Phosphate retention by soil in relation to waste disposal

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PHOSPHATE RETENTION BY SOIL IN RELATION TO WASTE DISPOSAL

Proefschrift
ter verkrijging van de graad van
doctor in de landbouwwetenschappen,
op gezag van de rector magnificus,
dr. H.C. van der Plas,
hoogleraar in de organische scheikunde,
in het openbaar te verdedigen
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des namiddags te vier uur in de aula
van de Landbouwhogeschool te Wageningen

STELLINGEN

1. Het karakteriseren van bodemfosfaten met behulp van een 'electron microprobe' of rasterelektronenmicroscoop voorzien van een energie dispersieve analysator verdient de voorkeur boven de tot nu toe veelal toegepaste fractionering met behulp van selectieve extractie methodieken.

2. Het vastleggend vermogen van een grond voor fosfaat wordt onderschat als alleen rekening wordt gehouden met een vastlegging via adsorptie-processen.

   Sawhney and Hill. J. Environ. Qual., 4: 342-346 (1975); Sawhney. J. Environ. Qual., 6: 86-89 (1977); Dit proefschrift.

3. Om in tijden van schaarste over enige fosfaat reserve te kunnen beschikken verdient het aanbeveling om vloeivelden in te richten op gronden met groot P-bindend vermogen om hierdoor zoveel mogelijk het fosfaat vast te leggen dat aanwezig is in huishoudelijk afvalwater.

4. Het gebruik, fosfaatgehalten van bodem, water en meststoffen wisselend uit te drukken in eenheden P_2O_5, PO_4 en P, geeft aanleiding tot misverstand.

5. In het bodemkundig museum zou een voorraad heide-ontginningsgrond aanwezig behoren te zijn om ook in de toekomst aan te kunnen tonen dat de zogenaamde ontginningsziekte inderdaad op een gebrek aan opneembaar koper berustte.

   J.M.L. Otten en G. Veenstra. Bemestingsleer (1949); Th.M. Lexmond and F.A.M. de Haan. Proc. Int. Seminar on Soil Environ. and Fert. Manage. in Intensive Agric., 383-393 (1977).

6. Verder uitstel van invoering van de Wet op de Bodembescherming zal automatisch leiden tot afstel van deze wet.

7. Voor een juist inzicht in de feitelijke situatie met betrekking tot overdosering van meststoffen moeten meststof-balansen per bedrijf worden berekend.

8. De mogelijkheid om door middel van de zogenaamde derde geldstroom meer toepassingsgericht onderzoek van enige omvang te kunnen verrichten in vakgroepsverband is van groot belang voor het meer fundamenteel gerichte onderzoek van de groep.

9. Het opnieuw invoeren van het systeem van de gasmunt zou in een koude periode een sterke stimulans betekenen voor het isoleren van woningen.

Stellingen behorend bij het proefschrift van ir. J. Beek,
getiteld 'Phosphate retention by soil in relation to waste disposal'
Wageningen, 23 maart 1979.

Aan Joan
Githa en
Henriette

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Het typewerk werd door mej. De Kat verzorgd. Karin, veel dank voor je enthousiaste en niet aflatende inzet. Ook de heer Matser wil ik graag bedanken voor het tekenen van de figuren. Op de valreep heeft Dr.Ir. A.R.P. Janse nog zijn artistieke blik laten gaan over de tekening op de omslag. Toon, mijn hartelijke dank.

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CONTENTS

1 INTRODUCTION

The enrichment of (shallow, standing) surface waters with phosphate (P) is generally considered to be a primary factor responsible for excessive biological production in such eutrophied waters. In order to prevent P-induced eutrophication, or to improve the existing situation, the relative contribution of different sources of P to this process has been investigated recently in different, mostly industrial and/or densily populated, countries. The major sources of P were identified as waste water, or the corresponding effluents after a biological treatment, that were disposed off directly or indirectly in surface water. In special cases also the P load derived from intensive methods of animal production or agricultural land contributed significantly (Ryden et al., 1973).

Focussing the attention here on the Dutch lakes it was estimated (Golterman, 1976) that 18 mln kg P accumulated in these waters during 1970. Approximately 48% of the latter amount was due to the inflow of water from the great rivers which derived their load of P mainly from waste water disposals in the upstream catchment area (i.c. outside the Dutch border). The contribution from inland disposals of industrial and domestic forms of waste water amounted to 7% and 38%, respectively. The remaining 7% was ascribed to a number of different sources, among which runoff and leaching of P from the soil. In view of the above summary of different P sources it has been strongly recommended (Golterman, 1976) to take measures to lower the phosphate load of waste water. A discussion of the technical, economical and political implications of the different measures is, however, beyond the scope of this study.

The minor contribution of (surface) runoff and leaching from agricultural land to the P load of surface water was obtained in spite of an estimated much larger annual accumulation of 87 mln kg P in the soil. The major sources were in this case the addition of manure (64 mln kg P) and chemical fertilizers (48 mln kg P) on agricultural land. Removal of P from the soil was brought about by harvesting of crops (31 mln kg P) and the above mentioned runoff (0.4 mln kg P) and leaching (0.7 mln kg P). Approximately 40-70% of the last two eventually reaches surface waters.

The addition of P to soils has been practised in agriculture for a long time because most virgin soils have low phosphate contents. In addition the soil P compounds are usually present in a form which is rather unavailable for plant uptake (cf Chapter 2 for more details). Before the introduction of chemical fertilizers (around 1870; Schuffelen 1974) the most wide-spread source of P was some form of manure. The P present in this manure was then transferred from e.g. grazed areas to the manured arable areas. A typical example is the situation around certain villages in some parts of the Netherlands, where P from grazed heatherfields became accumulated in arable fields close by the village (Enggrond). With the advance of modern agriculture such translocations reached global dimensions, as mineral phosphates mined in particular areas (e.g. Moroc) were applied in the form of industrially produced phosphate fertilizer to agricultural land elsewhere, particularly in the highly industrialized parts of the world. Due to these additions the total phosphate contents of certain soils were increased considerably. Referring to the earlier mentioned arable fields close to the villages (Enggrond) it was found at this laboratory (Lefers*, personal communication) that the P content in selected samples of the top layer amounted to about 800 mg P/kg soil as a mean value. In comparison samples of comparable nonfertilized soils had a mean P content of 250 mg P/kg soil. For soils in the United Kingdom it was estimated (in 1957) that 40% of the phosphates present were derived from phosphatic manures and fertilizers added to them since 1837 (Russell, 1961).

The man-induced P translocations mentioned here were intended to increase (locally) crop yields and once acceptable yields were attained, further addition of fertilizer P tended to be scaled to maintain a balance with the local removal of P from the land with

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*Lefers, H.G., 1967. Fosfaat in grond; voorkomen en beschikbaarheid der verschillende fracties. Verslag doctoraalproef. Laboratory of Soils and Fertilizers, Agricultural University, Wageningen.

crops plus some leaching.

Since several mineral soil components have a strong affinity for phosphate the ensuing interaction processes lead to the formation of (strong) chemical bonds between added P and the relevant soil components. Results of long-term fertilization experiments show that in most soils the excess of added P becomes accumulated in the surface layers (Roscoe, 1960, Cooke and Williams, 1970), with very little movement to deeper layers. The fact that P is rather immobile in the soil further explains the observation that, with some exceptions, the leaching losses of cultivated (i.e. fertilized) and virgin soils are practically the same (Cooke and Williams, 1970; Kolenbrander, 1972; Ryden et al., 1973). Referring to the above mentioned annual leaching losses of 0.7 mln kg P in the Netherlands it would mean that the concentration of P in the solution leaving the soil would be somewhere around 0.06 mg P/l (2.10^{-6} mol P/l), assuming a precipitation surplus of 350 mm. This concentration falls within the range of reported values for the P concentration in the soil solution (Russell, 1961).

Losses of P from cultivated soils via (surface) runoff, however, may reach significant values under specific conditions (Ryden et al., 1973). The relatively low losses of P by surface runoff reported for agricultural land in the Netherlands are then very probably the result of the presence of a number of factors which limit runoff.

More recently a third phase in phosphate translocation and local accumulation arose with the coming about of intensive methods of animal production. Thus the phosphate applied to grow feed

Table 1.1 Yearly excess of P in regions with intensive methods of animal production. Estimated from P present in manure produced within the region, plus P from chemical fertilizers (mean value 8.5 kg P/ha), minus removal (26 kg P/ha) by harvested crops (after Henselmans and Algra, 1976)

Region	Area of cultivated land (ha)	Excess P, in kg P/ha, per year
Western part of Northern Limburg	40168	79.4
Northern Peel area	35509	70.6
Southern Peel area	18818	87.5
Western Veluwe	32026	87.1
Utrecht (sandy soils)	12279	49.9

grains in one region of the earth became accumulated in localized areas somewhere else in the form of excessive amounts of manure. Moreover, addition of mineral phosphate directly to the feed has become practice in this type of intensive animal production. In table 1.1 some data are given, referring to certain regions in the Netherlands, as reported by Henselmans and Algra (1976). As most soils in these regions mentioned in table 1.1 have only relatively low amounts of mineral components capable of binding P, downward leaching towards groundwater becomes a matter of primary concern, following excessive additions of manure to the soil.

A related variant of translocation of phosphate, leading to local excesses, is the production of domestic sewage water in densily populated areas. In particular the fairly recent introduction of P-containing detergents has significantly increased the P level in the latter. Recent estimates (Kolenbrander, 1972) of the total daily discharge per inhabitant in the Netherlands are around 1.5 g P. Since discharge into open water is highly undesirable, application to soil, either as raw sewage water, effluent or sewage sludge further increases the potential danger of downward leaching. Particularly since with the addition of liquid manure or sewage water to the soil a large portion of P is supplied in a soluble form, a significant contribution of direct convective transport to the translocation of P in the soil system becomes possible. This may lead to higher leaching losses. It is also very likely that the supply of large amounts of liquid manure, sewage water or wet sludge affects the losses by surface runoff.

Referring to the above discussion, the main objectives of the present study were to investigate the magnitude of the P retention capacities of sandy soils and the leaching losses under conditions of high loads of soluble phosphate. In particular the behavior of dissolved orthophosphate species was studied.

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2 TRANSFORMATION PROCESSES OF PHOSPHATE COMPOUNDS IN SOIL (SOME FACTS FROM LITERATURE)

P in soil is subject to chemical and biological transformation processes. The nature and rate of these processes determine largely its behavior in terms of the availability for plant uptake or its behavior in terms of accumulation, mobility and leaching (of surface applied P compounds). The chemical processes comprise e.g. adsorption onto different soil components and/or the formation of solid phosphate compounds, alternated by desorption and dissolution under changing conditions. The biological processes include the formation of organic phosphates, which are in part incorporated in the soil organic matter fraction. In turn, living organisms may bring about mineralization of organic P to inorganic P. The processes mentioned here have recently been discussed, some in considerable detail, in: *J. Beek and W.H. van Riemsdijk (1979): Interaction of orthophosphate ions with soil, Chapter 8 in Soil Chemistry, part B, G.H. Bolt (ed)*, where reference is given to the original literature. Below the above publication is briefly summarized.

2.1 OCCURRENCE OF PHOSPHATE IN SOIL

The soil phosphate compounds are predominantly present as orthophosphate, the stable form of phosphorus in nature. Condensed phosphates[*], formed by living cells in situ or added by man, eventually hydrolyse to orthophosphate. Although reduced forms of phosphorus are known their presence in (reduced) soils is of no concern.

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[*] Condensed phosphates are defined as multiple units of PO_4 tetrahedra joined by shared oxygen atoms between the tetrahedra; the linear chain polymers are known as polyphosphates.

In this context it is mentioned that losses of gaseous forms of (reduced P) from the soil do not occur for that reason, in contrast to the situation with nitrate where denitrification can lead to substantial losses of nitrogen in gaseous form from the soil.

The total phosphate content of many virgin soils is in the range of 0.04 to 0.1 % P (by weight). Usually somewhat higher values are found in the topsoil than in the subsoil, very likely as a consequence of the upward cycling of phosphate by plants. The phosphate compounds in such soils are derived mainly from apatite minerals and P present as a substitution for silicon in silicate rocks of the earth's crust. Weathering and soil forming processes brought about a transformation and translocation of the original phosphate compounds. Due to the action of living organisms organic phosphate compounds were formed from inorganic phosphate and eventually returned via mineralization processes. The fraction of total P that is present in organic combination varies widely, and ranges roughly from 20 to 90 per cent. These large differences are explained, at least partly, by the strong dependence of the largely biological processes of formation and breakdown (mineralization) of organic phosphates upon local conditions of rainfall and temperature, various chemical and physical properties of the soil as well as on the plants and organisms present.

Results of fertilised soils indicate that the balance of organic phosphate in the soil is much more regulated by the local cycle of formation and breakdown of organic phosphate than source determined, viz. addition of P in the form of manure or chemical fertilizer (Van Diest., 1968; Oniani et al., 1973; Campbell and Raez, 1975).

Different organic phosphate compounds have been isolated and identified; in particular inositol (hexa) phosphates seem to constitute a large portion of the soil organic phosphate fraction. The inorganic phosphate fraction may constitute forms varying from adsorbed phosphate, amorphous and ill-defined compounds to (primary) and secondary phosphate minerals. Conclusive evidence that (virgin) soils contain phosphate minerals is scarce, however, possibly because identification of these compounds within the bulk of the soil sample is hardly possible with the direct methods of identification, used up to now.

The concentration of P in the soil solution is usually low - varying from 10^{-7} to 10^{-5} M (0.003-0.3 mg P/1) - due to strong interactions of soluble P with various soil components. The dissolved phosphate species may consist of dissolved or complex orthophosphates, condensed phosphates and organic phosphates. The distribution of all these species depends on the stability constants and local soil conditions, like e.g. pH and other relevant solution concentrations. Besides the dissolved species also suspended forms of P may be present; the latter may react differently with the soil components than the dissolved species.

2.2 THE REACTION OF P WITH SOIL MINERALS

The complex composition of soils and the possible occurrence of physical, chemical and biological processes concurrently or consecutively have stimulated the use of single soil minerals to study the chemical interaction mechanisms with P. Some of the results of such studies will be mentioned here, while referring for details to Beek and Van Riemsdijk (1979).

From studies using aluminum and iron oxides*, clay minerals and solid calcium carbonate it follows that dissolved orthophosphate species (in the pH range relevant for most soils the dominant species are the (partly) dissociated $H_2PO_4^-$ and HPO_4^{2-} ion) may react with active groups present on the surface of these solids. This reaction is assumed to be chemisorption.

Infrared studies have shown that phosphate ions exchange with singly coordinated hydroxyl or water groups located on specific faces of crystalline aluminum and iron oxides. The adsorbed phosphate may react further with another surface OH or H_2O group, either coordinated to the same metal ion or to a neighboring metal ion, in the last case resulting in a so-called binuclear surface complex. This would imply that the number of singly coordinated surface OH(H) groups and the stoichiometry of the reaction determine the maximum amount of phosphate which can be bound in this manner. In this context the question arises whether adsorption

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*The term oxides is used here as a comprehensive term for oxides, hydrous oxides and hydroxides.

is restricted to singly coordinated surface OH(H) groups only, or that exchange with e.g. doubly coordinated surface OH(H) groups might take place. The latter mechanism has been suggested to occur at higher concentrations of dissolved P with aluminum oxides. Other workers have speculated about the mechanism of the phosphate adsorption reaction on the basis of pH changes (sometimes) accompanying phosphate adsorption on metal oxides (viz. a pH increase is associated with exchange of surface hydroxyl groups). With clay minerals the exchange reaction might occur as was found for the metal oxides because on the edges of these minerals the same exposed AlOH(H) groups may be present as on aluminum oxides.

The active sites for adsorption on solid carbonate (calcite) are assumed to be exposed surface Ca^{2+} ions of which the vacant coordinate positions may be occupied with water, bicarbonate or hydroxyl groups. Phosphate ions may replace these groups.

Desorption studies with these phosphated components indicated that the bound phosphate was released very slowly when the material was suspended in a P free solution. The exchange of sorbed P with ^{32}P labelled species in solution is also a slow process. Indications exist that the above rates further decrease as the contact time between the solid and phosphate increased, likewise the rate of exchange with species competing for the same sites decreased at longer contact times.

The interaction of P with these solids is not restricted to adsorption only, because under the appropriate conditions a crystalline aluminum-, iron- or calciumphosphate may be formed. The latter process requires a certain threshold value of the concentration of dissolved P, which depends on the solubility products of the relevant minerals and some other characteristics of the system, like e.g. the pH. The rate of formation of these solid phosphates, which depends on the supersaturation of the system, is mostly slow (as follows from the decrease in concentration of dissolved P) in comparison to the adsorption reaction. Adsorption and (secondary) precipitation may therefore occur simultaneously, implying that a clear distinction of both processes may be difficult on the basis of measured concentrations of dissolved phosphate in suspensions of these solids. On the other hand it is clear that at short reaction times and low concentrations of dissolved P the adsorption process will dominate, though it is no guarantee that with this method the equilibrium adsorption isotherm can be determined. Freundlich and Langmuir isotherms are used to describe the (presumed) equilibrium adsorption. In particular the latter is frequently used for this purpose; very often more than one isotherm is necessary to describe the experimental data satisfactorily.

Experiments with a number of condensed inorganic phosphates have shown that in principle the same chemical processes may occur as with dissolved orthophosphate species. Also several organic phosphates have a high affinity for the metal oxides and clay minerals, in particular inositol (hexa) phosphates form strong bonds with the soil minerals. Moreover, it was found that the latter organic phosphate compounds may react with Al, Fe, Mg and Ca ions in solution, as a result of which (solid) complexes (phytates) may be formed under the proper conditions.

2.3 IMMOBILIZATION AND MOBILIZATION OF P IN SOIL

The removal of phosphate from solution by soil is denoted by the term retention; it represents the net effect of physical, chemical and biological processes involved in the transformation of mobile (i.e. present in the soil solution) into immobile (i.e. associated with the soil solid phase) forms of P. Since the rates of these processes differ it is found very often that when soluble phosphate is added to the soil, the concentration in solution decreases rapidly initially, followed by a slow decline, which may last for a long time period. The rapid decrease is associated with adsorption processes and the slow decline with a number of processes like e.g. precipitation processes, diffusion of dissolved P into less acessible parts of soil components and the incorporation of P in the organic matter fraction of the soil (when growing plants are present also uptake of P may be involved). Obviously, precipitation processes may contribute significantly to the retention of P at short reaction times if the solution is highly supersaturated. In soils such conditions may be present around dissolving granules of chemical fertilizers. Some calcium phosphates, for instance, give rise to high phosphate concentrations in combination with low pH values. Soil minerals in direct contact with such granules may (partly) dissolve giving rise to high concentrations of metal ions in solution, leading to direct precipitation of (metastable) metal phosphates from solution. As in the bulk of the soil much lower concentrations are present diffusion processes are responsible for some redistribution, followed by dissolution of the metastable compounds and formation of less soluble solids. The precipitation reactions predicted from solubility product relationships could be confirmed by experimental results under such conditions, because detectable amounts of (crystalline) phosphates were found. In most cases, however, direct identification of the reaction products is not possible, therefore indirect methods are used, like e.g. selective extraction techniques. Different soil phosphate fractions are distinguished in this manner, viz. organic and inorganic bound forms, the latter usually subdivided in aluminum and iron bound phosphate and calcium bound phosphates. Although a sharp distinction between the different fractions is usually not possible, and at best only a rough indication about the composition of the compounds is obtained, it provides information about transformation processes of phosphate added to soil. These results supported in a qualitative sense the reactions predicted from solubility product relationships (cf. fig. 6.11 of Novozamsky and Beek, 1976) viz. aluminum and iron bound phosphates dominate as inorganic bound forms in acid to neutral soils and calcium bound phosphates in calcareous soils.

Until recently it was assumed that variscite was the stable aluminum phosphate compound in acid soils. The latter assumption, however, may be incorrect as indications were found that possibly compounds like crandallite or wavellite might be the stable phases in acid to neutral soils (cf. also Chapter 3).

Biological immobilization of dissolved inorganic phosphate in the soil depends on e.g. the type, P-content and amount of organic material available at the site of decompostion. The rate is influenced by physical (e.g. temperature, moisture content, and reducing conditions) and chemical (pH) factors (Fuller et al., 1956; Birch, 1961; Ghoshal, 1975).

A transformation of immobile forms of soil P to mobile forms may occur when the concentration of dissolved phosphate is lowered, leading to desorption and dissolution reactions. Some other factors which may play a rôle in the release of solid P are e.g. pH changes, reducing conditions and the presence of inorganic and organic species competing with P for the same binding sites. Also decomposition of organic material and mineralization of organic phosphates may lead to the formation of dissolved (ortho)phosphate. Interaction of the organic phosphates with the soil minerals may have a retarding effect on the transformation to orthophosphate. Further evidence suggests that sorption of the enzymes catalyzing the dephosphorylation of organic P compounds (phosphatases) decreases the mineralization rate.

Hydrolysis of condensed phosphates to orthophosphate seems to be a rather rapid process in the soil. Reported half-life (i.e. the time period needed for hydrolysis of half of the amount added) varies from less than an hour to a few days. The half-life usually increases when the condensed phosphates react (via adsorption or precipitation processes) with the soil components.

As mentioned already, desorption and dissolution processes seem to have a low rate, which decreases further as the contact time between soil and retained phosphate increases. Since uptake by plants is limited to dissolved forms of (ortho)phosphate, the slow release processes largely determine the supply of this nutrient from the pool of soil inorganic bound P. This further implies that the efficiency of added fertilizer may be low in soils which contain high amounts of active (i.e. participating in the bonding of P) aluminum, iron and calcium compounds. Mineralization of organic bound P may have a strong beneficial effect upon plant growth in such soils since the growing plants then compete directly with the adsorbing surfaces during the liberation of P. This effect is more pronounced in regions with higher temperatures, because mineralization increases with a rise in temperature. The reported effect of a higher temperature on adsorption is ambiguous. Precipitation reactions are enhanced by higher temperatures in general. Various extracts and methods are in use to estimate the plant available fraction of soil P. Also in use is the term 'labile P', which represents then the fraction of soil P that exchanges with added ^{32}P within a certain time period.

It is evident that the formation of insoluble forms of soil P limits the movement of P and therefore the amount that is leached from the soil. In view of the reaction mechanisms and its kinetic aspects discussed in section 2.2, it follows that the retention capacity of a certain layer for P and the kinetics of the retention processes in relation to the flux (density) of (surface) applied P determine the depth of penetration into the soil. Compounds added in a soluble form, like e.g. disposal of waste waters or liquid manure, might therefore be more mobile in the soil than if solid forms of P were added. It is evident that the mobility also depends on the presence of other substances in the added material, because adsorption may be enhanced by, or have to compete with, other (specifically) adsorbing species. In addition it is clear that when soluble P species are added that have a very low affinity to the soil components, as is claimed of some organic P components, the mobility might be higher. The mineralization rate of such organic P components to orthophosphates in the soil is then an important factor regulating the leaching of P (Gerritse and Zugec, 1977, Gerritse, 1978). Also suspended forms of P seem to be leached from the soil more easily than most of the dissolved species.

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tal plain soils of New Jersey. Plant and Soil, 29: 241-247.
(Further references to the original literature consulted may be found in Beek and Van Riemsdijk, 1979, referred to on the first page of this chapter).

3 ACCUMULATION OF P IN A SANDY SOIL TREATED WITH SEWAGE WATER

Summary of results published in:
J. Beek, F.A.M. de Haan, and W.H. van Riemsdijk, 1977a,b. Phosphates in soils treated with sewage water: I. General information on sewage farm, soil and treatment results. II. Fractionation of accumulated phosphates. J. Environ. Qual., 6: 4-12, plus some additional information obtained more recently.

3.1 INTRODUCTORY REMARKS

The present concern about eutrophication of surface waters as well as the ability of soil to bind strongly phosphate (and some other) compounds, have greatly stimulated the disposal onto soil of liquid wastes that were formerly disposed of in surface water. Besides the removal of compounds from the added wastes by physicochemical processes, also soil biological processes may contribute to the purification of the added liquid wastes. If added to agricultural land, crops may benefit from the added nutrients and/or the supply of water. In view of the increasing amounts of liquid wastes that become available nowadays, like e.g. domestic sewage water, certain processing waters and liquid manure in areas with intensive animal production, it can be foreseen that large amounts will be supplied annually. It is of prime importance, however, that (most of) the added compounds should not reach the groundwater or otherwise leave the soil profile (e.g. due to the discharge of drainage water).

Focusing the attention on phosphate, it then follows that in view of the above requirements the amount added should never surpass the retention capacity of the relevant soil layer. Moreover, it has become clear that the retention of phosphate is a 'rate' process, implying that the penetration depth of phosphate in the soil depends on the flux (density) of the surface applied phosphate and the rate of bonding by the soil components. The latter rate may depend on the nature of the added compounds, such as orthophosphate species, condensed inorganic phosphates and organic phosphates. On the other hand, the flux is determined by the form of application, viz. solid, suspended or dissolved form. The general opinion that phosphate accumulates in the top layers of the soil, as is found in field experiments with long term additions of chemical fertilizer or farmyard manure, might therefore not be valid if phosphate is added in the form of waste water.

Since results of field experiments involving long term addition of waste water are scarce, some relevant data of soil and water analysis are reported here concerning a farm which has been in operation for the treatment of sewage water by means of land disposal during the past 50 years. As most of the results have been published already elsewhere only a brief summary will be given in this chapter, plus additional information obtained more recently.

3.2 GENERAL INFORMATION ON THE SEWAGE FARM

The sewage farm is situated in the direct vicinity of Tilburg, the Netherlands, and has been used during the past 50 years for land treatment of town sewage water (i.e. of domestic and industrial origin). In the beginning raw sewage water (i.e. without any treatment) was supplied, whereas from 1972 on the sewage water was subjected first to a primary treatment in a treatment plant prior to

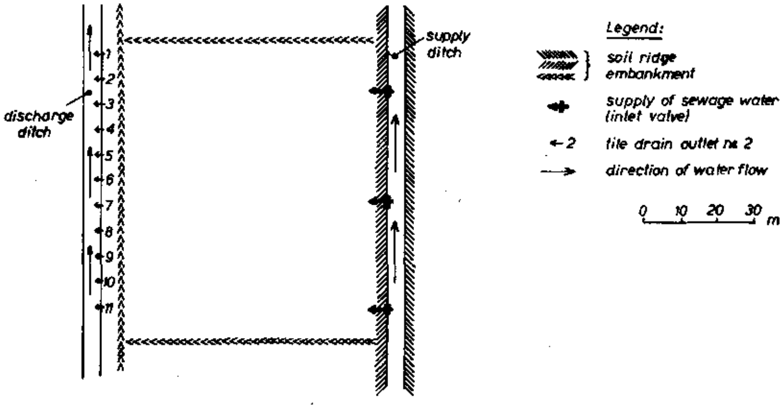

Fig. 3.1 Schematic plan of a single parcel of the sewage farm located near Tilburg.

the application to the soil. This primary treatment consists mainly of sifting out coarse substances and settling of solids. The farm has at present a total surface area of 100 ha and was reclaimed from uncultivated woodland on sandy soil; it has always been in agricultural use as permanent pasture, used mainly for grazing. When the area was reclaimed a system of tile drains was installed at a depth of 110-140 cm, with an average distance between drains of 14 m. Later new drains were laid at a depth of 70-100 cm, such that the drain distance now averages 7 m. The sewage water reaches the land by means of raised supply ditches which are connected with the adjacent parcels through simple syphons. The tile drains discharge into a lower system of discharge ditches which are connected with a discharge canal. Figure 3.1 shows schematically the situation of a single parcel.

The amount and rate of sewage water application has changed considerably since the establishment of the farm. At present the dose is maintained at approximately 200 mm monthly. The latter dose allows infiltration of the sewage water into the soil within 2 days after its application. Up to 1972 no additional fertilizers were applied because sufficient plant nutritive elements were added with the sewage water. From 1972 on, when sewage water was supplied which had undergone a primary treatment, a small application of nitrogen fertilizer twice yearly during the growing season was necessary. Supply of other nutrients by the sewage water is still sufficient. (Beek and de Haan, 1974, Beek et al., 1977a).

3.3 COMPOSITION OF SEWAGE WATER AND DRAINAGE WATER

The effectiveness of the present method of sewage water treatment may be judged by a comparison between the composition of the added waste water and that of the drainage water. In a first attempt samples of both were analyzed for some components which supposedly may undergo changes during their presence in the soil. The concentrations of different N and P fractions, BOD_5 values (and pH) are summarized in table 3.1. These data represent the average values of samples taken at different sampling times 2 days after the sewage water was added to the (different) parcels. As follows from table 3.1 soil treatment results in almost complete removal of BOD_5 (98%)

Table 3.1 pH, oxygen demand, and concentrations of nitrogenous and phosphorus compounds in sewage and drainage water.

	pH	BOD_5	Kjeldahl-N	NO_3	Total-P	P^*-ortho	Total P minus P^*-ortho
		mg O_2/l	--- mg N/l ---		-------- mg P/l -----------		
sewage water	7.1	381	20.5	0.23	10.8	6.53	4.24
drainage water	6.1	9	3.5	12	0.46	0.33	0.13

* Samples were filtered (0.45 μm) prior to orthophosphate analysis

and removal of P up to 96%. The P compounds present were distinguished in a fraction representing the dissolved orthophosphate species and a fraction representing the difference between total P and the former fraction. This fraction may comprise dissolved forms of condensed and organic P-compounds and suspended forms of P (i.e. P components which do not pass a 0.45 μm membrane filter). According to the results in table 3.1 there is no significant difference in the removal of both P fractions by the soil.

As follows from table 3.1 sewage water contained mainly NH_4 compounds, whereas drainage water contained N which was mainly in the NO_3 form, indicating that in the soil nitrification occurred. The latter transformation is probably also the main reason that the removal of N is relatively low.

In a second investigation, samples of drainage water were taken during a period of 100 hrs. after a parcel was flooded with sewage water. The main objective was to obtain more information about the phosphate concentration in the drainage water in relation to the residence time of the sewage water in the soil. The samples were analyzed for total phosphate, dissolved orthophosphate and dissolved hydrolyzable phosphate (the latter species most probably originating from polyphosphate present in detergents). In this experiment also the rate of dischare of the drainage water, pH, the concentration of some common constituents (Cl, Na, K, Ca, Mg, silica) and some (heavy) metals (Fe, Mn, Zn, Cd, Pb) was measured. Only the results related to phosphate will be reviewed here, the other data together with the methods of analysis were discussed by Beek et al. 1977a,b; Beek and Harmsen, 1977; Harmsen, 1977.

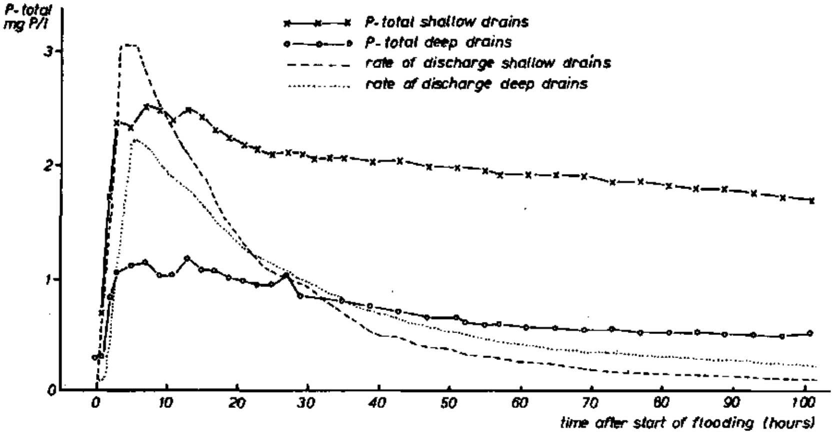

Fig. 3.2 Average values of P-total in effluent of shallow and deep drains (the corresponding rates of discharge of the effluent are shown in broken lines).

The amount of sewage water added in this experiment was equivalent to a layer of approximately 15 cm. The surface of the flooded parcel fell dry after about 1 day. The sewage water contained 10.4 mg P/l, of which 7.5 mg P/l was present in the form of dissolved orthophosphate species.

The average total P concentration of samples collected from drains situated at a depth of 70-100 cm (shallow drains) and from drains at a depth of 110-140 cm (deep drains) are shown separately in fig. 3.2. The average rates of discharge of the deep and shallow drains are indicated by broken lines. The phosphate concentration in the first samples is low (about 0.5 mg P/l), it represents very probably the phosphate concentration in the soil solution of the deeper layers of the soil. In the subsequent samples the phosphate concentration increases rapidly, particularly for the samples from the shallow drains. The simultaneously measured Cl concentration of the samples indicated that the drainage water comprised soil solution derived from the top layers, possibly mixed with some of the infiltrating sewage water.

In fig. 3.3 mean concentrations of chloride of selected samples from shallow and deep drains are plotted for the first 24 hours

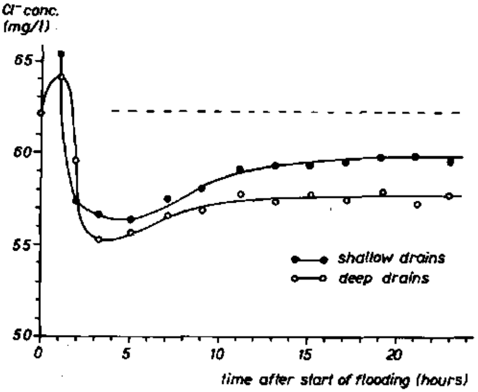

Fig. 3.3 Average concentrations of chloride in the effluent of shallow and deep drains (mean concentration of chloride in the sewage water, 62.3 mg/l, is indicated with a broken line).

after the start of flooding. The chloride concentration in the drainage water was used as a tracer in order to discern the discharge of groundwater and/or capillary soil water from the infiltrating sewage water. For various reasons it was postulated that the capillary soil water present in the saturated zone had a lower chloride content than the capillary water present in the nonsaturated zone, except for the top layers where dilution with rainwater again lowered the chloride concentration.
The effluent discharged by the deep and shallow drains during the first 2 hours of flooding (fig. 3.3) was therefore considered to be capillary water from the saturated and unsaturated zone. The subsequent steep decrease in chloride concentration was ascribed to the discharge of capillary water diluted with rainwater. After 3-4 hours of flooding the chloride concentration started to increase due to the discharge of capillary soil water mixed with the infiltrating sewage water. The chloride concentration in the latter is indicated with a broken line in fig. 3.3 (see for further details Beek and Harmsen, 1977 and Harmsen, 1977).

The higher P concentrations in the soil solution of the top layers were ascribed to the preceding percolations with sewage water. After 5 to 10 hours a maximum is reached which for the shallow drains amounts to 2.5 mg P/1 and for the deep drains to 1.1 mg P/1, followed by a slow decrease in the P concentration in samples collected after longer reaction times. The latter decrease is explained on the basis of the increasing residence time of the sewage water in the soil as a result of which more phosphate can be retained.

The determination of different phosphate fractions indicated that only orthophosphate species were present in the drainage water, except for the first 12 hours where the latter species comprised 70 to 80% of total phosphate present. The remaining fraction was then made up by hydrolyzable and suspended forms of phosphate.

