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Simulation of phosphorus losses from lysimeters

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Abstract

Because of water resources eutrophication and the need for water protection strategies, the estimation of diffuse phosphorus (P) leaching losses from agricultural soils has become an important issue. The objective of this study was to numerically depict P leaching and transformation processes to clarify the dominant factors controlling the P dynamics in soils and to investigate interactions between P and carbon (C) and nitrogen (N) cycles. We expanded the existing WASMOD modeling package with a P subroutine and tested model performance on an experimental data set from a 12 y lysimeter study.

The soil water regime, expressed in terms of yearly variation and the 12 y sum of seepage, was accurately depicted for the investigated soils under grassland. The experimentally observed average yearly P leaching losses varied between 0.03 kg ha^{-1} for a sandy loam and 1.4 kg ha^{-1} for a sand. The pronounced, texture-related differences in P leaching were generally reflected by the model, although an immobile water fraction needed to be introduced to obtain satisfactory modeling results. This demonstrated the strong effect of the flux field heterogeneity on P export. Phosphorus-sorption parameters were found to be more important for P leaching than the extent of the various P pools in the soils. Therefore, it is concluded that in P assessment studies, the sorption characteristics should be determined on an experimental and site-specific basis for top- and subsoils. Model sensitivity analysis revealed that the consideration of the P pools and their interrelation with the C and N cycles in the soil allows a differentiated analysis of the sorption-independent P dynamics. The WASMOD model is useful for the development of future agriculture management strategies to reduce P leaching losses, because its requirement for input data is relatively low.

Key words: grassland / leaching losses / modeling / WASMOD model

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1 Introduction

It has been widely accepted that phosphorus (P) losses from soils, in combination with other nutrients, may cause severe eutrophication problems in adjacent water resources (*Leinweber* et al., 2002; *Sharpley* and *Rekolainen*, 1998). Besides the surface-bound lateral transport of P *via* erosion, the vertical movement through the soil profile has been increasingly recognized as an important process. Results from different soil types cropped with grass have indicated that subsurface P transfer from soil to groundwater can occur at concentrations that could cause eutrophication. *Turner* and *Haygarth* (2000) found that total P concentration routinely exceeded 0.1 mg L^{-1}, with maximum P concentrations of >1 mg L^{-1}, in leachate from four contrasting soil types amended with mineral fertilizer.

The soil texture, land use, initial soil P concentration, fertilizer rates, fertilizer application time, and climatic conditions are important factors controlling the P transfer from soils (*Haygarth* and *Jarvis*, 1999; *Koopmans* et al., 2002). The influence of soil texture has been shown in soil column experiments with loamy sand and clay soils (*Djodjic* et al., 2004). Total P losses varied between 0.03 and 1.09 kg ha^{-1} y^{-1} with higher losses for clay soils. Similar results were presented by *van Es* et al. (2004) with P concentrations of up to 0.5 mg L^{-1} in leachate from clay loam and 0.013 mg L^{-1} from loamy sand cultivated with maize and grass. The P losses vary with time of fertilizer application. *Sims* et al. (1998) reported that the highest leaching potential was for early fall applications. In contrast, *Geohring* et al. (2001) suggested that late summer and early fall applications of dairy manure result in lower P losses. As an additional factor, the form of applied P influences the P leaching patterns. Significantly higher P losses were observed for combined mineral P fertilizer and dairy manure treatments (1.4–2.5 kg ha^{-1}) compared with a single mineral fertilizer application (0.6–1.3 kg ha^{-1}; *Toor* et al., 2004).

In this framework, an increasing number of estimation procedures including numerical simulation models have been developed to analyze and predict P leaching from agricultural

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land. A simple method to predict leaching losses is based on relationships between the indicators of the P status in soils and the downwards P leaching losses (quantity–intensity relationships) (*Heckrath* et al., 1995; *Sibbesen* and *Sharpley*, 1998; *Leinweber* et al., 1999; *Hesketh* and *Brookes*, 2000; *McDowell* and *Condron*, 2000). In general, the outcome of these studies suggests that simple P parameters from the topsoil alone are not suitable for a specific prediction of P transport. However, soil P status parameters may serve as an indicator for the leaching potential (*Djodjic* et al., 2004). Parameters such as the P sorption capacity (PSC) and degree of P saturation (DPS) were developed for acid sandy soils to calculate the risk of P leaching (*Schoumans* and *Groenendijk*, 2000). The P sorption index (P_{si}), a single-point method to characterize the relative P sorbing properties of the soil (*Bache* and *Williams*, 1971; *Heathwaite* et al., 2000, 2003), and the soil P capacity derived from a ^{32}P-isotopic method (*Frossard* et al., 1993), allow one to rank soils according to their sorption capacities.

Simple empirical factors such as quantity–intensity relationships, DPS, and P_{Si} take selected soil chemical features into consideration but do not account for soil physical properties and weather boundary conditions, both of which form the flux regime at a given site.

Alternatively, physically based numerical simulation models can be applied to evaluate P behavior. The basis for mechanistic solute transport modeling is an appropriate depiction of the water-flux regime caused by highly dynamic weather conditions (*Abdou* and *Flury*, 2004). Most models in use were originally developed for other nutrients such as nitrogen (N) and have been extended for P leaching. In addition, a number of P pools and processes for transformation, translocation, and distribution of P have to be considered. Land use is another important factor influencing the P dynamics in soils used for agriculture (*Heathwaite*, 1998). Most models only depict some of the processes (*McGechan* and *Lewis*, 2002). In the majority of the P leaching models such as Animo (*Groenendijk* and *Kroes*, 1999), Gleams (*Knisel*, 1993; *Shirmohammadi* et al., 1998), MACRO (*Jarvis*, 1994), Morpho (*Pudenz*, 1998; *Pudenz* and *Nützmann*, 1997), and Wave (*Ducheyene* et al., 1998), the dominant P forms and pools and their transformations are considered (*Lewis* and *McGechan*, 2002; *Schoumans* and *Chardon*, 2002). In general, the relevant P processes are considered in isolation, independent from the prevailing carbon (C) and N transformation processes. However, it has been shown that the soil organic matter (SOM) is not only important for the sorption of nutrients (*McGill* and *Cole*, 1981), but also plays a role in the dynamics of the various P pools. In addition, most of the currently published P leaching models do not account for physical nonequilibrium conditions which, because of small-scale heterogeneities, often affect the transport of nutrients in soils (*Lennartz* et al., 1999; *Šimùnek* et al., 2003).

