Diffusion of Inorganic Materials in Soil [and Discussion]

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Diffusion of inorganic materials in soil

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SUMMARY

Long-established theory concerning the diffusion of solutes in soil is described, with particular reference to the means by which pH changes are propagated through soil by acid-base transfer. The application of the theory is then demonstrated by way of models of the reaction with soil or two important fertilizer materials (urea and rock phosphate) and a model of the diffusion and oxidation of ferrous iron in the rhizosphere of lowland rice. Experimental verifications of the urea and rock phosphate models are given, in which reactant concentration profiles in the soil are compared with model predictions based on independently measured parameter values. No parameter-fitting is used. A sensitivity analysis of the urea model shows how loss of urea-derived nitrogen by ammonia volatilization depends on fertilizer, soil and atmospheric parameters. A sensitivity analysis of the rock phosphate model shows how the rate of rock-phosphate dissolution and the amount of dissolved phosphorus taken up by plant roots depend on fertilizer, soil and plant parameters including acid-base release by roots. A sensitivity analysis of the iron diffusion and oxidation model shows how rice roots may greatly alter chemical conditions in the soil near them, with major implications for nutrient and toxin transformations.

1. INTRODUCTION

Diffusion determines wholly or in part the rates of many important soil processes and it is one of the main mechanisms by which nutrients are delivered to plant roots. A comprehensive quantitative theory of diffusion in soil has emerged in the past decade or two, which has enabled the development of predictive mechanistic models of soil processes involving diffusion. In this paper, I give a brief overview of the theory and then show its application by way of three examples. In practical situations diffusion is often combined with convection (for example, in solute movement in the transpiration stream near plant roots), but I do not consider these aspects because they are dealt with in other papers in this symposium. A thorough review of diffusion in soil has been given by Nye (1979).

2. THE THEORY OF SOLUTE DIFFUSION IN SOIL

The bulk of the cations and often the anions and uncharged solutes in soil are adsorbed on minerals and organic matter; a small fraction are in the solution in the pores. Solutes may diffuse through both the solid and the solution, and the solid and solution pathways may partly operate in series. In so heterogeneous a medium as soil, it is impossible to develop exact equations for the mobilities and concentration gradients of solutes in all the constituent parts. But for volumes large enough to average microscale variations, the soil may be treated as a quasi-homogeneous body to which Fick's first law may be applied:

$$F = -D(dC/dx), \tag{1}$$

where F is the flux, dC/dx is the concentration gradient across a particular section, and D is a soil diffusion coefficient defined by equation (1). In most circumstances, although there are important exceptions (Staunton & Nye 1987; Kirk & Staunton 1989), the contribution of solid phase diffusion to the overall movement is small, and the total rate of movement through the soil may be considered as being because of a flux through the pore solution alone, together with an excess flux, F_E, created by any mobility of the solute on the solid. Thus

$$F = -D_L \theta f(dC_L/dx) + F_E, \tag{2}$$

where D_L is the solute diffusion coefficient in free solution, θ is the fraction of the soil volume occupied by solution, f is an impedance factor, and C_L is the concentration of solute in solution. Thus from equation (1), we have a combined diffusion coefficient,

$$D = D_L \theta f(dC_L/dC) + D_E, \tag{3}$$

where D_E is an excess term. The impedance factor, f, is empirical, accounting primarily for the geometry of the soil pore network but also for ion exclusion by negative adsorption from very narrow pores, and for the increased viscosity of water near charged surfaces. The impedance factor varies with soil type and with soil moisture content, but for simple ions in moist soil, it appears to be little influenced by the type of ion. The derivative dC_L/dC, describing the distribution of solute between solid and solution, varies widely between solutes: it is $1/\theta$ for non-adsorbed solutes such as Cl^- and NO_3^-, but it may be less than 10^{-4} for strongly sorbed ions such as $H_2PO_4^-$.

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For transient state conditions Fick's second law may be applied:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right). \tag{4}$$

For problems in which the diffusing solute is being added to or removed from the soil solution in time-dependent processes, source or sink terms may be added to the right-hand side of equation (4). For many practical applications, the boundary conditions for solving equation (4) are complex, and the derivative dC_L/dC is highly nonlinear, often depending on the diffusion and reaction of other solutes. The resultant sets of equations are mathematically crude and have no analytical solutions, so that recourse must be made to numerical methods.

An important application of soil diffusion theory is in predicting how pH changes are propagated through soil. Sources of pH changes in soil are legion: in the models described later in the paper, pH changes are central to the overall systems. A theory for the propagation of pH changes is soil was developed by Nye (1972). The theory uses a soil acidity diffusion coefficient, D_{HS}, defined by the relation

$$\frac{\partial pH}{\partial t} = \frac{\partial}{\partial x}\left(D_{HS}\frac{\partial pH}{\partial x}\right), \tag{5}$$

and for many practical purposes,

$$D_{HS} = \frac{2.303\theta f}{b_{HS}}(D_{LH}[H_3O^+]_L + D_{LC}[HCO_3^-]_L), \tag{6}$$

where D_{LH} and D_{LC} are the diffusion coefficients of H_3O^+ and HCO_3^- in free solution, b_{HS} is the soil pH buffer power $(-d[HS]/dpH)$, and HS is soil acid. The theory considers that when a pH gradient exists in a soil, a small portion of soil (S) may gain acidity either by access of H_3O^+ $(S+H_3O^+\rightleftharpoons SH^++H_2O)$, or by dissociation of H_2CO_3 (derived from CO_2) and removal of HCO_3^- through the soil solution $(S+H_2CO_3\rightleftharpoons SH^++HCO_3^-)$. In particular cases, other acid-base pairs (e.g. NH_4^+–NH_3, $H_2PO_4^-$–HPO_4^{2-}) may also make significant contributions. The relative importance of the pairs H_3O^+–H_2O and H_2CO_3–HCO_3^- is given by the term within the brackets in equation (6) and is plotted in figure 1a. Figure 1a shows that the soil acidity diffusion coefficient passes through a minimum in the pH range in which $[H_3O^+]_L$ and $[HCO_3^-]_L$ are both low: in this pH range a flux of acid or base through the soil results in steep pH gradients. This theory has been verified experimentally by Nye & Ameloko (1986) over a wide range of soil pHs (see figure 1b).