The phosphate concentrations of the shallow and deep drains, together with the rates of discharge were used to calculate the mean phosphate concentration of the drainage water. These values are plotted versus the time of sampling in fig. 3.4. This figure shows that the maximum concentration reaches a value of about 1.8 mg P/l, which decreases to 0.8 mg P/l after 4 days. On the basis of the total amount of P discharged with the drainage water (in 4 days), it was calculated that approximately 87% of the added amount was retained by the soil (Beek and Harmsen, 1977). These rates of P removal are extremely high in comparison with the results of secondary treatment plants, in fact the results of this land disposal system compete with the removal rates gained from tertiary treatment (Koot, 1970). On the other hand, however, the phosphate concentra-

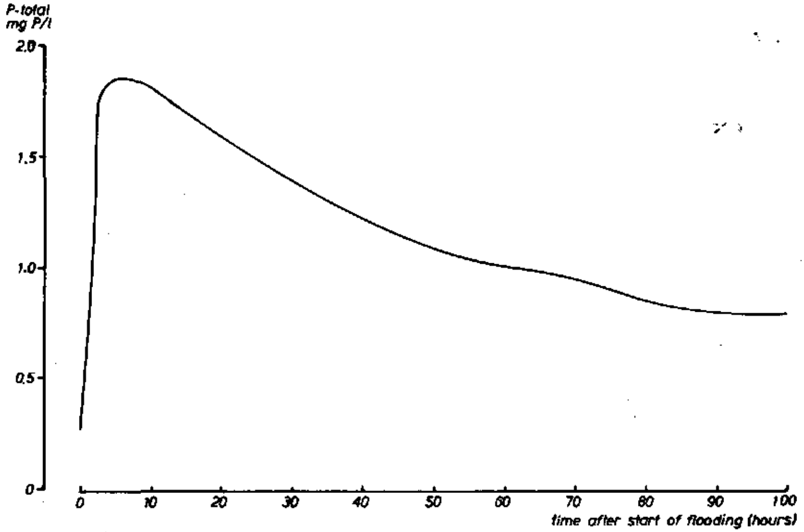

Fig. 3.4 Average values of P-total in effluent discharged from the tile drains in the flooded parcel.

tion level of the drainage water is still fairly high with respect to eutrophication (Sawyer, 1947; Dryden and Stern, 1968).

3.4 EFFECTS ON THE SOIL OF SEWAGE WATER ADDITIONS

The supply of large amounts of sewage water brought about different changes in the treated soil as compared to samples of corresponding layers derived from uncultivated woodlands (nontreated soil) surrounding the sewage farm. The pH-H_2O of the nontreated soil varied between 4.0 to 4.5 in the top 100 cm layer, whereas samples of the treated soil gave pH values varying from 6.5 to 6.8 (cf. table 3 in Beek et al., 1977a). It is evident that the increase in soil pH may affect the chemical and biological processes responsible for the purification of the waste water. The loss on ignition values for the treated soil were also higher, in particular for the top 20 cm layer. The increase in loss on ignition values illustrates the 'sieve' function of the soil and its vegetation cover for the organic matter contained in the sewage water (cf. table 3 in Beek et al., 1977a). The contents of Zn, Cd, Cu and Pb in different (top) layers of the treated soil followed the loss on ignition quite closely. According to Harmsen (1977) this might indicate that these metals were held by the organic matter or that the correlation was due to the fact that most metals reached the

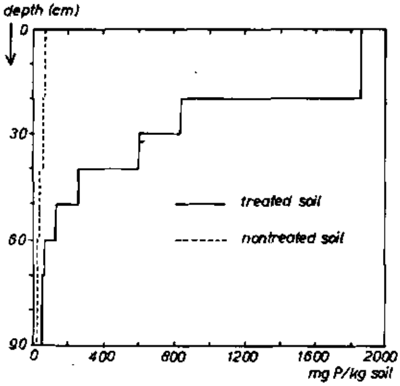

Fig. 3.5 Distribution of total soil phosphorus as a function of depth in the upper 90 cm layer of treated and nontreated soil.

soil in suspended form, presumably associated with organic matter. The cation exchange capacity (CEC) of the sandy soil is low (1-2 meq/100 g soil as measured by the ammonium acetate method using a pH of 7), except in the top layers where it may rise to 9 meq/100 g of soil, due to the high organic matter content.

Soil samples derived from the treated soil and nontreated soil were analyzed for total phosphate in order to determine the distribution pattern with depth of accumulated phosphate. It follows from fig. 3.5 that the accumulated phosphate is mainly present in the top 50 cm layers: in the layers below 70-80 cm no significant differences in total P were found. Taking into account the bulk densities of the relevant layers it was calculated that on a hectare base 7000 kg P had accumulated in this soil in a period of 45 years. This distribution pattern of accumulated phosphate in connection with the high rates of P removal from the sewage water and the relative short residence times of the latter in the soil were taken as indications that adsorption processes must be a major process in the initial retention of phosphate in these soils. The fact that the soil is still very effective in P removal after long-term addition of sewage water suggests that chemical or microbiological processes bring about a redistribution of the adsorbed P.

The accumulated phosphates were distinguished in different fractions with the help of fractionation methods, which are based on selective extraction techniques (cf. Beek et al., 1977b for the analytical aspects). It was found that in the top 50 cm layers 10 -20% of total soil P was present in an organic bound form and the remaining fraction as inorganic bound forms (cf. fig. 1 in Beek et al., 1977b). Accumulation of P in the form of immobile organic phosphate compounds is therefore of minor importance in these soils. A further subdivision of the inorganic bound fraction showed that Al- and Fe-bound forms of phosphate were dominant, the forms associated with Ca-bound phosphate were present to the extent of 9% of total P in the top layer and around 3% in the 20-50 cm layers (cf. table 3 in Beek et al., 1977b). Although a sharp distinction between the Al- and Fe- bound forms is not possible with the fractionation methods employed, it became clear that the Al-bound forms were the dominant ones in this soil (cf. fig. 2 in Beek et al., 1977b), indicating that the retention capacity of the soil for phosphate depends largely on the amount of reactive aluminum present (ch. Chapter 4).

The possible presence of crystalline phosphate compounds in the top layers of the treated soil was investigated with X-ray diffraction*. Since it was found that P was associated mainly with the finer particles, the coarser particles were removed from the sample by sieving or by settling in an aqueous suspension. Due to this pretreatment of the sample the P content of the remaining fine fraction rose 2 to 4 fold, what may facilitate the detection of crystalline phosphates, if present. The diffraction patterns of samples derived from the top layers of the treated soil were compared with the X-ray patterns obtained from samples of the nontreated soil. No significant differences were found, however, between the patterns of treated and nontreated soil, indicating that in the treated soil crystalline phosphates were either absent or present in too small amounts to be detected with this technique.

A second attempt to characterize the accumulated forms of P was the use of the scanning electron microscope (SEM) equiped with an energy-dispersive X-ray analysis system** (EDXRA). Details of this technique and of the apparatus used in this particular experiment were given by Bisdom et al. 1975, 1976. The objective here was to find out the chemical elements, apart from P, that were present in the accumulated forms of P. Thin sections, prepared from plastic-hardened soil samples were coated with a carbon layer prior to analysis. The secondary electron image of the surface of the thin sections suggested that a (very) small part of the accumulated phosphate may be present in the form of discrete particles. Chemical elements associated with P at such spots were e.g. Al, Fe, Ca and some heavy metals. These preliminary results seemed to indicate that complex phosphates might have been formed. Referring to comparable results obtained by Norrish (1968) and Sawhney (1973) it would mean that in the soil treated with sewage water precipitates were formed of which the composition agreed to some extent with that of the plumbogummite minerals (Lindsay and Vlek, 1977). Recently, it was found at this laboratory (Van Riemsdijk, et al., 1979) that in quartz sand columns, mixed with amorphous $Al(OH)_3$ associations were formed between P, Al and Ca upon treatment of the columns with sewage water. The above combination of P with Al and Ca is also present in crandallite, a member of the plumbogummite group of phosphate minerals.

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* Thanks are due to Mr. J.D.J. van Doesburg, Dept. of Soil Sci. and Geology for his work on X-ray diffraction.

** Thanks are due to Mr. S. Henstra, T.F.D.L., Wageningen and Dr. L. van der Plas, Dept. of Soil Sci. and Geology for performing the SEM-EDXRA analyses.

3.5 SOLUBILITY DIAGRAM OF DIFFERENT ALUMINUM PHOSPHATES

Information reported by e.g. Norrish (1968), Altschuler (1973) and Sawhney (1973) suggested that complex aluminum phosphates, like crandallite and wavellite might be the stable aluminum phosphate compounds in soils instead of variscite. In order to find out whether such compounds might be of any significance under conditions pertaining to soils treated with sewage water, the relative stabilities of the above aluminum phosphate minerals were depicted in a solubility diagram, shown in fig. 3.6. Since it was shown earlier (Beek and de Haan, 1974) that apatite might possibly play a rôle in this particular soil, also the latter compound was included in the diagram.

The solubility products of the different phosphates reported by Nriagu (1976) were used here. The diagram was further based on the assumption that solid $Al(OH)_3$ controlled the level of dissolved aluminum in this soil. A high and low reference level were assumed in the calculation scheme, corresponding to amorphous and crystalline $Al(OH)_3$, respectively. The solubility products, pertaining to the reaction:

$$Al(OH)_3 \rightleftarrows Al^{3+} + 3OH^- \qquad (2.1)$$

were for amorphous $Al(OH)_3$ taken as $\log K_s = -31.1$ and for crystalline $Al(OH)_3$ equal to $\log K_s' = -33.8$. The reference level of the calcium activity, (Ca^{2+}), in the soil solution (1.16 mmol/l) was calculated from the calcium concentration (1.78 mmol/l) found in the sewage water (cf. Table 1 in Beek et al., 1977a).

The solubility diagram (Fig. 3.6) was constructed on the basis of the equilibrium reactions given below:

variscite - $Al(OH)_3$

$$AlPO_4.2H_2O + H_2O \rightleftarrows Al(OH)_3 + PO_4^{3-} + 3H^+ \qquad (2.2)$$

where $\log K = -32.5$ for amorphous $Al(OH)_3$ and $\log K' = -29.8$, for crystalline $Al(OH)_3$.

crandallite - $Al(OH)_3$

$$CaAl_3(PO_4)_2(OH)_5.H_2O + 3H_2O \rightleftarrows 3Al(OH)_3 + 2PO_4^{3-} + 4H^+ + Ca^{2+} \qquad (2.3)$$

where log K=-58.0 and log K'=-49.9

wavellite - $Al(OH)_3$

$$Al_3(PO_4)_2(OH)_3 \cdot 5H_2O+4H_2O \rightleftarrows 3Al(OH)_3+2PO_4^{3-}+6H^+ \qquad (2.4)$$

where log K=-69.6 and log K'=-61.5

Apatite

$$Ca_5(PO_4)_3OH+H^+ \rightleftarrows 5Ca^{2+}+3PO_4^{3-}+H_2O \qquad (2.5)$$

where log K=-45.4

In order to convert the activity of (PO_4^{3-}) in a term comprising the concentration of total dissolved phosphate species, $[P_t]$, the following expression was used:

$$[P_t] = \alpha\ (PO_4^{3-}) \qquad (2.6)$$

where α is a function of pH, dissociation constants of phosphoric acid and the activity coefficients of the dissociation products (dissolved metal-phosphate complexes were not considered in the computation).

The solubility diagram is presented in fig. 3.6; it represents the equilibrium phosphate concentration pertaining to the different solids at the chosen conditions as a function of the pH. It can be inferred from this diagram that the formation of a particular compound is only possible when the actual phosphate concentration in the soil system is equal to or higher than the equilibrium value. Referring to the soil treated with sewage water it follows that the relevant pH values vary between pH 6 to 7. The phosphate concentrations of interest, expressed as log $[P_t]$, vary between the values -3.5 and -5, the upper limit representing the P concentration in the sewage water and the lower limit the concentration found in the drainage water. On the basis of these conditions it follows from fig. 3.6 that in the presence of crystalline $Al(OH)_3$ the formation of variscite and crandallite would be less likely than the formation of wavellite and apatite. In particular the formation of wavellite might play a rôle, according to this diagram, although the latter compound would be metastable with respect to apatite above pH 6.1. If, however, amorphous $Al(OH)_3$ would controll the reference level of dissolved aluminum it is clear that any of the solid compounds

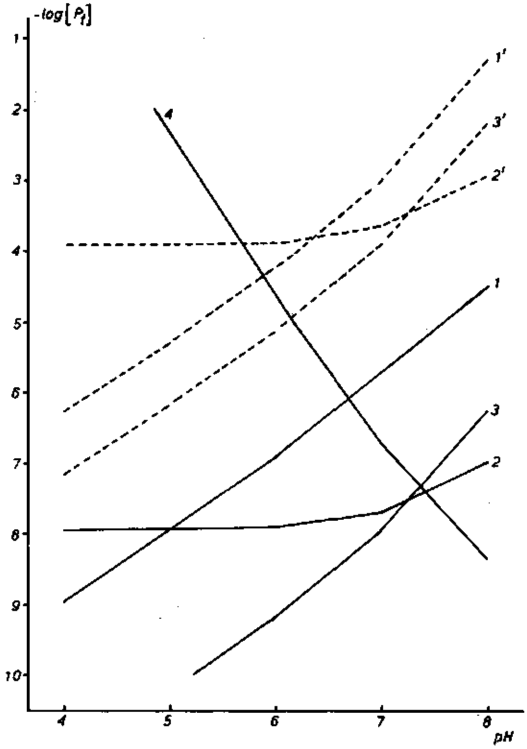

Fig. 3.6 Solubility diagram of different aluminum phosphates (1= variscite, 2=crandallite and 3=wavellite) in equilibrium with amorphous (solid line) and crystalline (broken line) $Al(OH)_3$. The solubility of hydroxyapatite (line 4) is based on a reference level of (Ca^{2+})=1.16 mmol/l.

considered here, could be formed in principle. Variscite, crandallite and apatite would be present then as metastable compounds with regard to wavellite.

In conclusion it follows that the conditions present in the soil treated with sewage water do not rule out the possible formation of crandallite and wavellite, though the formation of these compounds is unlikely at a very low level of dissolved aluminum. Above all, however, it should be realized that a discussion of precipitation reactions merely on the basis of a solubility diagram remains a matter of speculation.

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4 RELATIONSHIP BETWEEN SOIL ALUMINUM AND IRON FRACTIONS AND THE PHOSPHATE RETENTION CAPACITY OF SOME (DUTCH) SANDY SOILS

Summary of results published in:
J. Beek, W.H. van Riemsdijk and K. Koenders, 1976. Aluminum and iron fractions affecting phosphate bonding in a sandy soil treated with sewage water. Proc. Symp. Agrochemicals in Soils. Jerusalem, plus additional information obtained more recently (Section 4.3 and following).

4.1 INTRODUCTION

Fractionation of phosphate compounds accumulated in the soil treated with sewage water (cf. Chapter 3) indicated that aluminum was the main binding agent for added phosphate. In view of these findings the total Al and Fe content of selected layers of the treated and nontreated soil (sewage farm Tilburg) were determined. In addition the fraction of total Al and Fe that could be solubilized by different extracting agents was measured, and the relationship was established between the extractable forms of these elements and the retention of phosphate. This relationship was also determined for two other soils.

4.2 TOTAL AND EXTRACTABLE FORMS OF Al AND Fe IN A SANDY SOIL TREATED WITH SEWAGE WATER

The total Al and Fe content of selected layers of the treated and non-treated soil were determined by means of X-ray fluoresecence. In layers below a depth of 50 cm, approximately the same total amount of aluminum ($\approx$0.39 mol/kg soil or $\approx$2% Al_2O_3) was found for the treated and nontreated soil. For the top layers of the treated soil, however, a significantly higher content was found than in corresponding layers of the nontreated soil (cf. fig. 1, Beek et al., 1976). The excess aluminum in the treated soil amounted to 0.14, 0.09, 0.04 and 0.03 mol Al/kg soil for the layers 0-20, 20-30, 30-40 and 40-50 cm, respectively. The most plausible cause of the higher Al contents in the treated soil was the accumulation from sewage water. This was further supported by the distribution pattern of excess Al.

A direct proof of the above suggestion on the basis of the aluminum content present in the added sewage water could not be furnished because the sewage water was never analyzed for aluminum in the past. Taking into account, however, that textile, wooldressing and tannery factories were the main sources producing industrial waste water in the past, the discharge of aluminum compounds was very well possible because aluminum salts were used very probably in the different processing schemes. During 1976 samples of sewage water from Tilburg and Bennekom were analyzed for aluminum. Sewage water produced in the latter place is primarily of domestic origin whereas sewage water from the former place is mixed with industrial waste water. To this purpose the samples were evaporated to dryness and the residue treated with a mixture of concentrated HNO_3 and $HClO_4$. The diluted digest was analyzed for aluminum. In the samples derived from Bennekom only small amounts of aluminum (1-4 mg Al/l) were found, whereas in samples derived from Tilburg higher contents were present, occasionally amounting to 16-20 mg Al/l. Obviously the latter Al concentration is by no means a proof that in the past such concentrations were found; however, it points out that sewage water of industrial origin may contain relatively high amounts of Al. In this respect it is recalled that from 1972 on, sewage water was added to the soil which had undergone a primary treatment in the sewage water treatment plant (cf. Chapter 3). Samples analyzed before and after this pretreatment indicated that a large portion (60-70%) of the aluminum was removed by this treatment, implying that accumulation of Al in the soil probably is negligible at present.

The total iron contents in the samples of treated and non-treated soil were practically the same (≈0.04 mol/kg soil, or 0.3% Fe_2O_3), except for the top layer of the treated soil, which contained 0.06 mol Fe/kg soil.

The reactive portion of total soil aluminum and iron participating in the bonding of phosphate is generally estimated with the help of selective extractants. In the present study two different extracting solutions were used, viz. a solution of acid ammonium oxalate and a solution comprising citrate-dithionite-bicarbonate (CDB). The former extractant dissolves in principle the amorphous forms of iron oxides, whereas CDB also dissolves crystalline forms. On the other hand aluminum (and iron) present in the framework of silicate minerals is usually not brought into solution with either extractant. (Gorbunov et al., 1961; Schwertmann, 1964; McKeague and Day, 1965).

The oxalate extractable aluminum present in the samples of the non treated soil and in the lower layers of the treated soil amounted to roughly 6% of the total, suggesting that the remaining 94% of soil aluminum is very likely present in the form of silicate minerals. For the top 50 cm layers of the treated soil the extractable percentage rose to 19%. The latter higher percentages further supported the suggestion that the excess aluminum in those layers was present in the form of amorphous compounds and/or associated with organic matter. The ratio of oxalate over CDB extractable aluminum was close to 100% for the top layers of the treated soil; in the lower layers of the treated soil and in the non treated soil it varied between 63-80% (cf. fig. 3 in Beek et al., 1976). The higher amounts of aluminum dissolved by CDB were probably the result of dissolution of occluded aluminum present in iron compounds, the latter being dissolved by CDB but not by oxalate.

The fraction of total soil iron dissolved by oxalate was lower than found with an extraction using CDB; with the latter a fraction varying from 30% (for the lower layers) to 55% (for the top layers) of total iron was brought into solution (cf. fig. 5 in Beek et al., 1976)

The amount of P solubilized by both extractants corresponded roughly with the phosphate associated with aluminum and iron, as was found with the fractionation of accumulated phosphate in the treated soil (cf. Table 2 in Beek et al., 1976). On the basis of the above data, the molar ratio of the oxalate (c.q. CDB)- extractable aluminum and iron to the phosphate associated with these metals, $(Al+Fe)_{extr}/P-(Al+Fe)$, was calculated for the upper layers of the treated soil. The average values of this ratio varied from 2.9 for the top 20 cm layer to 12.3 for the 40-50 cm layer (cf. Table 3, Beek et al., 1976). Under the condition that the extractable (Al+Fe) in the lower layers reacted with P in a similar manner as in the top 20 cm, the higher values of this ratio indicate that the lower layers might retain additional phosphate.

4.3 THE PHOSPHATE RETENTION CAPACITY OF SOIL SAMPLES DERIVED FROM THE SEWAGE FARM IN RELATION TO THE SUM OF OXALATE EXTRACTABLE (Al+Fe)

Laboratory experiments were carried out to determine the amount of P that could be retained by samples of different layers of the treated and non-treated soil and to establish the ultimate ratio between extractable (Al+Fe) and P-retained.

Samples of different layers of the treated and non-treated soil were suspended in a solution containing the same concentrations of common cations and anions as were present in the sewage water, except for silicate and bicarbonate. The former was omitted and the latter was replaced by chloride (see Table 1 Chapter 5 for the actual composition). The initial P concentration was around 16 mg P/l and the total volume of solution about 500 ml. In order to arrive at a final P concentration of about 10 mg P/l the quantity of soil added was chosen on the basis of the oxalate extractable (Al+Fe) present in the material, thereby assuming that the final ratio would tend to a value around 3. The main motive to strive for a final concentration of 10 mg P/l was the fact that the latter value also represents the average P concentration in the sewage water, thus implying that the amount of P retained at this concentration would represent the retention capacity of that particular layer for phosphate added with the sewage water. Since the samples of the non-treated soil had a pH-H_2O around 4.5 (cf. Table 1. Beek et al., 1976), the pH of (suspended) samples was slowly raised (in a reaction period of 2 weeks) to 6.2 by adding NaOH. The pH of all suspensions were readjusted when necessary during a first month of continuous shaking, thereafter only occasional hand shaking was performed. The suspension was sampled by taking a 5 ml aliquot which was centrifuged, followed by filtration (0.45 μm membrane filter) of a small subsample of the clear supernatant which was then used for the determination of P. The remainder of the supernatant was used to resuspend the soil material which was then put back into the reaction vessel. The amount of P retained was calculated from the decrease in P concentration. Concurrently with the soil suspensions solutions with the same initial P concentration but without soil were sampled in order to find out if direct precipation of calcium phosphate from solution would occur. The latter process was theoretically possible, because the solution was supersaturated with respect to hydroxyapatite (cf. Chapter 5. for more details). In the present situation no direct precipitation of any phosphate from solution was observed over a reaction period of more than 2 years.

After a reaction period of 4 months the solution was removed from a selected number of samples and the retained phosphate was fractionated according to the method of Kurmies (cf. Beek et al., 1977b for more details). It was found that the freshly retained P (i.e. removed from the added solution) was predominantly present in the form of (Al+Fe)-bound P.

The amounts of P retained were determined with samples (prepared according to the procedure given in the small print section above) of different layers of the treated an non-treated soil after a reaction period of 1.2 year. In fig. 4.1 these amounts, added to the (Al+Fe)-bound P initially present, are plotted against the amount of oxalate extractable (Al+Fe). The linear equation following from the data points, using the least squares method, equals:

$$p = 0.356 + 0.326\ q \qquad (4.1)$$

where p and q stand for (Al+Fe)-bound P and the sum of oxalate extractable (Al+Fe), respectively, both expressed in mmol/kg soil. The correlation coefficient corresponding to equation (4.1),

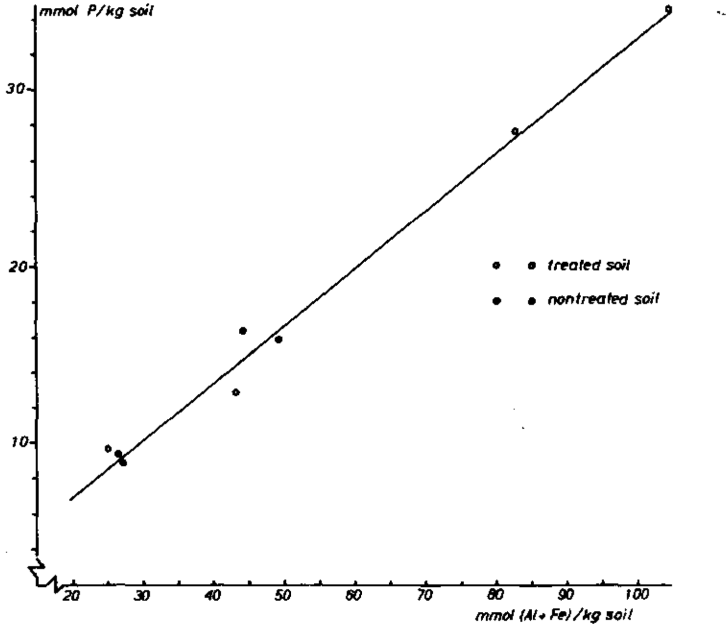

Fig. 4.1. Relationship between oxalate extractable (Al+Fe) and the phosphate retained after 1.2 years, for different layers of the treated and nontreated soil.

amounted to 0.996. Since the data points of the treated and nontreated soil could be described by one line it was concluded that the oxalate extractable (Al+Fe) derived from the soil parent material and/or from the compounds supplied with the sewage water reacted with P in a comparable manner. The molar ratio q/p calculated from equation (4.1) equaled 3 (rounded-off value). The latter ratio is under the prevailing conditions a fairly good estimate of the P retention of the different layers and was attained at a mean (final) concentration of P in solution of 10.9 mg P/l (s.d.=0.8).

In soil suspensions the removal of P from solution is a rapid process initially, followed by a much slower decline over longer reaction periods (cf. Chapter 5 for more details about this aspect). The amounts retained after 1.2 year are therefore a reasonable estimate of the retention capacity of that particular soil sample for P. The final value of q/p will strongly depend on the conditions present, like e.g. the pH and phosphate concentration. For instance, Williams et al. (1958) using P concentrations of about 1 g/l at a pH ≈ 4, attained values of q/p varying between 1.4 and 2.1 for different soil groups.

With the relevant value of q/p, the amount of oxalate extractable (Al+Fe), and the bulk densities of the different layers the P retention capacities of different layers of the treated and non-treated soil were calculated. For the treated soil it implied that in the top 50 cm layer another 2000 kg P per hectare could be retained in addition to the 4700 kg P/ha already present (the retention capacities mentioned in table 3 of Beek et al., 1976 were based on the value of q/p as was found in the top 20 cm layer, viz. q/p= 2.9). On the basis of 10 additions of sewage water per year of 20 cm each, with a mean concentration of 10 mg P/l, it would mean that the top 50 cm layer would be saturated with P after 10 years. Furthermore, it would imply that then the P concentration of the solution leaving the soil layer at a depth of 50 cm would equal the concentration present in the sewage water added to the surface.

In chapter 6, predicted concentrations of P in solution are given for the top layers of the treated soil in relation to increasing amounts of P retained.

Foregoing details in the present discussion it is very reasonable to assume that the P concentration in the soil solution will gradually increase as the amount retained reaches the maximum value, implying that part of the added phosphate will accumulate in the underlying layers, viz. below 50 cm.

4.4 THE RETENTION CAPACITY OF TWO SANDY SOILS FOR P

For 2 sandy soils, located in areas where intensive methods of animal production are practised, the oxalate extractable aluminum and iron was determined, as well as the amount of P that could be retained under the same experimental conditions as described in section 4.3. One of the soils was located near Vorden, the other one was located on an experimental farm in Vredepeel (information about precise location and the name according to the Dutch soil classification system are available). Both soils are in agricultural use, the one near Vorden as grassland, the second one as arable land. General characteristics of both soils are presented in table 4.1. The oxalate extractable aluminum and iron, expressed in mmol/kg or as a percentage of Al-total and Fe-total, respectively, are given in table 4.2.

It follows from table 4.2 that the oxalate extractable forms

Table 4.1 Some general characteristics of 2 sandy soils (Vorden, Vo and Vredepeel, Vr)

soil	pH-KCl	loss on*	fraction**		
layer (cm)		ignition %	<2 µm	2-50 µm %	>50 µm
Vo					
2-12	4.3	6.0	3.1	9.2	87.7
12-19	4.2	5.9	2.9	9.4	87.7
19-28	4.1	5.5	2.8	9.8	87.4
28-41	4.2	3.8	3.3	8.5	88.2
41.50	4.5	2.4	2.6	5.2	92.2
50-60	4.6	1.6	2.3	3.9	95.8
60-75	4.6	1.1	2.3	6.5	91.2
Vr					
0-20	5.6	5.6	3	10	87
20-30	4.3	5.9	3	9	88
30-40	4.2	3.3	2	8	90
40-50	4.4	1.4	1	4	95
50-60	4.5	1.0	1	2	97
60-70	4.6	0.5	1	2	97
70-80	4.6	0.5	2	1	98

*expressed as % of oven-dry soil material

** expressed as weight % of mineral fraction

Table 4.2 Oxalate extractable amounts of Al and Fe in mmol/kg soil and expressed as the fraction of Al-total* and Fe-total* for 2 sandy soils (Vorden, Vo and Vredepeel, Vr)

soil	Al		Fe	
layer (cm)	mmol/kg soil	% of Al-total	mmol/kg soil	% of Fe-total
Vo				
2-12	81.1	14.4	11.2	21.5
12-19	77.9	14.8	9.3	21.9
19.28	65.5	17.4	9.8	46.1
30-41	73.9	14.0	5.3	14.6
41-50	71.1	11.6	5.9	12.4
50-60	57.1	9.2	3.8	7.8
60-75	49.2	8.3	1.6	6.9
Vr				
0-20	50.0	16.3	10.1	37.6
20-30	59.0	19.2	3.9	14.9
30-40	52.7	17.4	3.0	10.8
40-50	39.5	9.7	1.5	4.0
50-60	30.2	9.2	1.6	5.1
60-70	26.5	9.6	2.0	8.0
70-80	18.9	6.3	0.8	3.4

*Total amounts were determined with X-ray fluorescence.

of aluminum and iron are higher in the samples derived from the top layers than in the samples derived from the deeper layers. The results further show that in corresponding layers of both soils almost comparable fractions of oxalate extractable aluminum and iron are present. Referring here to the samples derived from the non-treated soil surrounding the sewage farm it followed (cf. fig. 3. Beek et al., 1976) that the oxalate extractable fraction of aluminum was slightly lower (around 6.5%) than found for the samples mentioned in table 4.2. On the other hand, the oxalate extractable fraction of soil iron (cf. fig. 5, Beek et al., 1976) was somewhat higher (varying from 7-40%). The amounts of P retained, summed with the amount of P-(Al+Fe) initially present, are plotted in fig. 4.2 versus the sum of oxalate extractable (Al+Fe). The linear equation following from the data points, using the least square method, was represented by:

$$p' = 0.064 + 0.412\,q' \qquad (4.2)$$

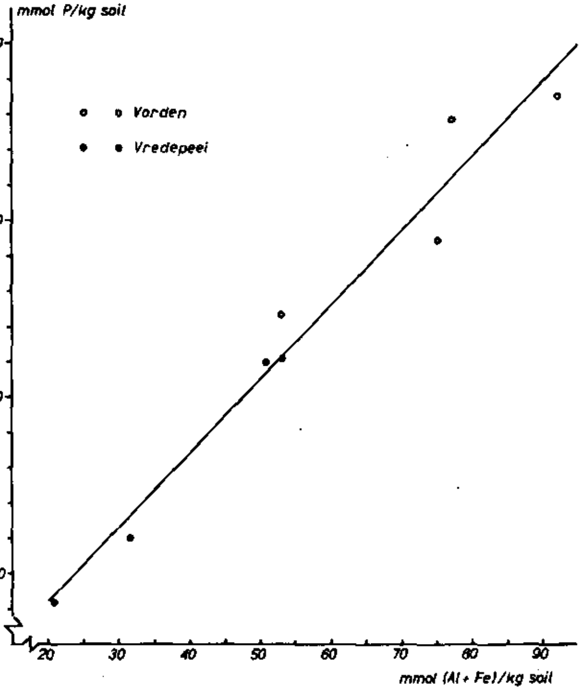

Fig. 4.2. Relationship between oxalate extractable (Al+Fe) and the phosphate retained after 1.2 years, for different layers of two sandy soils located at Vorden and Vredepeel, respectively.

where p' and q' represent the P-retained by Al and Fe and the oxalate extractable forms of these metals, respectively, both expressed in mmol/kg soil. The correlation coefficient corresponding to equation 4.2 was 0.968. The ratio q'/p' calculated from equation 4.2 amounted to 2.4, indicating that for these two soils the oxalate extractable (Al+Fe) is more effective in bonding of phosphate than the oxalate extractable (Al+Fe) derived from the samples of the sewage farm (cf. fig. 4.1). One possible reason of the greater efficiency of the oxalate extractable aluminum and iron in these two soils might be the result of the procedure used here to increase the soil pH from its original value to pH 6.2 in a relatively short period (3 days, instead of 2 weeks as used previously). The rapid neutralization may have favored the formation of poorly ordered amorphous aluminum and iron hydroxides which could have a greater ability towards P-bonding than those formed upon a neutralization period extended over 2 weeks. Counting for these two soils only the oxalate extractable (Al+Fe) as available for phosphate bonding, and using the above ratio of 2.4, together with the relevant bulk densities, one arrives at P-retention capacities for the top 50 cm layer of 7200 and 5000 kg P/ha for the soils located at Vorden and Vredepeel, respectively. Once such amounts would have been accumulated, the phosphate concentration in the soil solution would likely reach a value close to 10 mg P/l, implying a substantial leaching of added P to layers below 50 cm.

As was mentioned before, the removal of P from the solution by soil is a rapid process initially, followed by a (very) slow retention over long time periods. The rapid process is usually associated with adsorption processes and the slow process with the formation of a solid phosphate phase. In these samples the latter process very probably leads to the formation of an Al(Fe) phosphate compound, either present in the form of discrete particles or some form of occluded phosphate. As will be shown in chapter 5, the amounts removed by the rapid processes, viz. adsorption processes, can be approximated by the amount retained after a reaction period

Table 4.3 The amounts of P removed from the solution by different layers of 2 sandy soils (Vorden, Vo and Vredepeel, Vr) after a reaction period of 3 days and 1.2 year.

soil	layer (cm)	oxalate-P*	P-retained 3 days	P-retained 1.2 year	Fraction**
		-------- mmol P/kg soil -------			
Vo	5-12	12.1	13.3	24.9	0.36
	19-28	1.7	17.1	27.2	0.59
	41-50	1.1	21.2	34.8	0.59
	60-75	0.8	12.7	23.8	0.52
Vr	0-20	4.3	8.2	17.7	0.37
	30-40	1.3	12.3	21.1	0.55
	50-60	0.8	5.9	11.2	0.49
	70-80	0.5	3.9	7.8	0.47

* Original soil phosphate solubilized with oxalate.

** The fraction is defined as: P-retained (t = 3 days)/(oxalate -P + P-retained (t = 1.2 year)).

of 3 days. The latter amounts are given in table 4.3, together with the amounts retained after a reaction period of 1.2 years. Also the amounts of P originally present and solubilized with oxalate are presented. In particular the top layers contain relatively high amounts of oxalate soluble phosphate, very probably the result of supply of manure and/or chemical fertilizer. It follows from table 4.3 that the amount removed by adsorption (viz. retained after a reaction period of 3 days) equals roughly 54% of the total amount retained after 1.2 years, except for the top layers where the latter percentage amounted to 37%. The lower values found for the top layers are very likely the result of an occupation of some 'adsorption sites' by phoshate species derived from the forms of phosphate originally present in the sample. On the other hand it is also very likely that the relatively high values of around 54% found here, were largely due to the presence of (poorly ordered amorphous) Al- and Fe-oxides with relatively large surface areas, formed during the rapid neutralization of the samples.

4.5 DISCUSSION

A determination of oxalate extractable (Al+Fe) seems a relatively simple method to estimate the retention capacities of sandy soils for P. Although at present some uncertainties remain with respect to the different factors influencing the ultimate value of the ratio $(Al+Fe)_{ox,\ extr.}/P\text{-}(Al+Fe)$, its value is very likely close to 3 for soils with a pH-H_2O around 6 and for P concentrations around 10 mg P/l. With the above method a first guess can be obtained when breakthrough of a particular soil layer as a 'filter' for phosphate is to be expected, thereby keeping in mind that the retention of phosphate is a 'rate' process. This implies that before the maximum amount of phoshate has been retained, relatively high concentrations of dissolved phoshate may leach from that particular layer. These aspects will be discussed in more detail in chapter 5 and 6.