The main purpose of this study was to predict P losses from different grassland soils and different fertilizer application rates to help develop agriculture management practices to protect water resources. Our first objective was to develop a new P submodule for the existing WASMOD (**W**ater **a**nd **S**ubstance Simulation **Mod**el) model. The goal of this model development was to use simple and readily available soil-hydrology and soil-chemistry input data, as well as the careful consideration of the interactions between the pathways of C, N, and P transformations. The WASMOD model is based on an integrated description of water and heat dynamics, organic matter (OM) and N transformation processes in the unsaturated and saturated zones (*Reiche*, 1991). Because the hydrology of soil types differs widely, our second objective was to validate this model with lysimeter data. We tested model performance by comparing our numerical calculations with experimental data derived from an intensive 12 y lysimeter study (*Godlinski* et al., 2004). This experimental data base also facilitated investigation of the effects of soil texture and fertilizer application rates on P leaching losses.

2 Material and methods

2.1 Modeling concept

The WASMOD model is a modular, process-based package that simulates soil water and groundwater dynamics, surface runoff, soil heat budget, organic C, N transformation processes, and nutrient uptake by plants for a single location or entire catchment (*Fränzle* et al., 1989; *Reiche*, 1991, 1995; *Göbel* et al., 2001). In our study, the model was applied to a 1D-case with emphasis on the vertical transport through the soil profile.

Transport and transformation processes are considered in the vegetation, soil surface, unsaturated and saturated zones. The atmosphere represents the upper system boundary, characterized by daily measured meteorological data of air temperature, global radiation, and precipitation. The model system components, namely heat flow, N dynamic, and mineralization, and organic C processes, are described elsewhere in detail (*Reiche*, 1994, 1996) and will be considered here only with respect to the P dynamics.

Description of the water flow in the unsaturated zone is based on the Richard's equation using the methods of finite differences. The potential evapotranspiration is calculated according to a modified Penman approach (*ATV-DVWK*, 2002). The reduction of the potential to the actual evapotranspiration is based on the availability of soil water and plant root depth, which varies according to the physiological conditions of the vegetation. The vegetation cover and land use are described by calculating the N and P uptake by plants using a crop-specific plant uptake function following the Michaelis-Menten equation. Different types of soil tillage, crop seeding, fertilization, and crop harvest are included in an agricultural management system submodel.

In this study, a new P submodule was developed. Phosphorus is considered to be present in one out of four interconnected P pools: the dissolved (P_{sol}), adsorbed (P_{sorb}), fixed (P_{fix}), and organic P (P_{org}) pools (Fig. 1; *Godlinski*, 2005).

Phosphorus enters the system through fertilization, either as mineral or organic fertilizer (submodel for agricultural man-

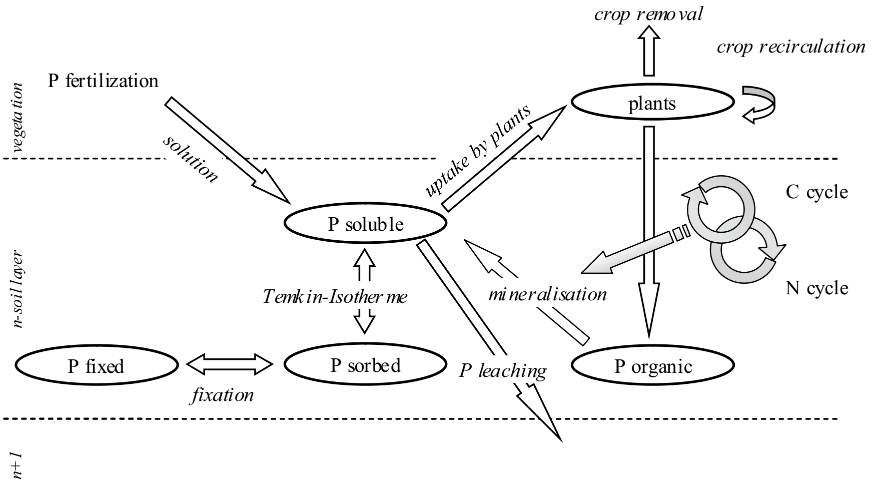

Figure 1: Phosphorus pools and P processes in the WASMOD model.

agement). The method of fertilizer application may also vary between surface application or incorporation into topsoil layer. Once the fertilizer is applied, P is assumed to dissolve and subsequently adsorb, according to given distribution coefficients.

The P uptake by plants (P_{Pl}) depends on a plant-specific uptake coefficient (a_{Pl} [–]), the P concentration of the soil solution (C_P [mg L^{-1}]), and the transpiration rate (t_{Pl} [L s^{-1}]) (Eq. 1).

$$P_{Pl} = a_{Pl} \cdot C_P \cdot t_{Pl}. \quad (1)$$

The P uptake is treated as passive process, *i.e.*, the P is transported into the plant with water that is taken up with the transpiration stream. The P assimilation depends on the plant growth and the resultant P need. At early stages of the vegetation period, potential maximum and actual P uptake may differ according to P availability. Deviations are less pronounced at the end of the vegetation period when the P demand of plants decreases. A reduction of the P uptake occurs under water shortage and dry soil conditions. The P uptake takes place to a plant-specific maximum value.

