Invited paper

USING RADIOTRACERS IN SOIL CHEMISTRY RESEARCH

O. TALIBUDEEN
Rothamsted Experimental Station,
Harpenden, Herts, United Kingdom

Abstract

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    Some models described summarize the more important chemical transformations in the soil-plant system and show how radioisotopes have helped recently to give a better and more precise understanding of these processes.

INTRODUCTION

    There has been an increase in the use of isotope tracers, aided by organizations such as the International Atomic Energy Agency. Soil science has not been slow to join in and is not alone, unfortunately, in using the technique unnecessarily and for reasons of prestige. Here work will be summarized that has contributed new knowledge to the basic and practical aspects of soil science relevant to the papers presented in this Session and the following one, where possible from work at Rothamsted. Even the most severe critic will concede that, intelligently applied, isotope tracers have given precision to subjects not readily attained by other techniques and, also, added a new dimension to the basic disciplines in soil science.
    Five models are discussed to illustrate these applications. The models can be recognized without much difficulty from the known characteristics of the soil and its environment (Fig. 1). Work on ion and water transport through soils is not considered — it is covered in Sessions 1 and 2. Mostly, chemical transformations in the soil affect such "transport" experiments less than the gross and micro- physical structure of the soil and plant growth characteristics.
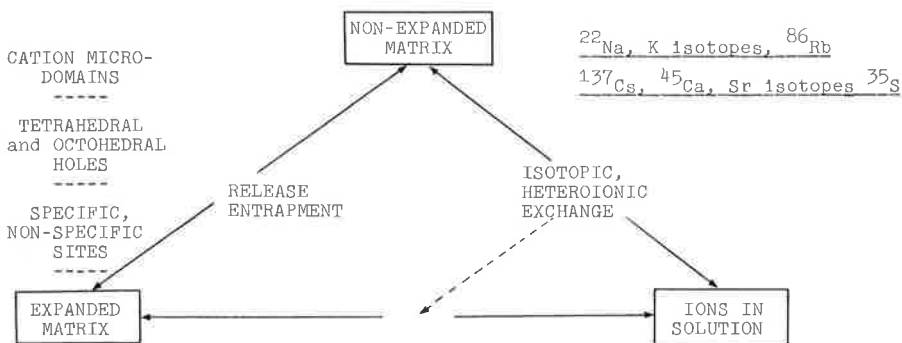
SOIL MINERALS

    The mineral matrix, pedogenetically derived from the parent mineral, forms the main framework supporting chemical reactions in the soil, and is therefore a logical starting point of the five models. Its main components are (Fig. 2) the micas, the kaolins and halloysites, the oxides of Fe, Al and Si mainly, the carbonates of Ca and Mg and, occasionally, zeolites and more exotic minerals. Of these, the layer-silicates with expanding inter-layer spaces are the primary seat of cation exchange reactions. Their various chemical compositions, attained in geologic and pedogenetic reactions, lead to subtle variations in crystal lattice dimensions, negative charge per unit cell and its siting in the crystal, the size of crystallites and, hence,

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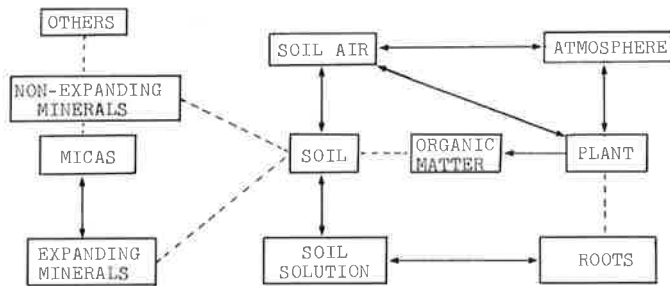
C, S, N cycles   Fall-out elements

Natural radioactivity   Industrial effluent

                                        Herbicides and pesticides

FIG. 1.   The soil complex.

^{22}Na, K isotopes, ^{86}Rb

^{137}Cs, ^{45}Ca, Sr isotopes ^{35}S

(micas, halloysites)

FIG. 2.   Soil minerals (micas, kaolins, zeolites, felspars, carbonates, oxides).

exposed specific surfaces. The resultant electrical charge-density and lattice dimensions of the surfaces are important parts of specific cation and water adsorption. Radiotracers play an important part in adding precision to this picture, and explain contradictions in results obtained by other methods. Much work has also been reported on the mobility and retention of fission elements in soils and also in model clay minerals.

