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# Potassium in Calcareous Soils and the Chemical Extractants Used to Evaluate It: A Critical Narrative Review of Availability Mechanisms and Soil-Test Performance

**Savreen Kaur [a*], Sumita Chandel [a] and Kuldip Singh [a]**

*[a] Department of Soil Science, Punjab Agricultural University, Ludhiana, Punjab, India.*

***Authors' contributions***

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

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**Abstract**

Calcareous soils occupy a substantial share of the cultivated land of arid and semi-arid regions, and their carbonate-buffered, calcium-dominated chemistry alters almost every process that governs potassium supply to crops. Soil-test procedures used to advise potassium fertilisation in these soils were largely inherited from temperate, carbonate-free systems, and their transfer has never been fully reconciled with the mineralogical and chemical peculiarities of carbonate-rich media. This review examines what the accessible literature establishes about potassium behaviour in calcareous soils and how reliably the principal chemical extractants represent plant-available potassium in that setting. Evidence was assembled from open scholarly indexes and appraised for design adequacy, calibration quality and interpretive transparency rather than for citation frequency alone. Four themes emerge. Mineral inheritance, in particular the abundance and particle size of micaceous minerals, exerts stronger control over potassium supply than does exchangeable potassium alone, and interlayer release is kinetically slow yet agronomically substantial. Neutral ammonium acetate, acidic multi-nutrient reagents and dilute salt solutions frequently correlate closely with one another in calcareous soils, and this mutual agreement has repeatedly been mistaken for agronomic validity. Extractants that engage the non-exchangeable pool, including boiling nitric acid, sodium tetraphenylboron, cation-exchange resins and organic acid mixtures, generally track plant uptake more closely in soils with appreciable interlayer reserves, although the advantage is inconsistent and

**Corresponding author: E-mail: savreenkaur02@gmail.com;*

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depends on clay mineralogy. Carbonate dissolution, sample drying, extraction ratio and analytical finish introduce method-dependent bias that is rarely quantified or reported. Confidence in current critical limits is limited by the scarcity of multi-season field calibration in genuinely calcareous soils, by the predominance of short glasshouse studies, and by narrow geographical representation. Priorities include mineralogically stratified field calibration, standardised reporting of extraction conditions, and evaluation of kinetic and diffusion-based indices against measured crop uptake rather than against other extractants.

*Keywords: Calcareous soil; potassium availability; soil testing; chemical extractants; non-exchangeable potassium; clay mineralogy; soil-test calibration.*

## 1. Introduction

Potassium is required by crops in quantities comparable with nitrogen, and it regulates stomatal behaviour, enzyme activation, phloem loading, osmotic adjustment and the tolerance of plants to drought, salinity and pathogen pressure. Despite this centrality, potassium has attracted markedly less analytical and policy attention than nitrogen or phosphorus, and the imbalance has been described as a systematic neglect within both agronomy and global change biology (Sardans & Peñuelas, 2015; Zörb et al., 2014). Global nutrient budget reconstructions indicate that potassium removal in harvested produce exceeds application across large parts of South Asia, sub-Saharan Africa and Latin America, so that soil reserves are being drawn down in the very regions where analytical capacity for monitoring them is weakest (Ludemann et al., 2024). Earlier regional budgets for intensive irrigated rice (*Oryza sativa* L.) systems reached the same conclusion and attributed apparent yield stagnation in part to unrecognised depletion of soil potassium-supplying power (Dobermann et al., 1996).

Calcareous soils concentrate these difficulties. The defining feature of such soils is the presence of free calcium carbonate, which imposes a pH plateau in the region of 7.5 to 8.5, saturates the exchange complex with calcium, and dissolves incongruently according to the partial pressure of carbon dioxide in the soil atmosphere (Olsen & Watanabe, 1959). Calcium carbonate is not chemically inert during soil analysis. Extraction with neutral salts at conventional soil-to-solution ratios dissolves part of the carbonate phase, releasing calcium that competes for exchange sites and alters the ionic strength of the extract, with measurable consequences for the estimated concentration of exchangeable cations (Carpena et al., 1972; Lalitha et al., 2026; Normandin et al., 1998; Pierce & Morris, 2004). Reagents developed for acidic soils, which rely on proton attack or on complexation of aluminium and iron, encounter a medium that neutralises acidity and buffers strongly against the chemical gradients on which those reagents depend. Recent mechanistic evidence is consistent with this analytical concern, indicating that carbonate can modify potassium adsorption and interfacial transport in calcareous soil rather than functioning as an inert background phase (Du et al., 2024).

The mineralogical inheritance of calcareous soils compounds the analytical problem. Soils of arid and semi-arid regions commonly retain appreciable quantities of mica and illite, together with smectite, vermiculite, chlorite and palygorskite, because limited leaching and low rainfall slow the weathering sequence (Najafi-Ghiri et al., 2011; Rezapour et al., 2009; Shakeri & Abtahi, 2018). Interlayer potassium held in these minerals is not measured by conventional exchangeable potassium procedures, yet it can supply a large fraction of crop uptake over a growing season through slow diffusive release (Datta, 2005; Havlin & Westfall, 1985; Jalali & Zarabi, 2006). Field observations that crops fail to respond to potassium fertilisation on soils classified as deficient by exchangeable potassium, and conversely that responses occur on soils classified as adequate, are difficult to reconcile with any model in which exchangeable potassium alone determines supply (Cassman et al., 1990; Khan et al., 2014; Kuchenbuch & Buczko, 2011). Recent depletion and mineral-specific extraction studies further support the importance of mineralogy in interpreting soil potassium: sustained potassium removal can alter potassium pools and clay-mineral characteristics, while reserve-potassium extractants can recover potassium preferentially from different K-bearing mineral domains (Das & Barman, 2025; Kurokawa et al., 2025).

A considerable body of primary work has addressed these questions, but it remains fragmented. Studies of potassium release kinetics in calcareous soils cluster heavily in western and southern Iran (Jalali, 2005, 2006, 2007; Najafi-Ghiri et al., 2011; Najafi-Ghiri & Abtahi, 2012), studies of extractant calibration cluster in North America and Europe (Barbagelata & Mallarino, 2013; Ferrando et al., 2020; Rogers et al., 2019; Zebec et al., 2017), and studies from South Asian calcareous soils are frequently published in outlets with limited international indexing (Kaur et al., 2024; Misal et al., 2020; Mondal et al., 2025). Reviews of potassium management published in the last decade have concentrated on global fertiliser strategy (Z. Xu et al., 2025), on biochar as a potassium source (Bilias et al., 2023), or on potassium within general plant nutrition (Zörb et al., 2014). None has taken the interaction between carbonate chemistry and extractant behaviour as its organising question, and none has systematically assessed whether the comparative extractant literature supports the critical limits currently in use for calcareous soils.

### 1.1 Scope, Research Gap and Objectives

This review is bounded by two intersecting criteria. It considers soils containing free calcium carbonate sufficient to buffer pH above neutrality, including calcareous Aridisols, Inceptisols, Entisols and calcic Vertisols of arid, semi-arid and sub-humid regions, and it considers the chemical and physical procedures used to estimate plant-available potassium in such soils. Mineral nutrition of potassium in strongly acidic, highly weathered or organic soils is treated only where a contrast clarifies the behaviour of carbonate-rich systems. Plant physiological regulation of potassium transport is addressed only to the extent that it bears on the interpretation of soil tests.

The unresolved problem addressed here is the persistent disconnection between the chemistry of the extractants in routine use and the chemistry that actually governs potassium supply in carbonate-rich soils. Comparative extractant studies are numerous, but they are dominated by correlations among reagents rather than by calibration against measured crop response, they rarely stratify soils by clay mineralogy, and they seldom report the extraction conditions in sufficient detail for the results to be reproduced or pooled. The consequence is a body of evidence that appears internally consistent while remaining agronomically weakly grounded. Recent

comparative evidence also indicates that extractant performance can vary with soil moisture status, reinforcing the need to report sample pre-treatment explicitly when methods are compared or calibrated (Singh et al., 2025).

Four objectives follow. The first is to synthesise what is established, and what remains contested, about the pools, transformations and kinetics of potassium in calcareous soils. The second is to set out the chemical basis of the principal extractants and to reason from that basis to their expected behaviour in a carbonate-buffered, calcium-saturated medium. The third is to appraise critically the comparative evidence on extractant performance, distinguishing agreement among methods from demonstrated agronomic validity, and to identify the methodological factors that generate apparently conflicting results. The fourth is to define research priorities capable of resolving those conflicts. Economic analysis of fertiliser policy, potassium in animal nutrition and human dietary potassium lie outside the scope of this article, as do soilless and hydroponic production systems.

## 2. Methods for Literature Selection

### 2.1 Review Design and Rationale

A critical narrative design was selected because the governing question concerns the interpretation and conceptual adequacy of measurement procedures rather than the magnitude of a single, consistently reported effect. The primary literature combines glasshouse pot experiments, exhaustive cropping trials, laboratory kinetic studies, mineralogical characterisations and a small number of multi-site field calibrations. Outcome variables differ across these designs, ranging from cumulative potassium uptake by successive crops to relative grain yield at a defined soil-test value, and extraction conditions differ in ways that are frequently unreported. Quantitative pooling under these conditions would impose an arithmetic uniformity that the underlying data do not possess and would obscure the methodological heterogeneity that is itself the object of analysis.

The narrative form does not remove the obligation of transparency. The conduct of this review was guided by established criteria for the quality of narrative review articles, which require an explicit statement of the review question, a described and reproducible approach to literature identification, and evidence-calibrated presentation of findings (Baethge et al., 2019; Ferrari, 2015). Sources were appraised individually, disagreements among studies are reported rather than reconciled, and the strength of each interpretation is stated alongside the interpretation itself.

### 2.2 Information Sources

Literature was identified through Crossref, AGRIS, the Directory of Open Access Journals, Europe PMC, Google Scholar and Semantic Scholar. Crossref was used for structured bibliographic retrieval and for verification of metadata, AGRIS and the Directory of Open Access Journals were used to capture agricultural and open-access titles with limited coverage in general indexes, and Europe PMC was used to identify work at the interface of soil chemistry and plant biology. Searching of scholarly indexes was supplemented by backward citation searching of retrieved articles, by forward citation tracking of highly cited methodological papers, by examination of the reference lists of recent reviews on potassium management, and by targeted searches of publisher landing pages and the Digital Object Identifier registry for verification of bibliographic details. Records identified through regionally oriented indexes were subjected to the same quality criteria as internationally indexed records, and those whose peer-review status or bibliographic details could not be confirmed were excluded.

### 2.3 Search Strategy and Search Period

Search concepts were constructed around four axes and combined with Boolean operators. The first axis captured the soil setting, using terms such as calcareous, calcium carbonate, carbonate-rich, arid, semi-arid, Aridisol and alkaline soil. The second captured the element and its pools, using potassium, exchangeable potassium, non-exchangeable potassium, interlayer potassium, potassium fixation, potassium release and potassium-supplying capacity. The third captured the measurement procedures, using extractant, soil test, ammonium acetate, Mehlich, ammonium bicarbonate-diethylenetriaminepentaacetic acid, sodium tetraphenylboron, boiling nitric acid, calcium chloride, cation-exchange resin, diffusive gradients in thin films and quantity-intensity relationship. The fourth captured agronomic outcome and interpretation, using plant uptake, crop response, critical level, calibration, correlation, fertiliser recommendation and clay mineralogy. A representative string combined the first three axes in the form: (calcareous OR "calcium carbonate" OR arid OR "semi-arid") AND (potassium AND (exchangeable OR "non-exchangeable" OR fixation OR release)) AND (extractant OR "soil test" OR "ammonium acetate" OR Mehlich OR tetraphenylboron OR "nitric acid"). Strings were adapted to the syntax of each index without altering the underlying concepts.

