7. *Chemical Elements in Living Organisms*

PS7.1 — MO

BARRY G. MORRELL
NICHOLAS W. LEPP
Department of Biology
Liverpool Polytechnic
Byrom Street, Liverpool L3 3AF
U.K.
DAVID A. PHIPPS
CARL A. HAMPSON
Department of Chemistry and Biochemistry
Liverpool Polytechnic
Byrom Street, Liverpool L3 3AF
U.K.

REDUCTION OF VANADIUM BY HIGHER PLANT ROOTS

INTRODUCTION

The mobilisation of metals in soils and their subsequent uptake by plants is a complex process. Within the soil there is a wide range of processes both biotic and abiotic which can alter the chemical form of the metal and hence its pattern of translocation. Precipitation and solubilisation are markedly affected by both complex formations and by redox reactions; these processes are themselves substantially affected by pH changes. Consequently, it is essential to consider such changes when attempting to examine the uptake of metals from soils by plants, since availability depends on chemical form. However, even if it is possible to establish the nature of the chemical species within the soil solution, there is no assurance that the same species will exist within the plant. Changes in both complex structure and redox state of the metal ion both occur readily and indeed, as is known for iron, the latter may play a significant part in the uptake process [1,2].

By using solution culture techniques it is possible to remove the effect of the soil components and to focus attention on the effect of plant roots on the uptake of the metal.

Vanadium is an element which exhibits a multiplicity of forms in soil systems. In parent materials, it is generally present as the reduced trivalent form, where it replaces Fe(III). Weathering of the parent material will lead to release of vanadium in the fully oxidized pentavalent form. This fully oxidized form (VO_3^-) is generally considered to be a mobile form of vanadium in soil solutions. There is, however, strong evidence of reduction, $V^V \rightarrow V^{IV}$, by soil organic matter [3]. This reduced vanadium is thought to exist as an anionic complex [4]; its presence in an uncomplexed form is highly unlikely since the VO^{2+} entity is only stable at pHs below 2.4 [5].

Previous studies on the uptake of vanadium utilizing excised roots and whole plants [6] have revealed a striking similarity between the uptake patterns of the two vanadium forms (V^{IV}, V^V). Such similarities would not be expected because of the dissimilarity of the ions. Vanadium injected into rats always adopts the V^{IV} state independent of injected form [7]. Thus it might be that vanadium in plants could always have a common form. This paper describes some initial work examining the form of vanadium in plants.

METHODS AND MATERIALS

Barley seeds (*Hordeum vulgare* L. cv. Maris Mink) were soaked for 12 hours in double distilled H_2O and then spread onto moistened tissue paper and allowed to germinate. After two days growth the seeds were transferred to beakers containing the appropriate uptake solution. The seeds were supported in glass tubes with a slight constriction at the neck. All solutions were aerated and changed every two days. Solution 1 contained 0.5 mM $CaCl_2$, solution 2 0.5 mM $CaCl_2$ and 0.1 mM VO^{2+}, solution 3 0.5 mM $CaCl_2$ and 0.1 mM VO_3^-. After 9 days growth the roots were removed from the solution, blotted and freeze dried to a constant weight.
Plant material was analysed using a Bruker EPR spectrophotometer.

RESULTS

Roots which had been in $CaCl_2$ alone produced no spectra. Roots which had been in a solution containing VO^{2+} produced an eight peak spectra (fig. 1a) characteristic of the VO^{2+} entity. Roots which had been exposed to VO_3^- also produced a similar eight peak spectra (fig. 1b).