It was shown that the additon of aluminum compounds to the soil (with the sewage water) greatly enlarged its phosphate binding capacity. Experiments performed at this laboratory (Van Riemsdijk et al., 1979) have shown that columns of pure (inert) quartz sand mixed with amorphous $Al(OH)_3$ are very effective in the removal of phosphate (and other constituents) from sewage water added at the top. The addition of reactive aluminum compounds to the soil may offer in principle a possibility to increase the P- binding capacity of the top layers.

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5 MODELING TRANSPORT AND ACCUMULATION OF (ORTHO) PHOSPHATE IN SOIL

The results of phosphate analyses of sewage water and drainage water presented in chapter 3 clearly demonstrate that the soil can act as scavenger for soluble phosphate compounds. Further support for this function of the soil is provided by the distribution profile of accumulated soil phosphates (cf. fig. 3.5).

In the particular soil investigated here, (hydr)oxides of Al and Fe turn out to be the main components responsible for the binding of the added phosphate compounds. On the basis of the amounts of these soil components the phosphate storage capacity of different layers has been estimated (cf. Chapter 4). In turn this capacity provides a guide line for predicting when breakthrough of the phosphate added to a given layer is likely to occur.

As was indicated already briefly in chapter 2, however, the retention of phosphate by soil is a 'rate process'. Accordingly the efficiency of removal of phosphate by a given soil layer will depend also on the flux (density) of the percolating solution (e.g. sewage water or liquid manure). This then implies that the construction of a simulation model for phosphate retention as envisaged here requires quantitative information about the kinetics of the retention processes in addition to equilibrium retention curves. Both types of information are obtained best from batch experiments. In the following section such studies are described in (some) considerable detail.

In section 5.2 it has been attempted to express the experimental findings of the preceding section in terms of a mathematical model of moderate complexity, which model was then tested out with additional batch experiments (Section 5.3).

In section 5.4 this model is incorporated into existing models describing water movement in soil. Results calculated with the combined simulation model were checked against experimental data obtained with the percolation of phosphate solutions through short soil columns assembled in the laboratory. On the basis of the simulation model obtained in this manner long-term predictions were made of the phosphate retention in the soil to which relatively large amounts of soluble phosphate were added (cf. Chapter 6).

5.1 COLLECTION OF BASIC INFORMATION WITH THE HELP OF BATCH-STUDIES

5.1.1 Discussion of the experimental procedure chosen

Very often batch type experiments are used as an alternative for the study of the kinetics of retention processes occurring in a soil through which a carrier solution is percolating. The main advantage of this (experimental) approach is the elimination of various complicating phenomena associated with the movement of the carrier solution through a non-homogenous medium. However, also disadvantages arise, like e.g. the difference in solid/solution ratio under experimental and field conditions, the possibility that soil aggregates may be destroyed during shaking and the situation that in batch experiments the kinetics of the processes are studied at a decreasing concentration whereas during percolation the solution is renewed continuously.

The interaction of dissolved orthophosphate species was studied with soil samples derived from different layers of a soil that had been treated with sewage water. Since samples of the treated soil were used and not of the nontreated soil, the experiments could be performed at pH values corresponding with field conditions, without a severe pretreatment of the samples with alkali in order to raise the pH (cf. Beek et al., 1977a). On the other hand, the initial presence of accumulated amounts of phosphate and aluminინum compounds may be a complicating factor.

In view of the physico-chemical processes involved in the retention of phosphate, like e.g. adsorption and formation of solid phosphates, the pH, ionic strength and composition of the supporting electrolyte solution were kept constant and comparable to field conditions. For the same reason the temperature was kept constant (at 20 °C ± 1°).

A complicating factor when dealing with soils are microbial transformations of phosphate. Suppressing microbial activity by the addition of bacteriocides frequently used for this purpose, like chloroform, toluene or propylene oxide was dissuaded by White (1964) on the grounds that these treatments cause the release of unkown amounts of phosphate from organic combinations. Also it was noticed that many phosphatases were not inactivated by those treatments (Cosgrove, 1967). Moreover, it should be a point of consideration that addition of substances, in order to inhibit microbial activity, may influence the chemical processes of phosphate retention. In view of these considerations no measures were taken to suppress microbial activity.

In order to ensure good contact between the soil particles and the solution and to prevent that diffusion processes of dissolved phosphate species are the rate limiting step, mechanical mixing of the suspensions was used. As was indicated earlier, shaking or other methods of mixing may destroy the soil aggregates, thus increasing the specific surface area. In preliminary experiments different methods of shaking were compared (cf. 5.1.2.3.). It was found that rotating very slowly a vertical disk onto which the vessels (centrifuge tubes) were clamped in horizontal position, provided satisfactory results.

In most experiments the initial phosphate concentration varied between 0-20 ppm P (0 - 0.65 mmol/l P). In this respect it is recalled that in sewage waters the phosphate concentration is often around 10 mg P/l. Secondly, relatively low concentrations of P in solution were preferred in order to minimize the possibility of direct precipitation of calcium phosphates from the solution, in view of the prevailing pH and calcium concentration of the solution (see also 5.1.2.2). The change in phosphate concentration of the suspension was followed as a function of reaction time, generally up to 30 days (a reaction time period of 1 month roughly agrees with the period between 2 successive doses of sewage water supplied to the soil). The difference in phosphate concentration of the suspension at the start of the experiment and at its termination was taken as a measure of the amount retained (or sometimes desorbed).

5.1.2 Rate of disappearance of dissolved phosphate added at different initial concentrations

5.1.2.1. Materials and methods

Bulk samples of air-dry soil were collected from the treated soil at the sewage farm. These samples were carefully mixed and divided into small subsamples by means of a mechanical sampling device. Of these subsamples 1 gram was placed in a 50 ml polypropylene centrifuge tube and wetted with 0.4 ml of demineralized water. The closed tubes were stored in a constant temperature room at 20 ± 1 °C for at least 10 days prior to the addition of the phosphate solution. Due to this pretreatment the reproducibility of the measurements of phosphate retention at short reaction times greatly improved in comparison to preliminary experiments were this pretreatment was omitted. Rewetting of the air-dry samples and storage for some time probably restores an (apparent) equilibrium condition (Aslyng, 1964; White, 1964). The composition of the solution added to the wetted samples is given in table 5.1. It contained all main inorganic ions present in the drainage water (cf. Beek et al., 1977a) and at the same average concentration, except for the silicate and bicarbonate. The former was omitted and the latter was substituted by chloride because it is impossible to obtain the same pH in the solution as in the drainage water if both contain the same amount of bicarbonate. This is caused by the fact that the drainage water is supersaturated with CO_2 with respect to

Table 5.1 Composition and pH of solution added to the soil samples

$CaSO_4.2H_2O$	0.84 mmol/l
$CaCl_2.2H_2O$	0.94 mmol/l
KCl	0.17 mmol/l
KNO_3	0.19 mmol/l
$MgCl_2.6H_2O$	0.35 mmol/l
$NaCl$	5.70* mmol/l
pH	6.2

* If P is added in the form of NaH_2PO_4 a correction was made for the added Na.

equilibrium with the atmosphere. For this solution the pH was adjusted to pH 6.2 by the addition of acid or base. Phosphate was added as NaH_2PO_4 (the sodium supplied by this salt was accounted for when adding NaCl). The solution/soil ratio (W) was roughly 20 and the suspensions were mixed as described in 5.1.2.3. The suspension pH was measured regularly and readjusted to pH 6.2 if necessary. In order to prevent the possible formation of anaerobic conditions moistened air was bubbled at regular time intervals as a safety measure (actually the centrifuge tubes are not closed air-tight by the screwcaps). At the termination of the experiment an aliquot of the suspension was either directly filtered through a 0.1 μm membrane filter or first centrifuged at 20.000 rpm for 10 minutes (at 20 °C) prior to filtration (with both procedures the same phosphate concentration was obtained). The filtered solution was used for the analysis of phosphate and sometimes other substances. Phosphate was determined colorimetrically according to the procedure of Murphy and Riley (1962), which presumably measures the orthophosphate species only.

5.1.2.2 Interpretation of the results

The decrease of the phosphate concentration of soil suspensions as a function of reaction time is given in fig. 5.1 on a semilog scale, for different initial phosphate concentrations (c_o). The interpretation of such curves in terms of mechanisms is largely based on results obtained with single soil minerals, like e.g. aluminum and iron oxides, clay minerals and solid carbonates (Stumm and Leckie, 1970; Chen et al., 1973; Griffin and Jurinak, 1973, 1974; Kuo and Lotse, 1972, 1974; Van Riemsdijk et al., 1975, 1977; Helyar et al., 1976; McLaughlin et al., 1977; Ryden et al., 1977a,b). The rapid decline in concentration is then ascribed to surface adsorption and the slow decline may represent the formation of a solid phosphate phase and/or diffusion of dissolved phosphate into the bulk of the adsorbent. When dealing with soil suspensions it is evident that here the same processes may also be operative. In addition the possibility exists that microbial transformation of phosphate is involved or that diffusion processes associated with

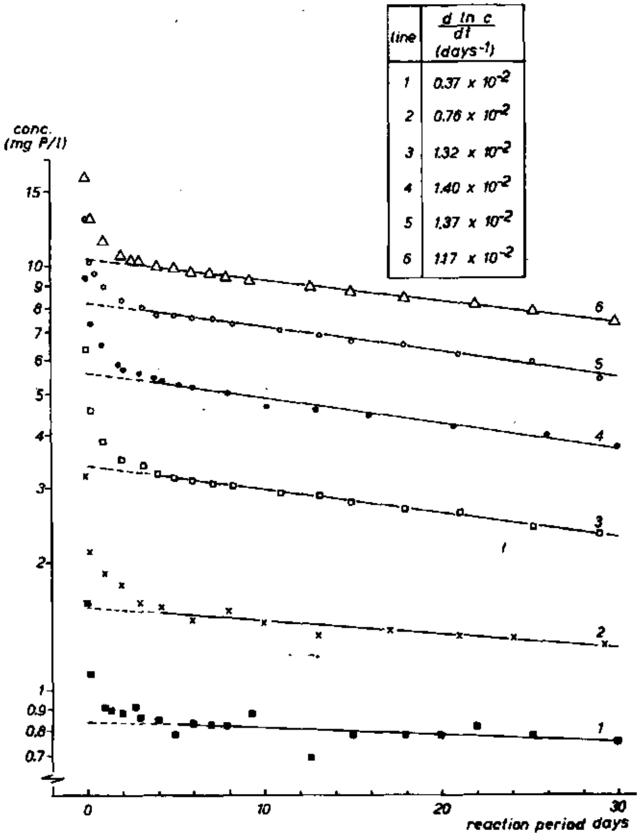

Fig. 5.1 The concentration of phosphate in solution (mg P/l) as a function of the reaction period for soil suspensions with different initial phosphate concentrations.

the aggregate structure of the soil occur (Vaidyanathan and Talibudeen, 1968), particularly at longer reaction times. In view of the foregoing the comprehensive term 'slow reaction' has often been used to denote the various possible processes involved in the slow, sometimes long lasting decline of the concentration. Adsorption processes are considered to be reponsible for the rapid decrease of the concentration.

With respect to the data presented in fig. 5.1 it is obvious then to associate the linear part of the curves with the 'slow reaction' and the non-linear part with adsorption. Provided the rate of the adsorption process(es) is sufficiently rapid in comparison to the concurrently occurring slow reaction, the former may have gone to completion and extrapolation of the linear line segments to time zero leads to a concentration, denoted here by c_o', which is lower than the corresponding initial P concentration (c_o) of the suspension. The difference (c_o-c_o') then represents the fall in concentration associated with the removal of P from the solution by adsorption process(es) only. If the latter difference is multiplied by the solution/soil ratio (W) one obtains the amount adsorbed per unit mass of soil. The equilibrium P concentration which corresponds to this amount adsorbed is under the presupposed condition of reversible adsorption (cf 5.1.3.2) the same as c_o'. The values derived from the different curves in fig. 5.1 according to the above considerations, have been tabulated in table 5.2. In fig. 5.2a the amounts adsorbed have been plotted as a function of the equilibrium P concentration. The contribution of the slow reaction in the retention of P is found from the total amount of P removed from the solution minus the amount removed by adsorption. The latter quantity can be derived from fig. 5.2a for the prevailing P concentration in the solution, provided the adsorption process(es) are reversible and in equilibrium with the P concentration in so-

Table 5.2 Amounts of phosphate retained by 'fast processes' from soil suspension with different initial phosphate concentrations (c_o). The 'equilibrium concentration' for the indicated processes (c_o') is found by a graphical extrapolation of the concentration curves to t=0 (fig. 5.1).

c_o	c_o'	P-retained $(c_o-c_o').W^*$
----- mg P/l	-----	mg P/kg soil
1.59	0.84	15.7
3.25	1.57	33.8
6.36	3.39	59.7
9.41	5.58	76.8
12.85	8.17	94.1
16.05	10.37	113.8

* W= solution/soil ratio

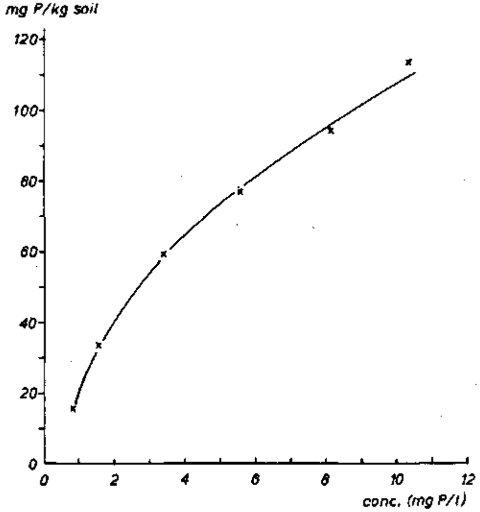

Fig. 5.2A Amounts of P (mg P/kg soil) removed from the solution by adsorption as a function of the equilibrium concentration in solution (mg P/l).

lution. It is thus assumed that different processes are involved in the removal of P from the solution and not one 'slow adsorption reaction'. At this point it is noted briefly that the curve in fig. 5.2a only represents an apparent adsorption isotherm as part of the adsorption sites will be occupied by phosphate already present in the soil at the time of sampling. Experiments with radioactive phosphate (^{32}P) have been carried out to determine the total amount of adsorbed P (cf. 5.1.3).

The usual method by which phosphate 'adsorption data' are obtained is based on a determination of the amounts of phosphate removed from the solution of soil suspensions with different initial phosphate concentrations after a certain reaction time. In order to limit the interference of the slow reaction, in particular the formation of a solid phase, short reaction times are preferred, especially if high solution phosphate concentrations are involved (cf. Chapter 2). On the other hand, however, the adsorption reactions are not instantaneous with the consequence that the chosen reaction times are always a compromise. The curves given in fig. 5.1 have been used to derive the amounts of P removed from the solution (and the corresponding concentration) after 1 through 5 days of reaction time. These amounts have been plotted in fig. 5.2b as a fraction of the equilibrium amounts removed for the corresponding initial solution phosphate concentrations. It shows that a termination of the 'adsorption' experiments at reaction times corresponding to ratio values <1 leads to an underestimation of the adsorption capacity. On the other hand at ratio values >1 it results in turn in an overestimation of the adsorption capacity. Figure 5.2b shows that at the prevailing experimental conditions a reaction time of 3 days gives a reasonable estimate of the 'equilibrium adsorption'. The determination of adsorption data for other layers (cf. 5.3.3) was, in

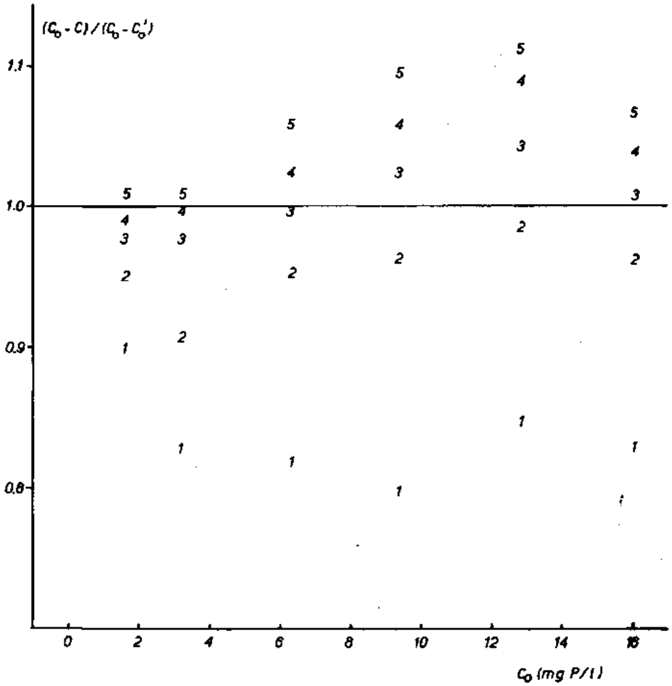

Fig. 5.2B Relative amounts of P removed from the solution (c_o-c) after different reaction times (1=1 day, 2=2 days, etc.), expressed as a fraction of the amount removed at equilibrium (c_o-c_o') for suspensions with different initial P concentrations (c_o).

view of the above information, usually based on results obtained after 3 days reaction time. Due to the contribution of the slow reaction, the amounts removed at the higher concentrations after 3 days of reaction time exceed already the estimate represented by the equilibrium 'adsorption' in fig. 5.2a, implying that the same contact time for suspensions with different initial phosphate concentrations may easily lead to underestimates of the amounts adsorbed at the lower concentration range and to overestimates at the higher concentration range. The fact that 3 days reaction time turns out to give the best estimate is obviously strongly dependent on the experimental conditions. For instance, Munns and Fox (1976) reported that the amounts removed from the solution at 6 days reaction time were less than derived from an extrapolation of the log c curves to time zero. Their explanation of such long reaction times was based on the argument that aggregation or gel coatings in the soil slow down the equilibration of the adsorption reaction.

Due to the fact that the adsorption process is relatively fast, it is of great importance for the removal of phosphate from waste water percolating through the soil. This explains the efforts made to arrive at a correct estimate of the adsorbed fraction of retained phosphate. In addition, this adsorbed fraction presumably represents reversibly bound forms of inorganic phosphate; accordingly it may respond rather rapidly to changes in the solution phosphate concentration.

According to fig. 5.1 the log c versus time data can be fitted to a straight line after 2 to 3 days reaction time. With other soils and minerals, like e.g. kaolinite and aluminum oxides, the slow decrease in solution phosphate concentration could also be described as a first-order process, i.e. $dc/dt = -k * c$ (Chen et al., 1973; van Riemsdijk et al., 1975, 1977; Munns and Fox, 1976; Sawhney, 1977). The responsible mechanism(s) causing this apparent first-order decline in concentration can not be derived (in general) from such data. For that purpose additional information has to be available, like e.g. X-ray or electron diffraction data. In this way it has been shown that the slow decline in solution phosphate concentration for the reaction of phosphate with different forms of aluminum oxides may be ascribed to the formation of an aluminum phosphate phase (Chen et al., 1973; van Riemsdijk et al., 1975, 1977). In particular the experiments carried out at this laboratory (cf. van Riemsdijk et al., l.c.) have practical significance because the (experimental) conditions were adjusted to those present in the sewage field. On this basis it is assumed that the reaction of available reactive soil aluminum (cf. Chapter 4) with (soluble) phosphate leads to the slow formation of an aluminum phosphate compound. Results of fractionation studies (cf. Chapter 3) of accumulated soil phosphate support this suggestion. It must be granted, however, that the suggested mechanism remains somewhat speculative because a direct experimental proof is not available. On the same grounds, it remains a matter of speculation which reaction or sequence of reactions is involved in the formation of the phosphate compound, because direct precipitation from the solution will be insignificant in view of the low solubility of most aluminum oxides at the prevailing experimental conditions, viz. pH around 6. At this point it is mentioned briefly (for details see small print below) that no experimental evidence has been obtained to the effect that direct precipitation of calcium phosphates has occurred during the reaction time, although the solution added to the soil samples (cf. Table 5.1) was supersaturated with respect to hydroxyapatite.

The (minimum) phosphate concentration necessary to attain a saturated solution with respect to dicalcium phosphate, octo-calciumphosphate and hydroxyapatite, respectively, at 25 °C has been calculated. To this purpose it is assumed that the solution pH remains at its original value of 6.2 and the calcium activity at a value of $10^{-2.93}$ mol/l. The latter activity follows from the calcium concentration in the solution ($10^{-2.75}$ mol/l) and the activity coefficient (0.65). This coefficient was calculated with the Debeye-Hückel equation for an ionic strength of 0.013 mol/l (see eq. 2.12 and Table 2.1 and 2.2 in Novozamsky et al., 1976). If these values are introduced in the ion product of the solid phoshate it follows that for the precipitation of $CaHPO_4.2H_2O$ (solubility product = $10^{-6.56}$) the phosphate concentration has to exceed $10^{-2.53}$ mol/l (92 mg P/l), for $Ca_4H(PO_4)_3.3H_2O$ ($10^{-46.91}$) it has to exceed $10^{-2.43}$ mol/l (115 mg P/l) and for $Ca_{10}(PO_4)_6(OH)_2$ ($10^{-113.7}$) it has to exceed $10^{-4.24}$ mol/l (1.8 mg P/l). Thus in view of the prevailing phosphate concentrations only direct precipitation of hydroxyapatite is theoretically possible.

In order to find out if precipitation of calcium phosphate actually occurs, centrifuge tubes were filled with solutions of which the phosphate concentration varied between 0 and 30 mg P/l and then treated in the same manner as if a soil suspension were present. In none of the treatments the solution became turbid and in the filtered and non filtered samples no significant decrease in P concentration was observed from the initial value at any reaction time studied. It is noted here that the results of P fractionation studies (Beek et al., 1977b) also show that in the presence of soil (components) the formation of calcium phosphate is insignificant.

Indications that adsorption and 'slow reaction' represent different processes have also been derived from the results with radioactive ^{32}P (cf. 5.1.3). Anticipating on the conclusions it can be stated that the phosphate removed by the slow reaction is hardly accessible to isotopic exchange, in contrast to the amount removed by adsorption.

A third argument that makes it unlikely that the slow decline of the concentration observed in fig. 5.1 is simply a 'tailing end' of the adsorption reaction, follows from fig. 5.3. In this figure the amounts retained during 100 days reaction time are presented for soil suspensions of which the (phosphate-depleted) solution was periodically replaced by a fresh solution with the same initial concentration of 5.9 and 12.4 mg P/l, respectively. Accounting for the fact that the amounts retained by the fast reaction amount to 83 and 115 mg P/kg soil at the relevant concentrations (cf. fig. 5.2a) it becomes clear that the contribution of the slow reaction in the retention of phosphate exceeds the amounts retained by adsorption.

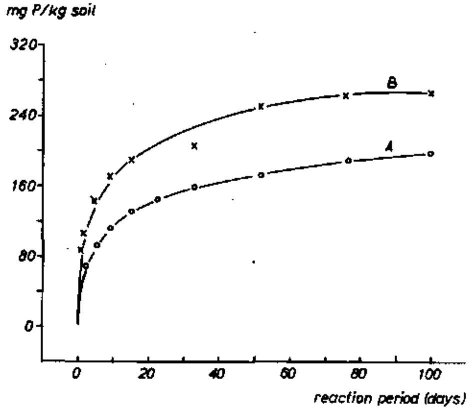

Fig. 5.3 Amounts of P removed from the solution (mg P/kg soil) of suspensions kept at a constant P concentration (A=5.9 mg P/l, B=12.4 mg P/l) after different reaction times.

The identification of the slow reaction with diffusion of phosphate species from the bulk solution into the matrix of the adsorbents (Vaydianathan and Talibudeen, 1968; Ryden et al., 1977b) is also rather unlikely, in view of the absolute amounts involved according to fig. 5.3. Obviously it is not postulated here that diffusion processes do not take place at all during the slow reaction.

5.1.2.3 Effect of mode of shaking on the interaction processes

The most plausible explanation of the slow decline of the concentration is, in view of the available evidence, undoubtly the occurrence of processes leading to the formation of a solid phosphate. At this point, however, it is recalled that the soil suspensions were mechanically shaken which may cause a degradation of the soil components. This may lead to an increase of the reactive surface and subsequent bonding of phosphate.

Different methods of shaking were compared, viz. shaking according to the method described in 5.1.1, by hand and end-over-end shaking. With end-over-end shaking the centrifuge bottles were placed in vertical position and turned 14 times/minute. In the alternative method (cf. 5.1.1) the bottles were placed horizontally and turned around 10 times/minute. Hand mixing was performed by

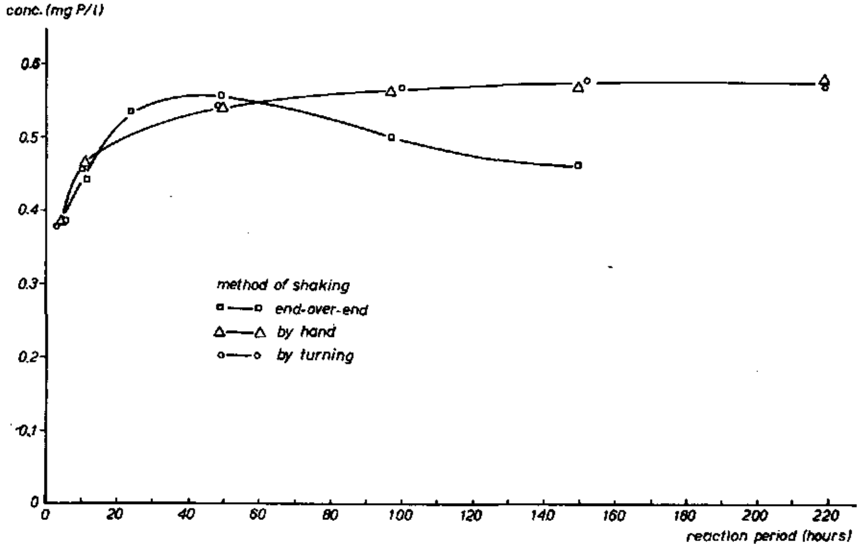

Fig.5.4 The effect of method of shaking on the release of solid P into the solution.

turning the bottles in horizontal position during working hours every two hours.

In order to demonstrate a possible decrease in dissolved P as a result of shaking, soil suspensions with low values of soluble P were preferred, because this minimizes the interfering effect of a decrease in concentration by chemical (precipitation) processes. Such conditions were obtained by using soil samples (for this preliminary experiment) which contained relatively high amounts of solid phosphate and by adding a solution initially free of phosphate. The release of solid phosphate increased the phosphate concentration in solution to a low but experimentally well measurable level. The pH of the soil suspensions was kept at pH 7 instead of pH 6.2 because with aluminum and iron as the reactive components, the slow reaction rate is expected to decrease at an increase in pH (Chen et al., 1973). The average values of duplicate desorption values have been plotted in fig. 5.4. End-over-end shaking gives rise to a rapid increase of the concentration followed by a decline at longer shaking times, in contrast to the results of the two other methods of shaking where the concentration increased monotonically. The decline in the concentration by end-over-end shaking has been interpreted as an indication that breakdown of the soil particles occurs which gives rise to exposure of new surfaces. It seems unlikely that the failure to obtain this effect with the two other methods of shaking was due to poor mixing of soil and solution because it was shown in an additional experiment that the decline in concentration of P in suspensions containing added phosphate is unaffected by (gentle) shaking after the rapid processes have been completed. On the basis of the above results the shaking procedure as described in 5.1.1 was selected for the present studies.

5.1.3 Isotopic exchange of P present in solid phases

Experiments with ^{32}P were performed to investigate the fraction of solid soil phosphate which is accessible to isotopic exchange with ^{32}P-labelled phosphate ions in solution. The solid phosphate could be separated into different fractions: the solid phosphate initially present in the samples and the solid phosphate retained during the batch studies. According to the results discussed in section 5.1.3 this latter fraction could presumably, be subdivided further into a fraction resulting from rapid retention processes and a fraction resulting from slow retention processes. A determination of the relative proportion of each of these fractions that is accessible to isotopic exchange may give valuable information about the physico-chemical nature of the soil solid phosphate and the retention processes involved.

5.1.3.1 Method employed

Pretreated soil samples (cf. 5.1.2) were suspended in a solution (cf. Table 5.1 for its composition) with and without added phosphate. The suspension pH was maintained at pH = 6.2 ± 0.2 by adding NaOH or HCl, if necessary, at regular time intervals. The other experimental conditions were the same as reported before. After 3 days or 4 weeks contact with the added solution (with or without phosphate) about 0.5 μCi ^{32}P was added as a carrier free solution (0.5 ml) to the suspension after which mechanical shaking was continued for time intervals varying from 0.5 hour to 7 days. For each time period duplicate soil suspensions were filtered through a 0.1 μm membrane filter. The ^{32}P activity was counted directly on duplicate 5 ml aliquots of filtered soil extract in a liquid scintillation spectrometer using Cerenkov radiation. In order to determine the correction factor for color quenching aliquots of the ^{32}P-labelled solution were added directly to samples of the solution in which the soil was suspended and to filtered samples of soil extracts (containing no ^{32}P). It turned out that the count rates in the filtered soil extracts were approximately 5-8% lower than in the solution to which no soil had been added. The use of ^{32}P further revealed that some 'adsorption' of phosphate might occur on the inside walls of the reaction vessels.

5.1.3.2 Interpretation of the results

Defining:

Y^* = amount of ^{32}P added to a suspension at time zero, in cpm per kg of soil;
y_t^* = amount of ^{32}P present in the solution phase at time t, in cpm per kg of soil;
y_t = amount of P present in the solution at time t, in mg P per kg of soil;

one may express the progressing isotopic exchange between solid phase and solution in terms of the amount of solid phase phosphate, $P_s(t)$, in mg P per kg of soil, that has acquired the same specific activity of ^{32}P as is found in the solution phase, viz. y_t^*/y_t.

Thus one finds:

$$P_s(t) = (Y^* - y_t^*)/(y_t^*/y_t) \qquad (5.1)$$

In the case of soil samples to which the phosphate-free solution was added, the quantity P_s refers to solid phase phosphate <u>originally</u> present in the sample, and will be indicated as $P_{s,o}(t)$. The amount in solution, y_t, then arises by dissolution of this solid phase phosphate. In table 5.3 the values of y_t, $(Y^* - y_t^*)/y_t^*$ and the corresponding $P_{s,o}(t)$ are given for different values of t, using samples that were pre-equilibrated with a phosphate free solution for 3 days and 4 weeks, respectively. In both series $(P_{s,o})$ increases with longer exchange times, implying that within a period of 7 days the exchange process has not reached an equili-

Table 5.3 Changes in the ratio of ^{32}P activity between solid/solution and the exchangeable soil phophate with time for samples pre-equilibrated with a phosphate-free solution for 3 days (A) and 4 weeks (B).

Exchange time	Ratio of ^{32}P activity between solid/solution $(Y^* - y_t^*)/y_t^*$	Exchangeable soil P $P_{s,o}(t)$
	A	
hours		mg P/kg soil
0.58	2.37	17.8
1	2.94	26.7
3	4.74	36.3
6	5.36	44.6
24	7.74	61.3
72	10.40	86.0
120	12.30	99.6

(The average value of y_t in these samples = 8.1 (s.d. 0.6) mg P/kg soil, leading to a concentration of 0.39 mg P/l)

Exchange time	Ratio of ^{32}P activity between solid/solution $(Y^* - y_t^*)/y_t^*$	Exchangeable soil P $P_{s,o}(t)$
	B	
0.53	1.17	9.7
1	1.88	14.2
3	2.47	20.4
6	3.49	30.8
24	5.58	49.3
74	8.00	64.0
120	9.60	79.4
168	11.05	91.5

(The average value of y_t in these samples = 8.3 (s.d. 0.6) mg P/kg soil, leading to a concentration of 0.44 mg P/l) brium state. The lower values of $(P_{s,o})$ for the 28 days series in comparison to the corresponding values of the 3 days series suggest that in this time interval changes in the (chemical) nature of the solid P have taken place. The presence of non-equilibrium conditions in the suspended soil samples might be a possible reason for these changes. On the other hand, however, the nearly equal average values of y_t for both series (cf. Table 5.3a,b) do suggest that an equilibrium state has been reached within 3 days of contact.

In general the exchange process can be divided into two distinct sets of reactions with respect to the rates of exchange (Jose and Krishnamoorthy, 1972). According to McAuliffe et al (1954) the two sets of reactions show up if the ratio $(Y^* - y_t^*)/y_t^*$, i.e. the ratio between ^{32}P in the solid phase and ^{32}P in the solution phase,

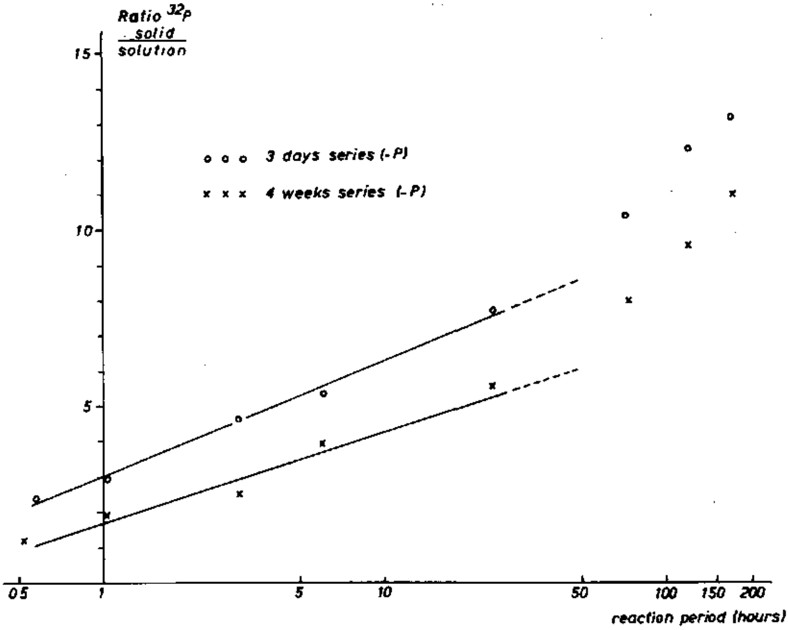

Fig. 5.5A Ratio of ^{32}P over solid/solution, $(Y^* - y_t^*)/y_t^*$, versus the reaction period (logarithmic time scale) for suspensions pre-equilibrated with a <u>phosphate</u> <u>free</u> solution for 3 days and 4 weeks, respectively.

is plotted versus log t and t, respectively. In fig. 5.5a,b this has been done for the data given in table 5.3, which shows convincingly that (at least) 2 sets of reactions are involved in the exchange process. At first the ratio changes logarithmically with time (cf. fig. 5.5a) and later presumably linearly with time (cf. fig. 5.5b). The latter conclusion, however, needs some reservation in view of the limited number of experimental points for exchange times exceeding 24 hours. It also implies that the separation between the rapid and slow sets of reactions from fig. 5.5 will be inaccurate. The 'equilibrium' values for the ratios have been estimated from the extrapolated linear portion of the curve at an (arbitrary) time of 48 hours; resulting in values of the above ratio equal to 8.6 for the 3 days series and to 6.1 for the 28 days series. The cor-

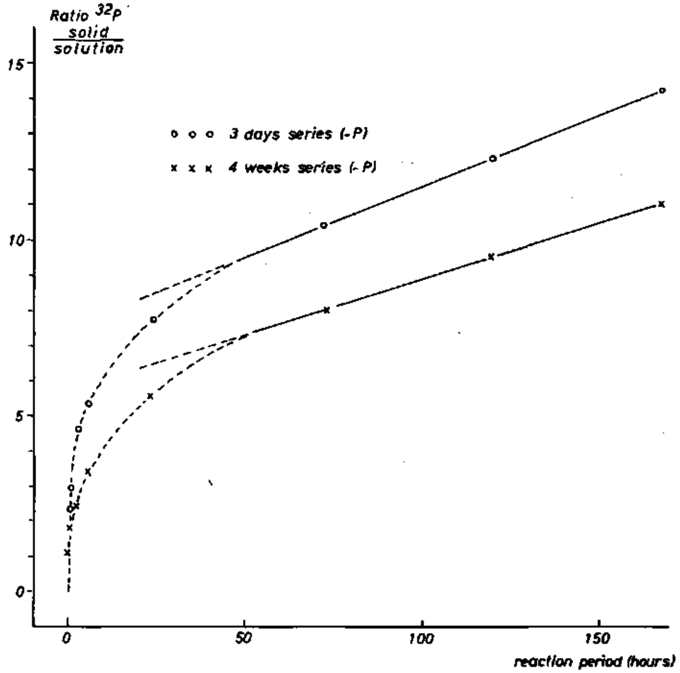

Fig. 5.5B Ratio of ^{32}P over solid/solution, $(Y^{*}-y_t^{*})/y_t^{*}$, versus the reaction period (linear time scale) for suspensions pre-equilibrated with a phosphate free solution for 3 days and 4 weeks, respectively.

responding (rounded off) amounts of rapidly exchangeable solid P are then 70 and 51 mg P/kg soil, (cf. eq 5.1) using for y_t the values 8.1 and 8.3 mg P/kg soil, respectively. The amounts of slowly exchanging solid P in the time period of 7 days are then 45 and 41 mg P/kg soil for the 3 days and 28 days series, respectively. The rapidly exchanging fraction is usually associated with P at 'external' surfaces and the slowly exchanging fraction with P held at less readily accessible sites (White, 1976). Isotopic exchange experiments with phosphated goethite and gibbsite, however, indicate that also the chemical configuration of the 'adsorbed' P on the solid-solution interface may be a rate-determining factor (Atkinson et al., 1972; Kyle et al, 1975).