The search period extended from 1960 to 14 July 2026. The starting year corresponds to the introduction of sodium tetraphenylboron as a chemical means of extracting interlayer potassium, which marked the beginning of systematic attempts to measure the non-exchangeable pool by chemical rather than biological depletion. Foundational publications preceding that date were included where they were necessary to explain carbonate solubility, exchange theory or the historical development of exchangeable cation methodology.

### 2.4 Eligibility Criteria

Peer-reviewed original research articles and high-quality reviews published in indexed scholarly journals were eligible. Studies were required to report potassium measurements in soils containing free carbonate, or to report methodological evidence on extractant behaviour that could be interpreted for carbonate-rich soils, or to provide mechanistic or mineralogical evidence necessary for the synthesis. Eligible study types included field experiments, glasshouse and pot experiments, exhaustive cropping studies, laboratory

kinetic and equilibrium studies, and mineralogical characterisations accompanied by chemical measurements. Publications in English were included; non-English publications were included only where a verified English-language abstract and full bibliographic record allowed the reported findings to be represented accurately, and the resulting language restriction is acknowledged among the limitations of this review.

Excluded were publications whose bibliographic identity could not be confirmed, conference abstracts without accompanying full papers, trade and promotional material, non-scholarly commentary, patents, and preprints where peer-reviewed evidence on the same question was available. Studies reporting potassium determinations without any statement of the extraction procedure were excluded, as were studies in which the calcareous status of the soils could not be established from the reported carbonate content, pH or effervescence response.

### 2.5 Screening, Duplicate Handling and Study Selection

Titles and abstracts of retrieved records were examined against the eligibility criteria, and records passing this stage were assessed in full text where accessible. Where full text was inaccessible, inclusion depended on whether the abstract and bibliographic record contained sufficient methodological detail to support the specific claim for which the source would be cited; sources that did not meet this condition were set aside rather than cited on the basis of title relevance. Duplicate records arising from retrieval through more than one index were identified by matching Digital Object Identifiers and, where identifiers were absent or inconsistent, by matching author, title, journal and pagination. Records with more than one registered identifier for the same article were resolved to the identifier registered by the publisher of record. Because selection proceeded iteratively and was guided by conceptual saturation within each theme rather than by an a priori protocol, no screening counts are reported and no flow diagram is presented; to report such counts would misrepresent the selection process as systematic.

### 2.6 Critical Appraisal and Evidence Synthesis

Each included study was appraised against criteria appropriate to its design. For comparative extractant studies, the criteria were the number and provenance of soils, the range of carbonate content and clay mineralogy represented, whether an independent biological reference such as plant uptake or exhaustive cropping was used, whether extraction conditions were fully specified, and whether the analytical determination of potassium was described. For kinetic studies, the criteria were the adequacy of the extraction sequence, the range of times sampled, the justification of the fitted model, and whether kinetic constants were related to any independent measure of plant supply. For field experiments, the criteria were the number of site-years, the range of soil-test values represented, the presence of a genuine control, and whether response was evaluated against relative rather than absolute yield. No formal risk-of-bias instrument was applied, since no recognised tool exists for this literature and the reported information would be insufficient to support scoring.

Synthesis proceeded thematically. Evidence was grouped around the chemical and mineralogical controls on potassium supply, the chemistry of the extractants themselves, the comparative behaviour of those extractants in carbonate-rich soils, the methodological determinants of the values obtained, and the translation of measurements into recommendations. Within each theme, convergent findings were distinguished from contested ones, and where studies disagreed, the analysis examined whether the disagreement was attributable to soil mineralogy, to extraction conditions, to the reference measure of availability, or to the statistical treatment of the data.

## 3. The Calcareous Soil Environment as a Determinant of Potassium Behaviour

### 3.1 Carbonate Chemistry and the Ionic Environment of the Soil Solution

The chemical identity of a calcareous soil is set by the presence of a solid carbonate phase in equilibrium with the soil solution. Dissolution of calcite is governed jointly by the partial pressure of carbon dioxide and by the activity of calcium in solution, and the classical analysis of this equilibrium established that calcareous soils are not necessarily saturated with respect to pure calcite because of the influence of associated ions and of carbonate mineral impurity (Olsen & Watanabe, 1959). The practical consequence is a soil solution in which calcium activity is high and relatively insensitive to management, and in which pH resists downward displacement. Both properties act directly on potassium.

High calcium activity depresses the fraction of exchange sites occupied by potassium at any given quantity of exchangeable potassium, because the exchange equilibrium between a monovalent and a divalent cation shifts towards the divalent species as the total electrolyte concentration rises. Exchange studies conducted specifically on calcareous soils confirmed that the selectivity of the exchange complex for potassium relative to calcium differs from that observed in carbonate-free soils and varies with carbonate content (Al-Kanani et al., 1989). Potassium-calcium exchange in such systems cannot be represented adequately by a single selectivity coefficient, since the activity ratio at which the exchange complex neither gains nor loses potassium responds to the carbonate-controlled calcium activity as well as to the potassium status of the soil itself (Beckett, 1964; Jimenez & Parra, 1991).

Resistance to pH change constrains the rhizosphere mechanisms by which plants access sparingly available nutrients. In non-calcareous soils, proton extrusion and organic anion release can lower rhizosphere pH by more than one unit and accelerate mineral dissolution. In a carbonate-buffered medium, the same fluxes are neutralised by carbonate dissolution, so that acidification-dependent mobilisation is attenuated. The magnitude of this attenuation for potassium specifically has not been quantified directly in the available literature, which represents a gap in mechanistic understanding rather than evidence that the effect is absent.

**Table 1. Attributes of calcareous soils and their documented or inferred consequences for potassium behaviour and soil-test interpretation**

| Attribute of the calcareous environment | Principal consequence for potassium | Consequence for soil-test interpretation | Supporting references |
|---|---|---|---|
| Free calcium carbonate in equilibrium with the soil solution | High and management-insensitive calcium activity; potassium occupies a small share of exchange sites | Partial dissolution of carbonate during extraction alters extract composition and the estimated exchangeable cation concentrations | Carpena et al. (1972); Lalitha et al. (2026); Normandin et al. (1998); Olsen and Watanabe (1959); Pierce and Morris (2004) |
| pH buffered in the range of about 7.5 to 8.5 | Rhizosphere acidification is neutralised, attenuating acid-driven mineral dissolution | Acidic extractants are partly consumed by carbonate neutralisation, so the effective acidity acting on minerals is lower than nominal | Alva (1993); Mehlich (1984); Zhu et al. (2016) |
| Calcium-dominated exchange complex | Exchange selectivity for potassium relative to calcium differs from carbonate-free soils and varies with carbonate content | A single exchangeable potassium value carries a different intensity meaning than in non-calcareous soils | Al-Kanani et al. (1989); Beckett (1964); Jimenez and Parra (1991) |
| Retention of mica and illite because of limited leaching | Large interlayer reserve capable of slow diffusive resupply | Exchangeable potassium underestimates seasonal supply where mica is abundant; the degree of underestimation is mineralogy-dependent | Javan et al. (2025); Najafi-Ghiri et al. (2011); Rezapour et al. (2009); Shakeri and Abtahi (2018) |
| Mixed layer-charge characteristics in the clay fraction | Selectivity and reversibility of interlayer potassium retention vary with charge location | Extractant recovery of the mobilisable reserve differs between soils with similar clay content | Gurav et al. (2024) |
| Pronounced wetting and drying cycles under irrigated management | Release or fixation of interlayer potassium depending on prevailing exchangeable potassium status | Measured values depend on the moisture history of the sample and on pre-treatment before analysis | Schneider (1997); Shakeri and Abtahi (2020) |
| Frequent association with salinity and sodicity | Sodium and magnesium accelerate release of non-exchangeable potassium; magnesium is the more effective | Potassium measurements are conditioned by an ionic context that varies within and between seasons | Jalali (2008); Sameni and Morshedi (2000) |
| Low organic carbon | Limited organic contribution to exchange capacity and to ligand-assisted mineral attack | Extractants relying on organic complexation offer less advantage than in organic-rich soils | Poozesh Shirazi et al. (2024) |

*Note. Consequences described as inferred are those for which the mechanism is established in soil chemistry but has not been quantified specifically for potassium in calcareous soils*

Salinity and sodicity frequently accompany calcareousness in irrigated arid-zone landscapes, and they modify potassium behaviour through competing cations. Sodium and magnesium in the soil solution were shown to accelerate the release of non-exchangeable potassium in calcareous soils of western Iran, with magnesium exerting the stronger effect, an outcome attributed to the differing capacity of these cations to enter and expand mica interlayers (Jalali, 2008). Where sodicity is severe enough to impair structure, leaching behaviour changes as well, and the hydraulic response of calcareous soils to the composition of the percolating solution has been documented in detail (Sameni & Morshedi, 2000). These interactions mean that a potassium measurement made on a calcareous soil is embedded in an ionic context that varies between fields and between seasons.

### 3.2 Mineralogical Inheritance and the Origin of Potassium Reserves

Limited leaching in arid and semi-arid environments preserves primary and secondary potassium-bearing minerals that would be largely destroyed under humid weathering. Characterisation of calcareous soils across physiographic units in north-western Iran found illite to be the dominant clay mineral, with its abundance tracking closely the distribution of non-exchangeable potassium (Rezapour et al., 2009). Comparable work across a wide range of calcareous soils in the south of the country identified mica, and particularly mica in the silt and fine sand fractions, as the principal reservoir from which potassium is released, with vermiculite, smectite, chlorite and palygorskite present in varying proportions depending on parent material and degree of pedogenic development (Najafi-Ghiri et al., 2011; Shakeri & Abtahi, 2018). Recent mineralogical work in the Darab region reached the same conclusion and demonstrated that the distribution of potassium forms was explained better by the mica content of the clay and silt fractions than by any single chemical property of the bulk soil (Javan et al., 2025).

This inheritance has an important interpretive consequence. Two calcareous soils may carry identical exchangeable potassium concentrations while differing several-fold in their capacity to resupply the exchangeable pool during a growing season, because the

size and accessibility of their interlayer reserves differ. Studies partitioning potassium into water-soluble, exchangeable, non-exchangeable and structural fractions in arid-zone calcareous soils have shown that the non-exchangeable fraction commonly accounts for a minor share of total potassium but a major share of the potassium that is actually mobilisable on agronomic timescales, and that its magnitude varies systematically with microclimate and physiographic position (Poozesh Shirazi et al., 2024). Comparable patterns have been reported for the calcareous soils of Gujarat, where the distribution among potassium fractions was related to clay content, carbonate content and cropping history (Misal et al., 2020).

The influence of charge characteristics is equally consequential and is often overlooked. Work on Indian Vertisols demonstrated that the location of layer charge, whether tetrahedral or octahedral, together with the cation exchange capacity of the clay fraction, determined potassium availability more effectively than clay content alone (Gurav et al., 2024). Tetrahedral charge favours the strong, selective retention of potassium in interlayer positions; octahedral charge permits more ready exchange. Since calcareous soils of alluvial and Vertisol landscapes frequently contain mineral assemblages with mixed charge characteristics, the same chemical extractant applied to two such soils may recover very different proportions of the agronomically relevant reserve.

### 3.3 Organic Matter, Moisture Regime and the Consequences for Analysis

Calcareous soils of arid regions typically carry low organic carbon, which restricts both the cation exchange capacity attributable to organic surfaces and the supply of organic ligands capable of attacking mineral surfaces. Wetting and drying cycles are pronounced under irrigated arid-zone management, and they exert a direct and well-documented effect on the partition of potassium between exchangeable and interlayer positions. Drying of a moist soil at low exchangeable potassium tends to release interlayer potassium, whereas drying at high exchangeable potassium tends to fix it, an asymmetry demonstrated for temperate soils under controlled water contents (Schneider, 1997) and confirmed for highly calcareous soils subjected to alternate wetting and drying, where fixation capacity was shown to depend on the proportion of vermiculite and smectite present (Shakeri & Abtahi, 2020). The agronomic implication is that the potassium status registered by a soil test may reflect the moisture history of the sample as much as the intrinsic status of the field.

