

TRANSPORT AND FIXATION OF PHOSPHATE IN ACID, HOMOGENEOUS SOILS

III. EXPERIMENTAL CASE STUDY OF ACID, SANDY SOIL COLUMNS HEAVILY TREATED WITH PIG SLURRY

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ABSTRACT

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A computer simulation model of the migration of orthophosphate in soils was applied to undisturbed soil columns treated with amounts of pig slurry up to the equivalent of 1000 t of wet slurry per ha. The kinetic parameters and adsorption data necessary in filling in the model were obtained from long-term batch phosphate fixation experiments. Computer simulation predicted a somewhat greater mobility of phosphate than was found in soil columns. The causes of this discrepancy are discussed. The necessity of taking into account the mineralisation of organic phosphorus is shown. The direct contribution of organic P in pig slurry to P-mobility in the soil was found to be negligible.

INTRODUCTION

In previous papers (Raats et al., 1982; De Willigen et al., 1982) a physico-mathematical model was formulated and simulation of orthophosphate mobility in soils was explored and exemplified with hypothetical situations. In this paper orthophosphate migration in an acid, sandy soil is simulated by computer and compared with soil column studies with pig slurry as the source of phosphorus.

Acid, sandy soils are of particular interest in The Netherlands as excessive amounts of phosphorus are released upon them in the form of animal wastes. In order to simulate the migration of orthophosphate in these soils, at least an empirical description of the mechanisms of fixation is required. Inorganic phosphorus when added to the soil as orthophosphate is not sorbed by the soil to an equilibrium value immediately. Various compartmental models have been assumed to describe this phenomenon. The relevant literature is discussed in some detail in Part I. As in Parts I and II, the total mobile ortho-

phosphate above a certain equilibrium level is taken to be the "driving force" in immobilising phosphate, as expressed in equation (3) below.

MATERIALS AND METHODS

Long-term phosphate fixation was studied, for which 1-l wide-necked polythene flasks were used containing 250 g air dry soil and 500 ml solution phase. The flasks were mounted in an overhead shaker and shaken continuously up to 80 days at 10 rev/min. Prior to sampling, the flasks were centrifuged at 300 *g* for 1 h after which 50 ml was withdrawn and centrifuged at 40,000 *g* for 45 min. Ortho-P was measured following Murphy and Riley (1962). Soil inorganic P was determined after extraction and soil organic P was determined as the difference between total P and inorganic P (Salomons and Gerritse, 1981). The volume of solution in the flask was then restored with 50 ml solution made up to the same P, Na, Ca, K contents as the solution in the flask. In this way a reasonably constant soil/solution ratio and solution composition was maintained, while the P concentration was affected as little as possible. All operations were done at ambient temperature (20°C). The flasks were aerated weekly. The long-term phosphate fixation experiments were done with initial phosphate solutions containing 5 ppm and 50 ppm P as ortho-P and total background electrolyte levels of 0.00035 *M* and 0.0035 *M* Ca+Na+K chlorides, respectively (molar ratio of Ca+Na+K in each case was 3:2:2), and corresponding blanks. The soil used was a "haarpodzol" sampled from the Ap horizon (0–19 cm) which had been stored in a polythene bag at 2°C for over a year. Characteristics of the soil are given in Table I. Twenty-four-hour adsorption isotherms were determined under similar experimental conditions except that 30 g soil and 60 ml solution phase were used.