The total amount of phosphate present in the samples used here amounts to 600 mg P/kg soil of which about 15-20% is present as organic bound forms (cf. Chapter 3) and the remaining as inorganic bound forms, the latter mainly associated with aluminum. The fraction of the above solid phosphate forms accessible to isotopic exchange was derived from table 5.3a,b; it varied from 15-19% after 7 days of exchange. The rapidly exchanging fraction contributed 8-12%; the contribution of the slowly exchanging fraction amounted to 7%. The results found here for the soil treated with sewage water fall in the range of 17-44% reported by Talibudeen (1958) for fertilized agricultural soils of comparable texture, viz. medium and light texture.

In the second part of the isotopic exchange studies samples were used that were equilibrated with a phosphate solution, before the addition of ^{32}P. The exchangeable phosphate (P_s) calculated from equation 5.1 for these samples includes in principle the exchangeable fraction of the original soil phosphate ($P_{s,o}$) and the exchangeable fraction of 'freshly' retained phosphate ($P_{s,r}$), i.e.

$$P_s = P_{s,o} + P_{s,r} \qquad (5.2)$$

The values of P_s, the total amount of retained phosphate (P-retained) and other relevant data are tabulated in table 5.4a, b for the 3 days series and 4 weeks series, respectively. As follows from a comparison between the values of P_s in table 5.3 and 5.4 the presence of 'freshly' retained phosphate leads to higher P_s values. Furthermore, an increase in reaction time from 3 days to 4 weeks leads to a decrease in P_s in spite of an increase in P-retained for the 4 weeks series.

An indication of the fraction of P-retained which is isotopically exchangeable, i.e. the ratio $P_{s,r}$: P-retained, can be derived from the data in table 5.4, provided the values of P_s obtained from the samples to which a phosphate free solution was added (cf. Table 5.3) can be used as an estimate for $P_{s,o}$. This approach is inevitable because $P_{s,o}$ and $P_{s,r}$ cannot be determined separately in the samples with added phosphate. It then follows that in the samples of the 3 days series the percentage of P-retained, accessible to isotopic exchange, reaches a maximum value of 80% after 24 hours of exchange. This fraction remains fairly constant at longer exchange times, implying that the increase in $P_{s,r}$ of 20.6

Table 5.4 Changes in the ratio of ^{32}P activity between solid/solution, exchangeable soil phosphate (P_s), the amount of soluble phosphate (expressed as mg P/l and as mg P/kg soil, y_t) and the amount retained (P-retained) with time for samples pre-equilibrated with a solution <u>with</u> phosphate for 3 days (A) and 4 weeks (B).

Exchange time hours	Ratio of ^{32}P activity between solid/solution $(Y^*-y_t^*)/y_t^*$	Solution P mg P/l	y_t mg P/kg soil	P-retained mg P/kg soil	Exchangeable soil P $P_s(t)$ mg P/kg soil
		A			
0.5	0.63	5.29	107.6	93.8	68
1	0.72	5.25	107.1	94.6	77
3	0.94	5.25	107.0	94.3	100
6	1.09	5.16	105.7	95.6	120
24	1.28	5.25	106.8	94.4	137
72	1.83	4.50	91.6	109.6	167
120	2.20	4.37	86.0	115.2	189
168	2.55	4.26	82.5	118.7	210
		B			
0.5	0.19	3.62	70.8	129.8	13
1	0.26	3.64	73.7	127.5	19
3	0.46	3.64	70.4	130.8	32
6	0.62	3.60	74.2	127.1	46
24	0.90	3.62	74.6	126.0	67
74	1.39	3.58	73.8	127.3	103
120	1.90	3.56	70.1	130.8	133
168	1.90	3.56	70.1	130.8	133

mg P/kg soil (96.3-75.7) in the period from 24 to 168 hours results from the concurrent increase in P-retained at 24.3 mg P/kg soil (118.7-94.4). For the samples of the 4 weeks series the percentage of P-retained accessible to isotopic exchange amount to 14% after 24 hours of exchange; this percentage increases to 32% after 7 days of exchange. Results of isotopic exchange studies with soil phosphate (Talibudeen, 1958; Barrow and Shaw, 1975; Ryden and Syers, 1977) and with phosphated gibbsite (Vanderdeelen and Baert, 1971) show the same tendency, viz. the retained phosphate becomes less accessible to isotopic exchange at longer contact times with the soil or gibbsite. A completely satisfying explanation of this behavior in terms of reaction mechanisms is not available at present.

Results of previous experiments (cf. 5.1.2.2) suggest that fast and slow reactions are involved in the retention of phosphate giving rise to a distinction of P-retained in an adsorbed fraction and a fraction representing a type of precipitated phosphate. If reversible adsorption is assumed (cf. Section 5.1.4 for the experimental support of the above assumption) one can estimate the fraction of P-retained present in an adsorbed form from fig. 5.2a and the phosphate concentration in the suspension. Also the P_s values can be distinguished in a rapidly and slowly exchanging fraction on the basis of a plot of the ratio's $(Y^* - y_t^*)/y_t^*$ versus log t (cf. fig. 5.5a and 5.6). The rapidly exchanging phosphate was associated with the adsorbed phosphate forms and the slowly exchanging fraction with less accessible forms of phosphate, like e.g. solid phosphate compounds.

The data of table 5.4 are plotted in fig. 5.6; the 'equilibrium' values of the relevant ratio's, indicating the rapidly exchanging fraction, were estimated from the linear portions of the plots extrapolated to an arbitrary exchange time of 48 hours. The values derived in this manner were 1.4 and 1.04 for the 3 days and 4 weeks series, respectively. The corresponding values of y_t (the amount of phosphate in solution) were 106.8 and 72.7 mg P/kg soil, respectively (cf small print below).

The above graphical procedure requires in principle a constant value of y_t; it follows from the data in table 5.4 however, that the latter decreases with longer exchange times. Since the rate by which y_t decreases is low, the latter was considered to remain constant over relatively short exchange times. The amounts of rapidly and slowly exchanging phosphate derived in this manner must be considered as rough estimates, in particular for the samples of the 3 days series, due to the decreasing value of y_t at longer exchange times. The values of y_t used to calculate the rapidly exchanging fraction from fig. 5.6, represent the average values for the first 24 hours of exchange.

The rapidly exchanging phosphate calculated from these values, P_s (fast), amounted to 150 and 76 mg P/kg soil for the 3 days and 4 weeks series, respectively. The corresponding slowly exchanging portions, P_s (slow), are then 60 (210-150) and 57 (133-76) mg P/kg soil, respectively. In the suspensions without added phosphate (cf. Table 5.3 and fig. 5.5) the rapidly exchanging phosphate, $P_{s,o}$ (fast), amounted to 70 and 51 mg P/kg soil and the slowly exchanging phosphate, $P_{s,o}$ (slow), to 45 and 41 mg P/kg soil for the

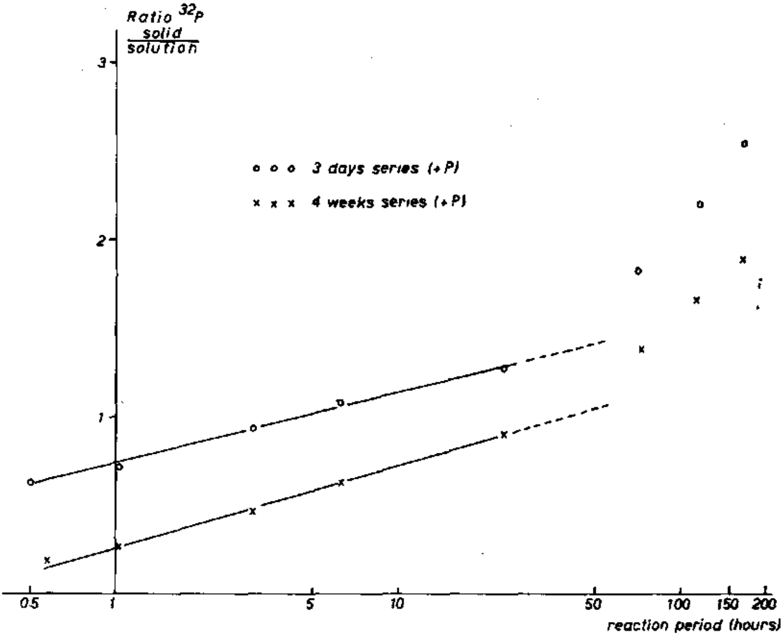

Fig. 5.6 Ratio of ^{32}P over solid/solution, $(Y^*-y_t^*)/y_t^*$, versus reaction period (logarithmic time scale) for suspensions pre-equilibrated with a phosphate solution for 3 days and 4 weeks, respectively.

3 days and 4 weeks series, respectively. A comparison of the different P_s (fast) and P_s (slow) values with the corresponding $P_{s,o}$ values indicated that the presence of 'freshly' retained phosphate increases the exchangeable phosphate in both fractions. The differences in rapidly exchanging phosphate, denoted here by $P_{s,r}$ (fast), amounted to 80 and 25 mg P/kg soil, the difference in slowly exchanging phosphate, denoted here by $P_{s,r}$ (slow) amounted to 15 and 16 mg P/kg soil for the 3 days and 4 weeks series, respectively.

The fraction of P-retained, present in an adsorbed form (see the above discussion for its calculation) amounted to 75 mg P/kg soil for the 3 days series (average phosphate concentration = 5.24 mg P/l) and to 62 mg P/kg soil for the 4 weeks series (average phosphate concentration = 3.62 mg P/l). If the values of $P_{s,r}$ (fast) are related to the adsorbed fractions it follows that for the samples of the 3 days series the adsorbed phosphate is completely accessible to isotopic exchange, in contrast to the samples of the 4 weeks series of which only 40% participated in the (rapid) exchange process. These results seem to indicate that part of the adsorbed phosphate became less accessible to isotopic exchange at longer reaction times between the soil and added phosphate. Whether this is caused by a change in the initial configuration of adsorbed phosphate at the solid/solution interface (cf. Chapter 2 for a discussion of the mechanism) or by the possible functioning of the adsorbed phosphate as a template in the formation of a type of precipitated phosphate (cf. Section 5.2.2) remains a matter of speculation.

The fractions of P-retained present in the form of a precipitated compound were calculated from the total amounts retained minus the portions present in an adsorbed form. The estimates obtained with this procedure were 44 and 66 mg P/kg soil for the 3 days and and 4 weeks series, respectively. The corresponding values of $P_{s,r}$ (slow) of 15 and 16 mg P/kg soil indicate that these solid compounds, very probably present in the form of an aluminum bound phosphate (cf. Chapter 3), are rather inaccessible to isotopic exchange. This is in agreement with the results found by Tandon and Kurtz (1968) that as much as 0.5 to 0.75 of the aluminum and iron bound phosphate was not exchanged in 147 hours. In conclusion, the fraction of P-retained present in presumably an adsorbed form is initially completely accessible to isotopic exchange, however, at longer reaction times with the soil changes occur by which it becomes less accessible to exchange processes. It is suggested here that the above changes are somehow related to the process(es) responsible for the formation of a type of solid phosphate. The latter forms of phosphate turn out to be rather inaccessible to isotopic exchange.

5.1.4 Effect of repeated additions of dissolved phosphate on phosphate adsorption

5.1.4.1 Preliminary considerations

The effects of previous additions of phosphate on phosphate adsorption by soil (components) have been studied in varying degree of detail by a limited number of workers, like e.g. Kurtz and Quirk (1965), Ozanne and Shaw (1968), Bache and Williams (1972), Kao and Blanchar (1973), Chen et al. (1973) and Barrow (1974). In general these effects are derived from phosphate adsorption isotherms of the (same) soil with and without a pretreatment with phosphate. Foregoing details one finds that either the isotherms coincide or that the isotherm of the pretreated soil falls below the isotherm of the original soil. The differences noted above are explained on the basis of (postulated) processes responsible for the slow retention of phosphate. If the isotherms coincide it is assumed that in the pretreated soil phosphate is removed from the original adsorption sites (in relation to the decrease in phosphate concentration of the solution) due to the slow formation of discrete phosphate compounds. If, however, the above reaction has not been completed, viz. some adsorption sites are still occupied in the pretreated soil at the time the isotherms are determined, the (apparent) isotherm of the pretreated soil will fall below the isotherm of the original soil. This is visualized in fig. 5.7 with help of hypothetical curves, representing the amounts of phosphate removed from the solution by adsorption and the corresponding 'equilibrium' phosphate concentration in solution. Curve 1 represents the above relation for the original soil whereas curve 2 is found for the pretreated soil. As follows from the latter curve, the amount of phosphate removed from the solution is lower than for the original soil at the same phosphate concentration, due to the presence of some phosphate on the adsorption sites. Under the presupposed condition that the latter fraction of adsorbed phosphate remains accessible to isotopic exchange it can be determined with the help of ^{32}P. If the amount of exchangeable phosphate is added to the amounts of phosphate removed from the solution curve 2 shifts upwards and must coincide with the corresponding portion of curve 1 because the total number of potential adsorption sites is the same in both cases. Curve 3 would be obtained if, in the pretreated soil, excess phosphate remains on the adsorption sites

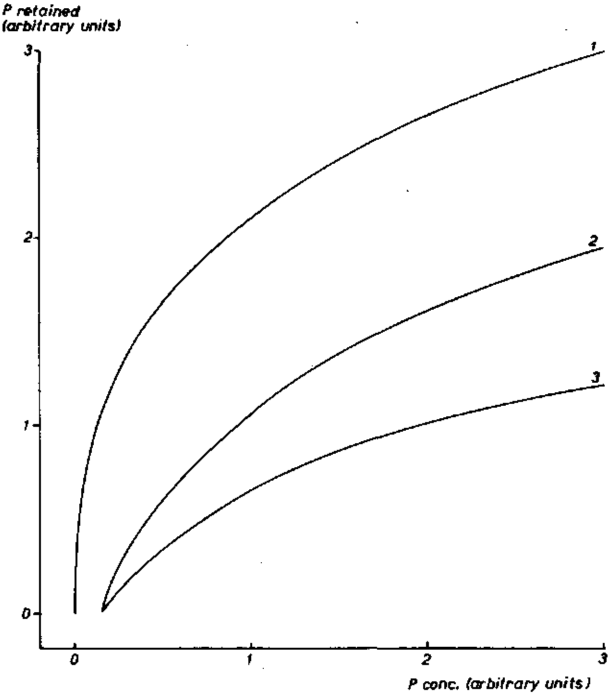

Fig. 5.7 Schematic representation of three possible relationships between the amounts of phosphate removed from the solution by adsorption and the equilibrium concentration; for explanation see text.

completely accessible to isotopic exchange, however, at longer reaction times with the soil changes occur by which it becomes less accessible to exchange processes. It is suggested here that the above changes are somehow related to the process(es) responsible for the formation of a type of solid phosphate. The latter forms of phosphate turn out to be rather inaccessible to isotopic exchange.

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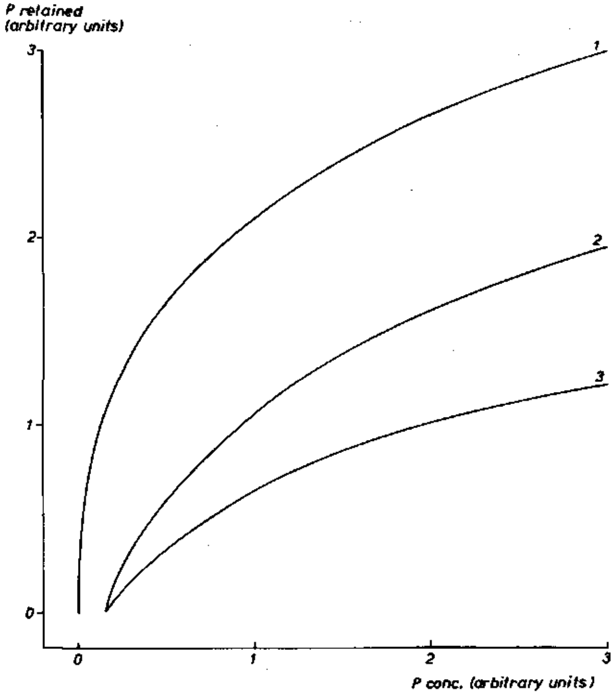


Fig. 5.7 Schematic representation of three possible relationships between the amounts of phosphate removed from the solution by adsorption and the equilibrium concentration; for explanation see text.

because it becomes more tightly bound or otherwise occluded at longer reaction times. Eventually this may lead to blocking of all the adsorption sites. If the above reactions have not gone to completion in the pretreated soil an (apparent) adsorption isotherm like curve 3 may be found. The latter curve is not only lower than curve 1 but will also have a different slope because there would be fewer sites free for adsorption.

Referring to the situation of repeated additions of sewage water to the soil, it is clear that when the initially adsorbed phosphate permanently blocks the adsorption sites the efficiency of phosphate removal from the solution decreases with each addition. Results of soil and water analysis of samples derived from the sewage farm (cf. Chapter 3) lead Beek and de Haan (1974) to suggest that between 2 successive additions of sewage water sites readily accessible to phosphate bonding become newly available. In view of the foregoing discussion of the retention process in terms of rapid and slow reactions it is suggested that as a result of the decline in solution phosphate concentration by the slow reaction, release of phosphate from the adsorption sites occurs. The hypothesis was tested with laboratory experiments with samples derived from the top layer of the soil treated with sewage water. The amounts of phosphate removed from the solution by adsorption were determined for samples with and without a pretreatment with dissolved phosphate in the laboratory.

5.1.4.2 Experimental set-up and results

Soil samples suspended in solutions with different initial phosphate concentrations were allowed to react for long time periods with the consequence that significant amounts of phosphate were removed from the solution by the slow reaction, in addition to the amounts retained by the rapid processes. After that period the suspensions were centrifuged. The clear solutions were removed and subsequently filtered through a 0.1 μm membrane filter (in order to prevent possible losses of soil particles the filters were rinsed afterwards with a few drops of the filtered solution which was added to the suspension). The phosphate concentration in the filtered solution was determined, thus allowing the calculation of the total amount removed from the solution and the estimation of the number of adsorption sites occupied in excess of the number of occupied adsorption sites in the samples without a pretreatment with dissolved phosphate (cf. discussion below). The above pretreated samples were resuspended in a solution with the same initial phosphate concentration as was added the first time and subsequently shaken for 3 days. Samples of the original soil material (i.e. without a pretreatment with dissolved phosphate) were suspended in solutions with different initial phosphate concentrations and also shaken for 3 days. After that period phosphate was determined in an aliquot of the filtered solution.

In view of the results shown in fig. 5.2b it was assumed that

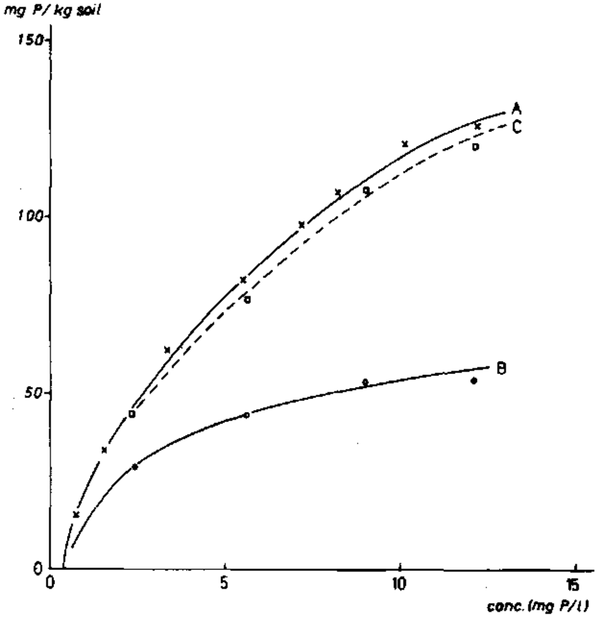


Fig. 5.8 Amounts of phosphate removed from the solution versus the phosphate concentration after 3 days reaction time. Curve A represents the above relationship for the original soil samples. Curve B represents the relationship if the samples had been pretreated with dissolved phosphate. If the adsorbed phosphate derived from the pretreatment is accounted for, curve C is obtained.

the amount retained in a 3 days reaction period gave a reasonable estimate of the amount that can be removed from the solution by adsorption under the prevailing conditions. These amounts, with the corresponding concentration (average values of triplicate samples), were plotted in fig. 5.8 for the original soil samples (curve A) and the pretreated samples (curve B). As was expected curve B is lower than curve A because in the pretreated samples more adsorption sites will be occupied than in the original samples. The number of sites still occupied at the end of the pretreatment period may depend on e.g. the amount of P removed from the solution, the nature of the slow retention processes and the phosphate concentration present in the solution at the end of the pretreatment period. Only under the condition that the slow reaction brings about a release of adsorbed phosphate in the present samples (as results of field studies seem to suggest) one can estimate the relative number of occupied adsorption sites with the help of curve A and the phosphate concentration in the solution at the end of the pretreatment period. According to this procedure the amounts of adsorbed phosphate were estimated for each of the experimental points in curve B. If the latter amounts were added to the corresponding experimental points in curve B, the latter shifts upwards, resulting in curve C. Since the latter closely agrees with curve A, as should be the case for the assumptions made here, it seems warranted to assume that the slow reaction brings about a release of phosphate from the adsorption sites, thereby maintaining the equilibrium adsorption relationship valid for the original samples.

On first sight the difference in slope between curve A and B in fig-5.8 would suggest a blocking of adsorption sites rather than a release of phosphate during the slow reaction. It is noted, however, that each of the experimental points of curve B represents a different pretreatment of the original sample, in contrast to curve 3 in fig. 5.7 where each of the samples was subject to the same pretreatment.

5.2 MATHEMATICAL FORMULATION OF PHYSICO-CHEMICAL INTERACTION PROCESSES OF ORTHOPHOSPHATE WITH SOIL

5.2.1 The equilibrium adsorption isotherm

According to the isotopic dilution experiments with ^{32}P (cf. 5.1.3) the original soil used in the batch experiments contains 51.6 mg P/kg soil exchangeable phosphate (at a solution phosphate concentration of 0.44 mg P/1 ($1.42 * 10^{-5}$M). Thus the adsorbed amounts of phosphate given in fig. 5.2a have to be increased with the above amount in order to obtain the total amount adsorbed (per unit weight of soil) at the corresponding equilibrium concentration.

With respect to the mathematical description of phosphate adsorption isotherms in soil either the Freundlich or Langmuir equation are used. The Langmuir equation seems favorite in this respect,

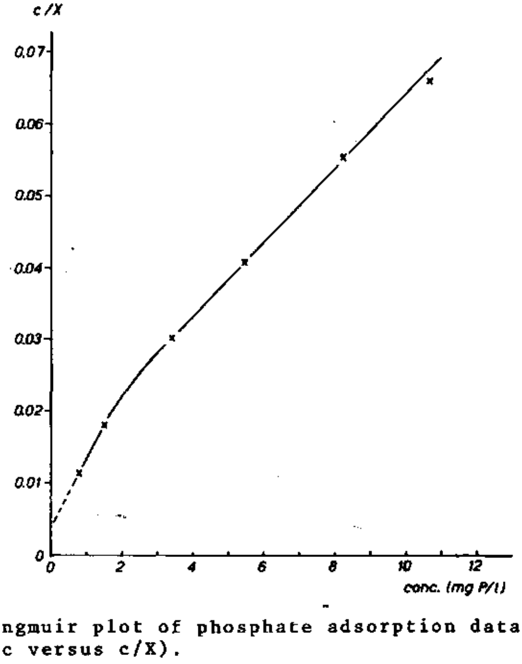


Fig. 5.9 A Langmuir plot of phosphate adsorption data for a top soil sample (c versus c/X).

but as will be explained below this choice may be based on rather weak grounds. The general form of the equation can be represented as:

$$X = kBc/(1 + kc) \qquad (5.3)$$

where X and c stand for the amount of phoshate adsorbed per unit weight of soil and solution phosphate concentration, respectively, k and B represent an 'affinity' and 'capacity' parameter, respectively. Equation (5.3) may be rearranged to give:

$$c/X = (1/kB) + c/B \qquad (5.4)$$

A plot of c/X versus c gives a straight line from which B (reciprocal slope) and k (slope/intercept) can be obtained. The experimental data in fig. 5.2a, increased with 51.6 mg P/kg soil were plotted according to equation (5.4) in fig. 5.9. Two linear relationships were obtained, one for concentrations below about 2 mg P/l and one for higher concentrations. The same phenomenon has been reported by Syers et al. (1973); in their soils the break occurred at solution phosphate concentrations varying from 1.5 to 3.2 mg P/l.

The two linear relationships were interpreted as an indication of the existence in the soil of two populations of sites which have a different affinity for P, each of which can be described by a Langmuir equation. Accordingly equation (5.3) may be rewitten as $X = X_1 + X_2$ where $X_1 = \frac{k_1B_1c}{1+k_1c}$ and $X_2 = \frac{k_2B_2c}{1+k_2c}$. The lower concentration range is (mainly) covered by X_1 and the higher concentrations by X_2. The procedure to derive the constants k_1, B_1, k_2 and B_2 form fig. 5.9 was based on successive approximation. The first estimate of k_1 and B_1 was obtained from fig. 5.9, the corresponding values of X_1 at the relevant concentrations were calculated and substracted from the experimental data (X), giving $(X-X_1)$. Then the regression equation for the points c and $c/(X-X_1)$ was calculated, thus giving k_2 and B_2. The corresponding (linear) correlation coefficient was used as the criterium for the acceptability of the first guess

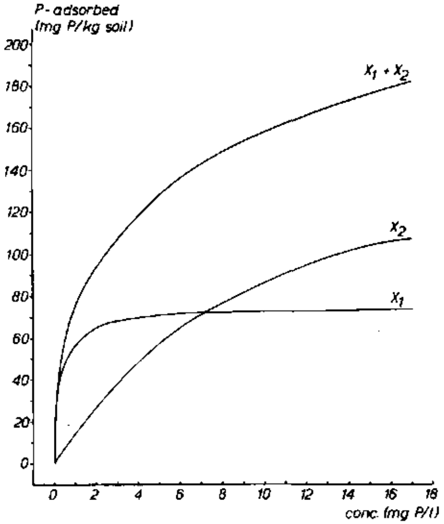


Fig. 5.10 Phosphate adsorption of a top soil sample described by two Langmuir isotherms (X_1 and X_2).

of k_1 and B_1. If the correlation coefficient was low the procedure was repeated in the sense that now k_2 and B_2 were used to calculate the difference $(X-X_2)$ leading eventually to a second estimate of k_1 and B_1. The general trend during this iteration was that the value of k_1 increased while that of B_1 decreased. The accepted values are given in table 5.5 and were derived from regression equations with correlation coefficients better than 0.99. With the values of k_1, k_2, B_1 and B_2 of table 5.5 the isotherms X_1, X_2 and $X=X_1 + X_2$ have been plotted in fig. 5.10.

The description of the reaction of orthophosphate species with a whole soil or its single constituents by the Langmuir equation has been subject of intensive discussion. In this respect it is recalled that the Langmuir adsorption equation (or isotherm) was originally derived (Langmuir, 1918) to describe the simple adsorption of gas molecules on a plane surface having only one type of elementary spaces, each of which could hold only one adsorbed molecule. It further assumed that the binding of a molecule on any one elementary space was independent of the binding on the remaining elementary spaces. The main criticism is that the above-mentioned assumptions underlying the Langmuir equation are not fulfilled when adsorption of phosphate (and other ionic species) in soils is involved.

In view of the above remarks in small print it is doubtful whether an absolute chemical meaning may be ascribed to the affinity (k) and capacity factors (B) given in table 5.5. As mentioned before, the occurrence of two linear Langmuir relationships has been interpreted as an indication of the existence of two populations of adsorption sites. From a mathematical point of view this may be allowed but whether it actually represents the adsorption onto two different components, like e.g. the adsorption onto iron hydroxide and solid calcium carbonate as was reported by Holford and Mattingly (1974), or different adsorption mechanisms as postulated by Ryden and Syers (1977), is obscure. Finally it is stressed here that Hsu and Rennie (1962a, b) and Veith and Sposito (1977) have shown that in systems where secondary precipitation reactions may occur, like e.g. the formation of solid aluminum or iron phosphates from the reaction of orthophosphate with solid aluminum or iron oxides, the description of the experimental data by the Langmuir equation cannot be considered as a direct proof of adsorption.

5.2.2 Kinetic aspects of the interaction processes

On the basis of the available evidence a model was developed of the transformation processes between phosphate in solution and the solid phase. As has been stated before it is assumed that under the prevailing experimental conditions the observed transformation processes are mainly the result of reactions between the inorganic soil phosphate fractions. In the present system the soil inorganic phosphates comprise those in solution (c), in two adsorbed states (X_1 and X_2) and in an another immobilized form (N). The solid phosphate in the pools X_1 and X_2 represents the fraction that exchanges (rapidly) with ^{32}P in solution, it is assumed to be present in a reversibly bound state. In contrast the N pool comprises phosphate of which the rate of exchange with ^{32}P in solution is small to zero; it represents the fraction that has a low degree of reactivity or solubility.

In most subdivisions proposed in the course of time, only two (solid) fractions have been distinguished, namely a fraction that responds rapidly to changes in the solution phosphate concentration and the second fraction that reacts relatively slowly to such changes. Those fractions were given different names depending on the purpose for which such a distinction was necessary. In comparison to the subdivision proposed here it is very likely that the phosphate present in the X_1 and X_2 pool represents the fraction that reacts rapidly to changes in the solution phosphate concentration and the N pool represents the slowly reacting fraction. In particular this latter fraction presumably still lumps together phosphate compounds of varying (low) degree of reactivity or solubility. No attempt has been made to subdivide those compounds in more fractions. The two principal reasons were that it is experimentally hardly possible, while the present recognition of the fractions X_1, X_2 and N seems the maximum permissible complexity in view of the envisaged use in a model covering the accumulation and transport of phosphate in soil systems.

In order to define the transformation processes, in terms of rate equations, the direction of phosphate flow from one pool to the other needs to be fixed. As in the present system four pools of phosphate have been recognized, different alternative models are (theoretically) possible. Usually these models are presented in the form of flow diagrams, as is illustrated in fig. 5.11. The main purpose of the diagrams in this figure is to visualize the transformation processes between the different pools, rather than expressing a physico-chemical concept of the relevant mechanisms. In the present system the rate equations were defined according to the transformation processes depicted schematically in diagram A.

Flow diagrams of simulation models are presented in general with the symbols given in the legend of fig. 5.11. In order to facilitate discussion, diagram A was presented in a very simplified form. Diagram B, representing a detailed version of diagram A, may facilitate reading of the computer program written in the simulation language CSMPIII (IBM, 1972) and given in appendix 1.

In the second part of this section different arguments will be given to elucidate the flow of phosphate shown in diagram A. In this context it is mentioned that also Gebhardt and Coleman (1974) suggested that P retention occurred in these stages, viz. two sorption sites in addition to precipitation of phosphates.

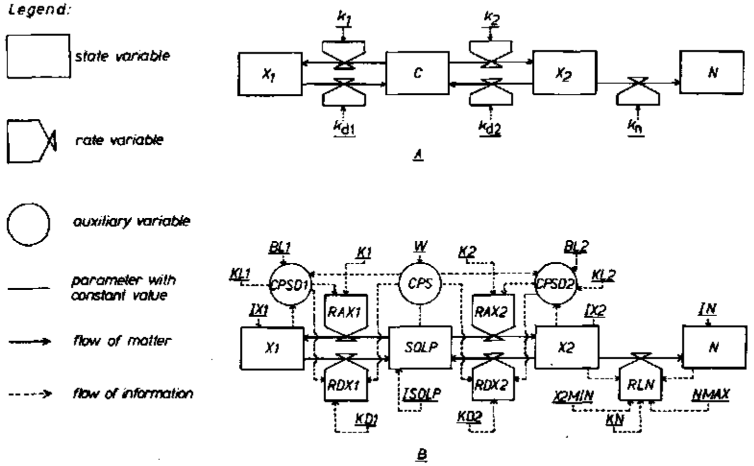


Fig. 5.11 Flow diagram of physico-chemical interaction processes of ortho-P with soil (see Appendix 1 for an explanation of the symbols used in diagram B).

The rate constants involved in the transformation reactions will be indicated with k_1, k_2 and k_n respectively. As will be commented on below the numerical values (pertaining to simple first order kinetics) given in table 5.5 refer primarly to forward reaction rates. As to the fast loading pool X_1, it was possible to show that its rate of unloading, k_{d1}, differed substantially from k_1. With regard to X_2, its unloading was limited by the very slow rate of formation of N. The unloading rate of the latter fraction was set to zero on the grounds that pool N comprises phosphate compounds of a low reactivity and solubility. (Results of desorption studies (cf. 5.2.2.1) seem to indicate that the above assumption is warranted). The rate equations defined below were rewitten in the appropriate form required by the simulation language CSMPIII (IBM, 1972) and integration was carried out with the Milne intergration method using a DEC-system-10 computer.

Rate equations of orthophosphate interactions with soil have recently gained increasing interest (Enfield and Shaw, 1975; Novak and Adriano, 1975; Enfield et al., 1976, Mansell et al., 1977a,b; Overman et al., 1976; Overman and Chu, 1977), leading to different expressions. Most of these equations merely describe the phenomenological aspects of the processes, rather than being based on some chemical concept of reaction mechanisms.

