availability by increasing Si content and pH in the Ferralsol.
- ii) The addition of sediment significantly increases barley production.

The results of the first field experiment using local, volcanically influenced sediments from Kenyan Rift Valley revealed that application of the sediments can improve the fertility of Ferralsols and increase barley yields. However, the underlying mechanisms were not clearly identified.

To clarify whether the observed effects are primarily due to an increase in soil pH or if other processes, such as silicon supply, play a significant role, a second field experiment was conducted. Here, lime treatments were integrated to compare the effects of the sediments to the effects of liming alone. Additionally, the globally established method of "straw return" was included as a further comparative treatment.

The following hypotheses were formulated for the second experiment:

- iii) The addition of local, volcanically influenced sediment reduces Al toxicity and increases P availability and barley yield in the second year after application through a combination of pH increase and Si supply.

- iv) The lime treatment increases soil pH, leading to improved P availability, reduced Al availability, and increased yields comparable to those from sediment treatment.
- v) The straw return method increases barley yields, but combining straw and liming achieves the highest yields.

To gain a deeper understanding of soil chemical processes in Ferralsol after adding local sediments, additional laboratory tests were conducted. Three incubation experiments were designed to analyse the mobilisation of Si, P, Al and Fe in the arable soils with corresponding sediment additions over defined time periods.

The first incubation experiment focused on the interaction between Si, P, and Al in the soil. In addition to the sediment treatments, a Si reference treatment with pure ASi addition was included to investigate the role of silicon specifically.

The second experiment examined the effects of increasing the pH through liming, particularly with regard to the availability of P and Al. In this experiment, a lime treatment was used instead of the Si reference.

The third experiment examined the release of P resulting from the reductive dissolution of Fe phases in Ferralsols after straw addition. Although Ferralsols are typically well aerated, temporary anoxic microsites can form during heavy rainfall, creating local reduction conditions that affect the solubility of Fe-bound P.

The following hypotheses were formulated for the laboratory tests:

- vi) The addition of sediment increases the availability of P and decrease the availability of Al to a similar extent as the Si reference treatment because Si can promote the mobilisation of P and bind Al from the soil solution.
- vii) The lime treatment results in stronger P release and lower Al availability compared to the sediment treatments because the pH value acts as a driving factor.
- viii) The P availability increases significantly as a result of the reductive dissolution of Fe phases promoted by the addition of straw, since a large proportion of the bound P is adsorbed on these phases.

For each part, a separate article was published in a peer-reviewed journal. These articles are given in Chapter 2 – 4 as self-contained articles with separate abstract, introduction, materials and methods, results, discussion, conclusion and references. In chapter 5, all results and

discussions are summarized before presenting a conclusion. Additionally, a further research recommendation is provided.

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## **Chapter 2: Local sediment amendment can potentially increase barley yield and reduce the need for phosphorus fertiliser on acidic soils in Kenya**

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### ***Abstract***

Soil acidification and low nutrient availability are two major challenges facing agriculture in most regions of East Africa, resulting in aluminium toxicity and poor crop yields. The amendment of local sediments to cropland can potentially alleviate these challenges, but responses are variable. In this study, we investigated the potential of two different local sediments influenced by volcanic deposits to increase soil pH, Si and P availability and reduce Al toxicity, thereby improve barley yield. Hence, a field experiment was established in Eldoret, Western Kenya, using 1% and 3% addition by weight of two sediments in barley cultivated plots. The Baringo 3% amendment significantly increased soil pH (from 4.7 to 7.0), the available P content (from 0.01 mg g<sup>-1</sup> to 0.02 mg g<sup>-1</sup>) and decreased the Al availability (from 3.03 mg g<sup>-1</sup> to 2.17 mg g<sup>-1</sup>). This resulted in a barley yield of 4.7 t ha<sup>-1</sup> (+1061%). The Nakuru 3% and Baringo 1% amendments increased yield to 2-3 t ha<sup>-1</sup>, while the Nakuru 1% did not significantly increase yield. These results highlight that, from a biophysical perspective, there are natural and local opportunities to reduce soil acidification and to partly replace mineral fertiliser, but its magnitude depends on the sediment and the amendment rate.

### ***Introduction***

Food security is a big challenge in many areas of tropical Africa. Soils in these regions are characterized by a low pH and nutrient availability, resulting in low crop yields (Du et al., 2020). About 29% of the tropical land area in tropical Africa is defined as acidic. In Kenya, acidic soils account for 13% of the total agricultural land, especially in the western part of the country (Pandey et al., 1994; Kanyanjua et al., 2002). This is due to the humid to sub-humid tropical climate with moderate to heavy rainfall and high temperatures, which promotes intense weathering and forms soils such as Ferralsols and Acrisols (Soil Survey Staff, 1999). As soils acidify, cations such as potassium ( $K^+$ ), calcium ( $Ca^{2+}$ ), magnesium ( $Mg^{2+}$ ), and sodium ( $Na^+$ ) are leached and replaced by hydrogen ( $H^+$ ) and aluminium ( $Al^{3+}$ ) ions (von Uexküll and Mutert, 1995; Agegnehu et al., 2021). In addition to the loss of nutrients through leaching, the increase in mobile and available  $Al^{3+}$  ions is a major problem of increasing soil acidification (von Uexküll and Mutert, 1995). Especially at  $pH < 5.5$ , Al toxicity increases because solubilized Al as  $Al^{3+}$  is plant available and phytotoxic (Sade et al., 2016; Vega et al., 2019). The main toxic effect of Al on higher plants is inhibition of root elongation and alteration of root system structure and functions, resulting in inadequate water and nutrient supply to affected plants (Foy et al., 2003; Kochian et al., 2004). In addition, high Al availability increases direct uptake and accumulation of Al in the plant, resulting in strongly decreasing crop yields (Cocker et al., 1998; Lal and Singh, 1998). Besides the very low pH value (pH 4-5), Ferralsols and Acrisols are also characterized by high contents of iron (Fe) and Al (Balland-Bolou-Bi and Livet, 2018). Minerals of these elements have a very high phosphorous (P)-sorption capacity, resulting in a P deficiency (Russel et al., 1974; Sanchez and Uehara, 1980; Beauchemin et al., 2003). The issue of P fixation in tropical soils has been under discussion for many decades and many studies on this topic have already been published (Kellogg, 1956; Russel et al., 1974; Sanchez and Uehara, 1980; Ayodele and Agboola, 1981). Due to the strong binding of P to Fe- and Al-oxides and hydroxides, relatively high total P contents are found, but very little of this total P is available to plants (Russel et al., 1974; Hengl et al., 2017; Du et al., 2020). Soil acidity, which occurs in large parts of tropical Africa, can additionally promote the P fixation in the soil (Agegnehu et al., 2021). A very low pH ( $<5$ ) can result in precipitation of Al- and Fe-phosphates, but already at  $pH < 5.5$ , phosphate can easily become unavailable to plants (Russel et al., 1974; Sanchez and Logan, 1992; Agegnehu and Sommer, 2000). As a consequence, farmers in tropical Africa need to apply large quantities of P fertiliser (up to  $150 \text{ kg ha}^{-1}$ ) to obtain high enough yields because the P deficiency caused by P fixation needs to be compensated for (Russel et al., 1974; Nziguheba et al., 2002). However, most smallholders do

not have access, due to poor availability and high prices, to these amounts of P fertiliser, resulting in a lack of P for crop production and low plus further declining yields (Sanchez et al., 1997; Nziguheba et al., 2002).

One option, to reduce the dependency on P fertiliser and to reduce Al toxicity might be the amendment of local sediments influenced by volcanic deposits. Kenya experienced high volcanic activities in the past, due to the East African Rift System (EARS) (Blegen et al., 2016). Large volcanoes, such as Menengai in the Pleistocene, have released large amounts of alkaline volcanic tephra during their eruptions, which have been deposited in large parts of the EARS (Tryon and McBrearty, 2006; Blegen et al., 2016). Volcanic tephra is characterized by a high content of silicon (Si), which can be released in large quantities by weathering (Dahlgren et al., 1999). The deposition of alkaline tephra over large areas of the EARS may have affected many sediments in the region, enriching the initial sediments in Si and increasing their pH (Blegen et al., 2016).

Silicon is the second most abundant element in earth's crust and is a component of many minerals (Wedepohl, 1995). It occurs in the soil in solid phases (primary, secondary minerals, and amorphous phases) and liquid phases (monomeric silicic acid, polymeric silicic acid) (Schaller et al., 2021a). The weathering of the solid Si phases releases silicic acid in solution, which is an important nutrient for many growth-promoting processes in plants (Schaller et al., 2021a). Depending on e.g., Si concentration in soil solution and solution pH, the forms of silicic acid can convert from monomeric to polymeric silicic acid or the other way around (Schaller et al., 2021a). Both forms may adsorb to mineral surfaces and compete with nutrients like P for binding sites, with a higher affinity of polymeric silicic acid than monomeric silicic acid (Dietzel, 2000; 2002; Reithmaier et al., 2017). Taylor (2004) even found that silicic acid can exchange phosphate from iron oxides, although having a slightly lower binding energy. Schaller et al. (2019; 2022) revealed that amorphous Si (ASi) fertilisation increases soil P mobility and plant availability. They suggest that the addition of ASi to soil may have promoted reductive dissolution of the Fe phases/minerals releasing P initially bound to or occluded in these minerals into solution. Additionally, the weathering of the added ASi releases silicic acid (mono- and polymeric) into solution which may exchange P adsorbed to Fe mineral surfaces. Thus, higher soil Si concentration may lead to higher P mobilisation in soil, which in turn may result in better plant nutrition, biomass production and crop yields (Neu et al., 2017). Additionally, it was shown that Si fertilisation may reduce the bioavailability of Al due to the precipitation of Al and Si as aluminosilicates (Pačes, 1978; Exley et al., 2019). Next to this, numerous studies have

shown that Si mediates various physiological processes in plants to mitigate metal toxicity of Al, As, Cd, Mn and Pb (Horiguchi, 1988; Li et al., 2009; Singh et al., 2011; Li et al., 2012; Emamverdian et al., 2018). Silicon modifies cell walls by depositing hydrous SiO<sub>2</sub>, which provides physical and mechanical protection against biotic stresses. It has also been suggested that Si causes changes in plant cell metabolism, reducing root uptake of potentially toxic elements and inducing the excretion of certain compounds such as organic acids (OAs) and phenolics (Cocker et al., 1998; Gu et al., 2011; Luyckx et al., 2017; Wang et al., 2017). In numerous crops like barley, maize and wheat, the amelioration of Al toxicity by Si has been shown to result from a competition for Si versus Al uptake by roots (Cocker et al., 1998; Pontigo et al., 2015; Vega et al., 2019). Therefore, a Si fertilisation effect by addition of local sediments with volcanic deposits could increase the P availability as well as decrease the aluminium toxicity in plants. However, it is important to note that, in addition to Si, other essential nutrients may also be enriched in sediment materials. As the sediments weather over time after incorporation into the soil, nutrients such as P, Na, Ca and K may be released into the soil solution and become available to plants (Manning, 2022).

While volcanic ash is known to improve soil fertility (Fiantis et al., 2019), much less is known about the effects of Si derived from local sediments of areas influenced by volcanic deposits on P availability and Al toxicity in acidic soils. Therefore, we investigated the effects on Si and P availability and Al toxicity of adding local sediments influenced by volcanic deposition to Kenyan arable soils where barley was grown and whether barley yields may be improved by the addition of sediments. We hypothesized that 1) the addition of Si rich sediments will increase P availability and decrease availability of potential toxic Al and 2) the increase in soil pH by the addition of local sediments will also lead to an increased P availability and decreased availability of potential toxic Al. We further hypothesized that 3) the increase in P availability and decrease in Al availability will strongly improve the plant growth and yield of barley.

### ***Materials and Methods***

#### *Chemical characterisation of the sediments*

To examine the effects of local sediment amendments to soil properties and plant growth in Kenya, two potentially suitable materials from different locations in the EARS were identified. One of the sediments was from a site in the Nakuru district, south of Lake Nakuru (0.49726S, 36.091794E), which is defined as tuffs, diatomaceous silts and superficial deposits (McCall, 1966). The other sediment was taken from an area west of Lake Baringo (0.574643N, 35.984597E) and is defined as a Ca-rich lacustrine sediment (Hackman, 1987). Both sediments

are alkaline, with a pH of 8.6 for the Baringo sediment and 9.4 for the Nakuru sediment. Because of their location inside the rift valley of the EARS, they might be influenced by volcanic tephra deposition (Tryon and McBrearty, 2006; Blegen et al., 2016).

To characterize the sediments, X-Ray fluorescence analysis (XRF), Energy dispersive X-ray analyses at a scanning electron microscope (SEM-EDX), calcium chloride extraction ( $\text{CaCl}_2$ ) and sodium carbonate extraction ( $\text{Na}_2\text{CO}_3$ ) were performed. The elemental composition of the sediments was determined by XRF analysis (SPECTRO XEPOS HE, SPECTRO Analytical Instruments GmbH, Kleve, Germany). Pellets for analysis were prepared from 4 g ground sample material and 0.9 g Licowax (Cereox, Fluxana GmbH, Bedburg-Hau, Germany) using a hand-operated hydraulic press (Specac Atlas 15t, Portman Instruments AG, Biel-Benken, Switzerland). The SEM-EDX analysis was examined using a SEM (EVO MA10, ZEISS, Jena, Germany) equipped with an element detector (QUANTAX EDS, Bruker, Billerica, Massachusetts, USA). The plant-available Si was extracted by  $\text{CaCl}_2$  according to Haysom and Chapman (1975). Briefly, 1 g of sample material was weighed into 50 ml centrifuge tubes and added with 10 ml of a 0.01 M  $\text{CaCl}_2$  solution, followed by shaking on a roller shaker for 16 h. Subsequently, the tubes were centrifuged (12,800 g for 5 min) and filtered with 0.2  $\mu\text{m}$  membrane filters. The ASi was determined by  $\text{Na}_2\text{CO}_3$  extraction (DeMaster, 1981). For this, 0.03 g of sample material was weighed into 50 ml centrifuge tubes and added with 40 ml of 0.1 M  $\text{Na}_2\text{CO}_3$  solution. After shaking, the samples were placed in a heating block for 5 h at 85°C. Subsamples were taken after 1 h, 3 h and 5 h by taking 10-15 ml of the supernatant and filtered through 0.2  $\mu\text{m}$  membrane filters. For both  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  extracts, Si was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; iCAP 6300 DUO, ThermoFisher Scientific Inc., Walham, Massachusetts, USA). The cation exchange capacity (CEC) was determined with 0.1 M  $\text{BaCl}_2$  solution and measured by ICP-OES. Total organic carbon (TOC) was measured by dry combustion using a multiphase detector (RC612, LECO Corporation, St. Joseph, Michigan, USA).

#### *Study site and experimental design*

The study site is located near Eldoret in the Uasin Gishu County in western Kenya (0.4448° N, 35.4685° E) on the cropland of a local farmer, and at an elevation of 2410 m. The climate in Eldoret is cool and temperate with diurnal mean temperature range from 8.4°C to 27°C. It has two rainy seasons with an annual mean of 900–1200 mm (Tsuma et al., 2015). The soils around Eldoret are predominantly characterized as Plinthic Ferralsols with a low pH and high Fe content (Nyachiro and Briggs, 1987). The soil of this study has a pH of 4.7, the cation exchange

capacity (CEC) is  $9.7 \text{ cmol}^+ \text{ kg}^{-1}$  and the total organic carbon (TOC) is 2.6%. The total Al content is  $104 \text{ g kg}^{-1}$ , the plant-available Al content ( $\text{CaCl}_2$ ) is  $0.04 \text{ mg g}^{-1}$ . An oxalate/dithionite Fe ( $\text{Fe}_o/\text{Fe}_d$ ) ratio of 0.04 indicates that it is a strongly weathered soil (Moody and Graham, 1995).

