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ASSESSMENT OF H3A-4 EXTRACTABLE POTASSIUM IN DIVERSE SOILS OF INDIA

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ABSTRACT

Potassium (K) is an essential macronutrient that plays a critical role in plant growth, physiological regulation, and crop productivity. Adequate availability of K is therefore indispensable for sustaining yield and improving produce quality. Plant-available potassium is conventionally assessed using 1 M ammonium acetate (NH_4OAc, pH 7) extractant. Although alternative extractants for K have been developed and evaluated in several countries, their applicability under diverse Indian soil conditions remains largely unexplored. The present study evaluated the suitability of H3A-4 as a potential K extractant for diverse soils of India. A total of twenty-five bulk surface soil samples (0-15 cm) were collected from seventeen states across India, representing major soil groups and a wide range of physicochemical characteristics. Potassium extracted by H3A-4 varied significantly among soil types, with higher extractability observed in alluvial and black soils compared to red soils. On average, H3A-4 extracted 1.39, 2.14, and 1.87 times more K from acidic alluvial, non-acidic alluvial, and black soils, respectively, than from red soils. The enhanced extractability in alluvial and black soils was attributed to differences in clay content, mineralogical composition, and cation exchange characteristics, which influence K retention and release. These findings demonstrate that H3A-4 is sensitive to soil-specific attributes governing potassium availability and may provide a more representative assessment of plant-available K in certain Indian soils. Overall, the study highlights the potential of H3A-4 as an alternative extractant for potassium and underscores the need for plant uptake related evaluation of K extractants under Indian conditions.

Key words: Potassium, macronutrients, extractants, ammonium acetate, H3A-4, alluvial soil.

Introduction

Potassium (K) is a key macronutrient that plays essential regulatory roles in supporting plant growth and development (Soumare *et al.,* 2022; Bharadwaj *et al.,* 2025). Potassium contributes to fundamental biochemical processes such as the synthesis of starch, cellulose, proteins, and vitamins and activating more than 60 enzymes involved in photosynthesis, nitrate reduction, starch synthesis, metabolic reactions, and sugar degradation (Hawkesford *et al.,* 2012; Nieves-Cordones *et al.*, 2016; Su *et al.,* 2022). A major physiological function of K lies in the regulation of stomatal opening and closing, which supports efficient gas exchange and helps plants manage water use (Sustr *et al.,* 2019). A sufficient supply of K^+ enhances photosynthetic carbon assimilation, promotes more efficient nutrient uptake, and supports proper leaf orientation through its role in regulating turgor pressure (Carroll *et al.*, 1994; Sardans and Peñuelas 2021). Plants facing drought stress often show a higher internal requirement for K, as adequate K levels assist in CO_2 fixation during photosynthesis, protect chloroplasts from oxidative injury, stabilize carbohydrate metabolism, and regulate hydric relations (Cakmak 2005; Wang *et al.*, 2013). Besides osmotic adjustment K also contributes significantly to ion homeostasis, thereby helping plants mitigate the adverse effects of salinity stress (Das *et al.*, 2022). Beyond vegetative growth, K plays essential role in reproductive development by enhancing flowering, pollen germination, and seed formation, improving utilization efficiency of nitrogen (N) and phosphorus (P), imparting resistance to biotic and abiotic stresses- all of which contribute to overall gains in crop yield (Hasanuzzaman *et al.*, 2018). Its influence on the biosynthesis, allocation, and conversion of essential metabolites further supports yield improvement (Islam *et al.*, 2025). Together, these K-dependent physiological and developmental functions highlight the crucial role of potassium in sustaining crop productivity and ensuring high-quality agricultural produce (Rawat *et al.*, 2022). However, in recent years, intensive cropping has led to widespread K depletion in many soils. K-deficient plants exhibit slower growth, poor root development and weak stems, increasing the risk of lodging particularly in cereal crops. Consequently, significant reductions in yield and crop quality are observed (Johnson *et al.*, 2022).