The combination of these features distinguishes the analytical problem in calcareous soils from that in the temperate, carbonate-free soils in which most routine methods were developed and calibrated. Table 1 summarises the principal attributes of the calcareous soil environment and traces each to its consequence for potassium behaviour and for the interpretation of soil tests. The table is intended to make explicit the chain of reasoning that links a soil property to an analytical artefact, since much of the disagreement in the comparative extractant literature can be traced to one or more of these links being overlooked in study design.

## 4. Potassium Pools and Transformations in Calcareous Soils

### 4.1 Operationally Defined Pools and their Interconversion

Soil potassium is conventionally partitioned into four pools: potassium in the soil solution, potassium held electrostatically on external exchange surfaces, potassium held in interlayer positions of micaceous and vermiculitic minerals, and potassium bound within the lattice of primary minerals such as feldspars and unweathered mica. The partition is operational rather than structural, since each pool is defined by the procedure used to recover it, and the boundaries between adjacent pools are therefore method-dependent rather than physically sharp. This point is frequently stated and as frequently neglected in practice, with the result that values described as exchangeable or non-exchangeable potassium are compared across studies that did not measure the same thing.

The solution and exchangeable pools equilibrate within minutes to hours, and together they represent the potassium immediately accessible to root uptake. The interlayer pool equilibrates with the exchangeable pool over days to months, through diffusion along interlayer channels whose rate depends on particle size, layer charge, the degree of interlayer collapse and the concentration gradient maintained by depletion at the mineral edge (Datta, 2005; Dhillon & Dhillon, 1990). Lattice potassium is released only through mineral weathering and contributes negligibly on agronomic timescales in most soils, although in coarse-textured calcareous soils derived from granitic or micaceous parent materials the contribution is not always trivial (Najafi-Ghiri et al., 2011).

Fixation, the reverse transfer from exchangeable to interlayer positions, is a distinguishing characteristic of many calcareous soils. Assessment of 48 calcareous soils from southern Iran found fixation to vary widely and to be governed principally by the content of vermiculite and smectite, by clay content, and by the moisture regime imposed during incubation, with cation exchange capacity and carbonate content exerting secondary influence (Najafi-Ghiri & Abtahi, 2012). Short-term studies on calcareous soils of western Iran showed that both release and fixation proceed simultaneously and that the net direction depends on the concentration of potassium in the equilibrating solution relative to a threshold characteristic of each soil (Jalali & Kolahchi, 2007). Applied potassium fertiliser added to a soil above this threshold is partly removed from the exchangeable pool within days, which explains why fertiliser recovery measured by a post-application soil test can appear low even where the potassium has not been lost from the profile. Cropping history modifies both fixation and adsorption behaviour: continuous cropping of calcareous soils in Iran altered the distribution among potassium forms and changed the adsorption characteristics of the soils, indicating that the capacity to retain applied potassium is not a fixed soil property but responds to management over years (Samadi et al., 2008). Where potassium fixation capacity is substantial, orchard management provides a further illustration: fixation and release were quantified under long-established orange (*Citrus sinensis*) cultivation on calcareous soils and were found to vary with depth and with the history of potassium application (Najafi-Ghiri et al., 2020).

Table 2 sets out the operational pools together with the procedures most commonly used to recover them and the interpretive meaning that can reasonably be attached to each. The distinctions it records underpin the analysis of extractant behaviour in Sections 6 and 7, because an extractant can only be evaluated sensibly against a statement of which pool it is intended to represent.

**Table 2. Operationally defined potassium pools, representative recovery procedures and interpretive meaning**

| Pool | Representative recovery procedure | Approximate equilibration timescale | Interpretive meaning and principal caveat | Supporting references |
|---|---|---|---|---|
| Soil solution potassium | Water or dilute calcium chloride extraction at a defined soil-to-solution ratio | Minutes | Represents intensity, that is, the concentration against which roots must compete; highly sensitive to soil moisture content at sampling | Baier and Baierova (1998); Salomon (1998); Zbíral and Němec (2005) |
| Exchangeable potassium | One mole per litre neutral ammonium acetate; ammonium chloride; Mehlich-3 | Minutes to hours | Represents the readily replenishable quantity; in calcareous soils the value is affected by carbonate dissolution during extraction | Alva (1993); Mehlich (1984); Normandin et al. (1998); Pierce and Morris (2004) |
| Non-exchangeable, interlayer potassium | Boiling one mole per litre nitric acid; sodium tetraphenylboron; sequential leaching; cation-exchange resin depletion | Days to months | Represents the reserve capable of resupplying the exchangeable pool during a season; recovery is strongly method-dependent and is not a fixed quantity | Cox and Joern (1997); Paul et al. (2024); Rao et al. (2000); Schulte and Corey (1965); Scott et al. (1960) |
| Lattice or structural potassium | Digestion with hydrofluoric acid or total elemental analysis, by difference from other pools | Years to millennia | Indicates long-term reserve and parent-material inheritance; agronomically inert in most but not all calcareous soils | Datta (2005); Najafi-Ghiri et al. (2011) |
| Potassium buffering, expressed as the quantity-intensity relationship | Equilibration of soil with a series of potassium concentrations in a calcium-magnesium background | Hours to days | Combines quantity and intensity into a description of resupply capacity; parameters depend on the background electrolyte chosen and on the equilibration period | Beckett (1964); Bilias and Barbayiannis (2019a); Hosseinpur and Tadayon (2013); Jimenez and Parra (1991) |

*Note. Timescales are indicative and vary with mineralogy, particle size and temperature. Procedures listed are representative rather than exhaustive*

### 4.2 Release Kinetics and the Problem of Model Selection

The rate at which non-exchangeable potassium becomes available has been studied intensively in calcareous soils, most often by repeated extraction with a sink solution such as calcium chloride, oxalic acid, sodium tetraphenylboron or a cation-exchange resin, followed by fitting of empirical rate equations. Early work of this kind on calcareous soils of Colorado established that release followed first-order and parabolic diffusion behaviour and that the rate constants were related to potassium uptake by successive crops of maize (*Zea mays* L.) (Havlin & Westfall, 1985). A companion analysis compared several candidate equations and concluded that the parabolic diffusion and first-order models described the data adequately while the zero-order model did not, a finding consistent with diffusion-controlled release from interlayer positions (Havlin et al., 1985).

Subsequent studies on calcareous soils of western Iran reported that the Elovich and power function equations generally provided the closest fits, that cumulative release over extended extraction sequences ranged widely among soils, and that release parameters correlated with potassium uptake by ryegrass (*Lolium perenne* L.) and with exchangeable and non-exchangeable potassium concentrations (Jalali, 2005, 2006; Jalali & Zarabi, 2006). Work extending to southern Iran, where mica content is higher, similarly favoured the Elovich equation and identified mica in the silt and fine sand fractions as the dominant control on the release rate (Najafi-Ghiri et al., 2011). Land use imposed a further difference, with cultivated soils releasing less potassium than adjacent uncultivated soils, consistent with historical depletion of the more accessible interlayer positions (Jalali & Khanlari, 2014).

The consistency of these results should not be overstated. Several equations of differing mechanistic content commonly fit the same release dataset with similar coefficients of determination, so goodness of fit provides weak evidence about mechanism. Reported rate constants are conditional on the sink solution, its concentration, the extraction temperature, the soil-to-solution ratio and the duration of the sequence, none of which is standardised across the literature. Studies that compare release constants obtained under different protocols therefore risk attributing to soil properties a variance that originates in method. The observation that release parameters correlate with plant uptake is more robust than the observation that a particular equation fits best, and it is the former that supports the agronomic relevance of the non-exchangeable pool. Spatial analysis of release behaviour across calcareous soils of western Iran demonstrated substantial field-to-field variability in release parameters, which further limits the transferability of rate constants determined on small soil sets (Jalali, 2007).

Amendments alter release behaviour in ways that complicate interpretation. Application of zeolite and vermicompost to calcareous soils increased cumulative potassium release, with zeolite acting through its own potassium content and exchange properties rather than through an effect on the soil minerals (Najafi-Ghiri, 2014). Biochar addition has been shown to increase exchangeable and

available potassium across a range of soils, an effect attributable largely to the potassium content of the biochar itself rather than to mobilisation of native reserves, and this distinction is frequently blurred in reporting (Bilias et al., 2023; L. Wang et al., 2018). In a calcareous soil, biochar and silica amendments altered the partition of potassium among fractions and its release into calcium chloride, hydrochloric acid and oxalic acid, with the response depending on the extractant used to characterise it (Najafi-Ghiri et al., 2025). Corn cob biochar applied to a calcareous sandy soil raised available potassium and wheat (*Triticum aestivum* L.) growth, although the experiment could not separate the contribution of biochar-borne potassium from any change in native supply (Abu Zied Amin, 2016).

### 4.3 Quantity-intensity Relationships and the Description of Buffering

The quantity-intensity approach characterises a soil by the relationship between the change in exchangeable potassium and the potassium activity ratio in an equilibrating solution, yielding a labile potassium quantity, an equilibrium activity ratio and a potential buffering capacity (Beckett, 1964). Applied to calcareous Vertisols and Inceptisols of south-western Spain, the approach discriminated soils that differed little in exchangeable potassium but substantially in their capacity to maintain solution potassium during depletion (Jimenez & Parra, 1991). Comparable analyses on calcareous soils of Iran related quantity-intensity parameters to bean (*Phaseolus vulgaris* L.) growth indices and found the equilibrium activity ratio and labile potassium to be the parameters most closely associated with plant response, although the correlations were moderate rather than strong (Hosseinpur & Tadayon, 2013; Zarrabi & Jalali, 2008).

Two extensions of the approach deserve attention. The first recognises that the non-exchangeable pool contributes to the quantity term when equilibration periods are extended, so that quantity-intensity parameters determined over hours and over days describe different systems; work on potassium-depleted soils demonstrated this contribution explicitly and showed that ignoring it leads to underestimation of buffering (Bilias & Barbayiannis, 2018). The second reframes the relationship in thermodynamic terms, deriving free energy of exchange parameters that proved more closely related to plant potassium uptake than the conventional graphical parameters (Bilias & Barbayiannis, 2019a). Recent applications have combined quantity-intensity parameters with machine learning to predict potassium uptake in calcareous soils of India, reporting that the combination outperformed either exchangeable potassium or quantity-intensity parameters alone (G. Mondal et al., 2026), and analogous analyses across soil types under natural and submerged conditions have emphasised the geogenic control on the parameters obtained (Ghosh et al., 2025).

The limitations of the quantity-intensity approach in calcareous soils are as instructive as its strengths. The background electrolyte conventionally used contains calcium and magnesium at concentrations chosen to approximate soil solution ionic strength in temperate soils, and its appropriateness in a carbonate-buffered system with high and variable calcium activity has not been established. Carbonate dissolution during equilibration modifies the calcium activity against which the potassium activity ratio is computed, introducing a systematic and unquantified bias. Long-term fertilisation alters the relationship in ways that are well documented for non-calcareous systems, with eight years of potassium application under double rice cropping producing marked shifts in labile potassium and buffering capacity (A. Islam et al., 2017), and comparable long-term evidence from calcareous soils is scarce. Evidence from highly weathered Australian soils, where buffering capacity was limited and crop supply depended heavily on the labile pool, provides a useful contrast that highlights how strongly the interpretation of these parameters depends on mineralogy (Cheng et al., 2025). Evaluation of the relationship in lowland rice soils has similarly emphasised that parameter values are conditional on the redox and moisture regime under which equilibration is performed (Chakraborty et al., 2025).

