Phosphate losses on four grassland plots used for dairy farming

Measured phosphate losses and calibration of the model ANIMO

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ABSTRACT

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Changes in phosphate concentrations and pools were measured at four experimental plots from 1997-1999. The plots received P surpluses of 0. 10 and 20 kg ha⁻¹a⁻¹ P. Significant changes in the phosphate pools were not yet found. Phosphate concentrations, phosphate budgets and changes in phosphate pools were simulated with the nutrient model ANIMO in combination with the hydrological model SWAP. The model simulated the order of magnitude of the measured concentrations and Pw values quite well, although the temporary fluctuations in ortho-P and organic Pdid not always correspond to the measured values. Overall leaching fluxes were quite well simulated by the model, except for the peat soils where leaching fluxes where overestimated. Leaching fluxes of ortho-P were somewhat overestimated whereas organic P fluxes were lower than measured values. The simulate phosphate balance indicated that on average 0.9 to 3.6 kg ha⁻¹ a⁻¹ P was lost by leaching and runoff. The largest losses were found on the sandy soils, which had the highest P contents in the lower part of the root zone.

Keywords: Phosphorus, phosphate, leaching, P sorption, P fixation, P surplus

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Contents

Prefa	ice	5
Sumr	nary	7
1	Introduction	9
2	Field experiments2.1 Experimental set-up2.2 Characteristics of the sites	11 11 12
3	 Modelling 3.1 The model ANIMO 3.2 Modeling Approach 3.2.1 Vertical and temporal resolution 3.2.2 Spatial variability 3.2.3 Calibration and validation 3.3 Model input 3.3.1 Manure applications 3.3.2 Hydrology 3.3.3 Soil chemical characteristics and parameters 	15 15 16 17 17 18 18 18 18 19
4	 Results 4.1 Observed changes in phosphate contents and concentrations 4.2 Calibration and Validation 4.2.1 Cranendonck 4.2.2 Heino 4.2.3 Waaiboerhoeve 4.2.4 Zegveld 4.3 Overview of phosphate losses on the four plots 	23 23 25 25 30 33 36 39
5	Discussion	43
6	Conclusions	47
Refer	rences	49
	e xes asured Phosphate uptake at the four sites asured Pw values at the sites	53 55

Preface

In this report the results of the first three years of the project 'Phosphate losses on grassland soils' are presented. This project is part of the research program 317 of the Ministry of Agriculture, focussing on nutrient management and losses to groundwater and surface water. The main aim of this project is to obtain more information on the relation between phosphate application, soil properties and phosphate losses and to demonstrate the effect of a reduction in phosphate application on agricultural productivity and soil fertility under field conditions. The project is carried out in close cooperation with the Research Station Cattle, Sheep and Horse Husbandry (PR) and the Nutrient Management Institute (NMI). The progress and results of the project were discussed twice a year in a project group consisting of René Schils (PR), Jantina van Middelkoop (NMI), Dirk-Jan den Boer (NMI), Wim Chardon, Phillip Ehlert, Oscar Schoumans and Caroline van der Salm (Alterra).

This report contains the overall results over the period 1997-1999 with respect to measured changes in the chemical composition of the soil solution and soil solid phase and the calculation of phosphate budgets. However this report could not have been written without the contribution of our partners from PR and NMI, who coordinated the monitoring program and provided us with all the agricultural data. Over the past three years a lot of field and laboratory measurements have taken place. We would like to thank Hans Zweers, Antonie van den Toorn, Jaap Pankow and Delia van Dijk for their efforts to measure the soil chemical and hydrological conditions over the past three years. We would also like to thank Bastiaan Roelofsen and Christel Engelen both students of Rijn IJssel College who contributed to the monitoring program as part of their educational program. Last but not least we would like to mention Harm Everts, Teun Kraak and Klaas Sikkema who coordinated the experiments on the farms and the members of the project group for their contribution to the project.

Summary

In this report the first results of a study on the effects of phosphorous surpluses on the leaching and changes in phosphate status of the soil are presented. To quantify the effects of (a reduction) in phosphate and nitrogen application to grassland soils, a monitoring program has been started in autumn 1996 on four experimental dairy farms in the Netherlands. Two of these farms are located on sandy soils, one on a peat soil and one on a clay soil. At each location, plots have been established that receive a P surplus of 0, 10 and 20 kg ha⁻¹ a⁻¹. At these plots the input and output fluxes of phosphate, the botanical quality of the grass and the changes in phosphate pools in the soil are measured. In this report the results of the first three years of the measurements and a preliminary calibration and validation of the nutrient model ANIMO on the measured data are described.

To obtain output fluxes both meteorological, hydrological and soil solution data have been collected. To calculate hydrological fluxes rainfall has been measured daily at the farms, other meteorological data are obtained from weather stations close to the sites. Groundwater levels have been measured two-weekly at the different plots to validate the hydrological calculations. Soil solution concentrations have been measured three times a year: in early spring before and after the first manure application and in autumn. The soil solution was collected by means of centrifugation using a soil sample collected on 40 randomly selected points at each plot. Samples were collected at four different depth: 0-5, 5-10, 10-20 and 20-30 cm below the surface. Each year in autumn the collected soil samples were also analysed for phosphate pools.

During the first three years of the measurements no significant changes in the phosphate pools were found. This is mainly caused by the large size of the pools compared to the applied phosphate surplus. On basis of the size of the pools, significant changes over the period 1997-1999 may only be expected for the amount of adsorbed P (Q) or in Pw values (water soluble P). However, these changes were obscured by a strong year to year variation in the measured values. Soil solution concentrations also showed a strong temporal variation in measured values. The observed temporal pattern of dips and peak in measured concentrations at the different locations and plots was quite comparable. However, the variation in concentrations could not be explained by differences in environmental conditions.

The hydrological model SWAP and the nutrient model ANIMO were applied to the different plots. The hydrological model simulated the measured groundwater level quite well. ANIMO simulated the order of magnitude of the measured concentrations quite good at all four sites. However, the model could not simulate the measured strong seasonal variation in ortho-P concentrations. Variations in organic P concentrations were somewhat better simulated, but the timing of peaks and tips in the organic P concentrations did not always correspond to the measurements. Simulated leaching fluxes of ortho-P and organic P were close to

measured values at the sandy soils and the clay soils. At the peat soil the simulated leaching fluxes of organic P were higher than measured values. However, measured leaching fluxes of organic P are somewhat uncertain due to the strong temporal variation in organic P concentrations and the limited number (three) of yearly measurements. The simulated Pw values were close to measured data, in particular at the sandy soils. However, the model tended to overestimate the decline in Pw values at the plots with a P surplus of 0 kg ha⁻¹ a⁻¹ and to overestimate the rise in Pw values at plots with a P surplus of 20 kg ha⁻¹ a⁻¹.

Simulated phosphate balances of the upper 30 cm of the soil profile indicate that on average 0.9 to 3.6 kg ha⁻¹ a⁻¹ was lost by leaching and runoff during the period 1997-1999. The largest losses were found on the sandy soils, which have relatively high phosphate contents in the lower part of the topsoil. The simulated storage of P in the topsoil ranged from -5.9 to 24.2 kg ha⁻¹ a⁻¹ and is closely related to the P surplus of the considered plots.

The simulated phosphate balances are still somewhat uncertain due to the fact that the measurement period on which the model could be validated was rather short and the measurement frequency of the soil solution concentrations was relatively low. Moreover, simulated losses of phosphate from the different solid phase pools could not yet be validated due to the fact that significant changes in these pools were not yet detected. Preliminary calculation also showed that the distribution of cow droppings across the field has a significant influence on the simulated storage of P in the soil solid phase. However, the effect of cow droppings on the simulated leaching of phosphorous appears to be rather limited.

On basis of the above results it may be concluded that the available data provide the opportunity to give a rather reliable quantification of the actual leaching fluxes. However, large uncertainty remains with respect to the storage of P in different solid phase pools and thus with respect to the long-term leaching of phosphorous from the soils. To decrease this uncertainty the monitoring project need to be continued over a longer time period of time to find significant changes in phosphorous pools in the soil. Moreover, more information is needed on the seasonal changes in both ortho-P and organic P concentrations to validate the process formulation for phosphorous and to improve the estimated leaching fluxes. To obtain these data the frequency of the soil solution need to be increased. Finally, a number of aspects in the model application need to be considered in more detail. In particular attention should be paid to the impact of heterogeneity in both the soil solid phase (adsorption capacity, degree of phosphate saturation) and in the manure application (cow droppings) and to the modeled seasonal changes in phosphate concentrations.

1 Introduction

Excessive use of manure in agriculture has led to high levels of nitrogen and phosphate in the soil and losses of nutrients to groundwater and surface water (e.g. Miller, 1979; Wadman et al., 1987; Sharpley and Rekolainen, 1997). Losses of nutrients to groundwater may cause a decline in drinking water quality or an increase in the costs of purification, whereas high nutrient losses to surface water may lead to eutrophication. To avoid these adverse effects the policy of the Dutch government is to reduce the use of manure and fertilizers to acceptable levels.

To formulate reduction plans for manure applications in farming systems insight into the acceptable losses to the environment and the effect of a reduction in manure application on soil fertility is essential. A preliminary study, initiated by the Dutch Ministry of Agriculture in 1995, indicated that a lot of uncertainty exists on the magnitude of the surplus necessary to maintain a constant soil P test value (Oenema and Van Dijk, 1996). Moreover, a large gap exists between the acceptable losses to the environment (0.5 kg ha⁻¹ a⁻¹ P) and the present surpluses on fertile soils (10-20 kg ha⁻¹ a⁻¹ P). To improve the scientific basis of the reduction plans, additional research has been started. The main aim of this research is to obtain additional data on phosphate losses and it's effect on soil fertility under field conditions. The obtained data are indispensable to validate existing models that simulate the losses of nutrients to the environment and changes in soil fertility. These validated simulation models may be used to obtain insight in the long-term effect of a reduction in the use of manure and fertilizers on soil fertility and ground water and surface water quality.

The main aim of this study is to quantify the effects of a reduction in phosphate application on grassland sites used for dairy farming. In the autumn of 1996 experiments have been started on four grassland sites. Two of these sites are located on sandy soils, one on peat soil and one on a clay soil. On each location plots were established that received a phosphate surplus of 0, 10 and 20 kg ha⁻¹ a⁻¹ P. In this report the results of the first three years of the measurements and a preliminary calibration and validation of the nutrient model ANIMO (Groenendijk and Kroes, 1997) on the measured data are described. A thorough validation of the model is not yet possible, due to the small changes in solid phase phosphate pools combined with a relatively high temporal and spatial variability. Therefore the main aims of this report are: (i) to investigate the possibilities to calibrate ANIMO on the measured results, (ii) to indicate the limitations of the present data set and to suggest improvements and (iii) to give a first indications of the losses of phosphate.

