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PHOSPHORUS CYCLING IN AGRICULTURAL SOILS

Part I: Introduction

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C O N T E N T S

1. INTRODUCTION

In areas with large livestock operations as well as in and around urban areas, large amounts of phosphorus are taken up and then released in wastes. Traditionally such wastes were an important source of minerals and organic matter for agriculture. However, economic pressures now often dictate direct release into the aquatic environment or into soils in excessive amounts. The excess of phosphorus brought into the soil system is subject to transformation processes and displacement. In general, the mobility of phosphorus in soil solution will remain low due to the very effective retention possibilities of soil. However, the mobility of phosphorus in sandy soils is relatively high (VAN DER ZEE and VAN RIEMSDIJK, 1986) which can result in phosphorus leaching out of the soil into the open-water system. Substantial addition of phosphorus into the open-water system results in increased algal productivity and increased decomposition of organic matter which causes depletion of oxygen. These changes are often referred to as eutrophication, which, in this framework, is an undesirable effect (RIWA, 1977). This means that agricultural practices should aim at a situation where the concentration of phosphorus in the water leaving the soil profile and entering the drains remains low and does not exceed certain limits. Computersimulation of the transformation and transport processes of phosphorus in soil possibly can contribute to this aim.

2. C, N AND P CYCLING IN SOIL

The interactions taking place in the N or P cycle are closely related to and interdependent of the processes taking place in the C-cycle.

MCGILL and COLE (1981) constructed a schematic illustration of the
interrelations of C, N, S and P cycling within soil-plant systems
(figure 1).
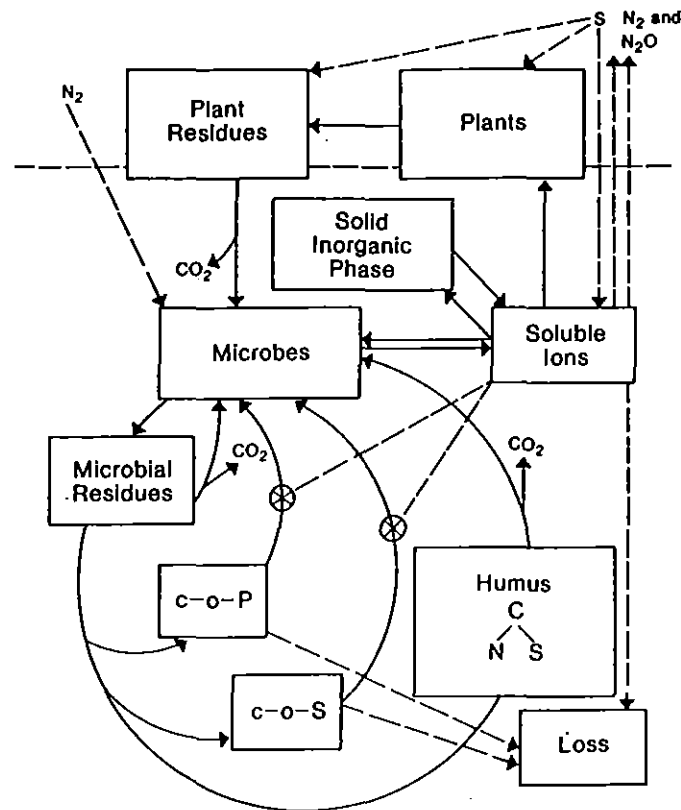
Fig. 1. Interrelations of C, N, S and P cycling withing soil-plant
systems (after MCGILL and COLE, 1981)

Three concentric cycles can be distinguished in this model. For P
and sulfate esters it is possible to 'short-circuit' their cycle if
plants need P and S respectively. MCGILL and COLE (1981) suggest that
C and N are stabilized together and mineralized through biological
mineralization, whereas organic P and sulfate esters are stabilized
independently of the main organic part and are mineralized through
biochemical mineralization. Biological mineralization, defined as
release of inorganic forms of N and S from organic materials during
oxidation of C by soil organisms to provide energy, is driven by the
search for energy. Biochemical mineralization, defined as release of
inorganic ions of P and S from organic form through enzymatic cataly-
sis external to the cell membrane, is strongly controlled by the
supply of and need for the element released rather than the need for
energy.

Splitting up the interrelated C, N, S, P cycle of figure 1 result in 4 separate ones. For modelling purposes schematization of these cycles is necessary to make quantification of the different processes less dificult.