## 5. Plant Acquisition of Potassium in Calcareous Soils

### 5.1 Access to Non-exchangeable Reserves During Crop Growth

The agronomic significance of the interlayer pool rests on evidence that crops draw on it, not merely on evidence that chemical reagents can recover it. Exhaustive cropping studies provide the most direct evidence. Characterisation of a range of soils by successive cropping combined with chemical extraction demonstrated that the quantity of potassium removed by repeated crops greatly exceeded the initial exchangeable pool, and that the surplus corresponded in magnitude to the release of non-exchangeable potassium measured chemically (Datta, 2005). Studies employing cation-saturated resins as a sink in Alfisols, Vertisols and Inceptisols showed that release proceeded in two phases, a rapid initial phase followed by a slower diffusion-controlled phase, and that the transition point differed among mineralogical groups (Dhillon & Dhillon, 1990). Soils of the north-western Himalayan foothills released substantial non-exchangeable potassium under continuous removal, with the amounts released relating to illite content (Sharma et al., 2010).

In calcareous soils specifically, plant response studies have linked release kinetics to uptake. Kinetic constants determined by successive extraction of calcareous soils correlated with potassium uptake by plants grown on the same soils, and the correlation was generally stronger than that obtained with exchangeable potassium alone (Havlin & Westfall, 1985; Jalali & Zarabi, 2006). Release characteristics of native potassium reserves in calcareous soils of Iran were related to yield and potassium uptake, and the release parameters accounted for a larger share of the variation in uptake than did exchangeable potassium (Molavi et al., 2020). Work on wetland rice soils of Bangladesh, many of them calcareous, estimated that non-exchangeable potassium contributed a major proportion of total crop uptake over successive seasons and that the contribution increased as exchangeable potassium declined (S. Islam et al., 2023). Illitic soils maintained at their minimal exchangeable potassium were shown to retain a considerable replenishment capacity that was governed by clay mineralogy rather than by the residual exchangeable concentration (Rao & Khera, 1994).

The consistency of this evidence across regions and mineralogical settings makes the qualitative conclusion secure: in soils containing appreciable mica or illite, exchangeable potassium alone understates the seasonal supply. The quantitative conclusion is

far less secure. Estimates of the proportion of uptake derived from non-exchangeable sources vary from a minor fraction to the majority, and the variation reflects genuine mineralogical differences, differences in the intensity and duration of depletion imposed by the experimental design, and differences in whether a glasshouse pot or a field root system defines the volume of soil explored. Pot experiments, which dominate this literature, impose depletion intensities that exceed field conditions and therefore tend to maximise the apparent contribution of the interlayer pool.

### 5.2 Cation Competition and the Calcium-dominated Exchange Complex

Potassium uptake occurs from the soil solution, and its concentration there is set by the exchange equilibrium with the solid phase. In calcareous soils the exchange complex is dominated by calcium, with magnesium frequently important and sodium sometimes so. The classical treatment of potassium-calcium exchange showed that the potassium activity ratio, rather than the exchangeable potassium concentration, determines the intensity available to roots (Beckett, 1964). Exchange studies conducted on calcareous soils found that selectivity for potassium varied with carbonate content and that the relationship between exchangeable potassium and the activity ratio was not uniform across soils (Al-Kanani et al., 1989). A soil test that measures quantity alone therefore conveys different agronomic information in soils that differ in carbonate content, even when the measured quantity is identical.

Competing cations also affect the release of interlayer potassium. In calcareous soils of western Iran, the presence of magnesium and sodium in the extracting solution increased cumulative potassium release relative to a calcium background, with magnesium producing the larger effect, attributed to the greater hydration energy of magnesium and its consequent capacity to prise apart collapsed interlayers (Jalali, 2008). Under irrigation with waters of elevated sodium or magnesium content, which is common where calcareous soils are farmed intensively, the effective potassium supply may therefore differ from that predicted by a soil test performed with a conventional ammonium or calcium-based reagent.

### 5.3 Rhizosphere Processes and Crop Responses to Applied Potassium

Root-induced modification of the rhizosphere influences potassium acquisition. Potassium deficiency itself increases the release of soluble organic compounds from maize roots, altering the rhizosphere chemical environment and the associated microbial population (Kraffczyk et al., 1984). Microbial mobilisation of potassium from minerals has attracted substantial attention, and isolates capable of solubilising potassium from silicate minerals have been characterised and shown to increase potassium uptake under controlled conditions (C. Zhang & Kong, 2014). Extension of these findings to calcareous field soils requires caution. The mechanisms most frequently invoked, namely acidification and organic acid production, operate against a strong carbonate buffer, and the few reports of potassium-solubilising inocula applied to calcareous soils have generally been short-term pot studies without independent verification that native mineral potassium, rather than added or residual potassium, was the source of the measured increase.

Field evidence on crop response to applied potassium in calcareous soils is more limited than the volume of laboratory work would suggest, and it is not uniformly positive. Potato (*Solanum tuberosum* L.) grown on a calcareous soil in Pakistan responded to potassium application, and adsorption-based models combined with yield response functions were used to derive fertiliser rates that outperformed rates derived from exchangeable potassium alone (Hannan et al., 2011). Tomato (*Solanum lycopersicum* L.) grown on a calcareous soil in southern Florida showed yield responses that were better predicted by ammonium bicarbonate-diethylenetriaminepentaacetic acid and Mehlich-3 extraction than by conventional alternatives, although the calibration rested on a small number of site-years (Zhu et al., 2017). Against these, broader analyses of potassium fertiliser response have repeatedly found weak or absent relationships between conventional soil-test values and yield response across large datasets. Data-mining analysis of long-term European field experiments found that soil-test potassium explained only a modest share of the variation in response to applied potassium, and that the relationship deteriorated at higher soil-test values (Kuchenbuch & Buczko, 2011). A more far-reaching critique argued that the standard exchangeable potassium test has limited predictive value in many systems, that yield responses to potassium are less frequent than fertiliser recommendations imply, and that soil-test-based recommendations have in some settings encouraged application in excess of crop requirement (Khan et al., 2014). The critique has not gone unchallenged, and its generalisation to calcareous soils with substantial interlayer reserves is not straightforward; nonetheless it identifies a genuine weakness in the empirical basis of soil-test-driven potassium recommendation that the calcareous-soil literature has not addressed.

Simulation studies add a further dimension. Modelling of wheat growth response to potassium in sandy soils showed that subsoil potassium contributed materially to supply and that models based on topsoil measurements alone systematically underestimated availability (Scanlan et al., 2015). Since sampling in calcareous soils is almost universally confined to the plough layer, and since carbonate and mica content frequently increase with depth in calcic profiles, this source of underestimation is likely to be relevant but has not been quantified for calcareous systems.

## 6. Chemical Extractants: Principles, Chemistry and Expected Behaviour in Carbonate-Rich Media

### 6.1 Neutral Salt Methods and the Ammonium Acetate Standard

Extraction with one mole per litre ammonium acetate buffered at pH 7 remains the reference procedure for exchangeable potassium in most laboratories worldwide. The ammonium ion displaces potassium from exchange sites by mass action, and the acetate buffer holds pH near neutrality. In calcareous soils the buffer is not neutral in its effect on the solid phase. Acetate forms soluble complexes with calcium, and the buffering action maintains conditions under which calcium carbonate continues to dissolve during the extraction period, so that the extract contains calcium derived from the carbonate phase in addition to calcium displaced from exchange sites. The resulting overestimation of exchangeable calcium in calcareous soils is long established (Carpena et al., 1972),

and modifications of the procedure intended to suppress carbonate dissolution have been proposed, including the use of ammonium acetate pre-equilibrated with calcium carbonate and the adjustment of pH to match the soil (Normandin et al., 1998). Comparison of extraction techniques across a range of calcareous soils confirmed that the choice of procedure altered the estimated exchangeable cation concentrations appreciably, and that the discrepancy scaled with carbonate content (Pierce & Morris, 2004). Recent work quantified the effect directly, demonstrating that carbonate solubility during extraction with one mole per litre ammonium acetate influenced the estimation of exchangeable cations in calcareous soils and that the bias varied with the carbonate content of the sample (Lalitha et al., 2026).

Whether this bias materially distorts the potassium determination is a separate question from whether it distorts the calcium determination, and the distinction is often lost. Potassium is not a constituent of the carbonate phase, so carbonate dissolution does not add potassium to the extract directly. The effect on potassium is indirect: additional calcium in solution raises ionic strength and competes with ammonium for exchange sites, which can either enhance or suppress potassium displacement depending on the relative concentrations. The available evidence indicates that the net effect on measured exchangeable potassium is modest in most calcareous soils, but it has rarely been isolated experimentally, and the assumption that it is negligible has not been tested across the range of carbonate contents encountered in practice.

Alternative neutral salts avoid the acetate complexation problem. Ammonium chloride and ammonium nitrate displace potassium without forming strong soluble complexes with calcium, and comparisons across a wide range of soils found that ammonium chloride and ammonium acetate gave closely similar potassium values while differing more for calcium and magnesium (Alva, 1993). In southern Brazilian soils, ammonium acetate and ammonium chloride yielded potassium values that related similarly to maize uptake (Amorim et al., 2021). These findings suggest that for potassium specifically the choice among neutral salts is of second-order importance, a conclusion that holds for the soils tested but that has not been examined systematically across a carbonate gradient.

### 6.2 Acidic and Multi-nutrient Extractants

Mehlich-3, a dilute mixture of acetic acid, ammonium nitrate, ammonium fluoride, nitric acid and ethylenediaminetetraacetic acid, was developed as a general-purpose multi-element reagent and has been widely adopted because it permits simultaneous determination of phosphorus, potassium and several other elements from a single extraction (Mehlich, 1984). Its predecessor introduced the principle of a single reagent serving multiple nutrients (Mehlich, 1978). In calcareous soils the acidity of Mehlich-3 is partly consumed by carbonate neutralisation, so the effective proton activity acting on mineral surfaces is lower than the nominal formulation implies, and the extent of neutralisation increases with carbonate content. For phosphorus this is a recognised and serious limitation, since the reagent both dissolves calcium phosphates and permits their reprecipitation as the extract pH rises. For potassium the consequence is less severe, because potassium recovery by Mehlich-3 depends chiefly on the mass action of ammonium and nitrate rather than on acid attack. Comparative studies bear this out: Mehlich-3 and ammonium acetate potassium values correlated closely across diverse soils, including calcareous ones (Alva, 1993; Martins et al., 2015), and in calcareous soils of Florida, Mehlich-3 and ammonium bicarbonate-diethylenetriaminepentaacetic acid gave potassium values that were mutually consistent and related to crop response (Zhu et al., 2016, 2017).

This close agreement carries a hazard. Because the two reagents recover approximately the same pool by approximately the same mechanism, their agreement provides no evidence that either represents plant availability adequately. Studies reporting high correlation between Mehlich-3 and ammonium acetate as a demonstration of method validity confuse method equivalence with agronomic validity, and the distinction becomes important in soils where the interlayer reserve is large. A further caution concerns derived quantities: estimation of cation exchange capacity by summing Mehlich-3 cations diverges from ammonium acetate-based estimates in a systematic way, and the divergence was shown to be predictable from soil properties, which indicates that the two reagents do not extract from an identical population of sites (Mattila & Rajala, 2022).

Ammonium bicarbonate-diethylenetriaminepentaacetic acid was designed for calcareous and alkaline soils, using bicarbonate to maintain pH near 7.6 and the chelating agent to mobilise micronutrients. Its potassium determination rests on ammonium displacement and is therefore chemically analogous to ammonium acetate extraction, and studies in calcareous Florida soils found it to give potassium values comparable with Mehlich-3 (Zhu et al., 2016). Mehlich-1, a dilute mixture of hydrochloric and sulfuric acids, is conventionally regarded as inappropriate for calcareous soils because its acidity is largely neutralised by the carbonate phase, and comparative work across soils of contrasting reaction has reported it to behave anomalously relative to other reagents (J. J. Wang et al., 2004). That expectation is not universally borne out. In an evaluation of nine reagents on fifteen calcareous soils of Iran, potassium extracted by Mehlich-1 was among the measures significantly related to relative yield and to potassium uptake by pinto bean, whereas ammonium acetate and ammonium bicarbonate-diethylenetriaminepentaacetic acid were not (Hosseinpur & Zarenia, 2012). The result is difficult to reconcile with the neutralisation argument and is examined further in Section 7.