The area of our experimental site was  $24 \times 19 \text{ m}$  with single plot size of  $3 \times 4 \text{ m}$  and was located within a farmland of a local farmer. The experimental design included for an addition of 1% and 3% by weight of each sediment to a depth of 20 cm. For Baringo, this resulted in  $24 \text{ t ha}^{-1}$  (1%) and  $72 \text{ t ha}^{-1}$  (3%) and for Nakuru, it was in  $18 \text{ t ha}^{-1}$  (1%) and  $54 \text{ t ha}^{-1}$  (3%). Additionally, control plots without any amendments were established and each treatment was replicated four times. We used a non-randomised block design (stripe design) for practical reason and set up buffering zones of one meter between each treatment and plot, to avoid interferences between the treatments (Supplementary Figure 1). The sediments were incorporated by hand followed by mixing to a depth of 20 cm. The mixing was performed in the same way for the control plots to ensure the same physical disturbance for all treatments.

Barley (*Hordeum vulgare L.*, cv. *Hessekwa*) was sown by hand in all plots on 30<sup>th</sup> of May 2022. Nitrogen (N) fertiliser was applied on every plot after germination ( $50 \text{ kg N ha}^{-1}$ ) and at stem extension ( $90 \text{ kg N ha}^{-1}$ ). Low P fertilisation ( $2.5 \text{ l ha}^{-1}$ , YaraVita Crop Boost, Yara UK Ltd., York, UK) was performed on all treatments, including the controls, in form of foliar application during the growing season. Harvest was conducted on the 13<sup>th</sup> of October 2022.

#### *Sampling and analyses*

Plant samples were taken at harvest in form of whole plants. Plants were randomly collected in areas of  $40 \times 40 \text{ cm}$ , weighed, washed, and dried to determine differences in crop yield and biomass. Additionally, soil samples (0-15 cm) of each plot were taken with a small shovel and air dried. The pH of each plot was determined in water at 1:2.5 solid to solution ratio (WTW pH/Cond 3320 with Sentix41 electrode, Xylem Water Solutions, Washington, DC, USA). Soil samples were analysed for available P, Si and Al using Mehlich III extraction according to the procedure used by Sparks and Bartels (2009). For extraction, 2 g of soil were weighed into 50 ml centrifuge tubes, mixed with 42 ml of Mehlich III extraction solution, and shaken on the overhead shaker for 5 min. The suspension was centrifuged ( $3,200 \text{ g}$  for 5 min), filtered through  $0.2 \text{ }\mu\text{m}$  filters and analysed by ICP-OES (iCAP 6300 DUO, ThermoFisher Scientific Inc., Walham, Massachusetts, USA).

To examine the nutrient translocation and accumulation in plant tissues during the growing season, the whole plants were separated into leaves, leaf sheaths, roots and grains and were subsequently analysed using different extraction methods. Microwave digestion was performed to estimate Fe, Al, and P contents in plant tissues. For this, 0.1 g of plant sample was weighed into closed vessels and mixed with 2 ml of H<sub>2</sub>O<sub>2</sub> and 3 ml of HNO<sub>3</sub> and placed in a closed vessel microwave digestion system (CEM-Mars6, CEM Corporation, Matthews, NC, USA). Subsequently, the extracts were made up to 20 ml with deionized water and filtered through 0.2 µm membrane filters. The ASi in plant tissues was determined by a Tiron extraction (Kodama and Ross, 1991). For this extraction, 0.03 g of plant samples were weighed into 50 ml centrifuge tubes, mixed with 30 ml of 0.1 M Tiron solution and heated in a water bath at 85 °C for 1 h. Immediately before heating and after 30 minutes, the samples were gently shaken by hand. Subsequently, the extracted solutions were centrifuged (5,000 g for 5 min) and filtered with 0.2 µm pore size. Both, the microwave and Tiron extracts were analysed for elemental contents by ICP-OES (iCAP 6300 DUO, ThermoFisher Scientific Inc., Walham, Massachusetts, USA). The C/N ratio of the dried and ground plant material was determined with CNS-Analyser to provide information about the nitrogen supply of the plants (CNS928-MLC, Leco Instruments Inc., St. Joseph, Michigan, USA).

### *Statistics*

The data of our study were analysed using R Studio (R Core Team, 2023). A mixed effect model with subsequent ANOVA and Tukey post-hoc test was carried out to determine statistical differences between the treatments. Blocks were treated as a random effect.

## **Results**

### *Characterisation of the sediments*

SEM-EDX analyses revealed that the Baringo sediment is characterized by a Ca-rich and aggregated sediment matrix (5-25 µm) with attached particles (< 1- 5 µm) containing Al and Si (Supplementary Figure 2). The XRF analyses confirmed the high Ca content (10.2%), but showed that Si is the main component of the sediment at 21% by weight (Table 1). In addition, the sediment was enriched in P (0.13%) and Mg (3.24%). The pH value of the Baringo sediment was 8.6 ± 0.1. The Nakuru sediment was characterized with SEM-EDX revealing the presence

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*Table 1: Element composition in weight percent or  $\mu\text{g g}^{-1}$  of the sediment and soil samples measured by XRF analysis. The absolute error of each measurement listed below each measured element. Detection limits are shown in Supplementary Table 1. Voltage=60 kV under vacuum.*

Element Dimension	Na %	Mg %	Al %	Si %	P %	K %	Ca %	Mn %	Fe %	Cu $\mu\text{g g}^{-1}$	Zn $\mu\text{g g}^{-1}$	As $\mu\text{g g}^{-1}$	Cd $\mu\text{g g}^{-1}$	Pb $\mu\text{g g}^{-1}$	S $\mu\text{g g}^{-1}$	Cl $\mu\text{g g}^{-1}$	Cr $\mu\text{g g}^{-1}$
Nakuru	4.46	0.18	8.31	30.18	0.09	4.27	0.93	0.26	4.54	3.8	199.3	1.4	<0.3	14.8	502	2183	156.7
(Abs. Error)	0.01	0.01	0.03	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	0.4	1.1	0.2	(0.0)	0.4	14	18	0.7
Baringo	0.70	3.27	7.22	21.14	0.13	1.09	10.15	0.15	5.09	30.4	95.9	2.9	<0.3	4.5	312	228.1	180.5
(Abs. Error)	0.04	0.04	0.03	0.04	<0.01	<0.01	0.01	<0.01	<0.01	0.8	0.9	0.2	(0.0)	0.4	12	8.1	0.8
Eldoret (Soil)	<0.01	0.17	15.85	18.81	0.08	0.80	0.07	0.19	8.37	23.5	164.7	3.5	<0.3	35.6	475	150.9	92.3
(Abs. Error)	(0.0)	0.01	0.05	0.04	<0.01	<0.01	<0.01	<0.01	0.01	0.8	1.1	0.3	(0.0)	0.6	13	6.8	0.7

of a mixture of splinter-like/molten Si-Al-containing particles of varying sizes. The small fraction, measuring between 20 and 50  $\mu\text{m}$ , and the coarse fraction, between 80 and 220  $\mu\text{m}$ , were observed to contain rounded particles (171.4  $\mu\text{m}$ ) with soil adhesions in the nanometer range. XRF analyses showed, that Si is the main component (30.2%) followed by Al (8.3%) and showed that it is enriched in Na (4.46%) and K (4.27%). The pH value of the Nakuru sediment was  $9.4 \pm 0.2$ . There was no amorphous Si detectable in Nakuru sediment, but the Baringo sediment had an ASi content of  $2.62 \pm 0.37 \text{ mg g}^{-1}$ . Calcium chloride extraction showed that the Baringo sediment had a much higher soluble Si ( $99.7 \pm 1.1 \text{ mg kg}^{-1}$ ) content than the Nakuru sediment ( $22.3 \pm 0.7 \text{ mg kg}^{-1}$ ) (Supplementary Figure 3). Both, the Baringo and Nakuru sediment did not show any enrichments and contaminations with potentially toxic elements like As, Cr, Pb or Cd. The Baringo sediment had a high  $\text{CEC}_{\text{eff}}$  of  $45.49 \text{ cmol}^+ \text{ kg}^{-1}$ , with  $\text{Ca}^{2+}$  ( $28.86 \text{ cmol}^+ \text{ kg}^{-1}$ ),  $\text{Mg}^{2+}$  ( $11.48 \text{ cmol}^+ \text{ kg}^{-1}$ ) and  $\text{Na}^+$  ( $6.78 \text{ cmol}^+ \text{ kg}^{-1}$ ) being the dominant cations in this sediment (Table 2). The  $\text{CEC}_{\text{eff}}$  of the Nakuru sediment was low ( $4.46 \text{ cmol}^+ \text{ kg}^{-1}$ ), with  $\text{Na}^+$  ( $3.78 \text{ cmol}^+ \text{ kg}^{-1}$ ) and  $\text{K}^+$  ( $1.15 \text{ cmol}^+ \text{ kg}^{-1}$ ) being the dominant cations in this sediment.

*Effect of local sediment amendments on biomass and yield*

Amending soils with local sediments significantly increased both the dry yield ( $p < 0.001$ ,  $F = 33.83$ ,  $df = 4$ , ANOVA) and dry biomass ( $p < 0.001$ ,  $F = 38.48$ ,  $df = 4$ , ANOVA) of barley (Fig. 1). Both 3% Baringo and 1% Baringo treatment had significantly higher dry yield compared with the control, with 3% Baringo having the highest yield of  $4.7 \pm 0.3 \text{ t ha}^{-1}$  ( $p < 0.001$  for both Baringo, Tukey). For Nakuru, only the 3% addition had a significantly higher dry yield ( $2.2 \pm 0.6 \text{ t ha}^{-1}$ ) compared with the control ( $0.41 \pm 0.37 \text{ t ha}^{-1}$ ;  $p = 0.003$ , Tukey). The same pattern was observed for dry biomass, with significantly highest biomass for 3% Baringo, and significantly higher biomass for 1% Baringo and 3% Nakuru than the control ( $p < 0.001$  for both Baringo,  $p = 0.002$  for Nakuru 3%, Tukey). For both biomass and yield, 1% Nakuru had higher values than the control, but not significantly.

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Table 2: CEC data of the sediment materials, the control soil (Eldoret) and the soil after treatment with different sediment amendments in  $\text{cmol}^+ \text{kg}^{-1}$ . Standard deviation is given ( $n=4$ , sediment references were homogenized, thus only one value is shown).

Element	Ca [ $\text{cmol}^+ \text{kg}^{-1}$ ]		K [ $\text{cmol}^+ \text{kg}^{-1}$ ]		Mg [ $\text{cmol}^+ \text{kg}^{-1}$ ]		Na [ $\text{cmol}^+ \text{kg}^{-1}$ ]		Al [ $\text{cmol}^+ \text{kg}^{-1}$ ]		Fe [ $\text{cmol}^+ \text{kg}^{-1}$ ]		Mn [ $\text{cmol}^+ \text{kg}^{-1}$ ]		CECeff [ $\text{cmol}^+ \text{kg}^{-1}$ ]	
Baringo (Reference)	28.86		1.59		11.48		6.78		<0.01		<0.01		<0.01		45.49	
Nakuru (Reference)	0.51		0.51		0.02		3.78		<0.01		<0.01		<0.01		4.46	
Eldoret (Soil)	1.66	$\pm 0.12$	1.70	$\pm 0.1$	0.93	$\pm 0.08$	<0.01	(0.0)	2.51	$\pm 0.16$	0.02	$\pm 0.01$	0.83	$\pm 0.03$	9.69	$\pm 0.20$
Baringo 1%	7.90	$\pm 2.68$	1.79	$\pm 0.04$	1.77	$\pm 0.27$	0.07	$\pm 0.06$	0.32	$\pm 0.39$	0.02	$\pm 0.01$	0.63	$\pm 0.13$	13.42	$\pm 2.32$
Baringo 3%	17.86	$\pm 4.04$	1.8	$\pm 0.09$	2.76	$\pm 0.44$	0.15	$\pm 0.07$	0.02	<0.01	0.01	<0.01	0.31	$\pm 0.15$	20.90	$\pm 3.12$
Nakuru 1%	2.14	$\pm 0.22$	1.96	$\pm 0.09$	1.12	$\pm 0.06$	0.01	(0.0)	2.02	$\pm 0.11$	0.02	$\pm 0.01$	0.81	$\pm 0.06$	9.72	$\pm 0.39$
Nakuru 3%	3.31	$\pm 0.11$	2.02	$\pm 0.07$	1.32	$\pm 0.13$	0.09	$\pm 0.03$	1.18	$\pm 0.01$	0.02	<0.01	0.73	$\pm 0.04$	10.35	$\pm 0.45$

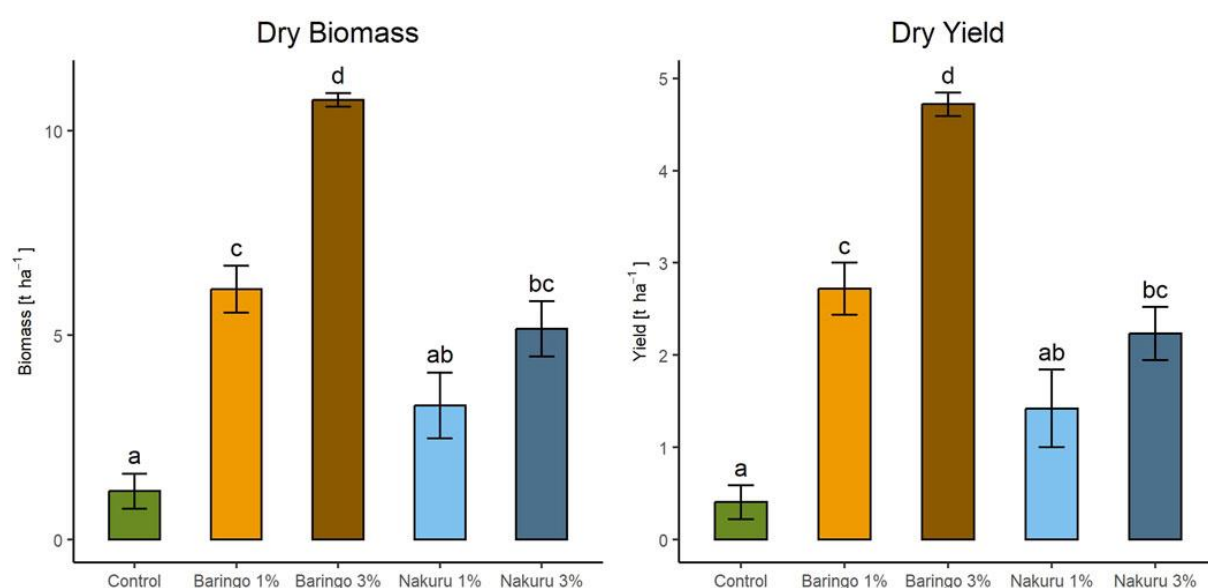


Figure 1: Increased biomass and yield of barley after amendment of different local sediments with 1% and 3% addition. Error bars indicate standard errors. Significant differences between all treatments are shown as different letters, common letters indicate no significant difference ( $p < 0.05$ ).

