Characterization, desorption, and mining of phosphorus in noncalcareous sandy soils

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Abstract

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In areas with intensive livestock farming, soils have been enriched with phosphorus (P), following heavy applications of animal manure. These soils are a risk for nearby surface waters, as the leaching of P from these soils contributes to eutrophication of these surface waters. This study was set up to better understand the speciation and desorption of P in noncalcareous sandy soils, so as to contribute to the development of management guidelines for these soils. Phosphorus speciation in soils sampled from the top 5 cm of grassland sites exposed to different fertilization regimes in a long-term field experiment was characterized using both classical wet chemical analysis and ^{31}P nuclear magnetic resonance spectroscopy. Phosphorus was mainly present in the inorganic form; orthophosphate monoesters were the main organic P compounds extracted. Thus, risk of P loss from the top 5 cm to the subsoil is mainly related to inorganic P.

Mining soil P can be defined as harvesting P taken up from the soil by a crop grown without external P addition, followed by the off-site removal of the above ground plant parts. In a long-term greenhouse experiment, the method of cropping grass was used to deplete a P-enriched potted soil. This caused a relatively large decrease of the P concentration in $CaCl_2$ extracts used to approximate P in soil solution. In contrast, the relative decrease of the total pool of P sorbed to the solid phase was much smaller. A simple tool, referred to as the dynamic bioavailability index (DBI), was used to determine whether kinetics of P desorption are expected to limit P uptake. The DBI is the dimensionless ratio of the maximal diffusive flux of P from the soil aggregates to the soil solution and the rate of P uptake by the plants. Based on the DBI, P uptake in the initial stage of the pot experiment was not limited by P desorption. However, with time, the supply rate of P from soil to the root could not meet the demand needed for an optimal P uptake anymore. The concept presented here could be seen as a promising onset to a new dynamic approach of bioavailability. It is concluded that mining soil P may be an effective remediation strategy to decrease the risk of P leaching from P-enriched soils. However, this suggestion has to be confirmed in the field.

Key words: bioavailability, depletion, desorption kinetics, dynamic bioavailability index, isotherm, mining, phosphorus, ^{31}P nuclear magnetic resonance spectroscopy, pot experiment, speciation, threshold, uptake.

Contents

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General introduction

Introduction

Phosphorus (P) is an essential nutrient for plant growth. Although plant roots are capable of absorbing P from the soil solution at low P concentrations (Hinsinger, 2001), most soils cannot supply sufficient amounts of P to the plant. In these soils, plant growth is limited by P deficiency. This is especially the case in highly weathered tropical soils, but also in many soils in temperate areas which have not received P fertilizers. Phosphorus deficiency is caused by low native P contents and by strong binding of P to the solid phase of the soil. To overcome P deficiency, application of P fertilizer is needed. With continued P fertilization, the amount of P in the soil increases, and more P in the soil becomes available to the crop. The increased availability of soil P can be easily detected via various chemical extraction methods. Relationships between the measured concentration in a certain extract and crop yields in the field can be established by comparing both sets of data. These relationships are widely used as a basis for P fertilizer recommendations (Tunney et al., 1997). Above a critical level of soil extractable P, which is considered as optimal for crop growth, the farmer is recommended to withhold P fertilizer application.

In areas with intensive livestock farming, application of P to agricultural soils often exceeds the amount of P removed by crop harvest. This causes the accumulation of P in soil to levels well above those needed for optimal crop growth. High levels of P in soils increase the risk of P loss to ground and surface waters. Examples of P accumulation in soils under areas with intensive livestock farming have been reported in Belgium (Lookman et al., 1995b), Germany (Leinweber, 1996), the Netherlands (Breeuwsma et al., 1995), and the USA (Pautler and Sims, 2000). In sandy, organic, or coarse-textured mineral soils with a high organic matter content, P can leach to deeper soil layers via matrix flow or accelerated flow through artificial drainage pipes to surface waters (Sims et al., 1998). Surface erosion (detachment and movement of soil by water) and runoff of P are more important in areas with steeper slopes (Heathwaite et al., 1999). Figure 1.1 shows the main hydrological pathways of P transport from soil to surface waters.

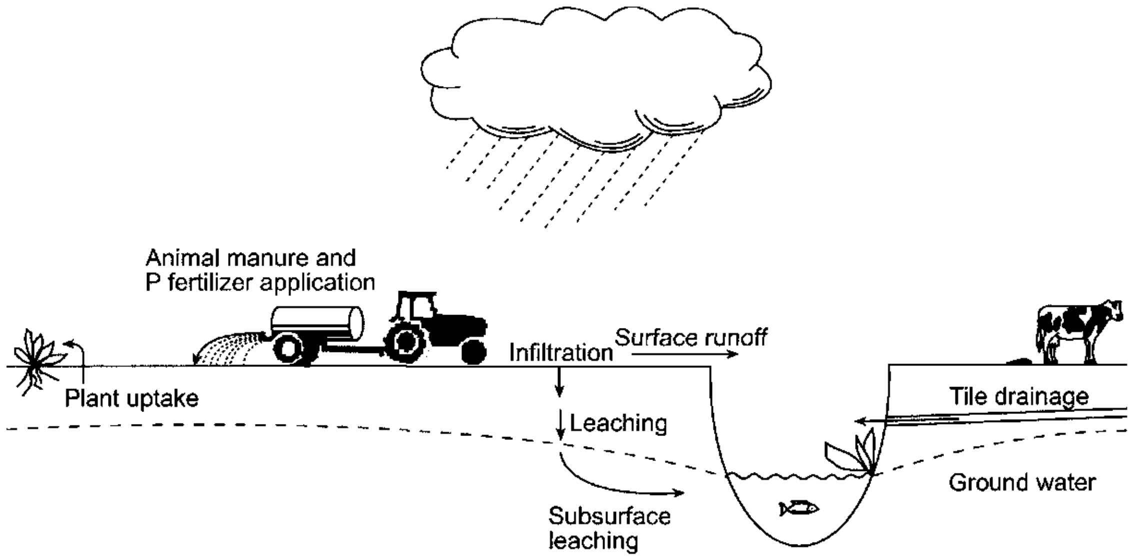

Figure 1.1. Concept of hydrological pathways of P transport from soil to surface waters.

Phosphorus enrichment of surface waters can contribute to eutrophication, because P often limits primary production in freshwater ecosystems (Sharpley et al., 1994; Correll, 1998). The impacts of eutrophication include excessive production of autotrophs, especially eukaryotic algae and cyanobacteria, causing green, turbid water with limited transparency. High primary production, in turn, increases bacterial populations and respiration rates, leading to depletion of dissolved oxygen in the water column. These conditions can result in fish kills and major shifts in species composition in all trophic levels. Anoxic surface waters are also conducive to the release of P stored in bottom sediments, which reinforces eutrophication (Correll, 1998). Eutrophic surface waters have reduced ecological value, because they are dominated by only a few species. Recreation becomes less attractive and the use of eutrophic surface waters for fisheries, industry, and drinking is restricted (Sharpley et al., 1994).

Phosphorus problems in the Netherlands

Livestock production was intensified in the Netherlands after 1950, as a result of the focus of the Common Agricultural Policy of the European Union (EU) on increasing agricultural productivity (see de Wit et al. [1987] and de Wit [1988]). Nowadays, agriculture in the Netherlands is one of the most intensive in the world in terms of capital and external inputs of nutrients (van Bruchem et al., 1999). To support the Dutch livestock population, a significant part of the animal feed needs to be imported, causing excessive surpluses of nitrogen (N) and P (i.e., the difference between total import of nutrients entering the country and total export of nutrients leaving the country) (Smaling et al., 1999). Table 1.1 shows the surface area of agricultural land, number of livestock, and imports and exports of P in the period between 1950 and 1995 in the Netherlands (Smaling et al., 1999). The surface area of agricultural land decreased slightly, but the P surplus and number of livestock increased markedly, especially between 1950 and 1980. Between 1950 and 1995, the average P surplus of Dutch agricultural land increased from 26 kg P ha^{-1} yr^{-1} in 1950 to 46 kg P ha^{-1} yr^{-1} in 1980, but decreased to 35 kg P ha^{-1} yr^{-1} in 1995.

Regionally, the P surplus has been much larger in the middle, east, and south of the Netherlands, where intensive livestock farming systems on noncalcareous sandy soils predominate. For decades, the animal manure produced was disposed of in the production area, especially on arable land cropped with maize (Breeuwsma et al., 1995). Between 1950 and 1990, the average P surplus of arable land cropped with maize on noncalcareous sandy soils in these areas ranged from 48 to 108 kg P ha^{-1} yr^{-1} (Reijerink and Breeuwsma, 1992). In these areas, plant available P, measured as Pw (water-extractable P at a soil to solution ratio of 1:60 [v/v]) (Sissingh, 1971) was between two and three times greater than optimum crop demand (Neutel, 1994). In general, the sorption capacity of noncalcareous sandy soils for P is limited, so these soils have become (nearly) saturated with P (Breeuwsma et al., 1995). This has drastically increased the risk of P transfer to surface waters, which in the Netherlands occurs mainly via (subsurface) leaching of soil solution, especially in flat areas with shallow ground water tables (Schoumans and Groenendijk, 2000).

Table 1.1. Changes in agriculture in the Netherlands in the period between 1950 to 1995. Surface area of agricultural land, livestock numbers, and P imports and exports for the whole agricultural sector (Smaling et al., 1999).

	Unit	1950	1960	1970	1980	1990	1995
Surface area	10^6 ha	2.3	2.3	2.2	2.0	2.0	2.0
Number of milking cows	10^6	1.4	1.6	1.9	2.4	1.9	1.7
Number of pigs	10^6	2	2	6	10	14	15
Number of chicken	10^6	41	45	55	81	93	84
P import via purchased animal feed	10^6 kg P	25	40	60	81	80	91
P import via inorganic P fertilizer	10^6 kg P	52	49	48	36	33	27
P import via other sources	10^6 kg P	0	0	3	6	7	1
P export via animal products	10^6 kg P	9	12	16	22	32	40
P export via harvested crops	10^6 kg P	8	9	10	9	9	10
P surplus	10^6 kg P	60	68	85	92	79	69
P surplus†	kg P ha^{-1}	26	30	39	46	40	35

†Phosphorus surplus in kg P ha^{-1} was calculated as the the P surplus in kg divided by the surface area of agricultural land.

Policies and measures in the Netherlands

In the Netherlands, the contribution of point sources to the total P load of surface waters has decreased greatly in recent decades. Enlargement of sewage systems and implementation of techniques that increase the removal of P from sewage water and industrial effluents have contributed to these decreased P emissions (Boers, 1996; van der Molen et al., 1998). Nevertheless, P concentrations in Dutch surface waters remain high and eutrophication persists as a major problem (Hosper, 1997; RIVM, 2002). In contrast to P emissions by point sources, P emissions from diffuse sources have not decreased (RIVM, 2002). Agriculture is the main contributor to diffuse emissions to surface waters. Nonseweraged urban areas also contribute to diffuse P emissions (van der Molen et al., 1998). In 2000, the estimated contribution of agriculture to the total P load of surface waters via P leaching was 44% (RIVM, 2002). Because of the high costs required to further reduce P emissions by point sources (Boers and van der Molen, 1993), attention has shifted to reducing P emission by agriculture (van der Molen et al., 1998).

From 1985 onwards, a series of policies and measures was implemented in the Netherlands to reverse the trend of increased P loading of agricultural soils (Boers, 1996; Oenema and Roest, 1998; van der Molen et al., 1998). A gradual approach was chosen for decreasing application rates of animal manure to give the agricultural sector the opportunity to adapt to a more efficient nutrient management system. The first measure was designed to prevent a further intensification of intensive livestock farming in order to stabilize the production of animal manure. The third step was the introduction of the Mineral Accounting System (MINAS) in 1998 with the aim to achieve balance fertilization in agriculture. The MINAS accounting system is a farm gate balance approach for both N and P: total input of nutrients entering the farm gate and total output of nutrients leaving the farm gate are quantified. Examples of inputs are purchased animal feed, fertilizer, and imported animal manure; examples of outputs are animal products (living animals, meat, milk, and eggs), harvested crops, and exported animal manure. The calculated N and P balance of a farm is expressed in kg N or P ha^{-1} yr^{-1}. The objective of MINAS is to reduce the nutrient surplus at the farm to the so-called 'levy-free surplus'. If the calculated surplus exceeds the levy-free surplus, the farmer has to pay levy over the excess. Levies encourage farmers to reduce the surplus by adoption of a more efficient nutrient management system. Since the introduction of MINAS, the levy-free surpluses of N and P have gradually been lowered. The target levy-free P surplus amounts to 9 kg P ha^{-1} yr^{-1} for the coming years and approximately 1 kg P ha^{-1} yr^{-1} in the long-term (RIVM, 2002). The loading of agricultural soils with P is expected to increase further, although at a decreased rate (Koopmans et al., 2001).

According to a recent judgement of the Court of Justice of the EU, MINAS does not sufficiently address the demands of the Nitrate Directive, issued by the EU. The EU Nitrate Directive is designed to protect water against pollution by nitrate (NO_3^-) from agriculture. The main objective is to ensure the quality of European drinking water by upholding a ground water quality standard of 50 mg NO_3^- L^{-1}. In the ground water of very well-drained sandy soils in the Netherlands, NO_3^- concentrations are generally (much) higher (RIVM, 2002). The judgement of the Court of Justice forces the Dutch government to replace MINAS by standards for the application of nutrients on agricultural land. These application standards will come into effect at the latest in 2006.

Identification of problem soils

Agricultural soils are generally considered to be a diffuse source of P to surface waters, whereas P-saturated soils are considered to be hot spots. Hot spots can be described as often small and well-defined areas typically contributing much of the total P loss in a watershed (Chardon and van Faassen, 1999). Hot spots of P loss occur where soil with a high level of P coincides with a soil of significant hydrological connectivity with receiving surface waters (Heathwaite et al., 1999). For the identification of hot spots, van der Zee et al. (1990) developed a method where the percentage or degree of P saturation (DPS) of the soil profile between the soil surface and the mean highest ground water level is compared with the P concentration in soil solution leaching from the soil profile in the long-term. Based on model calculations using average measured P sorption and desorption characteristics of Dutch noncalcareous sandy soils, a nonlinear relationship was derived between the DPS and the P equilibrium concentration in soil solution. At 25% saturation of the soil with P (25% DPS), the soil is called 'P-saturated' and the P concentration in soil solution leaching from the soil profile corresponds potentially to 0.1 mg orthophosphate P L^{-1} (van der Zee et al., 1990) or 0.15 mg total P L^{-1} (Schoumans and Groenendijk, 2000). The value of 0.15 mg P L^{-1} has been set as the Dutch limit for total P in surface waters to prevent eutrophication and associated adverse effects (TCB, 1990). Above 25% DPS, the P concentration in the soil solution increases nonlinearly with DPS (Schoumans and Groenendijk, 2000). Based on the DPS, the P concentration in the upper ground water is likely to exceed the surface water limit of 0.15 mg total P L^{-1} in an estimated 70% of noncalcareous sandy soils in the middle, east, and south of the Netherlands, an area of about 400 000 ha (Reijerink and Breeuwsma, 1992). These soils have the potential to contribute to P enrichment of surface waters. Figure 1.2 gives an overview of the P-saturated soils in the middle, east, and south of the Netherlands. The DPS method was developed for noncalcareous sandy soils, because intensive livestock farming systems with high application rates of animal manure predominate in these areas. Thus, the use of the DPS is restricted to these soils only (van der Zee et al., 1990). Evidently, to effectively reduce P loss from P-saturated soils, additional policies and measures are needed regionally. Because of the extent of the area of P-saturated soils, remediation is costly, and no site-specific policies and measures have been implemented yet. This is, in part, due to the large economic consequences this would have for intensive livestock farming systems (Chardon et al., 1996b; RIVM, 2002).

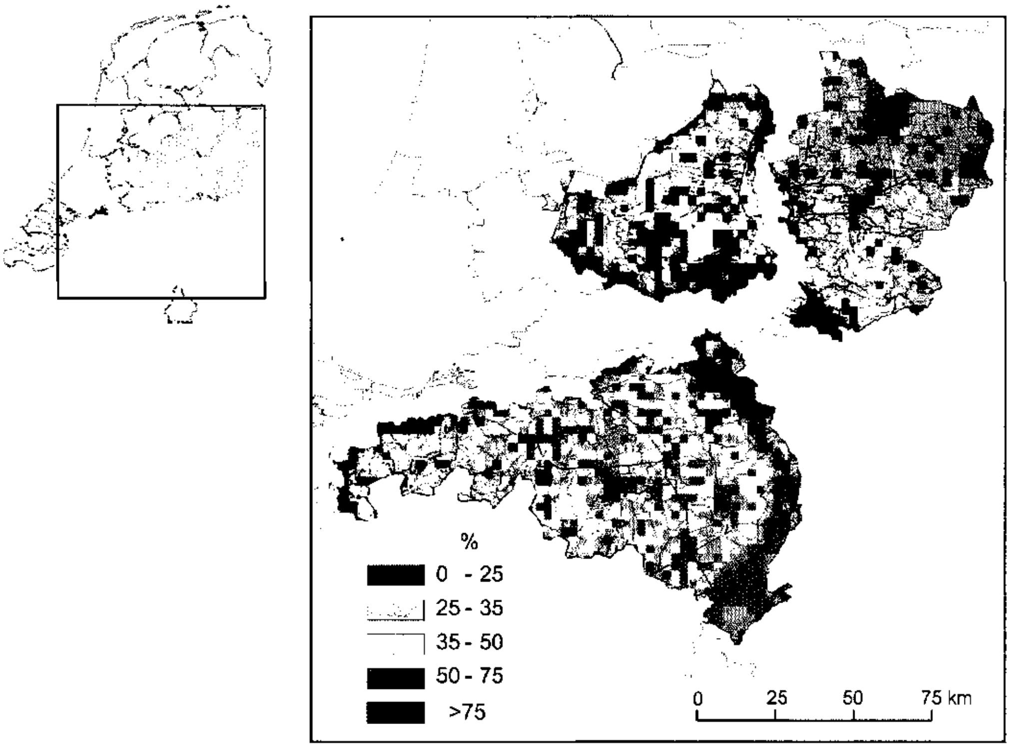

Figure 1.2. Degree of phosphorus saturation (DPS) of noncalcareous sandy soils in the middle, east, and south of the Netherlands (median value of DPS per cell of 2.5 by 2.5 km) (Reijerink and Breeuwsma, 1992).

A more recent approach to characterize P-enriched agricultural soils involves the application of split-line models to determine a threshold (change point or break point) in soil P quantity-intensity (q-i) relationships. Thresholds define a critical level in soil P quantity or soil extractable P above which a soil exhibits an increased risk for P loss. Thresholds can thus be used for the identification of problem soils. In many studies, strong relationships have been demonstrated between soil extractable P (quantity factor) and P concentrations in either surface runoff, drainage pipe water, and leachate (intensity factors) (Heckrath et al., 1995; Pote et al., 1996; McDowell et al., 2001a; Maguire and Sims, 2002). For example, McDowell and Sharpley (2001) used water and 0.01 M $CaCl_2$ to approximate P in surface runoff and leachate, respectively. These and other authors (Hesketh and Brookes, 2000) related these results to measurements of soil extractable P (Mehlich-3 and Olsen P) and fitted the results to a split-line model to calculate a threshold. Heckrath et al. (1995) and Maguire and Sims (2002) applied the split-line model to calculate thresholds in relationships between various extraction methods and P in drainage pipe water and leachate, respectively. The split-line model separates the relationship between soil extractable P and P loss into two sections: soils in the section above the threshold have an increased risk for P loss compared to the one below. Thus, for each unit increase in soil extractable P above the threshold, the release of P to leachate or runoff will increase at a greater rate than below the threshold. However, effects of experimental conditions, soil chemical characteristics, and soil P levels on calculated thresholds have received little attention so far.

Site-specific measure

Mining soil P (i.e., harvesting P taken up from the soil by a crop grown without external P addition, followed by the off-site removal of the above ground plant parts) has been proposed as a possible remediation strategy to decrease the risk of P leaching from P-enriched agricultural soils (van der Zee et al., 1992; Chardon et al., 1996b). However, quantitative information is scarce on the long-term change in soil P after P application has stopped. Previous studies in which soil P was mined by plant uptake were of relatively short duration (Delgado and Torrent, 1997; Guo and Yost, 1999; Yli-Halla et al., 2002), while in long-term field experiments of McCollum (1991) and those summarized by Sharpley (2000), where soil P was also mined, the change in soil P was mainly characterized with relatively strong extraction methods and only one extraction method per study. Thus, there is a need for more detailed information about long-term changes in different soil P pools caused by plant uptake after P application has ceased.

Phosphorus speciation in soil

Introduction

Soil P exists in many chemical forms, with the soil solution and solid phase containing both inorganic and organic forms. Figure 1.3 shows a simplified scheme of the speciation of P in soil. Organic P generally represents between 30 and 65% of total P (Harrison, 1987). Inositol phosphates are the most quantitatively important organic P compounds in soil, contributing over 50% to the total organic P content in many soils (Anderson, 1967). Inositol, a hexahydroxy cyclohexane ($C_6H_{12}O_6$), forms a series of orthophosphate monoesters ranging from monophosphate to hexakisphosphate, of which *myo*-inositol hexa*kis*phosphate is the most abundant form in soil (Turner et al., 2002). Phytic acid is the alternative name for its free acid form (Fig. 1.4). Because of the high number of phosphate groups of *myo*-inositol hexa*kis*phosphate, it has the ability to sorb strongly to Al- and Fe-(hydr)oxides, resulting in a low mobility but high stability in soil (Anderson, 1967). Other organic P compounds in soil include deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and phospholipids, a group of orthophosphate diester compounds (Anderson, 1967). The latter compounds have a lower charge density than orthophoshate monoesters, especially the inositol phosphates, resulting in a lower degree of sorption, but greater mobility and accessibility for microbial degradation (Turri6n et al., 2001).

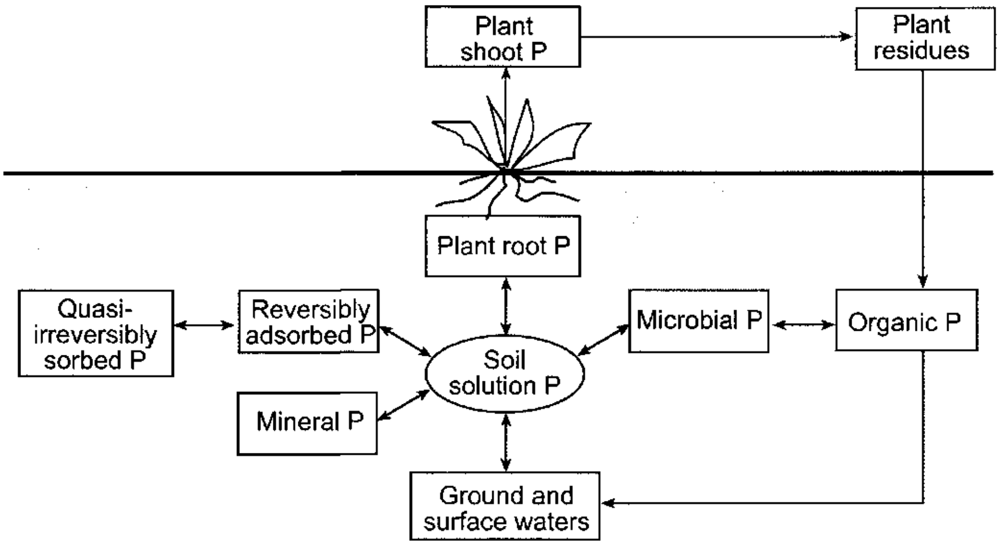

Figure 1.3. A simplified scheme of the speciation of P in soil.

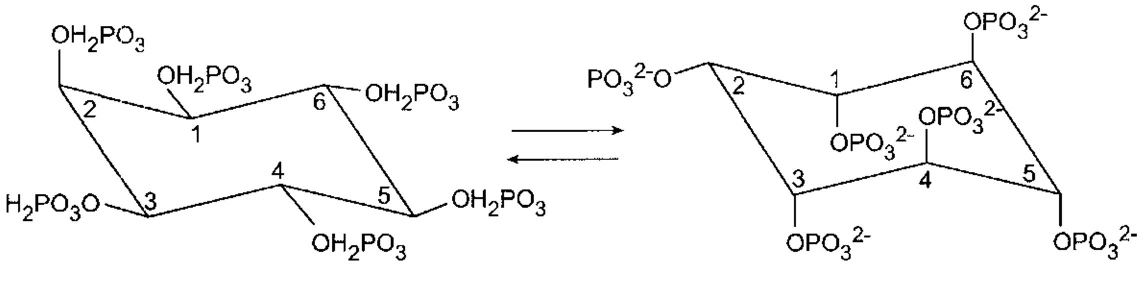

Figure 1.4. Structure of *myo*-inositol hexa*kis*phosphate in solution, between pH 0.5 and 9.0 (A) and between pH 10.0 and 13.0 (B) (Turner et al., 2003).

Phosphorus is added to the soil through the application of animal manure and P fertilizer and can be removed through processes such as uptake of P by plants and leaching of P to ground and surface waters. In soil solution, orthophosphate is the primary source of P for plant uptake. The decrease of the dissolved P concentration resulting from the uptake of P by plants is counteracted by desorption of P from the solid phase, by dissolution of P contained in minerals, or by mineralization of organic P compounds (Fig. 1.3). In animal manure, P is composed of both inorganic and organic P fractions, the latter varying from 5 to 25% of total P (Gerritse, 1981; Dou et al., 2000; Sharpley and Moyer, 2000). In other studies (e.g., Peperzak, 1959; Barnett, 1994), higher percentages of organic P have been found, depending on the type of animal manure. In agricultural soils treated with large amounts of animal manure, increased inorganic and organic P contents can be expected. However, little information exists on changes of inorganic and organic P fractions and the distribution of P among the various P compounds in soils exposed to high application rates of animal manure over long periods. Speciation of P in these soils is important, because the contribution of different P compounds to P loss via leaching may differ. In noncalcareous sandy soils treated with large amounts of pig and cattle slurry, P leaching through the soil profile was found to be mainly organic P (Gerritse, 1981; Chardon et al., 1997). Therefore, it is important to study speciation of P in soils amended with animal manure over long periods. For this purpose, solution ^{31}P nuclear magnetic resonance (NMR) spectroscopy, a relatively simple and direct technique, can be useful as it is has been applied successfully to characterize P in alkaline soil extracts (e.g., Cade-Menun and Preston, 1996).