2 Field experiments

2.1 Experimental set-up

To obtain information on the effects of reduction in phosphate and nitrogen application to grassland soils used for dairy farming, experiments have been started in autumn 1996 on four experimental farms in the Netherlands (Fig. 1). Two farms were located (Cranendonck and Heino) on well drained sandy soils, one on a shallow drained peat soil (Zegveld) and one on a well drained marine clay deposit (Waaiboerhoeve). On each farm six plots were established receiving different amounts of nitrogen and phosphate. The applied phosphate surplus (P application – P harvest) amounted to 0, 10 or 20 kg ha⁻¹ a⁻¹ P (annotated as P0, P10 and P20). These levels were chosen because they cover the range between the environmentally acceptable phosphate surplus (negligible P loss) and the present agricultural practice (20 kg ha⁻¹ a⁻¹ P). A surplus of 10 kg ha⁻¹ a⁻¹ P equals the acceptable phosphate surplus level for 2008 as proposed by the Dutch government in 1996. These phosphate levels were combined with nitrogen surpluses of 180 and 300 kg ha⁻¹ a⁻¹ N (N180, N300), which correspond to respectively the intended levels for 2008 and the present agricultural practice. Recently, lower values for the allowable nitrogen surplus have been proposed for sandy soil (140 kg ha⁻¹ a⁻¹ N) and the year of introduction of these lower surpluses has been accelerated to 2003.

The plots were managed in such a way that difference between the experimental situation and the normal agricultural practice on dairy farms was minimal. Therefore the grass on the plots was alternately grazed and harvested. To achieve the desired N and P surpluses both liquid manure and fertilizers were used. The actual surpluses were calculated at the end of each year from the total N and P application, the weight increase of the cows and the amount of grass removed by harvesting.

At the start of the experiment, in autumn 1996, soil samples were taken from each plot at a depth of 0-5 cm, 5-10 cm, 10-20 cm and 20-30 cm. To obtain a soil sample that represents the average condition of the plot, each plot was divided in 40 rectangles. In each rectangle a subsample was taken on a randomly selected point. The samples were analyzed for texture, carbon and nitrogen content, pH, total P, organic P (derived from total-P with and without oxidation), oxalate extractable Al, Fe and P and the P status. P status was measured using two different methods: (i) by water extraction (Pw; Sissingh, 1971) which can be directly linked to the phosphate concentration in the soil solution (Schoumans and Groenendijk, 2000) and (ii) by extraction with ammoniumlactate-acidic acid solution (P-AL; Egnér et al., 1960) a method that is commonly used in the Netherlands for grassland. Each year this sampling procedure was repeated to monitor changes in composition of the soil solid phase.

Soil solution concentrations were measured on the plots with a N surplus of 180 kg $ha^{-1}a^{-1}$ and a P surplus of 0 and 10 kg $ha^{-1}a^{-1}$ and on the plots with a N surplus of 300

kg $ha^{\cdot 1}a^{\cdot 1}$ and a P surplus of 20 kg $ha^{\cdot 1}a^{\cdot 1}$. The soil solution was obtained by centrifugation of soil samples that were collected using the same procedure (and the same depth) as used for sampling the soil solid phase. Measurements were carried out twice in early spring, before and after the first manure application, and in autumn. The advantage of this method compared to the use of lysimeter cups is that a field average concentration can be easily obtained. However, the method can only be applied with a limited frequency because of the destructive nature of the measurements. Finally, centrifugation may lead to slightly different concentrations due to the fact that gravitational forces put onto the samples are higher compared to the suction applied by the cups. A limited comparison of the composition of soil solutions on a number of plots indicated that these differences are probably small. Changes in soil solution concentrations and soil solid phase of the deeper soil layers (> 30 cm) are not considered in this study. This choice has been made because the largest changes in phosphate contents occur in the topsoil and these changes are most relevant in an agricultural perspective. Furthermore, losses from the plough layer (root zone) to deeper layers can be considered as environmental P losses. Finally, it may be expected that significant changes in the subsoil will not occur during the experiment.

2.2 Characteristics of the sites

The experimental plots at the sites Cranendonck and Heino are located on quite comparable sandy soils. Both soils have low clay contents and a carbon content between 2.0 and 2.5 % (Table 1), although Heino has a much lower silt content (7 %) compared to Cranendonck (approx. 25 %).

Site	Depth		xture	С	Bulk density
	(cm)	(%)	(%)	(kg m ⁻³)
		Clay	Sand		
Cranendonck	5	2	84	2.5	1132
	10	-	-	2.4	1430
	20	-	-	2.3	1448
	30	-	-	2.1	1399
Heino	5	3	83	2.5	1174
	10	-	-	2.0	1454
	20	-	-	2.1	1442
	30	-	-	1.6	1463
Waaiboerhoeve	5	20	26	3.8	1184
	10	-	-	2.1	1492
	20	-	-	2.1	1460
	30	-	-	1.8	1421
Zegveld	5	23	9	27.4	355
-	10	-	-	26.0	510
	20	-	-	23.5	447
	30	-	-	26.2	282

Table 1 General characteristics of the soils at the four experimental sites

Larger differences can be found in the subsoil: the soil at Cranendonck has a rather thick topsoil (40-60 cm thick) with a high carbon content (> 1.0 %), whereas the

topsoil at Heino is only 30 cm thick. The plots at Cranendonck are slightly better drained (groundwater level between 40 and 150 cm below the surface during the measurement period) compared to Heino (groundwater level between 20 and 130 cm). The amount of phosphate (Table 2) in the topsoil in Heino is slightly higher then in Cranendonck (higher P_{tot} , P-AL and a higher degree of phosphate saturation as expressed by the $P_{ox}/(Al+Fe)_{ox}$). The amount of water-extractable P (adsorbed P) are quite comparable.

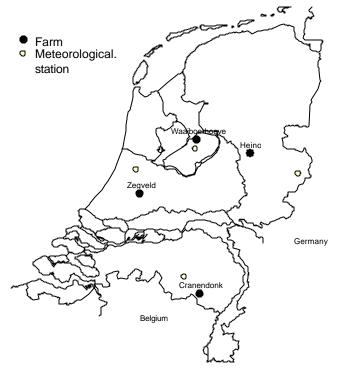


Fig. 1 Geographical location of the four experimental farms and the nearest meteorological station

The plots at the Waaiboerhoeve site are located on light textured (clay loam) marine clay soils. The ground water table generally fluctuates between 40 cm and 150 cm below the surface. Occasionally the ground water table reaches the surface after prolonged periods of extremely heavy rainfall (autumn 1998). In contrast to the sandy soils the amount of sorbed phosphate, Pw and P-AL decreases strongly with depth.

The plots at the site Zegveld are situated on a peat soil with a carbon content of approximately 25 % and 23 % clay. The amount of sorbed P is somewhat lower then at the other three locations and decreased strongly with depth in the topsoil.

Table 2 Phosphate pools in the topsoil of the four experimental sites

Site	Depth	(Al+Fe) _{ox}	Pox	P/	Ptot	Pw	P-Al
	•			(Al+Fe) _{ox}			
	(cm)	(mmol)	kg-1)	(-)	kg P ₂ O ₅	mg P ₂ O ₅	mg P ₂ O ₅ (100 g)-1
					ha-1]-1	
Cranendonck	5	71.5	21.3	0.30	152	40	40
	10	78.9	19.6	0.25	135	28	33
	20	82.4	19.7	0.24	141	26	37
	30	82.3	18.9	0.23	113	17	28
Heino	5	59.0	20.2	0.34	177	39	50
	10	66.3	20.7	0.31	152	28	39
	20	57.7	22.7	0.39	151	26	41
	30	60.3	17.8	0.30	132	24	38
Waaiboerhoeve	5	79.1	17.9	0.23	224	51	58
	10	84.9	11.0	0.13	153	19	24
	20	85.5	8.5	0.10	132	11	13
	30	86.9	7.8	0.09	120	8	12
Zegveld	5	279.0	49.6	0.18	615	31	42
-	10	354.4	44.6	0.12	548	15	25
	20	332.6	32.6	0.12	408	6	12
	30	388.6	18.6	0.08	284	4	5

3 Modelling

3.1 The model ANIMO

The impact of the different levels of phosphate application, on the phosphate contents in the solid and liquid phase has been simulated with the model ANIMO (Groenendijk and Kroes, 1997). The ANIMO model is a multi-layer dynamic simulation model, which was originally set up to simulate organic matter and nitrogen related processes in agricultural soils, recently the P cycle has been included in order to describe the fate of phosphate on agricultural land. Phosphate sorption is modeled by assuming a reversible adsorption reaction and an irreversible diffusion (fixation) process. The adsorption of phosphate is described by a Langmuir adsorption equation (Schoumans and Breeuwsma, 1995; Schoumans, 1997):

$$Q = \frac{KcQ_m}{(1+Kc)} \tag{1}$$

where Q is the amount of adsorbed P (mmol kg⁻¹ P), Q_m is the maximum amount of adsorbed P (mmol kg⁻¹ P), c is de phosphate concentration in solution (mg l⁻¹) and K is adsorption constant (l mg⁻¹). The incorporation of phosphate by diffusion is described by a time dependent Freundlich equation taking into account three types of sites with different affinities for phosphate:

$$S = \sum_{i=1}^{n} \left(K_i c^{N_i} - (K_i c^{N_i} - S_{o,i}) e^{-a_i t} \right)$$
(2)

where S is the amount of phosphate sorbed by diffusion (mmol kg⁻¹), K_i is de Freundlich sorption coefficient for site *i* ((mg l⁻¹)^{1/N} mmol kg⁻¹), N_i is the Freundlich exponent for site *i* (-), a_i is diffusion rate constant (d⁻¹) and $S_{a,i}$ is the initial amount of sorbed P for site *i*.

To compare the simulated amounts of adsorbed P with readily available agronomic soil tests, Pw values (mg $P_2O_5 l^{-1}$) were calculated from the amount of adsorbed P using the following equation (Schoumans, 1997; Schoumans and Groenendijk, 2000):

$$P_{W} = \frac{(a_{1} - \sqrt{D}) - (a_{1} + \sqrt{D})t}{2a_{2}(t - 1)} 137.42$$
(3)

where

$$a_{1} = -k_{a} (Q_{m} - Q) - \frac{k_{d} V_{H2O} 10^{-3}}{V_{soil} r_{d}}$$
(4)

$$D = a_1^2 - 4a_2k_dQ \tag{5}$$

$$\boldsymbol{t} = \frac{(2a_2c_1 + a_1 - \sqrt{D})}{(2a_2c_1 + a_1 + \sqrt{D})} e^{\frac{V_{soil}\boldsymbol{r}_d \cdot \sqrt{D}}{V_{H_{2O}} 10^{-3}}}$$
(6)

$$a_{2} = -k_{a} \frac{V_{H20} 10^{-3}}{V_{soil} \boldsymbol{r}_{d}}$$
(7)

$$c_1 = \frac{Q_T}{(36K(Q_m - Q_T))}$$
(8)

with k_a is the adsorption rate constant and k_d is the desorption rate constant (h⁻¹); V_{soil} is the incubated volume of the soil sample (ml); V_{H2O} is the volume of the extractant (ml); \mathbf{r}_d is the dry bulk density of the soil sample (kg m⁻³); *t* is the shaking time after dilution (1 hour) and Q_T is the total amount of phosphate adsorbed and in solution (mmol kg⁻¹).