Indeed the complexity of a soil system makes it rather doubtful whether an observed rate of disappearance of phosphate from solution could ever be used to derive the reaction mechanisms involved. In the present case this is certainly so, as at least three different forms of non-dissolved phosphates were distinguished, which are presumably all involved in the observed disappearance of phosphate from solution. Particularly if the ultimate goal - the construction of a mathematical model which approximates reasonably well the overall behavior of phosphates when fed into the soil at widely different rates of application - is kept in mind, one must be satisfied to use fairly simple rate equations.

In view of the above considerations the reactions leading to the formation of the isotopically exchangeable forms X_1 and X_2 were treated as simple first order reactions, the rate being proportional to the 'excess' concentration in solution. The ensuing rate equation, as is often used for diffusion controlled adsorption reactions (cf. Chapter 9 in Bolt, 1979), reads:

$$\frac{dX}{dt} = k \quad (c - c_e(X)) \tag{5.5}$$

where X specifies the amount adsorbed per unit mass of soil (here in mg P/kg soil) and $c_e(X)$ (in mg P/l) indicates the equilibrium concentration in solution corresponding with the momentary value of X according to an assumed adsorption isotherm. The first order reversible rate constant k is then specified in $l\ kg^{-1}\ t^{-1}$, i.e. the volume of solution from which the excess concentration is effectively removed by one kg of soil, per unit time.

If visualized as a film-diffusion controlled process, the ratio k:S, with S = surface area of active sites per kg of soil, would correspond to $D/\Delta l$, i.e. the ratio of effective diffusion coefficient (D) and the film thickness (Δl) (cf. Chapter 9 in Bolt, 1979).

As in the present case two pools of adsorbed phosphate were recognized, X_1 and X_2, respectively, the relevant equations are:

$$\frac{dX_1}{dt} = k_1 \ (c - c_{e1}) \qquad (5.6)$$

$$\frac{dX_2}{dt} = k_2 \ (c - c_{e2}) \qquad (5.7)$$

Referring to section 5.2 the corresponding momentary equilibrium concentrations are then given by:

$$c_{e1} = X_1/(k_1 \ (B_1 - X_1)) \qquad (5.6a)$$

$$c_{e2} = X_2/(k_2 \ (B_2 - X_2)) \qquad (5.7a)$$

where k and B indicate the 'affinity' and 'capacity' parameters discussed previously.

Even if the experimental data available for short initial periods of reaction as pictured in fig. 5.1 allow one to neglect the amount of P disappearing because of the formation of the N pool, the simultaneous occurrence of the reactions 5.6 and 5.7 make it difficult to obtain the values of k_1 and k_2 from such data. This follows from the fact that the conservation equation connecting the change of X with the observed change of c covers the two processes together, according to

$$\Delta(X_1 + X_2) = -W\Delta c \qquad (5.8)$$

where Δ indicates the difference with the initial values of X and c at the start of the adsorption experiment, X_i and c_i, respectively. Accordingly even the set of rather simple equations introduced above do not lead to an analytical solution allowing one to plot the relevant fraction of c against t in order to obtain the values of k_1 and k_2.

Such a procedure is fairly simple in case of a single reaction of the above type. In that case one may express ΔX in Δc with equation (5.8), which upon substitution into (5.6a) gives c_e in terms of c. With $dX/dt = -W(dc/dt)$ this leads to a first order differential equation in c. Upon integration this gives

$$kt = |W \ln F(c, W) \Big|_o^t \qquad (5.9)$$

where F(c, W) is an appropriate function of c and W. A semilog plot of F(c, W) against t then gives k/W as the slope. The actual form of F(c, W) has been derived by Novak and Adriano (1975) as given in Appendix 2.

In the present situation covering two simultaneous reactions, the values of k_1 and k_2 may be found by trial and error, using the limiting slope of c(t) at $t \to 0$ as a starting point. Thus for $t \to 0$ one finds $c_{e1} = c_{e2} = c_{ei}$, so:

$$\frac{d(X_1+X_2)}{dt} = -W \frac{dc}{dt} = (k_1 + k_2)\ (c-c_{ei}) \qquad (5.10)$$

Applying this to the data presented in fig. 5.1 it was concluded

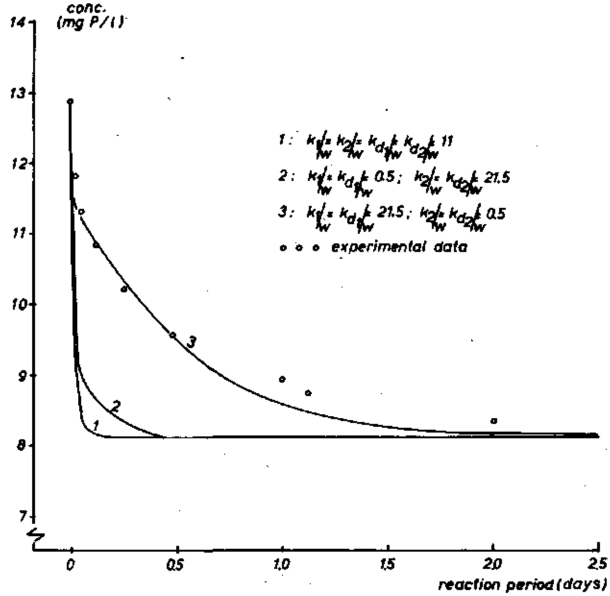


Fig. 5.12 The concentration of phosphate in solution versus the reaction period. Curves were calculated for different values of the rate constants (k_1 and k_2).

that $(k_1 + k_2)/W \approx 22$ day^{-1} (for W = 20.1 1/kg^{-1} and c_{ei} = 0.44 mg P/1). Next one may assume any distribution of this sum over its members and calculate the corresponding course of c(t). In fig. 5.12 the general trend of this procedure is demonstrated which shows convincingly that for the present system k_1 exceeds k_2 grossly.

Once this had been established it was possible to derive approximate values of k_1 and k_2 directly from the experimental data. This method consisted of solving k_1 from data of short reaction times with the help of the analytical solution presented in appendix 2, i.e. assuming $k_2 \approx 0$ (for details see appendix 2). This lead to a first estimate of $k_1/W \approx 21.7$ day^{-1}. Next the amount stored in X_1 following from equation 5.6 with this value of k_1 (or from the appropriate equilibrium adsorption isotherm at longer reaction periods, cf. fig. 5.10) was subtracted from $(X_1 + X_2)$ yielding a first estimate of $k_2/W \approx 0.6$. Using the latter, the amount stored in X_2 in small time periods can be substracted from (X_1+X_2) to give a second estimate of k_1, and so on. Final values of k_1/W and k_2/W obtained in this manner were ≈21.7 and ≈0.5, respectively. A small readjustment of these values was later necessary when comparing the calculated course of c(t) with the experimental data for reaction times up to 2.5 days. It is evident that then the assumption dN/dt = 0 does not hold any longer, because the (slow) formation of N may remove a significant amount of phosphate from solution.

Besides the derivation of the approximate values of k_1 and k_2 from experimental data as outlined above (in small print) it is also possible to derive the appropriate values of the rate constants by successive approximation as shown in fig. 5.12. Final values of k_1/W obtained were 21.6 and 0.4, respectively. In fig. 5.13 the ensuing course of c(t) is plotted for different values of c_i indicating a satisfactory overall check with experimental observation at all values of c_i.

In evaluating the significance of the deviations still present (which are partly inherent to the chosen simplified description in terms of equations (5.6 and 5.7) and the fact that for the time being only the adsorption processes have been included, thereby neglecting the amount of phosphate removed from the solution by the slow formation of N) the predicted amounts of phosphate adsorbed with time by X_1 and X_2 were compared with the experimental data of phosphate retained. As shown in fig. 5.14 the present description is indeed quite acceptable for this purpose.

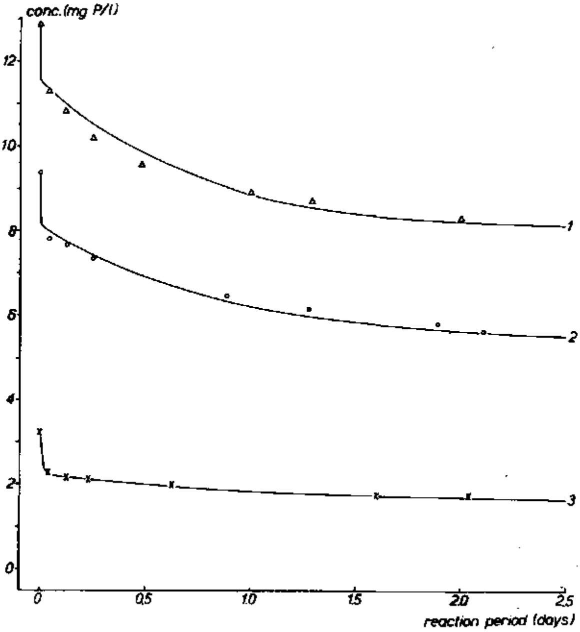


Fig. 5.13 Decrease of the phosphate concentration in solution versus the reaction period for soil suspensions with three different initial phosphate concentrations (1=12.9, 2=9.4, and 3=3.2 mg P/l). Curves were calculated with $k_1/W=k_{d1}/W=21.6$ and $k_2/W=k_{d2}/W=0.4$ day^{-1}.

At this stage the implied full reversibility of the adsorption reactions given in equations (5.6 and 5.7) deserves some attention. Although the experiments leading to the estimates of k_1 and k_2 were adsorption experiments, the observed substantial difference in the rate constants leads at a later stage to some desorption of the fast-loading pool X_1. It may then be concluded immediately that the present analysis yields no information as to the rate of desorption of X_2. It is also clear that the experimental data are only sensitive to the assumed rate constant for desorption from pool X_1, k_{d1}, if the rate of deloading X_1 becomes limiting in comparison to the rate of loading of X_2. Considering again the ratio k_1/k_2 54 this implies that k_{d1} must be very much smaller than k_1 before its effect becomes noticeable in the calculated (and

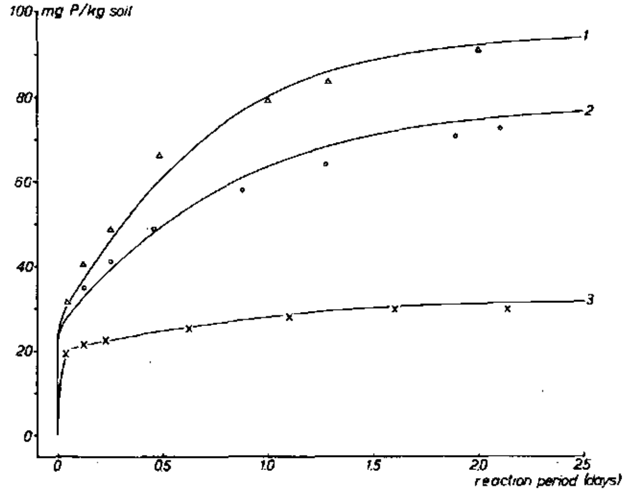


Fig. 5.14 Increase in phosphate retained versus reaction period for soil suspensions with three different initial phosphate concentrations. Symbols represent measured data, curves were calculated (details as in fig. 5.13).

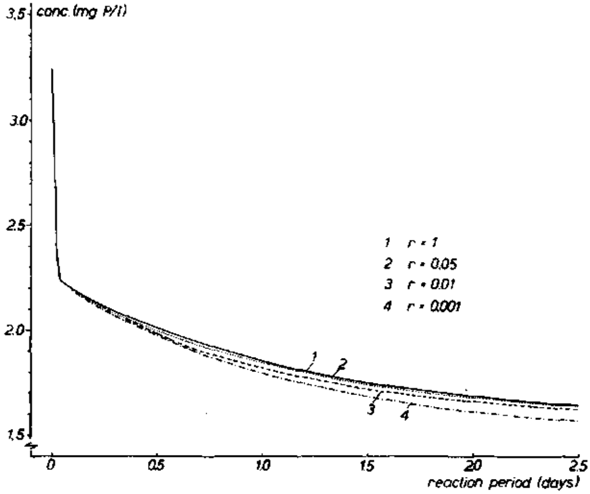


Fig. 5.15 Effect of the rate constant for the rate of unloading of X_1, k_{d1} ($k_{d1}=rk_1$), on the decrease of the phosphate concentration for a soil suspension with an initial concentration of 3.2 mg P/l.

measured) curves. In fig. 5.15 this is demonstrated by comparing dc/dt as found for the assumed full reversibility (i.e. $k_{d1} = k_1$) with the predicted course if $k_{d1} = rk_1$, taking r equal to 0.5, 0.1, 0.05, 0.01, 0.001. Clearly the effect becomes noticable only for r <0.05.

In conclusion it may be stated that the satisfactory check between calculated and measured curves shown in fig. 5.13 supports the use of $k_1/W = 21.6$; $21.6 > k_{d1}/W > 2$ and $k_2/W = 0.4$. day^{-1}.

Next it was attempted to develop an equation describing the slow formation of the (non-exchangeable) pool N. A first trial of first order kinetics on the basis of the solution concentration appeared untenable. As follows already from fig. 5.1, the observed linear plots of ln c against t at long time periods yield slopes which vary (considerably) with the concentration range. According-

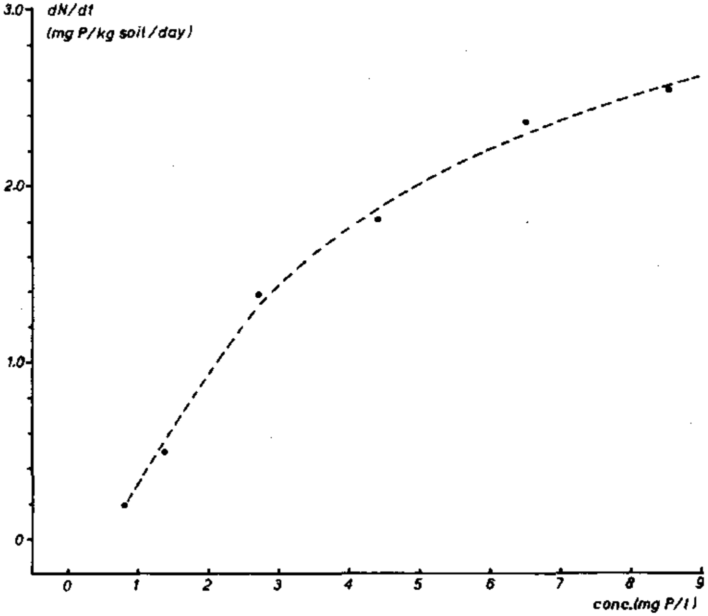


Fig. 5.16A Relationship between dN/dt and the concentration of phosphate in solution.

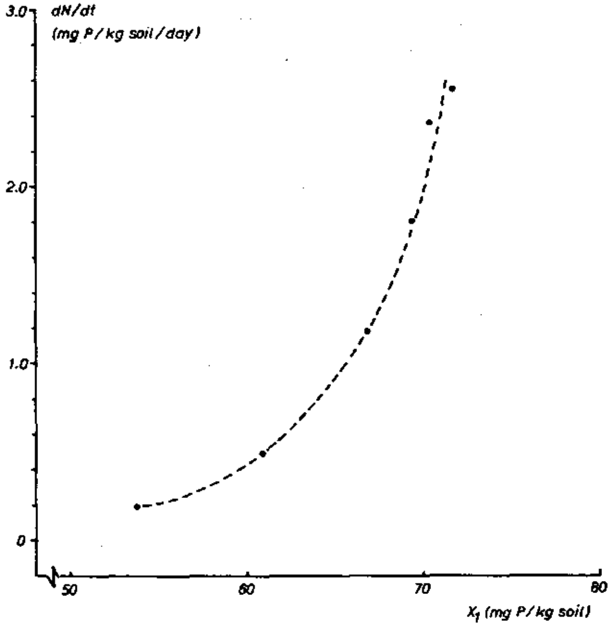


Fig. 5.16B Relationship between dN/dt and the amount of P present in pool X_1.

ly the value of dN/dt was derived for long time periods using:

$$\frac{dN}{dt} = -W\frac{dc}{dt} - \frac{dX_1}{dt} - \frac{dX_2}{dt} \qquad (5.11)$$

in which dX_1/dt and dX_2/dt were calculated according to equation (5.6 and 5.7) with the chosen values of k_1 and k_2. In fig. 5.16 these values were plotted against c, X_1 and X_2 indicating that first order kinetics could apply at best only with reference to the pool X_2. In itself this appears not unreasonable as other authors (cf. Mansell et al., 1977a,b; Overman and Chu 1977) come to the same conclusion, viz. the long-term, very slow immobilization reaction possibly takes place starting from an adsorbed phase.

It is pointed out again that the present study was not directed at

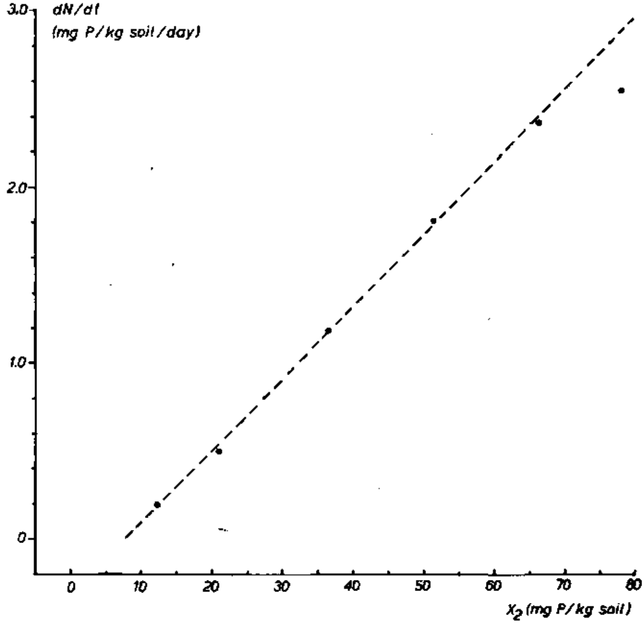


Fig. 5.16C Relationship between dN/dt and the amount of P present in pool X_2.

the elucidation of reaction mechanisms, but rather at finding a moderately simple descriptive model which seems plausible.

The need to explain the renewal of P-adsorbing sites observed in the present system with the formation of N should imply that N is formed at the cost of X, which in turn should tie dN/dt to X. On the basis of fig. 5.16c it is then logical to introduce a minimum level of X_2 ($X_{2,\mathrm{min}}$) and to write a first order equation according to:

$$\frac{dN}{dt} = k_n\ (X_2 - X_{2,\mathrm{min}}) \qquad (5.12)$$

Finally taking into account that the formation of the N pool must involve a P-binding agent with a limited supply for a given soil, one must obviously add a delimiting factor of the form $(N_{max} - N)$ in which N_{max} is an empirically determined P-binding capacity of the system. Here again pragmatism must prevail if the envisaged model is to work safely for long term predictions. Equation (5.12) would obviously fail because it leads to unlimited immobilization of P. Though a contention that pool N concerns a type of precipitated solid phase formed by using the adsorbed pool X_2 as a template seems not unreasonable, the present experiments were not designed to supply proof of such a reaction (cf. Van Riemsdijk et al., 1975, 1977, for some evidence in that direction). In conclusion the extension of equation (5.12) into a pseudo second

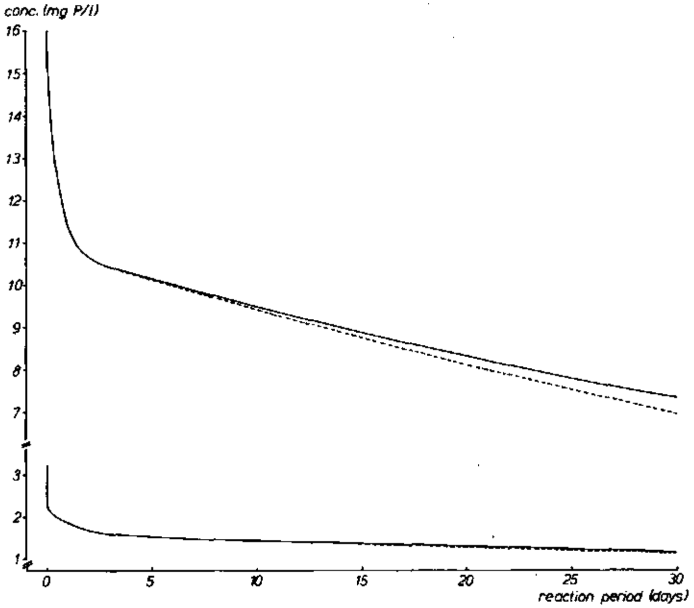


Fig. 5.17 The effect of the capacity factor (full line: capacity factor included (equation 5.13), broken line: capacity factor omitted (equation 5.12) in the computation) on the calculated decrease of the concentration of P in solution with time, for soil suspensions with different initial phosphate concentrations (3.25 and 16.1 mg P/l).

order one comprising the capacity controlled factor leads to:

$$\frac{dN}{dt} = k_n' \ (X_2 - X_{2,min}) \ (N_{max} - N) \tag{5.13}$$

Using the value of N_{max} as based on the ammonium oxalate (Tamm's reagent) extractable Fe and Al given in chapter 4, the results of this equation are presented in fig. 5.18. In order to demonstrate the effect of the capacity factor also the calculated course of c(t) is given in fig. 5.17 using equation 5.12, i.e. the course of c(t) in the absence of the limiting factor (N_{max}-N). (The value of k_n' in equation 5.13 is set equal to the quotient of k_n/(N_{max}-N) at t=0). As is shown in fig. 5.17 the difference in c(t) becomes significant at conditions that favor the formation of phosphate associated with pool N, i.e. at relative high solution phosphate concentrations and long reaction times. The rate constant k_n in equation 5.12 can be estimated from fig. 5.16c, which in turn leads to an estimate of k_n' (eq. 5.13) at a known value of the difference (N_{max}-N). The estimated value has been refined by a comparison of calculated results with the experimental data given in Fig. 5.1.

The final values of the rate constants and those of the other parameters as pertaining to the chosen soil are tabulated in table 5.5. The initial values of the amounts adsorbed, i.e. X_1 and X_2 at t=0, were obtained from the results of the experiments with ^{32}P. The amount of phosphate present in pool N at t=0 was derived from phosphate fractionation studies discussed in chapter 3. The inorganic phosphate fraction associated with Al and Fe, P-(Al+Fe), amounted for this soil layer to 434 mg P/kg soil, of which the amount present in an adsorbed state, i.e. X_1 and X_2 at t=0, equals in total 54 mg P/kg soil. The difference, amounting to 380 mg P/kg soil (434-54), is associated with phosphate compounds belonging to the forms present in pool N. The value of N_{max} is related to the sum of the ammonium oxalate extractable Al and Fe, which for the present samples amounted to 82.8 mM (Al+Fe) per kg soil. This corresponds to a phosphate bonding capacity of about 850 mg P/kg soil. The value of N_{max} given in table 5.5 is lower than 850 mg P/kg soil, because part of the available Al and Fe is presumably

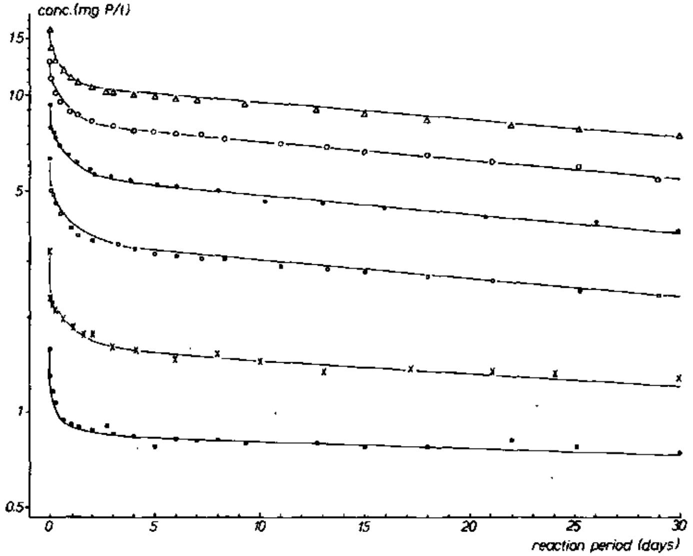


Fig. 5.18 A comparison between the calculated (curves) and measured phosphate concentration (symbols) of soil suspensions with different initial phosphate concentrations during a reaction period of 30 days.

Table 5.5 Numerical values of rate constants and other parameters used in the computation of the transformation processes of phosphate

k_1	434.3	(l/kg soil)/day	B_1	74.1	mg P/kg soil
k_{1d}	434.3	(l/kg soil)/day	B_2	164.8	mg P/kg soil
k_2	8.04	(l/kg soil)/day	k_1	3.383	l/mg P
k_{2d}	8.04	(l/kg soil)/day	k_2	0.107	l/mg P
k_n	0.046	day^{-1}	W	20.11	l/kg
k_n'	0.12	(kg soil/g P)/day			
			X_{1i}	45.7	mg P/kg soil
			X_{2i}	7.8	mg P/kg soil
			N_i	381.7	mg P/kg soil
			$X_{2,min}$	7.3	mg P/kg soil
			N_{max}	757	mg P/kg soil

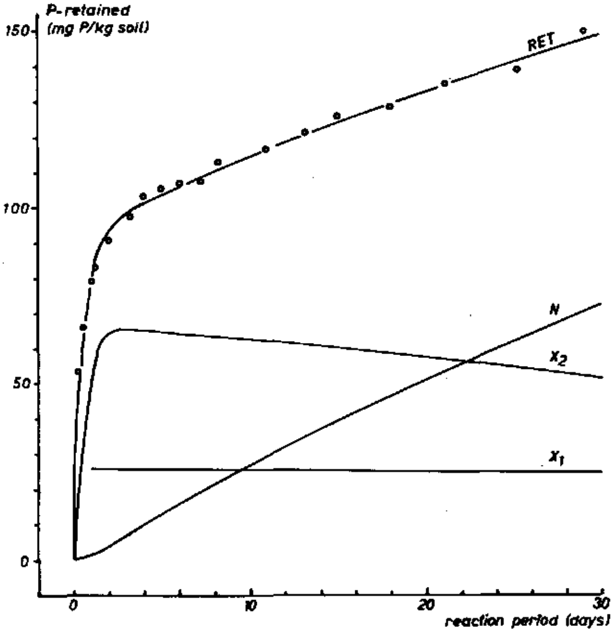


Fig. 5.19 The calculated (curve RET) and measured (symbols) increase in phosphate retained of a soil suspension with an initial phosphate concentration of 12.9 mg P/l. The distribution of the retained P over the pools X_1, X_2 and N is shown.

associated with P present in an adsorbed state of which is accounted for by X_1 and X_2. If N_{max} is set equal to 757 mg P/kg soil and the other parameters are given the values presented in table 5.5 it is shown in Fig. 5.18 that a close fit is obtained between the calculated course of c(t) and the experimental results, for soil samples to which different amounts of P were added and for a reaction period of 30 days. In fig. 5.19 the calculated changes in the amounts of different forms of solid phosphate are presented in relation to reaction time. It is shown that phosphate in pool N is formed at the cost of phosphate present in the pools X_1 and X_2. In other words phosphate that exchanges (rapidly) with radioactive P or presumably responds rapidly to changes in the solution phosphate concentration, is transformed into a rather non-reactive form.

5.2.2.1 Some comments on the formulation of the desorption processes

It was shown above that the rate equations (5.6 and 5.7) described the loading of the pools X_1 and X_2 satisfactorily. The reverse processes, i.e. unloading of the above pools were, in view of the experimental conditions, of no concern, exept that the loading of pool X_2 required some unloading of pool X_1. Therefore it was not possible to derive the proper value of the rate constant describing the unloading of pool X_2, k_{d2}, from the available experimental data. With respect to the rate constant describing the unloading of pool X_1, k_{d1}, it was shown in fig. 5.15 that the rate of unloading of X_1 would not effect the net removal of phosphate from the solution, provided $k_{d1} > 0.05\ k_1$. Since it was the main objective of the present study to describe the retention processes rather than the desorption of phosphate, only superficial attention was given to the latter processes.

In the experiment reported here, soil samples with different levels of adsorbed phosphate were suspended in solutions initially

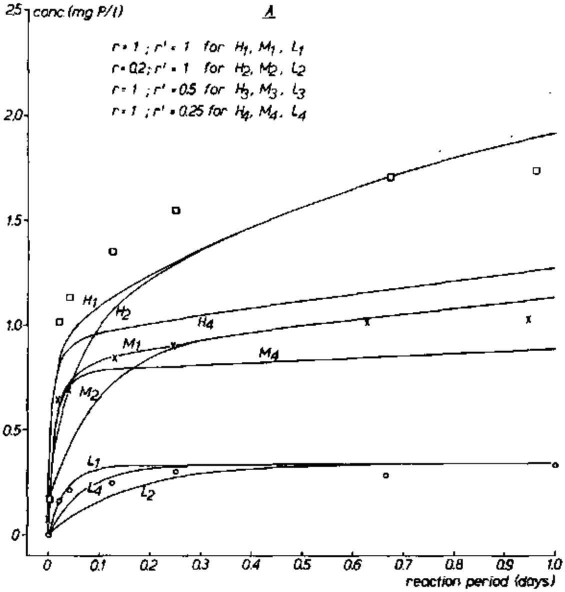


Fig. 5.20A The release of phosphate into the solution with time for soils with three levels of 'adsorbed' P (Low, Medium and High). Symbols represent measured concentrations, curves were calculated with different values of k_{d1} and k_{d2} ($k_{d1} = rk_1$; $k_{d2} = r'k_2$). The effect of k_{d1} is shown primarily at short reaction times.

free of phosphate. The amount desorbed was calculated from the phosphate concentration in the filtrate obtained after time intervals varying from 0.5 hour to 10 days. The samples containing higher levels of adsorbed phosphate then present in the original soil, were prepared by suspending the soil in solutions with an initial phosphate concentration of 6.4 and 13.1 mg P/l. After 3 days of reaction time these suspensions were centrifuged and the clear solution was almost completely removed. The small amount of phosphate left in the remaining solution was accounted for when the samples were resuspended in the phosphate free solution with the consequence that the initial phosphate concentrations in these samples were slightly above a zero level. The amounts of phosphate removed from the added (phosphate) solutions were then distributed over the pools X_1 and X_2 with the help of the adsorption isotherms shown in fig. 5.10, using the phosphate concentration in the solution at the end of the 3 days reaction period. The amounts of phosphate present in the above pools for the original sample were derived from the results obtained with the isotopic exchange studies with ^{32}P (as described on p).

The calculated course of the phosphate concentration in solution, c, for three levels of X_1 and X_2 are shown in fig. 5.20. These curves were calculated using different values of r and r', where $r=k_{d1}/k_1$ and $r'=k_{d2}/k_2$, respectively. Since the effect of k_{d1} on c is apparent only during the first 6 to 12 hours (for the r values as chosen), the ensuing curves are presented with two different time scales in fig. 5.20, the large scale (A) exposing primairly the effect of k_{d1}, the smaller one (B) that of k_{d2}. The effect of the latter rate constant manifests itself over the entire 10 days reaction period, although the effect for the original sample is hardly noticeable because the amount of phoshate in pool X_2 is only a fraction of the amount present in pool X_1. A change in k_{d2} also affects the loading rate of pool N, because the latter rate is related to the pool X_2 (cf. equation 5.13). This loading of pool N also explains the decrease in the concentration after 3 to 4 days of reaction time for the samples with medium and high amounts of adsorbed phosphate.

A comparison of the calculated curves with measured concentrations indicates that for a reaction period of 1 day the experimental data corresponding to the low and medium levels of adsorbed phosphate follow rather closely the curve calculated with r=1 and r'=1, viz. $k_{d1}=k_1$ and $k_{d2}=k_2$. The corresponding curve for the samples with the high level of adsorbed phosphate led to calculated values of the concentration lower than found experimentally during the first 12 hours of the reaction period. Since the calculated concentration for the medium and high level samples continue to increase at longer reaction times, in contrast to the measured concentrations, where a maximum value was reached after about 1 day, large deviations arise under the conditions mentioned first. Thus the curves in fig. 5.20b suggest that k_{d2} decreases as the contact time between phosphate and the soil increases, implying a stronger bond between phosphate and the soil with time. The same indication was derived from isotopic exchange experiments with ^{32}P.

In conclusion the rate equations (5.6 and 5.7) formulated on the basis of results derived from phosphate retention studies and employing constant values of k_d must be handled with care if long periods of desorption are involved. In the system described in

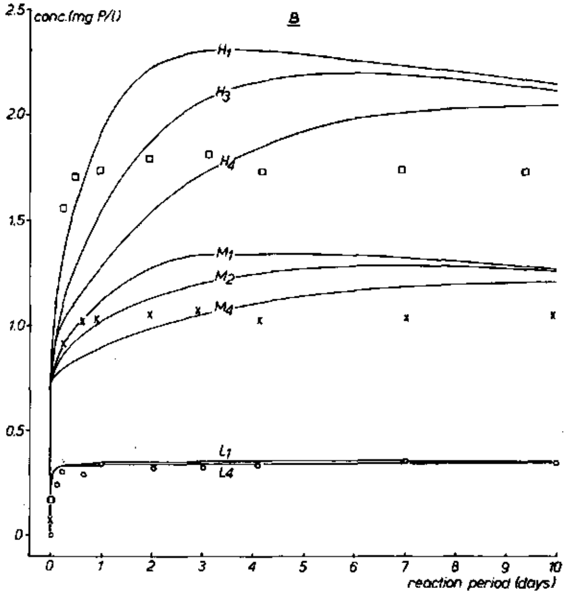


Fig. 5.20B The release of phosphate into the solution with time for soils with three levels of 'adsorbed' P (Low, Medium and High). Symbols represent measured concentrations, curves were calculated with different values of k_{d1} and k_{d2} ($k_{d1}=rk_1$; $k_{d2}=r'k_2$). The effect of k_{d2} is shown primarily at longer reaction times.

this treatise this is of minor concern, however, as here the process of retention of added phosphate is the dominant feature. If, on the other hand, release of phosphate from heavily loaded soils would be the subject of investigation, it appears advisable to use a time (c.q. 'history') dependent value for the rate parameters describing the release reaction. Alternatively one might consider using a suitable mean value as a constant, accepting that then either the long-term effect is overestimated or the short term effect underestimated. On the other hand, the assumption that release of phosphate from pool N could be ignored seems warranted, because the measured concentrations remain below the calculated concentrations.

5.3 A CHECK ON THE RELIABILITY OF THE MODEL FOR DESCRIBING BATCH-PROCESSES

5.3.1 Variation of the solution/soil ratio

The presumed independence of the *k* values on the solution/soil ratio, W, was checked with an experiment in which the course of c(t) was compared for soil suspensions having the same initial solution phosphate concentration (10 mg P/l) but with different values of W of 20, 10 and 5, respectively. At this point it is recalled that the values of the rate constants given in table 5.5 were derived from experiments in which W=20. In fig. 5.21 the course of c(t) is shown of experiments with the above values of W; mean values of duplicate soil samples are given. The close fit of computed and experimental results for the samples with the indi-

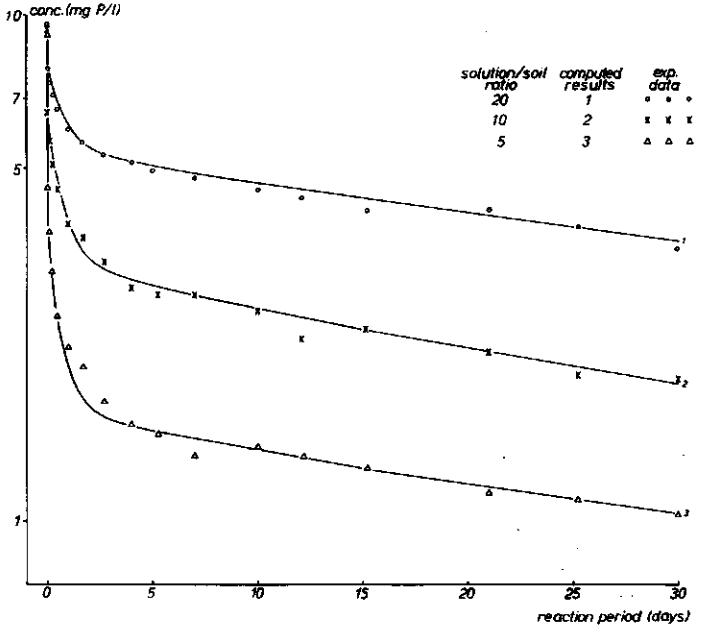


Fig. 5.21 The decrease of the phosphate concentration in solution with time for soil suspensions with the same initial phosphate concentration (≈ 10 mg P/l) but with different solution/soil ratio's.

cated W values supports the above assumption of *k* being independent of W, at least within the range of W values tested. In this respect it is mentioned that in 'field' soils or in experiments using soil columns (cf. Section 5.4) the solution/soil ratio attains much lower values than tested here, although conditions of saturated or near saturated leaching usually prevail.

