

## Subject 28

Experimental and research work  
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### Application of Potassium 40 and Potassium 42 in Agronomic Research

(L'utilisation du potassium 40 et potassium 42 en Agronomie)

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#### Summary

In this survey of the literature, the author reviews the chief studies in agronomic science, prior to 1967, made with the aid of the isotopes  $^{40}\text{K}$  and  $^{42}\text{K}$ . He concludes with suggestions for further experimentation likely to yield useful information for agronomists seeking to understand the problems of fertilization.

#### Introduction

In agronomy, as in other areas of research, radioelements may be employed for a variety of purposes. The effects of nuclear radiation can be of practical use in several ways, amongst these being the induction of mutations, preservation of foods, sterilisation of insects, and moisture measurement by the neutron probe.

Isotopes (radioactive or not) can be employed as tracers, notably as indicators of origin so that we may discover what befalls an element introduced into a medium that already contains the same element, but in a different isotopic form. The radioactive isotopes are particularly convenient here on account of the ease with which they can be detected.

In particular, plant breeding, entomology, and animal technology have benefitted greatly from the aid of these techniques. The present paper is concerned with summarising the results obtained with radioactive potassium in research in agronomy.

#### I. The isotopes of potassium

Potassium, a monovalent alkali metal of atomic weight 39.100, occurs in nature in the form of a mixture of three isotopes,  $^{39}\text{K}$ ,  $^{40}\text{K}$  and  $^{41}\text{K}$ . The two commoner ones,  $^{39}\text{K}$  (93.1 per cent abundance) and  $^{41}\text{K}$  (6.9 per cent) are stable, the third one  $^{40}\text{K}$  (0.012 per cent) being radioactive.

Other radioisotopes of potassium can be produced in atomic reactors. These are  $^{37}\text{K}$  (half-life 1.2 seconds),  $^{38}\text{K}$  (7.7 minutes),  $^{42}\text{K}$  (12.4 hours),  $^{43}\text{K}$  (22 hours),

$^{44}\text{K}$  (22 minutes), and  $^{45}\text{K}$  (34 minutes). The chief form of emission from these is  $\beta$ -rays.

The small quantities produced, the difficulties of separating them out and the short-lived character of most of the potassium isotopes leave us with the situation in which  $^{40}\text{K}$  and  $^{42}\text{K}$  are practically the only ones actually employed in agronomic research.

$^{40}\text{K}$  has a very long half-life ( $1.3 \times 10^9$  years) so that rather large amounts of it have to be introduced into the system being examined. For many purposes, this creates problems in its use. It is also very expensive (enriched to 30 to 55 per cent  $^{40}\text{K}$ , a milligram of potassium costs about 200 dollars). It gives out 11 per cent of gamma-radiation and 89 per cent of beta-radiation, being transmuted ultimately into  $^{40}\text{Ca}$ .

$^{42}\text{K}$  by contrast has a short existence (half-life 12.4 hours), limiting its use to experiments of brief duration (of the order of about one week at most). It emits 18 per cent of gamma-radiation and 82 per cent of beta. All in all, potassium has no radio-isotope that is really convenient to use, and no doubt this is the reason why it has been relatively little employed. Both a very long half-life and a too short half-life, force the experimentalist to bring a substantial dose of carriers into play, and this is likely to alter the dynamics of the element in question within the system being studied.

Chemically, potassium resembles the alkali metals of higher atomic weight, namely rubidium (85.5) and caesium (133). The radioactive isotopes of these being easier to use than those of potassium, a number of workers have hoped to use them in studying the dynamics of the latter (5, 6, 9, 10, 16, 28, 111). Rubidium is the only one suited for further attention in this field.

## II. General aspects of potassium

In the soil, the ions of an element, although all of the same kind may occur in different states:

- dissolved in the free water of the soil,
- held on solid particles, or within them, but capable at the given moment of diffusing into the free solution;
- firmly held in the solid phase and for the time being not diffusible, or only very slowly diffusible.