Plant nutrition and toxicants due to sediment amendments

The P content in grains was significantly higher ( $3.4 \pm 0.1 \text{ mg g}^{-1}$ ) with the 3% amendment of Baringo sediment, compared with the control ( $2.3 \pm 0.3 \text{ mg g}^{-1}$ ;  $p < 0.001$  Tukey; Figure 2c). Regarding to Al accumulation in grains, only the 3% Baringo treatment had a lower Al content ( $0.011 \pm 0.002 \text{ mg g}^{-1}$ ) compared with the control ( $0.021 \pm 0.005 \text{ mg g}^{-1}$ ;  $p = 0.017$ , Tukey), but not significantly ( $p = 0.307$ , Tukey). In contrast, the grains of both Nakuru treatments tended to have higher Al content and similar P content compared with the control, with lacking any significant differences. Baringo 3% treatment had significantly higher Si contents in the grains ( $1.9 \pm 0.1 \text{ mg g}^{-1}$ ) than the control ( $1.0 \pm 0.4 \text{ mg g}^{-1}$ ;  $p < 0.001$  for 3%, Tukey). However, both

Nakuru treatments and the Baringo 1% treatment did not significantly increase the Si content in grains ( $p = 0.138$  for Baringo 1%,  $p = 1$  for Nakuru 1% and  $p = 0.291$  for Nakuru 3%, Tukey).

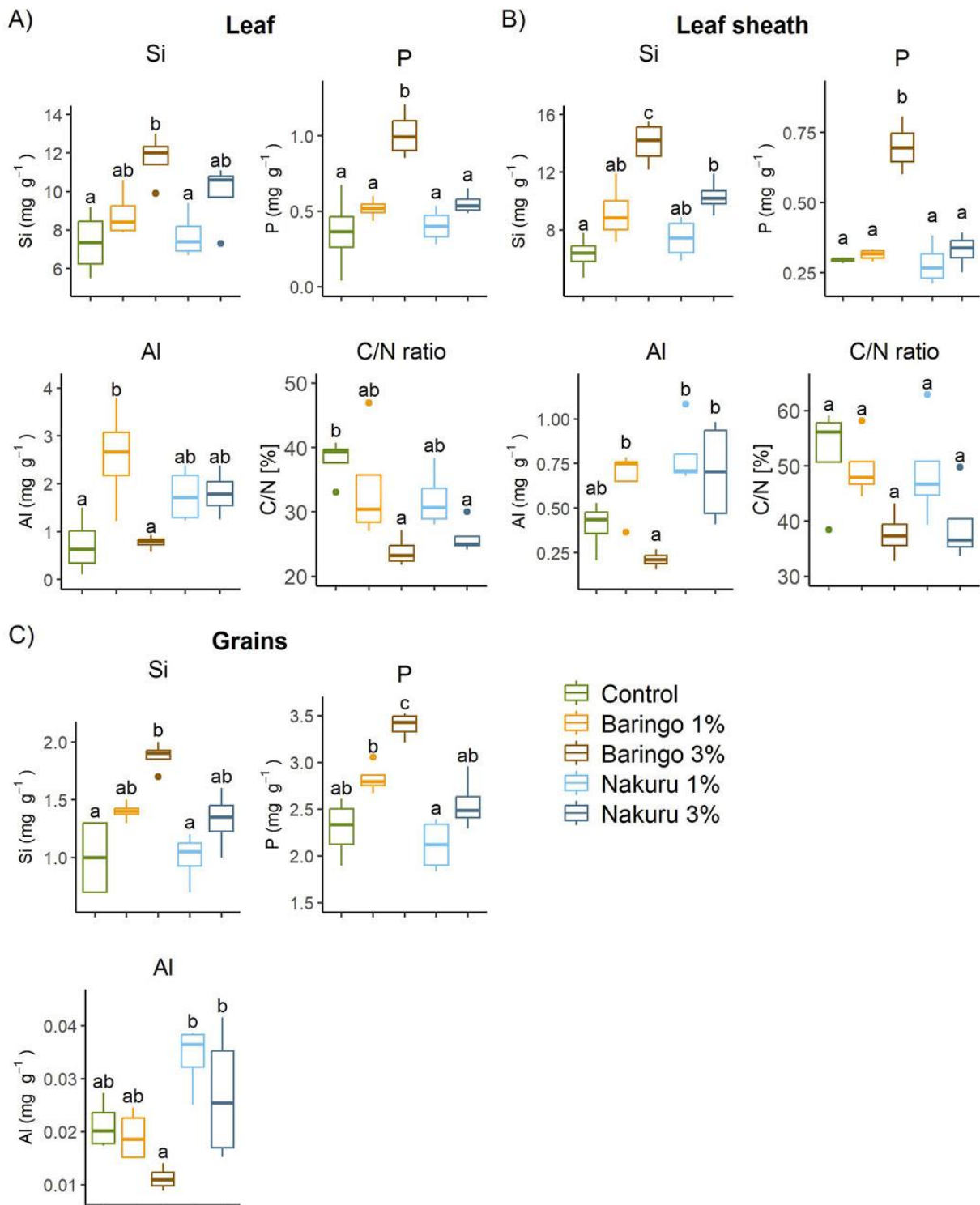


Figure 2: Element contents and C/N ratio at harvest in (A) leaves (B) leaf sheaths and (C) grains of barley with different sediment amendments. Significant differences between all treatments are shown as different letters, common letters indicate no significant difference ( $p < 0.05$ ).

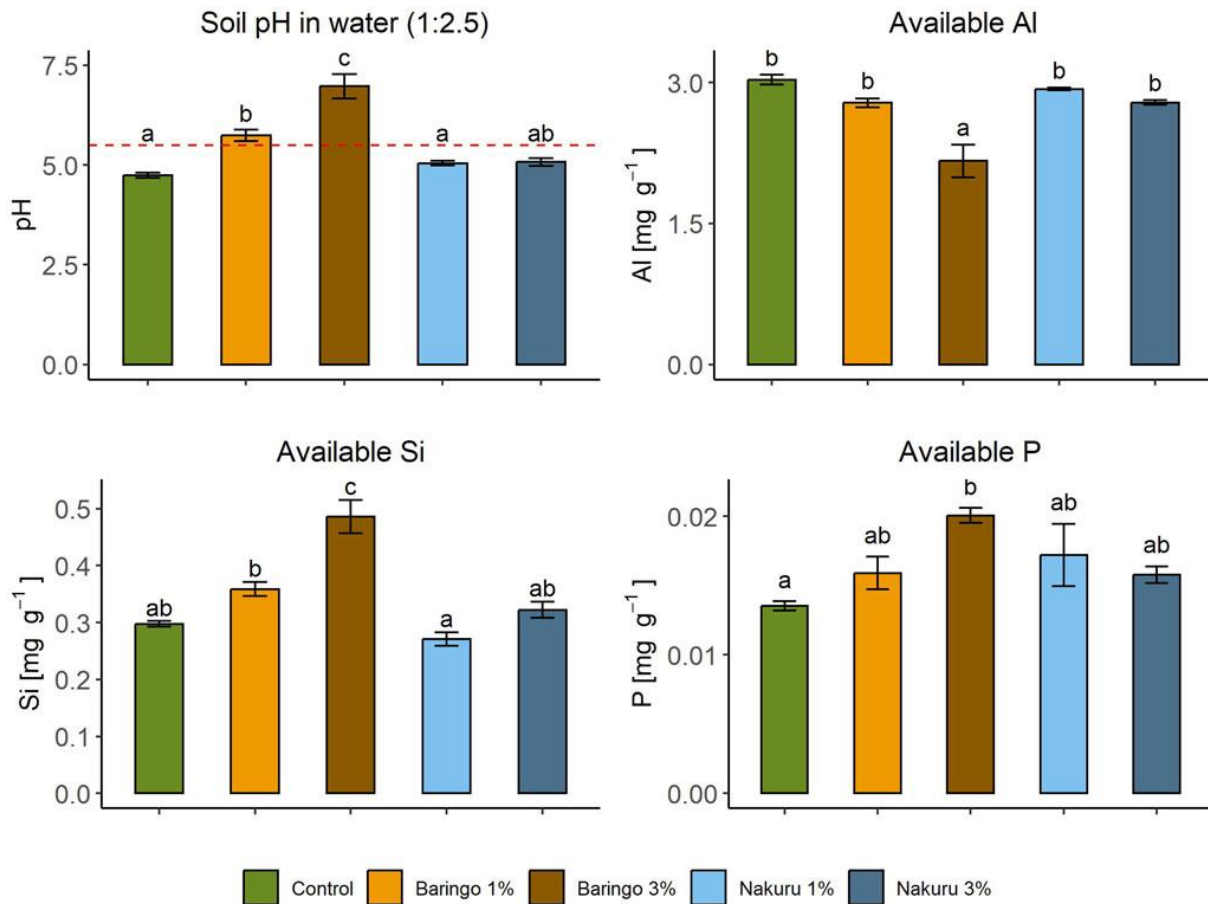


Figure 3: Sediment amendment effect on soil pH, available P, available Si and available Al in the soil. The red dotted line shows the pH threshold of 5.5. Error bars indicate standard errors. Significant differences between all treatments are shown as different letters, common letters indicate no significant difference ( $p < 0.05$ ).

Silicon contents showed significant differences between the sediment treatments and the control for both, leaves ( $p = 0.007$ ,  $F = 5.581$ ,  $df = 4$ , ANOVA) and leaf sheaths ( $p < 0.001$ ,  $F = 14.75$ ,  $df = 4$ , ANOVA) at the stage of harvest (Figure 2). However, only 3% Baringo treatment ( $11.73 \pm 1.31 \text{ mg g}^{-1}$ ) significantly increased Si contents in the leaves ( $7.4 \pm 1.7 \text{ mg g}^{-1}$  for control,  $p = 0.005$ , Tukey). Regarding the leaf sheaths, both sediments with a 3% amendment significantly increased the Si content ( $6.3 \pm 1.3 \text{ mg g}^{-1}$  for control;  $14.0 \pm 1.5 \text{ mg g}^{-1}$ ,  $p < 0.001$  for Baringo 3%;  $10.3 \pm 1.2 \text{ mg g}^{-1}$ ,  $p = 0.014$  for Nakuru 3%, Tukey), but not the 1% treatments. There are significant differences in P contents of leaves and leaf sheaths ( $p < 0.001$ ,  $F = 11.07$ ,  $df = 4$  for leaves;  $p < 0.001$ ,  $F = 5.915$ ,  $df = 4$  for leaf sheath, ANOVA), but again the significant effect was only shown with 3% Baringo treatment ( $1.0 \pm 0.2 \text{ mg g}^{-1}$ ,  $p < 0.001$  for leaves,  $0.7 \pm 0.1 \text{ mg g}^{-1}$ ,  $p < 0.001$  for leaf sheath respectively, Tukey). Adding Nakuru sediment had no significant effect on P contents in leaves and leaf sheaths. The Al contents in leaf sheaths decreased significantly with Baringo 3% compared with all other treatments, except of the control, which had also very low Al contents in leaf sheath tissues ( $p = 0.032$  for Baringo 1%,  $p = 0.005$  for Nakuru 1%,  $p = 0.018$  for Nakuru 3%,  $p = 0.634$  for control, Tukey). In leaf tissue,

the Al content of control and Baringo 3% were significantly lower than in the Baringo 1% treatment ( $p = 0.007$  for control,  $p = 0.009$  for Baringo 3%, Tukey), but not than in all other treatments. Regarding the C/N ratio at harvest, there are significant differences in leaves ( $p = 0.01$ ,  $F = 5.084$ ,  $df = 4$ , ANOVA), but not in leaf sheaths ( $p = 0.066$ ,  $F = 2.814$ ,  $df = 4$ , ANOVA). However, differences were only significant between the 3% treatments and the control (Leaves:  $23.8 \pm 2.4\%$ ,  $p = 0.009$  for Baringo 3%;  $26 \pm 2.7\%$ ,  $p = 0.03$  for Nakuru 3%; Tukey).

#### *Soil nutrient availability after local sediment amendment*

The Baringo sediment amendment significantly increased the pH in an amount-dependent manner ( $p < 0.001$ ,  $F = 38.62$ ,  $df = 4$ , ANOVA), with the 1% amendment increasing the pH from  $4.7 \pm 0.1$  to  $5.7 \pm 0.3$  ( $p = 0.004$ , Tukey) and the 3% amendment increasing it to  $7.0 \pm 0.6$  ( $p < 0.001$ , Tukey; Figure 3). In contrast, the Nakuru sediment amendment caused a slight but not significant increase in pH, rising to around 5.1 at both the 1% ( $5.1 \pm 0.1$ ,  $p = 0.673$ , Tukey) and 3% amendments ( $5.1 \pm 0.2$ ,  $p = 0.602$ , Tukey).

There were significant differences in nutrient availability between the control and the treatments (Figure 3). Only the 3% Baringo treatment, and not the 1%, significantly increased the contents of available P ( $0.02 \pm 0.001 \text{ mg g}^{-1}$ ) and Si ( $0.49 \pm 0.6 \text{ mg g}^{-1}$ ; for both  $p < 0.001$ , Tukey). Nakuru sediment amendment did not significantly increase the available P content in the soil ( $p = 0.213$ ,  $F = 1.845$ ,  $df = 2$ , ANOVA) and there is no significant difference for available Si between control and both Nakuru treatments. Only the 3% amendment of the Baringo sediment ( $2.17 \pm 0.35 \text{ mg g}^{-1}$ ) significantly decreased the available Al in soil ( $p < 0.001$ , Tukey). Again, there is no significant change with 1% Baringo treatment ( $p = 0.29$ , Tukey) and both Nakuru treatments ( $p = 0.916$  for Nakuru 1%,  $p = 0.302$  for Nakuru 3%, Tukey).

The amendment of sediments significantly increased  $\text{CEC}_{\text{eff}}$  ( $p < 0.001$ ,  $F = 28.03$ ,  $df = 4$ , ANOVA; Table 2), however only for the 3% Baringo treatment ( $p < 0.001$ , Tukey). Nevertheless, both Baringo treatments significantly increased exchangeable Ca ( $p = 0.008$  for Baringo 1%,  $p < 0.001$  for Baringo 3%, Tukey) and Mg ( $p = 0.001$  for Baringo 1%,  $p < 0.001$  for Baringo 3%, Tukey). Baringo 3% additionally increased Na significantly ( $p = 0.003$ , Tukey). The Nakuru amendment only significantly increased the exchangeable K ( $p = 0.004$  for Nakuru 1%,  $p < 0.001$  for Nakuru 3%, Tukey). Furthermore, the amendment of both sediments resulted in a significant decrease of exchangeable Al ( $p = 0.019$  for Nakuru 1%,  $p < 0.001$  for Nakuru 3% and both Baringo, Tukey). A stronger increase (or decrease for Al) was observed for all mentioned elements with a higher amendment of sediment.