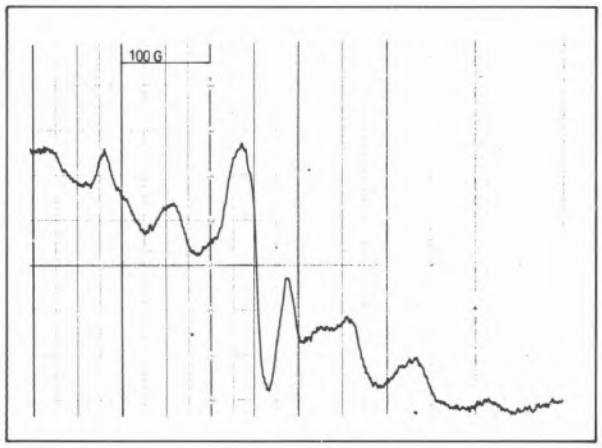


Fig. 1a
EPR spectra for roots grown in 0.1 mM $VOSO_4$ + 0.5 mM $CaCl_2$

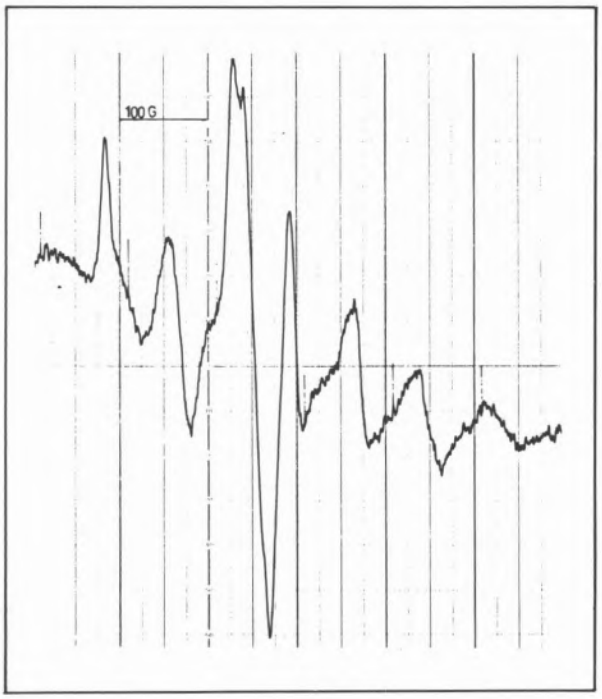


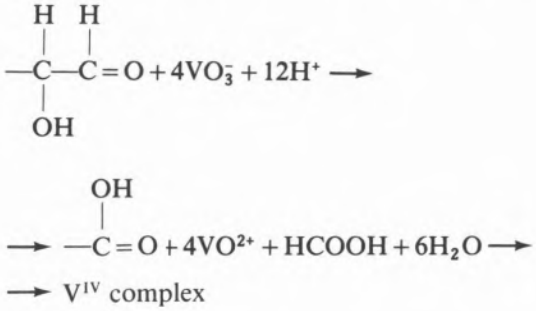
Fig. 1b
EPR spectra for roots grown in 0.1 mM NH_4VO_3 + 0.5 mM $CaCl_2$

DISCUSSION

Only substances with an unpaired electron will produce an EPR spectrum. V^{IV} with an outer electronic configuration of $4d^3\ 3s^1$ is thus EPR active and produces a characteristic eight peak EPR spectrum. The appearance of such a spectrum from root material exposed only to fully oxidized vanadium therefore indicates reduction has taken place. The reduction is unlikely to have occurred in the solution given its high pH and the constant aeration. The most probable explanation is that the roots have caused this reduction.

Reduction of metal ions by the roots of higher plants is a well documented phenomenon. UREN [8] has shown reduction of insoluble manganese oxides by the roots of sunflower seedlings. The reduction of Fe^{III} to Fe^{II} is also well understood [1,2]. CHANEY *et al.* [1] have proposed a mechanism of Fe reduction which involves reduction of an Fe^{III} chelate at the plasmalemma and subsequent uptake of the dissociated reduced ion. RÖHMELD and MARSCHNER [2] supported this hypothesis, as opposed to reduction in the intracellular space by secreted reductants.

The mechanism of vanadium reduction in plant roots is probably different to these, involving cell wall polyuronates as proposed by DEIANA *et al.* [9]. Polygalacturonic acid, a component of plant cell walls, will readily react with soil mineral species such as V^V because of the reducing properties of the polysaccharide end units. Reduction and subsequent complexation of the reduced species will occur, and DEIANA *et al.* [9] have proposed a mechanism for reduction of V^V to V^{IV}.



DEIANA *et al.* [9] pointed to the significance of these processes in maintaining a micronutrient supply for higher plant roots, especially in the case of Fe which can only be absorbed in

the reduced form. In the case of vanadium it is probably the reverse in that reduction and subsequent complexation of vanadium reduces its availability. Complexation no doubt prevents accumulation of V^V in the cell where its adverse effects on enzyme systems might cause severe cellular disruption.