Potassium concentration in cell cytoplasm ranges within 100-200 mM (Wang *et al.*, 2013) whereas, the concentration of K^+ in the soil solution generally varies between 0.1 to 1 mM (White 2013). Broadly, in soils, K occurs in four distinct pools: soil solution K, exchangeable K, non-exchangeable or fixed/interlayer K, and structural K held within the mineral lattice (Barber 1995; Brady and Weil 2012). The soil solution fraction- measured as water-soluble K-accounts for only 0.1-0.2% of the total soil K (White 2013). This form is directly accessible to plants and microbes and is also prone to leaching losses (Barre *et al.*, 2008; Dubus *et al.*, 2023). Exchangeable K generally represents 1-2% of total K, while the non-exchangeable or interlayer fraction contributes approximately 1-10%. The majority of soil K, however-around 90-98% is locked within the crystal structures of primary silicate minerals such as muscovite, biotite, orthoclase, feldspar, illite, mica, vermiculite, and smectite, making it largely unavailable for immediate plant uptake (Meena *et al.*, 2014a, b). The K accessible to crops is primarily derived from the soil solution, the exchangeable fraction bound to cation-exchange sites, and the non-exchangeable K associated with clay lattices (Römheld and Kirkby 2010; White and Greenwood 2013). Exchange between the soil solution and exchangeable K occurs quickly, whereas the transfer between the solution phase and non-exchangeable K is comparatively slow (Sharma *et al.*, 2024). Consequently, the amounts of K present in these fractions, together with the rate at which they interconvert, govern the short- and long-term availability of K to growing crops (Karpinets and Greenwood 2003; Römheld and Kirkby 2010).

On the basis of the rate of accessibility to plant, soil K can be grouped into three functional pools: (i) a readily available fraction comprising soil solution K and exchangeable K, (ii) a slowly available fraction represented by non-exchangeable K, and (iii) a very slowly available fraction consisting of structural K bound within mineral lattices (Das *et al.*, 2022). Exchangeable K is held as outer-sphere complexes on negatively charged surfaces of clay minerals or organic matter (Bourg and Sposito 2011; Bell *et al.,* 2021). Because this form of K can be readily displaced by competing cations in the soil solution, it is typically considered available to plants. However, the analytically defined “exchangeable K” does not always correspond fully to plant-available K.

Ammonium acetate (1 M NH_4OAc, pH 7) is conventionally used fir extraction for exchangeable K. NH_4OAc relies on a strong cation-exchange mechanism driven by high ionic strength. While NH_4OAc provides a reliable measure of exchangeable K, its chemistry does not reflect the conditions under which plant roots acquire nutrients. Use of highly buffered extractants does not reflect in situ soil conditions particularly in terms of soil pH, which strongly governs soil–solution chemistry (Nelson *et al.*, 1953).

Rengel (2002) highlighted that a more suitable extractant should operate close to the native soil pH and employ organic acids similar to those released by plant roots to mobilize nutrients. Although the rhizosphere is characterized by complex biological and chemical interactions, the pivotal influence of root exudates on nutrient availability provided the conceptual foundation for the development of the H3A extractant by Haney, Haney, Hossner and Arnold in 2006 with the aim of simultaneously extracting NO_3^- -N, NH_4^+ -N, and P from diverse soils (Haney *et al.*, 2006). To replicate root-driven processes, three organic acids commonly exuded by plants- citric, malic, and oxalic acids- were incorporated to enhance nutrient solubilization across a wide soil pH range (Rengel 2002; Baudoin *et al.*, 2003). Lithium citrate was added to partially neutralize acid strength and act as a weak buffer, while EDTA and DTPA served as chelating agents. The overarching goal of the H3A extractant was to support fertilizer recommendations based on bioavailable nutrient pools rather than total soil reserves (Chu *et al.*, 2019). The original H3A composition included lithium citrate (5.0 g; 0.02 M), citric acid (0.5 g; 0.0024 M), malic acid (0.5 g; 0.004 M), oxalic acid (0.5 g; 0.004 M), EDTA (0.25 g; 0.002 M) and DTPA (0.25 g; 0.001 M) (Haney *et al.*, 2006). The extractant pH remained within one unit of soil pH in more than 85% of the soils evaluated. In 2010, the extractant was further optimized to form H3A-2, enabling simultaneous determination of inorganic N, P, K, Ca, and Zn by eliminating EDTA and DTPA, reducing lithium citrate, malic acid, and oxalic acid, and increasing citric acid (2 g L^{-1} lithium citrate, 0.6 g L^{-1} citric acid, 0.4 g L^{-1} malic acid, 0.4 g L^{-1} oxalic acid) (Haney *et al.*, 2010). These adjustments produced a clearer extract and lowered the extractant pH from 5.0 to 4.4, while markedly improving the correlation between NH_4OAc-extractable K and H3A-extractable K. Subsequent refinement resulted in H3A-3, a weakly buffered extractant (pH ≈ 4.0) composed of 2 L deionized water, 2.6 g lithium citrate (0.006 M), 1.2 g malic acid (0.004 M), 1.0 g citric acid (0.002 M), and 0.6 g oxalic acid (0.003 M), allowing soil pH to exert greater control during extraction (Haney *et al.*, 2016). Since lithium citrate is not naturally present in soils and plants adapt nutrient acquisition by modifying the type and strength of organic acids they exude, H3A-4 was subsequently developed by completely removing lithium citrate to improve predictions of P, K, Ca, Fe, and Al (Crittenden *et al.*, 2024). This formulation, consisting only of malic acid (1.1 g), citric acid (0.7 g), and oxalic acid (0.45 g), yielded a weakly buffered extractant with pH H” 3.75 (Haney *et al.*, 2017). The exclusion of lithium citrate provided a more realistic evaluation of nutrient availability under natural soil conditions, rather than conditions imposed by strongly buffered chemical extractants.