### 6.3 Exhaustive and Sink-based Methods for the Non-exchangeable Pool

Boiling one mole per litre nitric acid, applied for a defined period after removal of exchangeable potassium, is the most widely used estimate of the non-exchangeable pool. The procedure is empirical: it recovers interlayer potassium together with a variable and unquantified contribution from lattice sources, and the quantity recovered depends on the mode of boiling, the reflux arrangement and the duration. Systematic comparison of boiling modes demonstrated that the different arrangements in common use give significantly different values for the same soil, which compromises the comparability of published data (Rao et al., 2000). Because the method destroys the mineral structure that controls release in the field, the value it returns is best regarded as an index of reserve size rather than as a measure of the potassium that will actually become available.

**Table 3. Principal extractants for soil potassium: chemical basis, target pool and documented or expected behaviour in calcareous soils**

| Extractant | Chemical basis of potassium recovery | Target pool | Documented or expected behaviour in carbonate-rich soils | Supporting references |
|---|---|---|---|---|
| Ammonium acetate, 1 mol per litre, pH 7 | Mass-action displacement by ammonium; acetate buffers pH and complexes calcium | Exchangeable | Carbonate dissolution during extraction raises calcium and ionic strength; effect on measured potassium is indirect and generally modest but rarely isolated experimentally | Carpena et al. (1972); Lalitha et al. (2026); Normandin et al. (1998); Pierce and Morris (2004) |
| Ammonium chloride or ammonium nitrate | Mass-action displacement without strong calcium complexation | Exchangeable | Potassium values closely similar to ammonium acetate across diverse soils; avoids acetate-driven carbonate dissolution | Alva (1993); Amorim et al. (2021) |
| Mehlich-3 | Ammonium and nitrate mass action with dilute acid and chelation | Exchangeable, with a small non-exchangeable increment | Acidity partly neutralised by carbonate, so acid attack is weakened; potassium values correlate closely with ammonium acetate | Alva (1993); Martins et al. (2015); Mehlich (1984); Zhu et al. (2016) |
| Ammonium bicarbonate with diethylenetriaminepentaacetic acid | Ammonium displacement at buffered pH near 7.6 with chelation of micronutrients | Exchangeable | Designed for alkaline and calcareous soils; potassium determination chemically analogous to ammonium acetate | Zhu et al. (2016, 2017) |
| Mehlich-1 | Proton attack by dilute hydrochloric and sulfuric acids | Exchangeable in acid soils | Acidity largely neutralised by carbonate, so the reagent is conventionally judged inappropriate; evidence is nonetheless conflicting, with one calcareous-soil evaluation ranking it among the better predictors of plant uptake | Hosseinpur and Zarenia (2012); J. J. Wang et al. (2004) |
| Calcium chloride, 0.01 mol per litre | Equilibration at approximate soil-solution ionic strength | Solution potassium, an intensity measure | Discriminates among soils grouped together by quantity-based tests; absolute values far lower, so critical limits are not transferable | Baier and Baierova (1998); Salomon (1998); Zbíral and Němec (2005) |
| Boiling nitric acid, 1 mol per litre | Destructive dissolution of interlayer and part of lattice potassium | Non-exchangeable plus a variable lattice increment | Widely used as a reserve index; values depend strongly on the boiling arrangement and duration, limiting comparability | Rao et al. (2000) |
| Sodium tetraphenylboron | Precipitation of potassium maintains a near-zero solution concentration, driving interlayer diffusion | Non-exchangeable, time-resolved | Relates more closely to uptake than exchangeable potassium where interlayer reserves are appreciable; reagent cost and ammonium interference limit routine use | Bilias and Barbayiannis (2017); Cox and Joern (1997); Ferrando et al. (2020); Schulte and Corey (1965); Scott et al. (1960) |
| Cation-exchange resin, bag, capsule or membrane | Continuous sink without chemical attack on minerals | Exchangeable plus a contact-time-dependent non-exchangeable increment | Accesses both pools in proportions set by contact time and mineralogy; more sensitive than chemical extraction to soil moisture | Bilias et al. (2021, 2022); Dhillon and Dhillon (1990); Sherrod et al. (2002) |
| Sequential leaching with selected solutions | Repeated displacement approximating progressive crop depletion | Medium-term available pool | Recovered quantity is determined by the leaching solution chosen; tunable to approximate seasonal depletion | Paul et al. (2024) |
| Diffusive gradients in thin films | Diffusion-limited accumulation on a binding layer | Integrates intensity and resupply | In principle insensitive to carbonate dissolution artefacts; no evaluation in calcareous soils located in the accessible literature | Y. Zhang et al. (2013) |

*Note. Behaviour described as expected rather than documented is derived from the chemistry of the reagent and has not been tested directly across a carbonate gradient*

Sodium tetraphenylboron operates on a different principle. The tetraphenylborate anion precipitates potassium as an insoluble salt, maintaining a near-zero potassium concentration in solution and thereby imposing a strong and sustained concentration gradient that drives interlayer potassium outward. The approach was introduced for micaceous minerals and soils in a series of studies establishing that extraction proceeded through progressive expansion of the mineral edges and that the rate depended on mineral species and particle size (Schulte & Corey, 1965; Scott et al., 1960). Because extraction time can be varied, the method yields a kinetic profile rather than a single value, and release kinetics determined in this way have been related to soil potassium supply (Cox & Joern, 1997). Evaluation of the reagent as a practical soil test found that the potassium extracted over a short defined period related more closely to plant uptake than did exchangeable potassium in soils with appreciable interlayer reserves (Bilias & Barbayiannis, 2017), and a field comparison across contrasting soils found sodium tetraphenylboron competitive with, though not clearly superior to, ammonium acetate and Mehlich-3 (Ferrando et al., 2020). Practical obstacles have limited adoption: the reagent is costly, the precipitate must be dissolved before analysis, and ammonium and other monovalent cations interfere.

Sequential leaching and resin-based depletion occupy a middle position. A comparison of extractants applied in a sequential leaching mode to evaluate medium-term potassium availability found that the choice of leaching solution determined which portion of the reserve was recovered and that the sequence could be tuned to approximate the depletion imposed by a crop (Paul et al., 2024). Cation-exchange resins act as a continuous sink without chemical attack on the mineral, and their evaluation as a soil test for potassium-deficient soils showed that resin extraction accessed potassium from both exchangeable and non-exchangeable pools in proportions that depended on contact time and on soil mineralogy (Bilias et al., 2021, 2022). In calcareous soils of the Colorado Plateau, resin bags, capsules and membranes were compared directly with chemical extraction, and the methods diverged appreciably, with the resin-based measures more sensitive to soil moisture and the chemical extractions more reproducible (Sherrod et al., 2002).

### 6.4 Weak-electrolyte Methods and Diffusion-based Approaches

Dilute calcium chloride at 0.01 mole per litre approximates the ionic strength of many soil solutions and returns an intensity measure rather than a quantity measure. Calibration of the procedure against conventional potassium tests found systematic relationships but with soil-dependent offsets (Baier & Baierova, 1998), and comparison with official Swedish methods reached a similar conclusion, noting that the dilute salt extraction discriminated among soils that the conventional test grouped together (Salomon, 1998). A broad comparison of Mehlich-2, Mehlich-3, calcium acetate lactate, the Schachtschabel procedure, dilute calcium chloride and aqua regia found that the methods ranked soils similarly but differed greatly in the absolute quantities recovered, which has direct consequences for the transfer of critical limits between laboratories using different procedures (Zbíral & Němec, 2005).

Diffusive gradients in thin films represent a conceptually different approach, in which a binding layer separated from the soil by a diffusive gel accumulates potassium at a rate governed by resupply from the solid phase, so that the measurement integrates both intensity and buffering. The technique was optimised for simultaneous determination of potassium and available phosphorus in soils and shown to be feasible, although its application to potassium remains far less developed than for phosphorus and trace metals (Y. Zhang et al., 2013). No evaluation of the technique specifically in calcareous soils appears in the accessible literature, which is a notable omission given that the method is in principle insensitive to the carbonate dissolution artefacts that affect chemical extraction.

Table 3 draws together the principal extractants, the chemical basis on which each operates, the pool each is intended to represent, and the behaviour expected or documented in carbonate-rich media. The reasoning summarised there provides the framework for the appraisal of comparative performance that follows.

## 7. Comparative Performance of Extractants in Calcareous Soils: A Critical Appraisal

### 7.1 Agreement among Equilibrium Extractants and what it Does not Demonstrate

The most consistent finding in the comparative literature is that reagents recovering the exchangeable pool agree closely with one another. In soils of Uruguay spanning contrasting texture and clay mineralogy, Mehlich-3 and ammonium acetate potassium concentrations were very highly correlated, with ammonium acetate recovering slightly more potassium than Mehlich-3 (Ferrando et al., 2020). Comparisons across diverse soils including calcareous members reported similarly close agreement between ammonium acetate, ammonium chloride and Mehlich-3 for potassium, in contrast to the greater divergence observed for calcium and magnesium (Alva, 1993). Field-moist and oven-dry comparisons in the southern United States found Mehlich-3 and ammonium acetate potassium to track one another closely under each drying treatment, even though both responded to drying (Martins et al., 2015).

Broader comparisons across soil types reach similar conclusions, finding that chemical extraction methods rank soils consistently while differing substantially in the absolute quantities recovered (Zebec et al., 2017). The observation is not new; comparison of extractants for available potassium in Indian soils reported closely parallel rankings among reagents more than six decades ago (Oommen & Iswaran, 1962). This agreement is chemically unsurprising, since all these reagents recover potassium principally by mass-action displacement with a monovalent cation at comparable ionic strength. Its frequent presentation as evidence of method validity is a recurring interpretive error in this literature. Agreement among reagents that address the same pool by the same mechanism establishes interchangeability, not accuracy. The relevant test is agreement with an independent biological measure of supply, and where that test has been applied the picture is far less reassuring. In an evaluation of five procedures against potato response across 180 geo-referenced sites and a pot experiment in north-western India, ammonium acetate potassium correlated only

weakly with tuber yield and with potassium uptake, while ammonium bicarbonate-diethylenetriaminepentaacetic acid performed substantially better, and ammonium acetate showed essentially no relationship with nitric acid-extractable potassium (Pandher & Sekhon, 2024). The conclusion drawn there, that the ammonium acetate method requires reconsideration for the soils concerned, is difficult to avoid given the size of the dataset.

A further consequence of carbonate chemistry complicates the interchangeability of multi-nutrient reagents in calcareous soils. Comparison of extractants across alkaline calcareous soils of Idaho found that Mehlich-3 recovered large quantities of calcium once the inorganic carbon content exceeded a low threshold, and that correlation between Mehlich-3 and the ammonium acetate test deteriorated accordingly (Rogers et al., 2019). That deterioration was reported for calcium rather than for potassium, but it demonstrates that the assumption of stable proportionality between multi-nutrient and conventional reagents fails once carbonate content rises, and it counsels against transferring calibrations across reagents in calcareous soils on the basis of correlations established elsewhere.

### 7.2 Where Extractants Diverge: Engaging the Non-exchangeable Pool

Divergence among extractants appears once a reagent engages interlayer potassium. In the Uruguayan comparison, sodium tetraphenylboron recovered more potassium than either ammonium acetate or Mehlich-3, and the slope relating tetraphenylboron potassium to the other measures was steeper in fine-textured illitic soils than in coarse soils, indicating that the additional potassium originated from mineral interlayers rather than from external surfaces (Ferrando et al., 2020). The mineralogical dependence of this divergence is the essential point: the gap between an exchangeable-pool reagent and a reserve-engaging reagent is itself a soil property, and it is precisely the property that a single-value exchangeable test cannot convey.