In this soil five undisturbed soil columns of 90 cm length were cored, for which the method of Bannink et al. (1977) was followed. The top 2 cm of the respective soil columns was mixed with 0, 20, 40, 60, and 80 g freeze-dried pig slurry, equivalent to doses of pig slurry of 0, 250, 500, 750, and 1000 t ha⁻¹. Analysis data of the pig slurry are given in Table II. Rainfall

TABLE I

Reclaimed "haarpodzol" — soil data

Horizon	Ap (0–19 cm)
pH-KCl	4.2
Sand	89.7%
Organic matter	5.3%
Fe	0.027 mol kg ⁻¹
Al	0.115 mol kg ⁻¹
Total P	0.021 mol kg ⁻¹
Inorganic P	0.014 mol kg ⁻¹

TABLE II

Analysis data for pig slurry

Dry matter	6.9%	(83.6% after freeze-drying)
organic matter	69.4%	
total P	2.40%	
inorganic P	1.96%	
organic N	1.64%	
In solution:		
total P	0.20%	
inorganic P	0.18%	
organic N	0.26%	
NH ₄ -N	8.7%	
chloride	2.36%	
pH	8.3	

was simulated at a rate of between 5 and 10 mm day⁻¹ using a solution of 0.00015 M CaCl, 0.0001 M NaCl and 0.0001 M KCl in water. After about 16 months the experiment was stopped and the soil columns were segmented and analysed. Computer calculations were done with CSMP modelling language. Details of the model are given in Part II.

RESULTS AND DISCUSSION

At slurry doses higher than 40 g (\approx 500 t ha⁻¹) the columns became anaerobic and temporarily impermeable due to formation of a gaseous layer below the surface. The time during which the columns remained anaerobic varied from 0 (0-, 20- and 40-g dose) to 4 months (60-g dose) and 6 months (80-g dose). Just before the onset of anaerobic conditions, concentrations of C₂-, C₃- and C₄-fatty acids peaked in the effluents and then quickly decreased. Maximum total concentrations reached were 0.015 M (60-g dose) and 0.035 M (80-g dose), 90% of which was due to acetic acid. The dispersion in the columns was calculated from the breakthrough of chloride in the column effluents. The effect of flow rate on this dispersion was investigated in the range of 0.1–1 cm day⁻¹. Results are shown in Fig. 1, from which a flow-independent dispersion length of 2–3 cm can be found. This justifies the use of equation (6) in Part I.

In Fig. 2, 24-h adsorption isotherms of phosphate in the podzol topsoil are shown. The isotherms are relative to the initial conditions, giving the increase of phosphate in the solid phase as a function of the increase of the phosphate solution concentration. Increasing ionic strength increased adsorption of phosphate. This was probably partly due to an accompanying drop in pH from 4.9 to 4.8. The long-term phosphate fixation data were processed as follows. First the differential 24-h adsorption isotherms of Fig. 2 were

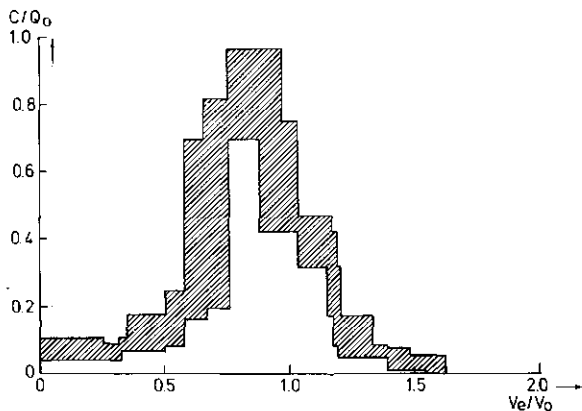


Fig. 1. Range of breakthrough curves for chloride in the effluents of 10 columns of a sandy soil at infiltration rates varying between 0.1 and 1 cm day⁻¹.

C = chloride concentration in effluent (mg l⁻¹).

Q_0 = total amount of chloride brought onto the column in pig slurry (= 260 mg).

V_e = total volume of collected effluent (l).

V_0 = pore volume of soil column (2.5–2.7 l).