This H3A-4 extractant can be used as a multi-nutrient extractant capable of simultaneously extracting macro- and micronutrients from the soils (Gunderson 2023). Although several studies in other countries have showed the extractability of H3A-4 for different nutrients, similar evaluations remain limited for the Indian soils. Therefore, the present study aimed to examine the extractability of H3A-4 for K in diverse soils of India. Based on the results from the literature, we hypothesized that: (a) significant amount of K can be extracted by H3A-4 from acidic, non-acidic alluvial, red and black soils of India (b) physicochemical and mineralogical properties of the soils could help to understand the difference in extractability of H3A-4 during the estimation of soil-test K. The outcomes of this experiment will provide a scientific basis for evaluating the suitability of H3A-4 as a potential K extractant for the diverse soils of India.

Materials and Methods

In the present study, twenty-five bulk surface soil samples (0 – 15 cm) with diverse physical and chemical properties were collected from seventeen states of India, viz., Lepa Rada, Arunachal Pradesh; Jorhat, Assam; Alipurduar, West Bengal; Cooch Behar, West Bengal; Uttar Dinajpur, West Bengal; Almora, Uttarakhand; Cuttack , Odisha; Nadia, West Bengal; Ludhiana, Punjab; Rewari, Haryana; Central Delhi, Delhi; Kota, Rajasthan; Kanpur, Uttar Pradesh; Gurugram, Haryana; Hisar, Haryana, Samastipur, Bihar; Karnal, Haryana; Hazaribagh, Jharkhand; Thrissur, Kerala; Kollam, Kerala; Birbhum, West Bengal; Hyderabad, Telengana; Bhopal, Madhya Pradesh; and Nagpur, Maharashtra. The first seven soils are acidic alluvial, next eleven soils are non-acidic alluvial then next four soils are red and lateritic in nature and last three soils are black soils (Table 1). Soil samples were first air-dried in the shade, after which the bulk portion was passed through a 10-mm sieve for use in the greenhouse experiment. A smaller subsample was gently crushed using a wooden mortar and pestle, sieved through a 2-mm mesh, and preserved in polypropylene containers for subsequent physicochemical analyses.

Table 1: Soil types of twenty-five locations

District	State	Soil type
Lepa Rada	Arunachal Pradesh	Acidic alluvial
Jorhat	Assam	Acidic alluvial
Alipurduar	West Bengal	Acidic alluvial
Cooch Behar	West Bengal	Acidic alluvial
Uttar Dinajpur	West Bengal	Acidic alluvial
Almora	Uttarakhand	Acidic alluvial
Cuttack	Odisha	Acidic alluvial
Nadia	West Bengal	Non-acidic alluvial
Ludhiana 1	Punjab	Non-acidic alluvial
Ludhiana 2	Punjab	Non-acidic alluvial
Rewari	Haryana	Non-acidic alluvial
Central Delhi	Delhi	Non-acidic alluvial
Kota	Rajasthan	Non-acidic alluvial
Kanpur	Uttar Pradesh	Non-acidic alluvial
Gurugram	Haryana	Non-acidic alluvial
Hisar	Haryana	Non-acidic alluvial
Samastipur	Bihar	Non-acidic alluvial
Karnal	Haryana	Non-acidic alluvial
Hazaribagh	Jharkhand	Red and laterite
Thrissur	Kerala	Red and laterite
Kollam	Kerala	Red and laterite
Birbhum	West Bengal	Red and laterite
Hyderabad	Telangana	Black
Bhopal	Madhya Pradesh	Black
Nagpur	Maharashtra	Black