REFERENCES

[1] R.L. CHANEY, J.C. BROWN, L.O. TIFFIN, *Plant Physiol.*, **50**, 208-213 (1972).
[2] V. RÖHMELD, H. MARSCHNER, *Plant Physiol.*, **71**, 949--959 (1983).
[3] A. SZALAY, M. SZILAGYI, *Geochim. Cosmochim. Acta*, **31**, 1-6 (1967).
[4] C. BLOOMFIELD, W.F. KELSO, *J. Soil Sci.*, **24**, 368-379 (1973).
[5] G.A. DEAN, J.F. HERRINGSHAW, *Talanta*, **10**, 793-799 (1963).
[6] B.G. MORRELL, N.W. LEPP, D.A. PHIPPS, *Minerals and Environ.*, **5**, 79-81 (1983).
[7] E. SABBIONI, E. MARANANTE, L. AMATINI, L. UBERTALLI, C. BIRATTORI, *Bioinorganic Chemistry*, **8**, 503-515 (1978).
[8] N.C. UREN, *J. Plant. Nutr.*, **4**, 65-71 (1981).
[9] S. DEIANA, A. DESSI, G. MICERA, C. GESSA, M.L. DE CHERCHI, *Inorg. Chim. Acta*, **79**, 231-232 (1983).

PS7.2 — MO

PAUL G. LOGAN
NICHOLAS W. LEPP
Department of Biology
DAVID A. PHIPPS
Department of Chemistry and Biochemistry

Liverpool Polytechnic
Byrom Street, Liverpool L3 3AF
U.K.

THALLIUM UPTAKE BY PLANT ROOTS: COMPETITIVE EFFECTS OF POTASSIUM IONS

INTRODUCTION

Thallium is a rare but toxic element, with a mean crystal abundance of approximately 1 ppm. Biologically, thallium is of interest due to its mimicry of K^+ in many biological systems [1]. Thallium shows many physico-chemico similarities to potassium, with the ionic radius of Tl^+ being very similar to the alkali metal cations Rb^+ and K^+ ($K^+ = 133$ pm, $Tl^+ = 144$ pm, $Rb^+ = 148$ pm). Tl^+ has been shown to be more effective than K^+, Rb^+ or Cs^+ at activating certain (Na^+/K^+) ATPases [2,3], whilst MULLINS and MOORE [4] have shown that both the kinetics of exchange and the electrochemical influences of Tl^+ and K^+ are virtually identical in the cells of the frog sartorius.
Levels reported in soils vary in the literature, between 0.05 and 0.5 $\mu g.g^{-1}$ dry weight, although recent studies by German workers report levels exceeding this value [5].
Thallium levels in plants have been reported as between 0.01 and 3800 ppm ash weight, with 0.5 ppm being typical for most species [1]. Plants with elevated thallium levels have been found in areas of natural thallium mineralization, and have been reported as toxic to grazing sheep and cattle [6].
The aim of this study is to examine the kinetics of uptake of thallium by excised barley roots, and to compare it with findings for K^+ by other workers.

MATERIALS AND METHODS

Low salt barley roots were grown hydroponically as described by EPSTEIN [7]. Barley seeds (*Hordeum vulgare* c.v. Maris Mink) were soaked in aerated distilled water for 4 hours, germinated and grown in the dark at 25°C for 7 days. Roots were excised, rinsed in distilled water, thoroughly mixed, and placed in aerated 0.5 mM $CaCl_2$ solution, prior to experimental use.
Uptake experiments were carried out as described by HARRISON *et al.* [8]. Roots were placed in aerated thallous acetate solutions at various concentrations, spiked with the isotope ^{204}Tl. After 15 minutes roots were removed, rinsed in chilled distilled water, and placed in chilled (2°C) unspiked thallous acetate solution for 30 minutes, after which they were removed, blotted to remove excess moisture, and weighed into digestion flasks. Samples were digested in 5 ml of a sulphuric acid/hydrogen peroxide mixture as described by ALLEN [9]. Samples were poured into scintillation vials, the flasks rinsed with 5 ml distilled H_2O, and the washings added to the samples. Activity was measured directly by measuring Cerenkov ra-