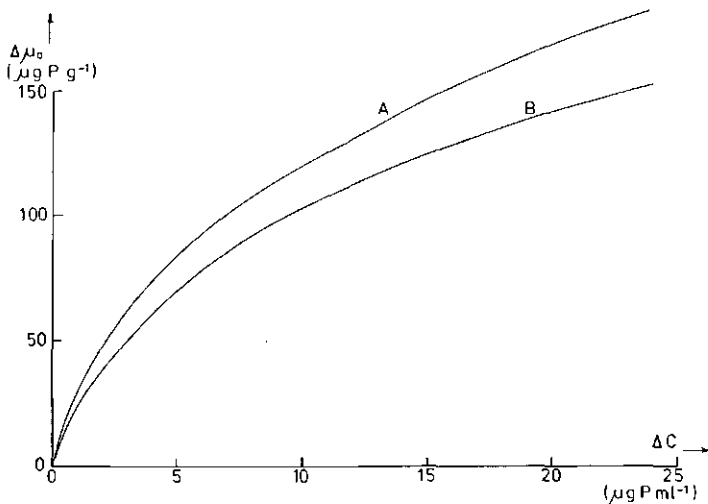


Fig. 2. Relative adsorption isotherms measured for phosphate in a soil system consisting of 26.1 g dry "haarpodzol" soil and 63.9 g water. The added water contained 0.0035 M (A) or 0.00035 M (B) Ca + Na + K chloride in the molar ratio 3 : 2 : 2. The data were obtained after 24 h equilibration. ΔC is the increase in adsorbed phosphate and $\Delta\mu_a$ the accompanying increase in the solution concentration of ortho-P.

fitted to a Langmuir function for the range $\Delta C < 1 \mu\text{g ml}^{-1}$ for orthophosphate in solution. Now an absolute isotherm giving the total amount of ortho-P adsorbed after 24 h (μ_a) as a function of the concentration of ortho-P in solution (C) could be constructed. Total mobile phosphate (μ) after 24 h

was then found from:

$$\mu = \mu_a + \theta * C \quad (1)$$

θ being the water content of the phase system per g or cm^3 , depending on how equation (1) is used in further calculations.

The change in total mobile phosphate (μ) as found from the long-term phosphate fixation data is assumed to be represented by a rate equation:

$$\text{RIM} = \frac{\delta \mu}{\delta t} = (1 - \sigma/\sigma_\infty) * K * (\mu - \mu_e) \quad (2)$$

in which: RIM = rate of immobilisation ($\mu\text{g g}^{-1} \text{day}^{-1}$); $1 - \sigma/\sigma_\infty$ = reduction factor, equal to the fraction of initially available Al + Fe not occupied by phosphate; K = rate constant (day^{-1}); μ_e = equilibrium value of μ at $t \rightarrow \infty$ ($\mu\text{g g}^{-1}$); t = time (days).

σ can be safely taken as zero for the conditions of the long-term fixation experiments. Equation (2) can be integrated to:

$$\ln(\mu - \mu_e) = K * t + \text{constant} \quad (3)$$

Plots of the long-term phosphate fixation data according to equation (3) are given in Fig. 3. μ_e is found by trial and error, assuming that all plots should have the same slope. The best fit was obtained with $\mu_e = 17 \mu\text{g P g}^{-1}$.

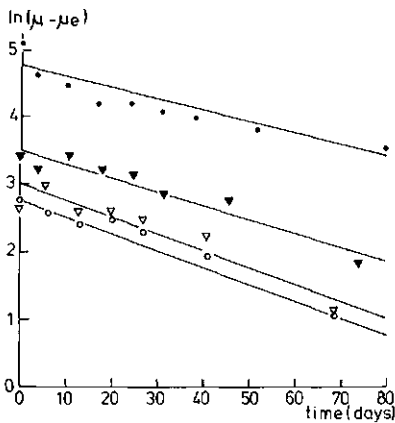


Fig. 3. Change of mobile orthophosphate with time for a "haarpodzol" topsoil. 250 g air-dry soil was shaken with 500 ml water containing:

in 0.0035 M Ca + Na + K chloride (3 : 2 : 2)

●, 50 ppm ortho-P

○, 0 ppm ortho-P

in 0.00035 M Ca + Na + K chloride (3 : 2 : 2)

▼, 5 ppm ortho-P

▽, 0 ppm ortho-P.

μ = total mobile orthophosphate.