Immobilization of inorganic P (and mineralisation of organic P) is related to organic matter dynamics in the soil. According to this model, four organic substances are distinguished: fresh organic matter, root exudates, dissolved organic matter and humus (dead soil organic matter and living biomass). The transformation of fresh organic material leads to the formation of a humus/biomass pool (assimilation). Depending on P availability, assimilation efficiency, and C/P ratio of the humus/biomass pool, organic matter transformation processes can result in a net production or net consumption of mineral P.

The hydrological model SWAP (Van Dam et al., 1997) calculates the hydrological fluxes and water contents, used in ANIMO. SWAP is a recent update of the model SWATRE (Belmans et al., 1983). The model calculates soil water movement in the soil matrix by providing a finite difference solution to Richard's equation.

3.2 Modeling Approach

3.2.1 Vertical and temporal resolution

The model ANIMO does not explicitly include a description of diffusion and dispersion of solutes, instead the numerical dispersion induced by the calculation scheme is used. To obtain an appropriate dispersion term a suitable combination of time step and thickness of the soil layers should be chosen. The numerical dispersion induced by the calculation scheme can be calculated as:

$$D_n = \frac{(\Delta z)^2}{t_{res}} \left(\frac{\frac{\Delta t}{t_{res}}}{1 - e^{-\frac{\Delta t}{t_{res}}}} - 0.5 \left(1 + \frac{\Delta t}{t_{res}} \right) \right)$$
(9)

where ? *z* is the thickness of the soil layers, ? *t* is the length of the time step and t_{res} is the residence time of the soil moisture in the considered layer (Groenenberg and Kroes, 1997). The physical dispersion coefficient can be calculated as a function of the dispersion length, the water flux and the water content:

$$D_{disp} = \mathbf{a} \frac{J_w}{\mathbf{q}} \tag{10}$$

where a is the dispersion length (m), Jw is the water flux (m d⁻¹) and ? is the water content (m³ m⁻³). At an average water flux of 200-400 mm a⁻¹, a dispersion length between 0.005 and 0.05 m and a water content of 0.25 m³ m⁻³, the dispersion coefficient ranges between 1 10^{-5} and 2.1 10^{-4} m² d⁻¹. This implies that the thickness of the soil layers in ANIMO should range between 0.5 and 20 cm when using a time step of one day. The use of site specific estimates for the parameters can decrease this range in values. However, the percentage of phosphate lost by leaching in relatively small and the impact of changes in the thickness of the layers on the total P balance will be limited. Therefore we used soil layers of 10 cm and a time step of one day for all sites in this preliminary study.

3.2.2 Spatial variability

Losses of phosphate from the considered plots may be influenced by spatial variability in soil properties and manure application within the plots. In this preliminary study the impact of spatial variability is not explicitly taken into account, instead input data for the models have been selected in such a way that they give the best representation of the average situation on the plots. For example data on the soil chemical composition of the solid phase are based on measurements from bulked soil samples for each plot (c.f. 2.1) and adsorption parameters are based on these same average data. Furthermore, we assumed that manure (liquid manure, fertilizers and cow droppings) was uniformly distributed over the plots. This assumption is questionable with respect to the cow droppings, an estimation based on the number of cows, the days of grazing and the average size of the cow droppings indicates that cow droppings are dropped on only 6 % of the surface area. These cow droppings are spread to a certain extend over the surface both by grazing and in particular by cutting the grass. However, little is known yet on the exact impact of these activities on the percentage of area effected by cow droppings. In this preliminary study we therefore assumed a uniform distribution in the standard application procedure (c.f. Discussion)

3.2.3 Calibration and validation

Both the hydrological model (SWAP) and the nutrient model (ANIMO) were calibrated on measured data during the first two years of the experiment (1997 and 1998). The third year (1999) was used for validation. The hydrological model was calibrated on the fluctuations in groundwater levels, whereas the nutrient model was

mainly calibrated on the measured Pw values. Details on the calibrated parameters can be found in chapter 3.3.

3.3 Model input

3.3.1 Manure applications

Nitrogen and phosphate were added to the soil by application of both liquid manure and fertilizers. Liquid manure was applied to the plots in early spring. P fertilizer was applied at the end of June and in early spring on the plots with high phosphate inputs. N fertilizer was applied approximately every month during the growing season.

Table 3 Application of phosphate (kg ha-1) by liquid manure, fertilizer and cow droppings to the experimental plots

Application	P surplus	Cran	endono	ck	Hein	0		Waai	boerho	oeve	Zegv	eld	
	(kg ha-1 P)	' 97	'98	'99	' 97	'98	'99	' 97	'98	' 99	' 97 [–]	'98	' 99
Liquid	0	13	15	11	10	8	7	9	6	9	10	8	11
Manure	10	17	15	11	10	8	7	9	6	9	10	8	11
	20	17	20	16	15	13	9	14	10	15	15	15	18
Fertilizer	0	15	10	18	11	12	15	7	7	12	6	10	14
	10	27	19	19	22	20	26	18	17	23	17	19	26
	20	33	27	36	32	32	36	28	24	32	24	25	33
Cow	0	18	21	17	19	17	21	16	10	14	12	10	15
Droppings	10	21	22	17	20	18	18	17	19	16	13	10	15
	20	20	32	20	21	21	22	19	32	18	16	13	18

Day of application, composition and amount of manure and fertilizers are input to the model ANIMO. These data were based on observations at the farm and chemical analysis of the liquid manure (Schils et al., 1998). Addition of phosphate and nitrogen during grazing was calculated from the loss of grass during the grazing period minus the increase in N and P in the cows (Table 3). The additions were assumed to be uniformly distributed over the plot (c.f. 3.2.2).

3.3.2 Hydrology

To calculate hydrological fluxes and water contents, the model SWAP uses meteorological data (rainfall, reference evaporation), data on soil physical characteristics (water retention characteristics and conductivity data), plant characteristics (amongst others root depth and root distribution) and drainage characteristics (depth of impervious layer, spacing of the drains etc.). These data were derived from measurements at the site and on generic data that were based on literature and previous studies at the experimental farms. Rainfall data were derived from daily measurements at the sites, the reference evapotranspiration for grass was calculated according to Makkink (Makkink, 1957) and based on data from the nearest meteorological station, which were located at a distance between 5 and 50 km from the site. Soil physical characteristics for Cranendonck, Waaiboerhoeve and Zegveld

were selected from the Staring soil series (Wösten et al., 1994) that provide soil physical characteristics for the topsoil and the subsoil of 18 common Dutch soil types. Data for Heino were based on measurements at plots involved in previous studies (Kroes et al., 1996). The root depth for grassland was set at a value of 30 cm for all plots and root distribution was calibrated on the changes in phosphate status in the topsoil over the period 1997-1998 (Table 4). Drainage characteristics were based on previous calibrations (Kroes et al., 1996) of the model on measured ground water levels and when available on measured fluxes from the drains (Waaiboerhoeve) or measured pressure heads (Heino). Data for Zegveld were based on calibration on measured groundwater levels.

Depth	Site			
	Cranendonck	Heino	Waaiboerhoeve	Zegveld
0-10 cm	75	71	67	76
10-20 cm	22	24	20	21
20-30 cm	3	5	13	3

Table 4 Calibrated root distribution (%) as a function of depth

3.3.3 Soil chemical characteristics and parameters

Organic matter dynamics

The dynamics of organic matter are described in ANIMO by using three solid phase organic matter pools (fresh organic matter, root exudates and humus) and a dissolved organic matter pool. Initial concentrations of dissolved organic matter were based on average concentrations in the soil solution during the first year of the measurements. Initial organic matter pools were derived from the measured amount of organic matter in the different soil layers. The total amount of organic matter was initially divided over the three pools using standard allocation fractions based on data for arable land on sandy soils (Kroes and Roelsma, 1998): 80 % of the organic matter was allocated to the humus derived from root exudates, 10 % to humus formed from fresh organic matter and 10 % to fresh organic matter. These values were slightly adapted during calibration, to avoid an excessive increase in organic matter content. This resulted in allocation of 80 % of the organic matter to humus from root exudates, 15 % to humus formed form fresh organic matter and 5 % to fresh organic matter.

The transformation of different organic matter pools into each other is regulated by a maximum rate constants and reduced by multiplication factors describing the influence of reduced aeration, low temperature and pH. The model uses a set of standard parameter values, for amongst others the oxygen diffusion coefficients, the amplitude of the yearly temperature wave and the damping depth, to calculate these multiplication factors (c.f. Groenendijk and Kroes, 1997; Kroes and Roelsma, 1998).

Table 5 Parameter values for the oxygen diffusion coefficients

Site	Texture	Standard	parameters ¹	Calibrated parameters		
		$\overline{P_1}$	P_2	P_1	P_{2}	
Cranendonck	loamy sand	2.5	3.0	2.5	3.0	
Heino	sand	1.5	3.0	1.5	3.0	
Waaiboerhoeve	clay loam	2.0	2.5	2.0	1.5	
Zegveld	peaty clay	2.0	2.5	2.0	2.0	

¹ Standard parameters based on Bakker et al., 1987

A sensitivity analysis of the model ANIMO showed that the results are strongly influenced by changes in the oxygen diffusion coefficient which regulate the aeration of the soil (Groenenberg et al., 1995). The oxygen diffusion parameters were thus calibrated, whenever the model calculated an excessive increase or decrease in organic matter content during the two-year simulation period (Table 5).

Phosphate sorption

Parameters for the adsorption of phosphate were derived from measurements of adsorbed P, combined with measured soil solution concentrations and Pw values in the field. The amount of adsorbed P was determined for each soil layer by repeated extraction of P with Fe oxide-impregnated paper for a total period of 90 h. For each site an average value for the adsorption constant *K* can be determined from Eq (1), by assuming that the average ortho-P concentration in the first year of the experiment equals the equilibrium concentration in the Langmuir equation. It was furthermore assumed that the maximum amount of adsorbed P (Q_m) in each soil layer could be calculated as a fraction of the Al and Fe content:

$$Q_m = \boldsymbol{b}(\mathrm{Al} + \mathrm{Fe})_{ox} \tag{11}$$

The Langmuir equation (Eq. 1) can now be rewritten to:

$$\frac{Q}{(\mathrm{Al} + \mathrm{Fe})_{ox}} = \frac{Kc_{avg,i}b}{(1 + Kc_{avg,i})}$$
(12)

where c_{avgi} is the average phosphate concentration in the soil solution at depth *i*. To solve *K* and **b**, $Q/(Al+Fe)_{ox}$ was fitted as a function of c_{avgi} using a Levenberg-Marquardt optimization routine (Marquardt, 1963). To calculate *Pw*, not only *K* but both the adsorption rate constant k_a and the desorption rate constant k_d have to be provided (Eq. 3-8). When *K* is known only k_d has to be determined because *K* equals k_a/k_d . To obtain consistent values of *K*, **b** and k_d equation 12 and 3 were solved simultaneously on respectively the measured adsorbed amount of phosphate and the *Pw*, as a function of the average concentration of phosphate in each layer (Table 6).