Basically, the radiotracer label enables the "pool" of the element (or molecule) in the soil in isotopic equilibrium with soil water (or in "steady-state" conditions) to be calculated by the conventional isotopic dilution relationship. Also, the rate at which this equilibrium is attained, by isotopic exchange or self-diffusion measurable only by using radiotracers, can be used to define diffusion parameters for both phases by suitably manipulating the experimental conditions. For the solid phase, this gives valuable

information about the energetics and kinetics of adsorption. Cations, anions and soil components continue to be added to the list of exchange reactions in soils and clays, revising their correct order in adsorptive reactions. However, to make such series useful practically, they must be obtained by standard methods so that they are strictly comparable [1, 2].

Cations

Small amounts of minerals, not identifiable in the whole soil by more direct methods, that control the release of cations to plants, e. g. analcime in saline soils for Na^+ [3], clinoptilolite in Harwell soil for K^+[4], were detected using ^{23}Na and ^{42}K, enabling the assay of these minerals in particle size fractions of the soil.

Again, ^{86}Rb and ^{45}Ca were used to show that soil organic matter and K saturation interact in opposing ways to affect the adsorption of Rb in soil – more residual K increases the soil's specificity for Rb, more organic matter decreases it except when Ca^{2+} dominates the soil complex [5]. This work illustrates the difficulties inherent in using ^{86}Rb as a tracer for soil K. These complex interactions in the soil can be unravelled easily and quantitatively using radiotracers. An elegant method was described [6] for tracing soil K using enriched ^{41}K and neutron activation analysis. However, it would deter users who prefer less elaborate and cheaper methods.

Many conventional "isotopic dilution" methods have been described for measuring the cation exchange capacity of soils and clays using various cations but none so elegant, simple, accurate and adaptable to cheap routine analysis as that described by Rosenqvist [7]; surprisingly, it has not been adopted. Experiments with labelled Ca-saturated soils (Ref.[1] and Fig. 3), show that the decrease in their negative charge (or cation exchange capacity) with increasing exchangeable K, is caused mainly by labelled Ca ions being entrapped rather than K^+ "fixation", implying the complete reversibility of "ion entrapment" and "release". This information cannot be obtained without isotope tracers. Many other combinations of cations need examining to eliminate current popular misconceptions in soil science.

Self-diffusion studies of cations abound in the literature; this depends on the exchanging entity and its structural disposition in the solid. The exchange equilibrium and kinetics of cation and anion adsorption and absorption are governed by lyotropic ion series, which differ slightly for different matrices (Table I). These series are directly involved, therefore, in the release and retention of plant nutrient and "fall-out", or "fission", cations. Basic and quantitative information of this kind for the various mineral and organic components of the soil concerning cation competition for exchange sites, together with knowledge of the gross composition of field soils, can go far to providing semiquantitative comparisons of practical use. This paper does not purport to catalogue these and other events comprehensively, but only those are selected that provide new information on cation release from soils and soil components. Some work has been described earlier [3, 4]. Self-diffusion of K into a soil illite using ^{40}K [8] provided an important parameter ($D_s = 10^{-23}$ cm^2/sec) for calculating very long-term K release by unfertilized Rothamsted soil containing an illitic mineral dominating the soil complex. Compared with K uptake by crops

that use K increasingly, the calculated "exchangeable" K provides a
strikingly suitable limiting value (Table II, [9]). More information of this
kind on all soil minerals is needed so that, when related to the mineralogical
compositions of different soils, their K reserves and their "availability"
rate can be predicted more precisely and usefully than determining "total"
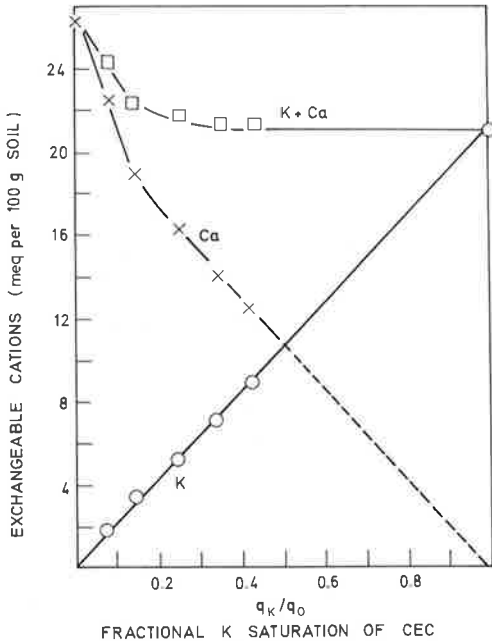K, "acid" extractable K, or K extracted with "tetraphenyl boron" or H^+
resins.