The crop removal and crop recirculation depend on the selected crop. Phosphorus can be present in the crop, in the remaining plant parts above ground (leaves, stems, *etc.*), and in the roots and is subsequently either removed from, or remains in, the system. Where there is permanent grassland, P is regularly removed with each grass cut. In nonperennial crop systems, P in plant residues after harvest is assigned to the organic-P pool of the upper soil layer.

The mineralization of the organic P (P_{org} [mg kg^{-1}]) is calculated on the basis of the C : P ratio and the C mineralization rate (ΔC_{org} [mg kg^{-1}]) (Eq. 2) which follows a first-order kinetic function of the soil water status and soil temperature.

$$\Delta P = \Delta C_{org} \cdot P_{org}. \quad (2)$$

The amount of mineralized P (ΔP [mg kg^{-1}]) depends linearly on C leaving the soil as CO_2. The net mineralization of N is calculated as a result of the C translocation and the turn-over processes. Furthermore, the nutrient dynamics are coupled to the general convection–dispersion equation for solute transport simulation.

For the P sorption process, the Temkin adsorption isotherm was found to be suitable to cover the entire P concentration range occurring in natural agricultural soil systems (Eq. 3; *Polyzopoulos* and *Pavlatou*, 1991; *Scheinost*, 1995). In addition, no modification of the function was needed to describe situations where P is already present in the system. This would lead to desorption of P in classical batch tests at low initial concentrations (*Bache* and *Williams*, 1971; *Barrow*, 1978).

$$\Delta S = A_T \cdot \ln\left(\frac{C_P}{P_{I0}}\right), \quad (3)$$

S = adsorbed P amount (mg kg^{-1}),
C_P = P concentration in solution (mg L^{-1}),
A_T and P_{I0} = Temkin parameters (mg kg^{-1} and mg L^{-1}).

The Temkin parameters depend on the amount of initial P in the system. In long-term investigations, isotherm parameters may change according to the variations in P storage. In WASMOD, the range of the initial P content is covered by moderately adjusting the Temkin parameters. The transfer of P into the fixed P pool is adjustable and in this study, it was assumed to be 10% of the average adsorbed amount per year (*Barekzai*, 1984). Remobilization of fixed P is possible when the adsorbed amount drops below 1/10 of the fixed P pool. In such cases, the annual remobilized amount (calculated on a daily basis) is assumed to be 1% of the fixed P pool.

2.2 Transport nonequilibrium conditions

Flow and transport processes in the unsaturated soil zone are often affected by nonequilibrium conditions (*van Genuchten* and *Wierenga*, 1976). In loamy as well as in sandy soils, soil water not participating in the transport of solutes has been observed (*Oliver* and *Smettem*, 2003; *Zurmühl*, 1998; *Bond* and *Wierenga*, 1990). Ignoring these immobile water phases may lead to a slower transport simulation compared with experimental results (*Lennartz* and *Meyer-Windel*, 1995). In WASMOD, immobile water and the resulting physical nonequilibrium are described by two parameters. While α (time^{-1}) is the rate parameter controlling the transfer of dissolved compounds from mobile to the immobile water phase, β (–) accounts for a permanent nonequilibrium resulting, *e.g.*, from an anion-exclusion volume. The nonequilibrium routine of WASMOD has no effect on the discharge regime, only on the solute behavior. During preliminary modeling, α and β were kept constant at unity to assume equilibrium conditions. Later, α was optimized manually while β remained fixed at 1.

2.3 Model input variables

The soil profile was divided into 15 compartments. The top two compartments were set to 5 cm, compartments 3–11 to 10 cm, and the remaining compartments were chosen according to the groundwater table (compartments 12–14 to 20 cm, compartment 15 to 100 cm).

The numerical investigations required a set of input variables for the weather, soil, plant, C, N, and P conditions (Tab. 1). All soil variables were derived from measurements on the original substrate from 1983 separated into top- and subsoil (Tab. 2).

The weather variables such as precipitation, minimal and maximal temperature, and the daily sum of global radiation were measured on-site on a daily basis. Most soil chemical and physical characteristics were determined from independent measurements. The soil water retention function was derived from soil texture and bulk density using pedotransfer functions (*Schaap* et al., 2001). The initial water content was adjusted to the water content at 30 hPa.

Table 1: Model input variables.

Variable	Unit	Determination method
Weather		
Precipitation and irrigation	mm	daily values, measured on site
Temperature (min and max)	°C	daily values, measured on site
Global radiation	J cm^{-2}	daily values, measured on site
Soil		
Texture		measured
Total organic carbon C_t	%	measured with dry combustion
Dry bulk density ρ_d	g cm^{-3}	measured
K_s	cm d^{-1}	estimated from soil texture
Water-retention function	hPa	assessed from soil texture (*Schaap* et al., 2001)
Initial water content	Vol%	water content at 30 hPa
pH	–	measured in $CaCl_2$, s:w 1:2.5
Plant		
LAI	cm^2 cm^{-2}	literature (*Reiche*, 1991)
Vegetation factor	mm mm^{-1}	literature (*Ernstberger*, 1987; *Löpmeier*, 1994)
Root depth	cm	30 cm (*DVWK*, 1996)
Fertilization	kg ha^{-1}	applied mineral P fertilizer
C : N		
Added organic material	kg ha^{-1}	model intern, calculated from harvest type
Microbial biomass	kg ha^{-1}	model intern, calculated from harvest type
Soil organic matter	kg ha^{-1}	calculated from literature (*Balesdent*, 1996; *Rühlmann*, 1999)
Soil nitrogen	kg ha^{-1}	calculated from literature (*Balesdent*, 1996; *Rühlmann*, 1999)
Phosphorus		
P_{sorb}	mg kg^{-1} and kg ha^{-1}	measured, DL- P
P_{org}	kg ha^{-1}	topsoil 40% (SL) and 35% (S), subsoil 20% (SL) and 15% (S) of P_t (*Harrison*, 1987)
P_{fix}	kg ha^{-1}	calculated as $P_{fix} = P_t – P_{sorb} – P_{org}$
P_{sol}	mg L^{-1} and kg ha^{-1}	calculated from measured isotherms
P_{l0} and A_T	mg L^{-1} and mg kg^{-1}	derived factors from measured isotherms

Table 2: Selected soil properties of the investigated lysimeters.