3. APPLICATIONS OF THE THEORY. I. AMMONIA VOLATILIZATION FROM APPLIED UREA

Urea is now the major nitrogen fertilizer in both temperate and tropical agriculture (FAO 1987). This is because it is the cheapest, per unit of nitrogen, of all the solid nitrogen fertilizers. In the Philippines,
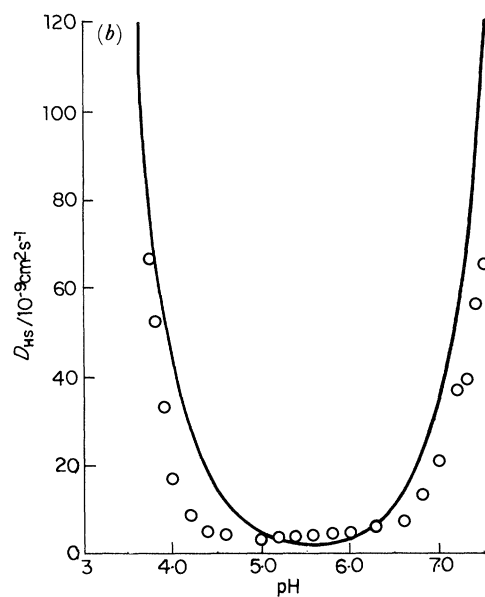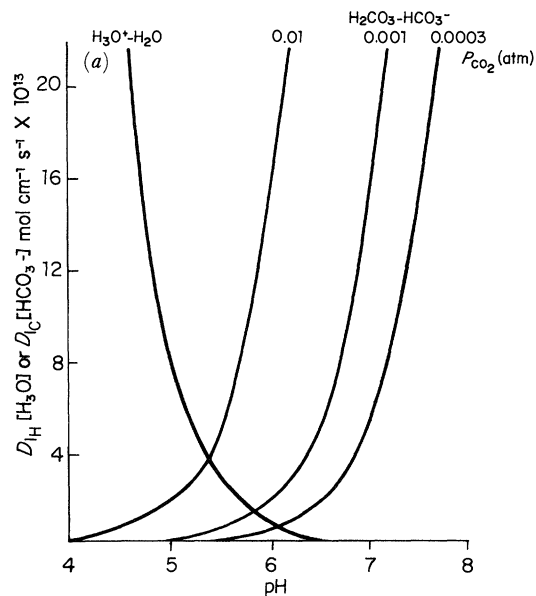

Figure 1. (a) Relative importance of H_3O^+ or HCO_3^- in acid-base transfer at different pHs, calculated using equation (6). (b) Comparison of experimental results (points) with the predictions of equation (6) for the P_{CO_2} maintained in the experimental soil (0.005 atm) (Nye & Ameloko 1986).

for example, a tonne of nitrogen from urea currently costs U.S.\$380 compared with U.S.\$590 for nitrogen from ammonium sulphate. It is also the most concentrated solid nitrogen fertilizer, and it is compatible with other materials in compound fertilizers such as urea phosphate. There are, however, problems in its use, the major one being high ammonia volatilization losses, often as much as 30% (Fenn & Hossner 1985) or even higher in flooded ricefields (Bouldin 1986). Urea applied to soil is hydrolyzed to NH_4^+ and HCO_3^- ions; the latter raise the soil pH. High pH and ammoniacal-nitrogen concentrations cause ammonia volatilization, but urea and its hydrolysis products will also diffuse into the soil. Thus ammonia volatilization results from the simultaneous operation of a series of complex,

interacting processes that are influenced by a multitude of soil and environmental variables. Therefore, it is not surprising that experiments in the past have often produced conflicting results. Suitable management practices to reduce ammonia losses can be developed only if the factors controlling ammonia volatilization are identified for all combinations of soil and environmental conditions. However, the cost of making experiments in all such conditions is prohibitive, and therefore a predictive model, based on mechanistic insight, may be invaluable for investigating the system. The purpose of the work described below was to develop and test such a model, enabling prediction of the fate of urea applied to soil and the loss of urea-derived nitrogen by ammonia volatilization.

(a) Development of the model (Rachhpal-Singh & Nye 1984, 1986)

The process of ammonia volatilization is the turbulent transfer of ammonia gas from the soil surface to the immediate atmosphere. The rate of ammonia loss is proportional to the concentration of ammonia gas at the soil surface. The following reactions show that during volatilization, the ammoniacal-nitrogen at the surface will be depleted, and the pH will decrease:

volatilization

↑

$NH_{3(g)}$

⇅

$NH_{4(aq)}^{+} + H_2O_{(l)} \rightleftharpoons NH_{3caq)} + H_3O_{(aq)}^{+}.$
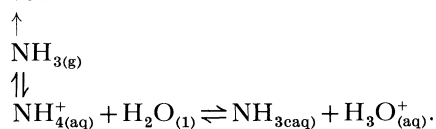
As a result, more ammoniacal-nitrogen in the soil solution and soil air will diffuse to the surface; also soil

acid will diffuse away from the surface and soil base towards the surface. Thus it was necessary to develop continuity equations for urea, ammoniacal-nitrogen and soil alkalinity, involving both solution and gaseous phase diffusion in soil and transfer of ammonia gas from the soil surface. In the movement of soil alkalinity, the major acid-base pairs are H_2CO_3–HCO_3^- and NH_4^+–NH_3, as described in §2. Furthermore, because CO_2 is produced from urea hydrolysis and since the concentrations of H_2CO_3 and HCO_3^- depend on the pressure of CO_2, the P_{CO_2} profile had also to be considered in the model calculations.

In the model, the four continuity equations (for urea, ammoniacal-nitrogen, soil alkalinity and CO_2) are solved numerically, subject to the relevant initial and boundary conditions. The key condition at the soil surface is that the total flux of ammoniacal-nitrogen in the soil moving upward in both the liquid and the gaseous phase be equal to the flux of ammonia gas moving out of the soil by volatilization. In the same way the latter is equal to the flux of soil acid moving down into the soil.

(b) Experimental testing of the model (Rachhpal-Singh & Nye 1986)

The model was tested against experimentally measured concentration profiles of urea, ammoniacal-nitrogen and soil pH, and data for ammonia volatilization losses. The agreement between the experimental results and the model predictions was excellent (figures 2 & 3). This suggests that all relevant processes were accounted for and that they are well understood. As all parameters in the model were obtained from
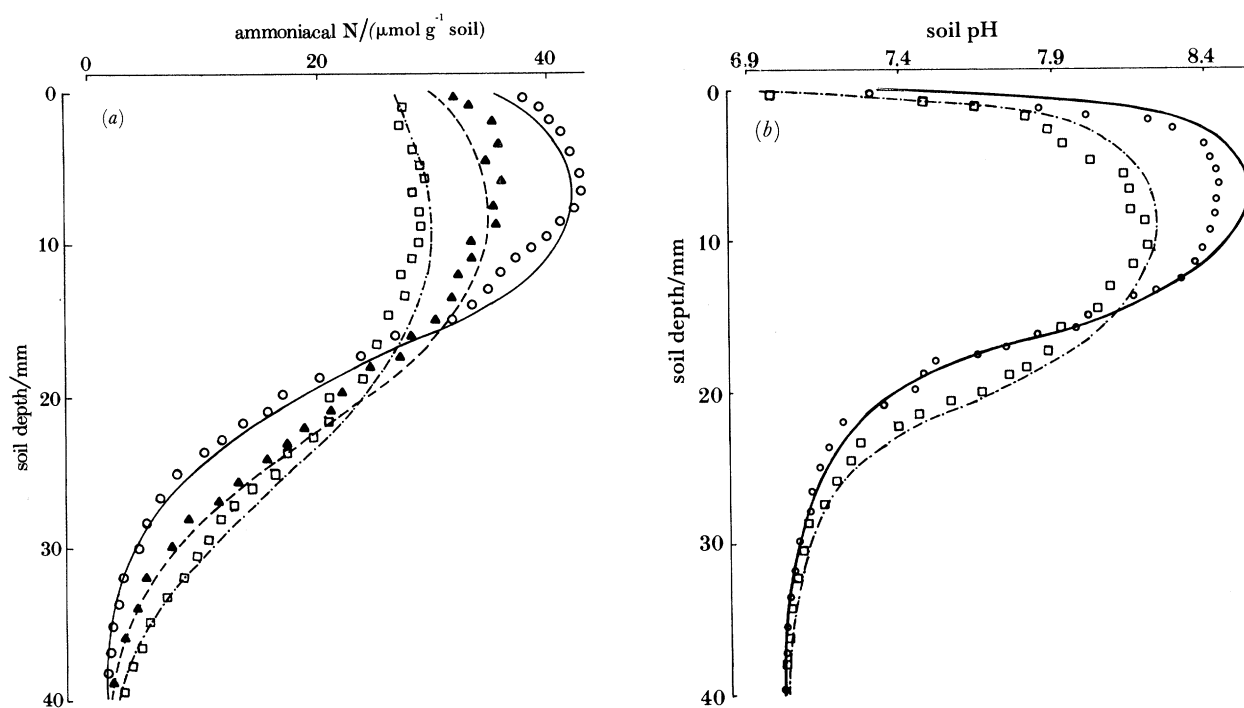