### ***Discussion***

#### *Barley P and Si nutrition and aluminium accumulation after amendment of local sediments with volcanic influence*

Our results indicate potential positive effects of amending local sediments including a certain share of volcanic ash on P, C/N and Si nutrition, as well as reduced aluminium availability in the soil using Baringo sediment at 3%. It is already known that volcanic tephra deposition can increase soil fertility in the surrounding areas, leading to better crop performance (Fiantis et al., 2019). However, in our study, sediments with volcanic influence were applied as a soil amendment in a less fertile region at field scale. The chemical composition of the sediments used in this study is comparable to that of several quaternary tephra deposits and bedded tuff members that have been analysed in previous studies in the same regions (Tryon and McBrearty, 2006; Blegen et al., 2016). Mineralogical evidence of the sediments using XRD was not carried out in this study. However, the high Ca content in the Baringo sediment fits to the geological map, which defines the materials at this location as lacustrine sediments (Hackman, 1987). The Pleistocene volcanism in the area north of Lake Baringo is characterized by alkali basalt-trachyte lava and may also have increased the Ca content in the sediments of the surrounding areas (Tryon and McBrearty, 2006). Both sediments have a high total Si content, consistent with volcanic materials (Baker et al., 1972; Blegen et al., 2016). Although the total Si content of the Baringo sediment is lower than that of the Nakuru sediment, it in particular showed higher Si mobilisation. One possible explanation for this may be the difference in crystallinity of the Si between the two sediments. While the Baringo sediment has a higher ASi content, the Si in the Nakuru sediment is mostly bound in crystalline minerals. Hence, since weatherability increases with lower crystallinity, Baringo has a higher release of Si than Nakuru sediment (Wolff-Boenisch et al., 2006). This is in line with the results of the SEM analyses where the Nakuru sediment was characterized by splintery/molten Si particles. The total Si content is higher, but the release through dissolution is much lower. The weathering of foreign material applied to the soil not only releases Si in solution, it may also provide a new source of other nutrients (Manning, 2022). In this study, the Baringo sediment released essential nutrients like Ca, Mg and Na which became available to plants and promoted plant growth. In addition, it released mentionable amounts of P, which becomes plant available by dissolution. Furthermore, the highly mobilized Si from the Baringo sediment may promote P availability in the soil. Previous studies revealed an increase in P availability after Si addition. A possible mechanism is the exchange of P from mineral surfaces by silicic acid (Schaller et al., 2019; Schaller et al., 2021b). Hence, Si mobilizes P from typically unavailable sources and thus

potentially enhancing its uptake by higher plants. Together with the P fertilizing effect from the Baringo sediment, this may explain the higher soil P availability and stronger P accumulation in plant tissues as shown for the grains yielded from the 3% Baringo treatment. However, these results were only significant for the 3% Baringo treatment. Besides the effect of Si on P availability, soil pH also controls P availability. Below a pH of 5.5, as in this study, P can become unavailable to plants due to binding to Fe and Al oxides and hydroxides and possible precipitation (Sanchez and Logan, 1992). Both sediments used in this study are characterized by alkaline pH of 8.6 (Baringo) or 9.4 (Nakuru), which is consistent with their characterisation as lacustrine sediments (Baringo) or tuffs (Nakuru), both probably influenced by the alkaline volcanism of the EARS (Hackman, 1987). The increasing pH (>5.5) with Baringo amendment may be explained by dissolution of carbonates buffering the soil solution pH. This is in line with the high Ca contents released by extraction, which can be attributed to the dissolution of carbonates. An increasing pH promotes the availability of P which may also have occurred in our study. The Nakuru sediment had a much lower influence on the soil pH and thus most likely no agronomic benefit despite also having an alkaline pH. This may be due to the much lower Ca content in the Nakuru sediment and the lack of carbonates. In addition to the pH effects on P availability, a pH value of 5.5 is an important threshold for the mobility of Al in soil solution as pH controls Al speciation. At a pH below 5,  $\text{Al}^{3+}$  is the dominant species, which is solubilized in soil solution and is phytotoxic (Kochian et al., 2004). With increasing pH, the phytotoxicity and solubility decreases and the dominant species changes from  $\text{Al}(\text{OH})_2^+$  (pH 5.5 – 6.5) to  $\text{Al}(\text{OH})_3$  at neutral pH (Bojórquez-Quintal et al., 2017). This change of speciation of Al results in a lower accumulation in plants and thus lower impact on plant growth (Bojórquez-Quintal et al., 2017). However, also the presence of silicic acid in soil solution may reduce the Al availability in soil solution (Exley et al., 2019). Silicic acid released into solution by weathering of the sediments may have interacted with Al forming short-range ordered aluminosilicates (SROAS) (Exley et al., 2019; Lenhardt et al., 2021). In addition, Si mediates physiological processes and induces changes in cellular metabolism that reduce the uptake and toxicity of heavy metals such as Al (Cocker et al., 1998; Gu et al., 2011; De Sousa et al., 2019). This is in line with the results of this study. In particular, Baringo 3% treatment increased pH and Si the most, resulting in a significant decrease of Al availability in soils and accumulation in plant tissues. Although the Nakuru treatments did not increase the pH above 5.5, the 3% amendment reduced Al availability and the proportion of exchangeable Al in the soil. This may indicate, that Si is also a driving factor in decreasing Al availability next to the soil pH. However, due to the experimental setup, we cannot separate the effects of Si versus the change in pH on the

increasing P availability upon addition of the sediments. Nevertheless, only Baringo 3% treatment resulted in a lower Al accumulation in plant tissues. Baringo 1% and both Nakuru treatments did not decrease Al contents in plant tissues. In fact, these treatments resulted in an increased Al accumulation compared with the control. Although the soil in the control treatment had a high availability of Al, the plants showed a very low accumulation of Al in the harvested plant tissue, less than in Baringo 1% and in both Nakuru treatments. This can be attributed to the negative impact of Al toxicity on plant growth. Numerous studies have demonstrated that the primary effect of Al toxicity is the inhibition of root elongation, which negatively affects nutrient and water uptake (Foy et al., 2003; Kochian et al., 2004). As a result, the plants do not grow properly. The plants in the control plots probably suffered from Al toxicity because the soil pH was lower than in all sediment treatments resulting in a higher Al availability in the soil. This led to inhibition of root growth and lower biomass production and therefore lower Al uptake by the plants. This is consistent with plant N uptake in this study, which was also lower in the control treatments. Despite the fact that all the treatments were fertilized with the same amount of N, the plants of the control treatment had a lower uptake of N compared to the other treatments.

#### *Plant performance and yield after soil sediment amendment*

In some cases, amending local sediments improved plant performance resulting in higher barley yield and biomass production. While Nakuru 1% did not significantly increase barley yield compared to the control, Nakuru 3% and Baringo 1% resulted in yield increases of about 500% (450% for Nakuru 3% and 569% for Baringo 1%) and Baringo 3% increased yield by as much as 1061%. However, the yield of the control, Nakuru 1%, Nakuru 3% and also Baringo 1% is still below the 5-year average for 2018/19 - 2022/23 ( $3.4 \text{ t ha}^{-1}$ ) (USDA, 2023). What stands out is the Baringo 3% treatment ( $4.72 \text{ t ha}^{-1}$ ) showing a higher yield than the 5-year average and also higher than the yield average of 2022 ( $4.0 \text{ t ha}^{-1}$ ) (USDA, 2023). These improvements of yield may be attributed to the new source of essential nutrients like Ca, Na, Mg and P, which are supplied by amending 3% of the Baringo sediment and the foliar P fertiliser. Another explanation may be the increased pH and Si availability resulting in an increase of P availability and a decrease of Al toxicity. These effects have caused better nutrient availability and growth conditions resulting in higher yields in the 3% Baringo treatment. The low yields of the control, Baringo 1% and the two Nakuru treatments may also be due to irregular rainfall with drought periods at the end of the growing season. Because of the less developed root system due to Al toxicity, plants in these treatments had a lower water uptake than plants in the Baringo 3% treatment. As a result, they senesced earlier and may have produced less grain.

Although the potential benefits of sediment amendments were demonstrated in this study, the underlying mechanisms are not yet fully understood. Further research on the used sediments and their interactions with the used soil is needed to improve knowledge on the underlying mechanisms. To find out whether some of our results can be explained more by the added Si or by the increased pH, another field experiment should be conducted. For this purpose, additional plots would need to be established that are limed only to compare whether it is only a pH effect or whether other mechanisms are also involved.

### ***Conclusion***

This study shows that amendment of volcanically influenced local sediments can improve plant growth and yield, but the improvement is dependent on the sediment source and the amendment rate. Of course, a new source of essential nutrients often has a fertilisation effect in a soil. However, a release of Si in the soil and a potential increase of soil pH by the sediment amendment are most likely also important drivers for the improvement of yields in this study. Higher Si availability in soil can improve P availability and, in conjunction with higher pH, also reduce Al mobility and its phytotoxicity. These effects can lead to better nutrient uptake of P and Si and less accumulation of Al in plant tissues resulting in better growth and yield of arable crops. The yields of the 3% Baringo treatment resulted in a higher yield compared with the average barley yield in Kenya. In conclusion, amendments of local sediments with volcanic influence could make agriculture in sub-Saharan Africa more sustainable from a biophysical perspective. Importantly, our study demonstrates that the outcomes are, however, dependent on the individual sediment and its amendment rate. Further studies are now needed to investigate possible long-term effects of the amended sediments and to understand the underlying mechanisms.

### ***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: Writing—original draft, Methodology, Formal Analysis, Data curation, Conceptualisation, Writing—review and editing. MS: Writing—review and editing, Methodology. JhS: Supervision, Writing—review and editing. TB: Methodology, Writing—review and editing. JrS: Writing—review and editing, Supervision, Funding acquisition, Conceptualisation.

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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.

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### **Supplementary material**

The Supplementary Material for this article can be found online at:

<https://www.frontiersin.org/articles/10.3389/fenvs.2024.1458360/full#supplementary-material>

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## **Chapter 3: Local sediment and lime but no straw amendments can potentially improve barley biomass and yield at the field plot scale in Kenya**

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### ***Abstract***

Soil acidification and nutrient leaching are major agricultural challenges in East Africa, leading to aluminium (Al) toxicity and poor crop yields. Various soil amendments are used worldwide to increase soil pH and crop production. Local sediment amendments have been identified as a potential soil improvement in Kenya, but the mechanisms remain unclear. This study examined the effects of liming, straw return, and local sediment amendments on nutrient availability and barley yield in Eldoret, Kenya. Plots were established with 1% and 3% of two local sediments (from Baringo and Nakuru) or with 0.15% lime, each with and without straw addition. Baringo 3% and lime treatments significantly reduced soil Al availability and increased soil pH, soil phosphorous (P) availability and barley yield (Baringo 3%: 1.3 t ha<sup>-1</sup>, Lime: 0.91 t ha<sup>-1</sup>), while the control had no yield. However, only Baringo 3% also increased soil silicon (Si) availability, achieving the highest yield. Other treatments and straw return had no significant impact on nutrient availability and plant production. These results indicate that the increase in barley yield with local sediment may be driven mainly by carbonate dissolution raising soil pH, while higher Si availability and accumulation could further enhance plant production. However, the beneficial effects are dependent on the sediment material and amendment rate.

### ***Introduction***

About 30 % of the global land surface is characterized as acidic (von Uexküll and Mutert, 1995), accounting for approximately 50 % of the global arable land area (Dai et al., 2017). Soil acidity is one of the major challenges for agriculture in tropical Africa. In Kenya, around 13 % of the total agricultural land is defined as acidified, resulting in barely fertile soils and low crop yields (Kanyanjua et al., 2002). The high incidence of acidic soils in Kenya is mostly due to the prevalence of Ferralsols in this region, which are characterized by pH of 4 – 5 (Nyachiro and Briggs, 1987; Soil Survey Staff, 1999). These soils are formed by long-term and intense weathering in a humid to sub-humid climate with high temperatures and moderate to high rainfall (Soil Survey Staff, 1999).

With ongoing soil acidification, hydrogen ( $H^+$ ) and aluminium ( $Al^{3+}$ ) ions are replacing essential cations such as calcium ( $Ca^{2+}$ ), magnesium ( $Mg^{2+}$ ), sodium ( $Na^+$ ) and potassium ( $K^+$ ), which are leached out during weathering processes (von Uexküll and Mutert, 1995; Agegnehu et al., 2021). Therefore, Ferralsols are characterized by low nutrient availability, a low pH and high contents of iron (Fe) and Al (Balland-Bolou-Bi and Livet, 2018; Du et al., 2020). Due to these characteristics, these soils are known to be less fertile, which results in low crop yields (Du et al., 2020). The decreasing pH and the replacement of cations by  $Al^{3+}$  ions promote Al toxicity for plants (von Uexküll and Mutert, 1995). At a pH value  $< 5.5$ , the toxic effect of Al increases, as Al is dissolved as  $Al^{3+}$ , which is plant available and phytotoxic (Sade et al., 2016; Vega et al., 2019). A higher Al availability in the soil promotes the direct Al uptake by plants and its accumulation in plant tissues, resulting in poor crop growth, especially the roots, and thus decreased yields (Cocker et al., 1998; Lal and Singh, 1998).

Another major challenge for agriculture on Ferralsols is a high phosphorus (P)-fixation in the soil due to the high Fe and Al content, which has been discussed and published in many studies for decades (Kellogg, 1956; Russel et al., 1974; Sanchez and Uehara, 1980; Ayodele and Agboola, 1981). Iron and Al minerals have a high P-sorption capacity, as P binds strongly to Fe- and Al-oxides/hydroxides, resulting in a relatively high total, but mostly plant unavailable P content in the soil (Russel et al., 1974; Hengl et al., 2017; Du et al., 2020). The P-fixation is additionally promoted by soil acidity (Agegnehu et al., 2021). At a pH value  $< 5.5$ , phosphates may already become inaccessible to plants; at a pH value  $< 5$ , Fe- and Al-phosphates may precipitate (Russel et al., 1974; Sanchez and Logan, 1992; Agegnehu and Sommer, 2000). To compensate for the P deficiency caused by the high P fixation in tropical Africa, farmers have to apply large quantities of P fertilisers (up to  $150 \text{ kg ha}^{-1}$ ) (Russel et al., 1974; Nziguheba et

al., 2002; Achieng et al., 2017). However, many smallholders have limited access to P fertilisers due to high prices and poor availability, resulting in a lack of P for crop production and low yields (Sanchez et al., 1997; Nziguheba et al., 2002).

There are various ways to improve soil fertility and soil pH with a reduced need for mineral fertilisers, some of which have been known for a long time or are still being examined. Scherwietes et al. (2024) showed that the application of local sediments might be one option to increase soil pH and reduce the need for phosphorus fertilisers in Kenya from a biophysical perspective. In some cases, the addition of local sediments significantly increased soil pH, soil P availability and barley yield, and significantly decreased soil Al availability (Scherwietes et al., 2024). However, the extent of the positive effects of the added local sediments depended on the material and the application rate (Scherwietes et al., 2024). In this study, it was not possible to differentiate between the effects of a pH increase versus nutrient addition (Scherwietes et al., 2024). Liming with materials rich in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is another common practice that is used all over the world to improve soil fertility and crop yield by increasing soil pH (Wang et al., 2021). By neutralizing excessive  $\text{H}^+$  ions in soil solution, liming could promote the immobilisation of toxic heavy metals such as Al (Bolan et al., 2003; Fageria and Baligar, 2008) and may increase the availability of essential nutrients (e.g. P) that are more available at higher pH (Thomas and Hargrove, 1984). Besides, liming could also directly supply important cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) for crop production (Fageria and Nascente, 2014; Li et al., 2019).

A third method for improving soil fertility and crop yield, which is commonly used in most parts of the world but not in Africa, is straw return (Liang et al., 2023). While in Africa, residue retention in the field is very little done as straw is used as feed for livestock, in other parts of the world it is a widely available and abundant resource. Straw is known to be rich in nutrients and has already shown positive effects on soil properties and functions when returned to the fields (Li et al., 2024). Decomposition of straw can replenish assimilated nutrients (such as carbon (C), nitrogen (N), P and K), thereby increasing nutrient availability and soil organic matter (SOM) stocks in the soil (Yan et al., 2019). By replenishing base cations, returning straw to the field is also widely recognized as a method to reduce soil acidification and has been observed in various studies (Wang et al., 2012; Butterly et al., 2013). However, the decomposition of straw may also result in an increase in organic acids, which in turn could accelerate soil acidification (Kato et al., 2005).

In this study, we aim to compare three soil fertility improvement methods—local sediment amendment, liming, and straw return—on acidic arable soils in Kenya. The study seeks to

determine whether the potential positive effects observed with some of the sediments are primarily due to changes in soil pH (liming effect) or if they result from other processes. Specifically, we investigated the effects of these treatments on P availability, Al toxicity, and barley yield. We hypothesize that: (i) local sediment application will decrease soil Al availability, increase soil pH, improve P availability, and enhance barley yield, even 2 years after incorporation; (ii) liming will similarly increase soil pH, P availability, and barley yield, while reducing Al availability, but at a lower application rate than local sediment amendment; and (iii) straw return will improve crop yield, with the best results likely occurring when combined with liming.