The soil pH and electrical conductivity (EC) were determined separately in 1:2.5 soil-to-water suspensions using a digital pH/Conductivity/TDS/!/°F-meter (Model number: PC 510, Eutech Instruments Pte. Ltd., United Kingdom) (Jackson 1973). H3A-4 extractable K was determined by taking 4 g soil with 40 mL of solution followed by shaking for 10 minutes and centrifugation at 3500 rpm for 5 minutes (Haney *et al.*, 2017). The K concentration in the extract of H3A-4 was measured with flame photometer (µController Based Flame Photometer Type-128, Systronics India Ltd., India) after filtering the suspension with a Whatman no. 1 filter paper.

Results and Discussion

Characterisation of the Experimental Soils

Out of the twenty-five soils evaluated, eleven were classified as acidic (pH < 6.5), while the remaining fourteen were non-acidic (pH > 6.5). Among the seven acidic alluvial soils, two sites (Lepa Rada and Jorhat) were extremely acidic (pH < 4.5), one site (Alipurduar) was very strongly acidic (pH 4.5–5.0), two sites (Cooch Behar and Uttar Dinajpur) were strongly acidic (pH 5.0–5.5), and two sites (Almora and Cuttack) were slightly acidic in reaction. Significant variability in soil pH was also evident among the four red soils, three black soils, and the eleven non-acidic alluvial soils included in the study. Electrical conductivity values across all soils were low, indicating the absence of salinity constraints.

The present study required the inclusion of soils exhibiting measurable variability in physicochemical attributes. The selected soils demonstrated limited to moderate variation in key properties known to directly or indirectly affect potassium extraction by different extractants. The set of soils represent the major soil groups of India, notably alluvial, red and black soils, which covered a range of physiographic conditions, climatic variability, parent materials, textural classes specially clay content and composition etc. Clay mineralogy of the experimental soils was not directly analyzed in the present study, which represents a methodological limitation. Nevertheless, a general understanding was inferred from previously published reports on soils from nearby locations. According to earlier literature, the red soils of Birbhum, Thrissur, Kollam, and Hazaribagh are predominantly kaolinitic, with illite occurring as the secondary mineral and only minor amounts of other clay minerals (Ghosh and Datta 1973; Paul *et al.,* 2024a; Kamarudheen *et al.*, 2025). The dominance of kaolinitic clay minerals reflects advanced stages of weathering, characterized by extensive leaching of easily hydrolysable bases and pronounced laterization (Papoulis *et al.*, 2004, Bertille Ilalie *et al.,* 2024). In contrast, the alluvial soils were dominated by illitic clay mineral, accompanied by appreciable amounts of kaolinite and minor proportions of other minerals such as smectite, vermiculite, and chlorite (Das *et al.,* 2021; Paul *et al.,* 2024b; Das and Barman 2025; Rezapour *et al.,* 2025). The black soils of India were characterized by a high clay content with the predominance of smectitic clay minerals, particularly montmorillonite, which impart distinctive physicochemical properties (Bhattacharyya *et al.,* 2025). The expansive nature, high surface area, and elevated cation exchange capacity of montmorillonitic clays strongly influence potassium dynamics by enhancing K retention on exchange sites (Simonsson *et al.,* 2009, Gurav *et al.,* 2024). These characteristics play a critical role in regulating K availability to plants, as smectitic clays can act both as reservoirs and sinks for K depending on soil moisture regimes and cropping intensity (Guo *et al.,* 2025). Consequently, the abundance of smectitic clay minerals in black soils has important implications for K buffering capacity and plant K nutrition, contributing to both short-term availability and longer-term K supply in these soils.