To define the fractions of K ions present in each of these states, and the possibilities of transition and rates of passage from the one to the other, is one of the problems dominating the dynamic of soil potassium.

Inside the plant, potassium (K) accounts for 20 to 40 per cent of the ash. Many aspects of its role in the plant are still only poorly understood. It has an important effect in photosynthetic assimilation of carbon and in the translocation of carbohydrates. In consequence of the latter function, potassium influences the distribution of the products of photosynthesis among the various organs of the plant, and hence their relative growth (e.g., ratio of roots to foliage; tillering index). Potassium also intervenes in nitrogen metabolism, including protein synthesis. It plays a part in regulating transpiration and hence the water balance of the plant. In certain crops a relation has been found between potassium nutrition and resistance to cold or to fungal diseases.

### III. The practical use of $^{40}\text{K}$ and $^{42}\text{K}$

#### A. Methodology, and analytical considerations

The necessary technique for counting  $^{42}\text{K}$  in presence of other radioelements, particularly by the use of selective screening, has been developed and published (14). A scintillation apparatus for localised counting, suitable for following *in vivo* the migration inside the plant of  $^{42}\text{K}$  added to the medium, has been developed (26). There have also been studies of special features of  $^{42}\text{K}$  utilisation connected with its short life, notably the possibility of replacing  $^{40}\text{K}$  by  $^{42}\text{K}$  in studying the absorption and release of K by minerals (96).

The radioactivity of  $^{40}\text{K}$  has been used in estimating the natural (that is to say isotopically normal) potassium content of fertilizers, soils, and plants, and also in following by autoradiography the movement of K out of the germinating seed into the young plant.

The radioactivity due to the  $^{40}\text{K}$  component of ordinary potassium has to be allowed for in studying other sources of radioactivity in soils and plants (25, 46, 76, 87, 88, 89, 138, 139, 150);—one milligram of ordinary, naturally occurring potassium is the site of 2.01 disintegrations per minute. The isotope  $^{42}\text{K}$  has been used in studying the kinetics of ion exchange in resins (7–20), losses of K from silicates by volatilisation (21), and the transport of K ions in electrophoresis (67).

#### B. Potassium and the soil

One of the chief possibilities that isotopes offer is the study of the diffusibility of ions held in the solid phase (72, 85). Through use of radiopotassium it has been established that in moist soil, K for K exchanges go on all the time, between the free solution and the external or internal adsorbing sites of the solid particles. The technique used to estimate the mass of K participating in these exchanges is that known as 'isotope dilution'. One puts into the system a known amount of an isotope (a radioisotope, usually), of the element in question, in that same ionic form as is being studied, and in a soluble condition. These ions mingle by diffusion with those pre-existing in diffusible condition within the system. At equilibrium the abundance ratio of the two isotopes is virtually the same in the various compartments accessible to diffusion, since the two isotopes have practically identical properties (except in a few elements with very light atoms and consequently, relatively very large differences in mass-numbers between isotopes). One then finds what this isotope ratio is, in the separable solution, and, knowing the total amount of one constituent present (*viz.* the added isotope), the total amount of the other may be deduced.

The chief advantage of this technique lies in the fact that elements held in a diffusible state on solid particles or inside them, can be estimated without its being necessary actually to separate out these elements, and so run the risk of changing the forms of combination of the ions present. This is particularly important in the case of potassium. Extracting this element, particularly with Ca, can render exchangeable some potassium that formerly was not so. On the contrary some exchangeable potassium can be converted to a non-exchangeable form by using an exchanger such as  $\text{NH}_4$  which is capable of 'closing up' clay minerals.

However, as already mentioned, in order not to disturb the dynamics of an element the addition of the isotope must not alter too much the mass of that element in the system. Ideally, what is desirable is a radio-isotope without carrier and with a high and sufficiently long-lasting specific radioactivity.