Figure 2. Experimental (points) and predicted (lines) concentration profiles of (a) ammoniacal-nitrogen, and (b) pH at diffusion times after surface application of urea. (o), 4 days; (△), 7 days; (□), 10 days.
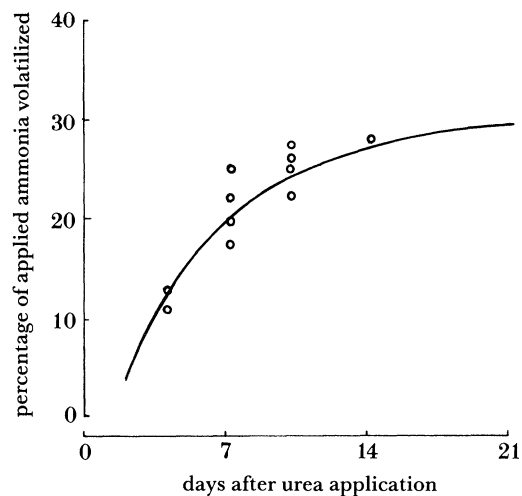
Figure 3. Comparison of experimental and predicted ammonia volatilization losses following surface application of urea at 210 kg N ha^{-1}; (○), experimental; (——), predicted.

independent experiments, the model predictions are absolute. The pH at the surface was 1–2 units lower than at a few millimetres below the surface. Such high pH gradients indicate that any simpler treatment of soil pH changes, particularly one neglecting the acidification of the soil surface during ammonia volatilization, would have been inadequate.

(c) *Effect of soil conditions on ammonia volatilization* (*Rachhpal-Singh & Nye* 1986)

Figure 4 shows the sensitivity of the predicted ammonia losses to different soil parameters. Losses are very sensitive to the initial pH of the soil, its pH buffer capacity, the rate of urea application and soil urease activity, but not very sensitive to the soil surface-
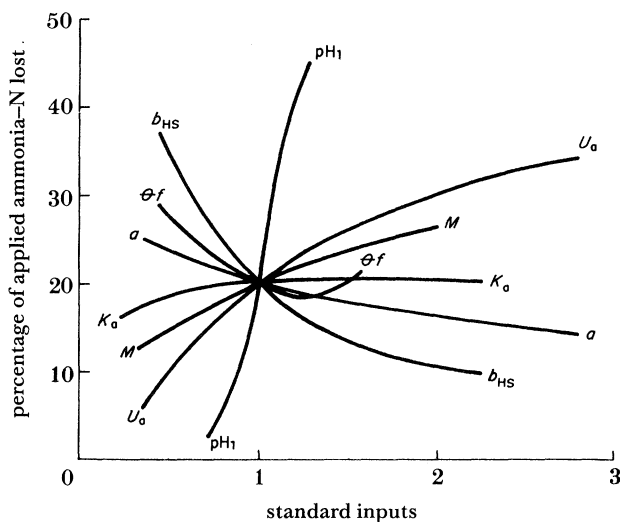

Figure 4. Effect of various model parameters on ammonia volatilization losses at seven days after surface application of urea. The standard parameter values are: K_a (gas transfer coefficient) = 133 dm h^{-1}; M (rate of urea application) = 210 kg N ha^{-1}; b_{HS} = 0.03 mol kg^{-1} pH^{-1}; a (NH$_4^+$ sorption Freundlich equation coefficient) = 0.35; initial soil pH = 7; θf = 0.086; U_a (soil urease activity, as described in Rachhpal-Singh & Nye (1986)).

atmosphere gas transfer coefficient. The coefficient for ammoniacal-nitrogen adsorption is less important than the soil pH buffer capacity. For near neutral soils, diffusion of bicarbonate to the soil surface is the rate-limiting step in ammonia volatilization. However, for very alkaline soils when the concentration of ammoniacal-nitrogen at and near the soil surface is very low, diffusion of ammoniacal-nitrogen to the surface is the rate-limiting step.

Volatilization tends to increase when the moisture level is above field capacity, and also when the soil is drier. Although in dry soil diffusion of NH$_4^+$ to the surface through the liquid phase is reduced, diffusion of NH$_3$ gas through the vapour phase is increased, and the net effect is to increase volatilization.

(d) *Further applications and development of the model*

The model described so far was developed in a basic form that would facilitate its experimental testing. The effects of other environmental factors and agronomic management practices can be incorporated in the model if their influences on the model parameters are known. For example, Rachhpal-Singh & Nye (1988) have adapted the model to investigate the effect of different methods of urea application. They showed that the reductions in losses to be gained from deep placement of urea could be accurately predicted.

Nitrification can be included in the model by evaluating the rate of nitrification of ammonium and incorporating in the model the continuity equations for nitrate and nitrite, and suitably revising the ammoniacal-nitrogen and soil alkalinity equations. Indeed, in other work (Darrah *et al.* 1986) it has been shown that the distribution of nitrate and soil acid formed by nitrification of ammonium fertilizers can be satisfactorily predicted. However, since nitrification is a rather slower process than urea decomposition, the main conclusions of the work on ammonia volatilization would not be seriously affected by the inclusion of nitrification. Other work (Kirk & Nye 1990) has shown that the upward flow of soil solution caused by evaporation of water from the soil surface enhances volatilization, but on the other hand downward flow by drainage can greatly decrease it.

The severity of ammonia volatilization losses from flooded ricefields was mentioned earlier. In ricefields, volatilization takes place from the floodwater standing in the field, and the dynamics of CO_2 in the floodwater and the soil are central to the system. In particular, CO_2 is taken up by algae respiring in the floodwater during the day, tending to increase the floodwater pH and consequently increasing volatilization; at night, the pH falls. One strategy for reducing volatilization might be to increase the CO_2 supply, for example by adding organic matter, to reduce floodwater pH. However, an increased CO_2 supply may also stimulate algal growth, resulting in the opposite effect. The model can be used to investigate such possibilities by adding a floodwater layer, in which algae are respiring, at the soil surface, and by suitably modifying the CO_2 and soil alkalinity sub-models.

These examples illustrate the power of this model to embrace the vast range of conditions in which urea is applied. The model poses precise questions to direct future research in particular conditions; and considering the scale on which urea is used, the model offers immense potential rewards.