Potassium retention in soils is largely governed by the interactive effects of clay content, dominant clay mineral species, and cation exchange capacity (CEC), which together determine the extent of K fixation and its accessibility to chemical extractants (Sparks 1987). Soils enriched with high-CEC clay minerals tend to hold a greater proportion of K on surface exchange sites as well as within interlayer domains, thereby limiting its short-term extractability while contributing to sustained K supply for plant uptake. In contrast, soils with coarse texture and low clay content possess fewer exchange sites, leading to diminished K retention and consistently lower extractable K regardless of the strength of the extractant applied. Soil pH further influences these dynamics by shaping the composition of the exchange complex. Under acidic conditions (pH < 6.0), exchange sites are predominantly occupied by H^+ and Al^{3+} ions, with aluminium occurring as hydrated monomeric species $[Al(H_2O)^{3+}]$ or as polymeric hydroxy-aluminium complexes $[Al(OH)_x(H_2O)_{6-x}{}^{(3-x)+}]$ (Jackson 1973; Bohn *et al.*, 1979; Sumner and Miller 1996; Lato *et al.*, 2025).

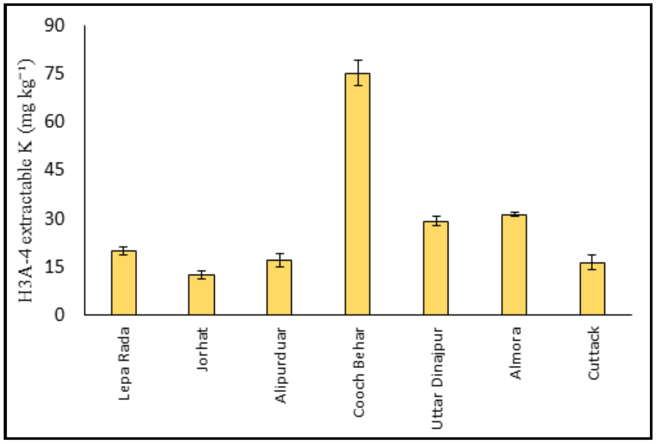

Fig. 1: Soil potassium (K) extracted by H3A-4 in acidic alluvial soils. Error bar represents standard deviation (SD, n=3).

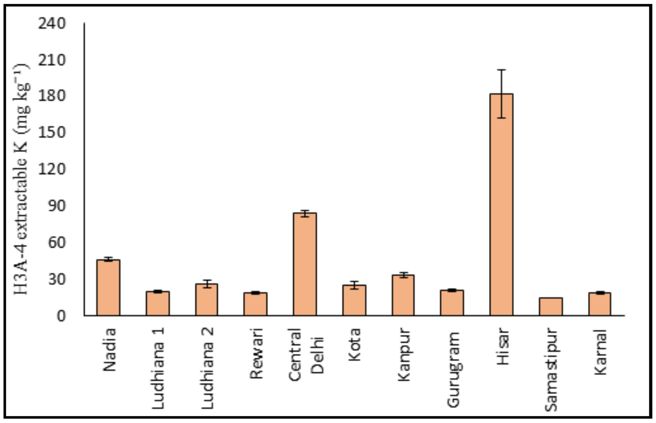

Fig. 2: Soil potassium (K) extracted by H3A-4 in non-acidic alluvial soils. Error bar represents standard deviation (SD, n=3).

These species modify cation-exchange equilibria and indirectly regulate K availability.

H3A-4 Extractable K content in soils

Substantial variability in potassium extraction was observed among the twenty-five experimental soils when categorized by soil type. In acidic alluvial soils, the range of H3A-4 extractable K varied from 12.5 mg kg^{-1} in Jorhat to 75.2 mg kg^{-1} in Cooch Behar, with a mean value of 28.8 mg kg^{-1} (Fig. 1). Non-acidic alluvial soils exhibited a wider range of extractable K, varying from 14.6 mg kg^{-1} in Samastipur to 181.2 mg kg^{-1} in Hisar, and recorded a higher average concentration of 44.4 mg kg^{-1} (Fig. 2). Black soils showed intermediate levels of H3A-4 extractable K, lower than those of non-acidic alluvial soils but higher than acidic alluvial soils, with values ranging from 33.4 mg kg^{-1} in Bhopal to 49.3 mg kg^{-1} in Nagpur and a mean of 38.7 mg kg^{-1} (Fig. 3). In contrast, red soils consistently exhibited the lowest levels of H3A-4 extractable K among all soil types, with concentrations ranging from 11.1 mg kg^{-1} in Kollam to 29.1 mg kg^{-1} in Hazaribagh and an average of 20.7 mg kg^{-1} (Fig. 4).