Reactions of inorganic phosphorus with the solid phase

In noncalcareous sandy soils, amorphous Al- and Fe-(hydr)oxides are the main reactive solid phases (Beek, 1979). The overall reaction of inorganic P with Al- and Fe-(hydr)oxides can be divided into a fast reversible adsorption reaction at surface sites (<1 d) and a slow one, that is, diffusion through the solid phase or through micropores of Al- and Fe-(hydr)oxides possibly followed by precipitation and/or adsorption inside the aggregates (van Riemsdijk and Lyklema, 1980a, 1980b; van Riemsdijk and de Haan, 1981; Barrow, 1983; van Riemsdijk et al., 1984a, 1984b; Bolan et al., 1985; Madrid and De Arambarri, 1985; Willett et al., 1988). The fast reaction has been described as a ligand exchange reaction between phosphate anions and OH^- or H_2O groups at the surface of Al- and Fe-(hydr)oxides (Breeuwsma, 1973; van Riemsdijk and Lyklema, 1980a). In the acid pH range (pH 4.5-6.5) of noncalcareous sandy soils, P adsorption is not very dependent on pH (van der Zee et al., 1989). The fast reaction in these soils can then be described using the kinetic Langmuir equation (van der Zee et al., 1987):

$$\frac{dQ}{dt} = k_a \times C \times (Q_{max} - Q) - k_d \times Q \qquad [1.1]$$

where Q is the amount of P adsorbed (mg P kg^{-1}), C is the P concentration (mg P L^{-1}), Q_{max} is the adsorption maximum (mg P kg^{-1}), k_a is an adsorption constant (L mg^{-1} h^{-1}), and k_d is a desorption constant (h^{-1}). At equilibrium (dQ/dt = 0), Eq. [1.1] reduces to the Langmuir isotherm where K (L mg^{-1}) is the affinity of the soil for P adsorption($K = k_a/k_d$):

$$Q = \frac{Q_{max} \times K \times C}{1 + K \times C} \qquad [1.2]$$

The slow reaction of P has been described as a slow diffusion process through the solid phase to the zone where a fast precipitation reaction occurs: the conversion of Al- or Fe-(hydr)oxides to Al- or Fe-P precipitates (van Riemsdijk and Lyklema, 1980a, 1980b; van Riemsdijk and de Haan, 1981; van Riemsdijk et al., 1984a, 1984b). In the chemical engineering literature, this is referred to as the unreacted shrinking core model (van der Zee and van Riemsdijk, 1991). In contrast, Madrid and De Arambarri (1985) and Willett et al. (1988) described the slow reaction as a slow diffusion through the micropores of synthetic Fe-(hydr)oxides followed by a fast adsorption reaction inside the aggregates. Consequently, the reaction may locally be described again with the Langmuir adsorption equation (Eq. [1.2]). Nevertheless, all studies agree on diffusion as a transport mechanism for P into aggregates of Al- and Fe-(hydr)oxides as the rate-limiting step in the slow P reaction. The total pool of sorbed P (F) in noncalcareous sandy soils has been interpreted as the sum of reversibly adsorbed P (Q) and quasi-irreversibly bound P (S), that is, F = Q + S (van der Zee et al., 1987; van der Zee and van Riemsdijk, 1988; Schoumans and Groenendijk, 2000). The acid ammonium oxalate extraction method of Schwertmann (1964) has been used to determine both the total pool of sorbed P (P_{ox}), which may be equated to F, as well as the sum of amorphous Al- and Fe-(hydr)oxides ($[Al+Fe]_{ox}$), which determine the total sorption capacity of inorganic P in noncalcareous sandy soils (Beek, 1979; van der Zee and van Riemsdijk, 1988).

Reversibility of the inorganic phosphorus sorption reaction

The reversibility of the overall reaction of inorganic P with the solid phase is of agricultural interest, because of the need to maintain an optimal soil fertility for crop production. It is also of increasing environmental interest, because of its consequences for the P enrichment of ground and surface waters resulting from leaching of soil solution. Upon the removal of P from soil solution, a fast initial desorption reaction for P adsorbed to surface sites of Al- and Fe-(hydr)oxides is expected (van der Zee et al., 1987). Desorption of P bound inside these metal-(hydr)oxides followed by diffusion to the outer layers of the aggregates may counteract the decrease of reversibly adsorbed P (Barrow, 1983). Phosphorus becomes available again upon desorption of adsorbed P or dissolution of precipitated P inside the aggregate, followed by slow diffusion of P to the soil solution. Since diffusion is slow, sorbed P becomes available again in the long-term, resulting in apparent hysteresis of P sorption and desorption (Ryden and Syers, 1977). Diffusion may be an important mechanism in controlling the bioavailability and transport of various reactive solutes in soils. Thus, intra-aggregate diffusion should be considered if realistic models are to be used to model long-term (de)sorption processes of reactive solutes in soil.

Quantitative information about the long-term reversibility of the overall reaction of P in P-enriched soils and its consequences for the total amount of P available for plant uptake and leaching is scarce. Theoretically, all sorbed P in soil is desorbable (Lookman et al., 1995a). In a long-term desorption study where P-enriched noncalcareous sandy soils were incubated with a P sink consisting of a dialysis membrane tube filled with hydrous Fe-(hydr)oxide (DMT-HFO) for approximately 67 d, up to 70% of P_{ox} was desorbed. Based on the model results of the long-term P desorption kinetics, all P_{ox} was practically desorbable over 100 to 400 d (Lookman et al., 1995a). Therefore, irreversibly bound P may not have been present in these soils. A desorption isotherm, describing the equilibrium relationship between P in soil solution and the total pool of sorbed P, can in principle be used to estimate the total amount of P available for uptake by plants and leaching. However, the relationship between the P concentration in soil solution and P sorbed to the solid phase is difficult to determine in laboratory experiments, due to the relatively slow desorption kinetics and other more practical problems (e.g., van der Zee et al., 1987; Freese et al., 1995). Furthermore, in the field kinetic factors may lead to a lower availability of P than would be estimated from the equilibrium desorption isotherm.

Objectives

Mining soil P has been proposed as a possible remediation strategy to decrease the risk of P leaching from P-enriched agricultural soils. However, little quantitative information exists on long-term changes in different soil P pools resulting from P uptake after P application has ceased. The available information has been obtained mainly from short-term pot experiments and long-term field experiments where the change in soil P was characterized with only relatively strong extraction methods. To fully evaluate the potential of mining soil P, additional quantitative information is needed on changes in different soil P pools induced by mining soil P. Another important issue concerns the extent to which P uptake from P-enriched soil may be considered as an equilibrium desorption reaction. In the case of equilibrium, a desorption isotherm, describing the long-term equilibrium relationship between P in soil solution and the total pool of reversibly sorbed P, can in principle be used to estimate the total amount of P available for uptake and leaching. However, in the case of disequilibrium, kinetics of P desorption from the solid phase to the soil solution determines the availability of P for uptake and leaching. Obviously, these issues should be studied in field experiments, but greenhouse pot experiments allow detailed information to be obtained much more rapidly. The general objective of the present study was to gain knowledge on the speciation and desorption kinetics of P in P-enriched noncalcareous sandy soils, with special emphasis on the analysis of soil samples at varying stages of P depletion.
Different approaches were chosen:

- soil samples enriched with P over a long period were used in a P speciation study; soils were sampled from grassland sites exposed to different fertilizer regimes in a field experiment, and
- soil samples at varying stages of P depletion were used in studies on P speciation and desorption kinetics. The P-depleted soil samples were created in a laboratory experiment and a pot experiment. In the laboratory experiment, an artificial P sink method (DMT-HFO) was used to deplete two P-enriched soils. In the pot experiment, the method of

cropping grass was used to deplete a P-enriched soil over a relatively long period in the greenhouse.

The specific objectives of the present study were:

- to characterize P speciation in soils sampled from grassland sites exposed to long-term application of different fertilizer regimes,
- to quantify the availability of P in a P-enriched soil for uptake by plants,
- to quantify the changes in different P pools resulting from depletion of soil P by either an artificial P sink or plant induced mining, and
- to quantify and model the changes in P desorption kinetics in a P-enriched soil subjected to P depletion.

Outline

In Chapter 2, effects of experimental conditions, soil chemical characteristics, and soil P levels on calculated thresholds, used for the identification of agricultural soils with an increased risk for P loss, are determined based on a simple modeling approach using the Langmuir adsorption isotherm. In Chapter 3, P speciation in soils sampled from the top 5 cm of grassland sites exposed to different fertilization regimes in a long-term field experiment is characterized. Classical wet chemical analysis and solution ^{31}P NMR spectroscopy are used to determine P speciation in both 0.25 M NaOH-0.05 M Na_2EDTA and 1:5 (w/v) water extracts. In Chapter 4, two P-enriched soils are incubated with an artificial P sink (DMT-HFO) in a laboratory experiment to create soil samples at varying stages of P depletion. Various extraction methods are used to characterize the changes in different soil P pools. Furthermore, the suitability of the DMT-HFO method to act as an 'infinite' P sink for P desorption is evaluated. In Chapter 5, the method of cropping of grass is used to deplete a P-enriched soil in a long-term greenhouse pot experiment. The effectiveness of mining soil P by grass is evaluated by characterizing the change in different soil P pools using various extraction methods. Phosphorus extractable with 0.01 M $CaCl_2$ is used to approximate P in the soil solution and P_{ox} is used as an indicator of the size of the total pool of sorbed P. Using these data for soil samples collected after various times of plant growth, an equilibrium desorption isotherm for P is constructed. The desorption isotherm is used to estimate the long-term availability of P for uptake by plants. In Chapter 6, the initial soil and some P-depleted soil samples selected from the pot experiment are used to determine the desorption kinetics of P in batch experiments and a diffusion model is used to simulate the P desorption kinetics from a spherical aggregate. The desorption isotherm, determined in Chapter 5, is then used to calculate P buffering during transport of P through the micropores of the aggregate to the soil solution. Furthermore, a new concept is proposed to interpret the bioavailability of nutrients based on the kinetics of desorption. This concept is referred to as the dynamic bioavailability index (DBI). The DBI is the dimensionless ratio of the maximal diffusive flux of a nutrient from the soil aggregates to the soil solution and the rate of nutrient uptake by the plant.

2

Soil phosphorus quantity-intensity relationships to predict increased soil phosphorus loss to overland and subsurface flow

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Abstract

Soil phosphorus (P) quantity-intensity (q-i) relationships, based on common extraction methods, may potentially be used to estimate the risk of P loss in overland flow and subsurface drainage water. Some workers have used nonlinear q-i relationships to derive thresholds in soil test P (STP; a quantity factor) above which the risk of P loss increases, while others find linear relationships and no threshold. We present here a simple modeling exercise (based on Langmuir adsorption theory) along with data from literature to explain the behavior of q-i relationships, and to give an explanation for this apparent discrepancy. The data indicate that q-i relationships are dependent upon the soil to solution ratio of the P intensity parameter, adsorption capacity (Q_{max}) and strength (K) of the soil, and the total range in STP. In turn, this affects the calculation of a threshold in STP. The q-i relationship tends towards linearity under conditions of a narrow total range of STP and/or when using a wide soil to solution ratio for estimating the P intensity parameter. Under such conditions, a threshold is difficult to detect, and uncertain. We conclude that the sensitivity of thresholds to experimental conditions and soils needs to be considered if thresholds are to be successful in environmental management to decrease P loss to surface waters.

Introduction

Soil phosphorus (P) contents of intensively managed agricultural soils in for example Europe and the USA have increased in the course of the 20th century, as the result of heavy P applications via fertilizer and animal manure exceeding the withdrawal of P by harvested crops (e.g., Breeuwsma et al., 1995; Pautler and Sims, 2000). This buildup of soil P can increase the potential for P loss to surface waters via hydrological pathways such as overland flow and subsurface drainage water, contributing to P enrichment of surface waters and eutrophication (Sharpley et al., 1994; Sims et al., 1998).

Various methods have been proposed to estimate the potential P loss from P enriched soils. For example, McDowell and Sharpley (2001) used water- and 0.01 M $CaCl_2$-extractable P to approximate P in overland flow and subsurface drainage, respectively. These and other authors (e.g., Hesketh and Brookes, 2000) have shown that such data can be coupled with measures of soil test P (STP; e.g., Mehlich-3- or Olsen-extractable P), and can be fitted to a split-line model to calculate a change point or threshold in STP. The split-line model separates the relationship between STP and P loss into two sections on either side of the threshold, whereby soils in the section above the threshold exhibit an increased potential for P loss compared to the one below. Others (e.g., Heckrath et al., 1995) have demonstrated a threshold in STP for P loss via tile drainage. These thresholds have been derived with the purpose to find a critical level in STP, above which the potential of P loss increases, to be used for environmental management (e.g., McDowell et al., 2001a).

A method, recently developed in the Netherlands, compares the percentage or degree of P saturation (DPS) of the soil profile between the soil surface and the mean highest ground water level, with the dissolved P concentration in soil solution leaching from the soil profile in the long-term (van der Zee et al., 1990). Based on model calculations using average measured P sorption and desorption characteristics of Dutch sandy soils, a relationship was derived between DPS and the P equilibrium concentration in soil solution. At 25% saturation of the soil with P (25% DPS), the P concentration in soil solution leaching from the soil profile corresponds to 0.1 mg dissolved P L^{-1} (van der Zee et al., 1990). The value of 0.1 mg P L^{-1} has been set as the Dutch limit for inorganic P in surface waters to prevent eutrophication and associated adverse effects (TCB, 1990). Above 25% DPS, the dissolved P concentration in the soil increases nonlinearly with DPS (Schoumans and Groenendijk, 2000). Indeed, experimental data often demonstrate nonlinear relationships between DPS and water-extractable P (e.g., Lookman, 1995; Chardon and van Faassen, 1999; Koopmans et al., 2001). McDowell et al. (2001a) applied the split-line model to laboratory extraction data of 0.01 M $CaCl_2$-extractable P (soil to solution ratio of 1 to 5 [w/v]) versus DPS in soils from New Zealand, the UK, and USA. Thresholds occurred at DPS values ranging from 25 to 34%, and corresponded to P concentrations in $CaCl_2$ extracts that were comparable to the dissolved P concentration in soil solution found by van der Zee et al. (1990) at 25% DPS. This method also applies to P loss via subsurface flow (Lookman, 1995).

The examples above have a commonality; they relate quantity (q; STP or DPS) to intensity (i; P in overland or subsurface flow or the approximation thereof, i.e., water- or 0.01 M $CaCl_2$-extractable P) in a nonlinear manner. In contrast, many other examples show a linear relationship between STP or DPS and P loss in overland flow or 0.01 M $CaCl_2$-extractable soil P, and as a consequence, no threshold (e.g. Sharpley, 1995; Pote et al., 1996; Pautler and Sims, 2000). This is puzzling, but methodology (soil to solution ratio of the P intensity parameter and rainfall intensity) and soil chemical characteristics (soil type) and conditions (land use and range of STP) were different in the various studies. For example, a narrow soil to solution ratio (i.e., a low suspended sediment concentration) in overland flow exhibited a nonlinear q-i relationship, while a wide soil to solution ratio exhibited a linear relationship (McDowell and Sharpley, 2001). Furthermore, apparent linearity of data can simply be caused by not testing soils of sufficiently wide range in STP to show a nonlinear relationship (McDowell et al., 2001a). So far, a coherent explanation for these divergent results does not exist to our knowledge. A simple modeling exercise, based on the Langmuir adsorption isotherm, may explain such an apparent discrepancy. Thus, the primary objective of this study is to explore with theory and data from literature, the variation in q-i relationships as influenced by methodology, soil chemical characteristics, and soil P levels. A secondary objective is to rationalize the existence of thresholds in STP, and to discuss the applicability and limitations of thresholds, and thus, place their calculation in perspective.

Materials and methods

Theory

The overall sorption reaction of inorganic P in soil may be simplified to consist of a fast reaction (reversible adsorption on surface sites), and a slow one (diffusion into soil aggregates followed by precipitation or sorption inside the aggregate) (e.g., van der Zee and van Riemsdijk, 1988). Phosphorus lost in overland flow and subsurface drainage water is significantly correlated only to the rapidly desorbable P pool, as revealed by recent data using radioactive ^{33}P (McDowell et al., 2001b). In our study, as an approximation, only reversibly adsorbed P is considered to be involved in the q-i relationships explored here.

Dispersing a known amount of soil (g; kg soil) containing a known amount of adsorbed P (T; mg P) in a known volume of solution (v; L) results in the establishment of an equilibrium within hours between the amount of P adsorbed to the soil (Q; mg P kg^{-1}) and the amount of P in solution (C; mg P L^{-1}), described by:

$$T = g \times Q + v \times C \tag{2.1}$$

The Langmuir adsorption isotherm can be used to describe reversible adsorption of P (van der Zee et al., 1988):

$$Q = \frac{Q_{max} \times K \times C}{1 + K \times C} \tag{2.2}$$

where Q_{max} is the adsorption maximum (mg P kg^{-1}) and K is a constant (L mg^{-1}) describing the affinity of the soil for P, or adsorption strength; Q_{max} and K are soil properties defined by the chemical characteristics of the soil. Substituting Eq. [2.2] in Eq. [2.1] gives:

$$T = g \times \frac{Q_{max} \times K \times C}{1 + K \times C} + v \times C \tag{2.3}$$

Equation [2.3] can be solved for C to yield Eq. [2.4] (see Appendix B):

$$C = \frac{-(g \times Q_{max} \times K + v - T \times K) + \sqrt{(g \times Q_{max} \times K + v - T \times K)^2 - 4 \times (v \times K) \times (-T)}}{2 \times (v \times K)} \tag{2.4}$$

For both adsorption and desorption processes, the Langmuir isotherm is linear at small amounts of T and thus the increase of C with T is linear at low values of T. As T increases and Q approaches Q_{max}, the Langmuir isotherm becomes nonlinear, and the relationship between C and T changes from linear to nonlinear. As T increases further, $Q \approx Q_{max}$ and any additional P remains in solution; the Langmuir isotherm becomes linear again, and likewise, the increase of C with T. This follows from Eq. [2.1], the slope of the C versus T relationship equals 1/v as $Q \approx Q_{max}$, and, thus, depends on the soil to solution ratio; widening this ratio decreases the slope. Using Eq. [2.4], we analyzed the behavior of q-i relationships, that is, C versus T, as a function of soil to solution ratio (g to v) at set values of Q_{max} and K. Next, we analyzed the effects of varying Q_{max} and K at a set soil to solution ratio for a range of T. We used the split-line model (Eq. [2.9]), described by McDowell et al. (2001a), to calculate thresholds in the q-i relationships.

Elaboration

We used laboratory extraction data of Schoumans et al. (1991) and Chardon (unpublished) to obtain relevant ranges of values of Q_{max} and K. Soil samples were collected from the plough layer (0-30 cm) of 151 sites representative for intensively managed agricultural sandy soils in the Netherlands. These data sets contained the following parameters: soil density, organic matter, water-extractable P at a soil to solution ratio of 1:60 (v/v) (Pw; Sissingh, 1971), ammonium oxalate-extractable P (P_{ox}) and Al and Fe ($[Al+Fe]_{ox}$), and P extractable with FeO-impregnated filter paper (Pi-test; Sissingh, 1983). Furthermore, the data sets contained the pH (KCl) (Schoumans et al., 1991) and the pH (H_2O) (Chardon, unpublished). We calculated DPS (%) according to van der Zee et al. (1990):

$$\mathrm{DPS} = \frac{P_{ox}}{\alpha \times [\mathrm{Al}+\mathrm{Fe}]_{ox}} \times 100 \qquad [2.5]$$

where P_{ox} and $[Al+Fe]_{ox}$ are expressed in mmol kg^{-1}; $\alpha = 0.5$ denotes the saturation factor, that is, sorption strength of $[Al+Fe]_{ox}$ for P. The value of α was calculated as the ratio between P_{ox} and $[Al+Fe]_{ox}$ from a set of sandy soil samples pre-saturated with P in a laboratory experiment. In sandy soils, Q_{max} depends upon the ammonium oxalate-extractable Al and Fe contents. The value of Q_{max} can be calculated from:

$$Q_{max} = \beta \times [\mathrm{Al}+\mathrm{Fe}]_{ox} \times 31 \qquad [2.6]$$

where $\beta = 0.135$, Al and Fe are expressed in mmol kg^{-1}, and 31 represents the atomic weight of P to obtain Q_{max} in mg P kg^{-1} (van der Zee et al., 1988). The value of β was calculated as the ratio between the amount of reversibly adsorbed P, as estimated by FeO-impregnated filter paper, and $[Al+Fe]_{ox}$ from a set of sandy soil samples pre-saturated with P in a laboratory experiment. Iron oxide-impregnated filter paper functions as an infinite sink for P, and maintains a negligible P concentration in suspension facilitating continuous desorption of reversibly adsorbed P (van der Zee et al., 1987).

We estimated K from P desorption in a Pw extract by solving Eq. [2.3] for K (see Appendix C):

$$K = \frac{T - v \times C}{g \times Q_{max} \times C + v \times C^2 - T \times C} \qquad [2.7]$$

We assumed equilibrium between P adsorbed to the soil and P measured in the Pw extract after 22 h of pre-equilibrating and 1 h of shaking at 20°C. Usually, the Pw value, used as STP in P fertilizer recommendation for arable land in the Netherlands, is expressed in mg P_2O_5 L^{-1} of soil. To obtain K, we expressed Pw in mg P kg^{-1} using soil density. To assess the amount of reversibly adsorbed P (T), van der Zee et al. (1988) used FeO-impregnated filter paper. We derived values of T from the data of the Pi-test.

Calculation of thresholds

Thresholds in the q-i relationships were calculated using a split-line model describing two linear relationships on either side of the threshold (McDowell et al., 2001a). Below the threshold, i varies with q according to:

$$i = a_1 \times q + b \qquad [2.8]$$

and above the threshold according to:

$$i = a_1 \times q + \Delta a \times (q - CP) + b \qquad [2.9]$$

where i is intensity (mg P L^{-1}), q is quantity (mg P kg^{-1}), CP is the threshold (or change point), a_1 is the slope of the linear relationship for values of q below the CP, Δa is the difference in slopes above the threshold compared to a_1, and b is the intercept. The four parameters (a_1, Δa, CP, and b) were estimated using the method of maximum likelihood (analogous to the least-squares method) in Genstat 5, release 4.1. The slope of the linear relationship after the threshold a_2 was calculated as $a_2 = a_1 + \Delta a$. A low ratio of a_2 to a_1 is indicative of a small change in the increase of i with q after the threshold, or in other words, the relationship between q and i tends to become linear. When the ratio of a_2 to a_1 is 1, then the relationship between q and i is linear by definition. Hence, when the ratio of a_2 to a_1 is low, a threshold is difficult to detect and uncertain.

Results and discussion

Soil characteristics

The 151 soil samples represent the wide range in soil conditions found in intensively managed agricultural sandy soils in the Netherlands. The samples provide a wide range in soil P levels (Pw, Pi-test-extractable P, P_{ox}, and DPS) and soil chemical characteristics (organic matter, pH, $[Al+Fe]_{ox}$, Q_{max}, and K) (Schoumans et al., 1991; Chardon, unpublished). The range, mean, and standard deviation of these parameters are presented in Table 2.1. The pH (KCl) of the soil samples taken from the study of Schoumans et al. (1991) was a little lower than the pH (H_2O) in the study of Chardon (unpublished). Because the pH of the soil samples selected is higher than the point of zero net charge, the pH in a high ionic strength medium (KCl) is lower than the pH in a low ionic strength medium (water) (McBride, 1994). Amounts of Pw- and Pi-test-extractable P were, on average, 3.4 and 19.5% of P_{ox}, respectively. Approximately 80% of the samples had Q_{max} and K values that ranged from 150 to 500 mg P kg^{-1} and from 0.3 to 3.3 L mg^{-1}, respectively. These results are similar to data presented by van der Zee et al. (1988).

Table 2.1. Measured data of organic matter (OM), pH, Pw, Pi-test, P_{ox}, $[Al+Fe]_{ox}$, and DPS of the 151 soil samples from the Netherlands (Schoumans et al., 1991; Chardon, unpublished), and estimated values of Q_{max} and K calculated according to Eq. [2.6] and Eq. [2.7] in this study.

Parameter	Range	Mean	Standard deviation
OM (%)	2.1-15.5	5.1	± 2.0
pH (KCl)†	3.7-6.2	4.7	± 0.5
pH (H_2O)‡	5.3-6.8	6.2	± 0.3
Pw (mg P kg^{-1})	2-65	16	± 12
Pi-test (mg P kg^{-1})	11-313	92	± 67
P_{ox} (mg P kg^{-1})	115-1211	485	± 213
$[Al+Fe]_{ox}$ (mmol kg^{-1})	25-185	70	± 23
DPS§ (%)	16-100	46	± 17
Q_{max} (mg P kg^{-1})	103-775	292	± 97
K (L mg^{-1})	0.1-6.2	1.5	± 1.1

†Schoumans et al. (1991); n = 67.
‡Chardon (unpublished); n = 84.
§DPS was calculated according to Eq. [2.5]. The DPS is calculated here for soil samples from the 0-30 cm layer only, while van der Zee et al. (1990) apply the DPS to the soil profile between the soil surface and the mean highest ground water level.

Influence of soil to solution ratio on q-i relationship

Figure 2.1 shows the relationship between quantity (as T/g to give mg P kg^{-1} soil) and intensity (C in mg P L^{-1}) calculated for soil to solution ratios of 1:0.3, 1:5, 1:10, and 1:50 (g to mL) for a soil of Q_{max} = 300 mg P kg^{-1} and K = 1.5 L mg^{-1}. According to Eq. [2.4], C may increase with T to infinity. However, P will precipitate as the concentration of P in soil solution exceeds the solubility product of the solid phase determining the solubility of P in soil. In acidic to neutral soils, heavily enriched with P, Ca- and Mg-P compounds may exist as metastable solid phases. An extreme example of a P-enriched soil was described by Dantzman et al. (1983). They investigated a site which had been used as a feedlot for 15 years and showed that P accumulated as Ca-P. Nair et al. (1995), Sharpley and Smith (1995), and Lookman et al. (1997) also observed accumulation of Ca-P on sites that received large amounts of animal manure. Also, de Haan and van Riemsdijk (1986) found indications for the existence of brushite ($CaHPO_4{\cdot}2H_2O$) in heavily pig manured sandy soils. They measured a maximum P concentration of approximately 90 mg P L^{-1}, and therefore, in Fig. 2.1, we showed C in the 1:0.3 extract up to this P concentration. The P concentration in the 1:0.3 extract shows a strong increase with T/g, and a large change in slope, but as the soil to solution ratio of the P intensity parameter widens, this increase lessens, and the slope of the relationship between T/g and C changes less (Fig. 2.1). Thus, at a wide soil to solution ratio, the relationship between T/g and C tends to become linear. To calculate a threshold in these q-i relationships, we applied the split-line model (Eq. [2.9]) (McDowell et al., 2001a), assuming that T/g ranges from 0 to 325 mg P kg^{-1} (T/g = 325 mg P kg^{-1} corresponds to C = 90 mg P L^{-1} in the 1:0.3 extract). In the 1:0.3 extract, a clear threshold is evident, however, as the soil to solution ratio widens, the threshold and the ratio of a_2 to a_1 decreased (Table 2.2). Decreasing the T/g range, used for calculating the threshold, from 0-325 mg P kg^{-1} to 0-150 mg P kg^{-1} has the same effect; the threshold and the ratio of a_2 to a_1 decreased (Table 2.2). In both cases, the corresponding Q and C values decreased as well. Summarizing, at a wider soil to solution ratio and/or a decreasing T/g range, the increase of C with T/g becomes smaller and the slope of the relationship between T/g and C changes less (Fig. 2.1), and as a result, the threshold calculated by the split-line model decreases.