Table 6 Parameters to describe the adsorption reaction

Site	Parameter		
	b (-)	K (l mg-1)	k_d (d-1)
Cranendonck	0.094	23.8	0.097
Heino	0.103	34.7	0.094
Waaiboerhoeve	0.063	10.5	0.770
Zegveld	0.077	17.0	0.270

Parameters to describe the diffusion (fixation) reaction (Eq. 2; Table 7) are based on large number of sorption experiments for sandy soils (Schoumans, 1995).

Sorption site	Parameter							
-	$a_{i}(d^{-1})$	$K_i\left((mg.L^{-1})^{1/N_i}mmol.kg^{-1}\right)$	N _i (-)					
1	1.1755	9.46 10 ⁻³ (Al+Fe)	0.54					
2	0.0334	3.80 10 ⁻² (Al+Fe)	0.20					
3	0.0014	5.19 10 ⁻² (Al+Fe)	0.26					

 $\mathbf{a}_{_i}~^{(d^1)}$ Table 7 Parameters to describe the diffusion (fixation) reaction

The initial amount of sorbed phosphate has been calculated from the amount of oxalate extractable P minus the amount of adsorbed P. The initial mount of sorbed P has been dived over the three terms by assuming equilibrium with a concentration c. The time dependant Freundlich equation (Eq. (2) can then be rewritten to:

$$S = k_i c^{N_1} + k_2 c^{N_2} + k_3 c^{N_3}$$
(13)

With this equation the equilibrium concentration c can be solved and the size of the three pools can be calculated.

Uptake of phosphate

Normally the uptake of phosphate is calculated by ANIMO on basis of the phosphate concentration in solution, the transpiration flux and a selectivity factor for phosphate. However, the results of this procedure were not accurate enough to reproduce exactly the measured phosphate uptake and the year to year variations. Therefore, yearly values for the selectivity factors for phosphate were used to reproduce exactly the yearly measured phosphate uptake. An overview of the measured phosphate uptake is given in Annex 1

4 Results

4.1 Observed changes in phosphate contents and concentrations

Both the P concentrations and Pw values varied considerably during the three-year measurement period (c.f. Fig. 5, 8, 10 and 12 and Annex 2). Due to these strong temporal variations no significant decline or rise in concentrations or Pw values was observed. The strong (seasonal) variation in concentrations may result from: (i) agricultural practices, (ii) meteorological conditions, influencing processes such as leaching and mineralisation, (iii) slight differences in sampling depth between the individual sampling events or (iv) analytical fluctuations. Impacts of agricultural practices, meteorological conditions or analytical flows may be expected to lead to a comparable pattern in the observed concentrations with time, e.g. high leaching rates will lead to low concentrations at all sites. Deviations in the measured concentrations due to fluctuations in sampling depth will likely lead to deviations in the measured concentration at a specific site.

The similarity of the patterns was investigated by statistical analyses of the data sets. When a uniform pattern exists the concentrations at a specific plot are approximately constant multiples of the concentration in another plot; i.e. the differences of the log of the concentrations of the two measurements are constant. In this case the log of the concentrations as a function of time can be fitted as a function of the plot and the individual points in time, representing the dips and peaks in the concentration measurements:

$$\log C_{i,t} = D_i + \log C_{r,t}$$
⁽¹⁴⁾

where $C_{i,t}$ is the concentration measured at plot *i* at a certain depth and time *t*, D_i is the difference between plot i and a reference measurement and $C_{r,t}$ is the concentration measured at the reference site. The reference measurement was chosen arbitrarily from the 12 plots. When the concentration measurements do not show a uniform pattern, the above model can be significantly improved by taking into account the interaction between time and plot (i.e. D_i has a different value each time) indicating that temporal variation are different at each site and depth. The interaction between time and site is described by a spline function, using a number of parameters, which is equal to a quarter of sampling dates.

Results indicated that the factor site explained 28-50 % of the observed fluctuations in ortho-P concentrations, an additional 26-30 % (total 60-77 %) was explained by common temporal variations. Interactions between time and site/depth did not improve the explained variance. These results indicate clearly that part of the observed concentration changes occur simultaneously at the different sites. Regression results indicated that measured ortho-P concentrations tend to be low in autumn and generally close to or above average during spring, except for 1999 when

all concentrations were clearly below average (Fig 2). The observed concentration pattern did not show a relationship with the slurry application in spring. In 1997 concentrations were higher two weeks after manure application whereas lower values were found in 1998 (and 1999). In 1999 concentration were measured much later (78 days) after the slurry application and it is thus not surprising that no effect was found in 1999. The lower values in 1998 are most probably due to the much higher precipitation between the two sampling dates in 1998 compared to 1997. In 1998 the average precipitation on the four sites was 102 mm whereas only 23 mm was recorded in spring 1997. Moreover a large part of the precipitation in 1998 fell directly after manure application, leading to an increased leaching of phosphate.

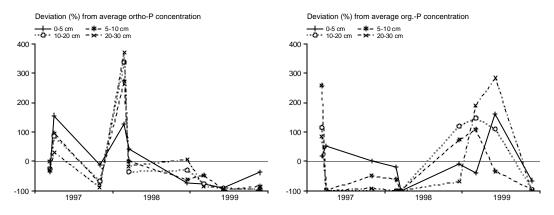


Fig. 2 General pattern of ortho-P (left) and organic P (right) concentrations at the four sites expressed as the deviation in the concentrations compared to the average concentration during the period 1997-1999

The variation in *organic* P (total P- ortho-P) concentrations was not explained as well (23-38 %) by the site and sampling time as the ortho-P concentrations. The explained variance was not improved when potential differences in pattern between the plots were considered. The observed pattern for the organic P concentrations was almost opposite to that found for ortho-P. Relatively low concentrations were found during 1997 and 1998 compared to the 1999 data. Organic P concentration after manure application were lower than concentration in early spring except for 1999

Fluctuations in Pw values were less pronounced then variations in ortho-P concentrations. However, a common pattern in the variations of Pw was found. Regression analysis showed that site and soil layer explained 75.4 % of the variance and an additional 1 % was explained by the time of sampling. Results indicated that Pw values measured in 1997 were significantly higher then those in other years, the Pw values in 1998 and 1999 were not significantly different from those in 1996. The fluctuation in Pw values did not correspond to the observed pattern in ortho-P concentrations. Ortho-P concentrations in 1997 were significantly lower. A plot of the measured ortho-P concentrations against measured Pw values clearly reflects this lack of correspondence. In an equilibrium situation a plot of the ortho-P concentrations against Pw should be comparable with the adsorption isotherm for the considered soil. In this case, the 1999 values are generally above the average adsorption isotherm, whereas 1998 values tend to be below the average isotherm (Fig. 3).

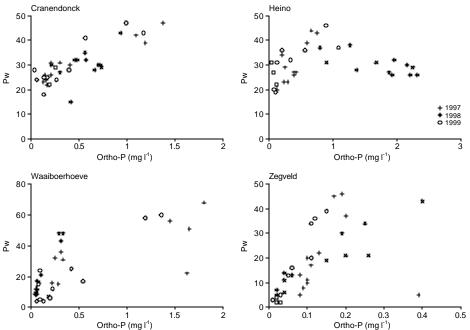


Fig. 3 Measured Pw values (mg $P_2O_5 l^1$) as a function of the measured ortho-P concentration in 1997, 1998 and 1999.

4.2 Calibration and Validation

4.2.1 Cranendonck

Hydrology

Groundwater level was measured at two points at the edges of each plot. The difference between the measured ground water level of these two points was negligible. The average groundwater level at the N180-P0 plot was slightly higher than at the N300-P20 plot and the N180-P10 plot (Fig. 4). However, these differences are too small to merit separate hydrological calculations.

The hydrological sub-model SWAP simulated the measured changes in ground water level quite good (Fig. 4) both during the calibration phase (1997-1998) and the validation phase (1999). Exceptions form the groundwater levels in autumn 1997 that were slightly overestimated. Precipitation in 1997 was slightly lower then the long-term average (736 mm). On the other hand 1998 was extremely wet, and continuous precipitation let to ponding at the soil surface and loss of water by runoff in autumn (Table 8). The high rainfall in 1998 led to a more than three times higher precipitation surplus (net downward flux) in 1998 compared to 1997. The precipitation in 1999 was also higher then the long-term average but ponding and runoff did not occur at Cranendonck

Table 8 Measured precipitation and simulated water fluxes (0- 30 cm depth) at Cranendonck

1 1	(1 /	
Water flux (mm a ⁻¹)	1997	1998	1999
Precipitation	709.0	938.6	879.0
Runoff	0.0	14.1	0.0
Interception	70.6	93.9	83.8
Transpiration	531.9	432.8	534.5
Lateral drainage	0.0	1.6	0.0
Net. Downward flux	109.4	387.1	247.4

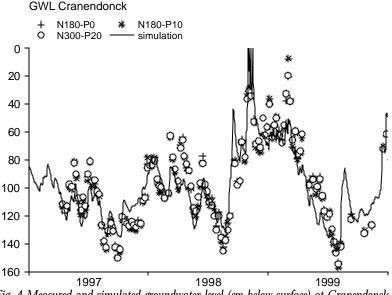


Fig. 4 Measured and simulated groundwater level (cm below surface) at Cranendonck

Phosphate

The short length of the data set and the strong temporal variation in the observed Pstatus slightly limit the possibilities of calibration and validation of the model ANIMO. With the present set of observations it is only possible to adjust the model parameters in a rough way such that measurements and model results are in the same order of magnitude and that unrealistic changes in solid phase pools are avoided.

In a first attempt to apply ANIMO to the Cranendonck site, only the root distribution was calibrated to avoid a decrease in phosphate amounts at a depth of more than 10 cm (c.f. Table 4 and Fig. 5). The results of this calibration showed that the model is not able to simulate the strong fluctuations in ortho-P concentrations with time. This may be due to the fact concentrations and adsorbed P are modeled by a Langmuir equation using a constant value for K, neglecting the potential impact of changes in temperature or redox potential (Barrow, 1983). The model simulated the dynamics in organic P concentrations better, except for the extremely high values in early spring 1997 and late autumn 1998. Although fluctuations in concentrations and Pw values were not very well simulated by the model the order of magnitude of both the modeled and simulated phosphate concentrations and Pw values are comparable on the plots with a P surplus of 0 and 10 kg ha⁻¹. On the plot with a 20 kg ha⁻¹ surplus the ortho-P concentrations and Pw values in 1998.