### ***Materials and Methods***

#### *Study site and experimental design*

The study site is located in western Kenya in Kaptagat, a village east of Eldoret in the Uasin Gishu County (0.4448 °N, 35.4685 °E). This area is characterized by a cool and temperate climate, the daily average temperature ranges between 8.4 °C and 27 °C. The average annual rainfall is 900 – 1200 mm, distributed over two rainy seasons (Tsuma et al., 2015). The pedology in this area is dominated by Plinthic Ferralsols, which are characterized as low in pH and high in Fe content (Nyachiro and Briggs, 1987). The experiment of this study was conducted on the cropland of a local farmer at an elevation of 2410 m. The pH of the soil of this study is 4.7, the cation exchange capacity (CEC) is 9.7 cmol<sup>+</sup> kg<sup>-1</sup> and the total organic carbon (TOC) is 2.6 % (Scherwietes et al., 2024). The element composition and the composition of exchangeable cations are described in Scherwietes et al. (2024). The soil is strongly weathered, which is indicated by an oxalate/dithionite Fe (Fe<sub>o</sub>/Fe<sub>d</sub>) ratio of 0.04 (Moody and Graham, 1995; Scherwietes et al., 2024).

Two suitable local sediments from different locations in the EARS were identified (Scherwietes et al., 2024). One of the sediments was defined as splinter-like/molten Si-Al-containing particles of varying size and was located in the Nakuru district, south of Lake Nakuru (0.49726 °S, 36.091794 °E, Scherwietes et al. 2024). The second sediment was defined as a Ca-rich and aggregated sediment matrix with attached particles containing Al and Si. This was taken from an area west of Lake Baringo (0.574643 °N, 35.984597 °E, Scherwietes et al. 2024). Baringo sediment had a pH of 8.6, Nakuru sediment had a pH of 9.4 (Scherwietes et al., 2024). The elemental composition and the composition of exchangeable cations of the sediments are described in Scherwietes et al. (2024). No harmful elements and heavy metal enrichments were identified in the sediment materials (Scherwietes et al., 2024).

The experimental site covered an area of  $30 \times 19$  m, with individual plot dimensions of  $3 \times 4$  m. The experimental design included the incorporation of two local sediments at application rates of 1 % and 3 % by volume to a soil depth of 20 cm. This corresponded to application rates of  $24 \text{ t ha}^{-1}$  (Baringo 1 %),  $72 \text{ t ha}^{-1}$  (Baringo 3 %),  $18 \text{ t ha}^{-1}$  (Nakuru 1 %), and  $54 \text{ t ha}^{-1}$  (Nakuru 3 %). Sediment incorporation was carried out in April 2022 (Scherwietes et al., 2024). In 2023, additional plots were established to assess the effects of liming, with calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] applied at a rate of 0.15 % by volume (equivalent to  $4.5 \text{ t ha}^{-1}$ ) to adjust the soil pH to a range of 7 to 8. Untreated plots without any amendments were included as controls. To investigate the effects of straw addition, each plot was divided into two equal subplots ( $3 \times 2$  m). One subplot received shredded wheat straw from the previous growing season at a rate of  $5 \text{ t ha}^{-1}$ , while the other did not. The C/N ratio of the used wheat straw was 76:1 (CNS928-MLC, Leco Instruments Inc., St. Joseph, Michigan, USA). Each treatment was replicated four times, and for practical reasons, a non-randomized block design with a split-plot structure was used, with straw addition applied at the subplot level. To avoid interferences between the treatments, buffering zones of one meter were set up between each plot (Supplementary Figure 1). All soil amendments were incorporated by hand and then mixed with hand hoes to a depth of 20 cm. To ensure the same physical disturbance for all treatments, the mixing was performed in the same way for the control plots.

Barley (*Hordeum vulgare* L., cv. Hessekwa) was sown by hand in all plots on the 10<sup>th</sup> of July 2023. Nitrogen (N) fertiliser was applied in form of urea on every plot after germination ( $50 \text{ kg ha}^{-1}$ ) and at stem extension ( $90 \text{ kg ha}^{-1}$ ). Low P fertilisation ( $2.5 \text{ L ha}^{-1}$ , YaraVita Crop Boost, Yara UK Ltd., York, UK) was performed on all treatments, including the controls, in form of foliar application during the vegetation period. At tillering stage, three irrigations of 200 L per plot were carried out once a week. Harvest was conducted on the 3<sup>rd</sup> of December 2023.

#### *Sampling and analyses*

Whole plants were taken at harvest, collected from random areas of  $40 \times 40$  cm of each treatment. The plant samples were washed, dried and weighed to determine crop yield and biomass. Soil samples from the upper 15 cm were taken randomly with a small shovel and air dried. Soil pH was determined in water at 1:2.5 solid to solution ratio for each plot with and without straw addition (WTW pH/Cond 3320 with Sentix41 electrode, Xylem Water Solutions, Washington, DC, USA). The soil samples were analysed for available Ca, P, Si, Al and Fe using Mehlich III extraction (Sparks and Bartels, 2009). For this, 2 g of the soil sample was weighed into 50 ml centrifuge tubes, mixed with 42 ml Mehlich III extraction solution and shaken for 5

min. The suspension was centrifuged (3,200 g for 5 min) and filtered through 0.2  $\mu\text{m}$  filters. The samples were then analysed by ICP-OES (iCAP 6300 DUO, ThermoFisher Scientific Inc., Walham, Massachusetts, USA).

To determine the nutrient contents in different plant tissues at harvest, the plants were separated into leaves, leaf sheaths and grains. Subsequently, the plant material was analysed using several extraction methods. Microwave digestion was performed to estimate Ca, P, and Al contents in plant tissues. Two ml of  $\text{H}_2\text{O}_2$  and 3 ml of  $\text{HNO}_3$  were mixed with 0.1 g of plant sample and placed in a closed vessel microwave digestion system (CEM-Mars6, CEM Corporation, Matthews, NC, USA). Subsequently, the extracts were made up to 20 ml with deionized water and filtered through 0.2  $\mu\text{m}$  membrane filters. By use of Tiron extraction (Kodama and Ross, 1991), Si contents in plant tissues were determined. Therefore, 0.03 g of plant samples were mixed with 30 ml of 0.1 M Tiron solution in 50 ml centrifuge tubes and heated in a water bath for 1 h at 85 °C. The samples were gently shaken by hand before heating and after 30 min. The extracted solutions were centrifuged (5,000 g for 5 min) and filtered through 0.2  $\mu\text{m}$  pore size filters. The elemental contents of both the microwave and Tiron extractions were analysed by ICP-OES (iCAP 6300 DUO, ThermoFisher Scientific Inc., Walham, Massachusetts, USA).

### *Statistics*

The data were analysed using RStudio (R Core Team, 2023). A linear mixed-effects model was fitted using treatment and straw addition as fixed effects, and block as a random effect. A two-way ANOVA was performed on the model, followed by Tukey's HSD post-hoc test using estimated marginal means (emmeans) to assess pairwise differences between treatment combinations.

## ***Results***

### *Soil nutrient availability depending on treatment*

Significant changes in soil pH and nutrient availability (Ca, Si, P, Al, Fe) were observed in some treatments with sediment and lime amendments without straw addition (Figure 1). Both Baringo sediment treatments significantly increased soil pH compared to the control (pH  $5.06 \pm 0.05$ ), with values of  $5.77 \pm 0.34$  ( $p = 0.004$ , Tukey) for Baringo 1% and  $6.73 \pm 0.51$  ( $p < 0.001$ , Tukey) for Baringo 3%. The highest pH was observed in the Lime treatment ( $7.49 \pm 0.30$ ;  $p < 0.001$ ). Neither Nakuru 1% nor Nakuru 3% significantly affected soil pH. Regarding nutrient availability, Baringo 1%, Nakuru 1%, and Nakuru 3% treatments did not cause significant changes in available Si, P, Al, or Ca compared to the control. In contrast, the

Baringo 3% treatment significantly increased available Si ( $0.44 \pm 0.06 \text{ mg g}^{-1}$ ;  $p < 0.001$ ), P ( $0.017 \pm 0.002 \text{ mg g}^{-1}$ ;  $p = 0.002$ ), Ca ( $2.43 \pm 1.16 \text{ mg g}^{-1}$ ;  $p < 0.001$ ), and Fe ( $0.081 \pm 0.002 \text{ mg g}^{-1}$ ;  $p = 0.011$ ), while significantly decreasing available Al ( $1.72 \pm 0.08 \text{ mg g}^{-1}$ ;  $p < 0.001$ ). Similarly, the Lime treatment significantly increased available

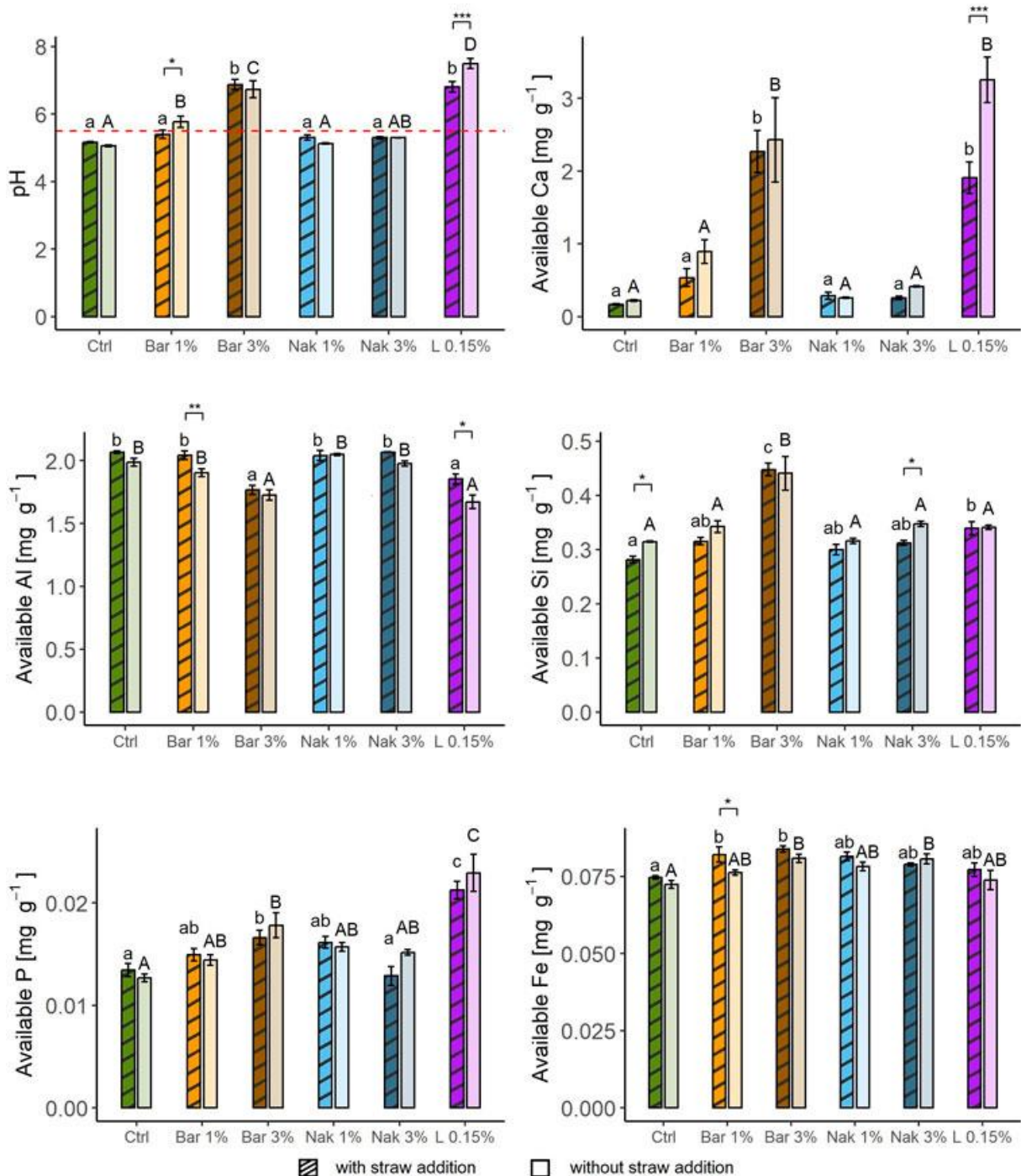


Figure 1: Sediment amendment and liming effects on soil pH, available Ca, Al, Si, P and Fe in the soil with (shaded) and without (not shaded) straw addition. The red dotted line shows the pH threshold of 5.5. Error bars indicate standard errors. Significant differences between all treatments with straw addition are shown as different lowercase letters, significant differences between all treatments without straw addition are shown as different capital letters. Common letters indicate no significant difference ( $p < 0.05$ ). Significant differences between with and without straw addition of each treatment are shown as stars ( $* = p < 0.05$ ,  $** = p < 0.01$ ,  $*** = p < 0.001$ ).

P ( $0.020 \pm 0.004 \text{ mg g}^{-1}$ ;  $p < 0.001$ ) and Ca ( $3.25 \pm 0.63 \text{ mg g}^{-1}$ ;  $p < 0.001$ ), and significantly reduced available Al ( $1.67 \pm 0.11 \text{ mg g}^{-1}$ ;  $p < 0.001$ ), compared to the control.

Similar patterns to those observed in the treatments without straw addition were found when comparing treatments with straw addition. Both the Baringo 3% and Lime treatments increased soil pH ( $6.88 \pm 0.29$  for Baringo 3%;  $6.80 \pm 0.31$  for Lime;  $p < 0.001$  for both, Tukey) and available Ca ( $2.27 \pm 0.58 \text{ mg g}^{-1}$  for Baringo 3%;  $1.91 \pm 0.43 \text{ mg g}^{-1}$  for Lime;  $p < 0.001$  for both, Tukey), while significantly decreasing Al availability ( $1.77 \pm 0.07 \text{ mg g}^{-1}$  for Baringo 3%;  $1.85 \pm 0.08 \text{ mg g}^{-1}$  for Lime;  $p < 0.001$  for both, Tukey) compared to all other treatments. The Baringo 3% treatment had the highest available Si ( $0.45 \pm 0.02 \text{ mg g}^{-1}$ ;  $p < 0.001$ , Tukey), but Lime treatment with straw also significantly increased Si availability ( $0.34 \pm 0.02 \text{ mg g}^{-1}$ ) compared to the control ( $0.28 \pm 0.01 \text{ mg g}^{-1}$ ;  $p = 0.013$ , Tukey). The highest available P was observed in the Lime treatment ( $0.021 \pm 0.002 \text{ mg g}^{-1}$ ;  $p < 0.001$ , Tukey), while Baringo 3% also significantly increased P availability ( $0.017 \pm 0.001 \text{ mg g}^{-1}$ ) compared to the control ( $0.013 \pm 0.001 \text{ mg g}^{-1}$ ;  $p = 0.014$ , Tukey). Both Baringo treatments significantly increased Fe availability compared to the control ( $p = 0.036$  for Baringo 1%,  $p = 0.005$  for Baringo 3%, Tukey), but neither the two Nakuru treatments ( $p = 0.066$  for Nakuru 1%,  $p = 0.486$  for Nakuru 3%, Tukey) nor the Lime treatment ( $p = 0.887$ , Tukey) showed significant changes.