μ_e = equilibrium value for $t \rightarrow \infty$.

The corresponding half-life time is 40 days (SD = 10%). It may be concluded that the calculation procedure and use of equation (3) describes the time course of the fixation of phosphate adequately. If the immobilisation reaction of phosphate is assumed to take place in the solid phase only, equation (2) should be written as (σ put at zero):

$$\text{RIM} = \frac{\delta \mu}{\delta t} = K * (\mu_a - \mu_{ae}) \quad (4)$$

By substituting (1) into (4) and integrating numerically, the rate constant K can be found. μ_{ae} is estimated by trial and error, assuming that in cases concerning one soil, the same rate constant (K) should result. In this way μ_{ae} was found to be $15 \mu\text{g P g}^{-1}$ with a rate constant of 0.02 day^{-1} (= half-life time of $\ln 2/0.02 = 35$ days).

Applying the above results to column studies, the results obtained using (3) were fitted to the computer simulation model described in Part II. Because pig slurry is considered here as a source of phosphorus, some extra points need consideration. In a pig slurry inorganic P is mainly present as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Gerritse and Eksteen, 1978).

To account for this in the simulation model the maximum solubility of added phosphate was put at $500 \mu\text{g P ml}^{-1}$ as a rough estimate. However, neglecting this and taking all added phosphate as initially mobile phosphate (PM) made no difference over the time span considered. Among other elements, Ca, Fe and Al are added with the slurry and will increase the fixation capacity of the soil for phosphorus. As the soil considered here is acidic, the effect of calcium may be neglected. With each ml of the pig slurry used in our experiments about $100\text{--}200 \mu\text{g Fe + Al}$ are added to the soil column.

This gives an increase of $500\text{--}1000 \mu\text{g cm}^{-3}$ Fe + Al in the top 2 cm of soil with the highest addition of pig slurry (80 g). In the soil itself (Table I) the Fe + Al content is about $6000 \mu\text{g cm}^{-3}$.

In the simulation model used here 20% of Fe + Al in the soil was taken to be available for fixation. It can then be said that with the highest addition of pig slurry the fixation capacity of the soil is almost doubled if Fe + Al added with slurry are taken to be completely available for phosphate fixation.

Another important parameter is pH. Even at the highest addition of slurry only a slight increase of pH in the topsoil was detected at the end of the experiment. Temporary large fluctuations in pH through nitrification or anoxic conditions are however possible. Also alternating anaerobic and aerobic conditions may greatly enhance phosphate fixation in soils due to oxidative precipitation of Fe-oxides with a large specific surface area (Fischer and Baumann, 1980). In the simulation model pH was assumed to be constant and the effect of anaerobic conditions was neglected.

In the effluents of the soil columns the inorganic phosphate concentrations ranged from 0.001 to $0.1 \mu\text{g P ml}^{-1}$, averaging $0.01 \mu\text{g P ml}^{-1}$. From the data of the long-term phosphate fixation experiment an equilibrium concentration of $0.3\text{--}0.4 \mu\text{g P ml}^{-1}$ in the soil solution was estimated for the top soil.