There is also in fact a further point on which the isotope dilution technique is open to criticism, as a means of studying the diffusibility of adsorbed ions. It turns out that the ions held in certain crystals can be exchanged against ions of the same species in the external solution but not against ions of different species. This is perhaps the case with a proportion of the potassium in some closed clay minerals, in particular a closed illite (136). The potassium estimated as autodiffusible (exchangeable against external potassium) cannot then be regarded as all diffusible in the usual sense since the aggregate of K ions held in the clay is not extensible in this instance (replacing one K ion by another K ion does not alter the spatial distribution of potassium). However, the self-diffusion of the potassium in this type of clay is extremely slow (a few Angstroms in 16 months), and only after a very long time can it affect any considerable quantity of potassium.

The potassium that is mobile, or exchangeable in a limited time (isotopically diluable), usually amounts to only a few units per cent of the total soil potassium (7, 32, 73, 76, 79).

Radiopotassium has also been used to investigate the laws of exchange of K against other cations in various clays (75, 124, 135, 136).

### Kinetics of isotopic exchanges of K

Potassium 42 has too short a life to allow the approach to the endpoint of isotopic exchange to be observed. There is no doubt that it would take no less than several months for this limit to be reached, reasoning from the kinetics of exchange of K against other cations. It is very likely that a stationary state would be established long before all the K in the soil had been isotopically exchanged, but it is just as likely that isotopic exchange would by then have involved an amount of K greatly exceeding the rapidly exchangeable K.

Only by using potassium 40, could the slow continuance of isotope exchange in soil particles be studied. This would clarify agronomists' ideas on the ability of soils to reconstitute their stock of rapidly assimilable K, or, in the reverse direction, to transform soluble fertilizer K into a form only slowly exchangeable. According to the writer's calculations this kind of work would call for the use of about 0.3 mg to 0.5 mg of isotopically enriched K (80 per cent  $^{40}\text{K}$ ) per 5 g of soil. It does not seem that this amount of added K would be enough to upset the normal dynamics of exchange appreciably. Potassium enriched to the 55 per cent  $^{40}\text{K}$  level could also be used, and would be less costly. The relative proportions of rapidly exchangeable K and slowly exchangeable K depend on the nature of the soil minerals, perhaps on the more or less porous structure of the primary aggregates, and possibly also on the presence of coatings capable of closing up the pores, temporarily or otherwise.

Alternations of drying and moistening greatly increase the amount of K isotopically exchanged in a limited time, just as they greatly increase the K that can be exchanged against other ions, whether in the direction of uptake or release. This increase in solid-phase exchanges by alternate wetting and drying can scarcely be explained only by the temporary opening of channels of communication between the outside and the inside.

## C. Potassium and the plant

### (a) Absorption by the roots

If a plant previously fed with a solution containing radioactive potassium is transferred to a medium containing ordinary potassium, it becomes apparent that the roots can excrete radioactive potassium, even though they are continuing at the same time to take in potassium for their nourishment. Some part of the K of the plant is, however, not exchangeable against the K of the medium. This potassium fraction is said to be actively absorbed. The use of radioisotopes has been crucial in establishing the concept of active absorption (2, 3, 56, 106).

The uptake of K by the plant organism varies according to species, being more intense with monocotyledons than with dicotyledons.  $^{42}\text{K}$  has been used to study K uptake in barley, maize, soya, beetroot, mustard, lucerne, sunflower, tomato, citrus fruits, fodder plants and timber trees (22, 35, 36, 69, 86, 95, 120, 129, 134, 145, 147, 148, 149).

The employment of radioelements, especially  $^{86}\text{Rb}$  and  $^{42}\text{K}$ , has helped considerably to strengthen the hypothesis of selective transporters, which can become temporarily attached to potassium ions or to similar ions that are specifically competitive with K, and so facilitate their transport across cell membranes.  $^{42}\text{K}$  has proved a convenient means of making comparative tests of K absorption by the plant, from different soils or different fertilizers. In this way it has been found that the plant takes up more K from the bicarbonate or the chloride than it does from the sulphate or the nitrate (100, 104, 131).