Fig. 2. The carbon cycle (after BERGHUIS-VAN DIJK et al, 1985)

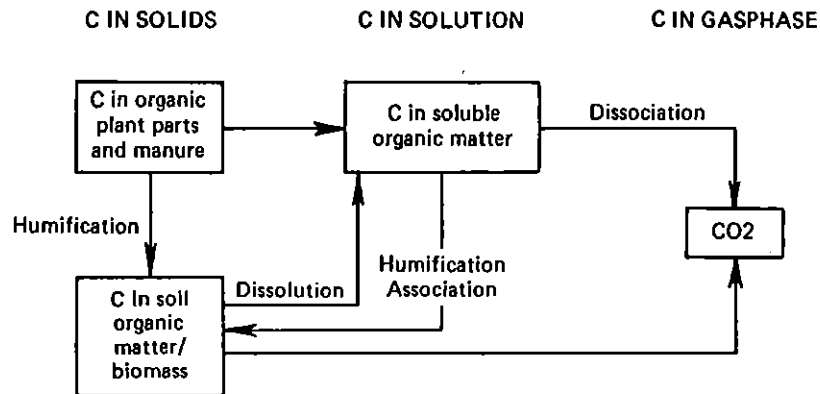In ANIMO (Agricultural Nitrogen Model) schematized C and N cycles have been introduced (BERGHUIS-VAN DIJK et al, 1985). Figure 2 gives the simplified soil organic matter or carbon cycle in soil as been used in ANIMO. Fresh organic material (i.e. dead plant parts and organic parts of manure) is partially oxidized to CO_2 and H_2O and partially transformed into soil organic matter. The ratio

$$a = \frac{\text{formed soil organic matter}}{\text{total amount of fresh organic material decomposed}}$$

is called the assimilation factor. At least a part of these transformation processes take place via the stage of soluble organic matter. The first step in the decomposition proces when big solid molecules like cell walls are involved is a splitting up of these molecules to smaller parts. Micro-organisms use exo-enzymes (operating outside the micro-organism cell) to perform this task. Generally spoken, the smaller the components formed, the higher their solubility is. The smaller molecules can be taken up by the micro-organism cell to be decomposed further.

The formed soil organic matter, in its turn, decomposes to CO_2 and H_2O, but at a much lower rate than the fresh organic plant parts. The biomass (micro-organisms) decomposes and renews itself at relatively high but often unknown rates; we can simplify and consider formation and decomposition of biomass as a one-direction overall process of the same kind as formation and decomposition of soil organic matter.

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Because it is quite difficult to distinguish experimentally between
the small fraction of living biomass and the total amount of dead soil
organic material, these two are often taken together in descriptions,
as is done by BERGHUIS-VAN DIJK et al (1985).

Living plant roots excrete soluble organic materials into soil
solution; also, dead root cells, discarded by the plant, become avai-
lable for decomposition; these products are called root exudates; they
partake in the carbon and nitrogen transformation cycles too.

Because it is uncertain which products are solubilized BERGHUIS-
VAN-DIJK et al (1985) have modelled the carbon cycle according to the
following schematization.

$$\text{fresh org. mat.} \rightarrow \text{soluble org. mat.} \nearrow^{CO_2} \text{soil org. mat.} \rightarrow CO_2$$
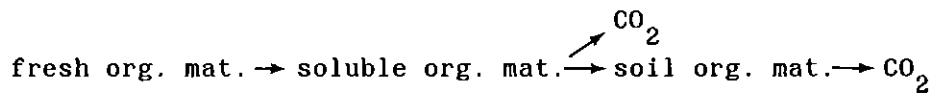
Root exudates are already partly soluble, and because it is known
that they disappear very quickly, transport possibilities will be very
small and there is no need to include an extra soluble stage here:

$$\text{root exudates} \nearrow^{CO_2} \text{soil org. mat.} \rightarrow CO_2$$
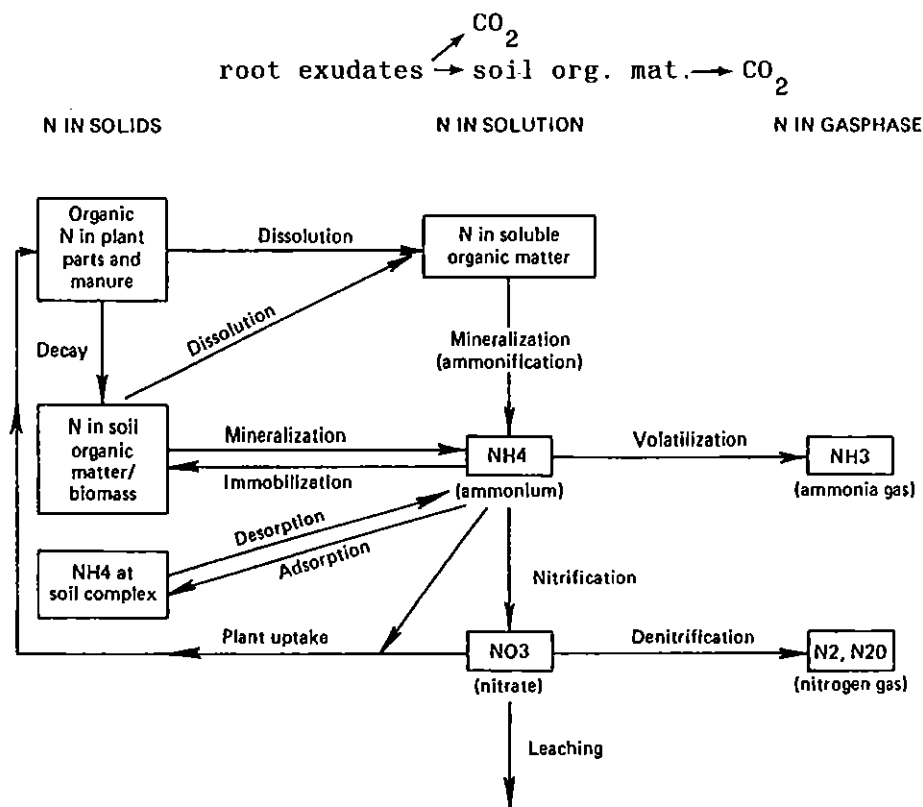
Fig. 3. The nitrogen cycle (after BERGHUIS-VAN DIJK et al, 1985)

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The different organic materials mentioned contain besides carbon
also nitrogen and phosphorus (except CO_2). So transformations in the
carbon cycle correspond with transformations in the nitrogen and phos-
phorus cycle. The schematized nitrogen cycle as been used in ANIMO is
shown in figure 3.

It can be seen that part of this cycle corresponds closely with
the C-cycle. The other part of the N-cycle describes processes such as
nitrification and denitrification.

The phosphorus cycle in soil can be schematized similarly as been
done with the N-cycle. An example is shown in figure 4.
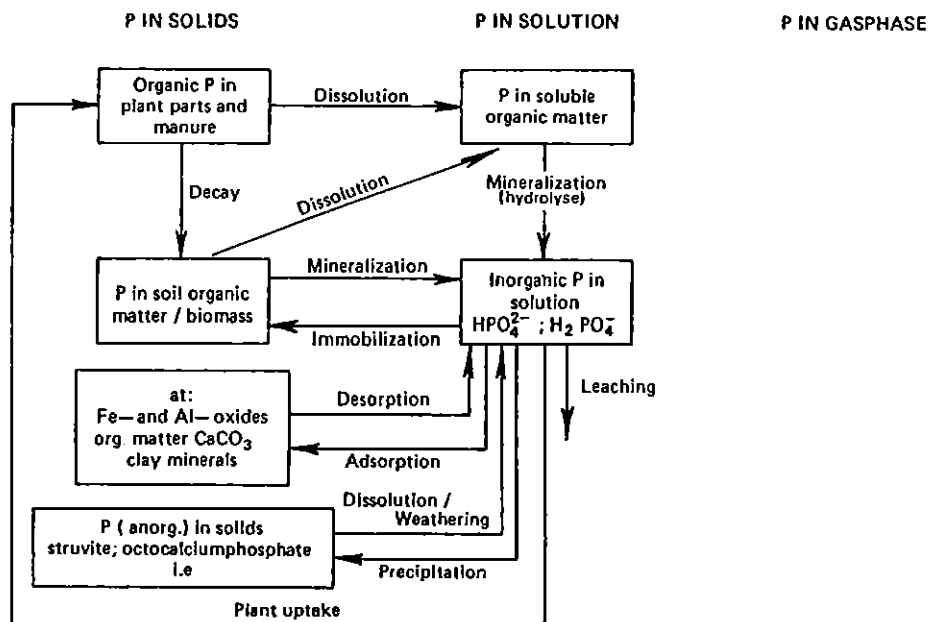
Fig. 4. The phosphorus cycle

It should be mentioned here that in agricultural areas liable to
high manure gifts, phosphorus is mainly added as inorganic P in solids
such as struvite, octocalciumphosphate and dicalciumphosphate
(GERRITSE, 1977; FORDHAM and SCHWERTMANN, 1977; GERRITSE and EKSTEEN,
1978) (see figure 5). These minerals are (very) soluble in soils with
pH up to 6.5. Dissolution of these minerals can increase the concen-
tration of inorganic P in soil solutions importantly which ultimately
can result in an increase in phosphate leaching.