Soil properties		**Sandy loam**		**Sand**		**Gravel**
		0–30 cm	30–100 cm	0–30 cm	30–100 cm	>100 cm
Sand (2–0.06 mm)	%	73.6	75.6	88.2	91.2	94.0
Silt (0.02–0.002 mm)	%	14.3	17.4	6.7	6.7	4.0
Clay (<0.002 mm)	%	12.1	7.4	5.1	2.1	2.0
Dry bulk density ρ_d	g cm^{-3}	1.48	1.84	1.34	1.66	1.30
K_s	cm d^{-1}	21	43	335	200	750
C_t	%	1.13	0.17	2.68	0.04	0.01
pH		5.8	5.6	5.6	6.0	5.5
Water content at 0 hPa	Vol%	39.8	29.3	43.7	33.8	44.0
Water content at 30 hPa	Vol%	27.2	18.7	18.5	10.9	9.0
Water content at 300 hPa	Vol%	15.3	11.6	7.1	4.9	5.5
Water content at 3000 hPa	Vol%	8.0	6.6	5.1	4.6	4.7
Water content at approx. 30000 hPa	Vol%	5.9	4.7	5.0	4.6	4.0

Plant variables to describe the seasonal plant growth were chosen according to fertilizer rates to account for a plant habitus–dependent transpiration scenario. The vegetation factor (VF) and leaf-area index (LAI) were selected from the literature (*Ernstberger*, 1987; *Löpmeier*, 1994; *Reiche*, 1991, 1996). The LAI is the ratio of the total area of all leaves on a plant to the area of ground covered by the plant, VF is necessary to calculate the vegetation-specific potential evapotranspiration rate. The rooting depth was fixed at 30 cm (*DVWK*, 1996). The management function included the type of fertilizer (mineral or organic) and the management practice (four cuts and removal of grass each year).

The added organic matter (OM) was divided into three main pools: added OM as plant residues and manure, microbial biomass, and SOM. The first two pools are divided into fractions of high and low mineralization intensity. The added OM was calculated from harvest type with the ratio of high to low mineralization set to 70:30. For microbial biomass, this ratio was set to 44:56. The SOM pool was divided in three pools: almost not decomposable, long-term, and fast mineralizable. These pools were set from the literature to 10:85:5 (*e.g.*, *Balesdent*, 1996; *Rühlmann*, 1999). Soil N as organically bound N, ammonium, and nitrate were distributed 99:0.5:0.5.

The values for the P_{sorb} concentration were measured as plant-available P with approx. 16% (sandy loam [SL]) and 20% (sand [S]) of the total P concentration (P_t) in the topsoil. Values for the P_{org} pool were taken from literature (dependent on soil texture, pH, and soil depth) with 40% (SL) and 35% (S) of the P_t concentration in the topsoil and 20% (SL) and 15% (S) in the subsoil (*Harrison*, 1987). The P_{fix} pool was calculated ($P_{fix} = P_t - P_{sorb} - P_{org}$). The Temkin parameters were derived from measured isotherms (Tab. 3).

During model runs, time steps were adjusted automatically according to the highest soil water flow rate from one spatial layer to another and were within the range of 10 min to 2 h. The basic time step of the temperature submodel was 4 h, while the submodel calculating the biological transformation processes had a fixed time step of 1 d. The phenological development of vegetation (root density distribution, LAI) was calculated in bi-weekly intervals.

Table 3: Input values of P pools and sorption isotherm (Temkin) used in the model runs.

Depth (cm)	P_{sorb} (mg kg^{-1})	P_{sol} (mg L^{-1})	P_{org} (kg ha^{-1})	P_{fix} (kg ha^{-1})	P_{l0} (mg L^{-1})	A_T (mg kg^{-1})
Sandy loam						
0–30	83.68	0.515	311.63	343.60	0.515	19.31
30–80	8.08	0.015	45.51	167.20	0.015	24.81
80–100	8.08	0.002	45.51	167.20	0.002	37.00
Sand						
0–30	246.34	2.067	577.66	742.71	2.067	12.25
30–80	43.10	0.008	122.67	623.61	0.008	25.00
80–100	43.10	0.001	122.67	623.61	0.001	40.00

2.4 Experimental set-up and condition

The lysimeters used in this study were located at the Falkenberg Lysimeter Station, Helmholtz Centre for Environmental Research – UFZ, Germany. The lysimeters were filled with disturbed top- and subsoil material in 1983 and were subjected to regular agricultural treatment thereafter. The six lysimeters selected for this study were managed as grassland with varying fertilizer rates and irrigation (*Meissner* et al., 1995; *Leinweber* et al., 1999; Tab. 4). For the current study, we used a time period of 12 y (from Oct. 1991 to Sep. 2003). During this period, the annual precipitation including irrigation varied from 617 to 1121 mm y^{-1}, with a mean of 845 mm y^{-1}. The irrigation amount varied between 105 and 270 mm y^{-1} depending on the plant demand (as calculated for a sandy soil) and was equal for all lysimeters. The time period from 1992 to 1994 was wet compared with the mean annual precipitation, whereas the years 1998 and 1999 were comparably dry.