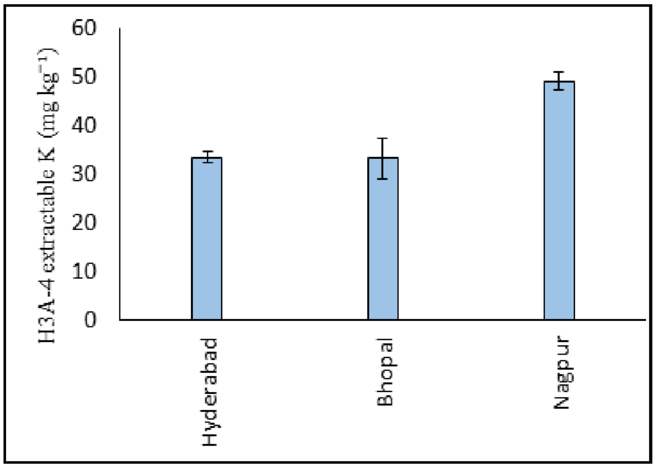

Fig. 3: Soil potassium (K) extracted by H3A-4 in black soils. Error bar represents standard deviation (SD, n=3).

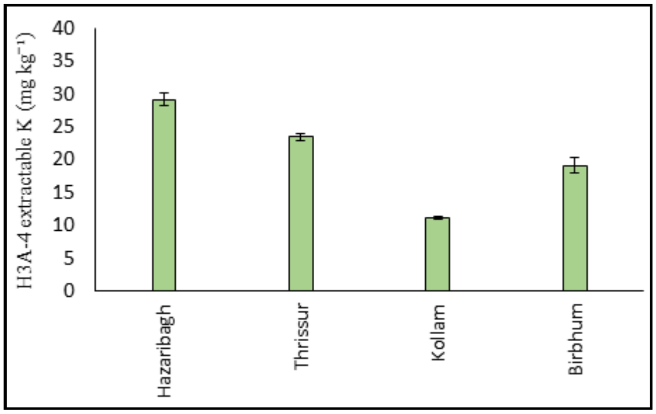

Fig. 4: Soil potassium (K) extracted by H3A-4 in red soils. Error bar represents standard deviation (SD, n=3).

The magnitude of K extraction by the H3A-4 extractant followed the order: non-acidic alluvial soils > black soils > acidic alluvial soils > red soils. On average, H3A-4 extractable K in acidic and non-acidic alluvial soils was approximately 1.39 and 2.14-fold higher, respectively, than that observed in red soils. Black soils likewise exhibited markedly greater K extractability, with values nearly 1.87 times higher than those recorded for red soils (Fig. 5). Statistical analysis revealed significant differences in H3A-4 extractable K among acidic alluvial, non-acidic alluvial, black, and red soils, clearly indicating distinct levels of K availability across these soil groups when evaluated using the H3A-4 extractant.

The consistently low K extraction in red soils, contrasted with substantially higher values in acidic alluvial, non-acidic alluvial, and black soils, highlights the influence of soil genesis, mineralogy, and weathering intensity on the size and accessibility of the labile K pool. Red soils, which are typically highly weathered and dominated by low-activity kaolinitic clays, possess limited cation exchange capacity and reduced K-bearing primary

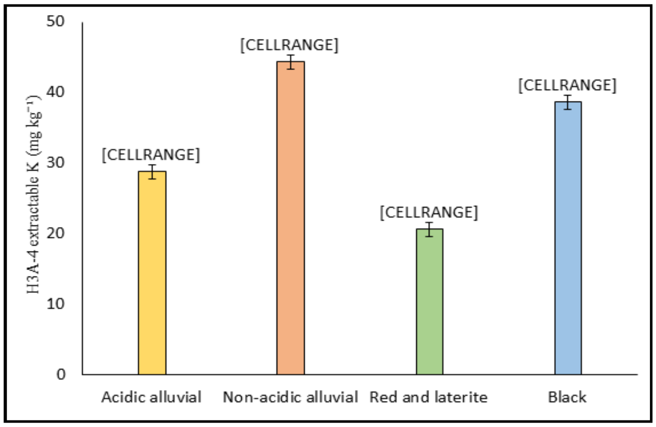

Fig. 5: Comparison of H3A-4 extractable potassium (K) among different soil types. values with no common letters are significantly ($p < 0.001$) different as per Tukey's HSD test. Error bar represents standard deviation (SD, n=3).