FIG. 3.   Effect of K saturation on cation
exchange capacity.

TABLE I.   ION ADSORPTION IN VARIOUS EXCHANGERS (FROM
THERMODYNAMIC DATA)

Source	Exchanger	Lyotropic series
Cruickshank & Meares, 1957	10% DVB resin	$K > Na > H > Li$
Merriam & Thomas, 1956	Attapulgite	$Cs > K > Na > Li$
Laudelout et al., 1968	Montmorillonite	$Cs > Rb > NH_4 > K > Na > Li$
Deist & Talib- udeen, 1967	Soil clays	$Rb > K > Na (> Ca)$
Barrer et al., 1963	Zeolite	$Na > K > Rb > Li > Cs$

TABLE II. K UPTAKE BY CROPS FROM UNFERTILIZED SOIL

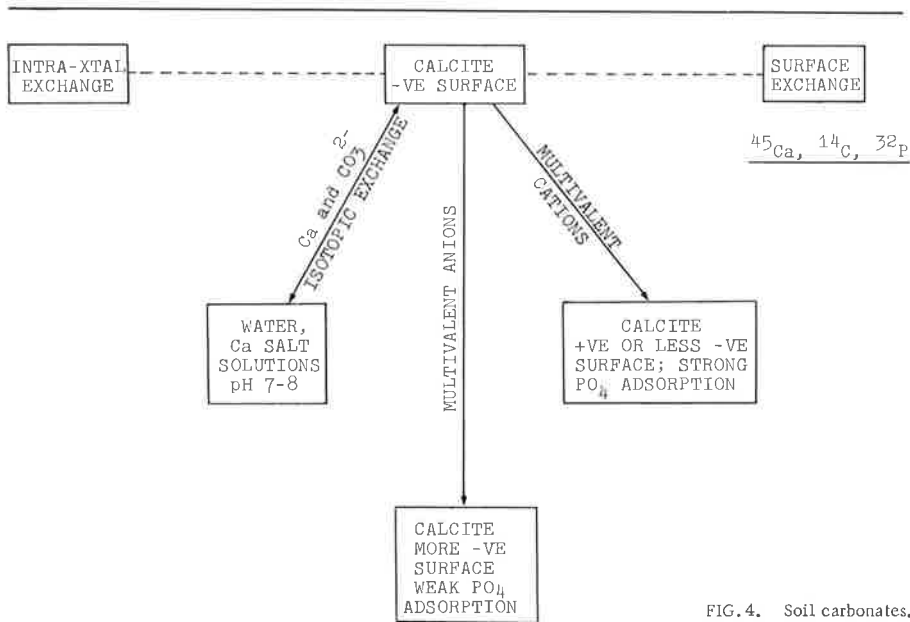| Calculated	lb K/acre per year
Broadbalk	125
Barnfield	180
Observed (Johnston) Exhaustion land	
Wheat	25
Potatoes	34
Barley	37
Swedes	79
Sugar beet	108
Kale	121

FIG.4.   Soil carbonates.