The soil monoliths had a surface area of 1 m^2 and a height of 1.25 m. The topsoil was 30 cm and the subsoil 70 cm. The lower boundary was a 25 cm gravel layer and a drainage pipe which routed the leachate continuously to a storage container. Annual seepage water fluxes were calculated from monthly samples. In three lysimeters, the dominant soil texture in the top- and subsoil was sand, with sandy loam in the other three lysimeters (Tab. 2).

The following P data were collected and used for comparison with simulated data: monthly P_t concentration in the leachate (one mixed sample per month), annual P uptake by plants and annual mineral fertilizer rate, P amount in the topsoil, and adsorption isotherms as determined from classical batch experiments. The P_t concentration in leachate was determined photometrically after digestion with potassium persulfate using the molybdenum-blue method (*Murphy* and *Riley*, 1962). Standard deviations of triplicate samples were generally <6%. Soil samples for P analysis were taken every year in spring. The plant-available P was analyzed with the "double lactate" method (DL-P) (*Hoffmann*, 1991). Total P concentration in the soil was determined after digestion with hypobromide (*Dick* and *Tabatabai*, 1977). For the derivation of the adsorption isotherms, a series of air-dried soil samples were shaken for 24 h with 30 mL of calcium chloride solution (0.02 M) using a soil-to-solution ratio of 1:10. Nine initial P concentrations ranging from 0 to 25 mg L^{-1} were processed (*Barrow* and *Shaw*, 1975). The P concentrations in the extracts were determined by inductively coupled–plasma spectroscopy (OES-ICP, Jobin Yvon 238 Ultrace, Instruments S.A. GmbH, Grasbrunn, Germany) at 214.9 nm. Standard deviations of triplicate samples were generally <2%.

3 Results and discussion

3.1 Seepage-flux simulation

Model simulations were carried out over a period of 21 y for equilibration purposes. Results from the last 12 y (1991/92 to 2002/03) corresponding to the experimental test period are presented in Tab. 5, corresponding measured flux rates are given in Tab. 4. The general differences in seepage flux between the two soil types as observed in the experimental investigations are reflected by the model. The higher amount of seepage from the sandy lysimeters was in accordance with the differences in the soil hydraulic properties, mainly the water retention function (Tab. 2). In general, a greater water

Table 4: Phosphor fertilizer rate, observed P uptake, and water balance components of selected lysimeters (means of the12 y period).

Texture	Identifier	P-fertilizer rate†	Mean P uptake‡	Mean flux rate§	Range of flux rate
		(kg ha^{-1} y^{-1})	(kg ha^{-1} y^{-1})	(mm y^{-1})	(mm y^{-1})
SL	SL I	20	37	207	16–339
SL	SL II	40	52	186	0–320
SL	SL III	60	61	166	0–303
S	S I	20	42	232	49–355
S	S II	40	47	213	57–382
S	S III	60	56	196	5–328

†P fertilization: mineral fertilizer
‡P uptake: mean of the period 1992–2002
§ flux rate: calculation period Oct. to Sep.

Table 5: Sum of precipitation and irrigation, observed and simulated seepage flux, for different soil textures over the 12 y period.

Soil texture		Sandy loam			Sand		
Fertilizer rate / (kg ha^{-1} y^{-1})		20	40	60	20	40	60
Precipitation and irrigation	(mm)	10104	10104	10104	10104	10104	10104
Observed seepage flux	(mm)	2479	2237	1995	2779	2556	2347
Simulated seepage flux	(mm)	2387	2175	1901	2855	2689	2480

retention capacity results in increased evapotranspiration and consequently in less groundwater recharge (*Knappe* et al., 2002).

With respect to the total sum of seepage, the water balance was better reproduced for the sandy loam lysimeters (underestimated up to 4.7%) than for the sand variants. Seepage flux from sand was generally overestimated (up to 5.7%). Note, however, that model input values which were generally determined from independent sources, and not from model optimizations, caused slight deviations between modeled and measured seepage flux.

It should be pointed out that the large variability in discharge generation between lysimeters is also a source for the uncertainty in the comparison between computed and measured values. As an additional factor contributing to deviations between computed and observed discharge, the construction of the lower boundary of the lysimeters has to be taken into account. Although the gravel layer was explicitly considered in all model runs, the embedded drainage pipe may have altered the flux compared with model predictions.

The numerical investigations did confirm the fertilizer effect on discharge generation (Tab. 5). A model sensitivity analysis (details not shown here) revealed that soil chemical features (pH, C_t) and the initial soil water content were of minor importance, whereas the saturated hydraulic conductivity value (K_s) and the water retention curve (as expected) modify model output significantly. Plant variables, especially the LAI and the VF, are also relevant for water balance estimations. The LAI influences the interception of plants, whereas the VF drives the transpiration (*Reiche*, 1996). The yearly discharge dynamics was satisfactorily reproduced with the model in all cases ($r \geq 0.873$, $p > 0.001$, df = 10, Fig. 2 a, b), and the importance of soil texture on seepage flux was confirmed.

To analyze the difference between measured and predicted values, the RMSE (root mean square error) was calculated (*Loague* and *Green*, 1991). The yearly amount of seepage from sandy loam was slightly overestimated by 9% over the 12 y period with a RMSE of 48 mm for yearly seepage. For the sand variant, the seepage flux was underestimated by 4% (RMSE 36 mm y^{-1}). Most seepage occurred during the winter months, and this seepage flux was accurately simulated by the model. In summer after a heavy rain or intensive summer irrigation, the simulations failed to reproduce large events of seepage fluxes. In these summer periods (April to September), the monthly RMSE was 8 mm for the sandy loam and 16 mm for the sand.

Minor deviations between the measured and modeled variations of seepage fluxes are possible because of an inappropriate depiction of the plant root system. As previously mentioned, a uniform rooting depth of 30 cm was assumed in all model runs independent of the fertilizer rate. In addition, root density which is enhanced by an increased fertilizer input (*Brye* et al., 2002) could not be simulated with the model package.