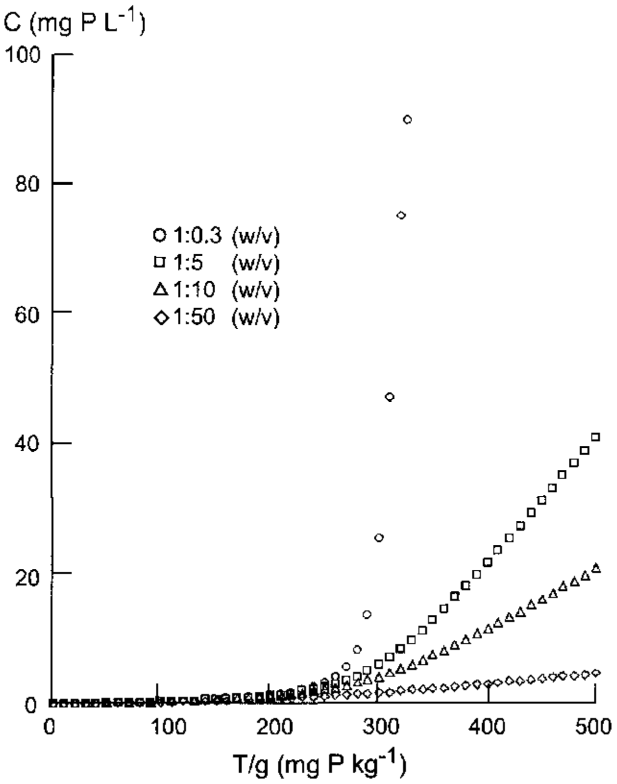

Figure 2.1. Modeled data of the phosphorus intensity (C) versus P quantity (T/g) at four different soil to solution ratios calculated using Eq. [2.4] (Q_{max} = 300 mg P kg^{-1} and K = 1.5 L mg^{-1}).

Table 2.2. Modeled data of the threshold in T/g, calculated from the split-line model (Eq. [2.9]), the corresponding amount of P adsorbed (Q) and P equilibrium concentration (C), and the ratio of a_2 to a_1 calculated at different soil to solution ratios for a soil of Q_{max} = 300 mg P kg^{-1} and K = 1.5 L mg^{-1} (Fig. 2.1). T/g ranged from 0-325 mg P kg^{-1} and 0-150 mg P kg^{-1}, respectively.

Soil to solution ratio	T/g	Threshold in T/g	Q	C	a_2 to a_1 ratio
	mg P kg^{-1}	mg P kg^{-1}	mg P kg^{-1}	mg P L^{-1}	
1:0.3	0-325	293	288	16.1	110.3
1:5	0-325	246	234	2.4	11.4
1:10	0-325	227	211	1.6	7.1
1:50	0-325	187	152	0.7	2.7
1:0.3	0-150	87	87	0.3	2.1
1:5	0-150	87	86	0.3	2.0
1:10	0-150	87	84	0.3	1.9
1:50	0-150	85	74	0.2	1.6

Clearly, q-i relationships calculated are highly dependent upon the soil to solution ratio used for determining the P intensity parameter and the total range in STP. As a result, the threshold, calculated by the split-line model, and the corresponding C value, are also affected by experimental conditions and soil selection. At a wide soil to solution ratio and/or a narrow total range in STP, the relationship between T/g and C tends towards linearity, and thus, a threshold may be difficult to detect.

Influence of soil chemical characteristics on q-i relationship

Figure 2.2 shows the relationships between T/g and C for a soil to solution ratio of 1:0.3, Q_{max} = 150 and 500 mg P kg^{-1}, and K = 0.3 and 3.3 L mg^{-1}. Similar to Fig. 2.1, C is shown up to a maximum of 90 mg P L^{-1}. Increasing Q_{max} and/or K has the effect of increasing the range in T/g before the slope of the relationship between T/g and C changes. Applying the split-line model to the data presented in Fig. 2.2 shows that at higher values of either Q_{max} or K, both the threshold and the ratio of a_2 to a_1 increase (Table 2.3). Conversely, widening the soil to solution ratio of the P intensity parameter to 1:50 caused the threshold and the ratio of a_2 to a_1 to decrease (Table 2.3). Thus, in theory, q-i relationships are highly dependent upon Q_{max} and K of the soil. As a result, the threshold and the corresponding C value are also affected by the selection of soils. For example, in sandy soils with a low adsorption strength, the threshold may be difficult to detect, especially at a wide soil to solution ratio used for determining the P intensity parameter.

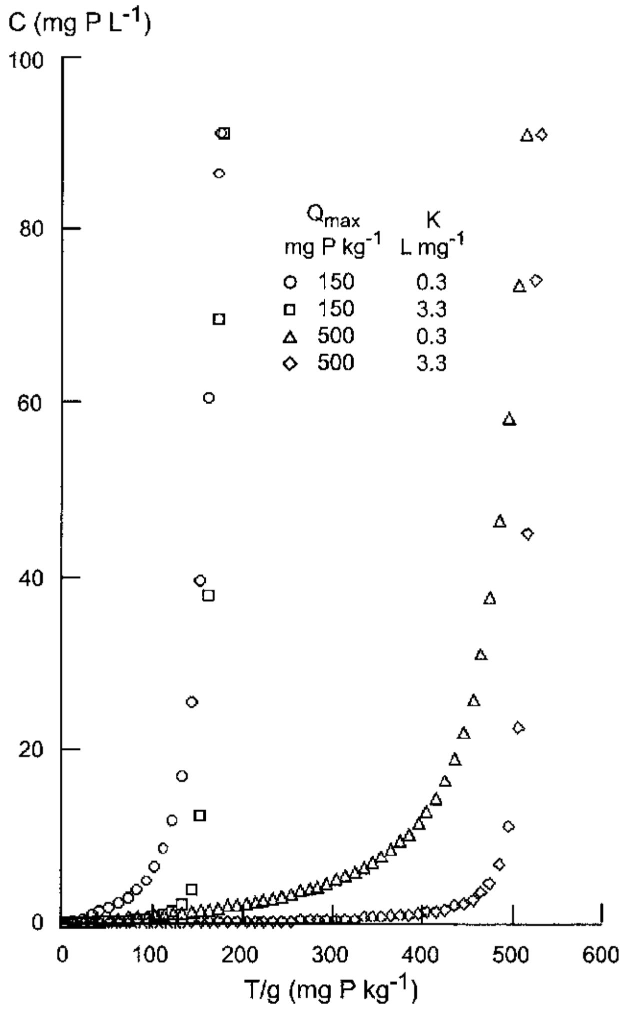

Figure 2.2. Modeled data of the phosphorus intensity (C) in a 1:0.3 extract versus P quantity (T/g) at two different P adsorption maxima (Q_{max}) and strengths (K) calculated using Eq. [2.4].

Table 2.3. Modeled data of the threshold in T/g, calculated from the split-line model (Eq. [2.9]), and ratio of a_2 to a_1 calculated at a soil to solution ratio of 1:0.3 (Fig. 2.2) and 1:50 for different values of Q_{max} (150 or 500 mg P kg^{-1}) and K (0.3 and 3.3 L mg^{-1}). T/g ranged from 0 mg P kg^{-1} to the value required to obtain C = 90 mg P L^{-1} in the 1:0.3 extract.

Q_{max}	K	Soil to solution ratio	T/g	Threshold in T/g	Q	C	a_2 to a_1 ratio
mg P kg^{-1}	L mg^{-1}		mg P kg^{-1}	mg P kg^{-1}	mg P kg^{-1}	mg P L^{-1}	
150	0.3	1:0.3	0-172	135	129	20.6	20.0
150	3.3	1:0.3	0-176	147	145	8.2	169.6
500	0.3	1:0.3	0-509	444	437	23.0	30.6
500	3.3	1:0.3	0-525	493	489	13.8	323.7
150	0.3	1:50	0-172	84	34	1.0	1.2
150	3.3	1:50	0-176	105	85	0.4	3.1
500	0.3	1:50	0-509	264	175	1.8	1.6
500	3.3	1:50	0-525	358	329	0.6	5.4

Examples in the literature

Many examples exist in the literature to demonstrate our theory. In a study by Hesketh and Brookes (2000), Olsen P was related to P loss in subsurface drainage waters from experimental columns containing soils of different P contents. They noted a threshold in Olsen P, above which P loss in subsurface drainage waters increased. This was mimicked by a plot of P extracted by 0.01 M $CaCl_2$ versus Olsen P (Fig. 2.3, adapted from Hesketh and Brookes [2000]). Widening the soil to solution ratio of the 0.01 M $CaCl_2$ extraction method caused the slope of the relationship between Olsen P and 0.01 M $CaCl_2$-extractable P above the threshold to decrease. They used this phenomenon to explain why plots of Olsen P from topsoils of the Broadbalk Continuous Wheat experiment (Rothamsted, Harpenden, UK) versus the P concentration in subsurface drainage waters yielded by approximation the same thresholds, but different slopes of the relationships between Olsen P and the P concentration in drainage waters, for rainfall events with a different intensity. The different volume of rainfall caused the soil to solution ratio to change and, thus, the slope of the q-i relationship. These results agree with our data presented in Fig. 2.1 and Table 2.2.

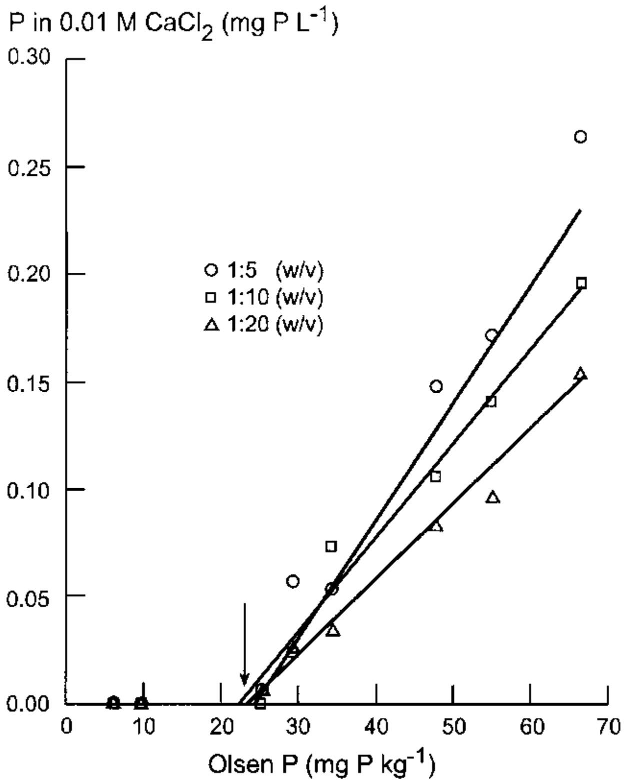

Figure. 2.3. Measured data of the P concentration in a 0.01 M $CaCl_2$ extract at three different soil to solution ratios versus Olsen P in experimental columns containing soils from different plots of Saxmundham (UK). Arrow indicates the thresholds (adapted from Hesketh and Brookes [2000]).

The importance of the soil to solution ratio was also suggested in a study by McDowell and Sharpley (2001). In Fig. 2.4, the dissolved P concentration in overland flow, generated from air-dried soil packed in boxes in response to a rainfall event of 65 mm hr^{-1}, is plotted against Mehlich-3 P (a measure of STP) (Pennsylvania soils, USA) and Olsen P (Devon soils, UK), respectively (adapted from McDowell and Sharpley [2001]). At the beginning of the event (i.e., the first 250 mL of overland flow), the dissolved P concentration increased in a nonlinear manner with both Mehlich-3 P and Olsen P, and in both relationships, a threshold was detected. In contrast, at the remainder of the event, a linear relationship between both Mehlich-3 P and Olsen P and the dissolved P concentration was suggested. This transition was attributed to the slaking and dispersion of soil in overland flow at the beginning of the event resulting in a larger amount of soil suspended in solution, and hence yielding a comparatively narrow soil to solution ratio. This was confirmed by measuring the suspended sediment concentration in a subsample of all overland flow combined, which contained <10% of the suspended sediment concentration in the first 250 mL.

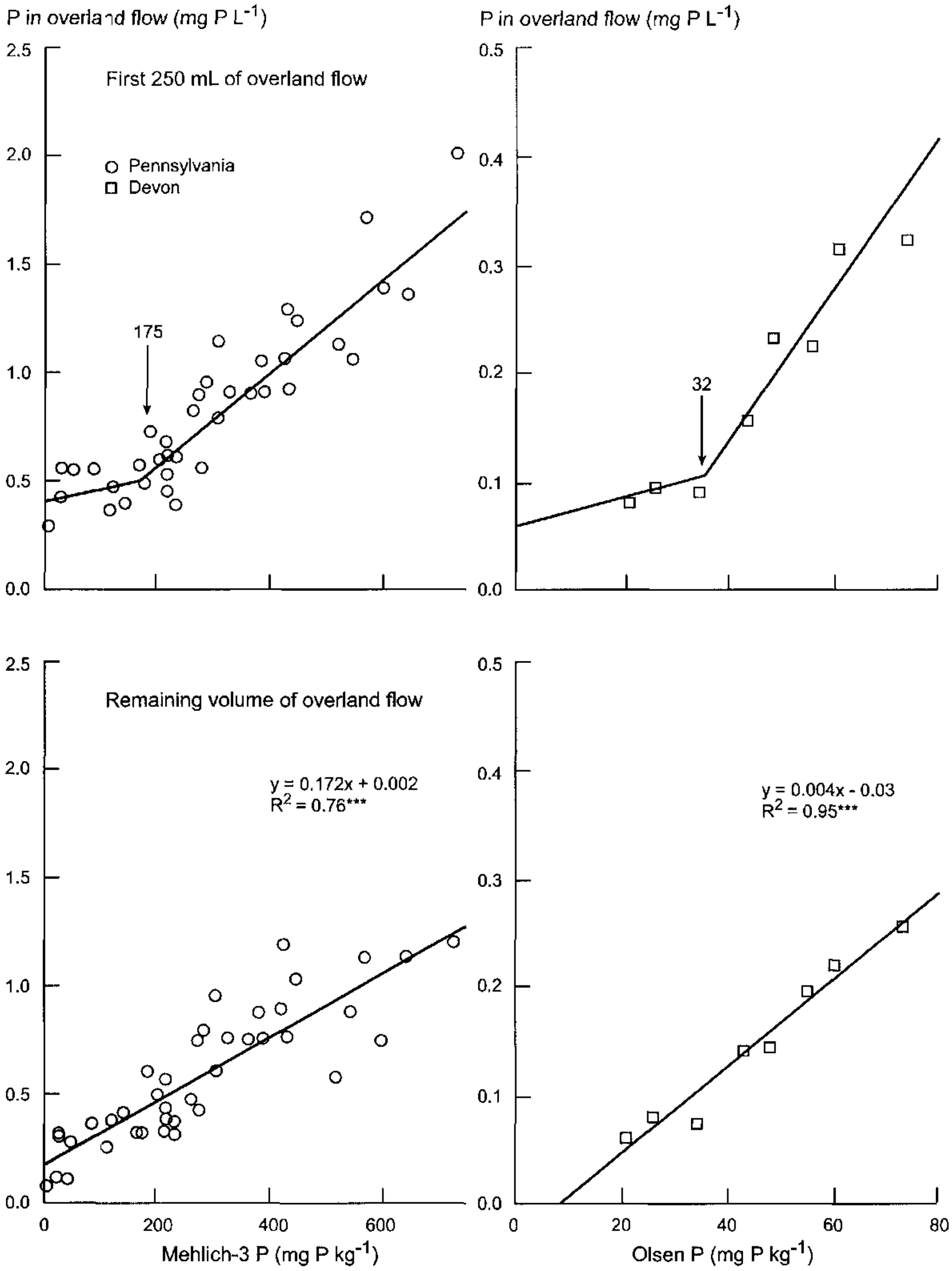

Figure 2.4. Measured data of the P concentration in the first 250 mL of overland flow and the remaining volume of overland flow versus Mehlich-3 P and Olsen P for selected soils from Pennsylvania (USA) and Devon (UK), respectively. Arrows indicate the thresholds (adapted from McDowell and Sharpley [2001]) (*** indicates significance at $P<0.001$).

Others (e.g., Sharpley, 1995; Pote et al., 1996) have suggested linear relationships between STP and P in overland flow. As a result, there was no threshold. The reasons for these contradictory results may be two-fold.

Firstly, the range of STP tested may not have been sufficiently wide to detect a clear threshold and secondly, the experimental conditions may have differed, that is, the soil to solution ratio is too wide. For example, the rainfall intensity of 25.4 mm hr^{-1} used in the study by Sharpley (1995) is much less than the intensity used by McDowell and Sharpley (2001), resulting in less loss of soil. Furthermore, the soils used by Sharpley (1995) were pre-wetted, negating the effect of slaking and the increased soil loss this would have caused. Little soil loss was also likely in the study by Pote et al. (1996) where plots were covered by a thick Fescue sward.

Application

In flat areas with a high ground water level, subsurface flow is an important transport route for P loss from soil (e.g., Sims et al., 1998). For most subsurface flow situations, we expect a nonlinear relationship between STP and the P concentration in solution, since compared with overland flow, much soil comes into contact with solution, yielding a narrow soil to solution ratio. In a study by Heckrath et al. (1995), a nonlinear relationship was noted even when transport was mediated by preferential flow through large macroporous cracks in the subsoil, and little contact with the soil occurred compared to matrix flow. In areas where overland flow predominates, nonlinear relationships will be likely, where conditions favor erosion of much sediment into solution during high-intensity rainfall events, and a high soil adsorption strength. However, we hypothesize that there must be a wide range in STP values, whatever the predominant hydrological pathway for P loss.

Clearly, q-i relationships depend upon the soil to solution ratio of the P intensity parameter, adsorption capacity and strength of the soil, and total range in STP. As a result, the threshold in STP calculated by the split-line model is also affected by experimental conditions and by the selection of soils, that is, the total range of STP and Q_{max} and K. Hence, thresholds derived from q-i relationships cannot be used in environmental management without considering their sensitivity to experimental conditions and soils. Furthermore, the P concentration in solution corresponding to the threshold depends on experimental conditions, soil chemical characteristics, and total range in STP. As a consequence, in some cases, the P concentration at STP values lower than the threshold still can be considerably high (e.g., see Fig. 2.4, <0.5 mg P L^{-1} for the Pennsylvania soils), and can exceed the critical P concentration mentioned for triggering eutrophication effects in surface waters, that is, 0.015-0.030 mg total P L^{-1} (USEPA, 1994). Clearly, this P concentration should also be considered before using thresholds for mitigating P loss from soil to surface waters in practice.

Conclusions

Experimental relationships between soil P quantity (e.g., STP or % DPS) and P intensity (e.g., P extracted by water or dilute $CaCl_2$ or P lost in overland or subsurface flow) are often nonlinear, and yield a threshold. However, in some cases, these q-i relationships are linear, and there is no threshold. Based on our exploration of q-i relationships, we conclude that under conditions of a narrow total range in P quantity being tested, and/or a wide soil to solution ratio of the P intensity parameter, q-i relationships tend towards linearity. Under such conditions, a threshold is difficult to detect and uncertain. What is clear is that q-i relationships are highly dependent upon experimental conditions, soil chemical characteristics, and total range in STP. This should be considered when calculating thresholds from these relationships to be used for environmental management.

Appendix A

List of symbols

a_1	slope of the linear relationship for values of q below the CP in the split-line model
a_2	slope of the linear relationship after the CP in the split-line model
Δa	difference between a_2 and a_1 in the split-line model
α	ratio $F_{max}/[Al+Fe]_{ox}$
b	intercept of the split-line model
β	ratio $Q_{max}/[Al+Fe]_{ox}$
C	concentration (intensity) of P desorbed in solution (mg P L^{-1})
CP	change point or threshold (mg P kg^{-1})
DPS	degree of phosphorus saturation (%)
F_{max}	total P sorption maximum (mg P kg^{-1})
g	mass of soil (kg)
i	intensity (mg P L^{-1})
K	constant Langmuir adsorption isotherm (L mg^{-1})
q	quantity (mg P kg^{-1})
Q	amount of P adsorbed to the soil (mg P kg^{-1})
Q_{max}	P adsorption maximum (mg P kg^{-1})
T	total amount of inorganic reversibly adsorbed P (mg P)
v	volume of extractant (L)

Appendix B

Derivation of C from mass balance

The amount of P extracted can be calculated at a set of values of g, v, Q_{max}, and K for a range of T by solving for C in Eq. [2.3]:

$$(1+K\times C)\times(T)=(g\times\frac{Q_{max}\times K\times C}{1+K\times C})\times(1+K\times C)+(v\times C)\times(1+K\times C) \qquad [B.1]$$

yielding:

$$(T)+(T\times K)\times C=(g\times Q_{max}\times K)\times C+(v)\times C+(v\times K)\times C^2 \qquad [B.2]$$

Equation [B.2] can be written as:

$$(v\times K)\times C^2+(g\times Q_{max}\times K+v-T\times K)\times C+(-T)=0 \qquad [B.3]$$

and solved using a quadratic equation of C:

$$C_{1,2}=\frac{-b\pm\sqrt{b^2-4\times a\times c}}{2\times a} \qquad [B.4]$$

Equation [B.4] gives two solutions of which one solution is negative. Obviously, a negative value of C does not exist. We used the positive solution, that is, Eq. [2.4].

Appendix C

Derivation of K from mass balance

Adsorption strength of the soil for P can be estimated at a set of values of T, g, v, Q_{max}, and C by solving for K in Eq. [2.3] leading to Eq. [B.1]. Equation [B.1] can be written as:

$$(T)+(T\times C)\times K=(g\times Q_{max}\times C)\times K+(v\times C)+(v\times C^2)\times K \qquad [C.1]$$

which can be solved for K according to Eq. [2.7].

3

Wet chemical and phosphorus-31 nuclear magnetic resonance analysis of phosphorus speciation in a sandy soil receiving long-term fertilizer or animal manure applications

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Abstract

In areas under intensive livestock farming and with high application rates of animal manure, inorganic and organic phosphorus (P) may be leached from soils. Since the contribution of these P compounds to P leaching may differ, it is important to determine the speciation of P in these soils. We determined the effect of various fertilization regimes on the P speciation in NaOH-Na_2EDTA (ethylenediaminetetraacetic acid) and water extracts of acidic sandy soil samples from the top 5 cm of grassland with wet chemical analysis and ^{31}P nuclear magnetic resonance (NMR) spectroscopy. These soils had been treated for a period of 11 years with no fertilizer (control), N (no P application), N-P-K, or different animal manures. Inorganic P was highly elevated in the NaOH-Na_2EDTA extracts of the soils amended with N-P-K or animal manures, while organic P increased only in the soil treated with pig slurry. Water-extractable P showed a similar trend. As indicated by ^{31}P NMR, orthophosphate monoesters were the main organic P compounds in all soils. Our results suggest that long-term applications of large amounts of P fertilizer and animal manures caused an accumulation of inorganic P, resulting in an increase of the potential risk related to mobilization of inorganic P in the top 5 cm of these soils.

Introduction

In areas under intensive livestock farming, soil phosphorus (P) content has increased due to high application rates of P fertilizer and animal manure for decades, often exceeding the rate necessary to maintain optimal soil fertility for crop production (e.g., Breeuwsma et al., 1995). In the Netherlands, intensive livestock farming is mainly found on sandy soils in the east and south of the country. Sandy soils are generally characterized by a low sorption capacity for P, and as a result, P can leach, especially in flat areas with a high ground water level (e.g., Sims et al., 1998).

In animal manure, P is composed of both inorganic and organic P fractions, the latter varying from 5 to 25% of total P (Gerritse, 1981; Dou et al., 2000; Sharpley and Moyer, 2000). Dissolved organic P compounds in liquid pig slurry (a mixture of feces, urine, and cleaning water), representing 1% of total P, were found to be of high molecular weight and related to deoxyribonucleic acids (DNA), that is, orthophosphate diesters (Gerritse and Eksteen, 1978). In sandy soils amended with large amounts of pig and cattle slurry, the P leaching through the soil profile was found to be mainly organic P (Gerritse, 1981; Chardon et al., 1997). In the study of Gerritse (1981), where pig slurry was used as an amendment, the organic P leached had molecular weight characteristics similar to dissolved organic P compounds in the liquid fraction of pig slurry found by Gerritse and Eksteen (1978). Therefore, some organic P compounds in animal manure may be more mobile in soil than inorganic P (Gerritse, 1981). In soils treated with large amounts of animal manure, increased inorganic and organic P contents can be expected. Since the contribution of these P compounds to P leaching may differ, it is necessary to determine the P speciation in these soils.

Various sequential extraction methods have been used to characterize P pools of different availability in relation to plant uptake of P (e.g., Tiessen and Moir, 1993). However, extraction methods do not give direct information on the structural composition of the various compounds of P in soil (Guggenberger et al., 1996). Liquid-state ^{31}P nuclear magnetic resonance (NMR) spectroscopy, a relatively simple and direct technique, has been used to characterize P in soil extracts (e.g., Tate and Newman, 1982; Hawkes et al., 1984; Dai et al., 1996). Characterization of P in soil extracts with ^{31}P NMR has indicated the presence of inorganic P compounds such as orthophosphate, pyrophosphate, and polyphosphate and organic P compounds such as phosphonate, orthophosphate monoesters (e.g., inositol phosphates), and orthophosphate diesters (e.g., phospholipids and DNA) (Cade-Menun and Preston, 1996).

The method used for extracting P from soil may affect the results obtained by ^{31}P NMR (Cade-Menun and Preston, 1996). In most ^{31}P NMR studies, P has been extracted by alkaline extracts, such as 0.5 M NaOH (e.g., Tate and Newman, 1982; Hawkes et al., 1984; Bedrock et al., 1994). However, 0.5 M NaOH usually extracts <50% of the total P content from soil, whereas an ideal method should extract all P from soil without altering the P compounds in soil (Cade-Menun and Preston, 1996). The use of 0.25 M NaOH-0.05 M Na_2EDTA extracts more P from soil with minimal alkaline hydrolysis of organic P to inorganic P (Bowman and Moir, 1993; Cade-Menun and Preston, 1996; Dai et al., 1996). Alkaline hydrolysis of orthophosphate diesters may occur, especially at higher NaOH concentrations (Leinweber et al., 1997).

Very little information exists on changes of inorganic and organic P fractions and the distribution of P among the various P compounds within these fractions in soils exposed to long-term application with animal manure. We therefore selected soil samples from the top 5 cm of grassland exposed to different fertilization regimes in a long-term field experiment, started in 1970 and ending in 1980 (van der Veen, 1985). These soil samples are part of an extensive archive for technical information and soil samples (TAGA) containing the results of about 20 000 field experiments, performed in the period between 1879 and 1998 in the Netherlands, and about 250 000 soil samples from selected experiments (de Willigen et al., 2001). Our first objective was to determine the P speciation in 0.25 M NaOH-0.05 M Na_2EDTA extracts of soils exposed to no fertilizer (control), or applications of N (no P application), N-P-K, or different animal manures. Phosphorus in the NaOH-Na_2EDTA extracts was characterized with wet chemical analysis and ^{31}P NMR. Our second objective was to characterize P in water extracts at a soil to solution ratio of 1:5 (w/v), representing the fraction of P in soil relevant for potential mobilization of P to surface waters (e.g., McDowell and Sharpley, 2001), again with wet chemical analysis and ^{31}P NMR.

Materials and methods

Field experiment

We used soil samples from a long-term field experiment (1970-1980) on an acidic sandy soil (van der Veen, 1985). Samples were taken in 1981 from the top 5 cm of eight grassland sites, located in a single field, exhibiting a size of 2 by 2 m and separated by 5-cm-wide and 3-cm-deep trenches. The sites had been treated with no fertilizer (control), N (no P application), N-P-K, or different animal manures. Table 3.1 shows the treatments and the amounts applied for each application. All soils were treated annually since 1970, except for the pig slurry and the N-P-K treatments, which were applied from 1971 onward. In 1970, the animal manures were applied once, but from 1971 onward, applications were twice each year: at the start of the growing season and after the second harvest of the grass. From 1971 up to and including 1973, the N and N-P-K fertilizers were applied twice each year. From 1974 onward, N was applied four times each year: 50 kg of N ha^{-1} was applied after the first, second, third, and fourth harvest of the grass, while the P and K fertilizers were applied once each year (before the start of the growing season). Fertilizers and animal manures were applied on the soil surface without mechanical incorporation. No tillage was applied during the field experiment. After sampling, soils were dried at 40°C, sieved (2 mm), and stored in closed cardboard boxes at constant temperature and humidity in the archive TAGA, as described before (de Willigen et al., 2001).