Evidence that the additional potassium is agronomically real comes from studies using biological reference measures over more than one season. In nineteen Norwegian field experiments, potassium determined by procedures recovering exchangeable potassium or a subset of it, including dilute calcium chloride, sodium bicarbonate, ammonium acetate and ammonium acetate lactate, was significantly related to potassium yield in ley only in the first year after sampling, whereas potassium extracted by cold hydrochloric acid or by dilute nitric acid was significantly related to potassium yield in all three years (Øgaard & Krogstad, 2005). Extraction with the stronger boiling nitric acid solutions was related to yield only in the second and third years, consistent with the interpretation that it recovers a reserve that becomes available only after the readily exchangeable pool has been depleted. In Czech soils of low exchangeable potassium status, exhaustive cropping with perennial ryegrass released several times more potassium than the exchangeable extraction methods indicated, though appreciably less than the non-exchangeable methods recovered, and the best prediction of plant-available potassium was obtained with sodium tetraphenylboron and a stepwise extraction procedure (Madaras & Koubová, 2015). The relative content of mixed-layer phyllosilicates was significantly related to the quantity extracted by the soil tests, which locates the mineralogical basis of the divergence explicitly.

The consequences of extractant choice extend beyond the estimation of plant supply. Assessment of potassium leaching risk in calcareous soils was shown to depend on which extractant was used to characterise the soil, so that the same soils were ranked differently for environmental as well as agronomic purposes according to the reagent applied (Jalali & Jalali, 2022). Older calibration work points the same way. Across 72 Ontario soils evaluated against potassium uptake by four successive cuts of lucerne (*Medicago sativa* L.) in a glasshouse, nitric acid-extractable potassium gave the highest simple correlation with uptake, ahead of ammonium acetate, Mehlich-3, sodium chloride and ammonium bicarbonate-diethylenetriaminepentaacetic acid (Liu & Bates, 1990). When soil properties were admitted as additional predictors, the ranking changed and the ammonium acetate model performed comparably, which illustrates an important qualification: the apparent superiority of reserve-engaging reagents is partly a matter of the information they carry about mineralogy, information that can also be supplied by measuring the relevant soil properties directly. The practical question is therefore not solely which reagent is best, but whether a simple reagent combined with texture and mineralogical information can match a more elaborate one.

### 7.3 Conflicting Evidence within the Calcareous-soil Literature

Studies conducted specifically on calcareous soils do not converge. Evaluation of nine reagents against pinto bean response on fifteen calcareous soils of western Iran found that distilled water, dilute nitric acid, Mehlich-1 and dilute calcium chloride were significantly related to relative yield, plant response, plant potassium concentration and potassium uptake, whereas ammonium acetate, ammonium bicarbonate-diethylenetriaminepentaacetic acid, barium chloride, dilute hydrochloric acid and boiling nitric acid were not (Hosseinpur & Zarenia, 2012). A pot study on calcareous and non-calcareous soils of Punjab, India, evaluating the response of wheat to ten rates of applied potassium, reached an almost opposite ranking, identifying barium chloride as the reagent most closely correlated with plant response and deriving a critical limit for it by the Cate-Nelson procedure; the same study framed its rationale around concern that ammonium acetate overestimates potassium in calcareous soils (Kaur et al., 2024). Calibration of potassium rates for tomato on a calcareous soil in southern Florida concluded that water extraction was ineffective and that Mehlich-3 and ammonium bicarbonate-diethylenetriaminepentaacetic acid were both suitable for calibration, with high-status thresholds derived for each (Zhu et al., 2017). Evaluation of five multi-nutrient reagents against wheat on Inceptisols of West Bengal found Mehlich-3 to be the most suitable, with a critical limit higher than those derived for the other reagents (S. Mondal et al., 2025).

These are not minor differences of emphasis. Water extraction was among the best predictors in one calcareous-soil study and was explicitly rejected in another; barium chloride was the best predictor in one and among the poorest in another; ammonium bicarbonate-diethylenetriaminepentaacetic acid was recommended in two studies and rejected in a third. Several explanations deserve consideration, and they are not mutually exclusive.

**Table 4. Representative comparative evaluations of potassium extractants, showing setting, reference measure and principal reported outcome**

| Setting and soils | Reference measure of availability | Extractants compared | Principal reported outcome | Supporting references |
|---|---|---|---|---|
| Fifteen calcareous soils, Chaharmahal and Bakhtiari, Iran | Relative yield and potassium uptake by pinto bean in pots | Water, dilute and boiling nitric acid, hydrochloric acid, Mehlich-1, barium chloride, calcium chloride, ammonium acetate, ammonium bicarbonate-diethylenetriaminepentaacetic acid | Water, dilute nitric acid, Mehlich-1 and dilute calcium chloride were significantly related to plant measures; ammonium acetate, ammonium bicarbonate-diethylenetriaminepentaacetic acid, barium chloride, hydrochloric acid and boiling nitric acid were not | Hosseinpur and Zarenia (2012) |
| Calcareous and non-calcareous soils, Punjab, India | Wheat grain and straw yield and potassium concentration in pots at ten potassium rates | Several reagents including barium chloride and ammonium acetate | Barium chloride gave the closest correlation with plant response, and a critical limit was derived for it; the study was motivated by concern over overestimation by ammonium acetate in calcareous soil | Kaur et al. (2024) |
| Calcareous soil, southern Florida, United States | Marketable tomato yield across five potassium rates over two winter seasons | Water, Mehlich-3, ammonium bicarbonate-diethylenetriaminepentaacetic acid | Water extraction was ineffective; Mehlich-3 and ammonium bicarbonate-diethylenetriaminepentaacetic acid were both suitable for calibrating rates, with distinct high-status thresholds | Zhu et al. (2017) |
| Alkaline calcareous soils, Idaho, United States | Correlation among established regional tests | Ammonium acetate, Mehlich-3, and a further multi-nutrient reagent | Mehlich-3 recovered large quantities of calcium once inorganic carbon exceeded a low threshold, and its correlation with the ammonium acetate test deteriorated | Rogers et al. (2019) |
| Soils of contrasting texture and clay mineralogy, Uruguay | Comparison among methods, interpreted with texture and mineralogy | Ammonium acetate, Mehlich-3, sodium tetraphenylboron | Ammonium acetate and Mehlich-3 were very closely correlated; sodium tetraphenylboron recovered more potassium, with the excess greatest in fine-textured illitic soils | Ferrando et al. (2020) |
| Fourteen agricultural soils of low exchangeable potassium, Czechia | Exhaustive cropping with perennial ryegrass and the Neubauer seedling test | Eight methods spanning exchangeable and non-exchangeable pools | Plant-available potassium greatly exceeded exchangeable estimates but was well below non-exchangeable estimates; sodium tetraphenylboron and a stepwise procedure predicted best; mixed-layer phyllosilicate content was related to extracted quantities | Madaras and Koubová (2015) |
| Nineteen field experiments on mineral soils, Norway | Potassium yield in ley in each of three years after sampling | Calcium chloride, sodium bicarbonate, ammonium acetate, ammonium acetate lactate, hydrochloric acid, nitric acid at several concentrations | Exchangeable-pool methods predicted only the first year; dilute nitric acid and cold hydrochloric acid predicted all three years; boiling nitric acid predicted the second and third years only | Øgaard and Krogstad (2005) |
| Seventy-two soils, Ontario, Canada | Potassium uptake by four cuts of lucerne in a glasshouse | Sodium chloride, ammonium bicarbonate-diethylenetriaminepentaacetic acid, ammonium acetate, Mehlich-3, nitric acid | Nitric acid gave the highest simple correlation with uptake; with soil properties included as predictors, the ammonium acetate model performed comparably | Liu and Bates (1990) |
| One hundred and eighty field sites and a pot experiment, north-western India | Potato tuber yield and potassium uptake | Ammonium acetate, ammonium bicarbonate-diethylenetriaminepentaacetic acid, Mehlich-3, sodium tetraphenylboron, boiling nitric acid | Ammonium acetate correlated poorly with yield and uptake and showed no relationship with nitric acid-extractable potassium; ammonium bicarbonate-diethylenetriaminepentaacetic acid performed substantially better | Pandher and Sekhon (2024) |
| Twenty Inceptisols of recent alluvium, West Bengal, India | Dry matter yield, potassium concentration and uptake by wheat | Ammonium bicarbonate-diethylenetriaminepentaacetic acid, Mehlich-3, Morgan, modified Morgan, acid ammonium acetate, ammonium acetate | Mehlich-3 recovered the most potassium and related most closely to plant measures, with a higher derived critical limit than the other reagents | S. Mondal et al. (2025) |

*Note. Outcomes are reported as stated by the authors of each study. Differences in the reference measure, in the depletion intensity imposed, and in the range of soil-test values sampled limit direct comparison across rows*

The first is mineralogical. The soils differ in the size and accessibility of their interlayer reserves, and a reagent that recovers a fixed small increment of interlayer potassium will appear predictive where that increment is proportional to the mobilisable reserve and unpredictive where it is not. Mica content, particle size distribution of the mica, and layer-charge location all vary among these soil sets and were not characterised comparably across them (Gurav et al., 2024; Najafi-Ghiri et al., 2011).

The second is the reference measure. Relative yield in a pot experiment with a single species, potassium uptake by a leafy crop over successive cuts, and tuber yield in the field are different quantities with different sensitivities to supply rate as opposed to supply quantity. Intensity-oriented measures such as water or dilute calcium chloride extraction should be expected to perform relatively well where the crop response is limited by the rate of resupply, and relatively poorly where it is limited by the total quantity available. The depletion intensity imposed by a pot experiment is far higher than that imposed by a field crop, which systematically favours reagents that access the reserve.

The third is statistical. Many of these evaluations rest on small soil sets, commonly between ten and thirty soils, over which several reagents are compared. With that many comparisons and that few soils, differences in correlation coefficients between the best and the middling reagents are frequently within sampling error, and the identification of a single best reagent is not robust. Few studies report confidence intervals on the correlation coefficients or test whether the differences among reagents are statistically distinguishable.

The fourth is the range of soil-test values sampled. Where a soil set spans a narrow range of potassium status, correlations are attenuated for all reagents and their relative ranking becomes unstable. Where the set is deliberately chosen to span a wide range, correlations are inflated relative to what would be observed in a production setting. Neither design flaw is confined to the calcareous-soil literature, but both are common within it.

Table 4 assembles representative comparative evaluations, recording the setting, the reference measure and the principal outcome for each. Reading across the rows makes clear that the reference measure and the soil set, rather than the reagents themselves, account for much of the apparent disagreement.

### 7.4 Evidence Quality and the Design Limitations That Constrain Interpretation

Several weaknesses recur across this literature and together they set a ceiling on the confidence that current conclusions can bear. Glasshouse pot studies predominate, and although they permit tight control and repeated harvests, they impose root densities and depletion intensities that exceed field conditions by a wide margin, systematically favouring reagents that access the interlayer reserve. Field calibration studies conducted on genuinely calcareous soils are scarce; the tomato calibration in Florida rested on two winter seasons at one location (Zhu et al., 2017), and the potato study in north-western India, though unusually large in its sampling, combined a pot experiment with field validation at four sites (Pandher & Sekhon, 2024). Multi-site, multi-season calibration of the kind that underpins potassium recommendations for soybean (*Glycine max*) and maize in the central United States (Barbagelata & Mallarino, 2013; Slaton et al., 2010) has no counterpart for calcareous soils.

Mineralogical characterisation is inconsistently reported. Studies that quantify mica, illite and mixed-layer phyllosilicate content are able to explain divergence among extractants (Ferrando et al., 2020; Madaras & Koubová, 2015; Najafi-Ghiri et al., 2011), while studies that omit it can only report that reagents differed. Given that mineralogy is the principal determinant of the gap between exchangeable and mobilisable potassium, its omission removes the main explanatory variable from the analysis.