minerals, resulting in a restricted pool of extractable K (Okusami *et al.,* 1997; Muslim *et al.,* 2025). This explains the significantly lower H3A-4 extractable K values recorded for red soils compared with other soil types. In contrast, both acidic and non-acidic alluvial soils exhibited markedly higher K extractability, with non-acidic alluvial soils showing the widest range and significantly higher K extraction than acidic alluvial soils. These soils are generally characterized by younger pedogenic development, mixed mineralogy, and greater proportions of illite and other K-bearing minerals, which contribute to larger reserves of exchangeable water-soluble K (Kneževiæ *et al.,* 2025; Farpoor and Moazallahi 2025). The lower extractable potassium in acidic alluvial soils is primarily associated with the dominance of H^+ and Al^{3+} ions on the soil exchange complex at low pH. Under such conditions, hydroxy-aluminium species strongly compete with K^+ for exchange sites, thereby reducing the proportion of K held in readily exchangeable forms and limiting its release during chemical extraction (Jackson 1973; Sparks 1987; Sumner and Miller 1996). Consequently, both extractable and plant-available K are constrained despite the presence of total soil K reserves, highlighting the strong influence of soil acidity on K dynamics (Sparks and Huang 1985). Black soils also displayed relatively high H3A-4 extractable K, intermediate between non-acidic alluvial and acidic alluvial soils, consistent with their high clay content and dominance of smectitic minerals (Gidigasu and Gawu 2013). The expansive nature and high surface charge of smectitic clays enhance K retention on exchange and interlayer sites, providing both a buffering reservoir and a sustained source of plant-available K (Laird 2006). These findings indicate that H3A-4 is effective in mobilizing K from exchangeable and weakly bound pools across a broad range of soil environments, without being overly sensitive to soil reaction alone.

The variation in K recovery among soils was strongly governed by inherent soil characteristics, particularly texture, clay content, and the nature of the clay minerals present (McCarthy *et al.*, 2025). Fine-textured soils with higher clay content and greater cation exchange capacity (CEC) consistently released larger quantities of exchangeable K (Nigon and Kaiser 2025), reflecting the abundance of negatively charged colloids capable of retaining and exchanging K^+ . In contrast, coarse-textured soils with limited clay and low CEC exhibited uniformly low extractable K irrespective of extractant strength, illustrating the dominant control of soil physical properties on K availability (Das *et al.,* 2019; Singh *et al.,* 2025). Pedogenic factors and native soil K status further shaped the extraction patterns (Haensel 2025; Surjeet *et al.,* 2025). Soils with depleted K reserves, often due to prolonged cropping or limited primary mineral inputs, showed smaller differences between the different extraction methods, indicating a restricted pool of readily exchangeable K (Das *et al.,* 2022). Conversely, soils containing appreciable quantities of interlayer or edge-held K displayed larger divergences between extractants, reflecting their differing capacities to mobilize structurally bound or partially fixed K. These outcomes emphasize that the efficiency of H3A-4 extractant must be interpreted in relation to the soil's physicochemical framework (Hosseinpur and samavati 2008), as interactions between extractant chemistry, mineralogical composition, and exchange processes collectively determine the magnitude of K released (Sparks and Huang 1985; Simard *et al.,* 1992; Lee *et al.,* 2017).

Conclusion

Potassium extractability was primarily controlled by extractant chemistry, soil physicochemical and mineralogical properties. Potassium extraction by H3A-4 decreased in the order: non-acidic alluvial soils > black soils > acidic alluvial soils > red soils, reflecting the controls of higher clay content, dominance of illitic and smectitic minerals, and greater cation exchange capacity on K availability in these soils. Lower K extraction in red soils is consistent with their advanced weathering and prevalence of low-activity clay minerals.

Overall, the results demonstrate the strong potential of H3A-4 as an alternative extractant for assessing plant-available K across diverse Indian soils. Further validation through comparison with the conventional 1 M NH_4OAc (pH 7) method and direct relationships with crop K uptake is required to establish its suitability as a biologically relevant and routine soil testing extractant.

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