Chemical analyses

For the soil samples, we used the following results from van der Veen (1985): pH (KCl), organic matter (estimated from loss-on-ignition), Pw (water-extractable P at a soil to solution ratio of 1:60 [v/v]), total soil P content, and the P balance of the field experiment. The method of Sissingh (1971) was used to determine Pw. In the Netherlands, Pw is used for P fertilizer recommendations for arable land. Normally, Pw is expressed in mg P_2O_5 L^{-1} of soil, but in this study in mg P kg^{-1}. For converting Pw, we calculated the density of the soil samples on the basis of the organic matter content. Other methods used are described in Vierveijzer et al. (1979). Van der Veen (1985) calculated the cumulative P balance as the difference between the P applied and P removed with the harvested grass. For calculating the P balance, the total P content of the grass and animal manure and the yield of the harvested grass were determined. We determined the organic P content of the soil according to the ignition method of Kuo (1996). The method of Schwertmann (1964) was used for determining oxalate-extractable P, Al, and Fe. Concentrations of P, Al, and Fe were measured by inductively coupled plasma (ICP) spectroscopy. The degree of phosphorus saturation (DPS) was calculated according to Schoumans and Groenendijk (2000):

$$\mathrm{DPS} = \frac{\mathrm{P_{ox}}}{0.5 \times [\mathrm{Al} + \mathrm{Fe}]_{\mathrm{ox}}} \times 100 \qquad [3.1]$$

where DPS is expressed as a percentage, P_{ox} and $[Al+Fe]_{ox}$ are expressed in mmol kg^{-1}, and the value 0.5 denotes the saturation factor of Al- and Fe-(hydr)oxides for P sorption in acidic sandy soils.

NaOH-Na_2EDTA extracts

A slight modification of the single-step extraction method (0.25 M NaOH-0.05 M Na_2EDTA) of Bowman and Moir (1993) was used to extract P from soil. It is a simple method needing minimal analytical prowess and extracts a large part of total P from soil with minimal alkaline hydrolysis of organic P (Bowman and Moir, 1993; Cade-Menun and Preston, 1996). The NaOH solubilizes the organic material and EDTA increases the effectiveness of organic P extraction by breaking P containing Al and Fe complexes from soil. Three grams of soil were suspended in 60 mL of 0.25 M NaOH-0.05 M Na_2EDTA in a centrifuge tube and shaken reciprocatively for 16 h at 85 strokes min^{-1} and 20°C. The suspension was centrifuged at 2100 x g for 10 min and filtered through a Schleicher & Schuell (Dassel, Germany) 589/5 filter (pore size 2 to 4 μm). An aliquot of 30 mL of filtrate was freeze-dried and stored at -18°C. Before ^{31}P NMR analysis, the freeze-dried extract was dissolved in D_2O, vortexed for 2 min, and kept at room temperature for 2 h. The remaining filtrate was used to determine inorganic P and total P, Fe, and Mn, and the pH. Inorganic P measurements were made colorimetrically (Murphy and Riley, 1962) after removal of a large fraction of the solubilized organic matter through acidification and centrifugation (Tiessen and Moir, 1993). Total P, Fe, and Mn concentrations were measured by ICP. Organic P was calculated as the difference between total and inorganic P. The pH was measured by pH indicator strips (pH of approximately 13). The ^{31}P NMR spectra were obtained on a Bruker (Rheinstetten, Germany) DPX 300 spectrometer, operating at 121.49 MHz and room temperature. Conditions used for ^{31}P analysis were a pulse angle of 90°, a pulse delay of 2 s, and an acquisition time of 0.67 s. For each sample, 512 scans were used to obtain an acceptable signal to background noise ratio. Chemical shifts (δ) of the peaks were measured according to an external 0.98 mM methylenediphosphonic acid trisodium salt tetrahydrate (MDP; 98%) standard, contained in a capillary tube measured simultaneously with each sample. In most other ^{31}P NMR studies, orthophosphoric acid is used as a standard. For comparison of our results with these studies, MDP was set at δ = 18.1 ppm. Interpretation of the ^{31}P NMR spectra was based on literature assignments (Bedrock et al., 1994; Cade-Menun and Preston, 1996; Amelung et al., 2001). Peak areas were calculated by instrumental integration. The ^{31}P NMR spectra were evaluated semiquantitatively, that is, the fractions of the different P compounds were calculated by relating the respective peak areas to the total area.

Water extracts

In addition to the Pw results of van der Veen (1985), we measured water-extractable P at a soil to solution ratio of 1:5 (w/v). Twelve grams of soil were suspended in 60 mL of water and shaken reciprocatively for 16 h at 85 strokes min^{-1} and 20°C. The suspension was centrifuged at 2100 x g for 10 min and filtered through a Schleicher & Schuell 589/5 filter. An aliquot of 40 mL of filtrate was freeze-dried and stored at -18°C. Before ^{31}P NMR analysis, the freeze-dried extract was dissolved in D_2O, vortexed for 2 min, and kept at room temperature for 2 h. The ^{31}P NMR spectra of the water extracts were obtained with the same ^{31}P NMR parameters as for the NaOH-Na_2EDTA extracts. Interpretation of the spectra was based on our experience with ^{31}P NMR analysis of solutions exhibiting a slightly acidic pH. The remaining filtrate was used to determine inorganic and organic P and total P, Fe, and Mn.

Test for alkaline hydrolysis of organic phosphorus

Alkaline hydrolysis of organic P to inorganic P was tested by measuring inorganic P before and after the addition of a volume of 0.25 M NaOH to a soil water extract. Five grams of soil were suspended in 25 mL of water and shaken reciprocatively for 16 h at 85 strokes min^{-1} and 20°C. The suspension was centrifuged at 2100 x g for 10 min, filtered through a Schleicher & Schuell 589/5 filter, and inorganic P and the pH were measured. On average, the pH was 5.34 ± 1.06. Three milliliters of 0.25 M NaOH were added to an aliquot of 10 mL of filtrate to increase the pH to approximately 13. The filtrate was shaken again for 16 h at 85 strikes min^{-1} and 20°C. Afterwards, inorganic P and the pH were measured (pH = 12.90 ± 0.03).

Results and discussion

Soils

Table 3.1 shows the selected characteristics of the soil samples and the P balance of the field experiment. After 11 yr of treatment, soil characteristics such as pH and organic matter were considerably affected. The pH increased in the soils amended with animal manures, while the organic matter content increased in all soils. Mugwira (1976) also found an increase in soil pH and organic matter after 3 yr of dairy manure application at rates varying from 22 to 267 Mg ha^{-1} yr^{-1}. A higher pH decreases sorption of P in sandy soils, increasing the soil potential for P mobilization, and favors the microbial mineralization of organic P (Beek and van Riemsdijk, 1982).

The Pw (plant-available P) and total P content of the soils amended with N-P-K or animal manures were 6.6 to 19.0 and 1.9 to 6.1 times higher than the corresponding values in the initial soil, respectively, due to the positive P balance. Interestingly, the relative increase of P available for plant uptake was much higher than the increase of total P. The DPS showed a large increase in the N-P-K- and animal manure-amended soils (Table 3.1). The sum of oxalate-extractable Al and Fe remained relatively constant. As soils become increasingly saturated with P, any additional soluble P applied through P fertilizer or animal manure remains as (readily) available P in soil, causing a large increase of Pw. In the soils treated with animal manures, the DPS is, however, (much) higher than expected on basis of the theoretical maximum (DPS = 100%) predicted by the sum of oxalate-extractable Al and Fe. This may indicate the buildup of a pool of Ca-P compounds in soil originating from the animal manures applied. In acidic to neutral soils, heavily enriched with P, Ca-P compounds may exist as metastable solid phases. De Haan and van Riemsdijk (1986) found indications for the existence of brushite ($CaHPO_4{\cdot}2H_2O$) in heavily pig manured sandy soils. The Pw value and total P content of the soil treated with N fertilizer (no P application) slightly decreased, due to the negative P balance. In contrast, Pw and total P of the control soil slightly increased. In the soils treated with animal manures, organic P was 1.4 to 2.2 times higher than in the initial soil, due to the accumulation of organic P resulting from animal manure application. In the control and N- and N-P-K-amended soils, organic P was 1.1 to 1.2 times higher. This slight increase may be explained by accumulation of organic P from plant residues. Since the increase of the total P content was much higher than the increase of organic P in the soils treated with N-P-K or animal manures, P had mainly accumulated in soil as inorganic P (results not shown). Similar results have been found in soils treated with large amounts of cattle feedlot manure over several years; this was attributed to the high inorganic P fraction (78%) found in the cattle feedlot manure (Sharpley et al., 1984).

Table 3.1. Treatments, amounts applied for each application, cumulative P balance, and selected characteristics of the soils (0-5 cm) from the field experiment.

Treatment	Application	P balance†	pH (KCl)	Organic matter	Pw‡	Total P	Organic P§	$[Al+Fe]_{ox}$§	DPS¶
		kg P ha^{-1}		%	mg P kg^{-1}	mg P kg^{-1}	mg P kg^{-1} (%)#	mmol kg^{-1}	%
Initial soil			4.4	5.4	2.1	393	240 (61)	56	34
No fertilizer (control)		-158	4.0	5.9	3.0	436	269 (62)	54	39
N fertilizer	200 kg N ha^{-1}	-219	4.0	6.8	1.4	349	286 (82)	45	35
N-P-K fertilizer	200 kg N, 52 kg P and 199 kg K ha^{-1}	236	4.1	6.3	13.8	742	288 (39)	56	66
Solid poultry manure	25 Mg ha^{-1}	2486	6.5	6.5	29.0	2400	529 (22)	57	194
Idem mixed with litter	25 Mg ha^{-1}	3542	6.3	6.8	39.8	2007	470 (23)	53	208
Poultry slurry	30 Mg ha^{-1}	1690	6.3	6.0	22.7	1658	477 (29)	50	155
Calf slurry	25 Mg ha^{-1}	1066	5.7	5.7	26.5	1134	328 (29)	56	111
Pig slurry	25 Mg ha^{-1}	1000	5.4	6.7	22.0	1222	441 (36)	60	107

†The cumulative P balance was calculated as the difference between the P applied and P removed with the harvested grass.
‡Water-extractable P at a soil to solution ratio of 1:60 (v/v) (Sissingh, 1971).
§Organic soil P and $[Al+Fe]_{ox}$ were determined in this study; other data were taken from van der Veen (1985).
¶Degree of phosphorus saturation (DPS) was calculated according to Eq. [3.1].
#Organic P as a fraction of total P is shown in parentheses.

Wet chemical analysis of NaOH-Na_2EDTA-extractable phosphorus

Figure 3.1 and Table 3.2 show inorganic and organic P measured in the NaOH–Na_2EDTA extracts. Total P in the NaOH–Na_2EDTA extracts represented 70 to 78% of the total P content in soil (Table 3.2) implying that it is a reasonably good extractant for total P in our sandy soil samples, although the method was originally developed for extracting organic soil P (Bowman and Moir, 1993). Our results correspond well with recoveries of total P found in other studies where 0.25 M NaOH-0.05 M Na_2EDTA was used as an extractant: Cade-Menun and Preston (1996) and Dai et al. (1996) extracted 71 to 91% and 39 to 99% of total P from forest soils, respectively. The P remaining in soil after extraction with NaOH-Na_2EDTA may represent some insoluble inorganic P compounds (Dai et al., 1996). Organic P in our NaOH-Na_2EDTA extracts represented 27 to 70% of organic soil P (Table 3.2). These results agree with the 22 to 103% extracted by Dai et al. (1996). Interestingly, the recovery of extracted organic P relative to organic soil P decreased with increasing soil pH (Fig. 3.2). In the soils with pH values close to neutral, only 27 to 37% of organic soil P was extracted (Tables 3.1 and 3.2; the solid poultry manure, solid poultry manure mixed with litter, and poultry and calf slurry treatments). Because of the higher soil pH of the latter treatments, the microbial mineralization rate may have been higher than in the soils of the other treatments; the remaining organic soil P may therefore have a lower extractability in NaOH-Na_2EDTA. Another explanation includes a lower extractability of organic P originating from solid poultry manure, solid poultry manure mixed with litter, and poultry and calf slurry. According to the sequential extraction method of Tiessen and Moir (1993), 0.1 M NaOH represents less available inorganic and organic P compounds. Since we did not use any other extraction prior to the NaOH-Na_2EDTA extraction, it thus contains both available and less available inorganic and organic P compounds, made available for characterization by ^{31}P NMR. Total P measured in NaOH-Na_2EDTA was 32 to 188 times higher than the corresponding Pw value (results not shown).

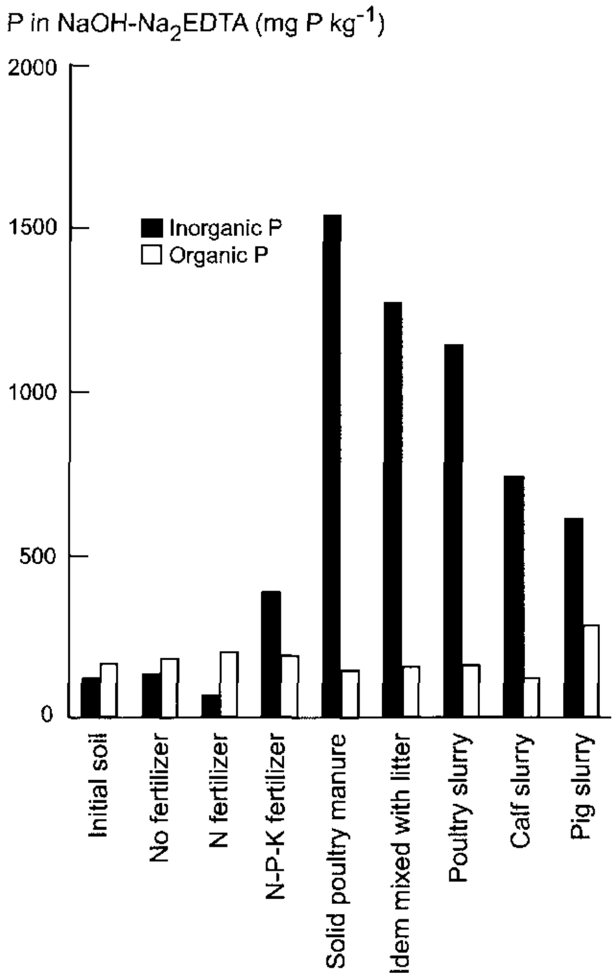

Figure 3.1. Inorganic and organic P for the different fertilizer regimes, measured in NaOH-Na_2EDTA extracts by wet chemical analysis.

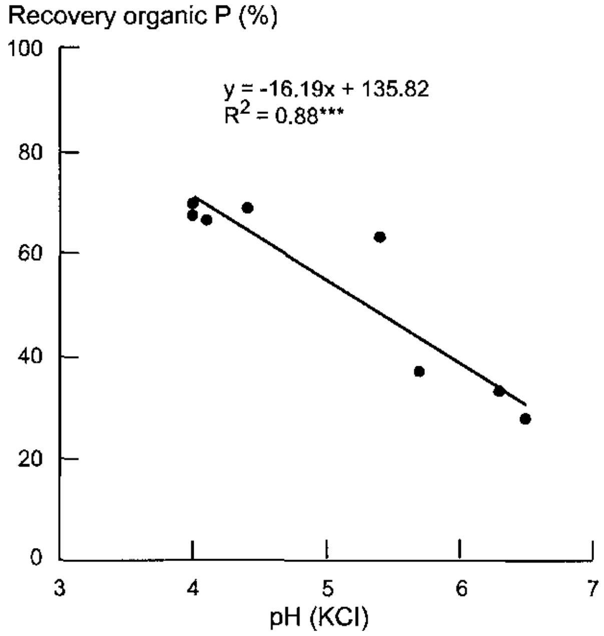

Figure 3.2. Recovery of extracted organic P by NaOH-Na_2EDTA relative to organic soil P plotted against the soil pH (KCl).

Table 3.2. Total, inorganic, and organic P measured in the NaOH-Na$_2$EDTA extracts by wet chemical analysis, and organic P as a fraction of total P, measured by wet chemical analysis or ^{31}P nuclear magnetic resonance (NMR).

	Wet chemical analysis				^{31}P NMR
Treatment	Total P	Inorganic P	Organic P	Organic P/ total P	Organic P/ total P
	mg P kg^{-1} (%)†	mg P kg^{-1}	mg P kg^{-1} (%)‡	%	% of total area§
Initial soil	285 (73)	120	165 (69)	58	52
No fertilizer (control)	310 (71)	128	182 (68)	59	54
N fertilizer	268 (77)	69	199 (70)	74	66
N-P-K fertilizer	574 (77)	383	191 (66)	33	29
Solid poultry manure	1681 (70)	1536	145 (27)	9	17
Idem mixed with litter	1424 (71)	1269	156 (33)	11	21
Poultry slurry	1298 (78)	1141	158 (33)	12	17
Calf slurry	857 (76)	736	122 (37)	14	24
Pig slurry	889 (73)	610	279 (63)	31	33

†Total P as a fraction of total soil P is shown in parentheses.
‡Organic P as a fraction of organic soil P is shown in parentheses.
§Sum of peak areas of organic P compounds as a fraction of total area.

Inorganic P in the NaOH-Na$_2$EDTA extracts of soils amended with N-P-K or animal manures was 3.2 to 12.8 times higher than in the initial soil (Fig. 3.1 and Table 3.2). In contrast, removal of P from soil by cropping of grass decreased inorganic P in the N fertilizer treatment. Organic P remained relatively constant in all treatments except in the soil treated with pig slurry. Our results are further illustrated by organic P as a fraction of total P. The organic P fraction decreased from 58% in the initial soil to 9 to 33% in the soils amended with N-P-K or animal manures (Table 3.2). The high levels of inorganic P found in the NaOH-Na$_2$EDTA extracts of the soils treated with animal manures can be attributed to the large inorganic P fraction generally found in animal manures (Gerritse, 1981; Dou et al., 2000; Sharpley and Moyer, 2000). Long-term field experiments indicate a tendency for intensively managed agricultural soils to contain a higher fraction of inorganic P rather than organic P, reflecting the long-term application of P fertilizer and animal manure (Hawkes et al., 1984; Sharpley et al., 1984). In contrast with the N-P-K- and animal manure-amended soils, the organic P fraction in the N-treated soil showed a large increase (74%), probably resulting from uptake of inorganic P by the grass and some accumulation of organic P from plant residues, but remained relatively constant in the control soil (59%). In nonagricultural soils without P input, organic P becomes more important (Condron et al., 1990; Cade-Menun and Preston, 1996; Dai et al., 1996).

Test for alkaline hydrolysis of organic phosphorus

With any extraction method, soil P compounds can be chemically altered during or after extraction (Cade-Menun and Preston, 1996). Hydrolysis of organic P in alkaline extracts has been reported in literature (e.g., Leinweber et al., 1997). Alkaline hydrolysis was tested by increasing the pH of the water extracts from 5.34 ± 1.06 to 12.90 ± 0.03. After shaking for 16 h, inorganic P in the water extracts increased to a small extent (on average 6.5 ± 5.4%), probably due to alkaline hydrolysis of chemically labile organic P compounds into inorganic P. Thus, the possibility of some transformation of organic P to inorganic P during our NaOH-Na_2EDTA extraction cannot be excluded.

Phosphorus-31 nuclear magnetic resonance analysis of NaOH-Na_2EDTA-extractable phosphorus

Figure 3.3 shows representative ^{31}P NMR spectra of the NaOH-Na_2EDTA extracts from the soils either amended with solid poultry manure mixed with litter or amended with calf slurry. Four distinct P compounds were detected: orthophosphate (δ = 7.0-7.1 ppm), orthophosphate monoesters (δ = 4.7-5.8 ppm), orthophosphate diesters (δ = 0.6-0.8 ppm), and pyrophosphate (δ = -3.6 to -3.7 ppm) (Cade-Menun and Preston, 1996). A peak appearing at δ = 7.6 to 7.9 ppm may reflect the presence of aromatic orthophosphate diesters (Bedrock et al., 1994; Amelung et al. 2001). The quality of our ^{31}P NMR spectra was good, with a good separation of the orthophosphate and orthophosphate monoester peaks. This contrasts with the ^{31}P NMR spectra obtained by Cade-Menun and Preston (1996), with a relatively poor separation of the orthophosphate and orthophosphate monoester peaks. This was attributed to the complexing of Fe and Mn by EDTA. Extraction of paramagnetic ions, such as Fe and Mn, causes line broadening and distortion of the ^{31}P NMR spectra (Hawkes et al., 1984). In our study, however, Fe and Mn concentrations after extraction were on average only 45 and 3% of those of Cade-Menun and Preston (1996), respectively.

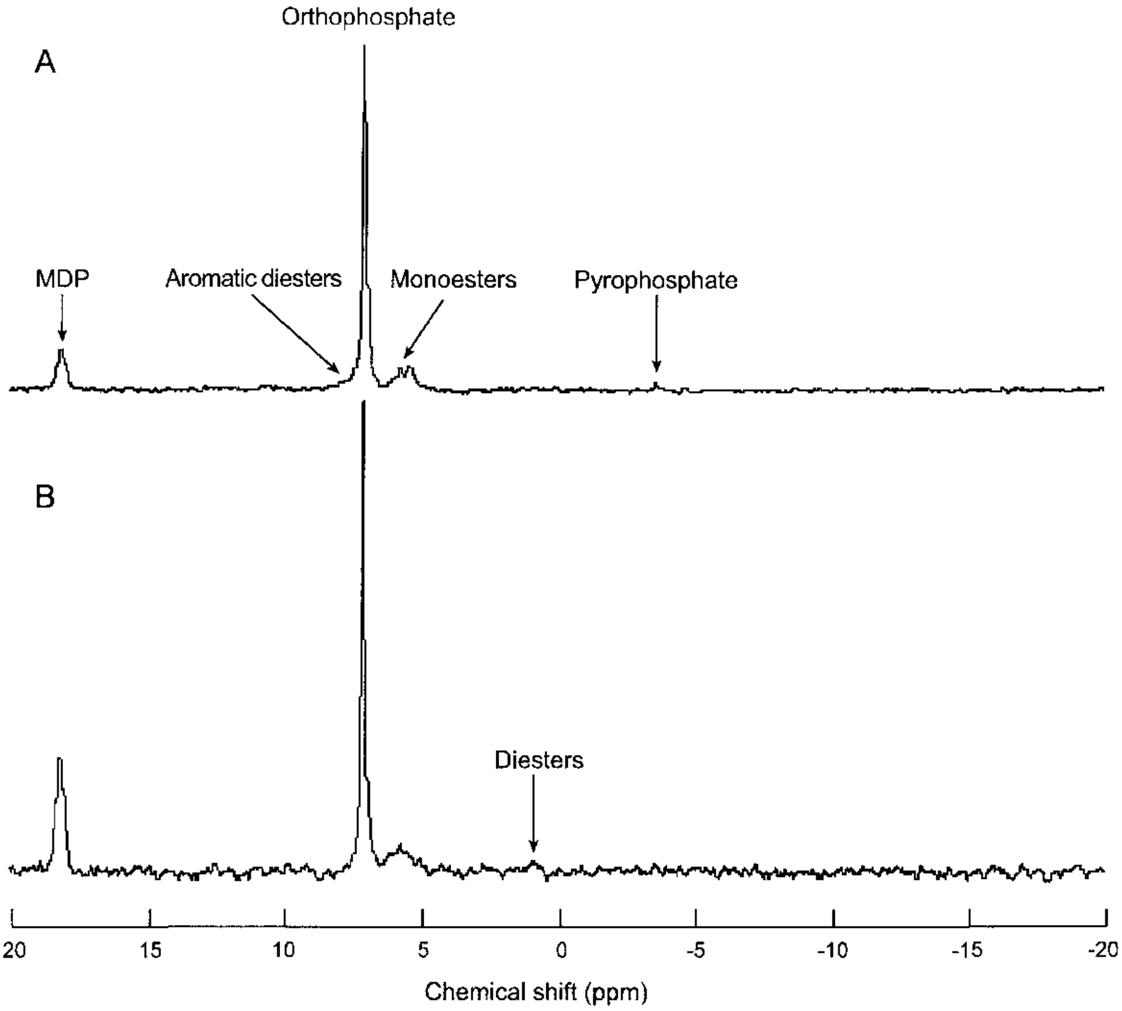

Figure 3.3. Phosphorus-31 nuclear magnetic resonance (^{31}P NMR) spectra of NaOH-Na_2EDTA extracts from soils either amended with solid poultry manure mixed with litter (A) or amended with calf slurry (B). MDP denotes the P standard.

Table 3.2 shows, for the different fertilizer regimes, organic P as a fraction of total P measured by wet chemical analysis or ^{31}P NMR (% of total area). Differences between both organic P fractions were relatively small (<11%) and agree well with results reported elsewhere in literature (e.g., Condron et al., 1985; Dai et al., 1996). Thus, both methods provided similar results in separating organic P from inorganic P and apparently no significant alkaline hydrolysis of organic P compounds occurred during concentration of the NaOH-Na_2EDTA extract and ^{31}P NMR analysis (Zhang et al., 1999). Differences between the two methods have been attributed to errors arising from the indirect wet chemical method used for estimating organic P (i.e., difference between total P and inorganic P) and to background noise in the ^{31}P NMR spectra (Dai et al., 1996).

Table 3.3 shows the P compounds as a fraction of total P (% of total area) measured by ^{31}P NMR. In all treatments, inorganic P was mainly found as orthophosphate, although some very small fractions of pyrophosphate were found in the solid poultry manure-, solid poultry manure mixed with litter-, and poultry- and pig slurry-treated soils. Pyrophosphate can be a product of biological cycling of P in soil, but it can also be formed by hydrolization of organic esters during or after the extraction by NaOH-Na_2EDTA (Condron et al., 1985). Pyrophosphate is a short-chain polyphosphate (n = 2), which is used as a microbial storage product appearing from microbial activity (Condron et al., 1985; Cade-Menun et al., 2000a, 2000b). The presence of pyrophosphate in the solid poultry manure-, solid poultry manure mixed with litter-, and poultry slurry-amended soils, with a pH close to neutral, further supports the idea of a higher microbial mineralization rate in these soils. Organic P was mainly found as orthophosphate monoesters. This agrees with results reported in other studies (e.g., Tate and Newman, 1982; Hawkes et al., 1984; Condron et al., 1985, Condron et al., 1990; Bedrock et al., 1994). Orthophosphate diesters were detected in the solid poultry manure- and calf slurry-amended soils. Orthophosphate monoesters and diesters in soil can be derived from a combination of plant and microbial residues (Anderson, 1967; Bedrock et al., 1994; Guggenberger et al., 1996) and animal manure application. Using ^{31}P NMR, Leinweber et al. (1997) detected these P compounds in poultry and pig manure. Orthophosphate monoesters consist mainly of inositol phosphates, amounting to >50% of total organic P in soil (Anderson, 1967). Due to the high charge density of inositol phosphates, these P compounds are strongly sorbed by (hydr)oxides of Al and Fe in soil (Turrión et al., 2001), protecting inositol phosphates from mineralization. Orthophosphate diesters comprise P compounds such as phospholipids, ribonucleic acids (RNA), and DNA. Because of their lower charge density, orthophosphate diesters are only slightly retained in soil, and are more mobile and more accessible for microbial degradation than monoesters (Gerritse, 1981; Turrión et al., 2001). Under favorable soil conditions, such as an optimal pH and moisture content for microbial activity, orthophosphate diesters can be transformed into monoesters (Hinedi et al., 1988). In intensively managed grassland soils with favorable conditions for mineralization, such as in our soils, orthophosphate diesters can be absent (Condron et al., 1990). In contrast, in nonagricultural soils where conditions favored a lower rate of mineralization (low pH and high moisture content), significant amounts of orthophosphate diesters have been found (Condron et al., 1990; Bedrock et al., 1994; Cade-Menun et al., 2000a). Moreover, alkaline hydrolysis of orthophosphate diesters into monoesters may have occurred to a small extent. Especially at higher NaOH concentrations (0.5 M NaOH), alkaline hydrolysis of orthophosphate diesters can occur (Leinweber et al., 1997). We used a lower NaOH concentration (0.25 M NaOH), possibly decreasing the potential of alkaline hydrolysis.