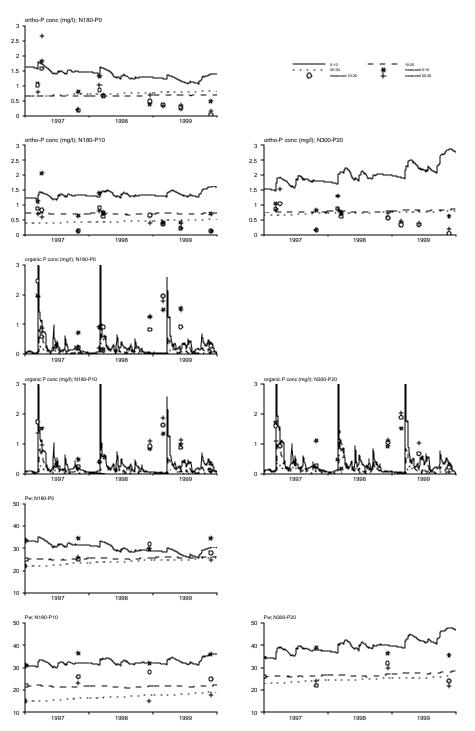


Fig. 5 Measured and simulated ortho-P, organic P and Pw values for the plots at Cranendonck after calibration of the root distribution

These results indicate that the model underestimates the fixation of phosphate, the immobilization of phosphate in organic matter or the transport of phosphate to deeper layers. Unfortunately, the storage of P in the solid phase pools can not yet be

derived from measurements because the increase in P is too small to lead to significantly measurable changes in the pools. It is therefore impossible to decide, on basis of the measurements, whether the observed overestimation of Pw is caused by an underestimation of the immobilization of P or by an underestimation of the P fixation. To optimize the model results several runs were carried out with ANIMO, using different parameter values and initial conditions. Changes in parameter settings and initial contents of the various organic matter pools that might influence the immobilization had little influence on the model results. Comparable results were found for the simulated hydrology; changes in the hydrological parameterization, leading to higher leaching fluxes, had little impact on the simulated Pw values. However, the model was able to simulate measured Pw values by calculating a higher fixation of phosphate. This was achieved by changing the initial pool size of one of the three pools and increasing the size of the others. For example Pw values during the calibration phase were quite well simulated when the initial amount of P in the fast reacting diffusion pool (c.f. Eq 2 and 13) was reduced, by assuming equilibrium with the average ortho-P concentration in the soil solution (Fig. 6).

Validation of the model on 1999 data showed that the calibrated model underestimated the Pw, in the upper 10 cm of the soil, at the plot with a P surplus of 0 kg ha⁻¹ and overestimated the Pw at the plot with a surplus of 20 kg ha⁻¹. However the measured changes in Pw values between 1998 and 1999 at the plots are quite unlikely. The P surplus during 1999 at the three plots increased from 17.4 kg ha⁻¹ at the plot with the lowest P surplus to 27.0 kg ha⁻¹ at the plot with the intermediate P surplus and 37.4 kg ha⁻¹ at the plot with the highest P surplus (c.f. Table 9). The increase in P surplus was not reflected in the measured change in Pw values between 1998 and 1999, which were +5 kg P₂O₅ l⁻¹ at the plot with the low and intermediate P surplus and -1 kg P₂O₅ l⁻¹ at the plot with the highest P-surplus. A longer validation period is thus necessary to conclude whether the model is able to simulate the trend in measured Pw values.

The model overestimated measured ortho-P concentrations at all plots in 1999. Measured ortho-P concentrations strongly declined at most sites (c.f. 4.1) from autumn 1998 onwards. This decline was not related to the P surplus and neither reflected in the measured Pw values (adsorbed P). The modeled organic P concentrations were close to measured values in autumn 1999. Spring values were less well simulated by the model.

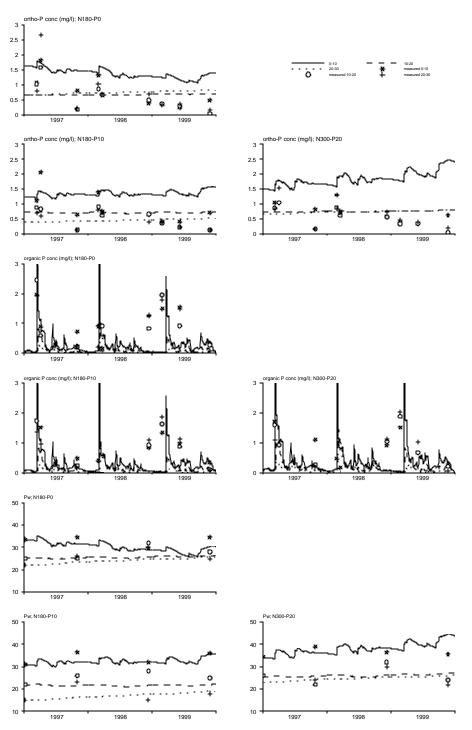


Fig. 6 Measured and simulated ortho-P, organic P and Pw values for the plots at Cranendonck, after calibration of the initial amount of sorbed P

A phosphate balance (Table 9) has been constructed for the three plots at Cranendonck, using the simulations with an increased P fixation (Fig. 6). This balance indicates that the average P loss by leaching, from the root zone (30 cm),

ranges between 1.7 and 3.0 kg ha⁻¹ a⁻¹. Losses from the plot with a P-surplus of 10 kg ha⁻¹ a⁻¹ are slightly lower than from the other plots because this plot has a lower P status in the deeper parts of the root zone compared to the other plots. Leaching losses in the wet year 1998 were twice as high as in 1997, which was relatively dry. Despite the much higher leaching losses in 1988, storage of P in the soil solid phase is still the largest sink for phosphate.

P balance terms (kg ha ⁻¹ a ⁻¹)	1997			1998			1999			Averag	ge	
Plot	P0	P10	P20	P0	P10	P20	P0	P10	P20	P0	P10	P20
Surplus	1.5	10.1	18.2	3.7	11.6	26.8	13.9	21.6	37.4	6.4	14.4	27.5
Leaching	1.9	0.9	1.9	4.0	2.5	4.1	3.2	1.8	3.1	3.0	1.7	3.0
Runoff	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Adsorption	1.5	9.7	14.6	-2.7	6.1	11.7	12.8	21.2	27.1	3.9	12.3	17.8
Fixation	0.0	0.0	5.5	0.0	0.3	2.4	0.0	1.4	5.8	0.0	0.6	4.6
Immobilization	-1.9	-0.5	-4.0	2.4	2.7	8.4	-2.1	-3.0	1.0	-0.5	-0.3	1.8
Others	0.0	0.0	0.2	0.0	0.1	0.2	0.2	0.2	0.4	0.1	0.1	0.3

Table 9 Phosphate balance for the root zone (0-30 cm) of the plots at Cranendonck

4.2.2 Heino

Hydrology

The ground water level was measured at the edge of the N180-P0 plot, at the border of the N180-P0 and the N180-P10 plot and at the edge of the N300-P20 plot. The ground water level measured at the N180-P0 was 15 to 20 cm higher than at the N180-P10 plot (Fig. 7), although the measurement points are located only 26 m. apart. The dynamics of the two points are almost identical, however. These differences in ground water table may influence the hydrological fluxes at the three plots.

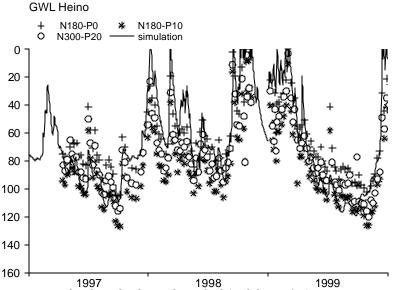


Fig. 7 Measured and simulated groundwater level (cm below surface) at Heino

For the time being these differences are however not taken into account, because the effect on the simulated phosphate balance is comparatively small. The hydrological submodel SWAP simulated the measured changes in ground water level quite good during 1997 and 1999, but slightly overestimated the groundwater level in 1998 (Fig. 7).

The simulated net downward flux at the bottom of the root zone (30 cm) was very low in 1997 and almost 10 times as high in 1998 (Table 10).

Water flux (mm a ⁻¹)	1997	1998	1999	
Precipitation	645.0	1060.0	770.8	
Runoff	0.0	249.7	50.0	
Interception	69.9	96.0	88.3	
Transpiration	524.7	386.3	507.6	
Lateral drainage	0.0	3.2	2.,2	
Net. Downward flux	34.0	324.0	120.4	

Table 10 Measured precipitation and simulated water fluxes (0- 30 cm depth) at Heino

The model also simulated a considerable runoff in September and October 1998. In these months the precipitation at Heino (372 mm) amounted to nearly half of the normal annual precipitation (751 mm). The total amount of precipitation in 1999 was close to the normal situation but the summer was relatively dry whereas December was extremely wet.

Phosphate

The model ANIMO was calibrated to the Heino data using the same calibration procedure as in Cranendonck: first the root distribution was optimized to avoid extreme changes in Pw in the subsoil and next the losses of phosphate by immobilization or fixation were calibrated. After calibration of the root distribution the model simulated a clear increase in Pw (from 33 to 39) at the site with a P-surplus of 20 kg ha⁻¹. To obtain a better correspondence between measured and simulated Pw values the initial amount of P in the fast reacting diffusion pool was reduced (c.f. 4.1.2) in such a way that fixation occurs when the ortho-P concentration rise above the average ortho-P concentration in the soil solution (Fig. 8).

After calibration the model simulated the measured Pw values in 1997 and 1998 generally quite good. However, the model tended to underestimate the Pw values at the plot with a phosphate surplus of 0 kg ha⁻¹ and to overestimate the Pw values at the plot with a surplus of 20 kg ha⁻¹ year. The average simulated ortho P and organic P concentration were close to measured values. However, the measured ortho-P concentrations showed a much stronger fluctuations with time then the simulated data.

Validation of the model at the 1999 data, showed that Pw values in the upper soil layer were lower then measured values at all plots. However, taking into account the uncertainty in the measured Pw values (sd: approx. 5 %) simulated values are generally within the 95% confidence interval of the measured data except for the site with a surplus of 0 kg ha⁻¹. At the later site Pw values were clearly underestimated by

the model in 1999. Ortho-P concentrations during 1999 were generally somewhat lower than simulated values. However, the deviation between model results and simulated values was not as pronounced as at the Cranendonck plots.