	% of O.M.	average % of total P
total inorganic P	0.7 - 1.7	80
total organic P	0.2 - 0.4	20
inorganic P in solution	0.01- 0.2	10
phytate P	0.05- 0.1	5
P in microorganisms	0.02- 0.04	3
organic P in solution	0.01- 0.03	1.5
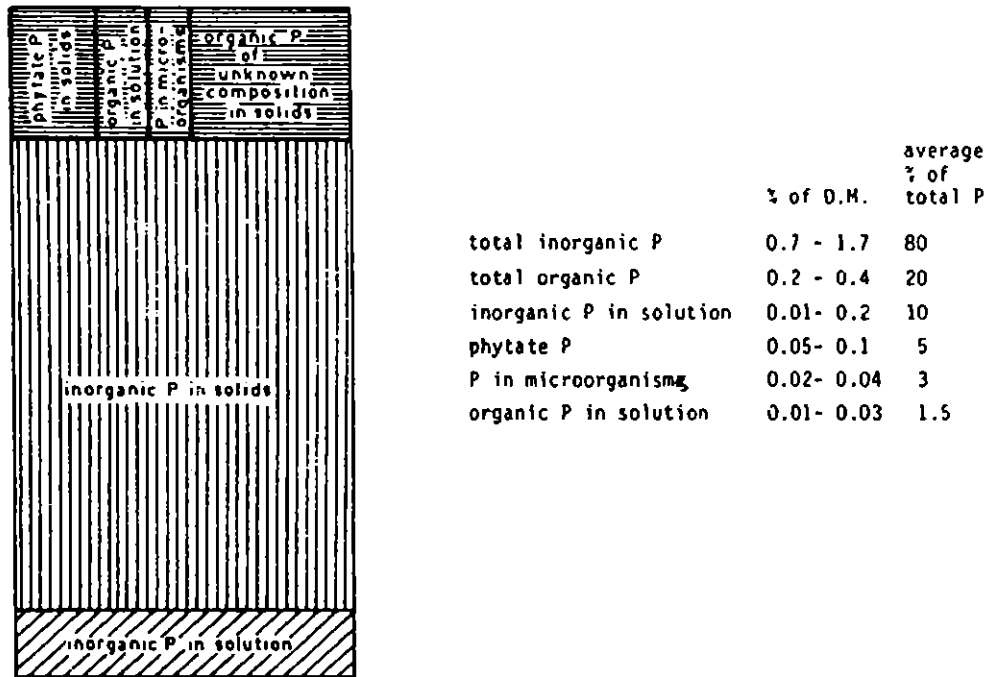
Fig. 5. The relative distribution of different phosphate forms in pig slurry (after GERRITSE, 1977)

3. PHOSPHORUS FORMS IN SOIL

3.1. Phosphorus in solids

3.1.1. Phosphorus minerals

Nearly 200 phosphorus minerals have been found in nature, but of these only one group is of significance, namely the apatites. The apatite unit cell has the chemical composition $M_{10}(PO_4)_6X_2$ and most frequently the metal ion M is calcium and X is fluorine. Thus calcium-fluorapatite $Ca_{10}(PO_4)_6F_2$ is the commonest phosphorus mineral. In igneous rock, fluorapatite always contains the theoretical amount of fluorine. It exists as well formed crystals which constitute 0.6 percent of the total rock. Fluorapatite is classified among the most easily wheathered minerals (MITCHELL, 1964); therefore, it very rarely occurs as a primary mineral in sediments.

The phosphorus content of sediments is on average lower than in igneous rock. The secondary phosphorus minerals present also belong to the apatite group, but they generally exist in poorly crystalline forms with many substitutions in the lattice. There are four main types of substitution, the pure end members of which are hydroxylapa-

tite, carbonateapatite, chlorapatite and secondary fluorapatite
(DEGENS, 1964).