Table 3.3. The P compounds as a fraction of total P (% of total area†) measured by ^{31}P nuclear magnetic resonance (NMR) in the NaOH-Na_2EDTA extracts.

Treatment	Aromatic diesters	Orthophosphate	Monoesters	Diesters	Pyrophosphate
Initial soil	nd‡	48.3	51.7	nd	nd
No fertilizer (control)	1.9	45.9	52.2	nd	nd
N fertilizer	4.8	34.4	60.8	nd	nd
N-P-K fertilizer	nd	71.3	28.7	nd	nd
Solid poultry manure	0.9	83.1	15.6	0.2	0.2
Idem mixed with litter	3.6	77.0	17.9	nd	1.5
Poultry slurry	3.1	81.6	13.5	nd	1.8
Calf slurry	1.7	75.9	19.2	3.2	nd
Pig slurry	6.4	66.3	26.6	nd	0.7

†Peak areas of the respective P compounds as a fraction of total area.
‡Not detected.

Summarizing, inorganic P was highly elevated in soils amended with N-P-K or animal manures, while organic P increased only in the soil treated with pig slurry. However, liquid-state ^{31}P NMR cannot be used to characterize inorganic P, since different inorganic P compounds (e.g., P associated with Al, Fe, or Ca) dissolved in the NaOH-Na_2EDTA extracts appear as one orthophosphate peak in the ^{31}P NMR spectra. Our results can therefore not be used to interpret whether long-term P applications resulted in accumulations of different inorganic P compounds. For this purpose, sequential extraction methods in combination with solid-state ^{31}P magic angle spinning (MAS)-NMR can be useful. Using the latter technique in acidic sandy soils amended with large amounts of animal manure, inorganic P was shown to be associated with Al and Ca; one of the Ca-P compounds was more soluble than the other P compounds (Lookman et al., 1997). However, solid state ^{31}P MAS-NMR has some limitations: paramagnetic ions, such as Fe and Mn, cause line broadening and large spinning-side bands complicating the interpretation of ^{31}P NMR spectra and the detection of P associated with these ions in soil (Hinedi et al., 1989; Lookman et al., 1997).

Wet chemical and phosphorus-31 nuclear magnetic resonance analysis of water-extractable phosphorus

Characterization of P in NaOH-Na_2EDTA extracts gives limited information on the soil potential for P mobilization, since both available and less-available inorganic and organic P compounds are extracted. For a better understanding of the potential mobility of P in our soils, water- or 0.01 M $CaCl_2$-extractable P needs to be characterized, since these extractants represent the P fraction in soil relevant for potential P loss to flowing water (e.g., McDowell and Sharpley, 2001). In addition to results of Pw, which has a low soil to solution ratio (1:60 [v/v]), taken from van der Veen (1985) (Table 3.1), we measured water-extractable P at a soil to solution ratio of 1:5 (w/v). Because of the higher soil to solution ratio of these water extracts, these results may be more indicative for the leaching of soil solution through the soil profile where a relatively large amount of soil comes into contact with a relatively limited volume of solution. Table 3.4 shows total, inorganic, and organic P measured in the water extracts by wet chemical analysis. Water extracted 1.5 to 3.7% of the total P content from soil (Table 3.4). The trend shown by inorganic P is similar to the one in the NaOH–Na_2EDTA extracts. Inorganic P increased by 7.5 to 24.8 times in the N-P-K- and animal manure-amended soils. In contrast, organic P increased only by 1.5 to 3.2 times. These results are further illustrated by organic P as a fraction of total P. The organic P fraction decreased from 67% in the initial soil to 20 to 32% in the soils amended with N-P-K or animal manures, but remained relatively constant in the control and N-amended soils (Table 3.4).

Figure 3.4 shows representative ^{31}P NMR spectra of the water extracts from the soils either amended with poultry or pig slurry. Two distinct P compounds were detected: orthophosphate (δ = 2.2-2.4 ppm) and orthophosphate monoesters (δ = 2.8-3.0 ppm). The chemical shifts of orthophosphate and orthophosphate monoesters in the water extracts differed from those in the NaOH-Na_2EDTA extracts. Since we did not adjust the pH of the solution containing the freeze-dried water extract prior to ^{31}P NMR analysis, the pH must have been lower than the pH of the solution with the freeze-dried NaOH-Na_2EDTA extract. As demonstrated by Crouse et al. (2000), the pH significantly affects the chemical shifts of the various P compounds in the ^{31}P NMR spectra: changing the pH causes a change in the chemical environment surrounding the P nuclei and as pH changes so do the chemical shifts. Thus, the differences between the chemical shifts of orthophosphate and orthophosphate monoesters in our NaOH-Na_2EDTA and water extracts can be attributed to a change in pH.

Table 3.4. Total, inorganic, and organic P measured in the 1:5 (w/v) soil water extracts by wet chemical analysis, and organic P as a fraction of total P, measured by wet chemical analysis or ^{31}P nuclear magnetic resonance (NMR).

	Wet chemical analysis				^{31}P NMR
Treatment	Total P	Inorganic P	Organic P	Organic P/ total P	Organic P/ total P
	mg P kg^{-1} (%)†	mg P kg^{-1}	mg P kg^{-1}	%	% of total area‡
Initial soil	6.7 (1.7)	2.2	4.5	67	nd§
No fertilizer (control)	7.5 (1.7)	2.7	4.8	64	21
N fertilizer	8.4 (2.4)	2.6	5.8	69	12
N-P-K fertilizer	24.7 (3.3)	16.7	8.0	32	nd
Solid poultry manure	35.5 (1.5)	28.5	6.9	20	12
Idem mixed with litter	69.4 (3.5)	55.1	14.3	21	nd
Poultry slurry	27.4 (1.7)	20.5	6.9	25	8
Calf slurry	41.5 (3.7)	31.6	9.9	24	nd
Pig slurry	43.8 (3.6)	33.5	10.3	24	4

†Total P as a fraction of total soil P is shown in parentheses.
‡Peak area of orthophosphate monoesters as a fraction of total area.
§Not detected.

Orthophosphate was detected in all treatments except in the initial soil. In contrast to the results of wet chemical analysis (Table 3.4), organic P was found (as orthophosphate monoesters) only in the control soil and the N-, solid poultry manure-, and poultry- and pig slurry-amended soils. Since orthophosphate monoesters are strongly retained in soil (Turrión et al., 2001), these P compounds may have been mobilized in water because of dispersion of colloidal soil particles. Table 3.4 shows organic P as a fraction of total P measured by ^{31}P NMR (% of total area). Organic P fractions measured by ^{31}P NMR were much smaller than those obtained by wet chemical analysis, showing that some organic P was not detected by ^{31}P NMR. McDowell et al. (1998) reported ^{31}P NMR results of P in 1:5 (w/v) 0.01 M $CaCl_2$ extracts from four P rich agricultural soils. They detected mainly orthophosphate and orthophosphate monoesters, and moreover, some small amounts of phosphonate, aromatic phosphate diesters, orthophosphate diesters, and pyrophosphate, indicating the potential mobility of these P compounds in soil. Most of these P compounds were also detected in the NaOH-Na_2EDTA extracts of our soils (Table 3.3), but apart from orthophosphate and orthophosphate monoesters, not in our water extracts. Concentrations of these P compounds may possibly have been below the detection limit of ^{31}P NMR. In the future, we will work on the development of an improved method for extracting potentially mobile P compounds for characterization with ^{31}P NMR. The choice of the extractant is important. Calcium chloride may affect results obtained by ^{31}P NMR, since $CaCl_2$ induces precipitation of dissolved organic matter and associated P, especially of high molecular weight compounds (Dolfing et al., 1999; Oste et al., 2002).

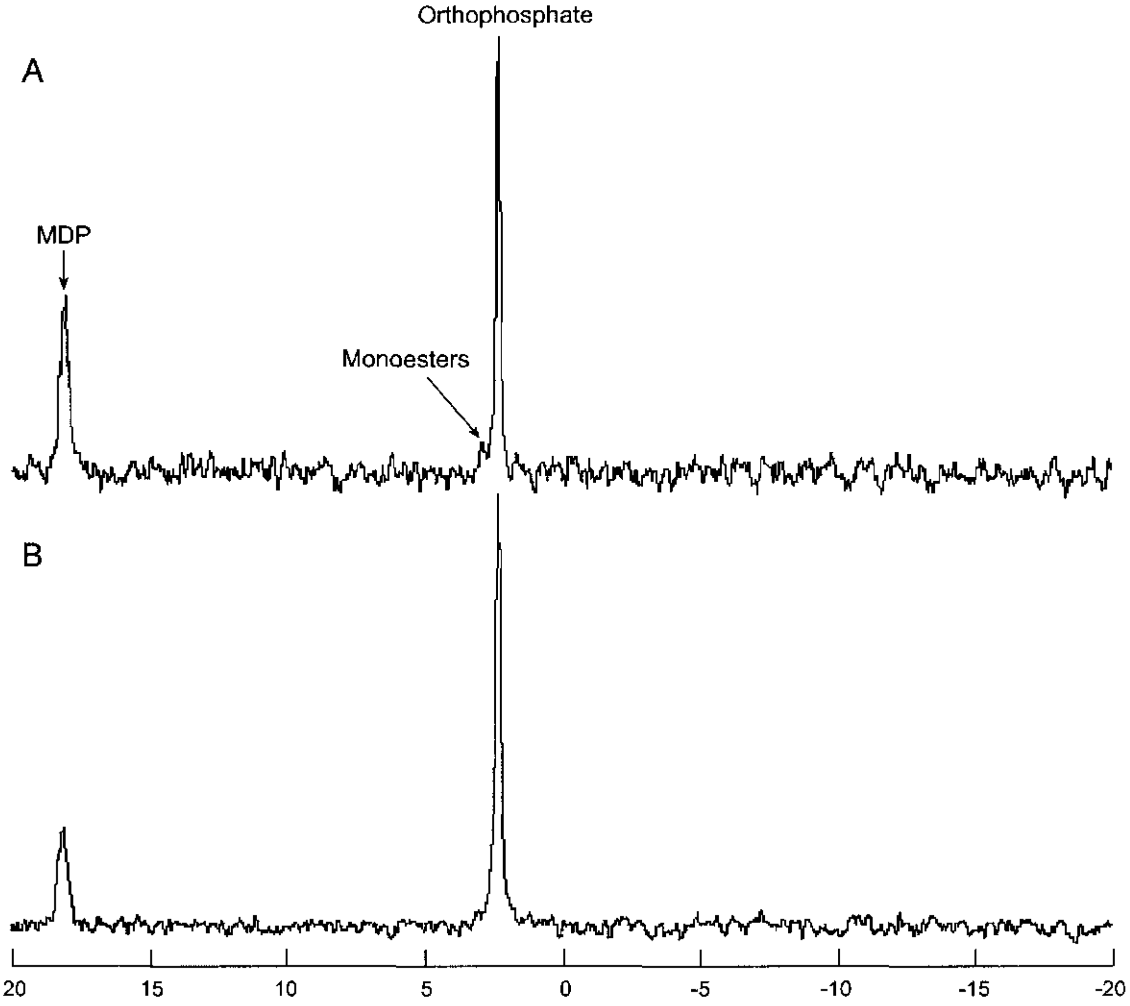

Figure 3.4. Phosphorus-31 nuclear magnetic resonance (^{31}P NMR) spectra of water extracts from soils either amended with poultry slurry (A) or amended with pig slurry (B). MDP denotes the P standard.

Conclusions

The speciation of P in the top 5 cm of an acidic sandy grassland soil exposed to different fertilization regimes was studied in $NaOH\text{-}Na_2EDTA$ and water extracts with wet chemical analysis and ^{31}P NMR spectroscopy. After 11 yr of treatment with N-P-K or different animal manures, inorganic P was highly elevated in the $NaOH\text{-}Na_2EDTA$ extracts, while accumulation of organic P was found only in the soil amended with pig slurry. In contrast, inorganic P remained relatively constant in the control soil (no fertilizer), while removal of P from soil by cropping of grass in the N-treated soil decreased inorganic P.

In both soils, organic P remained relatively constant. Hence, in soils without P input, organic P becomes more important. In all soils, orthophosphate monoesters were the main organic P compounds. In the water extracts, the same trend was found: inorganic P was highly elevated in soils treated with N-P-K fertilizer or animal manures, while organic P showed only a small increase. Orthophosphate monoesters were the only organic P compounds detected in the water extracts. Long-term applications of large amounts of N-P-K or animal manures resulted mainly in an accumulation of inorganic P in the soils as measured in both the NaOH-Na_2EDTA and water extracts. Since water-extractable P is considered to represent potentially mobile P in soil, risk of P loss to water in the top 5 cm of these soils was mainly related to inorganic P.

Acknowledgements

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4

Selective extraction of labile phosphorus using dialysis membrane tubes filled with hydrous iron hydroxide

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Abstract

Leaching of phosphorus (P) can be a serious problem in P-enriched sandy soils. Techniques which decrease the P content of such soils have been proposed as possible remediation methods. In this study, we determined the effect of P removal from two P rich sandy soils on extractability of soil P in a laboratory experiment. We created soil samples in increasing stages of P depletion by using a sink method, which consists of a dialysis membrane tube filled with hydrous Fe-(hydr)oxide (DMT-HFO). Total amounts of P removed were relatively small compared with the high initial ammonium oxalate-extractable P contents. However, amounts of water- and $CaCl_2$-extractable P in the depleted soil samples decreased by 57 to 80%, on average, for both soils. On the other hand, the ammonium oxalate-based P saturation index decreased by only 11%. Apparently, labile P forms were readily removed, which means that depletion by the DMT-HFO was selective. Our results suggest that remediation methods that remove a small but selective amount of P from soil may cause a significant decrease of the soil potential to release dissolved P. We also used our results to evaluate the suitability of the DMT-HFO to act as an infinite sink for P. For that, the desorption results were described with a simple kinetic Langmuir equation. Errors of k_d (desorption constant) and Q_0 (amount of P initially adsorbed) were calculated. Although the model fit was good for both soils ($R^2 = 0.98^{***}$ and 0.99^{***}), errors in k_d and Q_0 were large. Therefore, the DMT-HFO method could not be used to determine the desorption constants of our soils. Values of k_d and Q_0 obtained by this method should not be used in modeling studies.

Introduction

In areas with intensive livestock farming, soils are often enriched with phosphorus (P) as a result of decades of P addition, via animal manure, exceeding P removal in harvested crops (Breeuwsma et al., 1995). In the Netherlands, intensive livestock farming takes place mainly on sandy soils in the east and south of the country. In these areas, soil extractable P, measured as Pw (water-extractable P with a soil to solution ratio of 1:60 [v/v]) (Sissingh, 1971), has increased to values 2 to 3 times greater than optimum crop demand (Neutel, 1994). Sandy soils are generally characterized by low sorption capacity, and, as a result, P can leach from topsoil to deeper layers, especially in flat areas with a high ground water level (Sims et al., 1998; Chardon and van Faassen, 1999). Surface runoff of P is most important in areas with steeper slopes (Heathwaite et al., 1999). Currently, P in the upper ground water exceeds the surface water limit of 0.15 mg total P L^{-1} in an estimated 70% of the sandy soils in the east and south of the Netherlands, an area of about 400 000 ha (Reijerink and Breeuwsma, 1992). Such soils are likely to contribute to P enrichment and eutrophication of surface waters caused by (subsurface) leaching. Therefore, remediation is required to prevent (further) P losses (Chardon et al., 1996b; Oenema and Roest, 1998).

Techniques that decrease the soil P content, such as phytoremediation, have been proposed as effective remediation methods (Chardon et al., 1996b; Steinhilber and Weismiller, 1999). Plant uptake and harvesting of the crop remove P from soil. If no replenishment of removed P takes place, the (readily) available P content decreases rapidly (Sharpley, 2000), although the content of the more stable P forms decreases only very slowly (McCollum, 1991). In addition to plant uptake, conversion of P to less labile forms can also take place (Barrow, 1980). Knowledge of the extent of decrease in P extractability from the soil is important because extractable P is related to the potential of a soil to release P to soil solution and runoff. In several studies, P in soil solution and runoff has been shown to be highly correlated to water-extractable P or to degree of soil P saturation (Sharpley, 1995; Pote et al., 1996; Chardon and van Faassen, 1999).

In our study, we determined the effect of P removal from two P rich sandy soils on extractability of P in a laboratory experiment. We created soil samples in increasing stages of P depletion using a recently developed sink method of Freese et al. (1995), which consists of a dialysis membrane tube (DMT) filled with hydrous Fe-(hydr)oxide (HFO). Sink methods have been used widely in P desorption studies (Chardon et al., 1996a). Ideally, the DMT-HFO acts as an infinite sink for P desorbed from soil and maintains a negligible P concentration in solution, facilitating continuous P desorption (Freese et al., 1995). In contrast to the more widely used FeO-impregnated filter paper (Pi-test) introduced by Sissingh (1983), the DMT-HFO can be separated from soil suspension without contamination of the sink. Adhering soil particles may cause FeO paper to overestimate P desorption (Uusitalo and Yli-Halla, 1999). Freese et al. (1995) and Lookman et al. (1995a) used the DMT-HFO method to study long-term P desorption from a large number of P rich sandy soils. In the latter study, a kinetic model was used to describe P desorption. The extractability of P from such artificially depleted soils has, however, not been characterized yet. The first objective of our study was to characterize P extractability from artificially P-depleted soil samples using water- and $CaCl_2$-based methods and the ammonium oxalate-based P saturation index (PSI). Water- and $CaCl_2$-extractable P represent the more labile P forms in soil, whereas stable P is included in ammonium oxalate- but not in water- and $CaCl_2$-extractable P. The second objective was to discuss whether the DMT-HFO acted as an infinite P sink in our desorption experiment using the method of van der Zee et al. (1987).

Materials and methods

Soils

Samples were taken from the plough layer (0-30 cm) of two sites in Haren and Wijster, the Netherlands. The Haren soils were taken from three treatments of a long-term field experiment (Del Castilho et al., 1993), denoted as Har 7, Har 9, and Har 11. A sample from an adjacent field was denoted as Har 1. Har 11 had received the largest addition of P; an amount of 160 Mg pig manure slurry ha^{-1} was applied annually during a period of 11 years. The Har 11 and Wijster soils were used in the depletion experiment because these soils are believed to be representative of many sandy soils treated with excessive amounts of P in the Netherlands. Soil samples were dried at 40°C, and sieved through a 2-mm sieve. Table 4.1 shows some selected physical and chemical characteristics of the soils studied. Particle size distribution, pH (KCl), organic matter (Houba et al., 1997), and total P (Houba et al., 1993) were determined using standard analytical procedures. Particle size distribution was determined by the pipette method after removal of organic matter and $CaCO_3$. The pH (KCl) was measured in a 1:5 (v/v) suspension of soil in a solution of 1 M KCl. Organic matter was estimated from loss-on-ignition. Total P was determined after soil digestion with Fleischmann acid (a 1:1 [v/v] mixture of concentrated HNO_3 and H_2SO_4).

Table 4.1. Selected physical and chemical characteristics of the soils (analytical means of P_{ox} ± sample sd).

Soils	Clay (0-2 µm)	Silt (2-50 µm)	Sand (50-2000 µm)	Texture class	pH (KCl)	Organic matter	P_{ox}	Total P
	%	%	%			%	mg P kg^{-1}	mg P kg^{-1}
Har 1	4.1	17.3	78.6	loamy sand	4.7	3.6	461 ± 5.1	593
Har 7	3.6	21.3	75.1	loamy sand	4.6	3.6	522 ± 5.4	614
Har 9	3.8	23.0	73.2	sandy loam	5.2	3.7	731 ± 4.2	917
Har 11	3.6	17.3	79.2	loamy sand	4.5	3.7	833 ± 9.8	978
Wijster	4.0	17.0	79.0	loamy sand	5.2	4.8	614 ± 3.7	734

Preparation of hydrous Fe-(hydr)oxide

The HFO suspension was prepared according to the method of Freese et al. (1995). One hundred grams of $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 1 L demineralized water, and titrated automatically (Metrohm 736 GP Titrino) up to pH 7.5 using 1 M NaOH. After 5 min, the solution was again titrated up to pH 7.5, which is close to the zero-point of charge (pH_0) of HFO, thus facilitating flocculation (Schwertmann and Cornell, 1991). The HFO suspension was centrifuged (10 min at 670 x g), followed by decantation and resuspension in demineralized water, in order to remove salts. This was repeated 5 to 7 times until an electrical conductivity (EC) of about 300 $\mu S\ cm^{-1}$ was reached. Below this EC value, further dispersion of HFO complicated washing of the suspension. The volume of the HFO suspension was adjusted to 2 L with demineralized water. Afterwards, 0.5 M HCl was added in drops to acidify the mixture to pH 5, which is comparable to the pH (KCl) of the soils studied. The HFO suspension was stored at 6°C during the P desorption experiment to retard conversion of amorphous HFO to more crystalline Fe-(hydr)oxide compounds (Schwertmann and Cornell, 1991).

Phosphorus depletion experiment

Dialysis membrane tubes (Visking, size 3, diameter 15.9 mm, approximate pore size 2.5 to 5.0 nm, membrane thickness 3 μm) of 20 cm length were boiled 2 times for 5 min each time in demineralized water, and thoroughly rinsed with demineralized water. The DMT was then filled with 20 mL HFO, and closed with a plastic clip on both ends. The HFO suspension was stirred vigorously during the filling. Fifteen g of soil were suspended in 125 mL 0.01 M $CaCl_2$ in a 200-mL glass jar. The DMT-HFO soil suspension mixture was gently shaken during 72, 120, 240, 480, or 960 h (110 oscillations per minute at 20°C, opm) (n = 4). During the incubation periods of 480 and 960 h, the DMT-HFO was replaced after 216 h and after 240, 456, and 672 h, respectively, to maintain a low P concentration in solution.

After removal from suspension, the DMT-HFO was rinsed with demineralized water to remove adhering soil particles. The HFO was dissolved in 0.2 M H_2SO_4 in order to measure P and Fe. Standard P calibration solutions were adjusted to the same background Fe and H_2SO_4 concentrations as in the samples. Iron was measured using Atomic Absorption Spectrometry. On average, a DMT contained 143.0 mg Fe (sample standard deviation = 6.1 mg Fe, sd). Soil samples were obtained by centrifugation (10 min at 670 x g) of the suspension followed by decantation and drying at 40°C and 2-mm sieving of the deposited soil. Afterwards, soils of the four replicates were mixed. After the incubation periods of 72 and 480 h, a sample was taken from the supernatant of the centrifuged suspension followed by filtration (0.45 μm), and P was measured colorimetrically (Murphy and Riley, 1962).

Standard phosphorus solution experiment

The effectiveness of the DMT-HFO for uptake of P from solution was studied by determination of the k_s value (Eq. [4.1]). A DMT-HFO was shaken with 125 mL of 5 mg P L^{-1} standard P solution (KH_2PO_4) in 0.01 M $CaCl_2$ (110 opm at 20°C). A sample was taken from solution after 0, 2, 4, 6, 8, 10, 24, 27, 30, 48, 52, 56, 72, and 96 h, and P was measured colorimetrically using the method of Murphy and Riley (1962). For comparison, the k_s value of FeO paper, which was prepared according to a slightly modified method of Sissingh (1983), was determined: filter papers were immersed in 0.37 M $FeCl_3$ solution for 5 min and neutralized in 2.7 M NH_4OH for 45 s. One FeO strip in a fixed position was shaken end-over-end with 40 mL of 5 mg P L^{-1} standard P solution in 0.01 M $CaCl_2$ (4 rotations per min at 20°C, rpm), and P was measured after 0, 2, 4, 6, 8, 24, and 48.5 h. Results were fitted to:

$$\ln C(t) = \ln C_0 - k_s \times t \qquad [4.1]$$

where C(t) is the P concentration in time (mg P L^{-1}), C_0 is the initial P concentration, k_s is a constant (h^{-1}), and t is time (h).

Langmuir adsorption isotherm

Two grams of soil were suspended in 40 mL 0.005 M $CaCl_2$ in a 100-mL glass jar and in 10 different initial P concentrations using KH_2PO_4, which ranged from 0 to 50 mg P L^{-1}. Suspensions were shaken at 4 rpm and 20°C. After 24 h, the solution was filtered through a dense paper filter, and P was measured according to Murphy and Riley (1962). The initial amount of P adsorbed to the unamended soil was estimated with FeO strip-extractable P measured according to a slightly modified method of Sissingh (1983): 1 g of soil was shaken with one FeO strip in a fixed position in 0.01 M $CaCl_2$ at 4 rpm and 20°C for 16 h. Adhering soil particles were removed using an air brush as recommended by Chardon et al. (1996a). Amounts of P adsorbed were calculated by:

$$Q = \frac{v \times \Delta C}{w} + Q_0 \qquad [4.2]$$

where Q is the amount of P adsorbed (mg P kg^{-1}), v is the volume of solution used (L), ΔC is the difference between the initial and the equilibrium P concentration (mg P L^{-1}), w is weight of soil used (kg), and Q_0 is the amount of P initially adsorbed (mg P kg^{-1}). Results were fitted to the Langmuir adsorption isotherm:

$$Q = \frac{Q_{max} \times K \times C}{1 + K \times C} \qquad [4.3]$$

where Q_{max} is the adsorption maximum (mg P kg^{-1}), K is a constant (L mg^{-1}), and C is the P concentration (mg P L^{-1}). The constant K gives an indication of the affinity of the soil for P adsorption.

Phosphorus extraction methods

The extractability of P from the depleted soil samples was characterized using four extraction methods denoted as P-1:2, P-$CaCl_2$, Pw, and P_{ox} ($n = 3$). A modification of the method of Sonneveld et al. (1990) was used to determine P-1:2. Water extracts (1:2 [w/v]) were shaken on a reciprocating shaker (130 strokes per minute, spm) for 1 h. After centrifugation (10 min at 1800 x g), supernatants were filtered (0.45 μm), and P was determined in the filtrates. Calcium chloride-extractable P (P-$CaCl_2$) was determined in 0.01 M $CaCl_2$ according to Houba et al. (1986). The $CaCl_2$ extracts were shaken on a reciprocating shaker at 165 spm. The Pw extraction method of Sissingh (1971) was used. Water extracts were shaken end-over-end at 30 rpm. In the P-1:2, P-$CaCl_2$, and Pw extracts, P was measured colorimetrically (Murphy and Riley, 1962). Amounts of ammonium oxalate-extractable P, Al, and Fe were determined by the method of Schwertmann (1964). Extracts were shaken on a reciprocating shaker at 165 spm. Phosphorus, Al, and Fe were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The PSI was calculated according to:

$$PSI = \frac{P_{ox}}{[Al + Fe]_{ox}} \qquad [4.4]$$

where P_{ox} and $[Al+Fe]_{ox}$ are the amounts of ammonium oxalate-extractable P, Al, and Fe (mmol kg^{-1}).