Results of the computer simulations are shown in Figs. 4, 5, 6 and 7. In

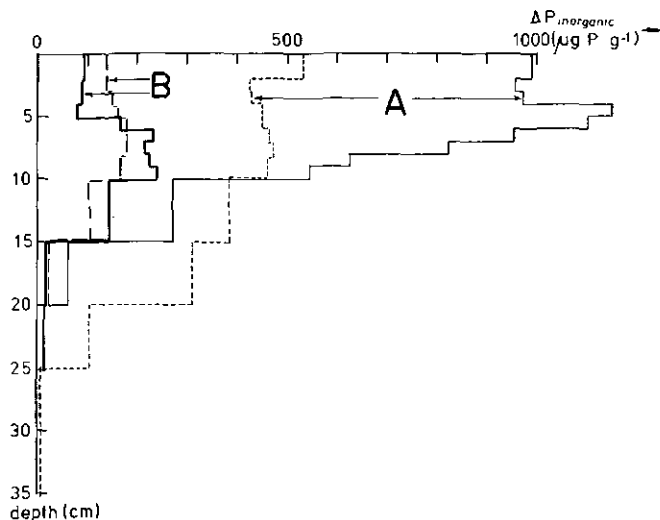


Fig. 4. The increase of inorganic P in the soil profile after adding 80 g (A) and 20 g (B) of freeze-dried pig slurry through the top 2 cm ($\approx 225 \text{ cm}^3$) of a "haarpodzol" soil column and simulating a rainfall of 2150 mm over 16 months (A) or 3600 mm in 12 months (B); 16.4 mg inorganic P and 3.7 mg organic P were added with each g of dried slurry. Solid lines represent the actual situation. Dashed lines were computer-calculated for similar conditions, considering inorganic P only and assuming it to behave as ortho-P.

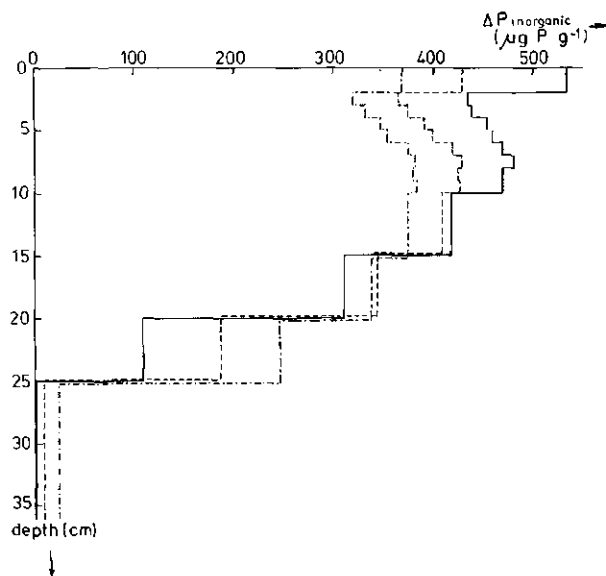


Fig. 5. The computed increase of inorganic P in the soil profile for various equilibrium soil concentrations of ortho-P. Simulation conditions are as described in Fig. 4 for situation A. Solution ortho-P at equilibrium, C_e :

- , $0.001 \text{ mg P l}^{-1}$
- - -, 0.1 mg P l^{-1}
- · - ·, 0.35 mg P l^{-1} .

Fig. 4 results for the soil column experiments with the highest dose and lowest dose of pig slurry are compared after eluting nine pore volumes. Only the distribution of *added inorganic P* is shown. The solid lines represent the actual distribution in the profile. The dashed lines represent the computed profile distribution of added inorganic P, assuming a half-life time of 35 days and an equilibrium solution concentration of $0.001 \mu\text{g P ml}^{-1}$. In Fig. 5 profile distributions of added inorganic P computed at equilibrium soil solution concentrations of 0.001, 0.1 and $0.35 \mu\text{g P ml}^{-1}$ are compared. As can be expected, increasing equilibrium concentration decreases the rate of immobilisation and results in a wider profile distribution and slightly, deeper total penetration. In Fig. 6 the effect of varying the half-life time is shown. Agreement with the practical situation is better when a shorter half-life time is used than was found from the batch experiments. In Fig. 7 profile distributions of the increase of inorganic P are shown for the case of the highest addition of pig slurry (80 g) after eluting 14 pore volumes. The slurry dose had now however been mixed through the top 10 cm of the soil column instead of the top 2 cm. No anoxic conditions resulted.