Conflicting but inconclusive evidence, based on multiple correlations, has appeared in the literature claiming that one or the other particle-size fraction of the soil is mainly responsible for holding or releasing K to plants. Recent "double isotope label" experiments [10], coupled with K release experiments with Ca-saturated resin and ryegrass, indicate directly that fine-clay-size (0.1 μm) micaceous particles ingrained in the coarse and fine silt fractions of the soil are involved equally with the soil clay fraction. Another important attribute of the "double-label" self-diffusion experiments in this work was the ability to distinguish microdomains in the soil fractions that were dominated by K^+ or Ca^{2+}, and were indistinguishable by physical methods.
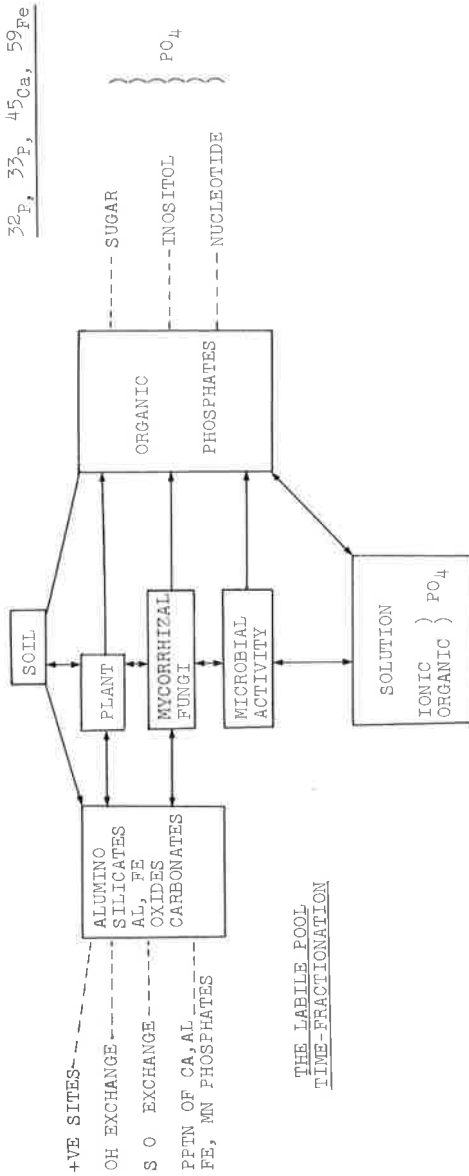
FIG. 5.   Phosphate equilibria in soils.

Anions

The phosphate chemistry of calcareous soils has attracted much attention. Our earlier work [11] indicated that increasing the specific surface of the calcium carbonate crystallites (i. e. smaller crystallites) in the soil, measured by [45]Ca exchange, decreased the self-diffusion of phosphate in the soil. This, and the contamination of calcite surfaces by foreign ions that abound in the soil, have an important effect on the phosphate chemistry of calcareous soils. Isotopic exchange of surface Ca in calcite and intra-crystalline Ca diffusion was measured using [45]Ca [12]; this work also showed that foreign ions strongly inhibit internal diffusion. Electro-endosmosis experiments show that calcite surfaces are negatively charged in water (Fig. 4), but polyvalent cations make the surfaces much more positive and polyvalent anions have the reverse effect. These results indicate that it should be possible to predict the nature and extent of residual phosphate in calcareous soils with relatively simple "labelled ion" experiments, using combinations of [45]Ca and other elements with [32]P.

Since work done in the 1950s on determining labile phosphate with ^{32}P label in soils, with and without growing plants, the literature on this subject continues to expand. Much of it repeats the same principles for a range of soils and crops, and it seems fair to say that knowledge and practice in this subject has not advanced significantly. Phosphorus-32 has been used to study the equilibrium and the kinetics of some chemical transformations of phosphate in the soil (Fig. 5).

Experiments were repeated in the 1960s to characterize the lability of soil phosphate by its rates of isotopic exchange [13 - 15] but no systematic attempt seems to have been made to relate this to the energetics of phosphate adsorption in model systems. Measuring ion mobility with (Na_2 EDTA) solutions, chemical association was observed between Fe and PO_4 in podzols and grey brown podzols but not in brown podzols [16]. A first attempt was reported recently [17] to characterize calcium phosphates on calcite by exchange with [45]Ca and [32]P. This work defines the limit of adsorbed phosphate above which octocalcium phosphate can be confirmed, by isotopic exchange, as a surface phase. The authors concluded that similar work on soils seems unlikely to be successful.

Little work has appeared in the literature on the rate at which organic phosphates from fresh plant residues become available to plants by soil incubation [18]. Because of the small amounts of P involved, ^{32}P and ^{33}P would be admirably suited to this purpose, using the "dilution" technique in radiochemical separation. The increasingly sophisticated use of P isotopes in the chemistry and translocation processes of the soil-plant system are illustrated by at least 7 papers in this symposium. Of particular interest are the "double-label" experiments described with ^{32}P and [33]P.