## 4. APPLICATIONS OF THE THEORY. II. DISSOLUTION OF ROCK-PHOSPHATE IN SOIL

Phosphorus deficiency is a major constraint to food production in the poorer countries of the tropics and sub-tropics. Because of the high cost of phosphorus fertilizers, it is essential that the cheapest, suitable forms be used in these regions and that fertilizer practice be efficient. Ground rock phosphate (R.P.) is the cheapest form of phosphorus available, the cost, per unit of phosphorus, often being less than half that of simple superphosphate (FAO 1987). But R.P. is only effective where soil and crop conditions favour a reasonable rate of dissolution. The rate of dissolution of a given R.P. varies with; (a) soil pH, soil solution calcium and phosphate concentrations, and with soil properties governing their buffering, and (b) crop differences in demand for phosphate and calcium, root effects on soil pH, and rooting density. The rate of dissolution of different R.P.s varies with their chemical and mineralogical characteristics, with the method and rate of application, and with particle size. In view of the large number of variables involved, it is not surprising that field trials with R.P.s have produced erratic and sometimes conflicting results, which have caused considerable disagreement about the usefulness of R.P., and this is reflected in the extent of their use. I consider that the use of R.P. would be far more widespread if all suitable situations for its use could be identified and if precise fertilizer recommendations could be given. However, as in the case of urea, the cost of performing the necessary field trials to cover all combinations of soil and crop conditions is prohibitive. Rather, an accurate predictive model is required, based upon readily and, if possible, routinely measured soil and crop parameters. Empirical models are unsatisfactory because such a large number of variables are important. So I shall describe the development of a mechanistic model, capable of predicting the rate of dissolution of R.P.s under any soil and crop conditions, from independently measured parameters.

(a) Development of the model (Kirk & Nye 1985)

Rock phosphates largely comprise complex micro-crystalline calcium phosphates. As a starting point from which to advance to these more complex forms, we chose dicalcium phosphate dihydrate (DCPD) as it is the most soluble of the sparingly soluble calcium phosphates, and the most convenient one for testing the model experimentally. The mechanisms governing the dissolution of the more complex calcium phosphates are essentially the same. To test the model, the case of a planar layer of DCPD in contact with moist soil was

considered first: this is the simplest system for measuring the solute concentration profiles close to the dissolving surface. This dissolution of a planar layer was then extended to the more practically relevant dissolution of particles of DCPD.

The dissolution reaction of DCPD in acid soils is:

$$CaHPO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + H_2PO_4^- + OH^- + H_2O. \quad (7)$$
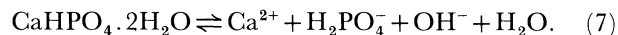
Hence, dissolution causes a rise in pH. The propagation of this rise in pH through the soil bulk can be considered in terms of a spread of 'base' away from the DCPD, effected by acid-base transfer as described in §2. In aqueous suspension, the rate of transfer of material from the crystalline phase to the solution is fast, and the net rate of dissolution is controlled by the diffusion of the mineral's components (phosphate, base and calcium) from the surface to the bulk solution. In soil, convective flow resulting from density or osmotic potential gradients will be negligible for the solute concentrations likely to exist near dissolving DCPD, and therefore diffusion, which is slower in soils than in water, will be rate-limiting. Thus the soil solution adjacent to the DCPD will be saturated, and its composition will be given by the solubility product relationship:

$$[Ca^{2+}]_L[H_2PO_4^-]_L/[H^+]_L = K_{DCPD}. \quad (8)$$

As one mole each of phosphate, base and calcium is produced for each mole of DCPD dissolved, steady state is attained when the fluxes of each component away from the DCPD are equal; otherwise, dissolution would not be continuous. To predict the rate of dissolution, the model calculates the fluxes of each of the components and balances them in accordance with these conditions.

The movement of phosphate through the soil is described by equations (3) and (4) with $D_E = 0$. The phosphate buffer power, b_p, is the inverse of the derivative dC_L/dC. For the movement of soil base, in very acid soils, H_3O^+–H_2O will be the major acid-base pair in the bulk of the soil, but close to the DCPD the contributions of the pairs H_2CO_3–HCO_3^- and $H_2PO_4^-$–HPO_4^- will also be significant as the interface pH and phosphate concentration are high. For the movement of calcium, having obtained the phosphate and base concentration profiles from the diffusion equations, the calcium concentrations can be found by balancing the ionic charges for electroneutrality. Thus considering the major ionic species in solution in this system, we obtain

$$[Ca^{2+}]_L = \tfrac{1}{2}([H_2PO_4^-]_L + 2[HPO_4^{2-}]_L + [HCO_3^-]_L + m[A^{m-}]_L - [H^+]_L - n[M^{n+}]_L), \quad (9)$$

where A^{m-} and M^{n+} represent any additional anions and cations in the soil.

The model solves the equations for phosphate, base and calcium, subject to their fluxes at the DCPD surface being equal and their concentrations obeying the solubility product relation, and it predicts the concentration profiles of each ion in the soil.
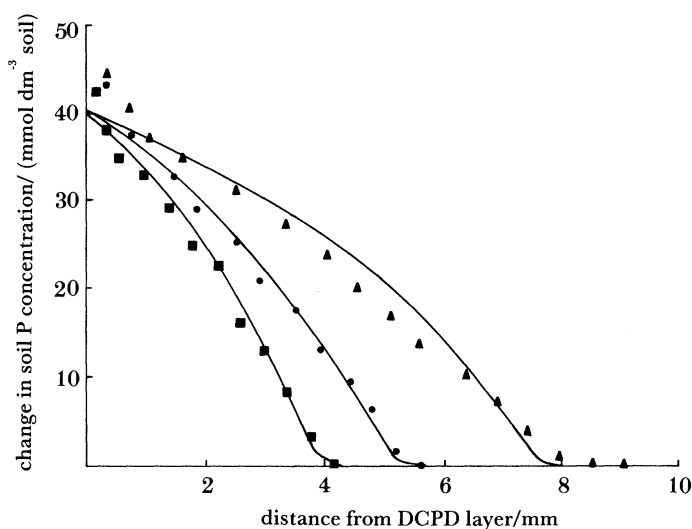
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Figure 5. Changes in total phosphate concentration profiles near dissolving DCPD after different times: points are experimental observations; lines are model predictions. Initial soil pH = 3.5; (■), 4 days; (●), 8 days; (▲), 16 days.

(b) Extension of the model to particles (Kirk & Nye 1986a)

Assuming that the particles are spherical, we need to calculate the concentration profiles in the sphere of soil surrounding each particle. Two additional effects must be accounted for. First, we must consider the effect of particle size: for a given total DCPD application, the finer the particles the higher will be the total surface area and the higher the rate of dissolution; but a particle's radius also decreases as it dissolves, which tends to reduce the rate of dissolution. Secondly, we must account for the effect of the rate of application: for a given particle size, the rate of application determines the mean distance between neighbouring particles and hence the time before the 'diffusion zones' around the particles overlap. In the model, the soil is divided into equal spherical volumes, one per particle, and the equations for the fluxes of phosphate and base are expressed in spherical geometry to obtain the rate of dissolution of particles and the concentration profiles in the soil. As in the planar model, the concentrations at the surface are found from the solubility product relation and by balancing the solute fluxes.

(c) Experimental testing of the models (Kirk & Nye 1985, 1986a)

Concentration profiles of phosphate, pH and calcium were obtained from columns of moist soil left with one end in contact with a planar layer of DCPD. Figure 5 compares the observed phosphorus profiles at different times with the model predictions using values for the soil parameters obtained for the experimental soil. Table 1 compares the measured total amounts of phosphate and base dissolved at these times with the model predictions. The good agreement between the observed and predicted results showed that the model provides a satisfactory simulation of the system, and that it was suitable for extension to the dissolution of DCPD particles.