$^{42}\text{K}$  has also been used to study competition between K and other cations, such as  $\text{NH}_4^+$  (68, 99, 100, 120, 152), Ca (31, 56, 71, 81, 100, 102, 115, 116, 148, 153, 156), Mg (100), Na (100, 105, 118, 119, 122, 133, 145, 154, 156). It has been established that  $\text{NH}_4^+$  and Ca are stronger inhibitors of K uptake by plants, than Mg and Na are.

Finally,  $^{42}\text{K}$  has been used in an attempt to resolve another question of importance to the agronomist, namely whether contact between the roots and the ion exchangers in soil favours the uptake by the plants of the ions held by these exchangers. Observations on rye seedlings growing in media with and without added kaolinite, illite or montmorillonite are in favour of an affirmative answer to this question (97).

### (b) Uptake by the leaves and stem. Leaching.

Radiopotassium like other radioelements has been used to study the practice of feeding plants by spraying nutritive solutions on to their leaves, stems or trunks. The autoradiograph technique is a particularly suitable one for detecting the penetration, and tracing the spread within the plants, of elements placed on the surfaces of these various organs. The effectiveness of the spraying method for feeding plants with potassium depends on their species, age, and vigour, and on the temperature, humidity, time of day, the pH of the solutions used, and the elements they contain. Absorption by the aerial organs, particularly by leaves, is generally very rapid (13, 15, 17, 18, 19, 24, 27, 36, 37, 38, 42, 58). But, although this method may allow a serious deficiency to be relieved for the time being, it is

not in itself sufficient to ensure optimal nutrition. It is to be regarded as supplementary to classical manuring. The plant does not absorb the different nutrients in the same proportions through its foliage as it does through its root system (66, 98).

When it rains, and the water runs off the aerial parts of plants, it takes with it perceptible amounts of some nutrient elements. The importance of this effect varies with the state of the tissues, the time of day, and the element concerned. Use of  $^{42}\text{K}$  has provided confirmation that the potassium in the growing plant is relatively resistant to removal by leaching (under 1 per cent removed in 24 hours), but as the plant matures it becomes much more easily removed (30, 33, 63).

#### *(c) Movements of K ions in the plant*

Radioactivity counts for different parts of the plant, and autoradiography, have allowed the movements of K ions in the plant organism and their partition amongst the various organs to be traced, after they have been taken up by roots or leaves (1). Young and healthy tissues are those which contain most of it, the foliage (leaf blades, and especially petioles) being the richest in potassium whilst the reproductive structures (seeds) have the lowest concentrations.  $^{40}\text{K}$  has made it possible to study conveniently the fate of potassium in the germinating seed; this potassium starts to migrate into the radicles as soon as these are forming (150). All seeds, whilst they are swelling, absorb potassium ( $^{42}\text{K}$ ) intensively; subsequently it is actively transported into the vegetative organs (82, 123).  $^{42}\text{K}$  has allowed demonstration of the rapidity of movement of K ions in the phloem. The absorption of potassium ( $^{42}\text{K}$ ) and sodium ( $^{22}\text{Na}$ ) by conifer seedlings has a rhythmic character with cycles of about 5 minutes, related to rhythmic changes in water movement and in the biopotential of the plant (86).

#### *(d) Other studies effected with radioactive potassium*

The radioactive potassium isotopes make possible the study, at the level of the cell itself, the movements of K ions and their linkage or association with its various other constituents (8, 83, 103, 127, 151). Chief uses of  $^{42}\text{K}$  have been: in studies of cell permeability, to investigate the mechanisms of absorption (84, 128, 129, 149), to elucidate the roles of  $\text{CO}_2$ , bicarbonates and carbohydrates in cation accumulation in the plant (53, 54, 64, 65, 117, 146, 155), and to study the relations between transpiration and the absorption of potassium (82, 126, 132).