Evaluation of DMT-HFO method

The evaluation of the DMT-HFO was done according to van der Zee et al. (1987). In acidic sandy soils, adsorption or desorption of P can be described by the kinetic Langmuir equation:

$$\frac{dQ}{dt} = k_a \times C \times (Q_{max} - Q) - k_d \times Q \tag*{[4.5]}$$

where k_a is an adsorption constant (L mg^{-1} h^{-1}), and k_d is a desorption constant (h^{-1}). At equilibrium ($dQ/dt = 0$), Eq. [4.5] reduces to the Langmuir isotherm where $K = k_a/k_d$ (Eq. [4.3]). In the presence of a DMT-HFO, P desorbs from soil to solution, and after transport over the dialysis membrane, P adsorbs to HFO. In case of infinite sink conditions, the P concentration in solution is negligible, and the backward adsorption reaction can be neglected. Under the condition $C \approx 0$ mg P L^{-1} at $t > 0$ h, Eq. [4.5] becomes:

$$\frac{dQ}{dt} = -k_d \times Q \tag*{[4.6]}$$

Integration of Eq. [4.6] gives:

$$Q(t) = Q_0 \times \exp(-k_d \times t) \tag*{[4.7]}$$

where Q(t) is the amount of P adsorbed in time (mg P kg^{-1}). Substitution of $Q(t) = Q_0 - Q\S(t)$ in Eq. [4.7] gives:

$$Q\S(t) = Q_0 \times [1 - \exp(-k_d \times t)] \tag*{[4.8]}$$

where $Q\S(t)$ is the amount of P desorbed in time (mg P kg^{-1}). In case the sink does not act as an infinite sink, desorbed P builds up in solution, which results in backward adsorption. Thus, desorption of P is limited causing bias in estimates of Q_0 and k_d. Van der Zee et al. (1987) incubated P rich sandy soils with four FeO strips. Since the buildup of a P concentration during their experiment was negligible (<0.02 mg P L^{-1}), errors in estimated Q_0 and k_d values were within experimental error. Apparently, the sink applied maintained infinite sink conditions. We estimated Q_0 and k_d in our experiment by fitting the desorption results to Eq. [4.8]. The error in Q_0 was obtained by inserting a constant P concentration during the P depletion experiment in the Langmuir isotherm (Eq. [4.3]). The error in k_d was calculated by (van der Zee et al., 1987):

$$\text{error } k_d = k_a \times C \qquad [4.9]$$

where C is a constant P concentration (mg P L^{-1}).

Results and discussion

Phosphorus desorption

Application of the DMT-HFO method removed relatively small amounts of P from either soil compared to the large amounts of P_{ox} initially present. Desorption of P was greatest in the Har 11 soil (Fig. 4.1). After 960 h, 13% of P_{ox} in the Har 11 soil, and 9% in the Wijster soil, was desorbed. These values are similar to the results found in a study after incubation of two P rich sandy soils with a DMT-HFO during periods of 648 and 840 h (C.L. van Beek, 2000, personal communication). Desorption of P in our experiment had not reached a maximum yet after 960 h. This is in agreement with results of Lookman et al. (1995a), who also used the DMT-HFO method; P desorption continued up to 1600 h, and equalled 15 to 70% of P_{ox}. Desorption depends on the degree of soil P saturation as the adsorption strength decreases with an increase in the level of P accumulation in soil (Ryden and Syers, 1977; Hooda et al., 2000). The PSI of the Har 11 soil was highest (Table 4.2). In addition to degree of P saturation, desorption depends also on the affinity of a soil for P adsorption. The affinity of the Har 11 soil, as indicated by the K value of the Langmuir isotherm (Eq. [4.3]), was lower than the affinity of the Wijster soil (Table 4.3). These findings are in agreement with the observation that P desorption was greatest in the Har 11 soil.

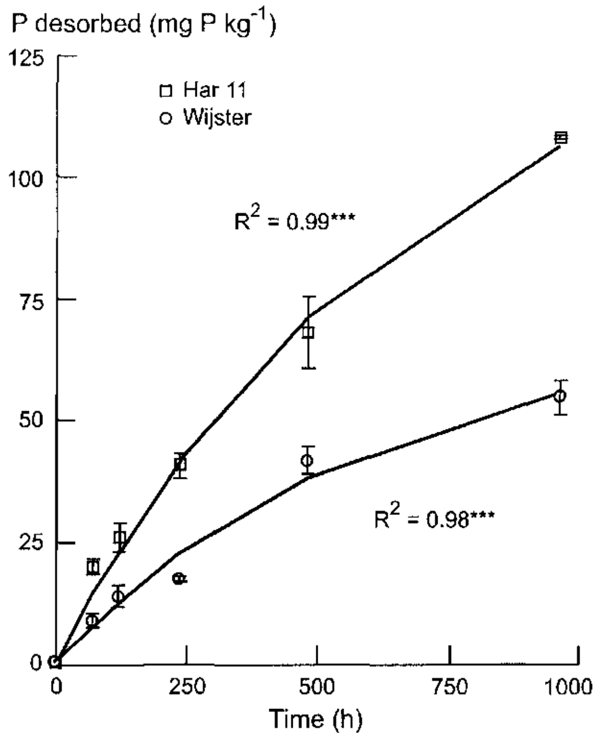

Figure 4.1. Experimental and modeled P desorption results of Har 11 and Wijster soils (average values with sample sd; the symbol *** indicates significance at the 0.001 level).

Table 4.2. Amounts of P extracted from depleted Har 11 and Wijster soil samples using four extraction methods (analytical means with sample sd), and P concentrations in suspension (average values ± sample sd).

Incubation periods	Har 11					Wijster				
	P-1:2	P-$CaCl_2$	Pw	PSI†	P concentration	P-1:2	P-$CaCl_2$	Pw	PSI	P concentration
h	mg P kg^{-1}	mg P kg^{-1}	mg P kg^{-1}		mg P L^{-1}	mg P kg^{-1}	mg P kg^{-1}	mg P kg^{-1}		mg P L^{-1}
0	7.40 ± 0.03	8.9 ± 0.09	33.9 ± 0.1	0.42 ± 0.002	nd‡	2.46 ± 0.02	3.2 ± 0.12	22.3 ± 1.1	0.22 ± 0.001	nd
72	2.61 ± 0.10	5.5 ± 0.06	22.0 ± 0.8	0.40 ± 0.010	0.45 ± 0.02	0.99 ± 0.05	2.4 ± 0.07	16.8 ± 0.6	0.22 ± 0.005	0.23 ± 0.02
120	2.31 ± 0.02	5.1 ± 0.03	21.2 ± 0.2	0.41 ± 0.003	nd	0.93 ± 0.09	2.3 ± 0.07	18.5 ± 0.2	0.22 ± 0.001	nd
240	1.59 ± 0.01	4.1 ± 0.07	18.7 ± 0.2	0.41 ± 0.005	nd	0.81 ± 0.02	2.1 ± 0.12	15.8 ± 0.6	0.22 ± 0.004	nd
480	1.64 ± 0.06	3.5 ± 0.01	17.2 ± 0.5	0.39 ± 0.009	0.32 ± 0.13	0.72 ± 0.03	1.6 ± 0.15	13.7 ± 0.3	0.21 ± 0.003	0.10 ± 0.01
960	1.27 ± 0.03	2.3 ± 0.08	13.0 ± 0.5	0.38 ± 0.005	nd	0.58 ± 0.04	1.1 ± 0.01	10.8 ± 0.6	0.19 ± 0.003	nd

†PSI calculated as $P_{ox}/[Al+Fe]_{ox}$ (Eq. [4.4]).
‡Not determined.

Table 4.3. Estimated constants of the Langmuir adsorption isotherm (Q_{max} and K) (Eq. [4.3]) and of Eq. [4.8] (Q_0 and k_d) ± se of the constants, and the calculated errors in Q_0 (Eq. [4.3]) and k_d (Eq. [4.9]) in Har 11 and Wijster soils.

Soils	Q_{max}	K	Q_0	Error Q_0	k_d	Error k_d
	mg P kg^{-1}	L mg^{-1}	mg P kg^{-1}	mg P kg^{-1}	h^{-1}	h^{-1}
Har 11	274 ± 12	0.22 ± 0.030	141 ± 15	18	0.0015 ± 0.0003	0.014
Wijster	469 ± 27	0.32 ± 0.058	71 ± 11	15	0.0016 ± 0.0004	0.006

Characterization of phosphorus extractability

Soil P depletion obtained by the DMT-HFO method resulted in a large decrease of water- and $CaCl_2$-extractable P in both soils. The decrease of water- and $CaCl_2$-extractable P was largest in the depleted Har 11 soil samples because of the larger amount of P desorbed (Table 4.2 and Fig. 4.1). On average, after 960 h, P-1:2 decreased by 83% in the Har 11 soil compared with 76% in the Wijster soil, whereas P-$CaCl_2$ and Pw decreased by 75% and 62%, respectively, in the Har 11 soil and by 67% and 52%, respectively, in the Wijster soil. The PSI, on the other hand, decreased only by 9% in the Har 11 soil and by 12% in the Wijster soil. This suggests that the more labile P forms, which are represented by water- and $CaCl_2$-extractable P, are readily removed. The more stable P, which is included in P_{ox} but not in water- and $CaCl_2$-extractable P, and which is the largest part of P in soil, is removed to a lesser extent. Therefore, the PSI decreased little. These observations give an explanation, in part, of the rapid decrease of soil test P values or crop yield when P applications are withheld for some years. Such observations have provided the justification for farmers to continue to apply excessive amounts of animal manure.

P-1:2 against Pw and PSI

Due to P depletion by the DMT-HFO method, water-extractable P (P-1:2 and Pw) showed a large decrease. Figure 4.2 shows the results of P-1:2 plotted against the results of Pw in the depleted and undepleted Haren soils. Results could be well described by a single nonlinear relationship (R^2 = 0.99***). Such a nonlinear relationship can be encountered when two methods, which extract different fractions of the total amount of desorbable P, are compared over a range of soils in increasing stages of P accumulation. The nonlinearity of this relationship is attributable to the nonlinear character of P adsorption isotherms (van der Zee et al., 1987).

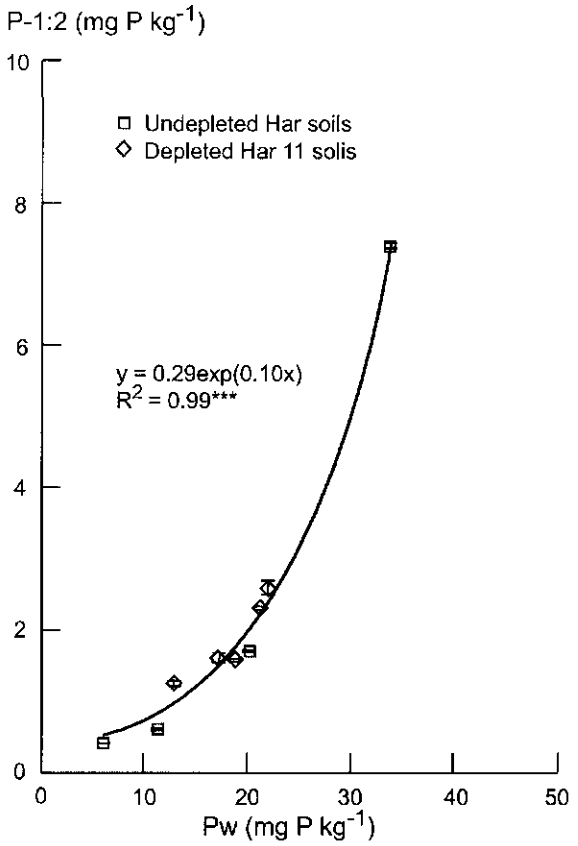

Figure 4.2. P-1:2 plotted against Pw in the undepleted Har 1, Har 7, Har 9, Har 11, and the depleted Har 11 soil samples (analytical means, sample sd of P-1:2 falls within symbols; the symbol *** indicates significance at the 0.001 level).

Soils have a finite capacity for P sorption. As the degree of P saturation of soil increases, as a result of accumulation of P in soil, the P concentration in soil solution increases nonlinearly. Hence, we expected to find nonlinear relationships between water-extractable P and the PSI. In Fig. 4.3, P-1:2 is plotted against PSI. Indeed, results of the four undepleted Har 1, 7, 9, and 11 soils could be well described by a nonlinear relationship (R^2 = 1.00***). However, after depletion by the DMT-HFO method, results of the depleted Har 11 soil samples fall below the relationship. Results of PSI plotted against Pw gave the same pattern (not shown). Thus, P depletion was indeed selective. In some studies, the P saturation degree has been proposed as an indicator for the potential of a soil to release P to the environment, because relationships with water-soluble P and P in runoff were highly correlated (Sharpley, 1995; Pote et al., 1996; Sims, 1998). Our results suggest that for our artificially P-depleted soils, the ammonium oxalate-based PSI may not be a good indicator for soluble P because it overestimates water-extractable P (Fig. 4.3). Other methods to determine a P saturation degree, for example, by calculating FeO strip-extractable P as a percentage of the P sorption maximum of the Langmuir isotherm (Sharpley, 1996), may give better results in P-depleted soils. It has to be investigated whether our observations hold for P-enriched soils which are depleted by plant uptake. The trend, as observed in Fig. 4.3, was also found in the results of a pot experiment in which a sandy soil, enriched with P in the past, was depleted by cropping grass at zero P application in a greenhouse (Koopmans et al., 2000).

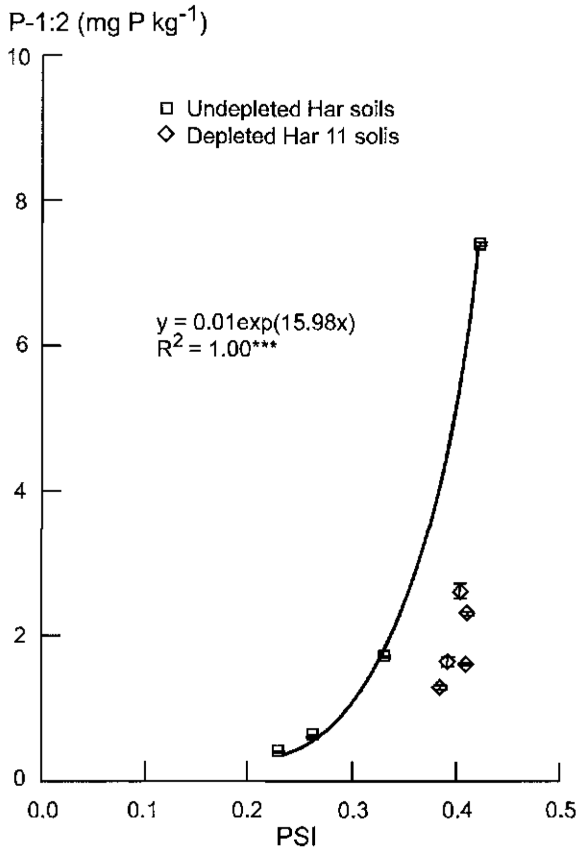

Figure 4.3. P-1:2 plotted against PSI in the undepleted Har 1, Har 7, Har 9, Har 11, and the depleted Har 11 soil samples (analytical means, sample sd of P-1:2 falls within symbols; the symbol *** indicates significance at the 0.001 level).

In summary, although total amounts of P removed from soil were relatively small, amounts of water- and $CaCl_2$-extractable P showed a large decrease. Hence, techniques such as phytoremediation, which remove labile P selectively, may result in a rapid decrease of water- and $CaCl_2$-extractable P. Strong indications for this were found in a phytoremediation experiment in which Koopmans et al. (2000) depleted a P rich soil by plant uptake. Water-extractable P is related to the potential of a soil to release soluble P to the environment (Pote et al., 1996; Chardon and van Faassen, 1999). Therefore, selective P extraction from soil may contribute to a rapid decrease in soil potential to release dissolved P. However, loss of particulate P to the environment may remain high because P_{ox} decreases much slower.

Evaluation of DMT-HFO method

We used Eq. [4.8] to model the P desorption results of both soils (Fig. 4.1). The fit of the desorption results was good (R^2 = 0.99*** of the Har 11 soil, and R^2 = 0.98*** of the Wijster soil). Table 4.3 shows the estimated values of Q_0 and k_d. The k_d values are much lower than those obtained by van der Zee et al. (1987) for sandy soils: they found an average k_d value of 0.2 h^{-1} (sample sd = 0.08 h^{-1}). Since soils had comparable characteristics, we expected to find similar k_d values. In addition to the low k_d values, P concentrations measured after 72 h and 480 h were well above zero, despite the presence of a sink (Table 4.2). The buildup of desorbed P in solution can lead to bias of estimated desorption constants. Errors in Q_0 and k_d were calculated assuming a constant P concentration during the desorption experiment, as measured after 480 h. This seems reasonable since P concentrations after 480 h were only slightly less than those after 72 h, although P concentrations must have been higher in the beginning of the experiment when desorption rates were highest. Errors in Q_0 in the Har 11 and Wijster soils were about 13% and 20% of Q_0, respectively, as calculated from the Langmuir isotherm (Eq. [4.3]) (Table 4.3). Errors in k_d were about 10 times the k_d value in the Har 11 soil, and about 4 times the k_d value in the Wijster soil (Eq. [4.9]). Values of k_a were calculated from $K = k_a/k_d$ using the average k_d value of van der Zee et al. (1987) and the K values as found in our study (Table 4.3).

A low effectiveness of the DMT-HFO for uptake of desorbed P from solution leads to the buildup of P in solution, and, therefore, might explain the observed high P concentrations and subsequent low k_d values in our experiment. Therefore, we determined the k_s value of the DMT-HFO, and compared it with results of Freese et al. (1995) and FeO paper. Figure 4.4 shows the decrease of the P concentration of a standard P solution, incubated with a DMT-HFO or an FeO strip, in time. The k_s value of the DMT-HFO was 0.06 ± 0.001 h^{-1} (± standard error, se), and corresponds well with results of Freese et al. (1995). We estimated a k_s value of 0.09 h^{-1} from their results. However, the k_s value of FeO paper was much higher: 0.54 ± 0.100 h^{-1}. After 6 h, the rate of the P concentration decrease became lower. With FeO paper the P removed from solution involves a fast reaction: adsorption on surface sites and a slow reaction ascribed to diffusion into FeO followed by sorption.

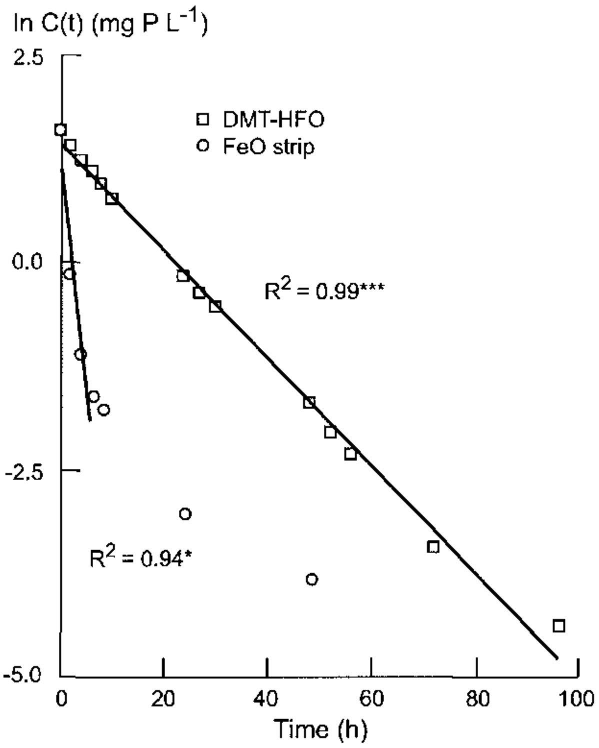

Figure 4.4. Phosphorus concentration decrease in a standard P solution (5 mg P L^{-1} and 0.01 M $CaCl_2$) incubated with a DMT-HFO or an FeO strip (the symbols * and *** indicate significance at the 0.05 and 0.001 levels, respectively).

In summary, since the DMT-HFO functioned as a sink for P, we succeeded in decreasing amounts of water- and $CaCl_2$-extractable P in our artificially depleted soil samples. However, due to a low k_s value, the DMT-HFO method did not act as an infinite sink for P. Thus, the DMT-HFO method should not be applied for determination of desorption constants for use in modeling studies describing P desorption, as done in Lookman et al. (1995a). We are currently working on an improved FeO strip method to use in P desorption studies.

Conclusions

The DMT-HFO method was used to create soil samples in various stages of P depletion. The selective depletion of the more labile P forms caused a large decrease of water- and $CaCl_2$-extractable P, although total amounts of P removed were relatively small compared with the large amounts of P_{ox} present initially. The PSI decreased little. Water- and $CaCl_2$-extractable P, representing the more labile P forms, are related to the potential of a soil to release P to the environment. Therefore, our results suggest that the environmental risk of P rich soils may decrease significantly when relatively small, but selective, amounts of P are extracted. Our evaluation of the suitability of the DMT-HFO method to act as an infinite P sink showed that this method caused large errors in the estimated Q_0 and k_d values as a result of the buildup of desorbed P in solution. Estimates of the desorption constants Q_0 and k_d obtained by the DMT-HFO should, therefore, not be used in modeling studies.

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Appendix

List of symbols

C	P concentration in solution (mg P L^{-1})
C_0	initial P concentration (mg P L^{-1})
$C(t)$	P concentration in time (mg P L^{-1})
ΔC	difference between initial and equilibrium P concentration (mg P L^{-1})
k_a	adsorption constant (L mg^{-1} h^{-1})
k_d	desorption constant (h^{-1})
k_s	constant P sink method (h^{-1})
K	constant Langmuir adsorption isotherm (L mg^{-1})
Q	amount of P adsorbed (mg P kg^{-1})
Q_0	amount of P initially adsorbed (mg P kg^{-1})
Q_{max}	P adsorption maximum (mg P kg^{-1})
$Q(t)$	amount of P adsorbed in time (mg P kg^{-1})
Q§(t)	amount of P desorbed in time (mg P kg^{-1})
t	time (h)
v	volume of solution (L)
w	weight of soil (kg)

5

Phosphorus availability for plant uptake in a phosphorus-enriched noncalcareous sandy soil

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Abstract

Mining soil phosphorus (P) (i.e., harvesting P taken up from the soil by a crop grown without external P addition) has been proposed as a possible management strategy for P-enriched soils to decrease the risk of P leaching. We performed a pot experiment in a greenhouse where grass was cropped on a P-enriched noncalcareous sandy soil at zero P application over a period of 978 d. We determined the long-term availability of soil P and evaluated the effectiveness of mining soil P to decrease P in different pools. There were two treatments: soil layers in the pots of either 5 or 10 cm thickness. Soils were analyzed at various stages of the experiment. Phosphorus in soil solution and the total pool of sorbed P were estimated using 1:10 (w/v) 0.01 M $CaCl_2$ extracts and acid ammonium oxalate (P_{ox}), respectively. A desorption isotherm was constructed, which described the relationship between P in soil solution and the total pool of sorbed P for the soils of the 5- and 10-cm treatments. The Langmuir equation gave a very good description of the isotherm. In the long-term, 65% of P_{ox} in the initial soil can be removed by plant uptake, as was calculated from the Langmuir equation and a critical P concentration in soil solution at which P uptake can just be maintained. Thus, P_{ox} may be largely plant available. From the strong nonlinearity of the desorption isotherm, it can be understood why the relative decrease of the P concentration in the $CaCl_2$ extracts was much larger than the relative decrease of P_{ox}. Mining soil P decreased the P concentration in soil solution effectively and, therefore, risk of P leaching from our P-enriched soil.

Introduction

In areas with intensive livestock farming, the soil phosphorus (P) content of arable land has increased considerably, mainly due to decades of animal manure application at rates that exceeded the rate necessary to maintain an optimal soil fertility for crop production (e.g., Pautler and Sims, 2000). In the Netherlands, intensive livestock farming is mainly located on noncalcareous sandy soils in the middle, east, and south of the country (Breeuwsma et al., 1995). In general, the sorption capacity of these soils for P is limited, and as a result, P can be transported to ground water through leaching, especially in flat areas with a high ground water level (Schoumans and Groenendijk, 2000). Currently, the P concentration in the upper ground water is likely to exceed the surface water limit of 0.15 mg total P L^{-1} in an estimated 70% of the noncalcareous sandy soils in the middle, east, and south of the Netherlands, an area of about 400 000 ha (Reijerink and Breeuwsma, 1992). These soils have the potential to contribute to P enrichment of surface waters through subsurface leaching. The enrichment of surface waters with P may lead to eutrophication and its associated adverse effects (Sharpley et al., 1994). To decrease the risk of P leaching, mining soil P, that is, harvesting P taken up from the soil by a crop grown without external P addition followed by the off-site removal of the above ground plant parts, has been proposed as a possible management strategy for P-enriched soils (e.g., van der Zee et al., 1992; Chardon et al., 1996b). However, quantitative information is scarce on the long-term change in soil P in P-enriched soils after P application has stopped. In previous studies of Delgado and Torrent (1997), Guo and Yost (1999), and Yli-Halla et al. (2002), pot experiments, where soil P was mined by plant uptake, were done over a relatively short period. Furthermore, in a long-term field experiment of McCollum (1991) and those summarized by Sharpley (2000), where soil P was also mined, the change in soil P was mainly characterized with relatively strong extraction methods and only one extraction method per study.

In noncalcareous sandy soils, amorphous Al- and Fe-(hydr)oxides are the main reactive solid phases (Beek, 1979). The overall reaction of inorganic P with Al- and Fe-(hydr)oxides is the result of a fast reversible adsorption reaction at surface sites (e.g., <1 d) and a slow one, that is, diffusion through the solid phase or through micropores of Al- and Fe-(hydr)oxides possibly followed by precipitation and/or adsorption inside the aggregates (van Riemsdijk and Lyklema, 1980a, 1980b; van Riemsdijk and de Haan, 1981; Barrow, 1983; van Riemsdijk et al., 1984a, 1984b; Bolan et al., 1985; Madrid and De Arambarri, 1985; Willett et al., 1988). The fast reaction has been described as a ligand exchange reaction between phosphate anions and OH^- or H_2O groups at the surface of Al- and Fe-(hydr)oxides (Breeuwsma, 1973; van Riemsdijk and Lyklema, 1980a). Filter paper strips impregnated with iron oxide have been proposed to determine the amount of reversibly adsorbed P (FeO-P) (van der Zee et al., 1987). The slow reaction of P has been described as a slow diffusion process through the solid phase to the zone where a fast precipitation reaction occurs: the conversion of Al- or Fe-(hydr)oxides to Al- or Fe-P precipitates (van Riemsdijk and Lyklema, 1980a, 1980b; van Riemsdijk and de Haan, 1981; van Riemsdijk et al., 1984a, 1984b), leading to a shrinking core of unreacted parts (van der Zee and van Riemsdijk, 1991). In contrast, in studies of Madrid and De Arambarri (1985) and Willett et al. (1988), the slow reaction was described as a slow diffusion through the micropores of aggregates of (hydr)oxides followed by fast adsorption inside the aggregates. Nevertheless, all studies agree on (reactive) diffusion as transport for P into the aggregates as the rate-limiting step in the slow reaction. The total pool of sorbed P (F) in noncalcareous sandy soils has been interpreted to be the sum of reversibly adsorbed P (Q) and quasi-irreversibly bound P (S), that is, F = Q + S (van der Zee et al., 1987; van der Zee and van Riemsdijk, 1988; Schoumans and Groenendijk, 2000). The acid ammonium oxalate extraction method of Schwertmann (1964) has been used to determine both the total pool of sorbed P (P_{ox}), which may be equated to F, as well as the sum of amorphous Al- and Fe-(hydr)oxides ($[Al+Fe]_{ox}$), which determine the total sorption capacity of inorganic P in noncalcareous sandy soils (Beek, 1979; van der Zee and van Riemsdijk, 1988).