Computer simulation of phosphate mobility as done here predicts a some-

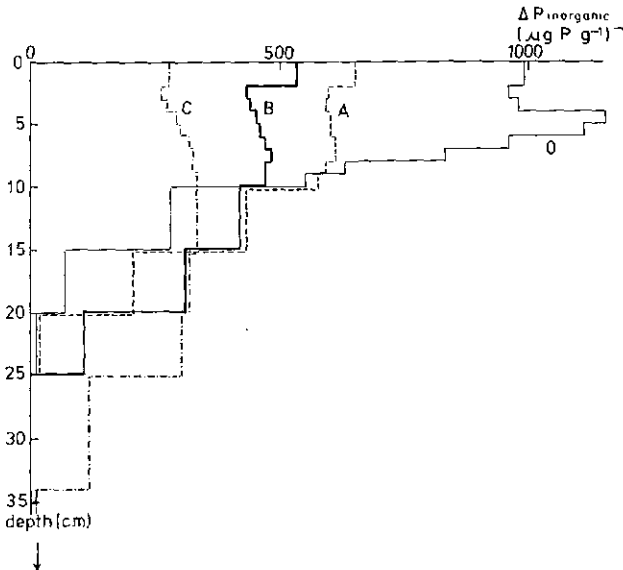


Fig. 6. The computed increase of inorganic P in a "haarpodzol" soil column profile after adding 80 g freeze-dried pig slurry through the top 2 cm ($\approx 225 \text{ cm}^3$) of the soil column and simulating a rainfall of 2150 mm over 16 months; with each g of slurry, 16.4 mg inorganic P and 3.7 mg organic P were added to the soil column.

O, practical situation after 16 months

A, computed profile for $K = 0.035 \text{ day}^{-1}$

B, computed profile for $K = 0.02 \text{ day}^{-1}$

C, computed profile for $K = 0.01 \text{ day}^{-1}$

C_e (solution ortho-P at equilibrium) was taken to be $0.001 \text{ mg P l}^{-1}$.

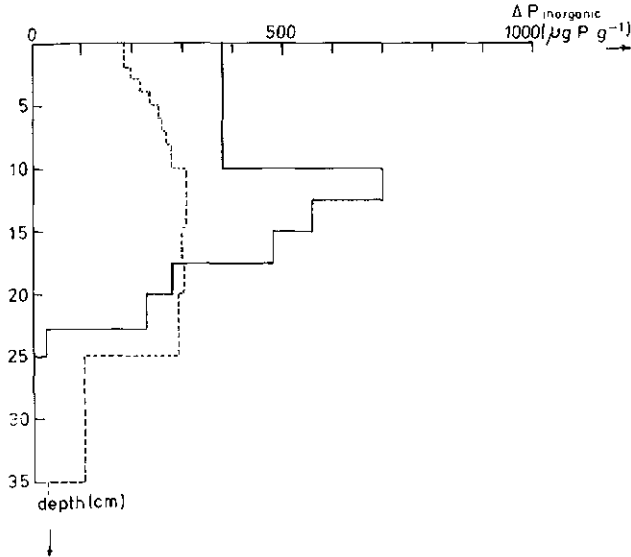


Fig. 7. Increase of inorganic P in a "haarpodzol" soil column profile after adding 80 g freeze-dried pig slurry through the top 10 cm ($\approx 1100 \text{ cm}^3$) and simulating a rainfall of 3600 mm in 12 months; 15.3 mg inorganic P and 3.2 mg organic P was added with each g of dried slurry. The solid line represents the actual situation after 12 months and the dashed line is computer-calculated for similar conditions, considering inorganic P only and assuming it to behave as ortho-P.

what greater infiltration of phosphorus than is met in practice. This may be due to various factors (pH, Eh, competitive adsorption, effective surface area, etc.) that effect both the adsorption isotherm and adsorption kinetics. Another factor is the possible large fixation of phosphorus in microbial biomass under the eutrophic conditions used. As long as these effects cannot be adequately quantified, a closer agreement between practice and model prediction is not very likely.