$^{42}\text{K}$  has been used to study the spatial distribution of the root systems of pasture plants in the soil profile, the uptake of K placed at various levels, and the existence of preferential zones of absorption (134). The isotope has made a contribution in studies of the relations between uptake of various ions and resistance to cold, in varieties and double hybrids of wheat (70).

Radioactive potassium, even though enclosed in a celluloid ampoule and not able to be taken up by the plants, was found markedly to enhance the growth of K-deficient barley plants (34).  $^{89}\text{Sr}$  and  $^{60}\text{Co}$  (radioactive) also exert effects of this kind.

### **IV. Use of Rubidium 86 to study the fate of potassium in the soil and the plant**

As mentioned at the beginning of this article, only Rb among the alkali metals resembles potassium closely enough to offer the prospect of using radioactive rubidium in place of radioactive potassium. The same certainly cannot be said of

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lithium (12, 57) or caesium (49, 50, 51, 52, 74). As  $^{86}\text{Rb}$  is much easier to use than  $^{40}\text{K}$  or  $^{42}\text{K}$ , there have been many tests on the possibilities of using rubidium to study the dynamics of potassium in the soil (12, 43, 45, 49, 50, 69, 77, 79, 92, 107, 114, 130) or in the plant (11, 23, 34, 43, 47, 48, 49, 50, 51, 60, 98, 112, 121, 157).

By investigating what happens when Rb and K are added in various concentrations to different soils and different plant species, it has been shown:

- that the dynamics of Rb and K in soils differ a great deal. Use of rubidium as a 'potassium tracer' has therefore to be ruled out in most cases. Fixation or release of one of these elements can, to an extent depending on soil conditions, interfere with that of the other,

- that in the plant on the other hand, in short-term experiments the mechanisms of transport for Rb and for K are similar, the ion transporters that convey them being the same. Inside plants (except for the reproductive organs which accumulate rubidium in higher proportion than the plant as a whole), one finds Rb/K ratios fairly constant between the various organs.

On account of these findings, use of  $^{86}\text{Rb}$  as a 'potassium tracer' has been almost entirely in the domain of plant physiology. Its main use has been in the study of absorption phenomena, in many plants (barley, beans, rice, sugar cane, etc.) (4, 29, 39, 40, 55, 59, 62, 78, 80, 93, 109, 110, 113, 140, 142, 143).

It has also been used in work on foliar uptake and foliar leaching (90, 91, 108, 113, 137, 141, 147), circulation of ions inside the plant (39, 41, 144), and their excretion into the surrounding medium (108, 43).

As regards the soil,  $^{86}\text{Rb}$  has been used to study the diffusion and exchange of cations (61, 94).

## Conclusion

Agricultural experimentation has shown that the fertilizing action of elements held by the absorbing power of the soil, as P and K are, is in general much more important in the long term than in the immediate future. Furthermore, building up the exchangeable K reserve can produce yield supplements such as cannot be obtained by recent dressings of a potassium salt, whatever the dose, on a soil poor in K.

It is important, therefore, that one should be able to follow, with the aid of labelled elements, what happens to the ions of the soil or of fertilizers over long periods, of the order of several years at least. Potassium 40 would lend itself well to such studies, whereas radiophosphorus whilst having very much the advantage over potassium for short-term studies, has much too short a life for use in long-term ones.

There do of course remain great possibilities for the use of short-lived radio-potassium ( $^{42}\text{K}$ ): the movements of potassium in the upper layers of the soil, the comparison of solid and liquid fertilizers in this respect, along with the effects of irrigation; the influence of contact of the plant with solid ion-exchangers in the soil on diffusion of potassium; and the specificity of ion transporters, and the nature of competition between cations in the plant.

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