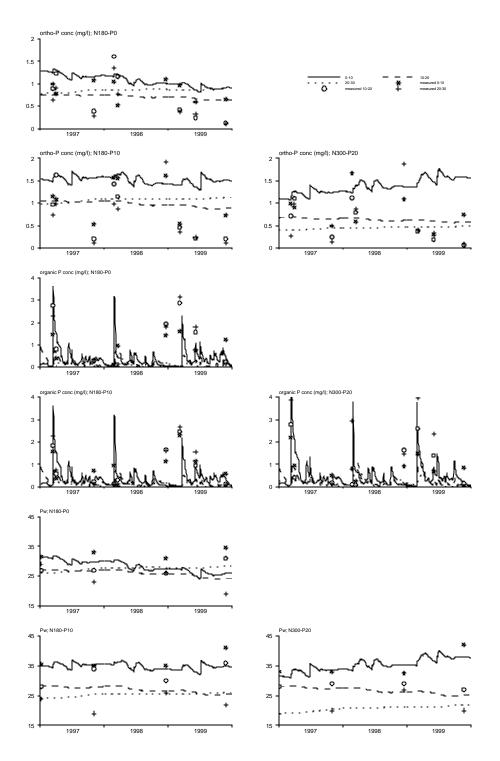


Fig. 8 Measured and simulated ortho-P, organic P concentrations and Pw values at the three plots in Heino

Table 11 Phosphate balance for the root zone (0-30 cm) of the plots at Heino

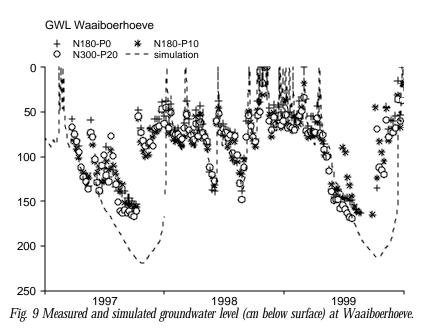
P balance terms	1997			1998			1999			Averag	ge	
(kg ha-1 a-1)		D10	DOO	DO	D10	Daa	DO	D10	Daa	DO	D10	D 00
Plot	PO	P10	P20	P0	P10	P20	P0	P10	P20	P0	P10	P20
Surplus	-0.7	8.0	16.9	-1.8	2.1	16.8	-3.5	5.9	17.4	-2.0	5.3	17.0
Leaching	1.4	2.0	0.5	4.0	5.1	2.5	2.3	3.1	1.1	2.6	3.4	1.4
Runoff	0.0	0.0	0.0	0.5	0.5	0.6	0.1	0.1	0.1	0.2	0.2	0.2
Adsorption	3.4	8.0	14.4	-16.0	-12.1	1.1	-9.9	0.6	8.6	-7.5	-1.1	8.0
Fixation	0.0	3.4	4.9	0.0	0.1	1.6	0.0	0.3	2.7	0.0	1.2	3.1
Immobilization	-5.9	-5.5	-2.9	9.4	8.7	11.0	3.7	1.4	4.2	2.4	1.5	4.1
Others	0.4	0.1	0.0	0.3	-0.2	0.0	0.3	0.4	0.7	0.3	0.1	0.2

Phosphate losses at Heino are comparable with simulated losses at Cranendonck (Table 11). The higher precipitation surplus at Heino leads to slightly higher losses of phosphate by leaching in 1988 compared to Cranendonck. An exception is formed by the plot that received a P-surplus of 20 kg ha⁻¹a⁻¹, at this plot the P leaching is lower than at Cranendonck due a lower P-status at the bottom of the root zone (20-30 cm).

4.2.3 Waaiboerhoeve

Hydrology

Hydrological differences between the three plots were relatively small (Fig 9). On general the N180-P0 plot was slightly wetter and showed a quicker response on precipitation.



SWAP simulated the average groundwater level for the three plots quite well in 1998 and during winter and spring of 1997. The model simulated too low groundwater levels during the dry summer of 1997 and 1999 and the recovery of the groundwater level in winter started too late.

Water flux (mm a ⁻¹)	1997	1998	1999
Precipitation	634.2	1147.0	853.9
Runoff	2.2	224.9	33.3
Interception	70.1	99.6	88.9
Transpiration	523.5	422.5	525.7
Lateral drainage	2.2	12.6	5.0
Net. Downward flux	28.5	333.1	179.8

Table 12 Measured precipitation and simulated water fluxes (0- 30 cm depth) at Waaiboerhoeve

Yearly precipitation and simulated water fluxes are comparable with Heino: precipitation and leaching fluxes are extremely low in the relatively dry year 1997, intermediate in 1999 and high in 1998 (Table 12).

Phosphate

To calibrate ANIMO on the Waaiboerhoeve data set the following procedure was followed: first the root distribution is calibrated to avoid extreme increases or decreases in the P-status of the deeper soil layers and next the oxygen diffusion coefficients were adjusted in such a way that extreme (im)mobilization of P in organic matter was avoided.

After calibration the order of magnitude of the simulated ortho-P concentrations was close to average measured concentrations but the measured fluctuations in ortho-P concentrations were not simulated. Organic P concentrations were quite well simulated, although the peaks in organic P concentrations that are simulated as a response to manure applications were not measured. To measure these concentrations sampling should take place sooner after manure application. Due to the strong year-to-year fluctuations in Pw it is extremely difficult to draw conclusions out of the simulated Pw values. The decline in Pw on the plot with a P surplus of 0 kg ha⁻¹ a⁻¹ appears to be somewhat overestimated. The simulated Pw values at the plot with a 10 kg ha⁻¹ a⁻¹ surplus remain in between the 1997 and 1998 values, whereas 1998 values for Pw are somewhat overestimated at the plot with the highest P surplus.

These trends are confirmed during the validation year 1999: Pw values at the plot with a 10 kg ha⁻¹ surplus are close to measured values, whereas Pw values are underestimated by the model at the 0 kg ha⁻¹ plot and overestimated at the 10 kg ha⁻¹ plot. Most likely simulated immobilization losses are slightly too high at the Waaiboerhoeve and fixation losses too low (c.f. 4.2.1 and 5.1).

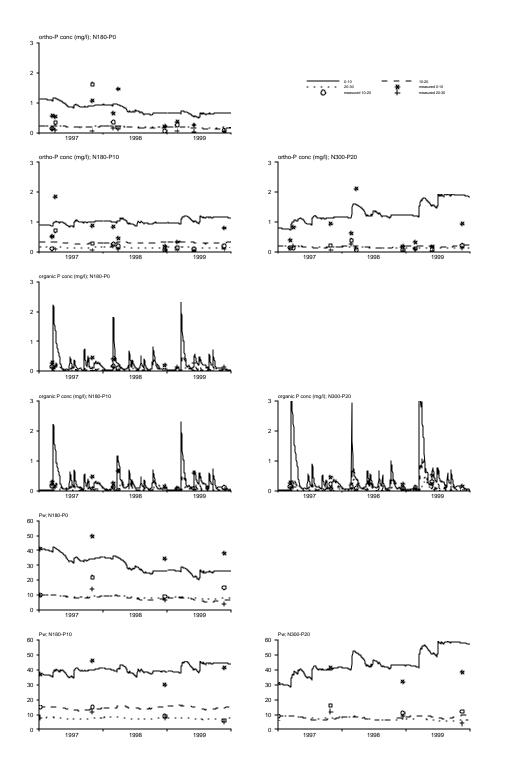


Fig. 10 Measured and simulated ortho-P, organic P concentrations and Pw values at the three plots at the Waaiboerhoeve

The phosphate balance (Table 13) indicates that simulated leaching losses at the Waaiboerhoeve are smaller than losses on the sandy soils, which have high P

contents in the deeper part of the subsoil. Losses of readily available phosphate due to immobilization of P in organic matter are quite comparable to the sandy sites. The adsorption of phosphate is slightly lower due to the fact that the P surplus, during the two-year period, was somewhat lower at Waaiboerhoeve compared to Heino and Cranendonck.

P balance terms	1997 1998			1999			Average					
(kg ha-1 a-1)												
Plot	P0	P10	P20	P0	P10	P20	P0	P10	P20	P0	P10	P20
Surplus	-7.6	6.1	17.3	-12.1	2.3	6.5	0.1	2.4	19.0	-9.5	3.6	14.6
Leaching	0.3	0.3	0.3	1.1	1.0	1.0	0.6	0.6	0.6	0.7	0.6	0.6
Runoff	0.0	0.0	0.0	0.6	0.5	1.4	0.1	0.1	0.1	0.2	0.2	0.5
Adsorption	-8.9	4.5	12.2	-16.3	-1.8	-0.2	-2.9	6.2	21.6	-9.4	3.0	11.2
Fixation	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Immobilization	0.9	1.1	4.5	2.7	2.7	4.3	-6.6	-4.5	-2.4	0.0	-0.2	2.1
Others	0.1	0.2	0.3	-0.2	-0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.1

Table 13 Phosphate balance for the root zone (0-30 cm) of the plots at the Waaiboerhoeve

4.2.4 Zegveld

Hydrology

Groundwater levels at the three plots were comparable in 1997, but in 1998 and 1999 higher (up to 10 cm) groundwater levels were measured at the N300-P20 plot compared to the other plots (Fig. 11). These differences in groundwater level between the plots were not yet accounted for in the model application. The simulated ground water level was in the range of measured values at the three plots, except for dry periods in spring 1998 where the groundwater level was somewhat underestimated by the model.

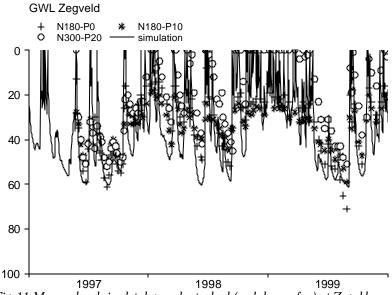


Fig. 11 Measured and simulated groundwater level (cm below surface) at Zegveld

Simulated water fluxes showed comparable year to year differences as found on the other three locations (Table 14). The year 1998 was extremely wet (1137 mm) compared to the thirty-year average precipitation at this site (813 mm). The high precipitation led to high runoff and leaching fluxes during 1998 compared to 1997. In all years runoff and lateral drainage fluxes at Zegveld are higher compared to the other three sites that are much deeper drained.