In virgin soil the total phosphorus content varies widely (LARSEN,
1967). Significant quantities of phosphorus are lost during soil for-
mation, probably by leaching and erosion. Soil, on a global scale, has
not received phosphorus from any source other than the parent mate-
rial. Some redistribution, however, is brought about by wind, water,
animals, and plants, causing depletion in some areas and enrichment in
others. In modern times this redistribution has been accelerated by
the activity of man; enrichment by manufacturing and applying fertili-
zers containing phosphorus on the one hand, and depletion through
cropping on the other. As mentioned before high manure gifts in agri-
cultural areas leads to an additional increase of phosphate minerals
in soils, e.g. of struvite ($MgNH_4PO_4.2H_2O$), octocalciumphosphate
($Ca_4H(PO_4)_3.3H_2O$) and dicalciumphosphate ($CaHPO_4.2H_2O$). Dissolution of
these minerals consequently leads to an increase of inorganic phospho-
rus in solution and ultimately to an increase in phosphate leaching.

3.1.2. Organic soil phosphorus

A significant proportion of the phosphorus which is present in the
top soil is in organic combination, either as specific organic phos-
phorus compounds or as organic compounds to which inorganic phosphorus
is linked. The organic phosphorus fraction may comprise between 20 and
80 percent of the total soil phosphorus.

The proportion of this organic phosphorus which is in the soil
solution is probably small. HANNAPEL et al (1964a) showed that a sub-
stantial part of the apparent organic phosphorus in extracts from
soils treated previously with easily decomposed organic matter, was
removed by filtration and centrifugation. This suggests that much of
what was earlier thought to be organic phosphorus in solution may in
fact have been microbial cells and coloidal debris.

The phosphorus content of organic matter in soils is influenced
by:

- rainfall	rainfall	>	org. phos. con. <
- temperature	temperature	>	org. phos. con. <
- drainage	drainage	<	org. phos. con. <
- soil pH	pH	>	org. phos. con. <
- cultivation	cultivation	>	org. phos. con. <
- manuring	manuring	>	org. phos. con. >

3.1.3. Sorbed phosphorus

The phenomenon of concentration of liquid or gaseous material on the surface of a solid is known as adsorption, while the incorporation of liquid or gaseous material into a solid is known as absorption. Removal of phosphorus from the soil solution has been considered to be due to both these mechanisms (HEMWALL, 1957) and is often called sorp-tion as a collective name for both reactions. The reverse process, the movement of phosphorus from the solid phase to the solution, is con-veniently called desorption.

Sorption of phosphorus can take place into the surfaces of:

- Al- and Fe-(hydro)oxides;

-- edges of clayminerals;

- Al- and Fe-bonded to organic substances;

- calciumcarbonates.

Measurement of the size of the phosphorus sorption system can be made by fitting sorption data to a previously described sorption iso-therm. Freundlich and Langmuir isotherms have often been used for this purpose.

The phosphorus sorption capacity of dutch sandy soils is mainly controlled by the presence of large quantities of Al- and Fe-hydroxides (KORZILIUS and BREEUWSMA, 1983).

Mankor (in press) uses a chemical equilibria method to quantify and calculate ratios between P-sorbed and P-solved in soils.

3.2. Phosphorus in solution

3.2.1. Inorganic phosphorus in soil solution

The concentration of phosphorus in the soil solution is of the order of 1 to 0.1 ppm. It varies with the properties of both the solid and liquid phases and also with the ratio between solid and solution. The forms in which phosphorus exists in solution are governed by the reactions of protonation and complex formation. These forms are ortho-phosphoric acid, $H_3PO_4^o$, the corresponding ions, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and the soluble complexes of these ions. The distribution of orthophos-phate ions in solution against pH is shown in figure 6. It is obvious from the graph that the ionic species $H_2PO_4^-$ and HPO_4^{2-} are the most abundunt in the pH range encountered in soil.
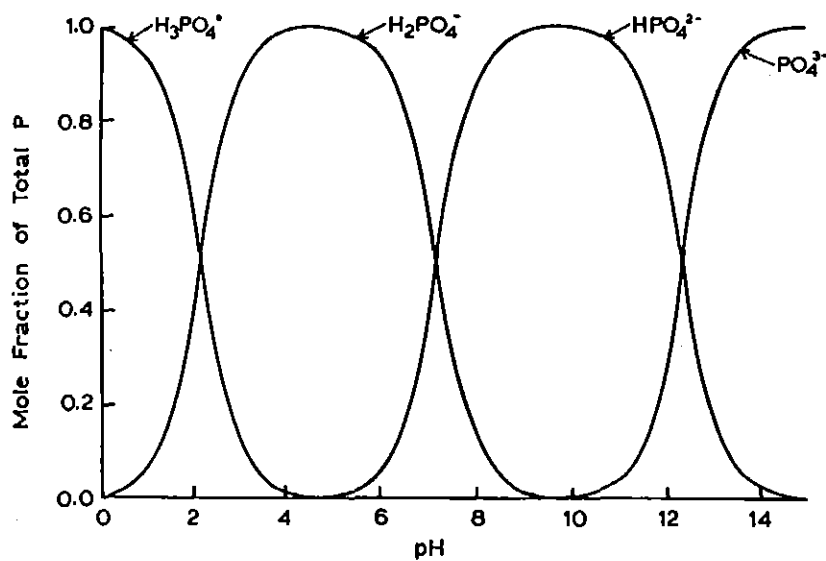
Fig. 6. Distribution of orthophosphate ions in solution against pH
(after LINDSAY, 1979)