5.3.2 Repeated additions of P during long time periods

A second aspect on which the attention is focussed concerns the effect of repeated additons of dissolved phosphate on the amount retained. As discussed in Section 5.1.4 experimental evidence seems to suggest that within certain limits of total P retained, the adsorption isotherms remain fairly constant. The slow reaction causes freeing of occupied adsorption sites, the latter presumably corresponding to the decline of the solution phosphate concentration below the 'equilibrium' value for the adsorption processes.

The above conclusions were checked under conditions of repeated additions of dissolved P. To this purpose soil suspensions were prepared of which the initial solution/soil ratio corresponded to W=20 and of which the initial phosphate concentration amounted to about 10 mg P/l. After 3 days of mechanical mixing the suspensions were centrifuged (15 minutes at about 20.000 rpm) and 15 ml's of the clear supernatant were removed and filtered through a 0.1 µm membrane filter. A small volume of the filtered solution was used to rinse the filter in order to remove soil particles that possibly might have been deposited on the filter surface; the solution used for rinsing was added to the soil suspension. The soil in the latter was resuspended by hand shaking, resulting in a solution/soil ratio approximating the value of 5 and the suspensions were left for further reaction periods varying between 1 and 8 weeks. After the indicated period the remaining solution was removed in the manner as described above and a 'fresh' solution (i.e. with a P concentration 10 mg/l) was added, after which the former procedure was repeated. A determination of phosphate concentration in the added solutions and the solution removed from the soil suspen-

Table 5.6 Amount of P retained by soil samples upon repeated additions of soluble P. After 3 days part of the added solution is removed causing the solution/soil ratio (W) to decrease from its initial value of about 20 to 5. The remaining solution is removed after 7 days (A), 28 days (B) or 56 days (C), respectively, followed by the addition of a 'fresh' solution (P conc. ≈10 mg P/l). Experimental (EXP) data are compared with results calculated with the simulation model (CALC). Cumulative reaction times are given.

A

Solution additions ≠	W ≈ 20 Reaction Time Days	EXP mg P/kg	CALC soil	W ≈ 5 Reaction Time Days	EXP mg P/kg	CALC soil
1	0 - 2.8	84.3	85.9	2.8- 10.0	11.1	6.8
2	10.0- 17.0	47.9	43.5			
3	17.0- 19.8	15.0	15.4	19.8- 26.7	9.9	9.3
4	26.7- 30.8	13.7	16.1	30.8- 37.8	6.1	7.6
5	37.8- 40.9	10.9	12.4	40.9- 44.7	4.0	4.0
6	44.7- 47.6	7.8	8.7	47.6- 54.5	5.2	6.4
7	54.5- 57.6	7.0	8.6	57.6- 65.4	4.6	5.8
8	65.4- 68.4	7.5	7.7	68.4- 72.3	2.4	2.5
9	72.3- 75.2	3.8	5.7	75.2- 79.2	3.0	2.6
10	79.2- 82.2	2.0	4.4	82.2- 89.2	3.1	3.8
Total		199.9	208.4		49.4	48.8

Total amount of P retained in 89.2 days: EXP = 249.3 mg P/kg soil and according to CALC = 257.2 mg P/kg soil.

B

1	0 - 2.8	82.0	85.5	2.8- 30.9	18.0	16.3
2	30.9- 35.2	46.4	50.1	35.8- 58.6	15.4	15.8
3	58.6- 61.7	25.4	30.3	61.7- 89.6	13.5	16.3
4	89.6- 92.4	13.9	22.0	92.4-120.7	13.6	12.4
5	120.7-123.6	9.1	14.0	123.6-153.5	8.8	9.7
6	153.5-160.4	5.4	9.9	160.4-188.4	9.0	7.0
7	188.4-191.4	4.5	3.0	191.4-222.4	8.8	5.7
Total		186.7	214.8		87.1	83.2

Total amount of P retained in 222.4 days: EXP = 273.8 mg P/kg soil and according to CALC = 298.0 mg P/kg soil.

C

1	0 - 2.8	83.1	85.7	2.8- 58.8	22.0	21.5
2	58.8- 61.9	43.4	57.3	61.9-121.8	22.9	23.2
3	121.8-125.8	30.5	44.0	125.8-184.7	15.8	18.3
4	184.7-187.7	17.6	23.4	187.7-245.7	10.5	7.8
5	245.3-251.9	10.0	11.4	251.9-300.8	11.8	7.7
Total		184.6	221.8		82.0	78.5

Total amount of P retained in 300.8 days: EXP = 267.6 mg P/kg soil and according to CALC = 300.3 mg P/kg soil.

sions made it possible to calculate the amounts of phosphate retained by the soil after different times of contact and for different values of W. These values are given in table 5.6a through c and represent the mean values of 4 soil suspensions for each treatment. In the same table also the calculated amount of P retained is given for the indicated reaction times and solution/soil ratios using the rate equations discussed before. The amount of P retained during the first 3 days after the 'fresh' solution had been added is mainly the result of adsorption processes, whereas the amounts removed from the solution in the following period is presumably caused by the formation of a solid P phase. As follows from table 5.6a to c, the predicted (i.e. calculated with the rate equations) and measured amounts of P retained by the latter process(es) agree closely. The effect of the delimiting factor (N_{max} -N), as introduced in equation 5.13, on the formation of a solid phase follows from the decreasing rate of P retained at longer reaction times. According to the procedure outlined in chapter 4 it was estimated that on the basis of the available reactive soil aluminum and iron, and the accumulated phosphate a P-binding capacity was left of about 300 mg P/kg soil, which amount according to the results shown in the indicated tables was roughly removed from the added solutions.

The agreement between predicted and measured amounts of P retained by the adsorption processes decreases as the time allowed for the 'slow reaction' increases, and the total amount removed from the solution has been increased. The fact that the calculated amounts of P retained by the adsorption processes are higher than the experimentally measured values is interpreted as an indication that the presumed constancy of the adsorption isotherm and the freeing of occupied (adsorption) sites in relation to the prevailing solution P concentration is probably not valid if the available reactive soil aluminum and iron becomes depleted. In other words the number of available (adsorption) sites decreases somewhat and the freeing of occupied sites is less than predicted from the relation between decreasing solution P concentration and the adsorption isotherm. According to table 5.6a to c the differences between predicted and measured total amount retained by adsorption vary between 4 and 20% of the experimentally measured values.

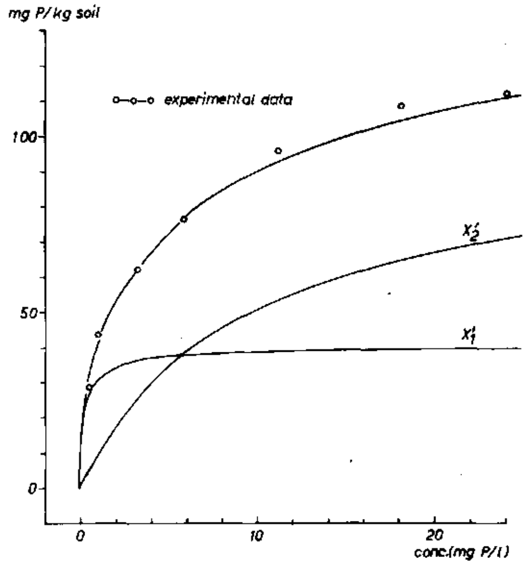


Fig. 5.22 The amount of phosphate removed from the solution in 3 days reaction time plus the ^{32}P exchangeable fraction of the original soil phosphate versus the phosphate concentration, for a subsoil sample. The Langmuir isotherms derived from these data are represented by X_1' and X_2'.

5.3.3 Behavior of a subsoil sample

In the various experiments reported above only soil samples were used that were sampled from the top 40 cm layers of the soil profile. These samples all contain approximately the same amount of oxalate extractable aluminum and iron (cf. Chapter 4) as a result of which the phosphate bonding capacity is also nearly equal. In the deeper layers of the profile the soil contains roughly only half of the amounts present in samples of the top layers, which very probably does not only affect the phophate bonding capacity but also the adsorption capacity as expressed by the Langmuir constants. Furthermore it is to be expected that the rate constants of the transformation processes of phosphate in the solution and the pools X_1 and X_2 differ from the ones used for the samples of the top layers. The above suppositions were tested experimentally with samples derived from the 60-70 cm layer of the soil treated with sewage water. Preparation of the soil suspensions and further experimental conditions were the same as reported before.

In fig. 5.22 the Langmuir isotherms are given together with the experimental data. These results are derived from samples that reacted with a phosphate solution for 3 days and are corrected for the original soil phosphate present in an 'adsorbed' state by the addition of the fraction of the latter that is accessible to isotopic exchange (4.9 mg P/kg soil). In the derivation of the Langmuir isotherm the procedure was followed of keeping the affinity constants the same value as obtained for the samples of the top layers, whereas the capacity (viz. B'_1 and B'_2) were adjusted in order to fit the experimental data. This leads to a value for B'_1=40 mg P/kg soil (at an affinity constant k_1=3.383 1/mg P) and for B'_2=99 mg P/kg soil (at a corresponding value of k_2=0.107 1/mg P).

In order to find out how the rate constants are affected, the calculated course of the solution phosphate concentration as a func-

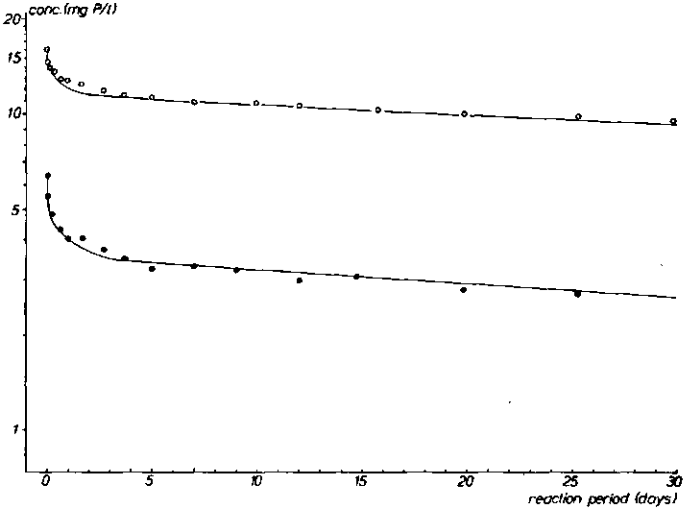


Fig. 5.23 The calculated (curves) and measured concentrations (symbols) for suspensions of a sub-soil (W=20) with different initial phosphate concentrations, during a reaction period of 30 days.

tion of reaction time was compared with experimental data for soil suspensions with 2 different initial phosphate concentrations. The experimental data shown in fig. 5.23 are the average values of duplicate samples. The contention that a change in the adsorption capacity of the soil affects the rate constants k_1 and k_2, included in the equations (5.6 and 5.7), describing the loading of the pools X_1 and X_2 was based on the consideration that these constants were defined with the dimensions of l (solution) kg^{-1} (soil) t^{-1} (days). Therefore the rate constants k_1 and k_2 (and also k_{d1} and k_{d2}) for the present sample were decreased in proportion to the Langmuir capacity constants of the samples derived from the top layer and the deeper layer (i.e. $k'=kB'/B$, where the prime refers to the present sample). As follows from fig. 5.23 satisfactory agreement was obtained between calculated and experimental data with the above derivation of k_1' and k_2'. It is noted here that no adjustment of k_n', the rate constant included in the equation (5.13) describing the loading of pool N, was necessary in the sense as applied for k_1 and k_2, because (5.13) contains explicitly the size of the pools involved. In view of the oxalate extractable amounts of alminum and iron the value of N_{max} (equation 5.13) was assigned the value of 178 mg P/kg soil.

5.4 SIMULATION OF COLUMN PROCESSES

5.4.1 Transport equations

The convective transport of phosphate with the liquid phase (j_{con}) may be described with the equation:

$$j_{con} = J^v c - D_{dis} \frac{\partial c}{\partial x} \tag{5.14}$$

in which j_{con} = flux of phosphate by convection with the liquid phase (μg P cm^{-2} day^{-1}), J^v=volume flux of the feed solution, in cm^3 (liquid) cm^{-2} (medium) day^{-1}, c = phosphate concentration in solution (μg P cm^{-3}), x = depth in cm and D_{dis} = the coefficient of hydrodynamic dispersion (cm^3 (liquid) cm^{-1} (medium) day^{-1}. This coefficient was calculated as $D_{dis} = J^v L_{dis}$ (Frissel et al. 1970).

For the dispersion distance (L_{dis}) a value of 2 cm was taken (this choice will be commented on later). The diffusion of phosphate through the liquid phase was described by

$$j_{dif} = -D_{dif} \frac{\partial c}{\partial x} \tag{5.15}$$

in which j_{dif} is the diffusive flux (μg P cm^{-2} day^{-1}) and D_{dif} is the diffusion coefficient for phosphate in the liquid phase of the soil (cm^3 (liquid) cm^{-1} (medium) day^{-1}). This coefficient was calculated with $D_{dif} = \theta D_o/\lambda$, with λ a labyrint factor for diffusion (cm^2 (medium) cm^{-2} (liquid), θ the volumetric liquid fraction (cm^3 (liquid) cm^{-3} (medium)) and D_o the coefficient for diffusion in the bulk liquid, in cm^2 (liquid) day^{-1}. The value of D_o for the orthophosphate species was taken as 0.8 cm^2 day^{-1} (Edwards and Huffmann, 1959). For $1/\lambda$ a value of 0.3 was taken (cf. also the discussion). Finally the conservation equation for

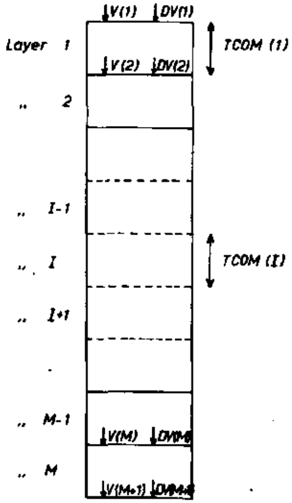


Fig. 5.24 A multilayer model with the corresponding mass fluxes V(I) and diffusion/dispersion fluxes DV(I). The thickness of each layer is represented by TCOM(I).

the transport in the soil system was described as:

$$\frac{\partial A_s}{\partial t} = - \frac{\partial j_{con}}{\partial t} - \frac{\partial j_{dif}}{\partial t} \qquad (5.16)$$

in which $A_s \equiv \theta c + \rho_b (X_1 + X_2 + N)$ indicates the total amount of phosphate present per unit volume of medium (μg P cm^{-3} medium), with ρ_b representing the bulk density of the soil in g (soil) cm^{-3} (medium).

The differential equations for transport of phosphate by convective flow and by diffusion were converted into the corresponding finite difference approximations with respect to the space coordinate (x).

To this purpose the soil column was divided into M, computational compartments (cf. de Wit and van Keulen, 1972). In this particular case the compartments are of equal thickness, (TCOM), water content (WC) and bulk density (BD), as indicated in fig. 5.24. For the computation of convective flow between the compartments 1 and M the concentration of phosphate in the solution (CPS(I)) present in adjacent compartments were averaged in order to suppress numerical spreading. The mass flux of phosphate, (V(I)) from layer (I-1) to layer (I) is defined as:

V(I) = VO * ((CPS(I-1) + CPS(I)) * 0.5) (5.17)

The system boundary fluxes V(1) and V(M+1) are taken as, respectively:

V(1) = VO * CPSF (5.17a)

V(M+1) = VO * (1.5 * CPS(M) - 0.5 * CPS(M-1)) (5.17b)

where CPSF represents the phosphate concentration in the feed solution and VO the influx rate. The rate of accumulation in layer (I), VV(I), is given by:

VV(I) = V(I) - V(I+1) (5.18)

The diffusion and dispersion fluxes from layer (I-1) to layer (I) are represented by DV(I) and are specified as:

DV(I) = DAV * (CPS(I-1) - CPS(I))/(0.5 * (TCOM(I-1)+TCOM(I))(5.19)

where DAV = WC * LAB * DI + VO * DISP, DI $\equiv D_o$ and LAB = $1/\lambda$. In view of the prevailing experimental conditions, the boundary fluxes were put to:

$$DV(1) = 0 \tag{5.20}$$

$$DV(M+1) = 0 \tag{5.20b}$$

The rate of accumulation in layer (I) by diffusion/dispersion phenomena, DIV(I), now equals:

$$DIV(I) = DV(I) - DV(I+1) \tag{5.21}$$

The rate of change of the solution phosphate concentration in layer (I), CPSR(I), is obtained as:

$$CPSR(I) = (VV(I) + DIV(I) - ((TCOM(I) * BD(I)) * (RCX1(I) + RCX2(I)))/(TCOM(I) * WC(I)) \tag{5.22}$$

where RCX1(I) and RCX2(I) represent the rate of transfer of phosphate between the solution and the pools X_1 and X_2, respectively. (The transfer of phosphate from pool X_2 to N is included in RCX2(I)). The feed solution is added with a constant rate, i.e. VO is a constant during a percolation run, likewise the phosphate concentration of the feed solution (CPSF) is constant. The ensuing set of ordinary differential equations with respect to time was combined into a model programmed in CSMPIII (IBM, 1972). Integration was carried out with the rectangular method (RECT), the length of the time step (DELT) was 0.0001 days (it meets the requirement that $DAV * DELT/(TCOM)^2 < 0.5$ (Frissel and Reiniger, 1974).

5.4.2 *Experimental set-up*

Soil column studies were used to test the rate equations of phosphate interaction processes (derived from batch studies) under conditions of liquid flow. This objective was achieved by measuring the phosphate concentration in the effluent from a column of soil to which a phosphate solution was added at a constant flow rate, under isothermal conditions. The composition of the feed solution was the same as used in the batch studies and the phosphate concentration was about 10 mg P/1. The soil columns were prepared by carefully adding, according to a standard manner, the (air-dry) soil material to a Buchner type funnel containing a porous glass plate at the bottom. The inside diameter of the funnel was about 2 cm. The feed solution was added at a constant rate to the top of the vertical soil column employing a peristaltic pump. To approximate a uniform flow rate, the solution was first dripped onto a layer of 2 mm diameter glass beads in order to spread the inflow. After passing through the glass beads, which were exposed to the atmosphere, the flow passed through a disc of blotting paper, which was in intimate contact with the soil sample. The soil column remained unsaturated at a constant water content during the percolation. The unsaturated condition of the soil was attained by maintaining a constant negative potential, equivalent to approximately 90 mbar of suction, at the bottom of the porous glass plate. The effluent from the column was then pumped by the same peristaltic pump to the sample collector. The samples were analysed for orthophophate (which under the present conditions equals total phosphate). Prior to the application of the phosphate solution to the soil column, the soil material was slowly wetted from the bottom layer upwards and kept in this prewetted condition for a week before the percolation started.

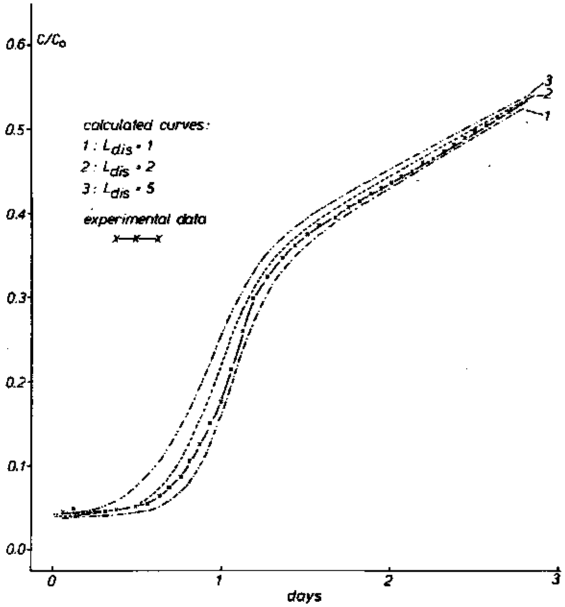


Fig. 5.25A The relative phosphate concentration in the effluent of a soil column (length: 1.1 cm, V0=6.37 cm/day) percolated with a solution with a constant phosphate concentration of 9.8 mg P/1. Curves were calculated for different values of the dispersion distance L_{dis}, given in cm.

The amount of soil material used in these studies varied between 5 to 15 gram, giving rise to column lengths of 1.1 to 3.3 cm. The advantages of using relatively short columns is that at moderate flow rates (i.e. comparable to the ones occurring in the sewage field) the phosphate concentration of the effluent starts to increase after relatively short percolation times. This allows separating out the effect of the relatively fast adsorption processes (i.e. the loading of the pools X_1 and X_2) from the slow formation of solid phosphate in pool N. The effect of the latter process was studied by a second percolation (with the same feed solution) after the column had been stored for about 3 weeks after termination of the first percolation run. During this period the column was kept at the same temperature of 20 °C and evaporation of the column solution was minimized by covering the funnel.

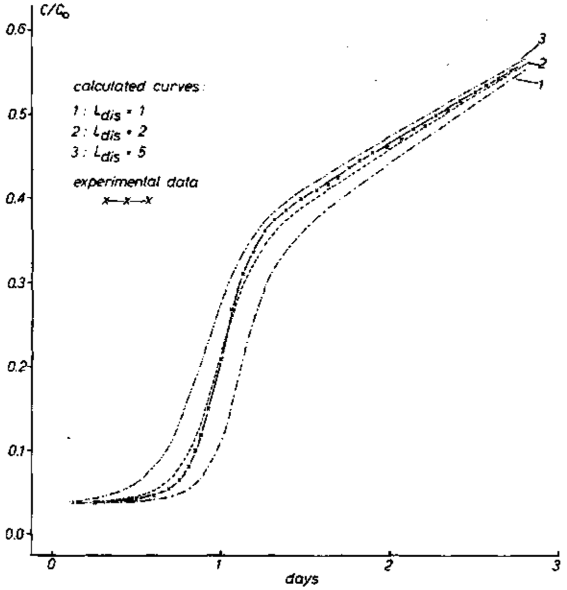


Fig. 5.25B The relative phosphate concentration in the effluent of a soil column (length: 2.1 cm, VO=16.6 cm/day) percolated with a solution with a constant phosphate concentration of 9.8 mg P/l. Curves were calculated for different values of the dispersion distance L_{dis} given in cm.

5.4.3 Results and discussion

It is evident that the effluent phosphate concentration is in principle also dependent on the coefficients D_{dif} and D_{dis}. This implies that the values of these parameters have to be determined for the particular soil column under study. As is indicated in section 5.4.1, D_{dis} is related to J^v and L_{dis}, whereas D_{dif} is related to θ, λ and D_o. The parameters J^v and θ are, in the present situation, easily accessible to experimental determination; the value of D_o was taken from Edwards and Huffman (1959). The experimental determination of L_{dis} and λ, however, is far from simple. Therefore the alternative method was followed of approximating L_{dis} and λ on the basis of a fitting procedure, which involved a calculation of the effluent phosphate concentration for different values of L_{dis} and λ and comparing the computed results with the experimental data of phosphate concentration in successive aliquots of the effluent. The estimated values of L_{dis} and λ were then used for the calculation of the effluent phosphate concentration of soil columns of different lengths and subject to different rates of influx of the feed solution. It is thus assumed that owing to the standard manner of soil column preparation the values of L_{dis} and λ will be rather uniform for the different columns.

Table 5.7 Physical parameters pertaining to the different soil columns of which the relative phosphate concentration of the effluent is presented in fig. 5.26

column nr.	bulk density (BD) g/cm^3	water content (WC) cm^3/cm^3	column length cm	weight of soil g	influx* of feed solution (VO) cm/day	
					1st	2nd
1	1.53	0.62	1.05	5	6.37	3.86
2	1.54	0.73	1.05	5	16.83	7.36
3	1.55	0.52	2.10	10	13.81	4.27
4	1.57	0.48	2.05	10	5.15	4.44
5	1.55	0.54	1.60	7.5	11.29	11.18
6	1.56	0.50	3.15	15	6.33	4.45

*The 2nd percolation was started 18 days after the 1st percolation was terminated. Each percolation run lasted about 3 days.

In fig. 5.25a,b the calculated effluent phosphate concentration (expressed as a fraction of the concentration of the feed solution) is given as a function of the time period of application of feed solution for two columns of approximately 1.1 and 2.1 cm length and subject to a different (constant) influx of the feed solution of 6.37 and 16.66 $\mathrm{cm.day^{-1}}$, respectively. The calculated curves and the curve drawn through the experimental points follow in general the same pattern, though the agreement in detail varies. On the basis of the curves shown in fig. 5.25a,b calculated with different values of L_{dis}, the latter was taken as 2 cm for further use in the calculation. The value of λ^{-1} in the above calculations was set to 0.3. Reported values of the labyrinth or tortuosity factor are usually above 2 (Porter et al., 1960; Rowell et al., 1967; Frissel et al., 1970; Vadianathan and Nye, 1970). On theoretical grounds it can be shown that the effect of a variation in $1/\lambda$ (be-

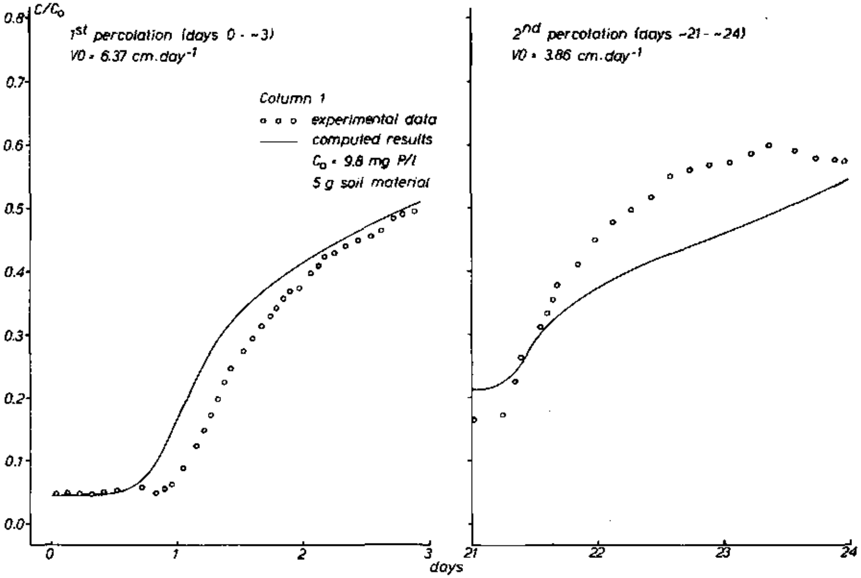
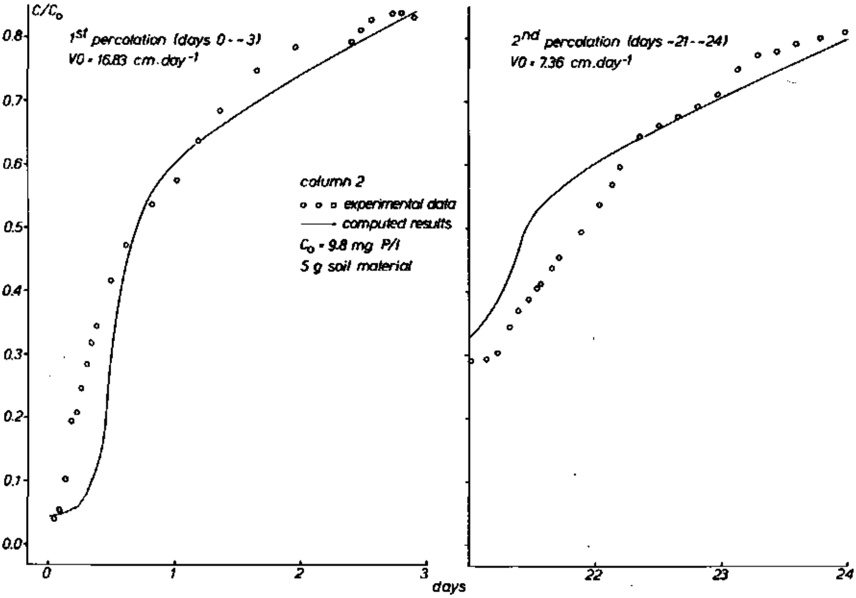


Fig. 5.26A to F The relative phosphate concentration in the effluent of short soil columns (1-6), prepared as described in text; the different column weights and influx rates (VO) are indicated on figure. Figure 5.26A is shown above.



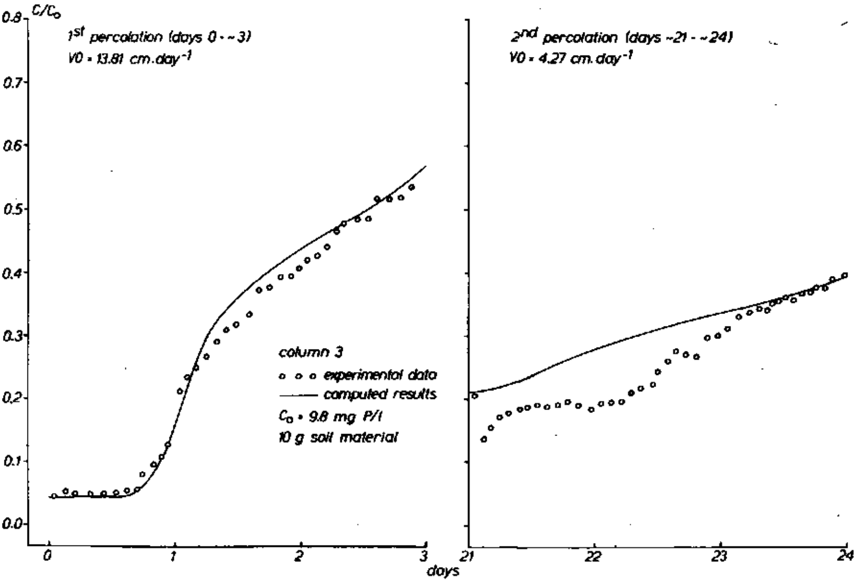
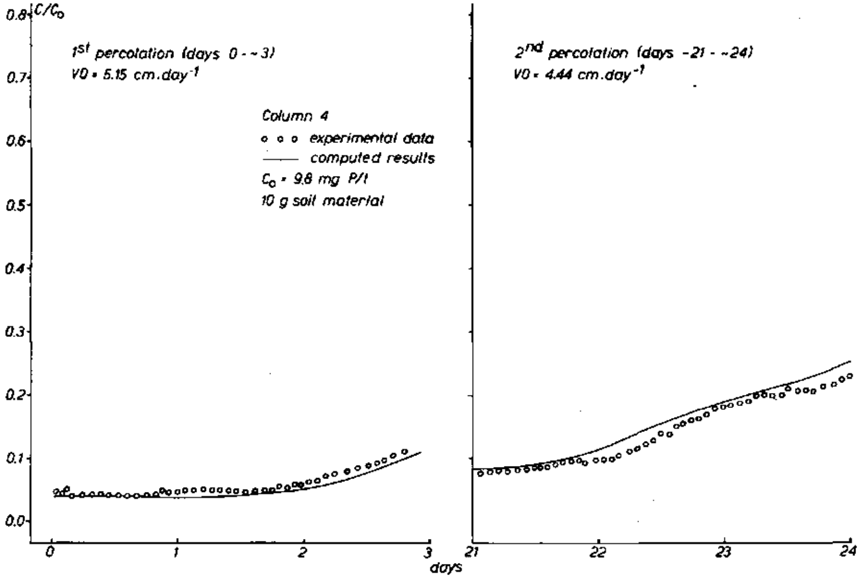


Fig. 5.26B (above), fig. 5.26C (below), for legend see fig. 5.26A.



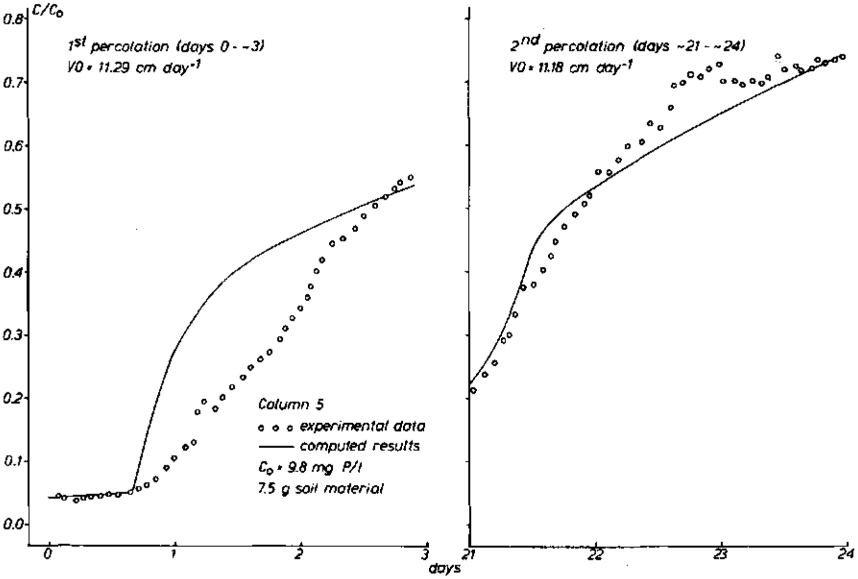


Fig. 5.26D (above), fig. 5.26E (below), for legend see fig. 5.26A.

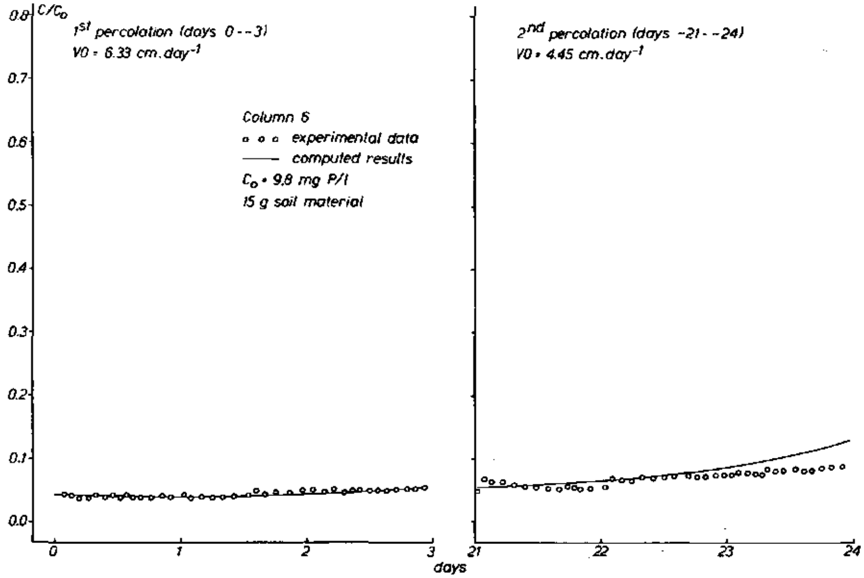


Fig. 5.26F, for legend see fig. 5.26A.

tween 0.1 and 0.5) on the effluent phosphate concentration is in general much smaller than the effect of a change in L_{dis} (between 1 and 5 cm), because the product of $J^v L_{dis}$ exceeds the product of $\theta D_o/\lambda$ already at low to moderate values of J^v (as compared to present experimental conditions). In the present study, however, the diffusion may have some effect on the redistribution of soluble phosphate during the time the column is not subject to percolation, which in an indirect way may influence the effluent phosphate concentration at the start of the second percolation run. Calculations in which $1/\lambda$ varied between 0.2 and 0.5 in combination with a variation of D_o between 0.7 and 0.9 resulted in small changes in the effluent phosphate concentration at the start of the second percolation. In view of the observed variation in experimental data the above calculated effects were to small to be used for a further refinement of the indicated parameter values in these soil columns.