SOIL ORGANIC COMPLEXES

Three kinds of complexes of organic molecules with soil (Fig. 6) have been identified: (a) complexes directly attached to soil minerals by proton exchange or Van den Waals forces; (b) complexes attached by "co-ordinate valency" bridge-linkages to, or precipitated on soil surfaces by, adsorbed cations; (c) complexes with soil organic matter. Radiotracers are used
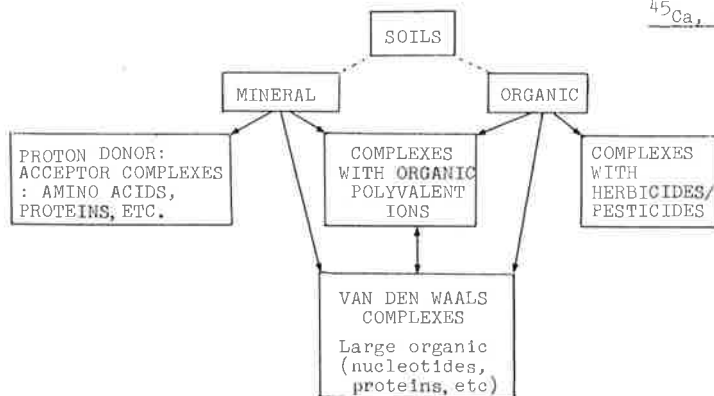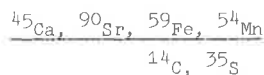
FIG. 6.   Organo-clay and organo-metallic complexes in soils.

in work on the formation and degradation of these complexes and in following
the fate of metabolites.

Work on the first kind of complexes with a few selected components was
completed and rules for complexing reactions established [19, 20] before
biosynthesis techniques of large organic molecules labelled with ^{14}C or ^{3}T
became commonplace.   Recently, ^{14}C-labelled humic-fulvic acid was used
to show that NH_4^+- and tryptophan-coated montmorillonites complexed more
humic acid than histidine-coated clay [21].   Information of this kind, using
a larger range of carefully selected labelled compounds and the clay surface
as a "reaction vessel", would rapidly extend the relatively meagre results
on the reactivity of soil organic matter and fill the gaps in existing results
more easily than earlier work.

Complexes formed by bridge - linkages have been extensively studied.
In the main, results [21] confirm most of the conclusions of earlier work
that the valency and nature of the bridging cations is all important in the
decreasing order of complexing intensity $Fe > Al > Ca > NH_4 > K > Na > H > Mg$.
The intensity of complexing by different clays [21] and soils, and functional
groups in soil organic matter [22], can also be characterized thus.   Basic
to the study of soil organic complexes is differentiating between functional
groups in the organic matter that reacts with various intensities with soil
cations [23], but even more important is the derivation of stability constants
for reactions of divalent Cu, Zn and Fe with fulvic acid [24].

Organic-organic complexes in the soil have been increasingly recognized
since herbicides and pesticides were applied to soils and plants.   Non-ionic
adsorbates are primarily involved, for each of which soil organic matter has
a near-constant sorption capacity.   Because the amounts of such compounds
in soil are in the "parts per million" range, their adsorption is most easily
studied using labelled compounds, and the literature contains many references
to their use.   The more important feature of such work is the rate at which
compounds are metabolized to CO_2.   The rate of degradation of ring-labelled
substituted urea herbicides in soils was thus followed [25] and showed that,
after the herbicide has been applied repeatedly, ring-splitting organisms

were more abundant in soil than those that decompose the urea side chain.
The results showed that despite this relatively rapid decomposition rate, the
substituted aniline residue was absorbed by soil organic matter.