Water flux (mm a ⁻¹)	1997	1998	1999
Precipitation	674.2	1137.0	952.5
Runoff	84.8	278.2	163.8
Interception	66.8	101.0	90.1
Transpiration	443.0	323.1	435.5
1			
Lateral drainage	86.4	243.8	162.5
Net. Downward flux	3.0	202.8	106.6

Table 14 Measured precipitation and simulated water fluxes (0- 30 cm depth) at Zegveld

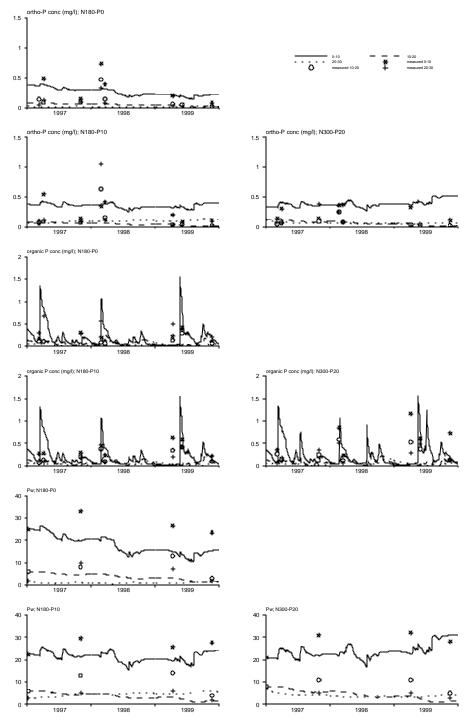
Phosphate

The model was applied to the Zegveld data in a comparable way as done for the Waaiboerhoeve: both the root distribution and the oxygen diffusion coefficients were adjusted. Measured P concentrations at Zegveld are considerably lower compared to the other plots and were generally below 0.5 mg L⁻¹ and fluctuations were relatively limited. The model simulated organic P concentrations quite good, except for the (high) concentration in early spring 1998 that were clearly underestimated. The order of magnitude of the ortho-P concentrations was quite well simulated by the model but the model did not simulate the measured temporary fluctuations in the concentrations. The model underestimated the measured Pw values in both 1997 and spring 1999, in particular at the plot with a 0 kg ha⁻¹ a⁻¹ P surplus. At this plot a strong decline in Pw value was simulated that could not be affirmed by the measurements. In autumn 1999, simulated Pw values for the plot with a P surplus of 10 and 20 kg ha⁻¹ were within the 95 percentile of the measured Pw values.

P balance terms	1997			1998			1999			Average			
(kg ha-1 a-1)													
Plot	P0	P10	P20	P0	P10	P20	P0	P10	P20	P0	P10	P20	
Surplus	-3.8	5.8	12.6	-11.8	-3.3	6.3	0.1	9.0	19.5	-5.2	3.8	12.8	
Leaching	0.3	0.5	0.5	0.8	1.3	1.4	0.3	0.9	0.8	0.5	0.9	0.9	
Runoff	0.2	0.2	0.2	0.5	0.5	0.7	0.4	0.5	0.5	0.4	0.4	0.5	
Adsorption	-15.8	-0.2	-7.9	-16.7	-8.2	-4.1	-2.8	7.0	13.2	-11.8	-0.5	0.4	
Fixation	8.2	1.9	12.1	3.6	2.6	4.2	3.8	2.3	2.9	5.2	2.3	6.4	
Immobilization	3.6	3.6	8.1	0.0	0.3	4.2	-1.6	-1.6	2.0	0.7	0.8	4.8	
Others	-0.3	-0.2	-0.4	0.0	0.2	-0.1	0.0	0.0	0.1	-0.1	0.0	-0.1	

Table 15 Phosphate balance for the root zone (0-30 cm) of the plots at Zegveld

Simulated phosphate losses due to leaching and runoff were somewhat higher compared to the clay site, despite the lower P contents at Zegveld (Table 15). This is caused by a higher contribution of the upper part of the soil profile to the overall losses due to a more shallow drainage of water from the soil profile at Zegveld. The simulation results indicated that a considerable amount of readily available phosphate is lost by fixation of phosphate, in the deeper parts of the topsoil (20-30 cm). However, these simulation results can not be confirmed by measurements, as these



changes are too small to result in significant changes in the amount of oxalate extractable P.

Fig. 12 Measured and simulated ortho-P, organic P concentrations and Pw values at the three plots at Zegveld

4.3 Overview of phosphate losses on the four plots

Simulated phosphate losses

An overview of the simulated phosphate losses by leaching, runoff and storage in the soil solid phase is given in Table 16. The loss of phosphate to the environment by leaching and runoff ranges from 0.9 kg ha⁻¹ a⁻¹ at plots at Waaiboerhoeve and Zegveld to 3.6 kg ha⁻¹ a⁻¹ at one of the plots in Heino.

Table 16 Overview of the simulated phosphate fluxes (kg ha⁻¹ $a^{-1} P$) in the topsoil (0-30 cm) for the four sites during the period 1997-1999

	Cra	nendon	ck		Heino		Wa	aiboerh	oeve	Zegveld			
-	P0	P10	P20	P0	P10	P20	P0	P10	P20	P0	P10	P20	
P surplus	6.4	14.4	27.5	-2.0	5.3	17.0	-9.5	4.2	11.9	-5.2	3.8	12.8	
Environmen	tal P los	ss:											
Leaching	3.0	1.7	3.0	2.6	3.4	1.4	0.7	0.3	0.7	0.5	0.9	0.9	
Runoff	0.0	0.0	0.0	0.2	0.2	0.2	0.2	0.6	0.7	0.4	0.4	0.5	
Storage in so	il:												
org. P	-0.5	-0.3	1.8	2.4	1.5	4.1	0.0	-0.2	2.1	0.7	0.8	4.8	
Inorganic P	3.9	12.9	22.4	-7.5	0.1	11.1	-9.4	3.0	11.2	-6.6	1.8	6.8	
Consisting of	f:												
Fixation	0.0	0.6	4.6	0.0	1.8	3.2	0.0	0.0	0.0	5.2	2.3	6.4	
Adsorption	3.9	12.3	17.8	-6.3	-2.1	7.8	-12.6	1.3	6.0	-11.8	-0.5	0.4	
Storage in Solution	0.1	0.1	0.3	0.3	0.1	0.2	0.0	0.0	0.1	-0.1	0.0	-0.1	

The losses of phosphate by leaching (subsurface runoff and vertical leaching) are not related to the current P surplus at the plots (c.f. Fig. 14) but are closely linked to the P status in the deeper layers of the topsoil (20-30 cm) from which the water is drained (Fig. 13):

 $P_{\text{leaching}} = -0.0178 + 0.11 \text{ Pw} \quad (R^2_{\text{adj}} = 0.80)$

The simulated storage of phosphate in the soil is closely related to the P surplus. (Fig. 14) and can be described by a linear relationship between P surplus and P storage according to:

$$P_{\text{storage}} = -1.67 + 0.97 P_{\text{surplus}}$$
 ($R^2_{\text{adj}} = 0.99$).

This relationship is comparable to data for a long-term (20 years) experiment at Rothmansted experimental station (Johnston and Poulton, 1995). They found a negligible loss of phosphorous (1:1 line between P surplus and P storage) when only fertilizer (superphopshate) was applied to the plots. However, when only animal manure was applied on average 7 kg ha⁻¹ a⁻¹ was lost at a P surplus of approx. 30 kg ha⁻¹ a⁻¹. These losses are slightly higher than the losses predicted at our experimental

plots (a loss of approx 3 kg ha⁻¹ a⁻¹ at a surplus of 30 kg ha⁻¹ a⁻¹) where both fertilizer and animal manure were used.

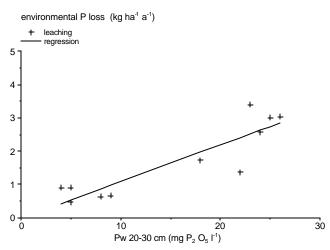


Fig. 13 Losses of P by leaching as a function of the average measured Pw of the soil at 20-30 cm depth

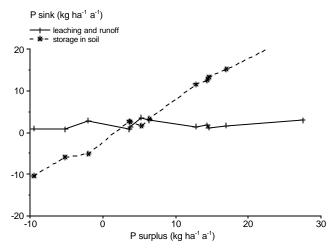


Fig. 14 Relationship between P surplus and P losses due to leaching and storage in the soil solution

A strong relation was also found between P surplus and adsorption (Fig. 15), which can be described by the following linear equation:

 $P_{adsorption} = -3.83 + 0.81 P_{surplus}$ ($R^2_{adj} = 0.87$).

The other sinks of phosphate show a much less pronounced increase with the P surplus and depend more strongly on the specific conditions at the individual sites (Fig. 15). For example the immobilization of organic P ranged from 0.1 kg ha⁻¹ a⁻¹ at Cranendonck to 4.8 kg ha⁻¹ a⁻¹ at Zegveld at a comparable P surplus.

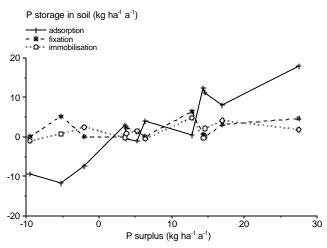


Fig. 15 Relationship between P surplus and P losses due to adsorption, fixation and immobilization in the soil

Comparison of simulated and measured phosphate losses

A comparison of the simulated storage of P in the soil with measured data is difficult due to the relatively small size of the P surpluses compared to the size of the phosphate pools. At the phosphate surpluses applied in this study a measurement period of a least two years will be needed to measure significant changes in Pw (adsorbed amounts of phosphate). To measure significant changes in organic phosphate and fixed phosphate measurement periods of 10 years or more are needed due to the large size of these pools. During the three-year measurement period significant changes in adsorbed amounts of phosphate were not yet found, due to strong temporal variation in measured phosphate pools.

Leaching losses at the plots can be derived from measured soil solution concentrations and calculated hydrological fluxes. These 'measured' leaching losses can be compared with modeled fluxes. Measured fluxes were derived on basis of the measured average yearly concentrations in the upper three soil layers and calculated (lateral) drainage fluxes and leaching fluxes. The average of these yearly fluxes was compared with the average leaching fluxes calculated by ANIMO (Fig. 16). Results indicate that simulated total P fluxes are generally close to measured values except for Zegveld, where simulated fluxes are lower then measured data. Simulated ortho-P fluxes tend to be somewhat overestimated by the model, whereas simulated organic P fluxes are generally lower than measured fluxes. One of the reasons for this discrepancy is that the model does not simulate the observed high organic P concentrations in early spring. However, the measured P leaching losses are rather uncertain because organic P concentrations tend to change strongly with time due to variations in temperature, moisture content and manure applications. It is thus likely that the measurement frequency (three times a year) is far too low to obtain an accurate estimate of the organic P leaching fluxes.

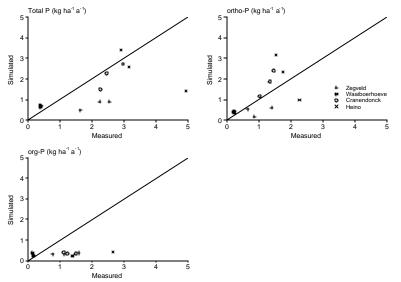


Fig.16 Measured and simulated leaching losses (kg ha⁻¹a⁻¹) of total-P, ortho-P and organic P (total minus ortho-P) from the upper 30 cm of the soil profile.

