The mechanism of rock phosphate solubilization in the rhizosphere

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Summary  A simple model is described, and experimentally tested, for predicting the rate of dissolution of rock phosphates in soil, including the effect of solubilization by plant roots. The sensitivity of the model to its input parameters is assessed and it is seen that plants may significantly increase their P uptake by acid secretion. The model provides a rational basis for the selection of P solubilizing crops and inter-crops.

Introduction

Per unit of P, rock phosphate is about one third the price of simple superphosphate, so it is obviously very important, particularly for poor countries often gravely short of phosphate in their soils, to know in what conditions it may be profitably used. Yet it is surprising that in 1986 the value of rock phosphates is still assessed by an ammonium citrate extraction and correlation with field trials. Here is an inorganic crystalline compound, whose composition we can measure, being added to soils whose properties we can also measure. We ought to be able to predict how rapidly it will dissolve from first principles. A complete account of the development of a predictive model has been given in a series of papers 1,2,3,4,5,6 that are physico-chemically and numerically rigorous. In this paper, only the main ideas and results will be given.

The dissolution of a planar layer of DCPD

When tackling a problem of this kind it pays to start with as simple a system as possible, test each assumption, and explore more complicated ground from an assured base. Dicalcium phosphate dihydrate (DCPD) is the most soluble, and therefore experimentally most convenient, of the insoluble calcium phosphates that typify rock phosphates. We started by considering the dissolution of a planar source of DCPD in contact with one end of a long column of moist soil (Fig. 1), so that the concentration profiles of the constituents of the DCPD could be measured, in order to test the model. The dissolution reaction of DCPD in acid conditions is
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Fig. 1. Experimental system for measuring concentration profiles of phosphate diffusing into soil from a planar source of DCPD.

\[
\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{H}_2\text{PO}_4^- + \text{OH}^- + \text{H}_2\text{O}
\]

The rate of dissolution is limited by diffusion of the constituents from the interface into the soil. This rate will depend upon the concentrations of the constituents at the interface and the diffusion characteristics of the soil. At the interface we have five unknowns: the concentrations in the soil solution of phosphate, base and calcium, and the fluxes of phosphate and base. These may be determined by the following five relationships.

1. The concentrations of phosphate, base and calcium must satisfy the solubility product condition

\[
[\text{Ca}^{2+}] [\text{H}_2\text{PO}_4^-] [\text{OH}^-] = K_{SP}
\]

2. The solution must be electrically neutral so that

\[
[\text{Ca}^{2+}] = ([\text{H}_2\text{PO}_4^-] + [\text{OH}^-])/2
\]

3. The flux of phosphate across the interface is given by

\[
F_p = ([\text{H}_2\text{PO}_4^-]_{\text{surface}} - [\text{H}_2\text{PO}_4^-]_{\text{soil}}) \left(\frac{D_p}{\pi t}\right)^{1/2} b_p
\]

where \(D_p\) = diffusion coefficient of phosphate in soil

\(b_p\) = phosphate buffer capacity

4. The flux of base across the interface is given by

\[
F_{\text{Base}} = (pH_{\text{surface}} - pH_{\text{soil}}) \left(\frac{D_{HS}}{\pi t}\right)^{1/2} b_{HS}
\]

where \(D_{HS}\) = soil acidity diffusion coefficient

\(b_{HS}\) = pH buffer capacity

5. For continuous dissolution the fluxes of phosphate and base must be equal. For example, if phosphate diffused faster than base, the concentration of \(\text{OH}^-\) at the interface would rise until the flux of base again equalled that of phosphate. Thus

\[
F_p = F_{\text{Base}}
\]