In fig. 5.26a to f calculated and experimental results are given of soil columns of different length and subject to different (constant) fluxes of feed solution. As mentioned before the calculations were made with L_d = 2 cm, λ^{-1} = 0.3, and D_o = 0.8 cm^2 day^{-1}, whereas the parameters J^v, θ, column length and bulk density were assigned the experimentally determined values given in table 5.7. The parameters specifically related to the phosphate retention reactions, like e.g. the rate constants and N_{max} and $X_{2,min}$ were obtained from the batch studies (cf. Table 5.5). As follows from fig. 5.25a to f the overall agreement between calculated and experimental data is satisfactory, though the agreement in detail varies. This leads to the conclusion that the rate equations describing the phosphate retention processes, as derived from the batch experiments, can be used under conditions of liquid flow.

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APPENDIX 1

The model of physico-chemical transformation processes of orthophosphate in soil, written in the simulation language CSMPIII, is given below:

```
TITLE PHYSICO-CHEMICAL TRANSFORMATION PROCESSES OF ORTHO-P ...
                    IN SOIL
****************J. BEEK----1978**************************************
INCON IX1=45.7,IX2=7.8,IN=331.7,ISOLP=188.0
PARAM KL1=0.383,BL1=74.1,KL2=0.107,BL2=164.0
PARAM K1=434.0,KD1=434.3,K2=8.04,KD2=8.04,KN=1.22E-4
PARAM W=20.11,X2MIN=7.31,NMAX=757.
***RATE OF LOADING/UNLOADING OF POOL X1***
CPSD1=CPS-CPSE1
CPSE1=1./(KL1*(BL1/X1-1.))
*****CPS=CONC. OF P IN SOLUTION (MG P/L)
*****CPSE1=EQUIL. CONC. OF P (MG P/L) CALCULATED FROM
*****LANGMUIR ISOTHERM FOR POOL X1
*****KL1=AFFINITY CONSTANT OF LANGM. ISOTHERM FOR POOL X1
*****(L/MG P)
*****BL1=CAPACITY CONSTANT OF LANGM. ISOTHERM FOR POOL X2
*****(MG P/KG SOIL)
***IF CPSD1>0.  LOADING OF POOL X1***
RAX1=INSW(CPSD1,0.,K1*CPSD1)
*****RAX1= RATE OF LOADING OF POOL X1 (MG P/KG SOIL/DAY)
*****K1=RATE CONSTANT (L/KG SOIL/DAY)
***IF CPSD1<0.   UNLOADING OF POOL X1***
RDX1=INSW(CPSD1,KD1*CPSD1,0.)
*****RDX1= RATE OF UNLOADING OF POOL X1 (MG P/KG SOIL/DAY)
*****KD1=RATE CONSTANT (L/KG SOIL/DAY)
RCX1=RAX1+RDX1
X1=INTGRL(IX1,RCX1)
***RATE OF LOADING/UNLOADING OF POOL X2***
*****MEANING OF VARIABLES, SEE COMMENT FOR  POOL X1
CPSD2=CPS-CPSE2
CPSE2=1./(KL2*(BL2/X2-1.))
RAX2=INSW(CPSD2,0.,K2*CPSD2)
RDX2=INSW(CPSD2,KD2*CPSD2,0.)
RCX2=RAX2+RDX2
X2=INTGRL(IX2,RCX2)
***RATE OF LOADING OF POOL N ***
X2D=X2-X2MIN
*****IF X2D>0.  LOADING OF POOL N
RLN=INSW(X2D,0.,KN*X2D*(NMAX-N))
*****RLN=RATE OF LOADING OF POOL N (MG P/KG SOIL/DAY)
```

```
*****X2MIN=THRESHOLD VALUE OF P REQUIRED IN POOL X2
*****(MG P/KG SOIL)
*****K1=RATE CONSTANT OF LOADING RATE POOL 1 ((KG SOIL/
*****MG P)/DAY)
*****MMAX=MAXIMUM OF POOL M (MG P/KG SOIL)
M=INTGRL(IM,RLM)
***AMOUNT OF P IN SOLUTION***
SOLP=ISOLP+(IX1+IX2+IM)-(X1+X2+M)
CPS=SOLP/W
*****SOLP=SOLUBLE P, EXPRESSED AS MG P/KG SOIL
*****ISOLP=INITIAL VALUE OF SOLP
*****W=SOLUTION/SOIL RATIO IN L/KG
RETP=ISOLP-SOLP
*****RETP=P RETAINED BY SOLID PHASE OF SOIL (MG P/KG SOIL)
PRINT CPS,X1,X2,M,RETP,RCX1,RCX2,RLM
METHOD MILNE
TIMER FINTIM=5.,PRDEL=0.01
END CONTINUE
TIMER FINTIM=30.,PRDEL=1.
END
```

APPENDIX 1

The symbols used in the computer program correspond to the symbols used in diagram B fig. 5.11. The meaning of the different symbols, presented in alphabetical order, is given below:

BL1 = Langmuir capacity constant of pool X_1 (mg P/kg soil)
BL2 = Langmuir capacity constant of pool X_2 (mg P/kg soil)
CPS = conc. of dissolved phosphate (mg P/l)
CPSD1 = auxiliary variable representing the 'excess concentration' for pool X_1 (mg P/l)
CPSD2 = auxiliary variable representing the 'excess concentration' for pool X_2 (mg P/l)
IN = initial amount of phosphate present in pool N (mg P/kg soil)
ISOLP = initial amount of dissolved phosphate present in pool SOLP (mg P/kg soil)
IX1 = initial amount of phosphate present in pool X_1 (mg P/kg soil
IX2 = initial amount of phosphate present in pool X_2 (mg P/kg soil
K1 = rate constant for the loading of pool X_1 ((l/kg soil)/day)
K2 = rate constant for the loading of pool X_2 ((l/kg soil)/day)
KD1 = rate constant for the unloading of pool X_1 ((l/kg soil)/day)
KD2 = rate constant for the unloading of pool X_2 ((l/kg soil)/day)
KL1 = Langmuir affinity constant for pool X_1 (l/mg P)
KL2 = Langmuir affinity constant for pool X_2 (l/mg P)
KN = rate constant for the loading of pool N ((kg soil/mg P)/day)
N = amount of phosphate in pool N (mg P/kg soil)
NMAX = maximum amount of phosphate that can be stored in pool N (mg P/kg soil)
RAX1 = rate of loading of pool X_1 ((mg P/kg soil)/day)
RAX2 = rate of loading of pool X_2 ((mg P/kg soil)/day)

RDX1 = rate of unloading of pool X_1 ((mg P/kg soil)/day)
RDX2 = rate of unloading of pool X_2 ((mg P/kg soil)/day)
RLN = rate of loading of pool N ((mg P/kg soil)/day)
SOLP = pool of dissolved phosphate ((mg P/kg soil)
W = solution/soil ratio (l/kg soil)
X_1 = fast loading pool of adsorbed phosphate (mg P/kg soil)
X_2 = slow loading pool of adsorbed phosphate (mg P/kg soil)
X2MIN = minimum amount of phosphate in pool X_2 above which loading of pool N is possible (mg P/kg soil)

Appendix 2

The following procedure was used by Adriano and Novak (1975) to derive the appropriate form of equation 5.8 from the equations:

$$dX/dt = k(c-c_e) \qquad \text{(A2.1)}$$

$$c_e = X/(k(B-X)) \qquad \text{(A2.2)}$$

$$X = X_i+(c_i-c)W \qquad \text{(A2.3)}$$

Substitution of A2.3 in A2.2 and rearranging, gives:

$$c_e = ((X_i/kB) + (c_iW/kB) - (cW/kB))/(1-(X_i/B) - (c_iW/B) + (cW/B)) \qquad \text{(A2.4)}$$

Substitution of A2.4 in A2.1, introducing $dX/dt = -Wdc/dt$ and rearranging, gives:

$$dc/dt = -k/W(\alpha c^2 + \beta c - \gamma)/(\alpha c + \phi) \qquad \text{(A2.5)}$$

where $\alpha = W/B$

$\beta = 1-(X_i/B) - \alpha c_i + (\alpha/k)$

$\gamma = (X_i/kB) + (\alpha c_i/k)$

$\phi = 1-(X_i/B) - \alpha c_i$

Equation A2.7 integrates (cf. Dwight, 1961, p 38, 39) to:

$$\tfrac{1}{2}\ln(\alpha c^2 + \beta c - \gamma)\Big|_{c(t=0)}^{c(t)} + ((\phi-\beta/2)/\xi)\ln((2\alpha c + \beta-\xi)/(2\alpha c + + \beta + \xi))\Big|_{c(t=0)}^{c(t)} = -k/W(t-0) \qquad \text{(A2.6)}$$

where $\xi = + \sqrt{4\alpha\gamma + \beta^2}$

The rate constant, k, can be calculated with equation A2.6 by inserting the proper parameter values and the concentration of phosphate in the suspension after different (short) time intervals.

The procedure used here to estimate the rate constants k_1 and k_2 with equation A2.6 will be illustrated, using the following data of the concentration of phosphate in the solution of soil suspensions (W=20.11) as a function of the reaction period:

Reaction period (minutes)	Concentration (mg P/l)
0	3.25
10	2.88
25	2.48
46	2.32
59	2.27

Since the rate of loading of pool X_1 is much faster than that of pool X_2 (cf. page), a first estimate of k_1 was obtained by assuming that the decrease in concentration during the first 10 minutes is merely the result of loading of pool X_1.

The corresponding parameter values introduced into equation A2.6 were: X_{1i} = 45.7 mg P/kg soil, c_i = 3.25 mg P/l, k_1 = 3.383 l/mg P, B_1 = 74.1 mg P/kg soil and W = 20.11 l/kg. This gives that for t=0 and $c=c_i$, the LHS of equation A2.6 equals 0.5285. For t=10 and c=2.88 mg P/l it gives: LHS=0.3777. If $\Delta(10)$ = LHS (t=0)- LHS (t=0) then $\Delta(10) = 0.3777 - 0.5285 = -k_1/W\ (10-0)$ and k_1/W 0.01508 min^{-1} or 21.72 day^{-1}. With the above value of k_1/W the value of $\Delta(t)$ was calculated for 25 min. The latter value of $\Delta(25)$ was used to find the value of c_{e1}, corresponding to t=25 minutes. This gives c_{e1} (t=25) = 2.508 mg P/l. Since the measured concentration equals 2.48 mg P/l it means that the loading of pool X_2 (thereby neglecting any loading of pool N) brought about a decrease in concentration of 0.028 mg P/l. Now equation A2.6 is used to obtain an estimate of k_2, using the following values of the parameters: X_{2i} = 7.83 mg P/kg, c_i = 3.25 mg P/l, k_2 = 0.107 l/mg P, B_2 = 164.8 mg

P/kg soil and $W = 20.11$ l/kg.
This gives that for $t=0$ and $c=c_i$ and for $t=25$ and $c = 3.222$ mg P/l;

$$\Delta(25) = 0.8521 - 0.8623 = -k_2/W\ (25-0)$$

and

$$-k_2/W = 0.00041\ \text{min}^{-1} \text{ or } 0.59\ \text{day}^{-1}$$

Now the procedure is repeated in the sense that c_{e2} is estimated with the above value of k_2 in order to arrive at corrected values of c_{e1}. The latter values are used to obtain a second estimate of k_1, and so on.

The above procedure has been applied to suspensions with different initial phosphate concentrations, leading to estimated values of $k_1/W = 21.7$ day^{-1} and $k_2/W = 0.5$ day^{-1}.

6 PREDICTION OF LONG-TERM EFFECTS OF PHOSPHATE MOVEMENT IN (SANDY) SOILS FOLLOWING APPLICATION OF DISSOLVED FORMS OF PHOSPHATE

The increasing potential risk of leaching losses of P from soil by direct convective transport after large additions of phosphate in the form of waste water or liquid manure has become a matter of great concern. In this context it is necessary to gain a quantitative insight into the interrelation between the flux density of the carrier solution through the soil profile and the reaction kinetics of phosphate retention processes as it affects leaching losses. The simulation model discussed in the previous chapter lends itself to this purpose.

In the following sections the model has been put to use to study long-term effects of variations in system parameters and in the regime of application of P-containing waste water to soils. Because of the singular information available on the effect of about 50 years of application of such water at a sewage farm in the Tilburg area, this information was used as a check on the reliability of the model (Section 6.2). In the next section (6.3) a number of hypothetical case studies were made. Part of these were meant to explore the existing possibilities with regard to further utilization of the sewage farm at Tilburg, using a regime of application alike the one presently in use. Thereafter the effect of varying the regime of application was studied in order to explore its limits with regard to leaching losses of phosphate during a complete loading operation (Section 6.3.2).

6.1 INITIAL SELECTION OF SYSTEM PARAMETERS

Using the sandy soil of the sewage farm at Tilburg as a reference base, a simplified description of the existing soil profile was constructed as follows. Accepting the top layer of 1 m depth as the zone of interest, this layer was subdivided into smaller layers exhibiting different physical and chemical properties of the comprising soil material. Moreover a subdivision into smaller layers or compartments is necessary for computational reasons. In this particular case the soil layer of 1 meter was divided into 20 compartments of equal thickness (i.e. 5 cm). A system of intermittent flooding with sewage water was considered, omitting possible complications associated with ponding of sewage water. It was assumed, therefore, that the rate of sewage water application equalled the flux of the effluent leaving the soil layer at a depth of 1 meter. This implied that the description of the movement of water in the soil was reduced to intermittent steady-state leaching at a constant volumetric water content, particular for the different layers. The fluxes considered here were based on average daily rates of discharge of effluent, observed in field studies (cf. Chapter 3). The values of the (volumetric) water content of different layers given in table 6.1 were derived from experimental data pertaining to (undisturbed) samples taken at a depth of 10, 30 and 65 cm below the surface. The values presented correspond to the water content under saturated conditions. The bulk density values given in table 6.1 were derived from experimental data pertaining to samples taken at the same depths as mentioned above. The dispersion distance (L_{dis}) was set at a 'reasonable' value of 3 cm. The diffusion coefficient (D_{dif}) and the tortuosity factor (λ) were given the same values as used in the soil columns discussed in chapter 5. The phosphate retention processes were formulated in accordance with the model discussed in chapter 5, viz. considering 3 pools of solid phosphate (X_1, X_2 and N) with their corresponding rates of loading and unloading. The remaining parameters are given in table 6.1 without further comment, except for the capacity (B_1 and B_2) and affinity constants (k_1 and k_2) pertaining to the Langmuir equations of pool X_1 and X_2, respectively, and the maximum storage capacity, N_{max}, of pool N.

In view of the presumed gradual accumulation of aluminum compounds in the soil treated with sewage water the term $k'_n (N_{max}-N)$ in equation (5.13) was replaced by $k'_n (0.5\ N_{max})$ at values of $(1-N/N_{max}) > 0.5$, thereafter the normal procedure was followed.

The decreasing values of N_{max} with increasing depth of the soil layer are directly related to the sum of oxalate extractable (Al + Fe) present in the various layers (cf. Chapter 4). As follows from the capacity constants (B_1 and B_2) given in table 6.1 it is assumed here that the adsorption maxima in the top 50 cm are identical;

Table 6.1 Physical and chemical parameters pertaining to different soil layers

Parameters	Soil layer (cm)				
	0-20	20-30	30-40	40-50	50-100
bulk density (g/cm^3)	1.1	1.3	1.45	1.45	1.6
water content (cm^3/cm^3)	0.6	0.45	0.4	0.4	0.3
Langmuir constants:					
B_1 (mg P/kg soil)	74.1	74.1	74.1	74.1	40.1
B_2 (mg P/kg soil)	164.8	164.8	164.8	164.8	99.2
k_1 (1/mg P)	3.383	3.383	3.383	3.383	3.383
k_2 (1/mg P)	0.107	0.107	0.107	0.107	0.107
Maximum value of pool N					
N_{max} (mg P/kg soil)	991	991	656	656	171
Minimum value of pool X_2					
$X_{2,min}$ (mg P/kg soil)	7.3	7.3	7.3	7.3	4.4
Rate constants:					
k_1 (day^{-1} 1/kg soil)	434.3	434.3	434.3	434.3	249.4
k_2 (day^{-1} 1/kg soil)	8.0	8.0	8.0	8.0	4.8
k'_n (day^{-1}/(g P/kg soil)*	0.12	0.12	0.12	0.12	0.12

L_{dis} (dispersion distance): 3 cm
$1/\lambda$ (tortuosity): 0.3
D_o (diffusion coefficient): 0.8 cm^2 day^{-1}
$k_{d1} = 0.05\ k_1$ and $k_{d2} = k_2$

* For $(1-N/N_{max}) > 0.5$ the term $k'_n\ (N_{max}-N)$ in equation (5.13) was replaced by $k'_n\ (0.5\ N_{max})$ thereafter the normal procedure was followed

likewise it is assumed that the adsorption maxima in the bottom 50 cm are identical. This assumption probably approximates the field situation closely in so far as it concerns the bottom 50 cm. With respect to the top 50 cm, however, it is difficult to asses to what extent this assumption approximates the situation in the field, due to the presence of accumulated amounts of aluminum in the soil treated with sewage water. The values of B_1 and B_2 given in table 6.1 correspond to experimental data pertaining to samples derived from the 30-40 cm and 60-70 cm layers, respectively. The choice to assign identical values of the affinity constants (k_1 and k_2) to all layers was based on the assumption that the reactions underlying the loading of the pools X_1 and X_2 were the same in the different layers.

The equations describing phosphate transport by mass flow and diffusion flow (cf. fig. 5.24) were formulated in accordance with the equations (5.18) through (5.21), with the exception of equation (5.20b). The latter equation was replaced by:

DV (M+1) = DAV * (CPS(M) - CPS(M+1))/(0.5 * TCOM (M)) (6.1)

where

CPS(M+1) = (1.5 * CPS(M) - 0.5 * CPS(M-1)) (6.1a)

In the present situation leaching of phosphate from the soil is then defined as:

POUT = V(M+1) + DV(M+1) (6.2)

where the definition of V(M+1) corresponds to equation (5.17b).

In view of the main objective of this model to obtain long-term predictions, special attention was paid to a procedure that limits the computation costs. These costs are highly related to the smallest time interval required for the proper integration of the fastest process. Referring to this model, where the rectangular integration method was applied, it implied that the length of the time interval (DELT) should be related to the fast (un)loading rate of pool X_1. The ensuing small time interval required a large number of computations per unit time of simulation. According to Goudriaan (1977) it is sometimes possible to decrease the necessary number of computations in models comprising fast and slow processes. Thus in so-called stiff systems, this may be effected by a conditional bypassing of either or both the slow and fast processes. The application of methods of bypassing in this model resulted in a four to eight fold reduction of the computation time. This reduction was predominantly achieved in the time periods between successive additions of dissolved phosphate to the soil. The underlying principle is that during these periods the rate of change of the solution phosphate concentration (CPSR in equation 5.22) is largely controlled by the relatively slow loading of pool N. The ensuing small rate of change of the solution phosphate concentration in the different compartments rendered it then possible to reduce the number of computations. A detailed description of the procedure as it was used in this model will be published elsewhere (series of Simulation Monographs, Pudoc), together with other methods of solving stiff systems.

6.2 CHECK OF THE MODEL AGAINST AVAILABLE FIELD DATA

The reliability of the model for long-term predictions was checked against the distribution of accumulated phosphate with depth as found in the soil treated with sewage water (cf. fig. 3.5). For the simulation it was assumed that the initial concentration of dissolved phospate in the soil solution amounted to 0.03 mg P/l (0.001 mmol P/l), that is identical with the concentration found in a neighboring non-treated soil. The initial amounts of phosphate present in the pools X_1 and X_2 were related to the above concentration of dissolved phosphate via the corresponding Langmuir

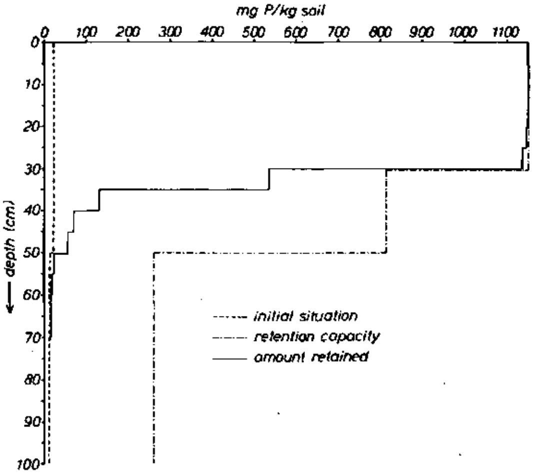

Fig. 6.1 The distribution profile of soil phosphate versus depth, for the situation present initially and after long-term treatment with dissolved phosphate. The retention capacity represents the maximum amount of phosphate that can be retained in the indicated layer.

equations. The amounts initially present in pool N were derived from the amounts of (Al + Fe)-bound P present at a corresponding depth in the non-treated soil, minus the initial amounts of phosphate accounted for in the pools X_1 and X_2; this calculation lead to initial values of 16.3 and 8.2 mg P/kg soil for the top and bottom 50 cm layer, respectively. In fig. 6.1 the corresponding total amounts of solid phosphate are plotted as a function of depth. In analogy to the system of intermittent flooding with sewage water in use at the sewage farm, the yearly phosphate load was split into ten equal portions, given after equal time intervals (i.e. a cycle of 36 days). The P concentration in the added solution was taken as 9.8 mg P/l and the (water) flux in the soil was fixed at a rate of 10 cm/day. The total load of P considered here amounted to 4464 kg P/ha; its value was estimated from the P distribution profile given in fig. 3.5, taking the fraction of the latter present as (Al+Fe)-bound P (cf. Beek et al., 1977b) and using the bulk densities of the relevant layers (Table 6.1). On the basis of a phosphate concentration in the added solution of 9.8 mg P/l this corresponded with a total water layer equivalent to 45.6 m. Using a yearly dose equal to the one applied in the field at present, i.e. about 196 kg P/ha, this amounted to 10 applications of 20 cm of water, each containing 19.6 kg P/ha.

It is pointed out that this regime implied the applications of sewage water during a period of 22.8 consecutive years. In reality the fields have been in use for about 50 years, the early ones comprising applications of lower amounts. Although in principle adjustment of the simulation program to lower applications at the outset is simple, the scant information available on actual rates of application in the early years did not warrant an effort to take this into account.

The distribution of accumulated P over the different layers as computed with the present model is shown in fig. 6.1. The strong accumulation in the top layers indicates that for the chosen regime of application - which coincides with the one presently in use at the Tilburg farm - the magnitude of the different rate coefficients, as determined from batch experiments, is amply sufficient to cause an efficient retention. In fact, the layers of the top 30 cm contain the maximum amount of P that can be retained, i.e. the sum of

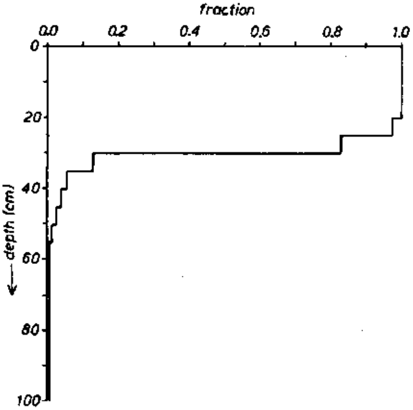

Fig. 6.2 The relative concentration of phosphate in the soil solution versus depth, expressed as a fraction of the concentration present in the added solution (9.8 mg P/l). The initial concentration in the soil solution amounts to 0.03 mg P/l.

N_{max} and the amounts present in pools X_1 and X_2 when in equilibrium with the feed solution. In fig. 6.2 the computed values of the concentration of P in the solution phase are plotted, expressed as a fractional value relative to the concentration of the feed solution at 9.8 mg P/l. Here again the efficient retention in the upper layers is obvious. It is also interesting to note that the zone of increased solution concentrations (as compared with the initial value at 0.03 mg/l) is practically limited to the upper 60 cm: because of the strongly convex adsorption isotherm of the X_1 pool the increase in retained P between 60 and 70 cm (fig. 6.1) hardly affects the solution concentration.

In order to compare the computed data with the situation prevailing in the field at the sewage farm, the distribution profiles given in fig. 6.1 (simulated data) and in fig. 3.5 (experimental data) were plotted together in fig. 6.3, expressing the amounts retained as a percentage of the retention capacity assigned to the first layer.

In this manner the curves where matched in the first layer, which was consistent with the chosen fixed value for the ratio (Al+Fe)/P determing the size of pool N, as discussed in chapter 5. Actually it might be preferred to plot the amounts retained as a percentage of the pool size of each layer, although such a plot tends to obscure the absolute amounts present in consecutive layers.

Depending on the viewpoint taken, the agreement between both curves may be considered as more or less satisfactory. From a practical standpoint the agreement is good: in both curves the penetration of applied P below a depth of 50 cm is negligible (<3%) and the bulk of the P applied is situated in the upper 30 cm. On a more detailed scale the field profile is definitely more spread out than the computed one. In order to establish whether possibly the computed profile was critically dependent upon the (independently determined, cf. Chapter 5) values of the rate coefficients, the computer simulation was repeated using *k* values equal to one half of the previously used ones. The effect of this on the ensuing retention profile was negligible: the amount of P retained below 50 cm increased only from 0.3% to 0.6%. Indeed, as will be shown in the following section, the effect of the magnitude of the rate coefficients becomes significant only once it is reduced below about one quarter of the value derived from the batch experiments reported in chapter 5; offhand there seems no reason to believe that in the field the rate coefficients would diverge so strongly from the ones determined in batch experiments. Moreover, also the

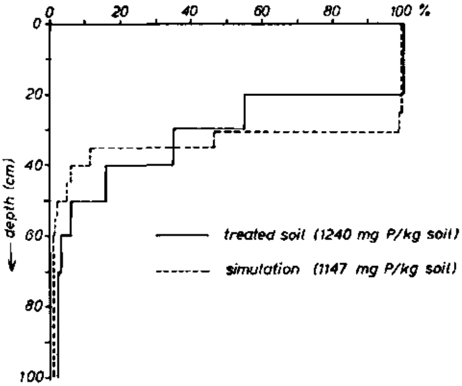

Fig. 6.3 Mass fractions of accumulated amounts of (Al+Fe)-bound soil phosphate versus depth, expressed as a percentage of the retention capacity assigned to the first layer.

short columns used in the laboratory appeared to check with the chosen values of the rate coefficients.

Another check on the sensitivity of the model was made by varying the rate of application. As was mentioned already (Beek and de Haan, 1974; Beek et al., 1977a) the monthly dose of sewage water varied from 150 to 350 mm during the past. In order to find out whether a higher dose rate might effect the P movement a calculation was made using an application regime of 30 cm per cycle instead of 20 cm. In other words the P load of 4464 kg/ha was added in a period of 15.2 years instead of 22.8 years. The effect of this on the retention profile was negligible: the amount of P retained below 50 cm increased only from 0.3% to 0.4%.

The above then leads to the important conclusion that under the present regime of sewage water application, the retention process is sub-critical with respect to the rate coefficients. While reassuring with respect to current practice at the sewage farm (cf. also the following Section), this conclusion is less gratifying in view of the present attempt to check the present model against the singular set of long-term experimental data available. The fairly small, though consistent, deviation as a result of the increased spreading of the penetration front in the field must be caused by other factors. The obvious ones in this case are the dispersive properties of the field system as compared to the one dimensional leaching assumed in the computation model. Two aspects of these are, respectively, the occurrence of short-circuits in flow channels due to cracks and animal tunnels ('bioperforation') and macro-dispersion inhaerent to fields flooded from one side and drained via localized tile drains. As the present study was not set up to investigate in any detail the actual flow pattern in the field it was impossible to account for such a pattern in the present model. Actually, even if known, the inclusion of two dimensional flow patterns in computer models of the present degree of complexity, would soon lead to excessive computation time. It thus seems warranted to use the present one based on a one dimensional flow pattern, keeping in mind that the field-peculiar dispersion pattern should be allowed for by means of a safety factor.

An indication of the correctness of the above viewpoint was found in the observed P concentrations in the effluent of field drains.

Whereas fig. 6.2 predicts an effluent concentration at a depth below 60 cm at the initial level of 0.03 mg P/l, it was found (see Table 3.1 and fig. 3.2) that the tile drains discharged levels between 0.2 and 2.5 mg P/l, with an average value of 0.3 mg P/l and a significant difference between shallow and deep drains. The rather early rise in the effluent concentration following the application of sewage water definitely points to the existence of routes to the drains with residence times in the soil much shorter than the average value used in the computation model.

6.3 SOME CASE STUDIES

6.3.1 Further use of the sewage fields at the Tilburg farm

Given the situation of a partly loaded soil at the Tilburg farm, the model was applied to establish whether a continuation of the current practice of sewage water application and some variations theron would yield satisfactory results with respect to the efficiency of P retention. To this purpose some major factors responsible for the movement of surface applied P to deeper layers were studied with a soil of which the top 50 cm layer could retain an additional amount of phosphate equivalent to 2055 kg P/ha.

The initial concentration of dissolved phosphate in this partly

Table 6.2 Effect of yearly dose on the downward movement of P at three application regimes

Yearly dose kg P/ha	Fraction* retained below 50 cm %	Leaching* losses %
	cycle 27 days	
196	2.7	4.4
392	4.1	4.4
783	6.8	4.4
	cycle 54 days	
196	2.8	4.4
392	4.4	4.4
	cycle 135 days	
392	5.6	4.4
783	9.4	4.4

* Expressed as percentage of amount supplied

loaded soil was set at a value of 0.43 mg P/l, that is identical to the concentration found in the top layer of the treated soil. The corresponding amounts of P present in the pools X_1 and X_2 in equilibrium with this concentration were calculated with the Langmuir equations. The amounts of P initially present in pool N for this partly loaded soil were distributed over the different layers in such a manner that a comparable distribution profile of accumulated phosphate was obtained as present in the soil treated with sewage water (cf. Beek et al., 1976; 1977a,b). The ensuing amounts of solid phosphate (i.e. the sum of X_1+X_2+N) per layer are plotted in fig. 6.4. On the basis of the amounts of solid P shown in fig. 6.4 and the retention maxima per layer plotted in fig. 6.1 it was calculated that in the top 50 cm an additional amount of P could be retained equivalent to 2055 kg P/ha.

The effect of the yearly dose on the downward movement of P was calculated for three loads of phosphate (196, 392 and 783 kg P/ha) at three different application regimes. These regimes were based on cycles of 27, 54 and 135 days; the fraction of the yearly dose supplied during each cycle then amounted to 8, 16 and 38%, respectively. The phosphate concentration in the added solution was set at 9.8 mg P/l and the carrier flux in the soil was maintained at 10 cm/day. The calculated effects of the different treatments are given in table 6.2, expressed as the fraction of the added amounts retained in the bottom 50 cm and the fraction lost from the soil by leaching. In view of the initial conditions assumed here (viz. a concentration of 0.43 mg P/l throughout the profile) a minimum loss of phosphate by leaching amounts to 4.4% at a total load of 2055 kg P/ha. So if the loss by leaching surpasses this minimum value, the surface added P has reached a depth of 1 meter. As follows from table 6.2 only the minimum values of losses by leaching were found for the different treatments, indicating that the surface added phosphate has not reached a depth of 1 meter. As follows from the fractions of phospate retained in the bottom 50 cm, the downward movement of P is affected by the yearly dose and the regime of application. For the lowest dose (196 kg P/ha) tried here it follows that a portion equivalent to 2.7% of the added amount is retained below a depth of 50 cm. This portion is not affected by the application regime. As follows from the other data the downward movement of P increases as the yearly dose becomes higher. The effect of the application regime manifests itself at higher annual doses of phosphate. On the basis of these results a yearly load of phosphate up to 400 kg P/ha seems possible in this soil. Although the downward movement related to the above doses is smaller for smaller portions added per time interval, the effect of the application regime remains minor. If, however, the yearly dose is increased to about 800 kg P/ha and it is supplied in portions of 300 kg P/ha, viz. corresponding to a cycle of 135 days, the fraction retained in the bottom 50 cm layers is about 9.5%. A problem closely associated with the dose and the application regime is the flux of the added solution in the soil, because the latter usually increases at larger amounts of water supplied, which might stimulate the downward movement of phosphate.

Table 6.3 The effect of the carrierflux on the downward transport of P at 3 different application regimes (annual dose = 392 kg P/ha, total amount supplied 2055 kg P/ha)

Average flux cm/day	Fraction* retained below 50 cm %	Leaching* losses %
	A	
	29.4 kg P/ha per cycle of 27 days	
10	4.1	4.4
15	4.4	4.4
30	4.9	4.4
	B	
	58.7 kg P/ha per cycle of 54 days	
10	4.4	4.4
20	4.9	4.4
30	5.4	4.4
	C	
	146.8 kg P/ha per cycle of 135 days	
10	5.6	4.4
50	8.1	4.4

* Expressed as percentage of amount supplied.

Preliminary results of (laboratory) experiments indicated that the hydraulic conductivity K_{con} in cm/day differed for the samples obtained from different layers. The minimum value was found in samples derived from the top 5-10 cm layer where K_{con} was about 50 cm/day.

The effect of a higher flux on the downward movement of added phosphate is shown in table 6.3 for an annual phosphate load equivalent to 392 kg P/ha supplied at three different regimes. If a flux of 10 cm/day is taken as a reference base it follows from table 6.3 that the effect of higher fluxes on the downward movement increases as the single dose becomes higher. The maximum difference amounts to 4% for the different fluxes tested here. These results support the former estimate that a load of 400 kg P/ha annually seems to be possible, although the top 50 cm layer is then nearly saturated with P after 5 years of application.

Table 6.4 Downward movement of P as a function of the rate constants k_1 and k_2 for 2 application regimes. The calculations were performed using fractional values (r) of the experimental data, presented in table 6.1. Total load of phosphate is equivalent to 2055 kg P/ha, annual load = 392 kg P/ha

Fraction of k_1 and k_2 r	Fraction* retained below 50 cm %	Leaching* losses %
	A	
	flux=10 cm/d, dose 29.4 kg P/ha per cycle of 27 days	
1	4.1	4.4
0.5	4.6	4.4
0.1	6.8	4.4
0.01	17.0	5.1
	B	
	flux=30 cm/d, dose 58.7 kg P/ha per cycle of 54 days	
1	5.4	4.2
0.1	10.1	4.4
0.01	20.3	6.3

* Expressed as percentage of amount supplied.