The addition of straw material significantly altered pH and element availability in some treatments compared to those without straw addition (Figure 1). Straw addition significantly decreased the pH of the Baringo 1% treatment ( $p = 0.044$ , Tukey) and of the Lime treatment ( $p < 0.001$ , Tukey). The addition of straw significantly decreased available Ca in the Lime treatment ( $p < 0.001$ , Tukey), while it significantly increased Al availability in the Baringo 1% ( $p = 0.006$ , Tukey) and Lime treatments ( $p < 0.001$ , Tukey), and significantly decreased available Si in the control ( $p = 0.049$ , Tukey) and Nakuru 3% treatments ( $p = 0.036$ , Tukey) compared to treatments without straw addition. No significant differences in P availability were observed between treatments with and without straw addition.

#### *Treatment effect on yield and biomass*

Significantly higher yields were obtained with the Baringo 3% treatment ( $1.32 \pm 0.33 \text{ t ha}^{-1}$ ;  $p < 0.001$ ) and the Lime treatment without straw addition ( $0.91 \pm 0.35 \text{ t ha}^{-1}$ ;  $p < 0.001$ ) compared to the control and the Nakuru 1% treatment, both of which produced almost no yield ( $< 0.1 \text{ t ha}^{-1}$ , Figure 2). Baringo 3% and Lime treatments resulted in significantly higher biomass than the control ( $p < 0.001$  for both; Tukey test). No significant differences in biomass or yield

were observed for Baringo 1% and either Nakuru treatments with straw addition compared to the control.

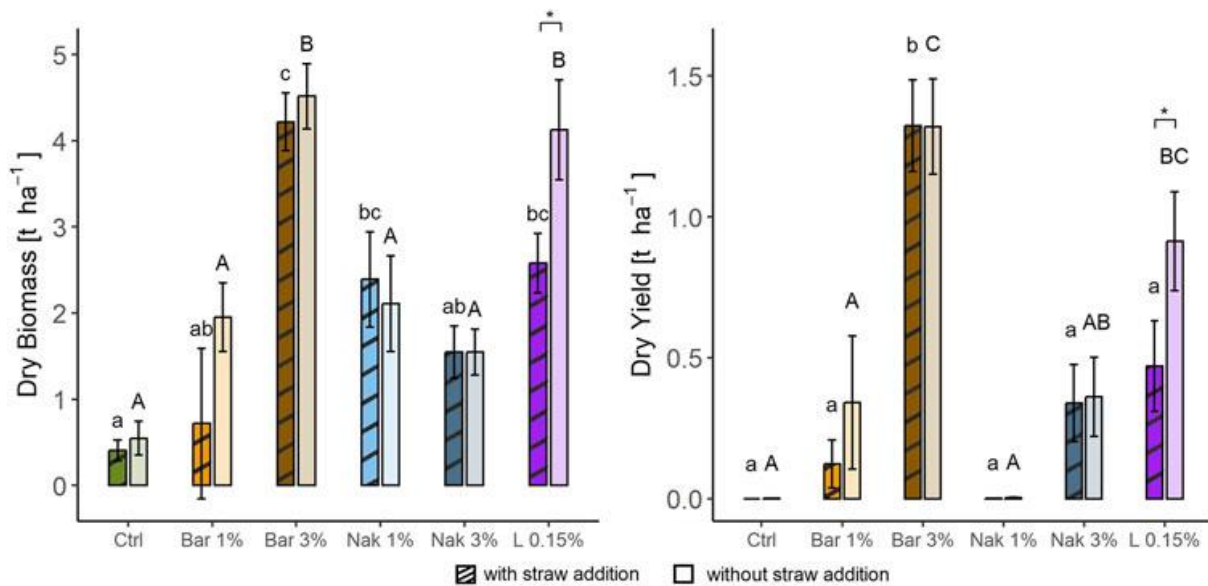


Figure 2: Effects of sediment amendment and liming on the biomass and yield of barley with (shaded) and without (not shaded) straw addition to the soil. Error bars indicate standard errors. Significant differences between all treatments with straw addition are shown as different lowercase letters, significant differences between all treatments without straw addition are shown as different capital letters. Common letters indicate no significant difference ( $p < 0.05$ ). Significant differences between with and without straw addition of each treatment are shown as stars ( $* = p < 0.05$ ).

When comparing all treatments with straw addition, Baringo 3% ( $4.22 \pm 0.67 \text{ t ha}^{-1}$ ,  $p = 0.02$ , Tukey), Nakuru 1% and Lime treatment showed a significantly higher biomass than the control ( $0.41 \pm 0.24 \text{ t ha}^{-1}$ ; Figure 2), but only Baringo 3% resulted in a significantly higher yield ( $1.32 \pm 0.32 \text{ t ha}^{-1}$ ,  $p < 0.001$ , Tukey). No significant differences in the yield were observed among the other straw-amended treatments, including the Control, Baringo 1%, the two Nakuru treatments, and Lime.

Straw addition only did significantly affect biomass and yield in the lime treatments, decreasing it significantly compared to the treatment without straw. However, a trend of reduced yield with straw addition was also observed in the Baringo 1% treatment ( $-63\%$ ) compared to the treatment without straw.

## Discussion

### Effects on soil pH and nutrient availability

Scherwietes et al. (2024) showed that the addition of local sediments to Kenyan ferralitic arable soil can potentially increase soil pH and nutrient availability (such as P and Si) and decrease Al availability. These findings are consistent with the results of the present study. Even two years after sediment incorporation, significant increases in soil pH, available P, available Si and

available Ca were observed in the Baringo 3 % treatment. In addition, the Al availability and thus potentially the Al toxicity for plants was reduced by the treatment with Baringo 3 %. However, no significant changes were observed in the availability of nutrients (Ca, Si, P) or in the levels of Al in the soil across the other sediment treatments. The decrease in Al availability in the 3% Baringo treatment may be due to two processes that may be the driving factors for the observed effects: (i) the increase in soil pH and (ii) the increase in available Si in the soil. Both are due to the chemical composition of the Baringo sediment, which is characterised as a Ca-rich lacustrine sediment with low crystalline Si as the main component (Scherwietes et al., 2024). During the weathering of the sediments, carbonates are released that buffer the pH value of the soil. A rising soil pH changes the mobility of Al in the soil solution, as it controls Al speciation (Bojórquez-Quintal et al., 2017). At a pH < 5, the phytotoxic and highly solubilised  $Al^{3+}$  is the dominant species in the soil solution (Kochian et al., 2004). As the soil pH increases, the dominant Al species changes to  $Al(OH)_2^+$  at pH 5.5 - 6.5 and to  $Al(OH)_3$  at neutral pH (Bojórquez-Quintal et al., 2017). In addition to carbonates, the weathering of the Baringo sediment also release Si, resulting in a higher available Si in soil solution. Scherwietes et al. (2024) found that the Baringo sediment has a high content of amorphous Si (ASi), which is less crystalline and releases a lot of silicic acid into the soil solution (Schaller et al., 2021). The presence of silicic acid in soil solution may also reduce Al availability as it could interact with Al and form aluminosilicates (SROAS) (Exley et al., 2019; Lenhardt et al., 2021). The observed reduction in available Al in the soil due to the addition of Baringo 3 % may therefore be attributed to both processes, the increase in soil pH and the increase in Si in the soil.

However, these processes not only promote the decrease in available Al, but may also favour the increase in available P in the soil observed with the Baringo 3 % treatment (Schaller et al., 2021). Particularly in Ferralsols with their high Fe and Al content, a low soil pH (< 5.5) may greatly reduce the availability of P due to binding of it to Fe- and Al-oxides and hydroxides (Sanchez and Logan, 1992; Agegnehu et al., 2021). Furthermore, previous studies revealed, that silicic acid may absorb to mineral surfaces, competing with P for binding sites and exchanging it from minerals like Fe-oxides (Taylor, 1995; Dietzel, 2002). The increase in soil pH, but also the increase in available Si in the soil due to the addition of Baringo 3 % may therefore promote lower Al availability and higher P availability in the present study. However, Scherwietes et al. (2024) have already pointed out the difficulty of distinguishing between these processes and finding out in a field study which is the driving factor for the change in nutrient availability. In the present study, additional lime treatments ( $4.5 \text{ t ha}^{-1}$ ) were applied to compare the effects on nutrient availability between the sediment treatments and liming. It is known that

lime increases soil pH by neutralizing excessive H<sup>+</sup> ions due to its high release of carbonates during weathering (Bolan et al., 2003; Wang et al., 2021). This process was also observed in the present study, with Ca availability and soil pH increasing with liming. Liming does not add any additional Si to the soil solution, but the increase in soil pH can potentially increase the Si availability (Haynes, 2019). However, this process was not observed in this study, as Si availability did not increase with liming while soil pH was increased. Nevertheless, the available Al decreased to a similar extent as in the 3 % Baringo treatment, and the P availability increased even more than in the 3 % Baringo treatment. This indicates that the increase in pH due to the supply of carbonates from the added material may be the driving factor for the reduction in Al availability and the increase in P availability in the soil.

Several studies have shown that straw return may serve as an effective method to increase soil pH and enhance the availability of essential nutrients, such as phosphorus, through the gradual release of nutrients during decomposition (Butterly et al., 2013; Yan et al., 2019). However, such effects were not observed in the present study. On the contrary, a significant decrease in soil pH was recorded following straw return in both the Baringo 1% and Lime treatments. Furthermore, when straw was applied in combination with sediment, no additional improvements in nutrient availability or soil pH were observed beyond those achieved by sediment alone. Initially, it was hypothesized that the combination of straw return and lime application would provide the most effective soil improvement. However, the results contradicted this hypothesis: a significant reduction in Ca availability was observed, which may have contributed to a subsequent decrease in soil pH and an increase in available Al.

#### *Effects on plant production*

Our results indicate potential positive effects of both amending local sediments and liming on barley biomass production and yield, which is in line with many other studies (Li et al., 2019; Wang et al., 2021; Scherwietes et al., 2024). Liming is already known for decades to be a very effective practice to promote plant production (Foy et al., 1965). In this study, liming (with a rate of 4.5 t ha<sup>-1</sup>) resulted in a significant increase in biomass production of 650 % (4.13 ± 1.16 t ha<sup>-1</sup>) compared to the control (0.55 ± 0.39 t ha<sup>-1</sup>). Scherwietes et al. (2024) found that the addition of local sediments could potentially increase the plant production and barley yield. In this study, these results could have been verified again two years after incorporation. However, the 3 % Baringo treatment was the only treatment with added sediment that showed a significant increase (4.52 ± 0.75 t ha<sup>-1</sup>, +722 % compared to control) in biomass production, which was even slightly higher than the lime treatment (+9 % compared to lime). The yield effect was even

higher for the 3 % Baringo compared to the lime treatment (Lime:  $0.91 \pm 0.35 \text{ t ha}^{-1}$ ; Baringo 3 %:  $1.32 \pm 0.34 \text{ t ha}^{-1}$ ; + 45 % compared to lime). However, due to the complete lack of rainfall in the tillering stage and irregular rainfall throughout the growing season, the overall yield in this study was very low. Irrigation was required at the tillering stage, which was carried out at 200 litres per plot once a week for three weeks. Apparently, the control and Nakuru 1 % treatments suffered the most from the low water supply, resulting in no heading and no yield by the end of the growing season. The yields of Nakuru 3 % ( $0.36 \pm 0.28 \text{ t ha}^{-1}$ ), Baringo 1 % ( $0.34 \pm 0.47 \text{ t ha}^{-1}$ ), Baringo 3 % and Lime treatment were all well below the 5-year average 2019/20 – 2023/24 ( $3.5 \text{ t ha}^{-1}$ ) and also well below the annual average of 2023 ( $3.0 \text{ t ha}^{-1}$ ; USDA 202).

Nevertheless, the addition of 3 % Baringo sediment and lime partially resulted in better plant growth compared to the control and may have promoted higher tolerance to drought stress at tillering stage, which was an advantage over the control and the treatment with 1 % Nakuru. One possibility is that the lower Al availability resulted in lower Al toxicity, the main toxic effect of which is inhibition of root growth and elongation (Foy et al., 2003; Kochian et al., 2004). Therefore, the plants may have developed a better root system from the beginning and may have had better water uptake under drought stress. In addition, the higher soil Si availability resulted in a higher Si uptake and accumulation in plant tissues (Supplementary Figure 2 + 3). Silicon is known to promote plant tolerance to drought stress through various mechanisms, which could explain the slightly better yield of Baringo 3 % compared to Lime (Coskun et al., 2016). For example, water uptake may be improved by promoting root growth and by the deposition of Si in the endodermal cell wall (Steudle and Peterson, 1998; Dakora and Nelwamondo, 2003). In addition, the deposition of Si in the stomata may reduce water loss via the stomata during drought stress (Gao et al., 2005).

In the present study, straw return at  $5 \text{ t ha}^{-1}$  had no positive effect on plant production or barley yield. It was initially assumed that straw return would enhance crop production, as reported in several studies (Butterly et al., 2013; Yan et al., 2019). However, a significant reduction in biomass production and barley yield was observed in the Lime treatment. This outcome may be attributed to a decrease in Ca availability, which led to a reduction in soil pH and an increase in Al availability, thereby contributing to enhanced toxicity.

As originally assumed, the lime treatment and local sediment amendment (but only in the form of treatment with Baringo 3 %) increased the biomass and yield of barley. These effects may be due to the increase in soil pH and the associated increase in P availability and decrease in Al

availability. Nevertheless, Baringo 3 % still performed slightly better in biomass production (+9 %) and yield (+45 %), which might be due to the supplementation of Si and its higher availability. However, the effects of the lime treatment appear to be more effective in the short term, as not significantly lower yields and biomass were achieved with significantly less added material (Lime: 4.5 t ha<sup>-1</sup>; Baringo 3 %: 72 t ha<sup>-1</sup>). However, the long-term effect of the added materials must also be taken into account, as the local sediments were already in their second growing season and still resulted in slightly better crop production. It is known that lime dissolves within a short time and thus loses its activity. Further studies should be carried out in order to evaluate the different amendments from an economic perspective in addition to the biophysical perspective of this study.

### *Conclusion*

The present study showed that there are differences between the effects of local sediment amendment, liming and straw return on soil fertility. While straw return did not improve soil fertility and barley yield, liming and certain local sediment amendments resulted in better growth and higher yield of barley. The results showed that the application of local sediment could be still effective even two years after incorporation. However, the improvement depends on the sediment source and amendment rate. One of the driving factors for the improvement in soil fertility with the addition of local sediments (Baringo 3 %) is probably the addition of Ca and consequently the increase in soil pH, which could promote a higher soil P availability and reduce the soil Al availability and its toxicity. However, Baringo 3 % still resulted in 45 % more yield compared to the Lime treatment. This indicates that Si supplementation by the sediment might also play a beneficial role in crop production, as Baringo 3 % increased soil Si availability, but Lime did not. Nevertheless, the yields of Baringo 3 % and Lime treatment were still well below the average barley yield in Kenya, probably due to lack of rainfall and water supply. In conclusion, the addition of local sediments or liming could make agriculture in Kenya more sustainable from a biophysical perspective. However, the effects of local sediment on soil fertility were still observed two years after incorporation, depending mainly on the sediment material and the rate of application. Lime was applied in smaller quantities, but is probably dissolved more quickly and thus loses its activity. Further studies are needed to investigate the potentials of local sediment amendments and liming for agriculture in Kenya from an economic perspective.

### ***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: Conceptualisation, Methodology, Visualisation, Writing – original draft, Writing – review and editing, Formal Analysis. JhS: Supervision, Writing – review and editing. TB: Writing – review and editing, Methodology. JrS: Writing – review and editing, Conceptualisation, Funding acquisition, Supervision.

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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***

The Supplementary Material for this article can be found online at:

<https://www.frontiersin.org/articles/10.3389/fenvs.2025.1572266/full#supplementary-material>

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## **Chapter 4: Phosphorus and aluminium mobilisation in ferralsols: effects of local sediment amendments, liming and straw application in a Lab Study**

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### ***Abstract***

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.