3.2 Phosphorus dynamics—simulation results

3.2.1 Model-sensitivity

The sorption process plays a crucial role in the mobility of solutes. Therefore, we first analyzed model sensitivity by varying the sorption parameter A_T, as well as variables for the C, N, and P pools. Secondly, we studied the importance of the nonequilibrium condition factor α on the P concentration level and its variability at the lysimeter's outlet. Figures 3–5 summarize the results of the sensitivity study.

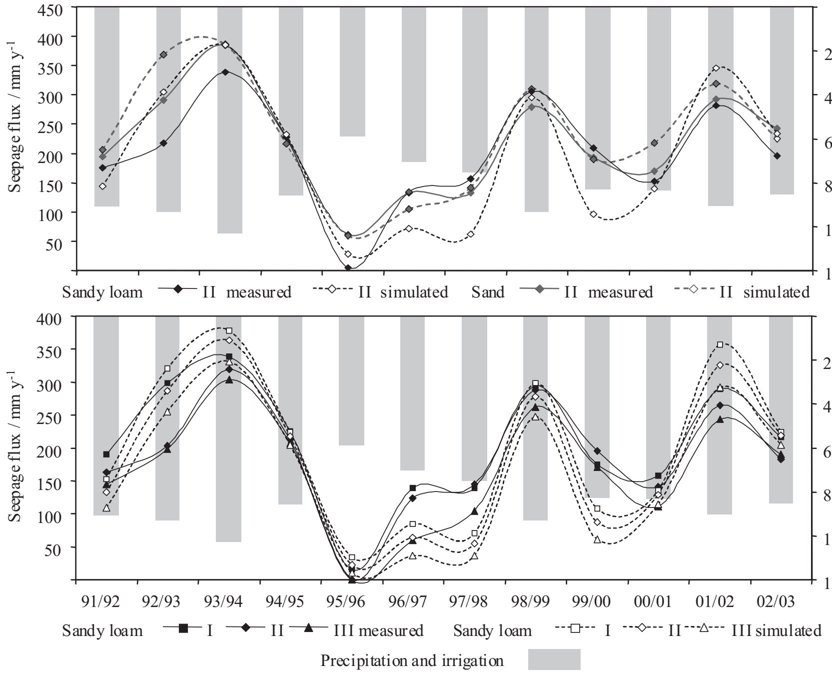

Figure 2: Observed and simulated annual seepage flux at (a) different soil textures and (b) different fertilizer rates over a 12 y period.

A larger sorption capacity, represented by higher parameter values of A_T (starting values given in Tab. 3), resulted in almost no variation in the sum of P leaching losses at given P input rates, whereas a reduction of A_T yielded increased P export rates for both soil types (Fig. 3). It seems that from a certain threshold onwards, an increased sorption capacity has no further effect on P leaching. Sorption of P is a function of the soluble P (Eq. 3, Fig. 1) which is influenced by the P input, P uptake by plants, and the P_{org} pool. From the threshold onwards, the P concentration in the soil solution is too low for further sorption. Only an increased P input into the system (P fertilizer) would lead to a larger P solution concentration and an enhanced adsorption.

To distinguish among the influences of the P_{sorb}, P_{org}, and C and N pools in the numerical experiment on P leaching, starting values of the P variables were set to equal for both soil types. The value of the P_{sorb} pool had almost no effect on the sum of P leaching losses (Fig. 4). Because of the exponential function for the sorption isotherm (especially for the subsoil), increased P_{sorb} pool values cause only minor changes in the solution concentration. Additional P in the soil solution is immediately absorbed by plant roots. In contrast, an increase in the P_{org} pool resulted in increased P transport and P uptake by plants, because the extent of mineralization is a function of the C transformation rate and the P_{org} pool. Conversely, an increase in the C and N pools produced lower P losses, predominantly because of a larger number of sorption sites at organic interfaces. The C and N transformation is independent of P and is controlled by soil temperature, water content, and pH.

The impact of the nonequilibrium conditions on P transport is shown in Fig. 5. For both soils, a smaller mass transfer rate between mobile and immobile water phases resulted in higher P export rates indicating an influence of immobile water regions on transport. This confirms results from field studies on a fine-texture soil where conservative tracers had been applied (*Ventrella* et al., 2000). Our results demonstrate that soil texture is important for the occurrence of immobile water in soil. The lower optimized value (α = 0.65) for the sandy soil is in agreement with results from *Phillips* and *Burton* (2005), who investigated nutrient leaching on a sandy podzol. Also, the soil depth was shown to be an important factor, because the effect of disregarding nonequilibrium conditions becomes more pronounced with increasing transport distance of a solute (*Oliver* and *Smettem*, 2003). However, in some other studies on sandy loam soils, immobile water had only minor effects on solute transport (*Abbasi* et al., 2003).

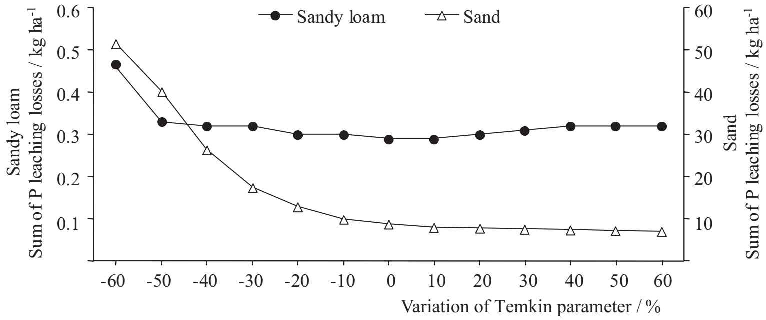

Figure 3: Effect of the Temkin sorption parameter A_T on P leaching losses.