The preceding calculations were based on the chosen dispersion distance L_{dis} of 3 cm. In order to illustrate the effect of a higher value of this parameter on the downward movement of phosphate, one of the cases was recalculated using $L_{dis} = 5$. The flux was in both calculations set to 10 cm/day, and per cycle (27 days) an amount of phosphate was supplied equivalent to 29.4 kg P/ha, yielding an annual dose of 392 kg P/ha. The leaching losses were in both cases equal to the minimum value of 4.4%; however, the fraction of added phosphate retained by the bottom 50 cm layers amounted in the case of $L_{dis} = 3$ cm to 1.1% and in the case of $L_{dis} = 5$ cm to 5.0%.

It was shown in section 6.2 that a simultaneous reduction of the rate constants k_1, k_2 and k'_n to one half of the original values had a negligible effect on the distribution profile of retained P. In order to separate out the effect of a reduction of the rate constants k_1 and k_2 from the effect of a reduction of k'_n a few additional calculations were made using a reduction factor up to 0.01 of the original values. An illustration of the effect of the rate constants k_1 and k_2 on the downward movement of phosphate may have further practical significance because the adsorption of (some) dissolved organic phosphate compounds might proceed with a slower rate than found for the orthophosphate species (Rolston et al., 1975).

The effects of a simultaneous reduction of the rate constants k_1 and k_2 by a factor r=1, 0.5, 0.1 and 0.01 on the fraction of added phosphate retained below 50 cm are given in table 6.4. The effect becomes noticeable for $r<0.1$ under the chosen conditions of application regime and water flux. On the basis of these results the conclusion seems warranted that adsorption processes are sufficiently rapid to establish an efficient removal of phosphate from a solution percolating through the soil at low to moderate rates. In part B of table 6.4 results are given of calculations based on a flux of 30 cm/d and an addition of 58.7 kg P/ha during each cycle of 54 days. As was expected the fraction of surface added phospate transported to deeper layers became higher. These results further show that substances containing slowly adsorbing (organic) phosphate compounds (as might be present in for instance liquid manure, Gerritse, 1978) should be added in small amounts per cycle. In order to minimize the downward flux of the carrier solution, addition in periods of a precipitation surplus should be avoided.

Finally the effect of different values of the rate constant, k'_n, was tested on the downward movement of phosphate. To this purpose the values of k'_n were reduced to a fraction, r, of 1, 0.5 and 0.1 of the original value. In fig. 6.4 the distribution profiles of accumulated phosphate versus depth are shown for r=1, 0.5 and 0.1. The flux was set to 10 cm/day and the annual phosphate load was equivalent to 392 kg P/ha, the latter was supplied in equal portions of 29.4 kg P/ha per cycle of 27 days. It follows from fig. 6.4 that a reduction of k'_n to a tenth of its original value leads to a higher mobility of the added phosphate at the chosen application regime. In table 6.5 the fraction of the added phosphate retained in the bottom 50 cm layers is given together with the losses by leaching. It shows that a reduction of k'_n has a large effect on the downward movement, thus stressing the important contribution of the relative slow retention process in the bonding of phosphate. Results presented in part B of table 6.5 agree with expectations that increasing the time period between two successive additions counterbalance the effect of a lower constant. Since the effective rate of loading of pool N strongly decreases as pool N becomes filled up with phosphate (cf. equation 5.13) it means that

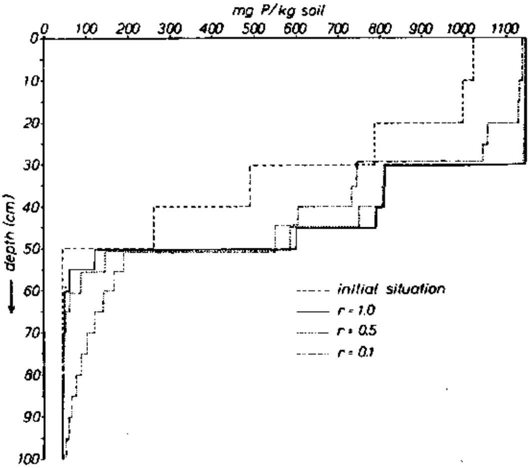

Fig. 6.4 The calculated distribution of phosphate versus depth for different values of k'_n, the latter constant was reduced by a factor r=1, 0.5 and 0.1 of the original value given in table 6.1.

the time period between two successive additions should be increased as more phosphate has been accumulated.

Available information suggests that the retention processes of phosphate in the soil slow down at lower temperature, especially the rate of precipitation reactions seems to decrease at a fall in temperature (Chen et al., 1973; Gardner and Jones, 1973; Barrow and Shaw, 1975). Since the rate constants used here were derived from (batch) experiments performed at a temperature of 20 °C it is possible that the occurrence of lower temperatures in the soil might give rise to lower values of the rate constants. Results presented in table 6.4, however, indicate that the downward movement of P is hardly affected by a 90% decrease of the rate constants k_1 and k_2, implying that it is rather unlikely that adsorption rates would become a limiting at lower soil temperatures. On the basis of the results shown in table 6.5 it follows that a 50% decrease in the rate constant k'_n due to lower temperatures would not lead to sifnificant changes in the retention process. This leads to the conclusion that the seasonal variation in soil temperature would have a minor effect on the retention processes of inorganic phosphate in the soil.

Table 6.5 Effect of the rate constant k'_n on the downward movement of phosphate for 2 application regimes. Original value of k'_n (table 6.1) was reduced by a factor r.

Fraction of k'_n r	Fraction* retained below 50 cm %	Leaching* losses %
	A	
	dose 29.4 kg P/ha per cycle of 27 days	
1	4.1	4.4
0.5	6.6	4.4
0.1	24.2	4.7
	B	
	dose 29.4 kg P/ha per cycle of 54 days	
1	2.8	4.4
0.1	14.2	4.4

* Expressed as percentage of amount supplied.

6.3.2 Establishing limits with respect to application regimes

As was pointed out in section 6.2, the regime as used in the past at the Tilburg farm was subcritical with respect to the effect of the chosen values of the rate coefficients. In the previous section it was shown that 'filling-up' the upper 50 cm is slightly more critical because of the then rapidly decreasing fraction of available P-binding sites.

In the present section it is attempted to present a survey of the limitations as to permissible rates of application for a given set of capacity and rate coefficients, if it is attempted to fill-up a layer of 25 cm depth without excessive penetration to deeper layers. It is then logical to adjust the single dose to the relatively fast loading pools X_1 and X_2. The upper limit of filling of these pools is fixed by the phosphate concentration present in the added solution (9.8 mg P/l). The lower limit is fixed by the minimum value of pool X_2 ($X_{2,min}$), because unloading of pool X_2 as a result of loading of pool N cannot proceed beyond this minimum value (cf. equation 5.13). On the basis of this reasoning the pools X_1 and X_2 could bind an amount of phosphate in the top 25 cm of the soil equivalent of 294 kg P/ha. Obviously an application based on the above dose might easily lead to deeper penetration if there is incomplete unloading of the pools X_1 and X_2 between successive applications. This implies that in addition to the application rate also the waiting period between successive doses might be critical. Starting with a dose of 294 kg P/ha as a guide line various other application rates were tried, which varied from a fraction equal to 1/6, 1/3, 2/3, to 4/3 of the above value. The waiting periods between successive doses were 15 and 50 days, thereby keeping in mind that the different application rates required different percolation times. Thus at a fixed value of the water flux of 20 cm/day and a fixed concentration in the solution added of 9.8 mg P/l, the number of days of percolation varied between 2.5 and 20 days. So one complete cycle required different time periods, depending on the waiting period of 15 or 50 days plus the number of days used for the supply of the water. The effect of the different treatments was based on the amount of phosphate that

Table 6.6 Effect of application regimes on the amount of surface added phosphate that has moved below the top 30 cm layer, in kg P/ha*

Days of percolation constituting a single dose**	Amount of surface added phosphate, kg P/ha (5% of this amount indicated between parentheses)												Time period for full load (3234 kg P/ha) (days)
	294 (15)	588 (29)	882 (44)	1176 (59)	1470 (74)	1764 (88)	2058 (103)	2352 (118)	2646 (132)	2940 (147)	3234 (162)	3528 (176)	
	Waiting period between successive applications amounts to 15 days												
A = 10	0	3	45	109	168	233	294	365	435	522	610	720	405
B = 15	0	6	74	156	239	322	405	490	578	674	777	890	330
C = 20	0	6	87	191	278	372	474	580	669	769	884	1014	285
	Waiting period between successive applications amounts to 50 days												
A'' = 2.5	0	0	0	2	6	14	26	41	59	81	113	$\underline{160}$	3465
A' = 5	0	0	2	7	17	31	48	68	94	$\underline{130}$	$\overline{178}$	245	1815
A = 10	0	1	8	28	48	72	$\underline{96}$	$\overline{129}$	165	222	280	376	965
B = 15	0	2	26	$\overline{62}$	97	134	173	217	268	330	405	497	715
C = 20	0	3	$\underline{43}$	102	141	193	252	318	365	432	520	633	565

* Underlined and 'over'lined numbers represent data closest to 5% of applied dose.

** The amount added per day amounts to 20 cm water containing 19.6 kg P/ha.

had penetrated deeper than 30 cm, thus accepting that the portion of surface added phosphate present in the 25-30 cm layer is due to dispersive spreading.

In the present soil the same initial conditions were assumed as were given in section 6.2. This implies that the initial amounts of solid phosphate present in the different layers were identical to the values plotted in fig. 6.1, while also the initial concentration amounted to 0.03 mg P/1. The amounts of phosphate present in pool X_1 and X_2 in equilibrium with the latter concentration where lower than the previously mentioned minimum value of pool X_2, i.e. $X_{2,min}$. This implied that the pools X_1 and X_2 were not completely loaded after the first addition of 294 kg P/ha. Again allowance was made for the presence of a gradually increasing value of N_{max} (cf. small print in Section 6.1).

The effects of the different treatments are shown in table 6.6, where the total amounts of phosphate applied are given in multiple units of 294 kg P/ha. The total capacity of the top 25 cm for phosphate bonding amounts to 3234 kg P/ha. It follows from table 6.6 that the maximum amount supplied surpasses this value by 294 kg P/ha, implying a penetration below 25 cm anyhow. The data in table 6.6 represent the amounts of phosphate in kg P/ha penetrated below a depth of 30 cm. In the first column on the left hand side the amounts applied per single dose are specified in terms of the number of days of percolation at a rate of 20 cm/day and at a concentration of 9.8 mg P/1, 15 days (case B) thus containing the capacity of the fast pool.

The conclusions following from this table are:

1. An application rate based on complete filling of the fast loading pools X_1 and X_2 must be dissuaded, unless one accepts long waiting periods between successive applications.
2. The relative amount of each single dose present below the depth of 30 cm increases for consecutive doses. At longer waiting periods between successive doses the relative increase is smaller.
3. The effect of smaller application rates is evident. As was expected the fraction present below a depth of 30 cm is higher if a higher application rate is used than the reference value (cf. treatment C = 392 kg P/ha).
4. Waiting periods between the doses should be selected in relation to the application rate, viz. higher application rates require

longer waiting periods. Moreover, it should be realized that the waiting period should be increased in relation to the amount present in pool N, because unloading of pool X_2 proceeds at a slower rate when the amount stored in pool N becomes higher. (In view of these results it is evident that intermittent flooding of the soil with waste water leads to higher P removal rates than when contineous flooding is used as indeed was found by Greenberg and McGauhey (1955), Logan and McLean (1973) and Lance (1977)).

5. On the basis of a fixed waiting period of 50 days it follows that the application rate should be lower than 1/3 of the reference value in order to limit the fraction present below 30 cm to 5% of the total amount added.

6.4 AN ATTEMPT TOWARDS GENERALIZATION

Concerning the aspect of P-binding in soil, some tentative conclusions on the minimum information needed for designing a land treatment scheme involving waste water containing orthophosphate could be:

1. The size of fast and slow loading pools must be determined, presumably using a method as described in chapter 5;
2. The rate coefficients of the pools should be checked with short soil column experiments as described in the same chapter.

Given these data one might think in terms of an application regime based on single doses not exceeding 20% of the capacity of the fast pool present in the layer to be used and then allow for a waiting period of three half times as applicable to the rate of unloading of the fast pool (X_2) at the moment that half of the slow loading pool N has been filled. The ensuing design should then be checked against the behavior of the computer model for the above applications. Thereafter one should consider applying a safety factor taking into account field-inhaerent irregularities not included in a necessarily schematized model.

Finally, it might be considered to run an optimalization procedure with the given variables, taking into account technical aspects associated with e.g. frequency of application, size of the land available, required minimum longevity of the treatment system as well as allowed leaching losses.

6.5 REFERENCES

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SUMMARY

The disposal of large amounts of domestic sewage water and liquid manure, both containing dissolved phosphates, is often problematic. Discharge of these into (shallow and standing) surface waters is highly undesirable, as phosphate is considered to be one of the prime causes of eutrophication. If, on the other hand, these materials are disposed of onto land, losses of P from soil via surface runoff and leaching are likely to increase, thus contributing again to eutrophication phenomena. An additional reason for concern about increased leaching losses in the case discussed is found in the simultaneous addition of large amounts of water. This may rapidly transport the phosphate to deeper layers, enhancing the chance of penetration into ground- or drainage water.

In the present text it was attempted to construct a model describing the movement of phosphate through soil following sizable applications of water. Such a model requires in the first place a quantitative insight into the kinetics of the processes governing the retention of phosphate in soil.

Since only scant information is available about phosphate retention in soils treated with soluble phosphate compounds, extensive analytical data were collected from a sandy soil profile that had been exposed to regular applications of (raw) sewage water during a period of about 45 years. As a result of these sewage water additions, phosphates accumulated in the soil, mainly in the top 50 cm. Fractionation of these accumulated forms of phosphate via selective extraction methods indicated that aluminum- and iron-bound phosphates constitute the largest fraction (60-75%). Organic-bound phosphates and calcium-bound phosphates were present in smaller quantities. Phosphate analysis of sewage water and effluent leaving the soil via a system of tile drains indicated that, in spite of 45 years prior usage, the removal of phosphate from the sewage water by the soil is still very effective (around 90%). Moreover, some other substances were partly or nearly completely

removed from the sewage water, during its percolation through the soil (Chapter 3).

In view of the above findings indicating that aluminum (and iron) were the main binding agents for phosphate, the total and oxalate extractable forms of these components were determined in the soil. These results strongly suggested that in the top layers (0-50) cm of the soil treated with sewage water accumulation of aluminum compounds had taken place in the past, most likely due to the supply of sewage water containing industrial waste water. Additional experiments showed, furthermore, that the phosphate binding capacity of different sandy soils could be related to the oxalate extractable forms of aluminum and iron. Under conditions as were found in soils treated with sewage water, the molar ratio of oxalate extractable (Al+Fe) over the phosphate retained tended to a value around three. A determination of the oxalate extractable aluminum plus iron thus presents a simple method to obtain a fair estimate of the phosphate bonding capacity of sandy soils, thereby assuming that the above value of the ratio (Al+Fe)/P remains valid (Chapter 4).

Kinetic aspects of the retention processes of dissolved orthophosphate with soil were studied with the help of batch shaking experiments, using samples of the soil treated with sewage water (Chapter 5). The samples were suspended in solutions containing most of the inorganic ions that were present in the sewage water, at the same concentrations. The soil suspensions were brought to pH 6.2 and adjusted when necessary. Determination of dissolved P as a function of time showed that P was removed rapidly from the solution initially, followed by a much slower rate of removal over longer periods. With the help of a graphical procedure the contributions of the fast and slow processes were separated out; adsorption processes were considered to be responsible for the fast removal, whereas the slow rate of removal was associated with the formation of a rather insoluble and non-reactive form of solid phosphate, presumably a (calcium) aluminum-phoshate.

The equilibrium adsorption processes could be described with two Langmuir equations, which lead to the introduction, in the model, of two pools of adsorbed phosphate, i.e. X_1 and X_2. In addition a third pool of solid phosphate was distinguished, viz pool N, comprising the solid phosphate compounds formed during slow retention processes. This division of retained phosphates into an adsorbed fraction and another immobilized form was supported by results of isotopic exchange experiments using ^{32}P. It was found that the adsorbed forms present in the pools X_1 and X_2 were relatively readily accessible to isotopic exchange whereas forms of phosphate present in pool N were rather inaccessible to exchange with ^{32}P labelled species in solution.

An important feature associated with the formation of phosphate in pool N was the apparent freeing of adsorption sites, suggesting that during the slow retention process part of the adsorbed phosphate was released from the adsorption sites.

The decrease of the phosphate concentration in the soil suspensions was described in terms of three rate equations. The reactions leading to the formation of the forms of phosphate present in the pools X_1 and X_2 were treated as simple first order reactions, the rate being proportional to the 'excess' concentration. The rate constants k_1 and k_2, defining the loading of pools X_1 and X_2, respectively, were derived from adsorption experiments. It was shown that k_1 differed significantly from k_2 viz, $k_1/k_2 \approx 50$. Since it was the main objective to study the retention of phosphate, only superficial attention was paid to desorption processes. The rate constants for desorption, k_{d1} and k_{d2} were therefore given the same values as the constants k_1 and k_2, although there are indications that the ensuing assumption of reversible adsorption is an oversimplification. The loading of pool N was defined as a second order equation, the rate being proportional to the 'excess' adsorbed phosphate present in pool X_2, implying that P present in pool N is formed at the cost of P present in pool X_2. Since the formation of P in pool N must involve a P-binding agent with limited supply for a given soil, a delimiting factor was introduced in the form of an available capacity. This factor was related to the oxalate extractable amounts of Al and Fe present in the soil. The rate constant of this slow reaction k_n', is presumably independent of the 'excess' amount adsorbed in pool X_2 and the available capacity of the P-binding agent.

On the basis of the presumed three pools of solid phosphate and a pool of dissolved phosphate a simulation model was developed; the transformation processes between the different pools were formulated on the basis of the rate equations written in the simulation language CSMPIII. Computed results were compared with experimental data of phosphate concentrations in solution of the soil suspensions to check the model. Finally short soil columns were assembled in the laboratory and subjected to percolation with a phosphate solution. The phosphate concentrations in the effluent leaving the column were used to test the computed result obtained with the model under conditions of liquid flow. To this purpose the model was extended with equations describing transport of phosphate by convective and diffusion/dispersion flow (cf. Chaper 5). The computed effluent concentration agreed satisfactorily with measured concentrations.

Since the check with column experiments indicated that the model could be used under conditions of liquid flow, it was applied to predict the effects of longterm additions of soluble (ortho)phosphate to the soil (Chapter 6). As for the present purpose the model required initially a long computing time, special procedures were introduced to reduce the latter to an acceptable level.

The reliability of the model for longterm predictions was checked against available field data of the scil treated with sewage water. To this purpose the distribution profile of accumulated (Al+Fe)-bound phosphate found in the field was compared with the computed data obtained after a load of phosphate was supplied identical to the (Al+Fe)-bound P present in the field. This load was equivalent to 4460 kg P/ha; in the program it was supplied in separate portions of 19.6 kg P/ha in the form of a solution containing 9.8 mg P/l. An application regime was sustained consisting of 10 applications per year, as is the normal practice used at the sewage farm. The agreement between the 2 sets of data was good from a practical standpoint, showing that the accumulated phosphate was mainly present in the top 30 cm with very little movement to deeper layers. On a more detailed scale, the field profile was definitely more spread-out than the computed one, very probably because the dispersive properties of the field soil differed from the ones present in the model, where only one dimensional leaching was considered. The downward transport of P appeared to be subcritical with respect to the chosen values of the rate constants and the yearly dose.

A partly loaded soil was used to study the effects of different application regimes, yearly loads, different fluxes and reduced values of the rate constants on the downward movement of P. To this purpose, the fraction of added phosphate that moved below a depth of 50 cm and the fraction of P lost from the soil via leaching (viz. at a depth of 1 meter) were used as criterions. The total amount of P supplied during these cases was always identical to the additional amount that could be bound in the top 50 cm. It could be shown that a variation in yearly load of 200 to 780 kg/ha, added in portions of different size, had only a small effect on the downward transport of P. A variation in the waterflux between 10 and 50 cm/day had the same minor effect on downward transport. A reduction of the rate constants controlling the loading of the pools X_1 and X_2 below 10% of their original values leads to higher leaching losses. A reduction of the rate constant defining the loading of pool N below 50% of the original value significantly increased the downward movement of P.

These calculations have shown that an application regime and yearly dose as are in use at the sewage farm studied, guarantee an effective removal of phosphate from solution. Of particular importance is the introduction of a sufficient waiting period between two doses, in order to allow for transformation of the adsorbed P to a less reactive form. This then leads to a regeneration of adsorption sites which is of great importance to remove the phosphate effectively from the sewage water during its relatively short residence time in the soil.

Finally the model was used to establish limits with respect to the application regime. These results indicated that the penetration depth of phosphate in the soil could be controlled on the basis of (a) the size of the single dose in relation to the capacity of the fast loading pools X_1 and X_2 and (b) the waiting period between successive doses, provided one does not surpass the maximum retention capacity of the relevant soil layer.

SAMENVATTING

Grote hoeveelheden huishoudelijk afvalwater en drijfmest, welke beiden opgeloste fosfaatverbindingen bevatten, leiden doorgaans tot afvoerproblemen. Lozing op (ondiepe en stilstaande) oppervlaktewateren moet worden voorkomen, aangezien fosfaat als een van de belangrijkste eutrofiërende voedingsstoffen in dit water wordt beschouwd. Anderzijds geeft toediening aan de bodem het risico dat oppervlakkige afspoeling en uitspoeling van fosfaat toenemen, waardoor op indirecte wijze wordt bijgedragen tot eutrofiëring. Een extra reden tot bezorgdheid over grote uitspoelingsverliezen in het geschetste geval is gelegen in de omstandigheid dat met het fosfaat ook relatief grote hoeveelheden water worden toegediend. Hierdoor kan het fosfaat snel naar diepere lagen worden gevoerd, waarbij de kans op doordringing in grond- of drainagewater toeneemt.

In het onderhavige proefschrift werd gestreefd naar een modelmatige beschrijving van de mogelijke verplaatsing van fosfaat in de bodem onder invloed van grote watergiften. Voor een dergelijk model is het in de eerste plaats van belang een kwantitatief inzicht te krijgen in de kinetiek van de processen van vastlegging van fosfaat in de bodem.

Aangezien alleen schaarse gegevens aanwezig zijn over de vastlegging van fosfaat in grond behandeld met opgeloste fosfaatverbindingen, werden uitgebreide meetgegevens verzameld van een zandgrond welke gedurende 45 jaar regelmatig was bevloeid met (onbehandeld) rioolwater. Als gevolg van de toediening van rioolwater was het fosfaatgehalte van de grond toegenomen, vooral in de bovenste 50 cm. Een fractionering van de geaccumuleerde fosfaten met behulp van selectieve extractie methodieken toonde aan dat aluminium-gebonden fosfaten de grootste fractie (60-75%) vormden. Organisch gebonden fosfaten en calciumfosfaten waren derhalve in geringere hoeveelheden aanwezig. Door in het rioolwater en in het effluent dat via drains uit de bodem werd afgevoerd het fosfaatgehalte te

bepalen kon worden aangetoond dat de grond, na 45 jaar in gebruik te zijn geweest als vloeiveld, nog steeds in staat was het fosfaat op zeer effectieve wijze uit het rioolwater te verwijderen (ongeveer 90% verwijdering). Bovendien werden nog andere bestanddelen geheel of gedeeltelijk uit het rioolwater verwijderd tijdens de bodempassage (hoofdstuk 3).

Omdat was gebleken dat het fosfaat vooral door aluminium (en ijzer) werd vastgelegd, werd het totale gehalte van deze bestanddelen bepaald, evenals de fractie die met een oxalaatoplossing kon worden geextraheerd uit de bodem. Deze gegevens wekten de stellige indruk dat in de bevloeide bovengrond (0-50 cm) een aanrijking met aluminium verbindingen had plaatsgevonden in het verleden, zeer waarschijnlijk een gevolg van toediening van rioolwater dat industrieel afvalwater bevatte. Aanvullende experimenten toonden aan dat het fosfaatvastleggend vermogen van verschillende zandgronden kon worden gekoppeld aan de met een oxalaatoplossing te extraheren hoeveelheden aluminium en ijzer. De molaire verhouding tussen deze in oxalaat oplosbare vormen van aluminum en ijzer en de vastgelegde hoeveelheden fosfaat bereikten een waarde van rond de drie onder omstandigheden zoals die voorkomen in het vloeiveld. Een bepaling van het met een oxalaatoplossing extraheerbare aluminium plus ijzer is dus een simpele methode om een redelijke schatting te kunnen doen naar de grootte van het fosfaatvastleggend vermogen van zandgronden, aannemende dat de eerder genoemde waarde van de molaire verhouding, (Al+Fe)/P=3, blijft gelden (hoofdstuk 4).

De kinetiek van de processen die een rol spelen bij de vastlegging van opgelost orthofosfaat in de bodem werd bestudeerd met behulp van schudproeven. Met dit doel werden grondmonsters afkomstig van het vloeiveld gesuspendeerd in een oplossing die de meest voorkomende anorganische ionen bevatte die ook in het rioolwater aanwezig waren en met overeenkomende concentraties. De suspensies werden op pH 6.2 gebracht en bijgesteld wanneer dit nodig was. Uit metingen van het verloop van de P-concentratie met de tijd bleek dat in het begin een snelle daling van de concentratie optrad gevolgd door een langzame verwijdering van P uit de oplossing over een langere periode. Door middel van een grafische methode werd de bijdrage van de snelle en langzame processen in de verwijdering van

P uit de oplossing gesplitst; de snelle verwijdering van P werd toegeschreven aan adsorptieprocessen terwijl de langzame afname werd toegeschreven aan de vorming van een weinig oplosbare en inactieve vaste fase, vermoedelijk een (calcium)aluminium-fosfaat.

De geadsorbeerde hoeveelheden P in evenwicht met de concentratie in oplossing konden worden beschreven met Langmuir vergelijkingen, op grond waarvan voor de modelbeschrijving werd aangenomen dat er twee vormen van geadsorbeerd P in de grond aanwezig waren, hier genoemd 'pools' X_1 en X_2.

Het fosfaat dat via de langzame processen wordt vastgelegd werd ondergebracht in een aparte derde 'pool' N. De indeling van het vastgelegde fosfaat in een geadsorbeerde fractie en een andere immobiele vorm wordt ondersteund door resultaten van isotopische omwisselingsproeven met behulp van ^{32}P. Het bleek dat het geadsorbeerde fosfaat betrekkelijk gemakkelijk kon omwisselen tegen met ^{32}P gemerkte ionen in de oplossing, in tegenstelling tot het fosfaat in 'pool' N, dat vrijwel niet toegankelijk was voor omwisseling.

Een belangrijke eigenschap die samenhing met de vorming van fosfaat in 'pool' N was het schijnbaar vrijkomen van adsorptieplaatsen hetwelk suggereert dat een gedeelte van het geadsorbeerde fosfaat tijdens de langzame vastlegging van de adsorptieplekken vrijkomt.

De afname van de fosfaatconcentratie in de suspensie werd beschreven met drie snelheidsvergelijkingen. De vorming van fosfaat in de 'pools' X_1 en X_2 werd beschreven met behulp van eenvoudige eerste-orde reactievergelijkingen. De snelheid was evenredig met de 'overmaat' P-concentratie; de snelheidsconstanten, k, werden geschat uit resultaten van adsorptieproeven. Er bleek een significant verschil te bestaan tussen k_1 en k_2, in die zin dat $k_1/k_2 \approx 50$. Aangezien het belangrijkste doel van dit onderzoek de vastlegging van fosfaat betrof werd alleen oppervlakkige aandacht besteed aan desorptieprocessen. Om die reden werden de snelheidsconstanten van de desorptiereacties, k_{d1} en k_{d2}, gelijkgesteld aan de overeenkomende adsorptieconstanten k_1 en k_2, hoewel er aanwijzingen zijn dat het veronderstellen van reversibele adsorptie een te simpele voorstelling van zaken is. Het vol lopen van 'pool' N werd beschreven met een tweede-orde reactievergelijking, waarbij de snelheid evenredig bleek met de hoeveelheid fosfaat in 'pool' X_2 (boven een minimum niveau). Het vol lopen van 'pool' N gaat dus ten koste van het fosfaat in 'pool' X_2. Omdat voor het vastleggen van fosfaat in 'pool' N een geschikte component nodig is die in beperkte mate voorradig is in de bodem werd in de snelheidsvergelijking een rem factor geintroduceerd op basis van de nog beschikbare hoeveelheid van deze component. Deze beschikbare hoeveelheid is gerelateerd aan de hoeveelheid Al en Fe die met een oxalaatoplossing geextraheerd kan worden. De snelheidsconstante van deze langzame reactie, k_n', werd onafhankelijk verondersteld van de geadsorbeerde hoeveelheid fosfaat en de beschikbare hoeveelheid (Al + Fe).

Op basis van de hier veronderstelde 3 'pools' van vast fosfaat en het mobiele opgeloste fosfaat werd een simulatiemodel ontwikkeld; de processen waarbij fosfaat vanuit de ene 'pool' naar de andere gaat werden hierbij gestuurd met behulp van de eerder geformuleerde snelheidsvergelijkingen, die voor dit doel werden herschreven in de simulatie taal CSMPIII. Het model werd getoetst op basis van een vergelijking van de berekende concentraties van fosfaat in de suspensies met de gemeten concentraties als functie van de tijd. Tot slot werden ook in het laboratorium een aantal korte kolommen gevuld met grond en vervolgens gepercoleerd met een fosfaatoplossing. De fosfaatconcentraties in het effluent werden vergeleken met de berekende concentraties volgens het model waarbij dit was uitgebreid met vergelijkingen die het fosfaattransport beschrijven als convectie aangevuld met diffusie/dispersie transport (hoofdstuk 5). De overeenstemming tussen berekende en gemeten fosfaatconcentraties in het effluent voldeed aan de gestelde normen.

Nu was aangetoond dat het model ook werkte onder omstandigheden van vloeistofstroming werd het gebruikt voor het doen van voorspellingen over de effecten van lange termijn toediening van opgeloste fosfaatverbindingen aan de bodem (hoofdstuk 6). Omdat er voor dit doel lange rekentijden nodig waren met dit model werden speciale voorzieningen getroffen die een verkorting van de rekentijd tot gevolg hadden.

De betrouwbaarheid van het model voor het doen van lange termijn voorspellingen werd getoetst door een vergelijking met gegevens afkomstig van de vloeivelden. Voor dit doel werd de verdeling van het geaccumuleerde fosfaat in de bevloeide grond vergeleken met de berekende verdeling nadat een vergelijkbare hoeveelheid fosfaat was doorgespoeld als in de bevloeide grond aanwezig was als (Al + Fe)-gebonden fosfaat. Deze hoeveelheid was gelijk aan 4460 kg P/ha; het werd toegediend in afzonderlijke porties van 19.6 kg P/ha in de vorm van een oplossing die 9.8 mg P per liter bevatte. Er werd een systeem gehanteerd van 10 toedieningen per jaar, hetwelk overeenkomt met de normale praktijk van bevloeiing. De overeenstemming tussen de twee groepen van gegevens was vanuit een practisch oogpunt bezien goed; het geaccumuleerde fosfaat was voornamelijk aanwezig in de bovenste 30 cm van het profiel met zeer weinig inspoeling in diepere lagen. Indien de resultaten werden bekeken op een meer gedetailleerde schaal bleek dat in de vloeiveldgrond het verdelingsprofiel een grotere spreiding vertoonde dan in het berekende profiel, zeer waarschijnlijk omdat de dispersieve eigenschappen van de vloeiveldgrond niet gelijk waren aan die in het model, waar slechts één-dimensionale stroming werd verondersteld. Het bleek dat het neerwaarts transport van fosfaat slechts weinig gevoelig was voor een halvering van de snelheidsconstanten, ook het verdubbelen van de jaarlijkse fosfaat gift had weinig effect op de diepte van indringing.

Een grond waarvan de capaciteit om fosfaat vast te leggen gedeeltelijk was gevuld, werd gebruikt om het effect van toedieningsregime, grootte van de gift, verschillende instroomfluxen en gereduceerde waarden van de snelheidsconstanten te testen. Om het effect van deze behandelingen te kunnen kwantificeren werden vergeleken de hoeveelheden fosfaat die inspoelden in de laag beneden 50 cm en de uitspoelingsverliezen op een diepte van 1 meter. De totale hoeveelheid fosfaat die werd toegediend was in alle gevallen juist gelijk aan de hoeveelheid die nog in de bovenste 50 cm kon worden vastgelegd. Het bleek dat een vergroting van de jaarlijkse gift van 196 to 780 kg P/ha weinig effect had op de inspoeling beneden de 50 cm bij verschillende systemen van toediening. Het zelfde geringe effect werd geconstateerd bij een vergroting van de instroomflux van 10 to 50 cm/day. Een reductie van de snelheidsconstanten k_1 en

k_2 tot beneden de 10% van hun oorspronkelijke waarde had een forse toename van de inspoeling op grotere diepte tot gevolg en leidde tot een hogere uitspoeling. Een reductie van de snelheidsconstante k_n' tot minder dan de helft van zijn oorspronkelijke waarde leidde eveneens tot een aanzienlijke toename van de inspoeling op grotere diepte. Uit deze berekeningen volgt dat de frequentie en grootte van de gift afvalwater zoals die op de vloeivelden van Tilburg wordt toegepast een effectieve verwijdering van fosfaat uit het afvalwater garandeert. Van speciaal belang hierbij is dat tussen twee giften afvalwater voldoende tijd wordt gelaten om het geadsorbeerde fosfaat in een weinig reactieve vorm om te zetten temeer daar deze omzetting tevens resulteert in het (schijnbaar) opnieuw beschikbaar komen van adsorptieplaatsen. Dit laatste is van belang omdat hierdoor in eerste instantie het fosfaat gebonden kan worden gedurende de relatief korte verblijftijd van het water in de bodem.

Tenslotte is het model gebruikt om grenzen vast te stellen voor een toedieningsregime. Uit deze berekeningen bleek dat de indringingsdiepte van het fosfaat in de bodem te beheersen is op basis van (a) de grootte van de enkele gift in relatie tot de capaciteit van de (snelle) adsorptie in de 'pools' X_1 en X_2 en (b) de wachttijd tussen twee giften. Vanzelfsprekend kan niet meer fosfaat worden toegediend dan overeenkomt met het vastleggend vermogen van de gekozen laag.

CURRICULUM VITAE

De auteur werd op 9 december 1940 te Elspeet geboren. Na het behalen van het diploma HBS-B aan het Christelijk Lyceum te Harderwijk in 1958 werkte hij als analist.

In 1965 begon de auteur zijn studie aan de Landbouwhogeschool te Wageningen. Gedurende zijn studie bleef hij voor een halve dagtaak verbonden aan het Instituut voor Toepassing van Atoomenergie in de Landbouw (ITAL) te Wageningen.

Het kandidaatsexamen werd in april 1969 afgelegd en in juni 1971 studeerde hij af in de richting bodemkunde en bemestingsleer met als (verzwaard) hoofdvak de algemene bodemkunde en bemestingsleer en als bijvakken de wiskunde en de theoretische teeltkunde.

Na zijn afstuderen bleef hij aan het ITAL verbonden tot februari 1972. Vanaf die datum trad hij als wetenschappelijk medewerker in dienst van de vakgroep Bodemkunde en Bemestingsleer. Binnen de vakgroep geeft betrokkene onderwijs op het gebied van de bodemscheikunde en verricht hij onderzoek naar transport en accumulatieverschijnselen van fosfaat in de bodem.

Gedurende de jaren 1974 tot en met 1977 is het hier gepubliceerde onderzoek medegefinancierd door de Commissie Hinderpreventie Veeteeltbedrijven.