Table 1. *The experimentally determined total amounts of phosphate and base dissolved in the planar system at different times and the corresponding predicted amounts of DCPD dissolved*

time (days)	experimental total phosphate (mmol)	total base (mmol)	predicted total DCPD (mmol)
4	0.51	0.52	0.52
8	0.60	0.65	0.63
10	0.93	1.00	0.97

To test the particle model, it is not feasible to measure the solute concentrations near the dissolving particles. Instead, the fraction dissolved at different times must suffice. These fractions were measured by labelling particles of DCPD with ^{45}Ca and recovering the dissolved ^{45}Ca from the soil using a $CaCl_2$ extractant that dissolved none of the undissolved DCPD. Figure 6 shows the results for two soil pHs and different sized particles, as compared with the model predictions. A plot of all the observed results against predicted results had a slope of nearly 1.0 and r^2 of 0.97, showing that the agreement was satisfactory.

(d) Extension of the model to carbonate apatites (Kirk & Nye 1986b)

The general form of the apatites in R.P. is

$$Ca_{10-x}[NaMg]_x(PO_4)_{6-y}(CO_3)_yF_z, \tag{10}$$
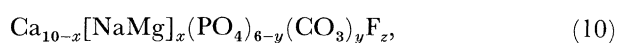
and the range in composition is from pure fluorapatite (FA), $Ca_5(PO_4)_3F$, to the most highly substituted form for which $y = 1.5$. Taking FA as an example, we see that the approach used to model DCPD dissolution may also be used for the dissolution of R.P. components. As with DCPD, dissolution of FA in acid
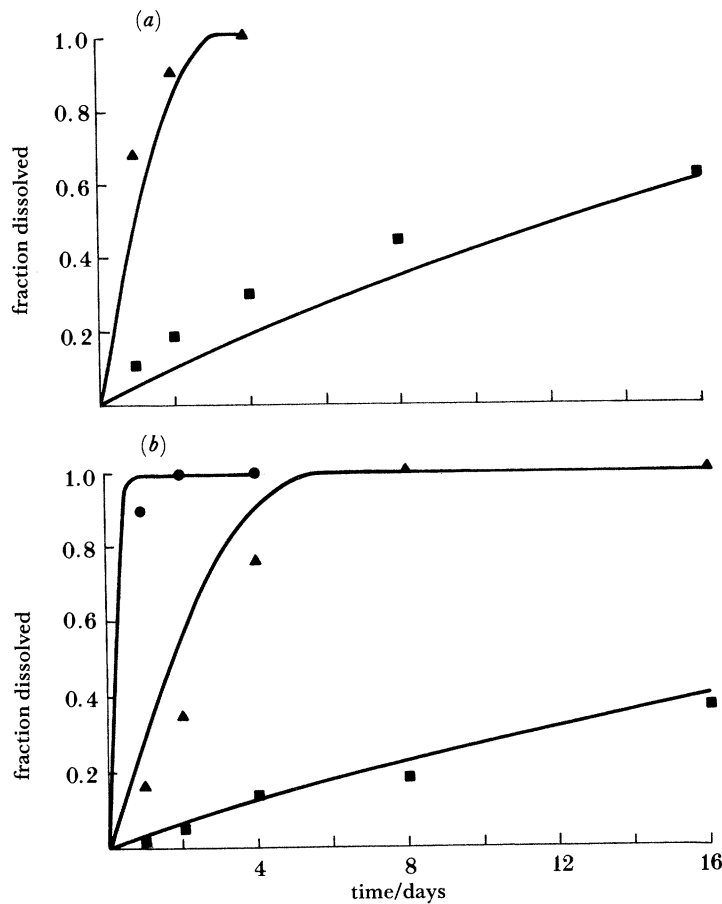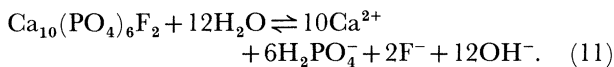
Figure 6. Rates of DCPD particle dissolution at initial pHs (*a*) 4.6, (*b*) 6.0. Particle radii (mm): (●) 0.021, (▲) 0.064, (■) 0.231.

conditions introduces phosphate, base and calcium ions to the soil:

$$Ca_{10}(PO_4)_6F_2 + 12H_2O \rightleftharpoons 10Ca^{2+}$$
$$+ 6H_2PO_4^- + 2F^- + 12OH^-. \quad (11)$$

The phosphate:base ratio for FA is 1:2, and the balance of fluxes must be adjusted accordingly. Also, F^- and any substituted ions must be included in equation (9), and the appropriate solubility product relation must be used. Therefore, only three changes need be made to adapt the model to carbonate-apatites. Figure 7*a* shows how the predicted fraction of maximally substituted carbonate-apatite that is dissolved after 80 days varies with model parameters. Bolland & Barrow (1988) have used the model so adapted to systematize measurements of rock phosphate dissolution under field conditions. They found that the model successfully predicted the trends in dissolution rates.

(*e*) *Effect of method of application and solubilization by roots* (*Kirk & Nye* 1986*b*)

The effect of non-uniform distribution of particles in the soil on the rate of dissolution was considered using a negative binomial distribution to describe the degree of clumping of the particles. A randomly distributed sample dissolved about 10% more slowly than a regularly distributed one. For a degree of clumping in which the sum of the spherical volumes influenced by

particles is only about 10% of the whole soil volume, the predicted rate of dissolution is reduced by about 85%. The effect of having a range of particle sizes in the applied material was also considered. Typical commercial grades of R.P. contain a high proportion of fine particles, resulting in a rapid initial rate of dissolution, but the rate trails off as the small particles are exhausted.

Uptake of dissolved phosphate by roots will tend to reduce the average phosphate concentration in the soil, and thus the rate of dissolution will be enhanced. Furthermore, in many situations (Nye 1986), the roots will simultaneously be secreting acid into the soil, which will tend to lower the soil pH, further enhancing the rate of dissolution. To incorporate these effects in the model, we used a classical model of nutrient uptake by roots (Baldwin *et al.* 1973) and assumed the effect of the roots to be spread across the whole soil volume. Since the model for the rate of dissolution and the model for the rate of root uptake both have the average phosphate concentration in the soil solution as the central variable, it is a simple matter to link them together. The effect of acid and base changes in the soil is obtained from the flux of acid or base across the root surface. In most soils, plant uptake of calcium is small compared with the amount present, so that uptake will generally not alter the validity of equation (9). The predicted effects of root acid excretion on dissolution of R.P. and root uptake are shown in figure 7.