### ***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 ( $Ca^{2+}$ ) and magnesium ( $Mg^{2+}$ ) (von Uexküll and Mutert, 1995). These cations are replaced on the mineral surfaces by hydrogen ( $H^+$ ) and aluminium ( $Al^{3+}$ ) 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 ( $Fe_2O_3$ ) 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; 2022) showed that amending amorphous Si (ASi) to soil increases soil P mobility and plant availability. Through the weathering of 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. 2025; 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.

### ***Material and Methods***

#### *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 1), 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<sup>+</sup> kg<sup>-1</sup> of soil, and a total organic carbon (TOC) content of 2.6% (Scherwietes et al., 2024). The total Al content is 104 g kg<sup>-1</sup>, with a plant-available Al content (CaCl<sub>2</sub>-extractable) of 0.04 g kg<sup>-1</sup> (Scherwietes et al., 2024). A Fe<sub>o</sub>/Fe<sub>d</sub> 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 1), 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 1) and hereafter called "Baringo," is a Ca-rich lacustrine sediment with an aggregated matrix (5-25 μm) and attached fine particles (≤1-5 μm) 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.

#### *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 3320 meter (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, USA).

#### *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 & 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 minutes (Centrifuge 5804, Eppendorf AG, Hamburg, Germany). The supernatant from each subsample was then filtered through 0.2 µm membrane filters.

*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 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 & 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 minutes and the supernatant was filtered through 0.2 µm membrane (Centrifuge 5804, 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.

*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, USA), 200 mL of deionized water was added to each sample, which was then sealed and shaken for 80 days (KS 501 D, Janke & 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 minutes and filtered through 0.2 µm membrane filters (Centrifuge 5804, Eppendorf AG, Hamburg, Germany). Each subsample's pH, redox potential, and EC were measured inside the anaerobic chamber to maintain consistent anaerobic conditions.

*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 hours and subsequently centrifuged at 10,000 g for 10 minutes (Centrifuge 5804, 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 (1960). 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 minutes and centrifuged at 10,000 g for 10 minutes (Centrifuge 5804, 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, USA).

#### *Statistics*

All statistical analyses were performed using R (Version 4.3.2; 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, 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).

### **Results**

#### *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

mobilisation ( $p = 1.000$ , 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 2).

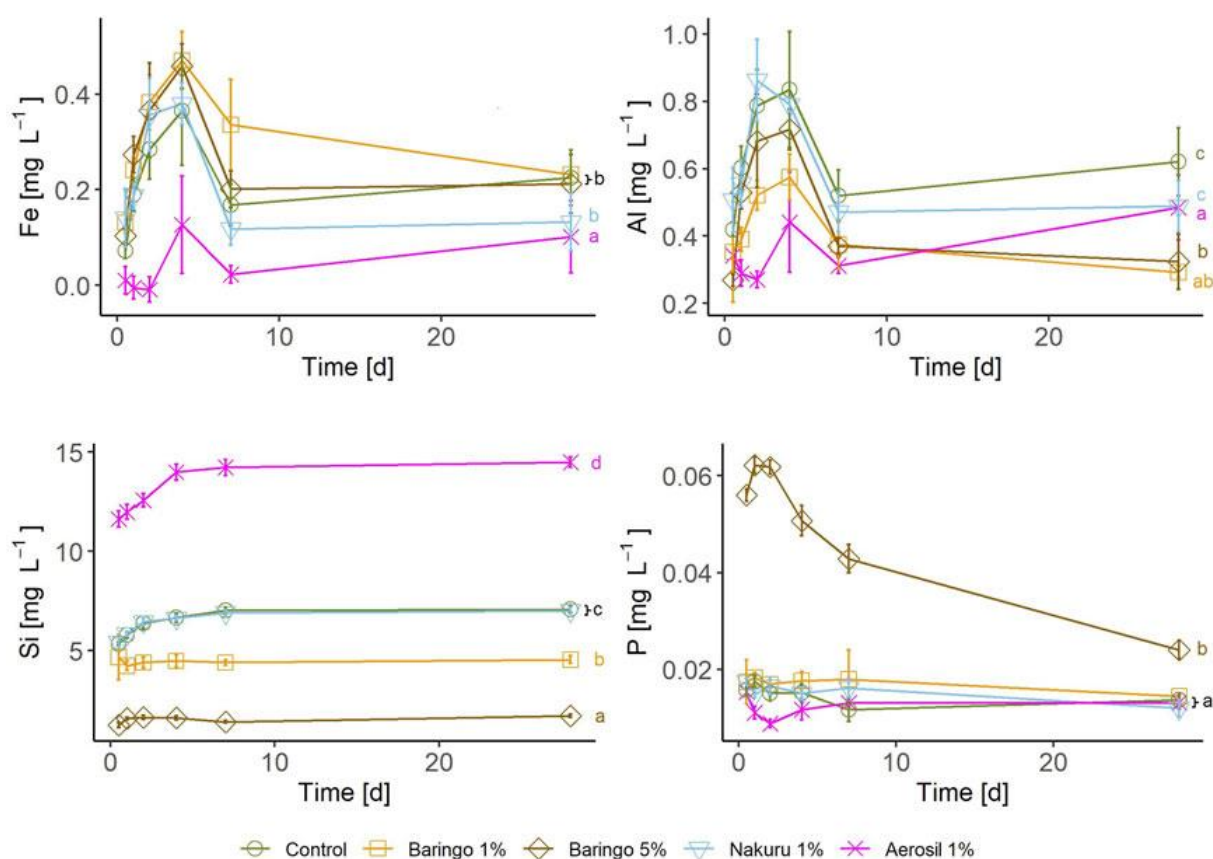


Figure 1: Dissolution of Fe, Al, Si and P while mixing sediment/soil treatments in water for 28 days. Error bars indicate standard deviation. Significant differences in the mean of all measurements between all treatments are represented by different letters, common letters indicate no significant difference ( $p < 0.05$ ).

In the reference materials, Aerosil released the highest amount of Si into solution (all  $p < 0.001$  vs. other materials, Tukey; Supplementary Figure 3). 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%.

#### *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). Baringo 1%, lime, and Baringo 3% increased pH, with Baringo 3% showing the highest value ( $6.1 \pm 0.08$ ;  $p < 0.001$ , 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 ( $313 \mu\text{S cm}^{-1}$ ;  $p < 0.001$ , 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 two 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 4).

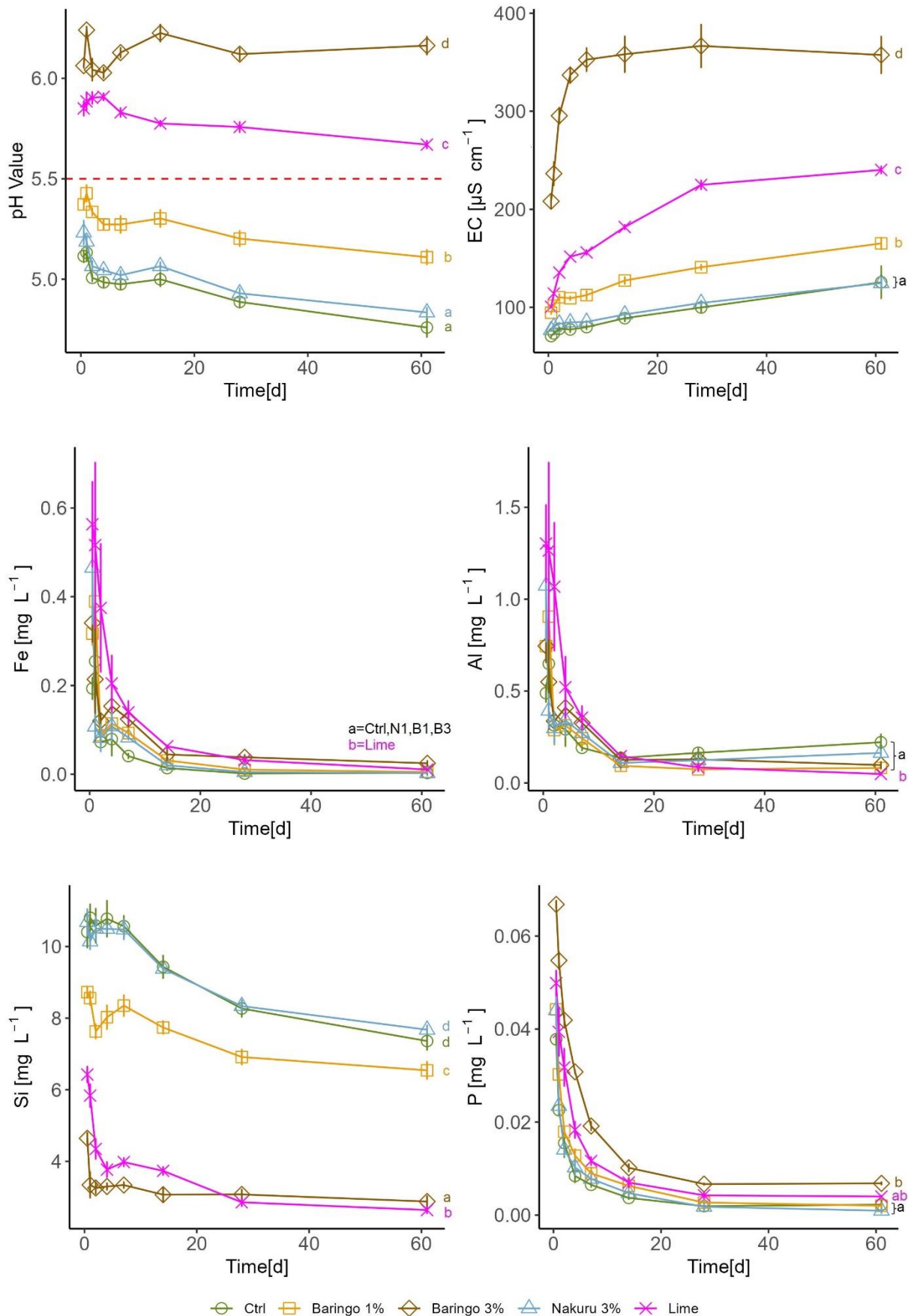


Figure 2: The physical parameters pH and electrical conductivity (EC) and the release of Fe, Al, Si and P of each treatment. The treatments were mixed with water and shaken for 61 days. The red dotted line shows the pH threshold of 5.5. Error bars indicate standard deviation. Significant differences in the mean of all measurements between all treatments are represented by different letters, common letters indicate no significant difference ( $p < 0.05$ ).

The pH of the reference materials was considerably higher than that of the soil/sediment treatments (Supplementary Figure 5). 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%.

#### *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  $5.7 \pm 0.06$  after 10 days and  $6.4 \pm 0.02$  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 6).

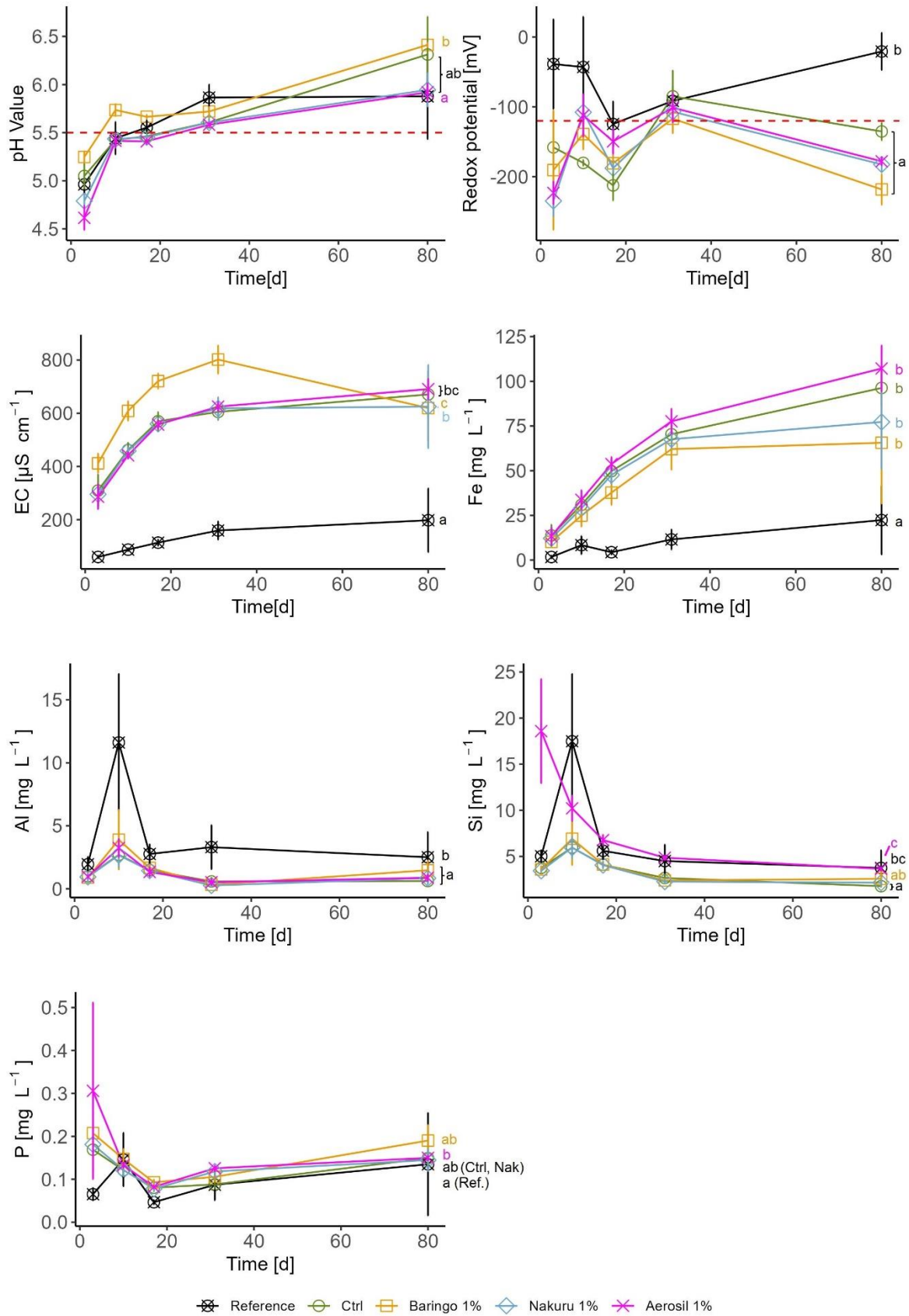


Figure 3: The physical parameters pH, redox potential and electrical conductivity (EC) and the release of Fe, Al, Si and P of each treatment under reducing conditions. The treatments were mixed with water and shaken for 81 days. The red dotted lines show the pH threshold of 5.5 and the threshold of redox 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 ( $p < 0.05$ ).

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).

#### *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 ( $Fe_{dith}=62.516 \pm 0.846$  g kg<sup>-1</sup>,  $p<0.001$ ,  $t=-179.31$ ,  $df=3$ , t-Test) than that extractable with oxalate ( $Fe_{ox}=2.615 \pm 0.339$  g kg<sup>-1</sup>, Table 1). Similarly, dithionite extraction released more P ( $P_{ox}=0.169 \pm 0.022$  g kg<sup>-1</sup>,  $P_{dith}=0.560 \pm 0.014$  g kg<sup>-1</sup>;  $p<0.001$ ,  $t=-78.76$ ,  $df=3$ , t-Test), more Si ( $Si_{ox}=0.327 \pm 0.037$  g kg<sup>-1</sup>,  $Si_{dith}=0.856 \pm 0.018$  g kg<sup>-1</sup>;  $p<0.001$ ,  $t=-26.25$ ,  $df=3$ , t-Test) and more Al ( $Al_{ox}=4.586 \pm 0.383$  g kg<sup>-1</sup>,  $Al_{dith}=8.336 \pm 0.089$  g kg<sup>-1</sup>;  $p<0.001$ ,  $t=-24.53$ ,  $df=3$ , 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 ( $Fe_{dith-ox}= 59.901 \pm 0.668$  g kg<sup>-1</sup>,  $p<0.001$ ,  $t=-179.64$ ,  $df=3$ , t-Test), P ( $P_{dith-ox}= 0.392 \pm 0.01$  g kg<sup>-1</sup>,  $p<0.001$ ,  $t=-14.35$ ,  $df=3$ , t-Test) and Si ( $Si_{dith-ox}= 0.530 \pm 0.04$  g kg<sup>-1</sup>,  $p=0.012$ ,  $t=-5.368$ ,  $df=3$ , 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<sup>-1</sup>,  $p=0.093$ ,  $t=2.432$ ,  $df=3$ , t-Test).