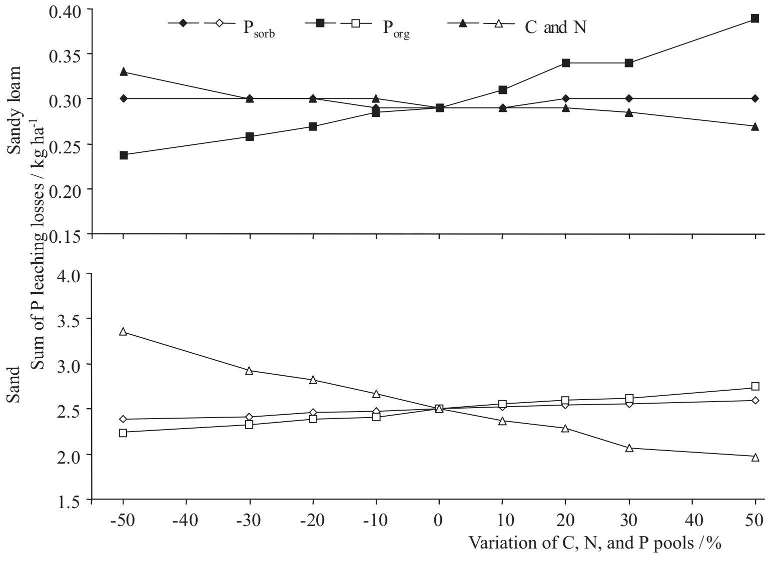

Figure 4: Effect of the C, N, and P pools on P leaching losses.

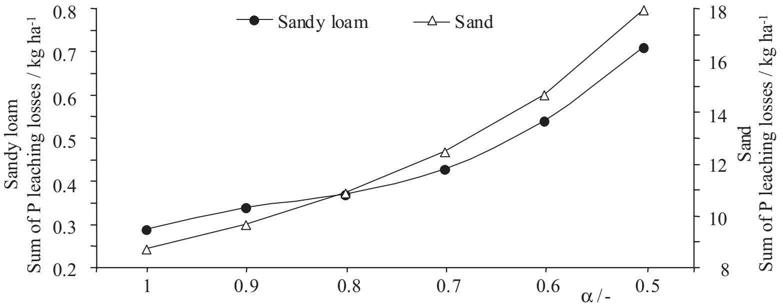

Figure 5: Effect of the nonequilibrium parameter α on P leaching losses.

3.2.2 Model performance

Three model simulation outputs were investigated, namely the monthly and total sum of P leaching losses and the yearly P uptake by plants. All simulation results are based on the input variables as listed in Tab. 2 and 3.

Variability of P losses: As a first result, Fig. 6 a, b shows a comparison between the measured and simulated P leaching losses at optimized nonequilibrium conditions on a monthly basis. The leaching variability was well reflected by the model with higher P losses in the years 1992 to 1994 and 2001 to 2002 but also with very low losses in the years 1995 to 1997. There were also higher values in winter than in summer. The low mean yearly measured P leaching losses in winter (0.0045 kg ha^{-1}) and summer (0.0023 kg ha^{-1}) for sandy loam were well reflected by the model (0.0036 and 0.0015 kg ha^{-1}, respectively). In contrast, the higher measured values for the sandy soil were underestimated (measured 0.241 kg ha^{-1}; predicted 0.136 kg ha^{-1}) in winter and overestimated (measured 0.078 kg ha^{-1}; predicted 0.102 kg ha^{-1}) in summer.

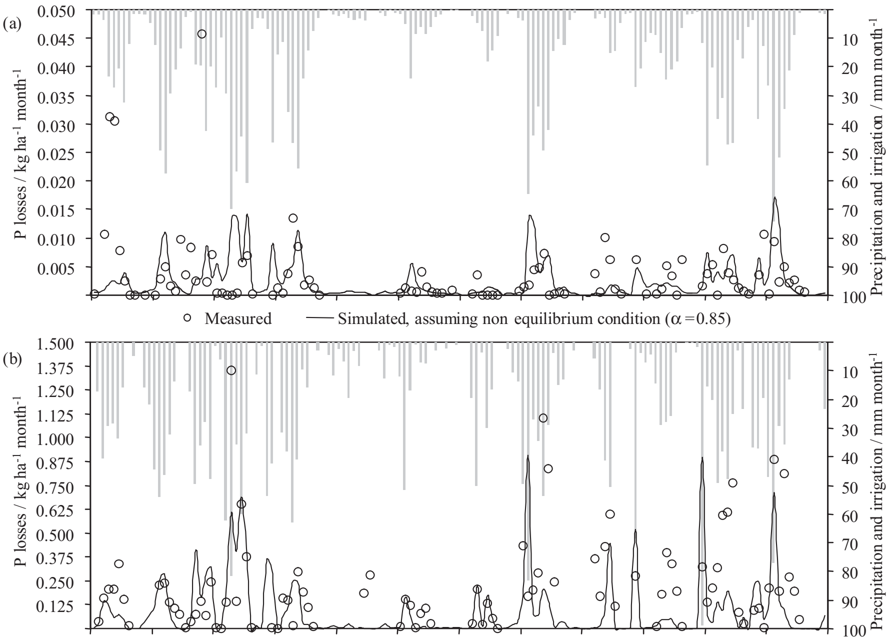

Figure 6: Monthly precipitation and irrigation and observed and simulated P losses from (a) sandy loam and (b) sandy soil (note scaling differences).

Table 6: Sum of observed and simulated P leaching losses for different soil textures over the 12 y period.