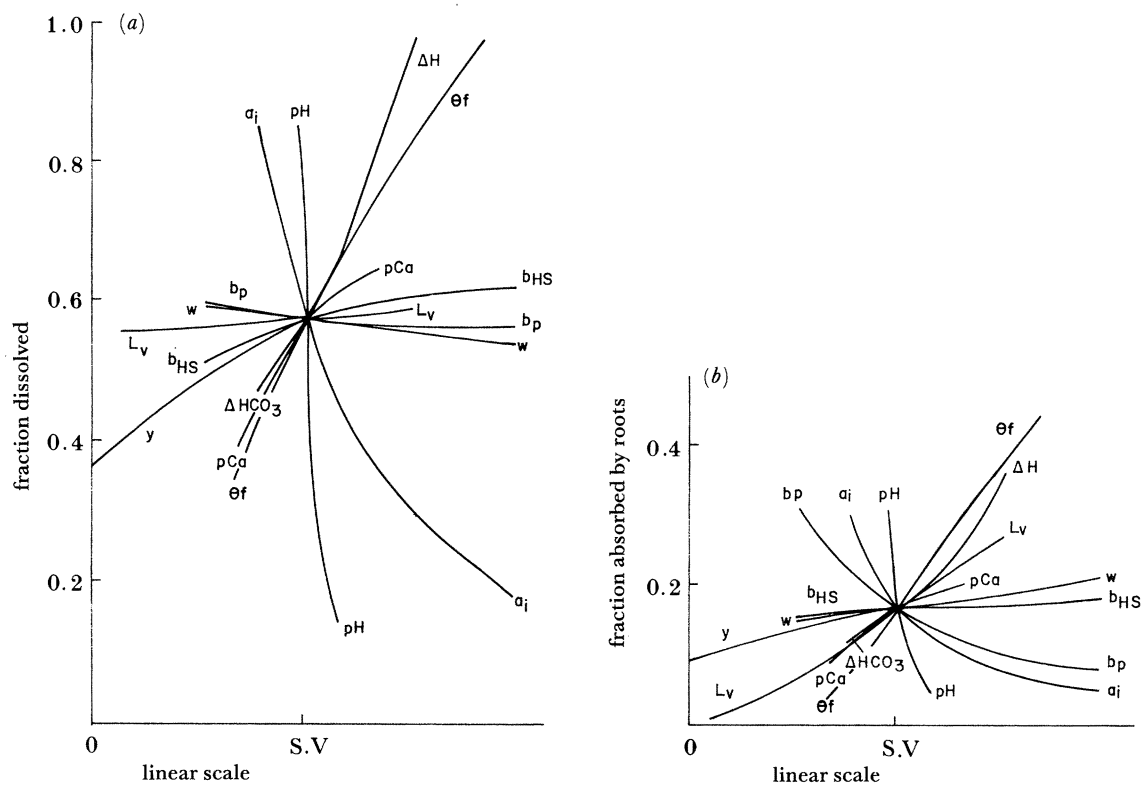The large variation in rate of dissolution of R.P.

Figure 7. Effects of important variables on the fraction of R.P. (*a*) dissolved, and (*b*) taken up by roots after 80 days. The standard parameter values (s.v.) are: $b_P = 70$ mol dm^{-3} soil mol^{-1} dm^{-3} solution; $b_{HS} = 0.07$ mol dm^{-3} soil pH^{-1}; $\theta f = 0.05$; w (application rate) $= 0.16$ kg P m^{-3} soil; a_i (particle radius) $= 0.1$ mm; y (degree of CO$_3$ substitution in FA) $= 1.5$; L_v (rooting density) $= 10^3$ dm dm^{-3}. Maximum ΔH (H$^+$ secreted by roots) $= 10^{-9}$ mol dm^{-3} soil s^{-1}; maximum ΔHCO_3 (HCO$_3^-$ secreted by roots) $= 5 \times 10^{-10}$ mol dm^{-3} soil s^{-1}.

shown in figure 7 shows the variability of agronomic effectiveness to be expected. It also means that there is considerable scope for using R.P.s on soils that are not usually thought suitable for them (i.e. other than strongly acid, low-calcium soils), and for manipulation of soil and crop management practices to suit the use of R.P.s.

5. APPLICATIONS OF THE THEORY. III. CHEMICAL CONDITIONS IN THE RICE RHIZOSPHERE

Rice is the most important cereal crop in the tropics and a staple for over half the world's population. To meet the projected growth in demand for rice, it is estimated that the world's rice production must increase by 65 % by the year 2020 (IRRI 1989). Much of this increase must come through the development of improved rice varieties, and an important part of the development of such varieties will be to advance understanding of processes in the rhizosphere of rice roots, where major nutrient and toxin transformations take place. The rice rhizosphere is poorly understood because rice root development is complicated and because parts of the root may be releasing oxygen and oxidizing materials into the rhizosphere greatly complicating rhizosphere chemistry and biology. The following pages describe a model of the simultaneous diffusion and reaction of oxygen and ferrous iron in soil, with which to investigate conditions near a rice

root releasing oxygen. Since the root-induced changes occur within a distance of the order of 1 mm from the root surface, and it is difficult to measure these changes experimentally with resolutions finer than 1 mm, simulation models such as this may be invaluable in investigating rhizosphere processes. The model deals with planar geometry to facilitate its experimental testing, but the predictions are also relevant to a cylindrical rhizosphere system.

(*a*) *Development of the model* (*Kirk et al.* 1990)

The model is based on a study by Ahmad & Nye (1990) of the kinetics of oxidation of Fe^{2+} in a stirred aqueous suspension of a thoroughly reduced low humus lowland rice soil. The study found that over a short period, less than five days, the main reaction is between Fe^{2+} and O$_2$ with formation of Fe(OH)$_3$ and acidity:

$$4Fe^{2+} + O_2 + 10H_2O \rightleftharpoons 4Fe(OH)_3 + 8H^+. \tag{12}$$
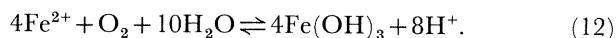
The study showed that the oxidation of Fe^{2+} adsorbed on soil solid surfaces was much faster than that of Fe^{2+} in solution, that some Fe^{2+} was adsorbed on Fe(OH)$_3$ formed during the reaction, and that, surprisingly, the adsorbed Fe^{2+} was oxidized at a rate nearly independent of pH. However, the distribution of Fe^{2+} between the solid and solution varied markedly with pH, and since this distribution greatly affects the mobility of Fe^{2+}, it is necessary to consider pH changes in modelling the system. The model solves equations
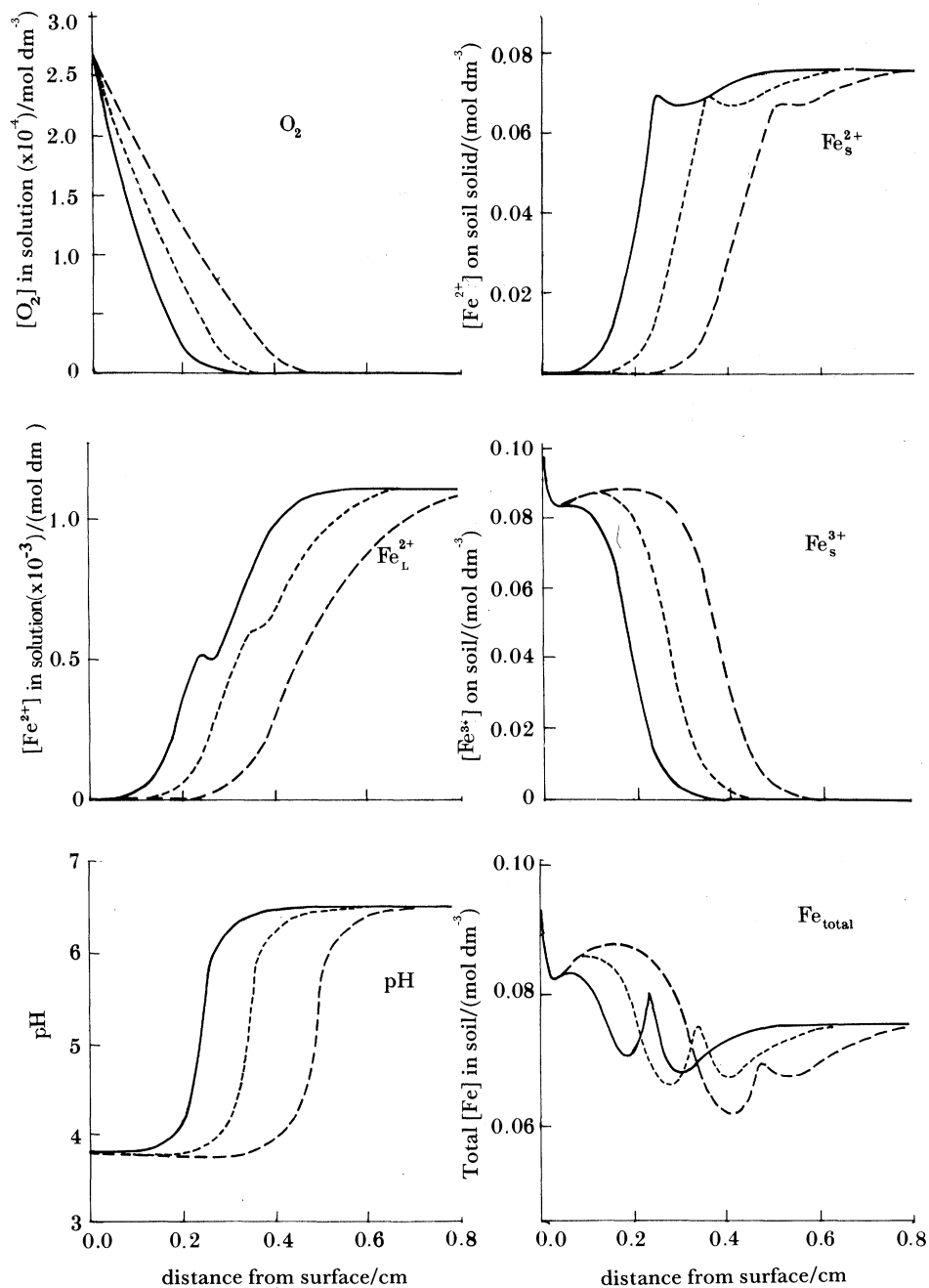
Figure 8. Profiles of oxygen, iron species in the soil solution and solid, and pH after 2.5, (———); 5, (------) and 10, (———) days. Parameter values are as the standards in figure 9.

(b) The model predictions

for the diffusion of Fe^{2+} and O_2, and for soil acids and bases that move in response to the fall in pH caused by the acidity generated in the oxidation reaction. It predicts the profiles of oxygen, pH and reduced and oxidized iron that develop in the soil for given values of the soil iron content, the pressure of CO_2 in the soil, the initial soil pH, the soil pH buffer capacity, parameters for Fe^{2+} sorption by the soil and for the effects of $Fe(OH)_3$ precipitation and pH on Fe^{2+} sorption, the oxidation rate constant and the soil moisture status and bulk density. The pressure of O_2 at the surface is set at atmospheric.

Figure 8 shows the model predictions for unexceptional lowland rice soil conditions. The model predicts that within a few days, substantial amounts of iron are transferred towards the oxidizing surface, leading to a well-defined zone of ferric hydroxide accumulation, and that the pH in this zone is more than two units lower than in the bulk soil. The profile of iron in the zone is banded, which can be explained by the dependence of the oxidation rate on both the O_2 concentration and the distribution of Fe^{2+} between solid and solution as influenced by pH. Such a banded iron profile is consistent with experimentally observed distributions of iron near oxidizing rice roots. Acidifi-

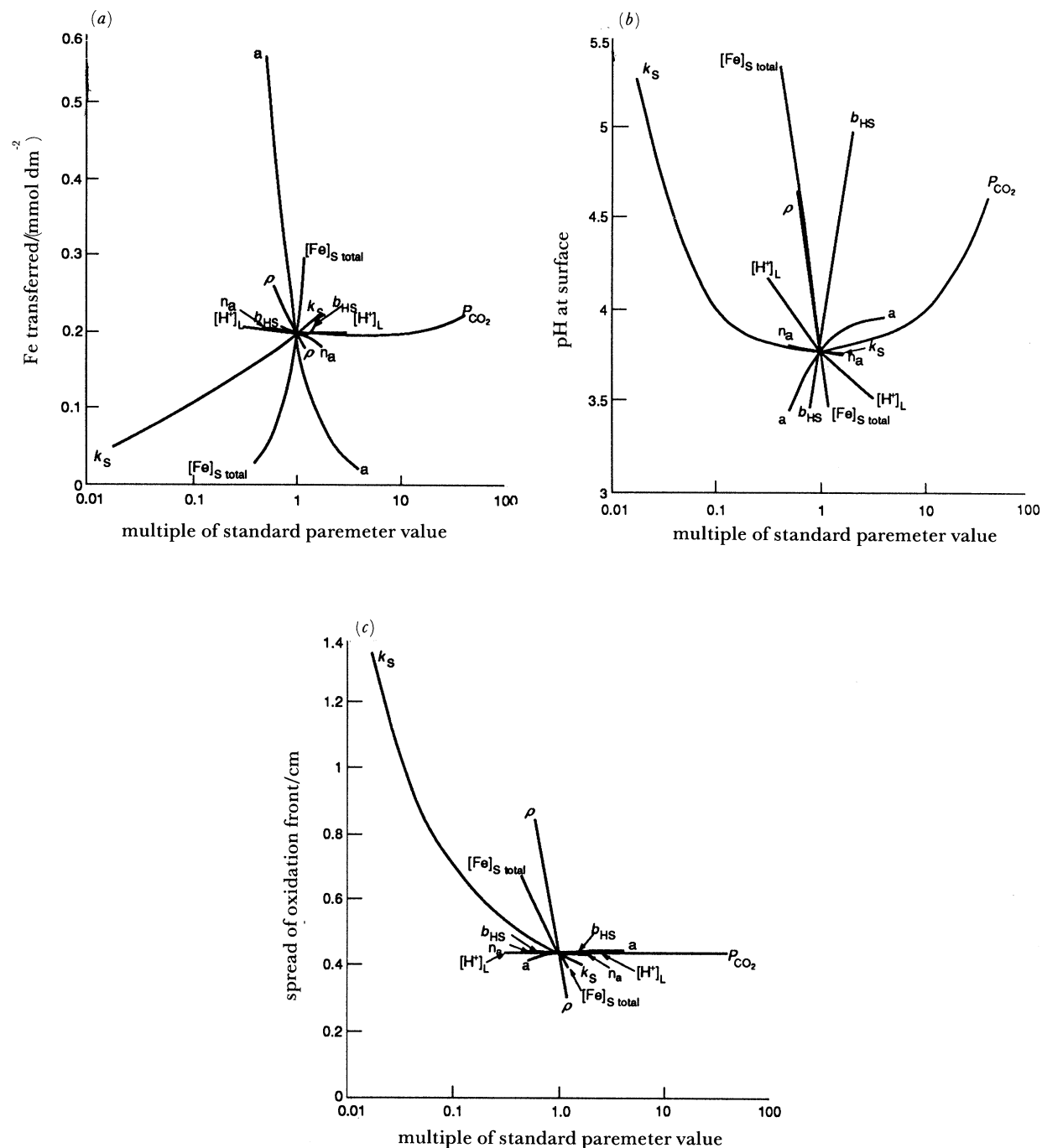340   G. J. D. Kirk   *Diffusion of inorganic materials in soil*