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

Element	Al <sub>ox</sub> [g kg <sup>-1</sup> ]	Fe <sub>ox</sub> [g kg <sup>-1</sup> ]	P <sub>ox</sub> [g kg <sup>-1</sup> ]	Si <sub>ox</sub> [g kg <sup>-1</sup> ]	Al <sub>dith</sub> [g kg <sup>-1</sup> ]	Fe <sub>dith</sub> [g kg <sup>-1</sup> ]	P <sub>dith</sub> [g kg <sup>-1</sup> ]	Si <sub>dith</sub> [g kg <sup>-1</sup> ]
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

### ***Discussion***

#### *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 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 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.

#### *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 3). 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 re-dissolution (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 3). 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 3). 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.

*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  $\text{Al}(\text{OH})_2^+$  or  $\text{Al}(\text{OH})_3$  (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  $\text{Al}(\text{OH})_2^+$  or  $\text{Al}(\text{OH})_3$ , 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.

*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 abiotic-chemical 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 Fe<sup>2+</sup> (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.

### ***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 Fe 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 fertilisers.

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: Visualisation, 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, Conceptualisation, 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

The Supplementary Material for this article can be found online at:

<https://www.frontiersin.org/articles/10.3389/fenvs.2025.1628554/full#supplementary-material>

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## Chapter 5: Epilogue

The present thesis explored the biogeochemical potential of volcanically influenced sediments from the Kenyan Rift Valley as a natural fertiliser for crop production on Ferralsols. Specifically, it examined the impact of applying two different sediments (Baringo and Nakuru) at two application rates (1 vol.% and 3 vol.%) on nutrient availability (Al, Si, P, and Fe) and on barley yield, growing on an acidic soil in Kenya. The effects were assessed in an arable field in Eldoret, western Kenya, across two consecutive growing seasons (Chapters 2 and 3). Additionally, the effects of these local sediment amendments were compared to globally used soil fertility improvement methods - liming and straw return (Chapter 3). To further understand the soil processes triggered by the sediment additions on a Ferralsol, laboratory experiments were carried out (Chapter 4).

The addition of volcanically influenced local sediments, combined with small amounts of P fertiliser, resulted in an increase in soil pH and Si availability in certain cases. Thereby, Al availability decreased and P availability increased. However, improvements in nutrient availability were only observed with the application of Baringo sediment, with more pronounced effects at higher application rate. Barley yield increased with both Baringo treatments and with the 3% Nakuru treatment. Therefore, hypotheses (i) and (ii) can only be partially confirmed, as the effects of the sediments depended on both the sediment type and the application rate.

Similar effects were observed in the second growing season after sediment application. Once again, Baringo 3% treatment showed the most pronounced impact, enhancing barley yields, increasing the availability of Si and P, raising soil pH, and reducing Al availability. Both Nakuru treatments did not improve the nutrition and yield of barley. Hence, hypothesis (iii) can only be partially confirmed. Since it remained unclear whether the improved nutrient availability was driven by the added Si or the rise in pH, a lime treatment was introduced for comparison in the second growing season. Both the Baringo 3% and lime treatments resulted in higher soil pH and increased available P, while also reducing available Al. In both cases, barley yields were significantly improved, supporting hypothesis (iv). In contrast, hypothesis (v) must be rejected, as straw return had no positive effect on nutrient availability or yield.

Laboratory experiments were conducted to elucidate soil processes occurring after the addition of volcanically influenced local sediments to a Ferralsol. Similar findings were observed in both the laboratory and field experiments. However, hypothesis (vi) could only be partially

confirmed, as the Si reference treatment decreased Al availability but did not affect P availability. Liming resulted in a significant increase of soil pH, increased P concentration shortly after addition and reduced Al availability, supporting hypothesis (vii). Adding straw under anoxic conditions resulted in a strong reductive dissolution of Fe phases with increased P availability, supporting hypothesis (viii).

***Sediment amendment can improve barley yield and soil fertility***

Over two consecutive growing seasons (2022 - 2023), the Baringo 3% treatment consistently resulted in a significant increase in barley yield. In the first year (2022), yield increased by 1061% compared to the control, reaching 4.72 t ha<sup>-1</sup>. This yield was well above the 5-year average for Kenyan barley production for 2018/19 – 2022/23 (4 t ha<sup>-1</sup>; UDA, 2023). Baringo 1% (2.7 ± 0.6 t ha<sup>-1</sup>) and Nakuru 3% (2.2 ± 0.6 t ha<sup>-1</sup>) also resulted in significant yield increases of around 500%, while Nakuru 1% had no significant effect in the first year. In the second season (2023), overall yields were low due to the complete lack of rainfall during tillering stage and irregular rainfall throughout the growing season. Despite irrigation in tillering stage, the control and Nakuru 1% treatments failed to produce grain. Under the same conditions, Baringo 3% was the only sediment treatment that still delivered a significant yield (1.32 ± 0.34 t ha<sup>-1</sup>). These yield improvements align with observed changes in soil pH and nutrient availability. Baringo 3% raised the soil pH above 6 and maintained it over both growing seasons. This effect is attributed to a strong release of carbonates through the weathering of the Ca-rich lacustrine sediment, which is buffering the soil solution pH. Along with Ca, the Baringo sediment also released large amounts of Si, significantly increasing Si availability in both years. Both the increase in pH above 5.5 and the release of Si from the sediment may explain the observed reduction in Al availability. At pH levels above 5.5, the release of toxic Al<sup>3+</sup> from Al(OH)<sub>3</sub> dissolution is inhibited (Bolan et al., 2003; Sade et al., 2016; Bojórquez-Quintal et al., 2017). Additionally, Al<sup>3+</sup> is increasingly transformed through hydrolysis into Al(OH)<sup>2+</sup>, Al(OH)<sub>2</sub><sup>+</sup> or Al(OH)<sub>3</sub>, which are less soluble or even precipitate and thus Al<sup>3+</sup> is removed from soil solution (Li and Johnson, 2016; Bojórquez-Quintal et al., 2017). Silicon may further contribute to the reduction in Al availability through the formation of aluminosilicates and SROAS (Exley et al., 2019; Lenhardt et al., 2021; Schaller et al., 2021a). Moreover, Si can enhance plant physiological functions, influencing cellular metabolism and thereby reducing Al uptake and toxicity (Coskun et al., 2016). In both growing seasons, a strong decline in Al availability was observed following Baringo 3% application. This treatment also resulted in a significant increase in P availability. This effect can be attributed to the direct release of P through sediment

weathering, but it is also likely influenced by the increase in pH and the addition of Si. Under low pH conditions, Fe and Al oxides are highly protonated, resulting in a positive surface charge that promotes electrostatic adsorption of negatively charged phosphate ions (Liu et al., 2013; Li et al., 2019). As pH increases, these surfaces become deprotonated, weakening the electrostatic bond and allowing phosphate to be released into the soil solution (Fageria and Baligar, 2008). Additionally, numerous studies have shown that the supply of Si can also increase P availability in the soil (Weng et al., 2012; Schaller et al., 2019; Schaller et al., 2021a; Schaller et al., 2021b; Uhuegbue et al., 2024). The silicic acid that enters the soil solution through weathering is able to adsorb to mineral surfaces and compete with and displace other anions such as phosphates (Schaller et al., 2019; Schaller et al., 2021a). However, an increase in P availability was only observed after the addition of Baringo sediment. Nakuru showed no significant effect on nutrient availability or on the pH of the soil solution. This is likely due to its higher crystallinity of the Nakuru material, which makes the sediment less reactive and less prone to weathering, thereby limiting the release of plant-available nutrients.

Liming was applied in the second growing season to compare its effect with the previously observed positive effects of the 3% Baringo sediment treatment. While liming significantly increased barley yield, it did not reach the yield achieved with Baringo 3%. In terms of nutrient availability, both treatments performed similarly: pH and P availability increased, while Al availability decreased. In fact, liming resulted in a stronger increase in pH and P availability than Baringo 3%. This indicates that the increase in pH due to release of carbonates by liming and neutralising of excessive H<sup>+</sup>, rather than the supply of easily weatherable Si, was likely the driving factor behind reduced Al availability and improved P availability. Although higher pH can promote Si availability (Haynes, 2019), this was not observed in the studied Ferralsol following liming. Due to intense weathering and desilification, Ferralsols contain only small amounts of Si (von Uexküll and Mutert, 1995), so increasing pH was not sufficient to increase Si availability. However, Baringo 3% still resulted in higher yield than liming (+45%). This may be explained by the additional supply of weatherable Si, which increased Si availability and may have supported physiological processes in the plants, contributing to improved growth (Dakora and Nelwamondo, 2003; Gao et al., 2005; Coskun et al., 2016).

#### ***Laboratory experiments confirmed field observation***

To better understand the processes behind the yield increase after Baringo sediment addition, incubation experiments were carried out under controlled laboratory conditions. Several results confirmed the field observations from Kenya. The addition of Baringo 3% resulted in an

increase in P concentration in the soil solution, an increase in pH, and a reduction in Al mobility. As in the field, the Nakuru sediment showed no significant effects compared to the control. Liming had similar effects on pH and nutrient mobilisation as Baringo 3% treatment, confirming field observations as well.

To investigate potential Si effects on element mobilisation, a Si reference was included in the incubation experiments under laboratory conditions. It was assumed that higher Si availability might reduce Al concentration and promote the P release into the soil solution. The interaction between Si and Al was confirmed after the incubation experiment. The Si reference as well as the Baringo treatments showed a decrease in Al mobility. This was likely due to electrostatic adsorption and surface complexation between Al and Si, resulting in the formation of aluminosilicates or SROAS, which can precipitate and reduce Al concentrations in solution. However, an associated release of P was not observed in the Si reference treatment. This suggests that the increase in P availability observed after Baringo sediment addition in both, the field experiment and the incubation experiment, is more likely due to the increase in pH and the direct release of P from the sediment. In the incubation experiment, the P availability rapidly decreased after short time, probably due to direct re-adsorption to Fe and Al oxide surfaces or to immobilisation by formed aluminosilicates.

In the first incubation experiment, only the Baringo treatments maintained low Al concentrations in the soil solution over time. This was likely due to the increase in pH, which prevented Al from re-dissolving. The Si reference had no effect on pH, so Al gradually re-dissolved and re-entered the soil solution. This was also confirmed in the second incubation experiment with the liming treatment. A sustained pH increase above 5.5 resulted in a long-term reduction in Al availability, which aligns with the field results from Kenya. Both liming and Baringo 3% reduced Al concentrations, likely due to the pH-driven transformation of mobile  $Al^{3+}$  into less mobile species like  $Al(OH)_2^+$  or precipitated  $Al(OH)_3$ . At the start of the incubation, both treatments also showed a strong increase in P mobility, likely due to direct release from the Baringo sediment or desorption at higher pH. However, P levels quickly dropped again, likely due to rapid re-adsorption to Fe and Al oxide surfaces or to formed aluminosilicates.

Ferralsols are generally known for being well-aerated soils (FAO, 2014). However, during periods of heavy rainfall in the rainy season, temporary anoxic microsites may develop. This may occur due to natural soil heterogeneity and the accumulation of organic material. Under anoxic conditions, the reductive dissolution of Fe(III) oxides can take place in Ferralsols, as Fe

oxides act as electron acceptors during the microbial oxidation of organic matter by bacteria (Bonneville et al., 2004). Since a significant proportion of P is either adsorbed onto or occluded within these Fe oxides (Owusu-Bennoah et al., 1997), it is assumed that reductive dissolution of these oxides may result in a substantial P mobilisation. This hypothesis was investigated in the third incubation experiment. The induced anoxic conditions resulted in a strong release of Fe, accompanied by approximately ten times higher P mobilisation compared to the first two incubation experiments. However, no significant differences were observed between the individual treatments. A combined oxalate/dithionite extraction further revealed that the investigated Ferralsol contains a high proportion of highly crystalline Fe oxides such as hematite and goethite. Due to higher crystallinity, these minerals dissolve under more negative redox potentials that were not achieved in this experiment (Lovley and Phillips, 1986; Gorski et al., 2016). It can therefore be assumed that considerable amounts of P are still retained in these more stable mineral phases. The results of the third incubation experiment demonstrate that temporary anoxic conditions in Ferralsols can result in the mobilisation of substantial amounts of P. At the same time, they highlight the strong binding of P to Fe oxides, supporting the assumption that the P mobilized in the first two experiments was rapidly re-adsorbed onto Fe oxides following a pH increase or the addition of Si.

### ***Conclusion and further research recommendation***

While volcanic ash is known to improve soil fertility (Fiantis et al., 2019), little is understood about the impact of volcanically influenced sediments on P availability and Al toxicity in acidic soils such as Ferralsols. This study demonstrates that the use of these sediments can improve plant growth and yield from a biogeochemical perspective, though the effectiveness strongly depends on the sediment source and the application rate. Over two growing seasons, a single application of Baringo sediment significantly increased barley growth and yield, even under the challenging conditions of low rainfall in the second year. These effects were attributed to the direct release of nutrients such as P, enhanced supply of Si, and the increase in soil pH from carbonate release. Both Si release and increase in pH mitigated two major agricultural challenges on Ferralsols: Aluminium toxicity and high P fixation by Fe and Al oxides. Comparison with liming indicated that the increase in pH was the driving factor behind these effects. While liming proved to be more efficient in terms of quantity applied, achieving similar yields with smaller amounts of amendment, it is likely to dissolve faster and therefore lose its effectiveness over time. In contrast, Baringo sediment continued to show positive effects on barley growth and yield even in the second year after application. However, the increased

availability of Si additionally showed beneficial effects on barley growth and yield, likely due to supporting plant physiological processes. Laboratory results confirmed the field observations, showing reduced Al availability and increased P availability after Baringo sediment addition. The sustained reduction of aluminium availability in the soil due to the pH increase as a result of sediment treatment could also significantly increase the efficiency of subsequent P fertilisation, as less P would be adsorbed on Al minerals. The laboratory experiments also highlighted the challenge of P fixation and quick re-adsorption by Fe oxides and aluminosilicates.

In conclusion, the use of volcanically influenced sediments from Kenyan Rift Valley shows promising potential to support more sustainable agriculture on Ferralsols in sub-Saharan Africa by reducing the need of mineral P fertilisers from a biogeochemical perspective. However, in this study, the effects of sediment amendment on crop production were only tested for barley. It would be recommended to examine possible effects also on other relevant crops in East Africa, such as millet, wheat and maize. Further research should also investigate the use of this material from a socio-economic perspective. This would involve assessing the availability of the sediment, conducting a cost-benefit analysis of its transport and application, and evaluating its long-term effects through a long-term field trial. A further recommendation for research is to investigate the potential P fixation by different forms of SROAS. To accomplish this, SROAS could be synthesized with varying Si/Al ratios, both with and without added phosphorus, to evaluate its impact on P fixation.

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