The orthophosphate ions form soluble complexes with many metallic
ions, and part at least of the phosphorus in the soil solution may be
complexed. Soluble complexes that are likely to occur and their equi-
librium constants are given by LARSEN (1967), LINDSAY (1979) and
others. Calculation of the proportion of the phosphorus that is likely
to be present in a complexed form in a given soil solution can be
carried out by using an adjusted version of the model COMPLEX as been
formulated originally by ABDEL KHALIK and BLÖMER (1984).

3.2.2. Organic phosphorus in soil solution

Relatively little information is available on the nature of orga-
nic phosphorus in the soil solution. WILD and OKE (1966) identified
the myoinositol monophosphate as the major constituent of organic P in
the $CaCl_2$ extract of soil. MARTIN (1970) obtained some evidence of
phosphate esters in cold water extract of soil, but the other compo-
nents could not be identified. It appears that a significant propor-
tion of the intracellular organic phosphorus is released into soil
solution from the damaged microbial cells with the phosphate ester
bond intact. Since organic phosphorus in soil solution is not utilized
by a large variety of plants this led to the conclusion that either
organic phosphorus does not contain the correct phosphorus compounds
necessary for plant growth or that organic phosphorus in the soil
solution is present in complex form. According to HANNAPEL (1964b)

most of the organic phosphorus in the soil solution is actually
colloidal in nature and associated with microbial cells and cellular
debris. Therefore availability of organic phosphorus in soil for
plants may be very low.

According to GERRITSE (1981) significant migration of organic
phosphorus in soil solution takes place only if high gifts of manure
(pig slurry) are added to the soil. With low or normal doses under
average rainfall, no significant leaching of P in this fraction could
be detected (GERRITSE, 1981).

4. PHOSPHORUS TRANSFORMATIONS IN SOIL

4.1. Dissolution ⇌ precipitation

The upper limit for the phosphorus concentration in solution is
set by the heterogenerous equilibria in which it takes part. The reac-
tions involved are the dissolution and precipitation of sparingly
soluble phosphorus salts, controlled by the solubility product prin-
ciple.

BJERRUM (1949) found two solubility products for octocalcium phos-
phate and two for hydroxylapatite; one when the equilibrium was
approached by precipitation and the other when it was approached by
dissolution.

WILD (1954) examined a large number of early analytical data but
found no agreement between the concentration of phosphorus in the soil
solution and the concentration predicted from solubility products.
More recently, other workers in this field (for instance BACHE, 1963)
have also found that the phosphorus concentration of the soil solution
did not conform to solubility product principles. A further complica-
tion is the strong influence that impurities seem to have on phosphate
solubility products.

The lack of agreement between the phosphorus concentration of a
soil solution and the solubility of pure hydroxylapatite does not
necessary imply that hydroxylapatite is not determining the phosphorus
concentration. A degree of acidity at which all calcium phosphates are
so soluble that they cannot possibly control the phosphorus concentra-
tion will, of course, eventually be encountered. For instance for pH
levels below 4 phosphate concentrations in soil solutions can be con-

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trolled by the solubility of aluminium phosphates such as variscite
(LARSEN, 1967).

Nature reserves located in the sandy middle-east parts of the
Netherlands contain generally soil solutions with very low phosphate
concentrations (Mankor, in press). Consequently possible phosphate
precipitation reactions can be ignored.

However, in agricultural areas exposed to high manure gifts this
need not to be the case. Added manure gifts contain large quantities
of soluble inorganic P-minerals. Dissolution of these minerals result
in an increase in inorganic phosphate in soil solutions. This increase
can continue upto a maximum level where precipitation of other, less-
soluble, P-containing minerals will take place.