Figure 9. Sensitivity of (a) the net transfer of iron, (b) the pH at the exposed surface, and (c) the spread of the oxidation front, after 5 days. The x-axis is logarithmic. The standard parameter values are: a (Fe^{2+} sorption parameter) $=$ 1.5 mol kg^{-1}; n_a (parameter for the effect of pH and $Fe(OH)_3$ precipitation on Fe^{2+} sorption) $= 30$; $P_{CO_2} = 0.5$ kPa; initial pH $= 6.5$; $b_{HS} = 0.033$ mol kg^{-1} pH^{-1}; k_S (oxidation rate constant) $= 0.3$ dm^3 s^{-1} mol^{-1}; $[Fe]_{total} =$ 0.05 mol kg^{-1}; ρ (bulk density) $= 1.5$ kg dm^{-3}.

cation by rice roots has also been observed, but not measured quantitatively.

Figure 9 shows the model's sensitivity to its input parameters over likely ranges of values, in terms of the net transfer of Fe (figure 9a), the lowering of pH at the surface (figure 9b), and the position of the oxidation front (figure 9c). All three of these are very sensitive to the oxidation rate constant. The stirred aqueous suspension kinetic experiments suggested that the rate controlling step in oxidation may involve the access of O_2 to Fe^{2+} adsorption sites between clay lamellae;

hence a very wide variation in rate constants should be expected between soils, probably as much as a 1000-fold. A small decrease in the Fe^{2+} sorption parameters strongly increases the transfer of iron and to a lesser extent the lowering of the pH; small increases have the opposite effect but to a lesser extent; the spread of the oxidation front is little influenced. Increases in the pressure of CO_2 and initial soil pH result in increased diffusion of HCO_3^- to the oxidation region, thereby decreasing the lowering of pH; an increase in soil pH buffer capacity also reduces the lowering of pH in the

oxidation region. A smaller lowering of pH in the oxidation region results in a smaller net transfer of iron, but scarcely influences the spread of the oxidation front. The spread of the oxidation front is strongly influenced by the diffusion of O_2 and the oxidation rate constant. Also, the soil bulk density greatly influences the system. At low bulk density, and correspondingly high saturated moisture content, rates of solute diffusion are high so that the net transfer of iron and rate of oxidation are high. Allowing for a small gaseous porosity in the soil greatly increases the rate of O_2 diffusion and spread of the oxidation front. With just 1% of the total porosity gas-filled, the oxidation front spreads four times further than in water-saturated soil.

(c) Additional rice rhizosphere processes and implications of the findings

In the rice rhizosphere, acidification caused by Fe^{2+} oxidation is likely to be compounded by acid release from roots to balance excess uptake of cations over anions, nitrogen being supplied in reduced soils chiefly as NH_4^+. The model suggests that this acidity would tend to increase the mobility of Fe^{2+} but reduce the net oxidation rate. Further potential complexities in the rice rhizosphere include a restricted flux of O_2 across root surfaces; microbial consumption of O_2 and liberation of CO_2, and passive uptake of soil CO_2 by roots and its subsequent conveyance to the atmosphere in the aerenchyma, which conveys O_2 in the opposite direction (in flooded conditions, much higher pressures of CO_2 arise in the soil than in the root). These processes are in need of quantification. Microbial consumption of O_2 would result in a decrease in the diffusive spread of O_2 and the oxidation front. The flux of CO_2 into roots probably exceeds the flux of O_2 out, because greater concentrations of CO_2 arise in the soil than of O_2 in the root. Therefore CO_2 may be depleted near roots even though aerobic microbial activity is stimulated by root C and O_2 release with concomitant increases in CO_2 production. A net loss of soil CO_2 would result in a loss of acidity, but also in a decrease in the diffusion of HCO_3^- to neutralize acid generated by Fe^{2+} oxidation and by roots.

The large iron transfers and pH reductions indicated by the model have numerous implications for rhizosphere processes. Table 2 gives some examples of rice rhizosphere processes that are likely to be influenced. The phosphorus buffer capacity of freshly precipitated, poorly crystalline ferric hydroxide at low pH would be very high, tending to reduce the diffusive supply of

phosphorus to roots; but the low pH would also favour release of soil phosphorus. Also, nitrification in an acid although oxidized rhizosphere would be very slow, and a low pH might hinder biological nitrogen fixation. Thus a thorough understanding of rice rhizosphere processes promises interesting possibilities for developing improved rice varieties and agronomic management practices.

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Table 2. *Some effects of rice rhizosphere oxidation*

effect	example
concentration of toxic solute	Fe^{2+}
concentration of major nutrient	$H_2PO_4^-$
concentration of micro-nutrient	Zn^{2+}
N_2 fixation	azospirillum
nitrification	nitrosomonas
enzyme activity	
oxidation of methane	

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Discussion

S. P. S. ANDREW (*1 The Wynd, Stainton, Middlesbrough TS8 9BP, U.K.*). Whereas Dr Kirk employed a 3-dimensional analysis for the spread of nutrient from a phosphate source, you only employed a 2-dimensional analysis for the urea source. As fertilizer particles are on average spaced at some 2 cm apart horizontally, would not a 3-dimensional analysis of the spreading of the urea and its initially high concentration ammonia containing 'plume' immediately beneath the urea particle be valuable particularly as the plume will locally have ammonia concentration above the toxic limit and could cause local damage to roots near the soil surface?

G. KIRK. Yes this would be valuable. The present model describes the reaction of urea crystals applied in a uniform layer on the soil surface; for large granules of urea, inter-granular diffusion may well be important in the early stages of the reaction. The effect will depend on the relative rates of urea diffusion and hydrolysis, as well as the granule size and rate of application. The model could quite easily be adapted to investigate this. Ammonia damage to roots growing near bands of urea is recorded in the literature.

J. M. LYNCH (*AFRC Institute of Horticultural Research, Littlehampton, West Sussex, BN17 6LP U.K.*) In Dr Kirk's paper and those of the preceding speakers, little mention was made of the biological populations as the third component of the soil–plant ecosystem. Many years ago Dr Barber at Letcombe demonstrated the role of the rhizosphere population in nutrient uptake. It is now clear that up to 40 % of the plant's dry matter production can be released in rhizodeposition (carbon loss from roots including respiration from roots and that derived from associated microorganisms). This has been found for some annuals and whereas the figure can be less, in perennials such as mycorrhizal trees, the figure might be even greater. It is dangerous to ignore this in any modelling approaches.

G. KIRK. I agree. We need much more information on the nature and quantity of carbon materials released from roots, and on their effects on chemical and microbiological processes in the rhizosphere. Of Professor Lynch's estimated total carbon release, a large part will be CO_2 respired by roots, and much of the other material is probably rapidly converted to CO_2 in microbial respiration. In aerobic soils, this CO_2 will diffuse rapidly away from the roots in the soil air pore system. On the other hand for rice roots growing in flooded soils, as discussed in the paper, CO_2 may be passively taken up by the roots. The rate of oxygen consumption by microbes in the rice rhizosphere is in general likely to be much slower than its consumption in ferrous iron oxidation.