The reversibility of the overall reaction of P with the solid phase is of agricultural interest, because of the need to maintain an optimal soil fertility for crop production. It is also of increasing environmental interest, because of its consequences in terms of the enrichment of ground water and surface waters with P resulting from leaching of soil solution. Upon the removal of P from soil solution, a fast initial desorption reaction for P adsorbed to surface sites of Al- and Fe-(hydr)oxides is expected (van der Zee et al., 1987). Desorption of P bound inside Al- and Fe-(hydr)oxides followed by diffusion to the outer layers of the aggregates may counteract the decrease of reversibly adsorbed P (Barrow, 1983). Because diffusion is slow, quasi-irreversibly bound P becomes available again only in the long-term, which may result in apparent hysteresis of P sorption and desorption (Ryden and Syers, 1977). In the short-term (e.g., within a growing season), desorption of P bound by the slow reaction has been considered as irrelevant (van Noordwijk et al., 1990). The term P fixation has been used to indicate P sorption, which sometimes is treated as an irreversible sorption reaction (Schoumans and Groenendijk, 2000).

Quantitative information about the reversibility of the overall reaction of P in P-enriched soils and its consequences for the total amount of P available for plant uptake and leaching in the long-term is scarce. Theoretically, all sorbed P in soil is desorbable (Lookman et al., 1995a). However, the rate of desorption of P and the equilibrium relationship between the P concentration in soil solution and P sorbed to the solid phase are difficult to determine experimentally, due to the relatively slow desorption kinetics and other more practical problems (e.g., van der Zee et al., 1987; Freese et al., 1995). Removal of P from the soil-solution system over a short time may cause a fast decrease of P in soil solution and of reversibly adsorbed P. This may, in term, result in a disequilibrium with P bound inside Al- and Fe-(hydr)oxides, because of its slow desorption kinetics. On the other hand, a slow removal of the same amount of P over a much longer time may be in equilibrium with the rate of desorption of P bound by the slow reaction. As yet, it is unknown to what extent plant uptake of P from P-enriched soil may be considered as an equilibrium desorption reaction. A desorption isotherm, describing the long-term equilibrium relationship between P in soil solution and the total pool of sorbed P, can in principle be used to estimate the total amount of P available for plant uptake and leaching. To test this hypothesis, one needs to establish the equilibrium relationship between P in soil solution and the total pool of sorbed P.

We performed a pot experiment in a greenhouse where grass was cropped on a P-enriched noncalcareous sandy soil at zero P application over a relatively long period (978 d). Our first objective was to determine the availability of P sorbed to Al- and Fe-(hydr)oxides for plant uptake in the long-term. Our second objective was to study P-depleted soil samples and the effectiveness of mining soil P to decrease P in different pools. Soil was sampled from a plot of a long-term field experiment that had been treated with large amounts of animal manure previously (Del Castilho et al., 1993). On this plot, the reaction time of the applied P varied from years to decades. Thus, the slow sorption reaction may have reached equilibrium. To determine whether plant uptake of P caused a disequilibrium between P in soil solution and reversibly adsorbed P on the one hand and P bound by the slow reaction on the other, we applied two treatments: soil placed in a pot in a layer of either 5 or 10 cm thickness. We expected a faster decrease of the P content in the soils of the 5-cm treatment due to an initially higher plant uptake of P in terms of amount of P harvested per unit of weight of soil. At various stages of the pot experiment, soil samples were analyzed. An estimate of the P activity in soil solution can be obtained by performing an extraction with water (Sonneveld et al., 1990) or 0.01 M $CaCl_2$ solution (McDowell and Sharpley, 2001). In our pot experiment, the P concentration in soil solution was estimated using both 1:2 (w/v) water and 1:10 (w/v) 0.01 M $CaCl_2$ extracts. Furthermore, reversibly adsorbed P and the total pool of sorbed P were estimated. In the Netherlands, water-extractable P (Pw) and P extractable with acetic acid and ammonium lactate (P-AL) are used in agricultural practice as soil tests in P fertilizer recommendation systems of arable land and grassland, respectively. To place our pot experiment in a more practical context, we also determined the change in soil P using Pw and P-AL.

Materials and methods

Soil

Soil was sampled in 1997 from the tillage layer (0-30 cm) of a noncalcareous loamy sandy soil (mesic Typic Haplorthod) of a plot from a long-term field experiment (see Del Castilho et al. [1993]). The soil sampled is believed to be representative of many noncalcareous sandy soils treated with large amounts of animal manure. Between 1971 and 1982, the soil was treated with 160 Mg of pig slurry ha^{-1} yr^{-1} (a mixture of feces, urine, and cleaning water). Between 1982 and 1987, inorganic P fertilizer was applied in a dosage equivalent to 40 Mg of pig slurry ha^{-1} yr^{-1}. From 1987 onward, the soil received variable mixtures of cattle slurry and inorganic P fertilizer (superphosphate). The soil was subjected to conventional Dutch agricultural practice: a crop rotation of forage maize (*Zea mays* L.), potato (*Solanum tuberosum* L.), wheat (*Triticum aestivum* L.), sugar beet (*Beta vulgaris* L.), and barley (*Hordeum vulgare* L.). After sampling, soil was dried at 40°C and passed through a 2-mm sieve. Before placement of soil in the pots, soil was homogenized.

Pot experiment

The pot experiment was performed in a greenhouse. The temperature was controlled and ranged from 12 to 14°C at night and from 19 to 21°C during daytime. In the winter, a 12-h day was provided through the use of artificial light to supplement natural light. Relative humidity was maintained at 75%. There were two treatments: in a pot with a volume of 2.5 L, soil was placed in a layer of either 5 or 10 cm thickness representing 1.65 or 2.85 kg of soil, respectively. The soil surface was 254 cm^2. Before placement of the soil, quartzitic sand, pretreated with acid to remove P, was placed in a layer of either 9 or 4 cm thickness. During the placement of soil in the pots, the lower 3 and 8 cm of the 5 and 10 cm soil layers were fertilized with 62.5 mg N equally divided between NH_4NO_3 and $Ca(NO_3)_2{\cdot}4H_2O$, 50 mg K as K_2SO_4, 75 mg Mg as $MgSO_4{\cdot}7H_2O$, 4.5 mg Cu as $CuSO_4{\cdot}5H_2O$, and 0.5 mg B as $Na_2B_4O_7{\cdot}10H_2O$. For each treatment, 16 pots were sown with a 1:1 seed mixture of average- and late-stalking perennial ryegrass (*Lolium perenne* L.). The grass was topped after germination; this day was taken as the start of the pot experiment. Approximately 7 d after topping, soil of each pot received the same fertilization as previously applied during the placement of soil in the pots. Supplemental fertilization was applied after approximately 200 d consisting of 150 mg Mg, 1.5 mg Zn as $ZnSO_4{\cdot}7H_2O$, 4 mg Fe as FeEDTA, 4 mg Mo as $Na_2MoO_4{\cdot}2H_2O$, and Mn as a 1% (w/v) $MnSO_4{\cdot}4H_2O$ solution as a spray. After 589 and 699 d, 140 mg N, 390 mg K, 150 mg Mg, 10 mg Cu, 1 mg B, 1.5 mg Zn, 4 mg Fe as FeEDDHA, 4 mg Mo, and 10 mg Mn as either $MnSO_4{\cdot}H_2O$ or MnDTPA were applied. Furthermore, 100 mg Mg was applied after 236 and 319 d. To prevent N and K limitation of plant growth, N and K were applied after each harvest in addition to the supplemental fertilization: after the first harvest, soil of each pot was fertilized with 200 mg N and 175 mg K, after the second harvest, 240 mg N and 200 mg K, from the third harvest onward 150 mg N and 150 mg K, after the ninth harvest, 430 mg N and 430 mg K, and from the tenth harvest onward, 360 mg N and 360 mg K. Pots were watered on top of the pot with demineralized water two times per week to 80 to 100% of the maximum soil water holding capacity. Once a week, water was given on the plate. Grass was harvested 31 times, at an interval of 19 to 47 d by cutting the grass manually at approximately 2 to 3 cm above the soil surface. Weight of the grass was determined after drying at 70°C. At various stages of the pot experiment, soil of 2 pots per treatment (duplicate pots) was destructively sampled (22, 41, 88, 151, 236, 319, 692, and 978 d, further denoted as t1 up to and including t8). Soil was dried at 40°C and passed through a 2-mm sieve. The initial soil, denoted as t0, was sampled before placement of the soil in the pots. Solely after the pot experiment had stopped (t8), roots were sampled and cleaned manually. Moist soils of the 5- and 10-cm treatments, which were sampled after the pot experiment had stopped (t8), were incubated in closed plastic bags in the dark at 20°C. Soil moisture content was maintained at 20%. Soil was sampled after 968 d of incubation (denoted as t9), dried at 40°C and passed through a 2-mm sieve.

Plant analyses

For each pot, grass samples harvested between two subsequent samplings of the soil were mixed, ground, and homogenized. The N and P contents were determined according to Temminghoff et al. (2000). The dry weight of the mixed grass samples was determined at 105°C. The dry matter production and N and P contents were expressed as g dry matter dried at 105°C and g P or g N kg^{-1} of dry matter dried at 105°C, respectively.

Soil analyses

The pH and organic matter content were determined according to Houba et al. (1997). The pH was measured in a settling 1:5 (w/v) suspension of soil in demineralized water and organic matter was estimated from loss-on-ignition. Organic P was calculated as the difference between total inorganic P measured after combustion of organic matter in a muffle furnace (550°C) and subsequent digestion of soil with 0.5 M H_2SO_4, and inorganic P measured after digestion of soil with 0.5 M H_2SO_4 (Kuo, 1996). Total P was measured after soil digestion with Fleischmann acid (a 1:1 [v/v] mixture of concentrated HNO_3 and H_2SO_4) (Houba et al., 1993). Phosphorus in soil solution was estimated using both 1:2 (w/v) water extracts and 1:10 (w/v) 0.01 M $CaCl_2$ extracts (Houba et al., 1986; reciprocative shaking at 165 strokes per min [spm]). For the 1:2 (w/v) water extracts, a modified method of Sonneveld et al. (1990) was used. The water-based soil suspensions were shaken on a reciprocating shaker at 130 spm for 1 h. After centrifugation (10 min at 1800 x g), supernatants were filtered (0.45 μm) and P was measured in the filtrates. The elemental composition of the soil solution of the initial soil and the soils sampled at t4 and t8 was estimated using 1:2 (w/v) water extracts. For this purpose, the soil of only one of the duplicate pots was used. The water extracts were shaken reciprocatively at 75 spm for 24 h. After filtration (0.45 μm), concentrations of Al, Ca, Cu, Fe, K, Mg, Mn, Na, P, and S were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Concentrations of NH_4^+ and NO_3^- were measured colorimetrically (Houba et al., 1997). Reversibly adsorbed P was estimated using a modified method of van der Zee et al. (1987). Filter papers were immersed in a 0.37 M $FeCl_3$ solution for 5 min and neutralized in 2.7 M NH_4OH for 45 s. One FeO strip in a fixed position was shaken end-over-end with 1 g of soil in 40 mL 0.01 M $CaCl_2$ at 4 rotations per min (rpm) for 16 h. Adhering soil particles were removed from the FeO strip using an airbrush as recommended by Chardon et al. (1996a). The FeO with adsorbed P was dissolved by shaking the FeO strip end-over-end at 30 rpm in 0.1 M H_2SO_4 and P was measured in the extracts. The total pool of sorbed P was estimated using the acid ammonium oxalate extraction method of Schwertmann (1964). Concentrations of P, Al, and Fe were measured using ICP-AES. The Pw (water-extractable P at a soil to solution ratio of 1:60 [v/v]) (Sissingh, 1971) and P-AL (Egnér et al., 1960) extraction methods were used to determine the agronomic P status of the soils for arable crops and grassland. In all extracts except the acid ammonium oxalate and the 1:2 (w/v) water extracts used to estimate the elemental composition of soil solution, P was measured colorimetrically according to Murphy and Riley (1962). The results of the soil analyses, except the 1:2 (w/v) water extracts used to estimate the elemental composition of soil solution, were reported as the average ± standard deviation of the duplicate pots of the 5- and 10-cm treatments.

Results and discussion

Dry matter production and phosphorus and nitrogen uptake

In the initial stage of the pot experiment (236 d), the slope of the cumulative dry matter production as a function of time in the 5- and 10-cm treatments was lower than in the remaining part (Fig. 5.1). In the next 742 d, the dry matter production rate increased and the slope of the cumulative dry matter production remained relatively constant. The dry matter production rate was lower in the 5-cm treatment than in the 10-cm treatment. Continuous cropping of grass for 978 d under greenhouse conditions removed considerable amounts of P from soil. The cumulative plant uptake of P from the soils of the 5- and 10-cm treatments amounted to 320 and 259 mg P kg^{-1} of soil, corresponding to 36 and 29% of P_{ox} in the initial soil, respectively (Fig. 5.2 and Table 5.1). The slope of the cumulative P uptake as a function of time showed a decrease with time, which can be explained by the decrease of the P content of the harvested grass (Table 5.2). In the 5- and 10-cm treatments, the P content of the grass decreased with time by 87 and 82%, respectively. Interestingly, the cumulative plant uptake of P was larger than the amount of FeO-P extracted from the initial soil (Fig. 5.2 and Table 5.3). The FeO strip method has been used to estimate the total amount of P available for plant uptake within a growing season (van Noordwijk et al., 1990). Apparently, the grass was able to remove P from the quasi-irreversibly bound P pool over the course of our pot experiment. The input of N with the added fertilizer to the pots of the 5- and 10-cm treatments was 1.5 and 1.4 times higher than the cumulative plant uptake of N, respectively. Neglecting the contribution of the soil to plant uptake of N, the recovery of N in the harvested grass was 67 and 71% in the 5- and 10-cm treatments, respectively. The N content of the grass in the 5- and 10-cm treatments decreased with time by 65 and 70%, respectively (Table 5.2). Thus, the N use efficiency of the grass decreased as the P content of the grass decreased. The P content of the harvested grass decreased at a higher rate than the N content. The N to P ratio of the grass in the 5- and 10-cm treatments increased from 8.0 and 9.3 to 22.3 and 15.1, respectively (Table 5.2). The ratio between the N and P contents of vegetation gives an indication of limitation of plant growth by either N or P: at a N to P ratio >16, P acts as a limiting factor (Koerselman and Meuleman, 1996). From t7 (692 d) onward, the N to P ratio of the harvested grass in the 5-cm treatment was >16. Therefore, somewhere in the interval between t6 and t7 (between 319 and 692 d), P may have become limiting for plant growth. This may explain the lower dry matter production in the 5-cm treatment (Fig. 5.1).

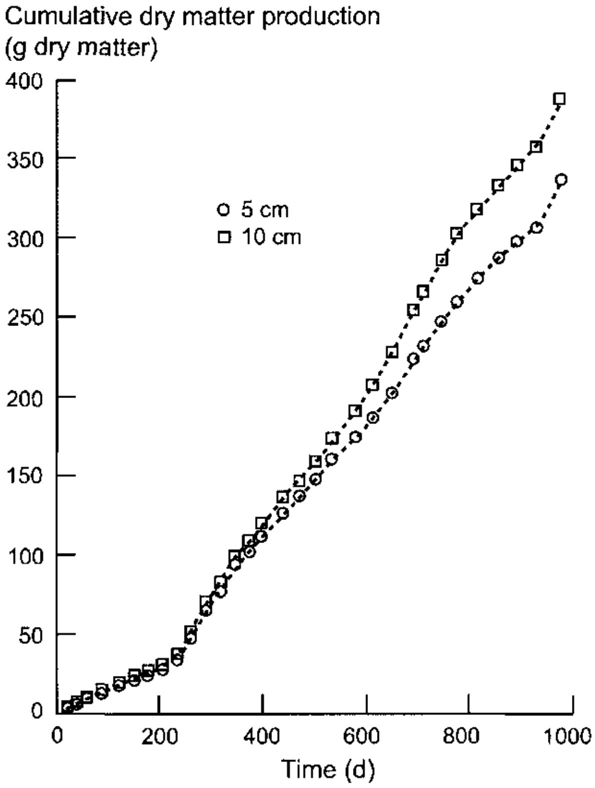

Figure 5.1. Cumulative dry matter production in the 5- and 10-cm treatments.

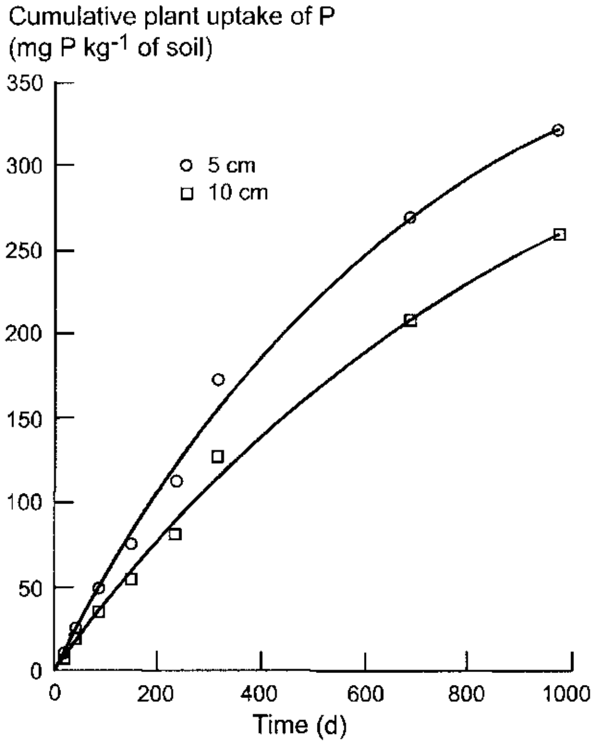

Figure 5.2. Cumulative plant uptake of P from the soils of the 5- and 10-cm treatments. To guide the eye, lines, fitted to the data using an exponential curve, have been added.

Table 5.1. Selected characteristics of the soils of the 5- and 10-cm treatments.†

	5 cm						10 cm					
Time	pH (H_2O)	Organic matter	$[Al+Fe]_{ox}$	P_{ox}	Organic P	Total P	pH (H_2O)	Organic matter	$[Al+Fe]_{ox}$	P_{ox}	Organic P	Total P
d		%	mmol kg^{-1}	mg P kg^{-1}	mg P kg^{-1}	mg P kg^{-1}		%	mmol kg^{-1}	mg P kg^{-1}	mg P kg^{-1}	mg P kg^{-1}
0 (t0)	5.18	3.41	69.0	896	184	1022	5.18	3.41	69.0	896	184	1022
22 (t1)	4.88 ± 0.02	3.58 ± 0.02	71.7 ± 2.0	902 ± 17	270 ± 53	980 ± 3	5.10 ± 0.04	3.83 ± 0.07	71.3 ± 1.4	925 ± 3	237 ± 26	1019 ± 8
41 (t2)	4.87 ± 0.02	3.25 ± 0.28	68.9 ± 0.0	847 ± 4	261 ± 8	935 ± 31	5.19 ± 0.01	3.48 ± 0.08	68.8 ± 0.8	888 ± 5	251 ± 36	976 ± 10
88 (t3)	4.99 ± 0.00	3.14 ± 0.53	68.5 ± 2.5	834 ± 57	248 ± 36	913 ± 49	5.32 ± 0.07	2.59 ± 0.68	67.1 ± 0.9	854 ± 12	229 ± 29	927 ± 5
151 (t4)	4.93 ± 0.04	2.59 ± 0.76	68.7 ± 1.4	814 ± 3	240 ± 19	896 ± 31	5.26 ± 0.08	3.89 ± 0.13	68.1 ± 0.8	847 ± 4	186 ± 14	936 ± 1
236 (t5)	5.13 ± 0.03	3.66 ± 0.19	62.8 ± 1.7	696 ± 18	189 ± 8	819 ± 49	5.35 ± 0.04	3.57 ± 0.22	62.6 ± 0.9	745 ± 16	221 ± 26	812 ± 40
319 (t6)	5.03 ± 0.08	3.57 ± 0.04	62.9 ± 1.3	643 ± 12	222 ± 30	765 ± 64	5.42 ± 0.02	3.76 ± 0.05	65.6 ± 3.7	750 ± 27	192 ± 28	855 ± 83
692 (t7)	5.52 ± 0.37	5.21 ± 0.33	66.1 ± 0.3	558 ± 18	252 ± 11	653 ± 18	5.71 ± 0.06	4.30 ± 0.22	68.7 ± 0.1	682 ± 10	247 ± 7	766 ± 6
978 (t8)	6.07 ± 0.20	5.12 ± 0.10	65.1 ± 3.3	468 ± 24	251 ± 6	595 ± 9	5.83 ± 0.08	4.22 ± 0.10	69.8 ± 2.1	611 ± 39	263 ± 4	666 ± 18

†Values are averages of duplicate pots ± standard deviations

Table 5.2. Nitrogen and P contents of the harvested grass† and N to P ratio‡ of the 5- and 10-cm treatments.

	5 cm			10 cm		
Time	N	P	N:P ratio	N	P	N:P ratio
d	g kg^{-1} of dry matter			g kg^{-1} of dry matter		
22 (t1)	47.6 ± 2.1	5.93 ± 0.33	8.0	55.0 ± 1.7	5.94 ± 0.23	9.3
41 (t2)	47.6 ± 2.5	6.81 ± 0.32	7.0	43.7 ± 2.0	7.61 ± 0.21	5.7
88 (t3)	46.3 ± 4.8	5.80 ± 0.15	8.0	47.3 ± 2.0	6.70 ± 0.16	7.1
151 (t4)	33.0 ± 1.8	5.32 ± 0.16	6.2	33.1 ± 1.0	6.54 ± 0.17	5.1
236 (t5)	24.5 ± 1.5	4.61 ± 0.25	5.3	24.0 ± 0.8	5.52 ± 0.34	4.4
319 (t6)	17.4 ± 0.7	2.34 ± 0.12	7.4	15.4 ± 1.2	2.87 ± 0.27	5.4
692 (t7)	18.2 ± 0.9	1.09 ± 0.08	16.7	16.0 ± 0.7	1.34 ± 0.07	11.9
978 (t8)	16.7 ± 0.4	0.75 ± 0.03	22.3	16.4 ± 0.5	1.09 ± 0.19	15.1

†Values are averages ± standard deviations.
‡The N to P ratio was calculated on a weight basis.

Soil characteristics

In the initial soil, the pH and organic matter content were 5.18 and 3.41%, respectively (Table 5.1). The pH showed an irregular increase during the pot experiment. The N fertilizer applied during the pot experiment was equally divided between NH_4NO_3 and $Ca(NO_3)_2{\cdot}4H_2O$. Thus, three-fourths of the N applied was in the form of NO_3^-, suggesting that N may have been mainly taken up as NO_3^-. Uptake of excess anions over cations may have been compensated for by root excretion of OH^- and HCO_3^- leading to an increase of the rhizosphere pH (Hinsinger, 2001). Denitrification of some of the NO_3^- applied may also have contributed to an increase of the pH (Šimek and Cooper, 2002). Organic matter showed an irregular increase during the pot experiment, due to an increase of root biomass with time, of which a part remained in soil after sampling and pretreatment; organic P was higher in the soils sampled at the end of the pot experiment than in the initial soil (Table 5.1). The $[Al+Fe]_{ox}$ content remained relatively constant as expected (Table 5.1). In the soils of the 5- and 10-cm treatments, P_{ox} decreased with time by 48 and 32%, respectively (Table 5.1). The decrease of P_{ox} in the soils of both treatments was larger than the cumulative plant uptake of P (Fig. 5.2). This may, in part, be explained by the buildup of a P pool contained in root residues. The ratio between P_{ox} and $[Al+Fe]_{ox}$ (both expressed in mmol kg^{-1}), α, is a measure of the degree of P saturation of a soil with respect to its content of amorphous Al- and Fe-(hydr)oxides (van der Zee and van Riemsdijk, 1988). The α of the initial soil was 0.42 and decreased with time to 0.23 and 0.28 in the soils of the 5- and 10-cm treatments, respectively.

Phosphorus desorption behavior

Figure 5.3 shows the relationships between the P concentration in 1:2 (w/v) water extracts and FeO-P and α. Due to continuous cropping of grass, FeO-P decreased by 83 and 72% in the soils of the 5- and 10-cm treatments over the course of the pot experiment (Table 5.3), respectively, whereas the relative decrease of α was much smaller. For both FeO-P and α, the curves are clearly different for the soils of the 5- and 10-cm treatments. Obviously, both curves should converge in the data point of the initial soil and in the origin. In the intermediate part, the curves of both treatments do not coincide, suggesting that P in soil solution is not in equilibrium with reversibly adsorbed P and P bound by the slow reaction. However, the elemental composition of the 1:2 (w/v) water extracts differs for both treatments (Table 5.4). In general, Ca is the main cation, contributing on average 57% to the total amount of cations in the water extracts of the initial soil and the soils of the 5- and 10-cm treatments sampled at t4 and t8. The Ca concentration in the water extracts obtained from the soils of the 5-cm treatment is (much) higher than the one obtained from the soils of the 10-cm treatment. This may be caused by the fertilization history of the pot experiment: the pots of the 5- and 10-cm treatments received the same amount of Ca fertilizer, but per unit of weight of soil, the soils of the 5-cm treatment received a much higher Ca input with the added fertilizer. The sorption of P to metal-(hydr)oxides increases and the desorption of P decreases with an increase of the Ca concentration in solution (Barrow and Shaw, 1979a; Koopmans et al., 2001; Rietra et al., 2001). The difference between the curves with FeO-P (Fig. 5.3A) and α (Fig. 5.3B) for the soils of the 5- and 10-cm treatments may be due to differences in Ca concentration, which affect the P concentration in the water extracts. The irregular fluctuations in the decrease of the P concentration in the water extracts over the course of the pot experiment may be explained by (temporal) fluctuations of the Ca concentration.