PLANT RESIDUES IN SOIL

The turnover of organic matter in the soil (Fig. 7) has been much studied
and many variables found that affect the rate of turnover — the environment,
soil properties and plant material. Uniformly labelled plant material has
proved very useful for such work, much of which was reviewed earlier
[26, 27]. This work includes investigations of the priming action of green
manuring [28, 29]. Visual and optical methods were devised to measure the
rate of decomposition [30]. The transformation and humification of labelled
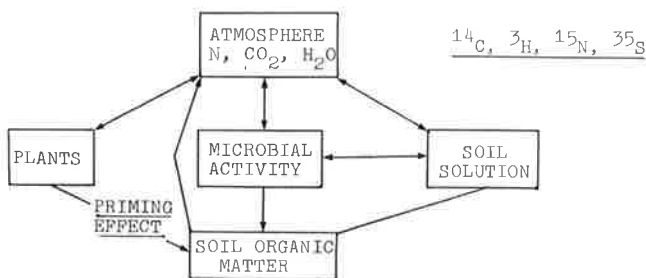sugars and starches in the soil were also followed [31-33].

FIG. 7.   Turnover of soil organic matter.

SULPHUR

Four aspects of the use of radiotracer ^{35}S are illustrated from the
literature. The S cycle, dominated by man's activities, has not been examined
in any detail. As crop production becomes more intensive, S-free N and P
fertilizers produced increasingly, the atmosphere cleaned of S pollution and
S deficiency better recognized, the S cycle will need closer study. Reliable
estimates are needed of reserves of S in the atmosphere and in soils,
especially where industrial pollution is small. The leaching of sulphate-S
down columns of solonzetic soil [34] showed that surface soils retained
more than subsurface soil zones. On virgin, pasture and cultivated podzols,
isotopically exchangeable sulphur [35], related to Na-acetate-extracted S,
was 8-10 times more in the B horizon than in the A horizon. Extracted S
was also more in the B horizon but total S was randomly distributed. These
examples illustrate the need for characterizing soil sulphur non-empirically
as has been done with soil phosphorus, and the need for labelled sulphate
solutions to measure positive sulphate adsorption needs emphasis [36].
Because of negative adsorption of the divalent anion in negatively charged
soils and clays, positive adsorption is too small to be measured chemically,
in contrast with ionic phosphate. Theoretical relations were derived and
checked by experiment for mixed uni-divalent cation-saturated soils and
clays of known negative surface charge to predict negative adsorption of the
sulphate ion.

Finally, to assess the contribution of atmospheric S to a crop, its concentration and the effective leaf area exposed per unit area of soil must be evaluated. Recent work [37] describes how this can be done using nutrient solutions containing ^{35}S-labelled sulphate given in pots growing mustard.

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DISCUSSION

R. CALVET: When discussing cations in silicate minerals, you men-
tioned the existence of "microdomains" associated with each cation. How
would you define a microdomain?

O. TALIBUDEEN: Perhaps "sub-microdomains" would describe more
exactly the concept I have in mind. These are volumes of submicron di-
mensions within crystallites that, superficially, seem structurally homo-
geneous when subject to physical analysis. However, methods based on
reversible and irreversible thermodynamics, such as you and I use, reveal
marked differences between the behaviour of strongly basic cations, sug-
gesting the presence of islands of microdomains, structurally related (or
unrelated) to the main matrix and randomly distributed within it.

C.G. LAMM: If I understand you correctly, you stated that by isotopic
labelling of metal ions it was possible to calculate complex stability constants.
This necessitates knowledge of the metal ion activities as well as the mole-
cular weights of the organic ligands. Could you elaborate a little on this?

O. TALIBUDEEN: The method referred to in the paper is used by
Schnitzer and co-workers in Canada, and is based on Schubert's method
of partitioning the chelated and unchelated ions on an ion-exchange resin
to determine the activity of the free ion. For more detail see Ref. [24]
of my paper.

H.E. OBERLÄNDER: I should like to comment on your reference to
"priming action", investigated, among others, by Jenkinson. It should
be borne in mind that this effect — the decomposition of "old" soil organic
matter under the influence of newly added fresh manure — is so small that
it can only be detected when the CO_2 generated is measured, but not when
carbon differences in the remaining soil are determined. We do quite a
lot of work of this type with ^{14}C-labelled manures, but we have never de-
tected any priming action by determining carbon differences. I should also
like to state that any carbon losses by priming action are certainly over-
compensated by the quantities of added manure carbon as well as by the
carbon from humic substances formed therefrom. Hence, this priming
action is of no practical importance in agriculture.