Soil texture		Sandy loam			Sand		
Fertilizer rate / (kg ha^{-1} y^{-1})		20	40	60	20	40	60
Observed P losses	(kg ha^{-1})	0.38	0.36	0.30	15.76	19.76	15.02
Simulated P losses (equilibrium conditions)	(kg ha^{-1})	0.34	0.29	0.24	9.05	8.73	8.53
Simulated P losses (nonequilibrium conditions)	(kg ha^{-1})	0.39	0.35 α = 0.85	0.29	13.62	13.48 α = 0.65	13.52

Discrepancies between measured and simulated data might be related to the seepage flux simulation. Extreme summer-rainfall and irrigation events were not well reflected by the model, which results in smaller P losses compared with measured values. In addition, some single but pronounced P leaching peaks could not be simulated, especially after fertilizer application in January and March and after first events following a dry summer period. We believe that macropore flow and preferential solute transport contributed significantly to these observed deviations. Although the model accounts for nonequilibrium conditions as they are generally encountered within mobile/immobile flux fields, it does not reflect extreme preferential transport situations as described in the literature (*McGechan* et al., 2005; *McGechan*, 2003; *Preedy* et al., 2001; *Hooda* et al., 1999).

Cumulative P losses: As a second result, the P leaching losses (simulated on a daily basis) are presented as the sum of losses over 12 y in Tab. 6. The magnitude of predicted values differed widely between the two textures, with very low values for the sandy loam. The simulated losses calculated as percentage of P input (20, 40, 60 kg ha^{-1} y^{-1}) varied between 0.16%, 0.07%, and 0.04% for the sandy loam and between 5.68%, 2.81%, and 1.93% for the sand, for the respective application rates. These results correspond to the following measured values: 0.16%, 0.08%, and 0.04% for sandy loam and 6.56%, 4.12%, and 2.09% for the sand.

Unexpectedly, the ratio of fertilizer input and P losses from both soils decreased with increasing fertilizer rates indicating the complexity of the system. We would intuitively assume that system input and output are positively correlated. The observed opposite correlation may be related to the plants functioning as an additional regulator in addition to various fixation and transformation processes. An increased nutrition-amplified plant growth resulted in an increased uptake of the fertilizer, although, in general, an opposite behavior can be expected (*Kutra* and *Aksomaitiene*, 2003; *Helyar*, 1998). From a plant physiologist's point of view, the enhanced nutrient use efficiency can be explained by a denser and more effective root system. For *Trifolium* species, it has been observed that root dry matter increases with an enhanced P fertilization (*Mugwira* et al., 1997). For modeling purposes, the plant growth optimized by fertilization is described by increased LAI and plant coefficients.

P uptake: The measured and simulated P uptake by grass is given in Fig. 7. For the sandy loam variants, the simulated P uptake is in the range of measured values, but it was in general overestimated for the lysimeters filled with sand. This is probably related to the higher P concentration in soil solution of the sandy soil and the calculation of P uptake as a passive process. The measured P uptake is in the range of other long-term studies on grassland (*Gallet* et al., 2003) and also confirms results from *Schils* and *Snijders* (2004) who reported increasing P uptake for grassland with increasing fertilizer rates.

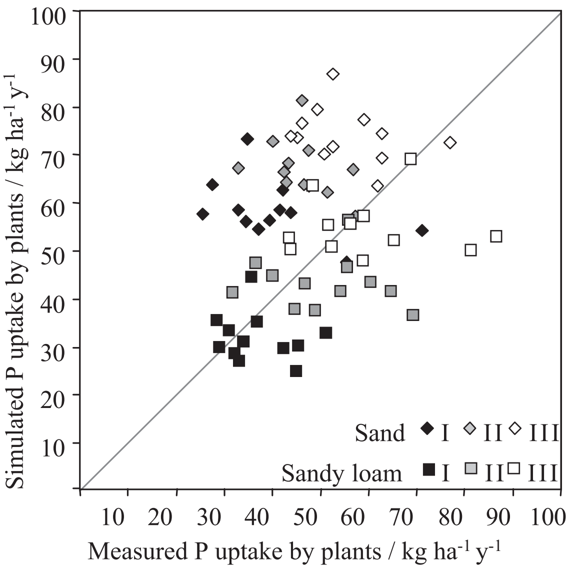

Figure 7: Observed and simulated annual P uptake by plants in differently textured soils at various fertilizer rates over a 12 y period.

4 Conclusions

Phosphorus is commonly considered as the limiting factor in the eutrophication process of water bodies, emphasizing the necessity to assess P leaching from soil. In this study, we developed a new P submodule for the process-based WASMOD model in which the soil C and N transformation and vegetation cover are simulated. The integration of four relevant P pools (dissolved, adsorbed, organic, and fixed P) with P transformation processes resulted in plausible estimates of P leaching and uptake by plants. The measured P leaching losses expressed as the 12 y sum and the annual and monthly variations from long-term sandy loam and sand-filled lysimeters with permanent grassland were adequately simulated using the WASMOD model.

Numerical investigations indicated that the P losses from soil were controlled by the P sorption process, the amount and transfer of P pools, and the physical nonequilibrium conditions caused by immobile water phases as follows:

(1) Model sensitivity analysis indicated that the P concentration in the soil solution is the limiting factor for the P sorption and is controlled by the P input (fertilizer and mineralization rate) and the P export (uptake by plants). Sorption parameters should be determined independently and individually for each investigation because they vary with soil texture, land use, and fertilization history and strongly affect modeling output.

(2) Considering certain P pools and their interaction with the soil's C and N cycles allows a differentiated analysis of the sorption-independent P dynamics.

(3) Simulation of experimentally obtained P leaching losses was only plausible when physical nonequilibrium conditions were assumed, indicating strong effects of immobile water

regions on P leaching. This indication is based on simplified assumptions in the WASMOD model. Generally, other soil physical factors such as the distribution of mobile and immobile water and the dispersion coefficient also have an influence on P leaching. These factors will be considered in the forthcoming development of the WASMOD model.

Overall, the newly developed P approach for the WASMOD model was successful for predicting P losses from soils in lysimeters. Subsequent research could include testing the model on a larger scale for the development of P management strategies for agricultural land use.

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