TABLE III

Distribution of phosphorus among organic and inorganic phosphorus compounds in pig slurry; 10 slurries were analysed; dry matter content ranged from 5 to 10% and time of storage from 1 to 6 months

	P content (% of dry matter)	Average of total P (%)
Total inorganic P	1.5—2	85
Total organic P	0.2—0.3	15
Inorganic P in solution	0.01—0.2	5
P in inositol hexaphosphates (IHP)	0.01—0.1	2
P in microorganisms	0.02—0.04	1.5
P in adenosine-5-triphosphate (ATP)	0.000—0.1	1
Organic P in solution	0.01—0.03	1

Differences in area covered by the actual inorganic-P profile and the computed profile must be ascribed to column heterogeneity and to organic phosphorus. Organic P is mineralised during the column experiment and this adds to the increase in inorganic P found in the profile. Pig slurry contains both organic and inorganic P (Table II) while in the computer simulation of the soil columns only inorganic P was considered. In Table III the distribu-

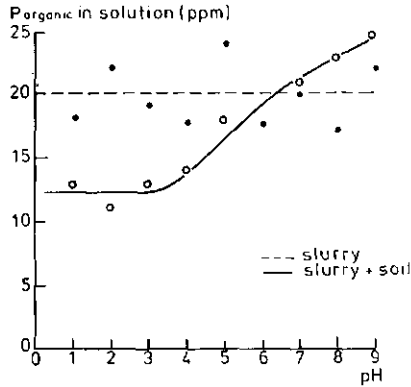


Fig. 8. Adsorption of organic P from pig slurry solution to soil; 10 g of a "haarpodzol" soil was shaken 24 h with 40 ml of pig slurry solution. The slurry solution was obtained from pig slurry after centrifuging 1 h at 40,000 g.

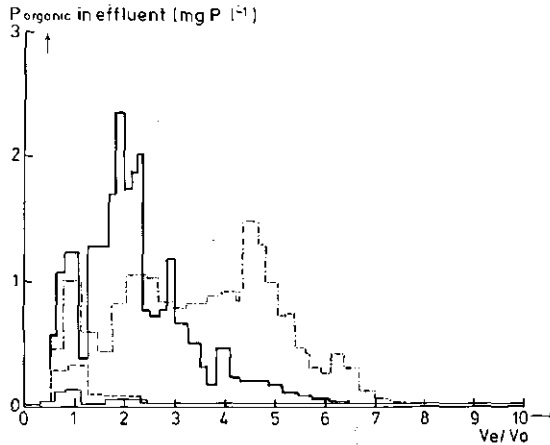


Fig. 9. Concentration of organic P in the effluents of a series of "haarpodzol" soil columns. The soil columns had been treated with freeze-dried pig slurry (mixed through the top 2 cm \approx 225 cm³) at an amount of:

- , 20 g
- - -, 40 g
- , 60 g
- · - ·, 80 g

Rainfall was simulated at about 1 cm day⁻¹;

V_e = total volume of collected effluent (l).

V_o = water-filled pore volume of soil columns (2.5–2.7 l).

tion of phosphorus in various inorganic and organic fractions is shown. An estimate of the amount of organic P mineralized during the soil column experiments was difficult to make due to soil heterogeneity. From tracer studies with ^{32}P it is known that all organically bound P in pig slurry is cycled microbially and thus in principle is completely bio-degradable (Gerritse and Zugec, 1977).

Of course phosphorus mobility in soils will not only be due to inorganic P. More often than not the greater part of phosphorus in the soil solution as well as in the soil (Gerritse, 1978, 1981) consists of organically bound phosphorus. In pig slurry only a small part of organic phosphorus is in solution, roughly 10–20 mg P per litre slurry or (Table III) 5–10% of total organic P. This soluble organic P is of microbial origin and of high molecular weight (Gerritse and Zugec, 1977; Gerritse and Eksteen, 1978). It is also only weakly adsorbed to the soil (Fig. 8). Only at very high doses of pig slurry does this fraction however appear to migrate through the soil rapidly (Fig. 9).

Summarizing it may be concluded that mobility of phosphorus added with animal wastes can best be described by considering all added P as ortho-P. On this basis modern computer simulation techniques will give an estimation of the build-up of phosphorus in a soil profile.

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