4.2. Sorption ↔ desorption

The phosphate sorption may consists of adsorption and/or absorp-
tion like reactions. Due to the low solubility of several phosphate
containing minerals, absorption may already occur at very low phos-
phate concentration. However, in general it is very difficult to unra-
vel the total sorption into its different contributions.

Under average conditions a strong sorption of inorganic P in soils
can be expected. The main factors affecting this sorption appear to be
Fe, Al and Ca content of the soil, specific surface area, pH and redox-
potential. Time is also an important parameter (GERRITSE, 1982;
RIEMSDIJK and VAN DER LINDEN, 1984). After an initial rapid adsorp-
tion, fixation of inorganic P in soils increases slowly with time due
to chemical immobilization reactions with rate constants of the order
of $(months)^{-1}$, $(years)^{-1}$ (GERRITSE, 1982). The slower reaction follo-
wing the initial adsorption is then assumed to be due to absorption of
phosphate on metaloxides/hydroxides. Although Langmuir isotherms can
succesfully describe analytical data for the initial reaction, the
underlying mechanism is not necessarily an adsorption reaction (VEITH
and SPOSITO, 1977). VAN RIEMSDIJK and LYKLEMA (1980) found that
adsorption contributed very little to the total soprtion at P concen-
trations above one $mmol.l^{-1}$, and already after 5 to 15 min absorption
(i.e. formation of metal-phosphate coatings) appeared to be the domi-
nant reaction.

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Whatever the exact processes might be sorption/desorption of phosphate onto (pure) Al- and Fe-oxides/hydroxides can be described succesfully by chemical equilibrium reactions as proposed by GOLDBERG and SPOSITO (1984 a,b). For modelling purposes such an approach is attractive.

4.3. Mineralization ↔ immobilization

The conventional approach to predict whether net mineralization or immobilization of P occurs when organic matter decomposes rests upon identifying a critical ratio of C to P in the substrate used by the micro-organisms, in a manner analogous to identifying a critical C/N ratio above which N immobilization occurs and below which there is mineralization. A review of recent literature reveals a wide range of critical C/P ratios, varying from 50 upto 300 (WHITE, 1982).

In this study WHITE (1982) conclude that the balance between mineralization and immobilization of P during the decomposition of fresh residues or humified organic matter will depend on the C/P ration of the substrate on which the micro-organisms are actually feeding, their growth yield (CF) and the C/P ratio within their tissues (C_m/P_m) according to the equation:

$$P/C \text{ substrate} = (1-CF) \frac{P_r}{C_r} + \frac{CF}{C_m/P_m} \qquad (2)$$

Solving this equation using data from literature suggests that the critical C/P ratio of the substrate from which micro-organisms mineralize P, vary between 50 and 70 (WHITE, 1982).

5. TRANSPORT OF PHOSPHORUS IN SOIL

Convective transport of inorganic and organic phosphorus in soil solution to deeper layers is possible (BEEK and VAN RIEMSDIJK, 1982). The removal of phosphate from percolating liquid manure and its distribution in the soil profile depends on the ratio of the carrier flux density to the rate constants of the processes by which the phosphate species are retained or transformed. Whether inorganic and organic phosphate compounds present in percolating liquid manure give different distribution patterns in soil will depend on the retention

characteristics of these compounds and the rate constant of the mine-
ralization process by which organic phosphate in solution is transfor-
med into orthophosphate and the rate constant of the process by which
inorganic phosphate in solution can be immobilized into soil organic
matter (BOUWMAN et al, 1967; HASHIMOTO and LEHR, 1973; ROLSTON et al,
1975). Obviously the presence of substances in the added liquid manure
that compete for the same sites as the phosphate compounds also
influences the distribution pattern (CAMPBELL and RACZ, 1975).

According to GERRITSE (1982) only a small part of organic phospho-
rus in liquid manure appears to be mobile. This mobile organic phos-
phorus amounts to 1% of total P or 10-20 mg P/l pig slurry. It is of
microbial origin, of high molecular weight and is only slightly absor-
bed to soil. With high doses of pig slurry only, this fraction appears
to migrate through the soil fairly rapidly. With low or normal doses
no significant leaching of P in this fraction could be detected. The
remaining organic phosphorus compounds in pig slurry are strongly
retained in the soil and are rapidly taken up in the phosphorus cycle.
The mobility of phosphorus added to soils with low or normal doses of
pig slurry can be said to be governed mainly by orthophosphate and can
be modelled quite adequately by considering all added phosphorus as
orthophosphate (GERRITSE, 1982; GERRITSE et al, 1982). However, if
high doses of pig slurry are added into the soil mobile organic phos-
phorus can participate significantly to total leaching of phosphorus
out of the soil system.