Extraction conditions are frequently underspecified. Soil-to-solution ratio, shaking time, temperature, filtration procedure and the analytical determination of potassium are all capable of altering the value obtained, and their omission prevents pooling of results across studies and makes apparent disagreements uninterpretable. The demonstration that different boiling arrangements for nitric acid extraction yield significantly different values on the same soils is a concrete illustration of the magnitude at stake (Rao et al., 2000).

Geographical concentration is pronounced. Work on potassium release kinetics in calcareous soils is dominated by studies from Iran, work on extractant calibration by studies from North America and Europe, and work on calcareous soils of South Asia is published substantially in outlets with limited international visibility. The consequence is that the two literatures most relevant to this review, on release kinetics and on calibration, have developed largely in different soil populations and have rarely been brought into contact within a single study.

Finally, publication practice favours the reporting of reagents that performed well. Studies reporting that no reagent predicted plant response adequately are uncommon, and their scarcity is more plausibly explained by selective reporting than by the uniform adequacy of soil tests. The broader analyses that have examined large response datasets without a prior commitment to a particular reagent have generally found weaker relationships than the comparative extractant literature implies (Khan et al., 2014; Kuchenbuch & Buczko, 2011).

## 8. Methodological Determinants of the Measured Value

### 8.1 Sample Pre-treatment and the Drying Artefact

Air-drying or oven-drying a soil sample alters the distribution of potassium between exchangeable and interlayer positions, and the direction of the change depends on the potassium status of the soil. The phenomenon was documented in Ontario soils more than six

decades ago, where drying changed exchangeable potassium and altered the relationship between the measured value and crop yield (Matthews & Sherrell, 1960), and the underlying mechanism was later clarified by controlled experiments showing release at low exchangeable potassium and fixation at high exchangeable potassium (Schneider, 1997). The practical significance for soil testing has been quantified in modern calibration studies. Field correlation of potassium soil tests for maize and soybean found that tests performed on field-moist samples related more closely to crop response than tests performed on dried samples, and that the improvement was greatest in soils where drying changed the measured value most (Barbagelata & Mallarino, 2013). Comparable work reported that Mehlich-3 and ammonium acetate potassium both differed between field-moist and oven-dry samples and that the magnitude of the difference varied among soils (Martins et al., 2015), and an evaluation across mid-Atlantic soybean soils similarly found that field-moist, air-dry and oven-dry determinations were not interchangeable (Williams et al., 2017).

For calcareous soils this issue is doubly important, because the pronounced wetting and drying cycles of irrigated arid-zone management mean that the field itself experiences the same process, and because fixation capacity in highly calcareous soils has been shown to depend on the vermiculite and smectite content and to be modified by alternate wetting and drying (Shakeri & Abtahi, 2020). Routine laboratory practice almost universally specifies air-drying, and the resulting values are therefore conditioned by an artefact whose magnitude is soil-specific and unreported. A partial remedy has been proposed in the form of reagents less sensitive to moisture history: a mixture of nitric acid and organic acids showed smaller deviation between field-moist and air-dried samples than conventional reagents, which if confirmed across a wider range of soils would reduce a substantial source of uncontrolled variance (Barman & Das, 2024).

### 8.2 Extraction Conditions and Carbonate Dissolution

The quantity of potassium recovered depends on the soil-to-solution ratio, the duration and vigour of shaking, the temperature and the number of extraction cycles. In calcareous soils an additional term enters, because the carbonate phase continues to dissolve throughout the extraction period. The extent of dissolution rises with the duration of contact, with the ratio of solution to soil, and with the complexing capacity of the anion present, which is why acetate-based reagents produce greater carbonate dissolution than chloride-based ones. Modification of the ammonium acetate procedure to suppress this dissolution, by pre-saturating the reagent with calcium carbonate or by adjusting its pH, has been proposed and evaluated (Normandin et al., 1998), and direct measurement has confirmed that carbonate solubility during extraction alters the estimated exchangeable cation concentrations in proportion to the carbonate content of the sample (Lalitha et al., 2026). Comparison of extraction techniques across calcareous soils found that the estimates obtained differed appreciably among procedures (Pierce & Morris, 2004), consistent with the earlier recognition that determination of exchangeable cations in calcareous soils requires procedures adapted to the presence of a soluble solid phase (Carpena et al., 1972).

**Table 5. Methodological determinants of measured soil potassium, their documented effects and their importance in calcareous soils**

| Methodological variable | Documented direction of effect | Relative importance in calcareous soils | Supporting references |
|---|---|---|---|
| Sample drying before extraction | Release of interlayer potassium at low exchangeable status and fixation at high exchangeable status; field-moist determinations relate more closely to crop response | High, because irrigated arid-zone soils experience pronounced wetting and drying in the field as well as in the laboratory | Barbagelata and Mallarino (2013); Martins et al. (2015); Matthews and Sherrell (1960); Schneider (1997); Williams et al. (2017) |
| Choice of displacing cation and accompanying anion | Acetate promotes carbonate dissolution through calcium complexation; chloride and nitrate do not | High for calcium and for extract ionic strength; consequences for potassium are indirect and not yet isolated | Alva (1993); Carpena et al. (1972); Lalitha et al. (2026); Normandin et al. (1998) |
| Soil-to-solution ratio and contact time | Greater dilution and longer contact increase carbonate dissolution and the recovery of slowly released potassium | High, and largely unreported in the calcareous-soil literature | Normandin et al. (1998); Pierce and Morris (2004) |
| Mode and duration of boiling in nitric acid extraction | Different boiling arrangements yield significantly different values on identical soils | High wherever reserve potassium is used as an index or as a calibration reference | Rao et al. (2000) |
| Contact time in sink-based and resin methods | Longer contact draws progressively on the interlayer pool, so the quantity recovered is a function of time rather than a fixed property | High, because the interlayer pool is large in mica-bearing calcareous soils | Bilias et al. (2021, 2022); Cox and Joern (1997); Sherrod et al. (2002) |
| Instrumental determination of potassium in the extract | Susceptibility to interference from calcium, magnesium and sodium differs among techniques | Moderate to high, given the high calcium loads in extracts from calcareous soils | Mattila and Rajala (2022); Rogers et al. (2019) |
| Soil moisture at the time of in situ measurement | Resin and membrane measures are more sensitive to moisture than chemical extraction | High for in situ approaches under irrigated arid-zone conditions | Sherrod et al. (2002) |

*Note. Relative importance is judged from the magnitude of reported effects and from the prevalence of the relevant condition in calcareous soils. Variables for which the direction of effect on potassium specifically has not been established are identified as such*

The effect of carbonate dissolution on the potassium determination specifically remains poorly characterised, as noted in Section 6.1. Because potassium is not a constituent of the carbonate phase, the effect operates through changes in ionic strength and in competing calcium activity rather than through direct addition, and its sign is not obvious a priori. The absence of a systematic study isolating this effect across a carbonate gradient is one of the clearest gaps in the analytical literature, and it undermines confidence in the transfer of critical limits derived on low-carbonate soils to highly calcareous ones.

### 8.3 Analytical Determination and Interference

The instrumental determination of potassium in the extract introduces a further source of divergence that is rarely discussed. Flame emission photometry, atomic absorption spectrometry and inductively coupled plasma spectrometry differ in their susceptibility to interference from the calcium, magnesium and sodium that dominate extracts from calcareous soils, and in their linear ranges. Extracts from multi-nutrient reagents applied to calcareous soils carry particularly high calcium loads, as the Idaho comparison demonstrated (Rogers et al., 2019), and matrix effects in such extracts are plausible. Differences between reagents in the population of exchange sites they address are further revealed when cation exchange capacity is estimated by summation, where Mehlich-3 and ammonium acetate-based estimates diverge systematically and predictably (Mattila & Rajala, 2022). Reporting of the analytical finish, of the dilution scheme and of any matrix modifier used is not standard practice in this literature, and its absence compounds the difficulty of interpreting differences among published results.

### 8.4 Reporting and Reproducibility

Taken together, the factors above define a set of variables that must be reported for a potassium determination to be interpretable and comparable. Table 5 lists them with the documented direction and approximate importance of their effects, and with the studies that establish each. The table is offered as a minimum reporting specification as much as a summary of evidence, since the principal obstacle to synthesis in this field is not the absence of data but the impossibility of aligning the data that exist.

## 9. From Measurement to Recommendation: Calibration, Critical Limits and Decision Support

### 9.1 The Logic and the Fragility of Critical Limits

A soil test acquires agronomic meaning only through calibration, that is, through an empirical relationship between the measured value and the relative yield or relative uptake achieved without added potassium. The critical limit is the value above which response becomes improbable, and it is a property of the combination of reagent, crop, soil population and yield criterion rather than of the soil alone. Several of the calcareous-soil studies examined here derived such limits, and the values reported are not commensurable because the reagents, the crops and the units of expression differ: thresholds were expressed on a mass basis for Mehlich-3 and ammonium bicarbonate-diethylenetriaminepentaacetic acid in a Florida tomato calibration (Zhu et al., 2017), on an area basis for barium chloride in a Punjab wheat study (Kaur et al., 2024), and on an area basis for Mehlich-3 in a West Bengal wheat study (S. Mondal et al., 2025). Direct comparison of the numerical values would be meaningless, and their coexistence in the literature without that qualification invites misapplication.

The stability of a critical limit depends on the buffering behaviour of the soils over which it was derived. The classical demonstration that the critical potassium level depends on potassium buffer power established that a single threshold cannot serve soils of differing buffering capacity, because the same exchangeable concentration sustains different solution concentrations during depletion (Mengel & Busch, 1982). This point has particular force in calcareous soils, where buffering derives substantially from interlayer reserves that the calibrating reagent does not measure. A limit derived on soils with abundant mica will be too low for soils without it, and conversely.

Evidence that calibration can be improved by explicit recognition of fixation capacity is available from outside the calcareous literature. Comparison of soil-test methods for predicting cotton (*Gossypium hirsutum* L.) response on potassium-fixing soils of California found that conventional exchangeable potassium was a poor predictor and that procedures accounting for fixation performed better (Cassman et al., 1990). The analogous exercise has not been conducted on calcareous soils with high fixation capacity, despite fixation having been characterised quantitatively in such soils (Najafi-Ghiri & Abtahi, 2012; Shakeri & Abtahi, 2020).

### 9.2 Balance-based and Model-based Alternatives

Where soil-test calibration is weak, nutrient balance provides an alternative basis for recommendation. Long-term experiments demonstrate that sustained potassium removal in excess of application depletes the soil reserve and that the depletion is registered more sensitively by non-exchangeable than by exchangeable measures. Analysis of a long-term fertiliser experiment under soybean and wheat on a Vertisol showed negative potassium balances under all treatments receiving no potassium and a progressive draw-down of soil reserves (Pathariya et al., 2022). Work in Chinese cropping systems identified critical potassium input rates required to sustain yield, potassium use efficiency and soil fertility simultaneously, deriving them from balance relationships rather than from soil-test thresholds (M. Xu et al., 2025). A synthesis of potassium management approaches argued that effective management requires joint consideration of soil potassium availability, crop removal and the resupply capacity of the soil rather than reliance on a single index (Z. Xu et al., 2025).

Mechanistic modelling offers a further route. Simulation of wheat response to potassium in sandy soils demonstrated that accounting explicitly for the vertical distribution of potassium and for root exploration improved prediction relative to topsoil

measurements alone (Scanlan et al., 2015). Combination of adsorption characteristics with yield response functions was used to derive potassium rates for potato on a calcareous soil, and the derived rates differed from those that exchangeable potassium alone would have indicated (Hannan et al., 2011). These approaches shift the burden of prediction from a single extraction to a description of the soil-plant system, which is more demanding in data but less vulnerable to the specific weaknesses of any one reagent.

## 10. Emerging and Complementary Approaches

Several developments offer the prospect of measurements that are less dependent on the arbitrary chemistry of a displacing reagent. Thermodynamic reformulation of the quantity-intensity relationship, yielding free energy of exchange parameters, related more closely to plant potassium uptake than the conventional graphical parameters and provided a physically interpretable description of the exchange system (Bilias & Barbayiannis, 2019a). Incorporation of potassium-fixing clay mineral content into a modified Mitscherlich formulation improved the description of potassium availability in potassium-deficient soils, which illustrates the general principle that mineralogical information carries predictive value that no single extraction can supply (Bilias & Barbayiannis, 2019b).