5 Discussion

A thorough calibration and validation of the model was not yet possible because significant changes in the pools of organic matter and phosphate bound by fixation were not found at different P surpluses. Changes in these pools during a three-year period are too small compared to the magnitude of the solid phase pools. This uncertainty can only be decreased by continuation of the measurements, while focussing on quantifying and minimizing the uncertainty introduced by sampling and analyses of the soil samples. Despite these limitations the results indicated that the model reasonably simulated the measured concentrations, leaching fluxes and change in phosphate status (Pw) at most sites. Although, the model showed a slight tendency to overestimate the rise in Pw values at the sites with the highest P surplus and the decline in Pw values at the sites with low P surpluses. Likewise some uncertainty remains with respect to the ratio of ortho-P to organic-P in the leaching losses. To decrease this uncertainty more frequent measurements of soil solution concentrations are required. Validation of ANIMO on such data should increase confidence in the model formulation and the calibration of the different process fluxes.

Apart of the general results there are a number of other aspects in this study that give cause of concern. For example the model did not simulate the measured temporal fluctuations in phosphate concentrations. On basis of the available information it is not yet clear whether this discrepancy between measurements and model results is due to measurement errors or due to an inadequate process description. Results of this study indicated that a large part of these fluctuations occur simultaneously at all sites and depth, indicating that the fluctuations are not caused by incidental errors in sampling. However, the variations in concentrations could not be explained by differences in environmental conditions. For example soil temperature and moisture content were almost the same in spring 1997 en 1998, however measured ortho-P and organic-P concentrations varied considerably between these two years. To obtain more insight in the variation in phosphate concentrations more frequent measurements, using lysimeter cups are indispensable. Such measurements might lead to slightly different values for the year average concentrations, requiring a change in the adsorption constants used in the model (c.f. Chapter 3.3.3). However, the overall parameterization of the model will remain almost unchanged as the leaching fluxes form only a minor component of the whole phosphate balance.

Another important aspect that might lead to errors in the calculated phosphate fluxes is the assumption that cow droppings are distributed evenly over the plot area. It is well known that cow droppings are only deposited at approximately 6 % of the pasture. Subsequent harvesting of grass may spread the cow droppings over a somewhat larger area, but the affected area will certainly be lower than 100 % as assumed in the standard simulations. An inhomogeneous distribution of manure may be expected to lead to a somewhat higher fixation, a higher storage of phosphorous in organic matter and probably to higher leaching fluxes compared to a situation where the manure is evenly distributed over the area.

To investigate the potential impact of such an inhomogeneous manure application, calculations were carried out for the Cranendonck plot with a P surplus of 10 kg ha⁻¹ a⁻¹. The plot was divided in 168 subplots, each year 6 % of the plots were selected to receive cow droppings, the remaining 94 % only received the regular application of liquid manure and fertilizer. To calculate the changes in concentrations and Pw values for the whole plot, the results of the 168 runs were averaged (Fig. 17).

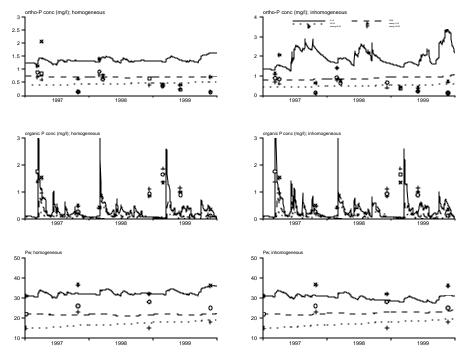


Fig. 17 Simulated ortho-P, organic P concentrations and Pw values for the plot with a P surplus of 10 kg ha⁻¹ a⁻¹, assuming a homogeneous distribution of the cow droppings (left) over the plot and an inhomogeneous distribution in which only 6 % of the area is affected by cow droppings (right).

Results showed that Pw values decreased more strongly when the actual distribution of cow droppings was taken into account. Simulated ortho-P concentrations were higher and showed a stronger temporal fluctuation using the actual distribution of the cow droppings. The increase in ortho-P concentrations and the simultaneous decrease in Pw values in caused by the fact that the maximum adsorption capacity of the soils was reached underneath the cow droppings. At these spots the ortho-P concentration showed a relatively stronger increase than the adsorbed amount of P. Despite the higher ortho-P concentrations the effect of an inhomogeneous manure application on the simulated P leaching fluxes was relatively small (P leaching fluxes increased from 1.7 to 2.0 kg ha⁻¹ a⁻¹). The inhomogeneous manure distribution mainly affected the adsorption and fixation of phosphate: the fixation of phosphate increased from 0 to5.5 kg ha⁻¹ a⁻¹, whereas adsorption decreased from 12.9 to 7.5 kg ha⁻¹ a⁻¹.

On basis of the above results it may be concluded that the use of a more realistic distribution of the manure over the plot led to stronger dynamics in the field average concentrations. However, the decrease in Pw values was overestimated. This may be due to the fact that adsorption constants were based on field average data. Better results may probably be achieved when adsorption constants are based on concentration and adsorbed amounts using data for both points that are recently affected and not affected by cow droppings. The larger discrepancy between measured and modeled Pw values may also be caused by factors such as: errors in the calculated P uptake near the cow droppings or underestimation of the area affected by cow droppings or the release of P from the cow droppings. To improve the insight in the potential effect of cow droppings on the phosphate balance and on changes in soil fertility, soil solution concentrations and soil P contents will be measured beneath cow droppings in the forthcoming year. Furthermore the distribution of cow droppings as a result of the agricultural practices (like harvesting) will be monitored to obtain information on the actual area affected by cow droppings.

6 Conclusions

Changes in phosphate concentrations and phosphate pools were measured at four experimental farms from 1997-1999. At each farm measurements took place at three plots receiving a P surplus of 0, 10 and 20 kg ha⁻¹ P. A significant rise or decline in yearly measured P pools was not yet found due to the considerable size and the strong temporal variation in the magnitude of the measured pools. Measured ortho-P and organic P concentrations, measured three times a year, showed strong seasonal variations. These variations occurred simultaneously at all sites. However, the variations could not be easily explained by differences in environmental conditions like temperature and moisture content.

Phosphate concentrations in the soil solution, phosphate budgets and changes in phosphate pools were simulated with the nutrient model ANIMO in combination with the hydrological model SWAP. Both models were calibrated on the measurements during 1996 and 1997. Data from 1999 were used for validation. The model ANIMO simulated the order of magnitude of the measured concentrations reasonably to quite good at the four sites. However, the model could not simulate the measured strong seasonal variation in ortho-P concentrations. Variations in organic P concentrations were somewhat better simulated, but the timing of peaks and tips in the organic P concentrations did not always correspond to the measurements. Simulated yearly leaching fluxes of total P were close to measured values at the sandy soils and the clay soils. However, at the peat soil the simulated leaching fluxes of total P were higher than measured values. It has to be taken into account that measured leaching fluxes are somewhat uncertain due to the limited number (three) of yearly measurements and the strong temporal variation in the measured concentrations in particular of organic P. The simulated Pw values were close to measured data, in particular at the sandy soils. However, the model tended to overestimate the decline in Pw values at the plots with a P surplus of 0 kg ha⁻¹ a⁻¹ and to overestimate the rise in Pw values at plots with a P surplus of 20 kg ha⁻¹ a⁻¹.

Simulated phosphate balances of the upper 30 cm of the soil profile indicate that on average 0.9 to 3.6 kg ha⁻¹ a⁻¹ was lost by leaching and runoff during the period 1997-1999. The largest losses were found on the sandy soils, which have relatively high phosphate contents in the lower part of the topsoil. The simulated storage of P in the topsoil ranged from -5.9 to 24.2 kg ha⁻¹ a⁻¹ and is closely related to the P surplus of the considered plots.

The simulated phosphate balances are still somewhat uncertain due to the fact that the measurement period on which the model could be validated was rather short and short and the measurement frequency of the soil solution concentrations was relatively low. Moreover, simulated losses of phosphate from the different solid phase pools could not yet be validated due to the fact that significant changes in these pools were not yet detected. Preliminary calculation also showed that the distribution of cow droppings across the field has a significant influence on the simulated storage of P in the soil solid phase. However, the effect of cow droppings on the simulated leaching of phosphorous appears to be rather limited.

On basis of the above results it may be concluded that the available data provide the opportunity to give a rather reliable quantification of the actual leaching fluxes. However, large uncertainty remains with respect to the storage of P in different solid phase pools and thus with respect to the long-term transformation and leaching of phosphorous from the soils.

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Annex 1 Measured Phosphate uptake at the four sites

Site	Surplus	Phosphate	Phosphate uptake							
	$(kg ha^{-1} a^{-1})$	1997	1998	1999						
Cranendonck	0	44.9	41.4	32.7						
	10	50.9	44.5	33.9						
	20	52.4	54.4	34.4						
Heino	0	41.3	40.6	47.8						
	10	45.1	44.9	45.3						
	20	52.0	50.3	49.8						
Waaiboerhoeve	0	40.3	47.1	44.9						
	10	38.2	43.8	46.4						
	20	44.5	53.9	46.3						
Zegveld	0	32.8	34.3	41.8						
0	10	40.6	41.7	47.7						
	20	41.3	44.8	50.5						

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Annex 2 Measured Pw values at the sites

Site	Depth	n P surj	plus (k	g ha-1 a	r ⁻¹)								
	(cm)	0				10				20			
		1996	1997	1998	1999	1996	1997	1998	1999	1996	1997	1998	1999
Cranendonck	0-5	39	39	32	41	39	42	35	43	39	47	43	47
	5-10	28	30	27	28	23	31	29	29	30	31	30	24
	10-20	25	25	32	28	22	26	28	25	26	22	32	24
	20-30	22	26	30	25	15	23	15	18	23	24	30	22
Heino	0-5	38	39	31	37	40	44	38	46	37	43	37	53
	5-10	25	27	31	32	31	26	32	36	29	23	28	31
	10-20	27	27	26	31	28	34	30	36	28	29	29	27
	20-30	29	23	26	19	24	19	26	22	19	20	27	20
Waaiboerhoeve	0-5	60	68	48	52	57	56	43	58	42	51	48	60
	5-10	22	31	21	24	17	36	17	25	19	32	16	17
	10-20	10	22	9	15	15	15	9	6	9	16	11	12
	20-30	10	14	7	4	8	12	8	5	6	12	9	4
Zegveld	0-5	32	46	34^{1}	34	30	37	30 ¹	39	26	45	43^{1}	36
-	5-10	18	20	19 ¹	13	15	22	21^{1}	16	16	17	21^{1}	20
	10-20	6	8	13 ¹	3	6	13	14^{1}	4	8	11	111	5
	20-30	2	10	7^{1}	2	3	5	6 ¹	2	7	5	5^{1}	3

Measured Pw values (mg $P_2O_5 l^{-1}$) at the four sites as a function of the P surplus

¹ Measured in april 1999