6. MODELLING PHOSPHORUS CYCLING IN AGRICULTURAL AREAS

The wish to model the phosphorus cycle in agricultural areas is a
complex one that should not be underestimated.

The inorganic phosphorus in solution is of particular importance
since it represents the mobile portion of soil phosphorus immediately
available for uptake by plant roots and/or leaching. The concentration
of inorganic phosphorus in solution is influenced and controlled by
the interaction of the different phosphorus transformation processes
and the existing hydrological regime in soil.

Phosphorus transformation processes are generally thought to occur
as a complex series of multistep kinetic reactions (TALIBUDEEN, 1974;
ARAMBARRI and TALIBUDEEN, 1959; MATTINGLY, 1975). However, as stated
by SCHUFFELIN (1974), a serious lack of experimental data exists to

describe the rate coefficients for these reactions. Unfortunately,
this deficiency in current knowledge of phosphorus chemistry has appa-
rently inhibited application of reaction mechanisms for the purpose of
quantitatively describing the dynamics of phosphorus applied to soil.
The rates of competing reactions are as important if not more so than
the final equilibrium state in determining the quantities of the
various phosphorus phases. Thus a need exists to determine the
influence of the kinetics of phosphorus transformations as well as the
equilibrium states upon phenomena such as leaching loss and plant
uptake of applied phosphorus.

In several models (ENFIELD and SHEW, 1975; NOVAK et al, 1975; SHAH
et al, 1975; HARTER and FOSTER, 1976; OVERMAN et al, 1976; MANSELL et
al, 1977a,b; RAATS et al, 1982; VAN DER ZEE and VAN RIEMSDIJK, 1986)
adsorption is treated as a reversible process, i.e. the adsorbed phos-
phate may desorb, though with a slower rate that during the adsorption
step. Adsorption (chemical immobilization, fixation) and precipitation
are usually considered as irreversible processes, generally with a
much slower rate than adsorption.

Kinetic expressions for these processes may vary from instanta-
neous equilibrium for adsorption to simple or complex rate equations
(ENFIELD, 1974; NOVAK and ADRIANO, 1975; ENFIELD et al, 1976; RAATS et
al, 1982; VAN DER ZEE and VAN RIEMSDIJK, 1986). Usually absorption,
precipitation and mineralization reactions are expressed in terms of
first-order rate equations (OVERMAN et al, 1976; ENFIELD et al, 1976;
COLE et al, 1977).

Although several investigators have combined both reaction rate
and mass transport theories to describe the dynamics of transforma-
tions and transport of applied phosphorus in soil (ENFIELD and BLEDSOE,
1975; MANSELL et al, 1977; SELIM et al, 1975; HELGAR and MUNS, 1975;
CHO et al, 1970; RAATS et al, 1982; VAN RIEMSDIJK et al, 1984; VAN DER
ZEE and VAN RIEMSDIJK, 1986) most if these models involve only a few
phosphorus transformation processes of the ones actually taking place
in soil. The most extensive but at the same time most simplified phos-
phorus cycling models are those developed for undisturbed natural eco-
systems (COLE et al, 1977; HALM et al, 1972; JONES et al, 1984). A far
more detailed model describing the phosphorus cycle in nature reserves
is being developed at present at the ICW (Mankor, in press).

Detailed models describing the phosphorus cycle in agricultural
areas exposed to varying manure gifts are not available so far.
Simplified ones, describing phosphorus transport, sorption, desorption

and/or precipitation processes are developed abundantly (RAATS et al,
1982; BERGHUIS-VAN DIJK, 1981; VAN DER ZEE and VAN RIEMSDIJK, 1986).
Usually these models predict phosphate transport quite adequately in
areas (or soil colums) where such simplified conditions occur. In more
heterogeneous areas subject to varying (high!) manure gifts other pro-
cesses such as phosphorus mineralization, immobilization, dissolution,
plant uptake and transport of organic phosphorus influence the distri-
bution pattern of phosphorus in soil significantly. Consequently these
processes have to be taken into account if one wishes an accurate
approach of the phosphorus cycle. Probably large parts of ANIMO
(BERGHUIS-VAN DIJK et al, 1985) can be of use in the development of a
future 'agricultural phosphorus model' because for instance the
complex carbon cycle is extensively described in it.

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