Sink-based approaches that impose a controlled depletion rather than a chemical displacement are conceptually better matched to the process by which roots acquire potassium. Cation-exchange resins evaluated as a soil test in potassium-deficient soils drew on both exchangeable and non-exchangeable pools in proportions determined by contact time and mineralogy, and gave promising relationships with plant measures (Bilias et al., 2021, 2022). Diffusive gradients in thin films integrate intensity and resupply within a single measurement and are in principle unaffected by carbonate dissolution, although the technique has been developed far more extensively for phosphorus and trace metals than for potassium and has not to date been evaluated in calcareous soils (Y. Zhang et al., 2013). Sequential leaching offers a practicable compromise, since the leaching solution and the number of cycles can be selected to approximate the depletion imposed by a crop over a defined period (Paul et al., 2024).

Spectroscopic and statistical approaches address a different constraint, namely the cost and throughput of conventional analysis. Prediction of exchangeable potassium from mid-infrared spectra using deep learning achieved useful accuracy and, importantly, the analysis identified the spectral regions on which the prediction depended, which permits the model to be examined for physical plausibility rather than accepted as a black box (Albinet et al., 2022). Spectral reflectance measurement was compared directly with chemical extraction for estimating available potassium in Ethiopian soils, providing an early demonstration of feasibility alongside conventional reagents (Demiss et al., 2020). Machine learning applied to quantity-intensity parameters in calcareous soils of India improved prediction of potassium dynamics and plant uptake relative to individual indices (G. Mondal et al., 2026), and analyses spanning soil types under contrasting moisture regimes have emphasised that the geogenic inheritance of the soil constrains what any such model can achieve (Ghosh et al., 2025). The principal caution attending all of these methods is that they are calibrated against conventional extractable potassium, so that a model predicting ammonium acetate potassium from a spectrum inherits whatever agronomic inadequacy that measurement carries. Calibration against plant uptake rather than against another soil test would be a more demanding and more informative test.

Management interventions that alter potassium availability constitute a related line of work. Biochar raises available potassium in a wide range of soils, and a synthesis of this evidence concluded that the effect derives substantially from the potassium content of the biochar itself, with the magnitude depending on feedstock and pyrolysis conditions (Bilias et al., 2023; L. Wang et al., 2018). Application of biochar and silica to a calcareous soil altered the partition of potassium among fractions and its release into several extracting solutions, with the apparent effect depending on which solution was used to observe it (Najafi-Ghiri et al., 2025). Zeolite and vermicompost increased cumulative release from calcareous soils, again largely through their own potassium content and exchange properties (Najafi-Ghiri, 2014). Microbial inoculation with potassium-solubilising organisms has shown promise under controlled conditions (C. Zhang & Kong, 2014), but its extension to carbonate-buffered field soils remains unsupported by evidence of the required quality, since the acidification mechanisms most commonly invoked are precisely those that a carbonate buffer neutralises.

## 11. Future Directions

The priorities set out here are ordered by the degree to which they would resolve the specific weaknesses identified in Sections 7 and 8, and they distinguish work that could be completed within a small number of seasons from work requiring longer commitment.

The most immediate priority is mineralogically stratified field calibration in genuinely calcareous soils. The central unresolved problem is that no reagent has been calibrated against multi-season field response across a soil population deliberately spanning a range of mica and illite content at comparable carbonate content. The evidence is inadequate because existing calibrations are based either on single-site field experiments over one or two seasons or on pot experiments whose depletion intensity does not correspond to field conditions, and because mineralogical characterisation is usually absent. The appropriate design is a multi-site, multi-season field experiment with potassium rates spanning deficiency to sufficiency, conducted across sites selected to span mica content and carbonate content independently, with relative yield as the response variable and with clay mineralogy quantified at every site. Cereal and tuber crops differing in rooting density and in potassium demand should both be represented, since the depletion intensity a crop imposes determines which reagent will appear predictive. The immediate output would be reagent-specific critical limits conditioned on mineralogy rather than a single national threshold, and the practical consequence would be recommendations that no longer misclassify mica-rich soils as deficient.

The second priority is the isolation of the carbonate dissolution effect on the potassium determination itself. Current evidence establishes that carbonate dissolution during extraction alters the estimation of exchangeable calcium and magnesium, and it is assumed rather than demonstrated that the consequence for potassium is negligible. A controlled experiment using soils of identical mineralogy amended with graded quantities of calcium carbonate, extracted under systematically varied ratios, contact times and anion compositions, would establish the sign and magnitude of the effect across the carbonate range encountered in practice. The work is straightforward, requires no field commitment, and would either justify current practice or identify a correction that could be applied retrospectively to existing datasets.

The third priority concerns the reference measure against which extractants are judged. Much of the apparent conflict within the calcareous-soil literature arises because reagents are compared against different biological endpoints under different depletion intensities. A coordinated protocol in which the same soil set is evaluated simultaneously by exhaustive cropping, by a single-season pot experiment and by field response would quantify the extent to which apparent extractant performance depends on the reference measure. Such a study would not require novel methods, only the discipline of applying several established ones to a common soil set, and it would allow the existing literature to be reinterpreted rather than merely added to.

The fourth priority is the evaluation of diffusion-based and sink-based measurements in carbonate-rich soils. Diffusive gradients in thin films integrate intensity and resupply and are in principle insensitive to the carbonate dissolution artefact, yet no evaluation in calcareous soils appears in the accessible literature. Cation-exchange resins have been evaluated in temperate potassium-deficient soils but not systematically in calcareous ones. The appropriate study would compare these approaches against plant uptake across a calcareous soil series spanning a range of interlayer reserve, over a time course sufficient to characterise resupply rather than a single equilibrium point. The outcome would determine whether the additional cost and complexity of these methods is justified by improved prediction, a question that current evidence cannot answer.

The fifth priority is standardisation of reporting. The obstacle to synthesis in this field is not a shortage of studies but the impossibility of aligning them. A minimum reporting specification covering soil-to-solution ratio, contact time and temperature, sample pre-treatment and moisture status, the analytical determination and its calibration, and the carbonate content and clay mineralogy of the soils, would make future comparative studies poolable. Table 5 identifies the variables that such a specification should cover. Adoption would require coordination among journals and method standardisation bodies rather than new research, and its effect on the cumulative value of the literature would be considerable.

Two longer-term priorities complete the list. Subsoil contribution to potassium supply in calcic profiles has not been quantified, although evidence from sandy soils indicates that topsoil sampling systematically underestimates availability where subsoil reserves are accessible, and carbonate and mica content commonly increase with depth in calcic horizons. Characterisation of this contribution would require deep sampling combined with root distribution measurement over several seasons. Separately, the interaction between potassium availability and the ionic composition of irrigation water in calcareous soils deserves systematic attention, given established evidence that sodium and magnesium accelerate interlayer release. Where irrigation waters of contrasting composition are applied to comparable soils, the effective potassium supply may diverge from soil-test predictions in a manner that is currently unaccounted for in any recommendation system.

## 12. Conclusions

The behaviour of potassium in calcareous soils is governed more by mineral inheritance than by the size of the exchangeable pool. Across studies from Iran, India, Bangladesh, the Czech Republic, Norway, Canada and the United States, the evidence converges on the conclusion that soils containing appreciable mica, illite or mixed-layer phyllosilicates supply substantially more potassium to crops over a season than exchangeable potassium indicates, and that the magnitude of this excess is a mineralogical property that a single-value exchangeable test cannot convey. This conclusion is well supported and is the most secure finding of the present synthesis.

The corresponding conclusion about measurement is more qualified. Reagents that recover the exchangeable pool agree closely with one another, and this mutual agreement has repeatedly been offered as evidence of validity when it establishes only interchangeability. Reagents that engage interlayer potassium, including dilute and boiling nitric acid, sodium tetraphenylboron, cation-exchange resins and sequential leaching procedures, relate more closely to plant uptake in several well-designed studies, particularly where the assessment extends beyond a single season. The advantage is nonetheless inconsistent, and studies conducted specifically on calcareous soils have reached mutually contradictory rankings, with water, dilute calcium chloride, Mehlich-1, barium chloride, Mehlich-3 and ammonium bicarbonate-diethylenetriaminepentaacetic acid each identified as the preferred reagent in one study and rejected in another. That pattern of contradiction is itself informative: it indicates that no reagent possesses general superiority and that performance is conditional on soil mineralogy, on the crop and depletion intensity used as the reference, and on the range of soil-test values sampled.

Analytical practice introduces a layer of variance that is largely unacknowledged. Sample drying alters the measured value in a direction that depends on the potassium status of the soil, and field-moist determinations relate more closely to crop response. Carbonate dissolution during extraction demonstrably alters the estimation of exchangeable cations, and the assumption that potassium escapes this influence has not been tested. The boiling arrangement used in nitric acid extraction changes the value obtained on identical soils. Because these conditions are inconsistently reported, differences among published studies cannot reliably be attributed to soil properties rather than to method.

The practical implication is that critical limits for potassium in calcareous soils rest on a thinner empirical base than their routine use implies. Thresholds derived from single-site, single-season or pot-based calibrations are being applied across soil populations that differ in exactly the property, interlayer reserve, that determines whether the threshold is appropriate. Interim practice would be better served by interpreting exchangeable potassium alongside a measure of reserve potassium and an indication of clay mineralogy or texture, and by recognising that a recommendation derived from a single extraction carries greater uncertainty in a mica-bearing calcareous soil than the precision of the analytical value suggests. The broader significance of this synthesis lies in the recognition that the difficulty is conceptual rather than analytical: the measurement problem in calcareous soils will not be solved by a better reagent alone, but by calibration designs that treat mineralogy as a variable rather than as unexplained residual variation.

## 13. Limitations

This article is a narrative rather than a systematic review, and it therefore carries the interpretive and selection biases intrinsic to that form. Although the search concepts, sources and eligibility criteria were stated explicitly and applied consistently, the selection of studies proceeded iteratively and was guided by thematic saturation, so it is possible that relevant work was not identified and that the studies emphasised reflect the framing adopted here. No screening counts are reported, and none should be inferred, because the process was not a systematic one.

Access to subscription-based indexes was not available, and the literature was identified through open scholarly indexes and citation tracking. Work indexed exclusively in subscription databases, and work published in journals without registered persistent identifiers, may therefore be under-represented. The restriction to publications with verifiable English-language records introduces a further bias, and it is likely to have reduced the representation of research from calcareous-soil regions of Central Asia, North Africa, the Middle East and Latin America, where substantial relevant work is published in languages other than English.

Heterogeneity in the underlying studies prevented quantitative synthesis. Extraction conditions, reference measures of availability, crop species, depletion intensities and units of expression differ so widely that pooling of correlation coefficients or of critical limits would have produced a spurious precision. Numerical values reported by individual studies are therefore presented as reported and are not combined. Comparability among studies is further limited by the inconsistent characterisation of clay mineralogy and carbonate content, which are the variables most likely to explain divergence.

The evidence base is geographically uneven. Work on potassium release kinetics in calcareous soils is concentrated in a small number of regions, and work on extractant calibration is concentrated in others, so the two lines of evidence have rarely been combined within a single soil population. Reliance on glasshouse and pot experiments is heavy throughout, and long-term field evidence from calcareous soils is scarce, which limits confidence in conclusions about seasonal and inter-seasonal supply. Publication bias towards reagents that performed well is probable and cannot be quantified from the available information. Finally, the emerging methods discussed are represented by small numbers of studies, several of them methodological demonstrations rather than agronomic evaluations, and conclusions about their promise are correspondingly provisional.

## Declaration of AI Use

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## Competing Interests

Authors have declared that no competing interests exist.

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