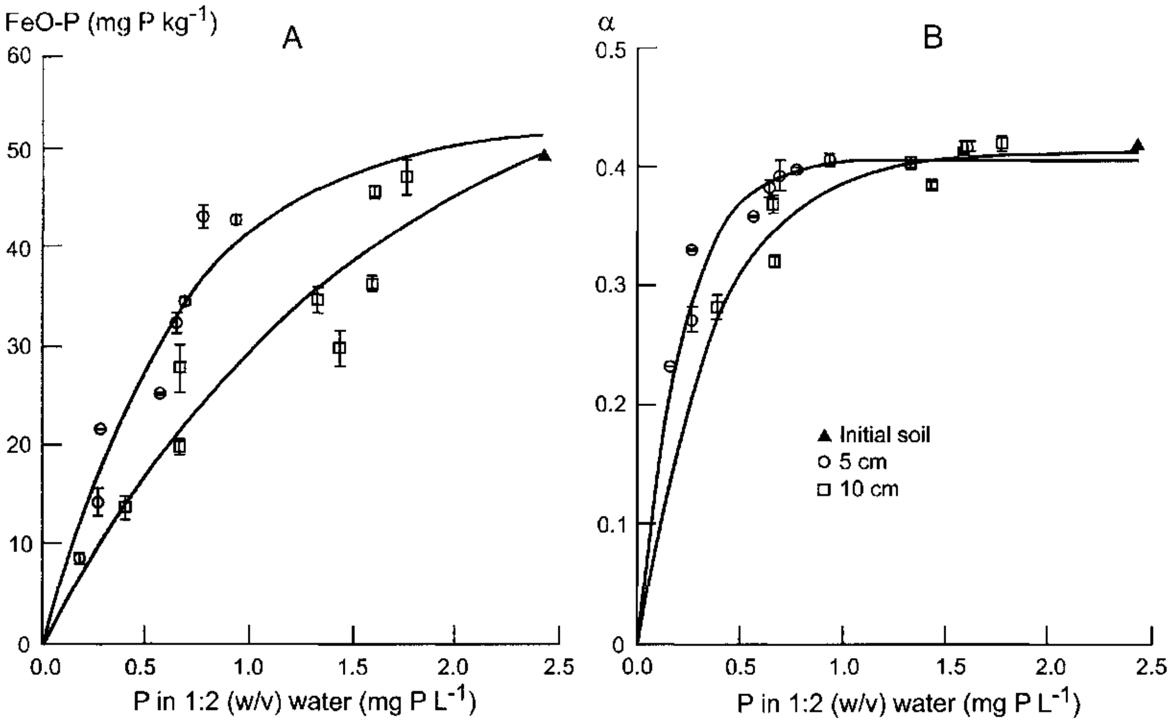

Figure 5.3. Relationship for the soils of the 5- and 10-cm treatments between the P concentration in 1:2 (w/v) water extracts and (A) FeO-P, and (B) α, which was calculated as $P_{ox}/[Al+Fe]_{ox}$ (with P_{ox} and $[Al+Fe]_{ox}$ in mmol kg^{-1}). To guide the eye, lines, fitted to the data using an exponential curve, have been added.

Table 5.3. Soil extractable P in the 5- and 10-cm treatments.†

Time	5 cm					10 cm				
	1:2 (w/v) water	1:10 (w/v) 0.01 M $CaCl_2$	Pw	FeO-P	P-AL	1:2 (w/v) water	1:10 (w/v) 0.01 M $CaCl_2$	Pw	FeO-P	P-AL
d	mg P L^{-1}	mg P L^{-1}	mg P kg^{-1}	mg P kg^{-1}	mg P kg^{-1}	mg P L^{-1}	mg P L^{-1}	mg P kg^{-1}	mg P kg^{-1}	mg P kg^{-1}
0 (t0)	2.42	0.84	25.5	49.2	398	2.42	0.84	25.5	49.2	398
22 (t1)	0.93 ± 0.04	0.52 ± 0.02	16.1 ± 0.7	42.7 ± 0.3	387 ± 3	1.76 ± 0.09	0.68 ± 0.00	21.4 ± 1.2	46.9 ± 1.7	402 ± 6
41 (t2)	0.77 ± 0.01	0.45 ± 0.02	15.3 ± 0.3	43.1 ± 1.1	374 ± 15	1.60 ± 0.00	0.60 ± 0.00	20.4 ± 0.1	45.4 ± 0.6	405 ± 3
88 (t3)	0.68 ± 0.08	0.41 ± 0.05	13.4 ± 1.0	34.5 ± 0.4	327 ± 40	1.58 ± 0.06	0.58 ± 0.09	19.7 ± 0.3	36.3 ± 0.7	398 ± 13
151 (t4)	0.64 ± 0.10	0.35 ± 0.03	12.9 ± 0.7	32.2 ± 1.0	327 ± 3	1.33 ± 0.05	0.46 ± 0.01	17.3 ± 0.5	34.6 ± 1.3	372 ± 6
236 (t5)	0.56 ± 0.07	0.25 ± 0.01	9.6 ± 0.6	25.2 ± 0.1	277 ± 0	1.43 ± 0.12	0.37 ± 0.01	13.6 ± 0.3	29.7 ± 1.8	316 ± 18
319 (t6)	0.27 ± 0.05	0.15 ± 0.00	6.1 ± 0.7	21.5 ± 0.0	249 ± 21	0.65 ± 0.03	0.21 ± 0.01	10.7 ± 0.1	27.7 ± 2.4	268 ± 61
692 (t7)	0.26 ± 0.15	0.10 ± 0.01	3.9 ± 0.7	14.1 ± 1.4	179 ± 9	0.66 ± 0.10	0.14 ± 0.02	7.9 ± 0.9	19.7 ± 0.8	240 ± 15
978 (t8)	0.17 ± 0.01	0.06 ± 0.00	3.8 ± 0.2	8.5 ± 0.5	154 ± 21	0.39 ± 0.08	0.07 ± 0.01	6.9 ± 0.3	13.6 ± 1.2	219 ± 9
1946 (t9)‡	nd§	0.05 ± 0.00	3.4 ± 0.1	nd	nd	nd	0.10 ± 0.01	6.9 ± 1.0	nd	nd

†Values are averages of duplicate pots ± standard deviations.

‡Moist soils of the 5- and 10-cm treatments sampled after the pot experiment had stopped (t8) were incubated in closed plastic bags in the dark at 20°C. After 968 d of incubation, soil was sampled (t9) and the P concentration in 1:10 (w/v) 0.01 M $CaCl_2$ extracts and Pw were measured.

§Not determined.

Table 5.4. Elemental composition of 1:2 (w/v) water extracts. Results were expressed in mmol L^{-1} and were obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis.

Treatment	Time	Al	Ca	Cu	Fe	K	Mg	Mn	Na	N-NH_4	N-NO_3	P	S
	d												
Initial soil	0 (t0)	0.04	0.81	0.0010	0.0048	0.25	0.31	0.023	0.36	0.13	1.759	0.11	0.19
5 cm	151 (t4)	0.05	3.00	0.0012	0.0040	0.12	0.45	0.084	0.14	0.11	0.003	0.04	3.69
5 cm	978 (t8)	0.04	1.11	0.0013	0.0049	0.06	0.25	0.029	0.07	0.06	0.031	0.06	1.25
10 cm	151 (t4)	0.04	0.65	0.0014	0.0089	0.40	0.01	0.001	0.14	0.14	0.024	0.03	0.56
10 cm	978 (t8)	0.05	0.28	0.0010	0.0067	0.09	0.01	0.003	0.09	0.01	0.009	0.03	0.07

Figure 5.4 shows the relationship between the P concentration in the 1:10 (w/v) 0.01 M $CaCl_2$ extracts and α. In this case, the salt level and Ca concentration is dominated by the 0.01 M $CaCl_2$ solution and will thus be identical for the soils of the 5- and 10-cm treatments. The data points of the 5- and 10-cm treatments now follow one curve. These are strong indications that the total pool of sorbed P is close to equilibrium with the fast reacting part and thus an apparent overall equilibrium between P in soil solution and P sorbed to the solid phase of the bulk soil is obtained. Local disequilibrium in the rhizosphere, resulting from the sink effect induced by plant roots (Hinsinger, 2001), would not be detected by our experimental setup, because we mixed the soil sampled from the pots before analysis. Even at a dense rooting, the volume of soil that is strongly depleted is relatively small (Geelhoed et al., 1997). Depletion of dissolved P in the rhizosphere may have caused variation in the amount of P sorbed to soil particles as a function of the distance to plant roots. Due to redistribution of P from sorption sites high in P to sorption sites low in P during the extraction, the variation in the amount of sorbed P has been undone (Del Campillo et al., 1996). Based on the method of Houba et al. (1986), the $CaCl_2$ extracts were shaken for 2 h. In principle, it is questionable whether the P concentration measured in these extracts has reached equilibrium. Results presented by van Erp et al. (1998) showed that at an extraction time longer than 2 h, the P concentration measured in 1:10 (w/v) 0.01 M $CaCl_2$ extracts did not further increase, indicating that equilibrium had been reached. To further test the hypothesis of an apparent overall equilibrium, we incubated moist soils of the 5- and 10-cm treatments sampled after the pot experiment had stopped (t8) in closed plastic bags in the dark at 20°C. Soil was sampled after 968 d of incubation (t9). The P concentration in the $CaCl_2$ extracts obtained from these soils remained relatively constant (t8 and t9 in Table 5.3). Thus, during incubation, there was virtually no replenishment of the reversibly adsorbed P pool by desorption of P from the quasi-irreversibly bound P pool to counteract the decrease of P in soil solution. This is another strong indication that the total pool of sorbed P is indeed close to equilibrium with P in soil solution in our pot experiment.

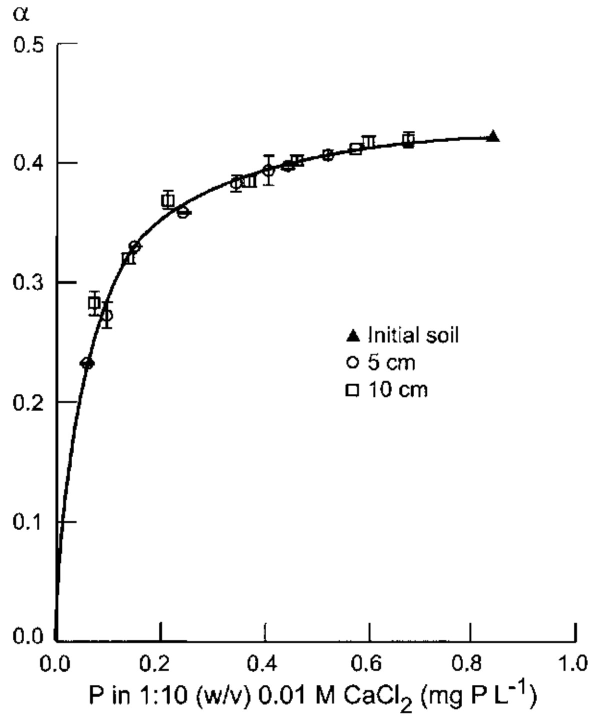

Figure 5.4. Relationship for the soils of the 5- and 10-cm treatments between the P concentration in 1:10 (w/v) 0.01 M $CaCl_2$ extracts and α, which was calculated as $P_{ox}/[Al+Fe]_{ox}$ (with P_{ox} and $[Al+Fe]_{ox}$ in mmol kg^{-1}). To guide the eye, a line, fitted to the data using a double exponential curve, has been added.

Phosphorus desorption isotherm

We derived a desorption isotherm that describes the long-term equilibrium relationship between the P concentration in the $CaCl_2$ extracts and the total pool of P sorbed to the solid phase of the soils of the 5- and 10-cm treatments (Fig. 5.5). The major part of the measured desorption is the result of P uptake by the grass over the course of the pot experiment whereas the contribution of the amount of P desorbed in the $CaCl_2$ extracts is relatively small. In laboratory experiments, it is difficult to determine such an isotherm, because of practical problems associated with the use of different desorption methods complicating these long-term desorption studies (van der Zee et al., 1987; Freese et al., 1995). In deriving the desorption isotherm, we corrected the total pool of sorbed P as measured by extraction with acid ammonium oxalate for the amount of P in the $CaCl_2$ extracts. The Langmuir equation gives a good description of the desorption isotherm. However, this fact may not be used to interpret the sorption behavior on a molecular scale. The exact mechanism is at this moment not known. Furthermore, the apparent equilibrium of the P desorption isotherm cannot be used to determine whether desorption processes of P inside Al- and Fe-(hydr)oxides have reached equilibrium. This requires a dynamic modeling approach of the P desorption kinetics inside aggregates of metal-(hydr)oxides. This will be part of a future study. In noncalcareous sandy soils, amorphous Al- and Fe-(hydr)oxides are the main reactive solid phases (Beek, 1979). Therefore, normalization of the total pool of sorbed P with respect to $[Al+Fe]_{ox}$ may give an isotherm, which is also of general use for other noncalcareous sandy soils. In comparison with Fig. 5.4, the data points in Fig. 5.5 show more variation around the fitted curve. This may be due to small variation in the measured $[Al+Fe]_{ox}$ contents (Table 5.1). The shape of the isotherm is highly nonlinear. This nonlinear shape results in a relatively fast decrease of the P concentration in soil solution in the initial stage of the pot experiment, due to a relatively low buffering by the solid phase in that part of the desorption isotherm (Lookman et al., 1995a). The buffering in the last stage of the pot experiment is much stronger, and then prolonged cropping is needed to obtain a relatively small decrease of the P concentration in soil solution. During the first 319 d of continuous cropping, the P concentration in the $CaCl_2$ extracts of the soils of the 5- and 10-cm treatments decreased by 82 and 74%, respectively, but in the following 659 d, it further decreased by only 10 and 17%, respectively. This effect is not only due to the strong nonlinearity of the desorption isotherm, but also to the decrease of plant uptake of P with time (Fig. 5.2 and Table 5.2). The latter is caused by the decrease of the availability of P in soil for plant uptake with a lowering of the P content in soil. This is illustrated in Fig. 5.6: for the soils of the 5- and 10-cm treatments, the P content of the harvested grass shows a clear decrease with the average P concentration calculated from the P concentration measured in the $CaCl_2$ extracts of soils sampled at two subsequent sampling points. As follows from Fig. 5.5, a fast decrease of a high P concentration in soil solution may be expected upon continuous cropping without external P addition, whereas a lower P concentration may persist and leach to ground water and surface waters for a much longer time.

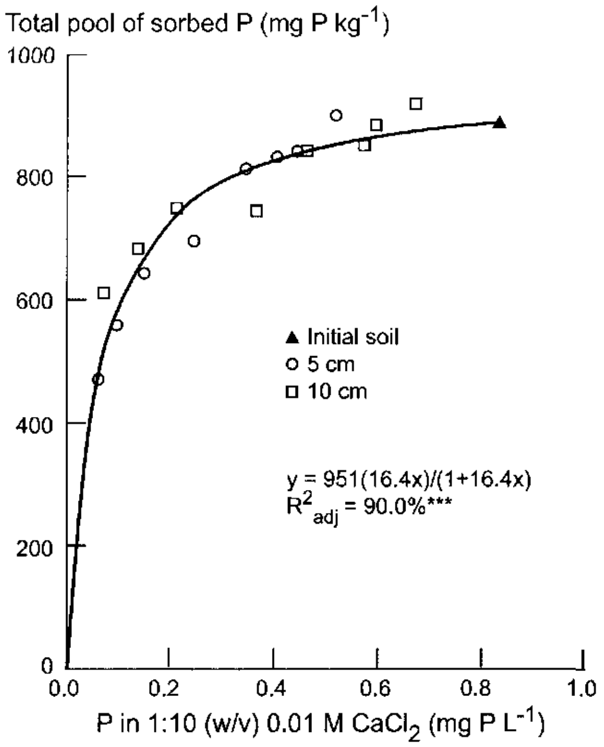

Figure 5.5. The desorption isotherm for the soils of the 5- and 10-cm treatments describing the relationship between the P concentration in 1:10 (w/v) 0.01 M $CaCl_2$ extracts and the total pool of sorbed P (P_{ox} corrected for the amount of P in the $CaCl_2$ extracts). The Langmuir equation was fitted to the data.

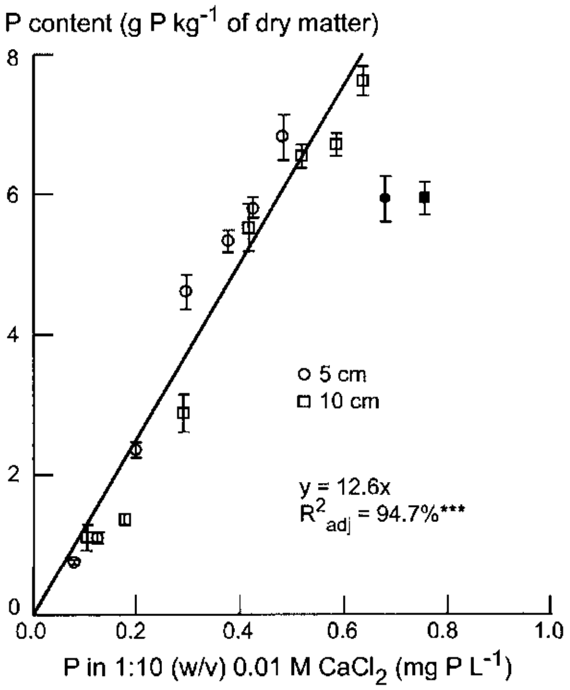

Figure 5.6. Relationship for the soils of the 5- and 10-cm treatments between the average P concentration, calculated from the P concentration measured in 1:10 (w/v) 0.01 M $CaCl_2$ extracts at two subsequent sampling points, and the P content of the grass harvested since the previous sampling point. The filled symbols of the 5- and 10-cm treatments, representing the average P concentration in the $CaCl_2$ extracts at t0 and t1 and the P content of the grass harvested since t0, were not included in the linear regression analysis, because these data points deviate significantly from the line.

Maximum of the desorption isotherm

In Fig. 5.5, we used the Langmuir equation to describe the desorption isotherm. The asymptote of the Langmuir equation at a high P concentration gives an estimate of the maximum amount of P sorbed to the solid phase of the soil used in our pot experiment, which may be equated to F_{max}. The estimated F_{max} was 951 ± 23 mg P kg^{-1} (mean ± standard error). We estimated the maximum saturation factor α_{max} of the amorphous Al- and Fe-(hydr)oxides with respect to P sorption by calculating the ratio between F_{max} and $[Al+Fe]_{ox}$ (both expressed in mmol kg^{-1}). For $[Al+Fe]_{ox}$, we used the average $[Al+Fe]_{ox}$ content of the initial soil and the soils sampled during the pot experiment (Table 5.1). The estimated α_{max} is 0.46, whereas the α of the initial soil was 0.42. Thus, the Al- and Fe-(hydr)oxides of the initial soil were almost completely saturated with P. Our estimated value of α_{max}, which was obtained from the desorption isotherm, is in very good agreement with values of α_{max} reported in sorption studies of van der Zee et al. (1988) and Freese et al. (1992), who found α_{max} values of around 0.4. However, somewhat higher α_{max} values of around 0.6 can also be found in literature (van der Zee and van Riemsdijk, 1988; Maguire et al., 2001).

Plant available phosphorus pool

The desorption isotherm (Fig. 5.5) can be used to estimate the cumulative plant uptake of P. The P concentration measured in the $CaCl_2$ extracts (Table 5.3) was used as an input variable in the equation given in Fig. 5.5 to calculate the total pool of sorbed P. Subsequently, the sum of the total pool of sorbed P and P in the $CaCl_2$ extracts of the soils of the 5- and 10-cm treatments at each sampling point was calculated. The cumulative differences between these sums should correspond with the cumulative plant uptake of P from these soils if inorganic sorbed P is the main source of P for plant growth. Figure 5.7 shows the relationship between the measured and calculated cumulative plant uptake of P. We obtained a good estimation of the measured cumulative plant uptake of P, although the soils of the 5- and 10-cm treatments sampled at later stages of the pot experiment, especially those at t8, clearly deviate from the 1:1 line. This may have been due to the buildup of a P pool contained in root residues in soil. Inclusion of P in root residues, which was determined after the pot experiment had stopped, in the measured cumulative plant uptake of P causes a clear shift of the data points of the soils of the 5- and 10-cm treatments sampled at t8 towards the 1:1 line.

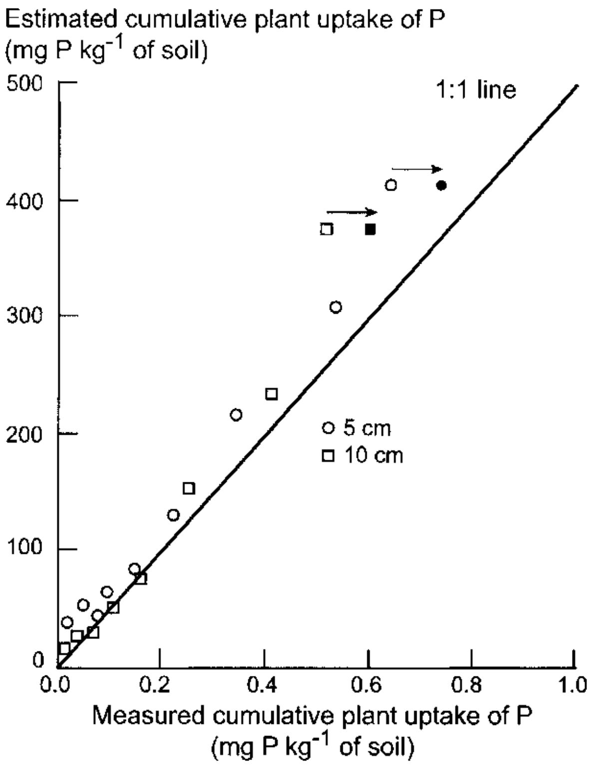

Figure 5.7. Relationship between the measured and estimated cumulative plant uptake of P. In the filled symbols of the 5- and 10-cm treatments, representing the cumulative plant uptake of P at t8, P measured in root residues was included.

Eventually, continuous cropping without external P addition may lead to a situation where the availability of P in soil is too low for crop growth. Van Noordwijk et al. (1990) reported a critical value of 0.03 mg P L^{-1} where plant uptake of P can just be maintained. Based on the desorption isotherm of Fig. 5.5, the total pool of sorbed P corresponding to a P concentration of 0.03 mg P L^{-1} in the $CaCl_2$ extracts, calculated from the Langmuir equation, is 314 mg kg^{-1}. This suggests that plant uptake can remove 582 mg P kg^{-1} from soil in the long-term, representing 65% of P_{ox} in the initial soil (Table 5.1). Thus, P_{ox} may be largely available for plant uptake in the long-term. This is in agreement with results of Lookman et al. (1995a) and Guo and Yost (1999). In a long-term desorption study of Lookman et al. (1995a), where P-enriched noncalcareous sandy soils were incubated with a P sink consisting of a dialysis membrane tube filled with hydrous Fe-(hydr)oxide for approximately 67 d, up to 70% of P_{ox} was desorbed. Based on their model results of the long-term P desorption kinetics, all P_{ox} was practically desorbable over 100 to 400 d, suggesting that irreversibly bound P was not present in these soils. In a pot experiment of Guo and Yost (1999), where maize and soybean (*Glycine max* [L.] Merr.) were cropped without external P application, P_{ox} was also largely available for plant uptake.

Practical implications

The relative decrease of the P concentration in the $CaCl_2$ extracts was much larger than the relative decrease of P_{ox} after 978 d of continuous cropping under greenhouse conditions. The P concentration in the $CaCl_2$ extracts and P_{ox} decreased by 93 and 48% in the soils of the 5-cm treatment and by 91 and 32% in the soils of the 10-cm treatment, respectively (Table 5.1 and 5.3). This is due to the strong nonlinearity of the desorption isotherm (Fig. 5.5). These results were achieved after 31 harvests, corresponding to approximately 6 yr of intensive cropping in the field when assuming five harvests per growing season. Based on the relatively large decrease of the P concentration in the 0.01 M $CaCl_2$ extracts used to simulate soil solution in our pot experiment (McDowell and Sharpley, 2001), mining soil P can be considered as an effective management strategy to decrease the risk of P leaching from our P-enriched soil on a relatively short-term basis. However, further testing of mining soil P under practical field conditions is necessary. Application of supplemental nutrients, such as N and K, may be necessary to prevent limitation of plant growth. In our pot experiment, the average N recovery in the harvested grass was 69%. This is a common recovery for intensively managed grassland (Prins, 1980).

Grass harvested during mining soil P may serve as feed for livestock. In our pot experiment, the P content of the grass decreased with a lowering of the availability of P for plant uptake (Fig. 5.6). In conventional agricultural practice in the Netherlands, the P content of grass is approximately 4 g kg^{-1} dry matter (Agterberg and Henkens, 1995). For an optimal nutritional value of grass to serve as feed for high yielding dairy cows, it should not contain less than 3 g P kg^{-1} of dry matter if grass is the only component of the diet (Valk et al., 1999). However, the P content of the grass harvested in the last stage of the pot experiment was far below 3 g kg^{-1} of dry matter (Table 5.2), implicating that the grass would have too little nutritional value. Thus, additional P supply will be needed if the harvested grass will be used as the sole component of the diet for high yielding dairy cows. Our results indicate that meeting 3 g P kg^{-1} in the dry matter requires a P concentration in a $CaCl_2$ extract of 0.24 mg L^{-1} (calculated from the equation given in Fig. 5.6). This P concentration is 71% lower than the initial P concentration (Table 5.3). From the Langmuir equation given in Fig. 5.5, it can be calculated that a P concentration of 0.24 mg P L^{-1} in a $CaCl_2$ extract can already be reached when only 15% of P_{ox} in the initial soil has been mined (Table 5.1).

In the Netherlands, Pw and P-AL are used in agricultural practice as soil tests for P fertilizer recommendation systems of arable land and grassland, respectively. In the soils of the 5- and 10-cm treatments, Pw decreased by

85 and 73% whereas P-AL decreased by 61 and 45%, respectively (Table 5.3). Due to the dilution effect of the relatively wide soil to solution ratio of Pw (1:60 [v/v]), P extracted with Pw can be interpreted as the sum of P in soil solution and part of the reversibly adsorbed P, whereas P-AL represents both reversibly adsorbed P and a large part of P bound inside Al- and Fe-(hydr)oxides (Schoumans and Groenendijk, 2000). Therefore, from the strong nonlinearity of the desorption isotherm (Fig. 5.5), it can be understood why the relative decrease of Pw was larger than the relative decrease of P-AL. Our results also explain why in a long-term field experiment of McCollum (1991) and those summarized by Sharpley (2000), the decrease of soil extractable P with continuous cropping after P application had stopped was relatively small. In these studies, relatively strong extraction methods, indicative of P sorbed to the solid phase rather than P in soil solution, were used. Thus, the result of evaluating the effectiveness of mining soil P as a possible management strategy strongly depends upon the P pool taken into consideration. In the soils of the 5- and 10-cm treatments sampled at t8, P-AL was 154 and 219 mg P kg^{-1}, respectively (Table 5.3). These P-AL values are considered as medium/optimal and high, respectively (Tunney et al., 1997). At this level, little or no additional fertilization is needed in practice to reach a P content in the harvested grass of about 3.5 to 4.0 g P kg^{-1} of dry matter. This evaluation is in marked contrast with the low to very low P contents of the grass as found in our pot experiment (Table 5.2). Evidently, the results of this study cannot be directly transfered to practice, especially because the thickness of the soil layers was restricted in our pot experiment. In a homogenized soil layer under field conditions thicker than 5 or 10 cm, the plant roots would have access to more available P at a given P content. In our incubation experiment, which was discussed before, the Pw was measured. The Pw did not change as a result of incubation of moist soil sampled at the end of the pot experiment (t8 and t9 in Table 5.3). This supports the hypothesis that the total pool of sorbed P was indeed close to equilibrium with P in soil solution. Therefore, after stopping mining soil P, in case the soil is kept fallow or when there is virtually no plant growth (e.g., winter), the P concentration in soil solution may be expected to remain relatively constant.

Conclusions

- In our pot experiment, performed over a relatively long time (978 d), an apparent overall equilibrium between P in soil solution and the total pool of P sorbed to the solid phase was obtained. A desorption isotherm was derived, describing the relationship between the P concentration in 1:10

(w/v) 0.01 M $CaCl_2$ extracts and the total pool of sorbed P, which was measured with the acid ammonium oxalate extraction method and corrected for the amount of P desorbed in the $CaCl_2$ extracts.

- The Langmuir equation gave a good description of the desorption isotherm, and could be used very well to calculate the measured cumulative plant uptake of P from soil.
- The maximum saturation factor α_{max} of the amorphous Al- and Fe-(hydr)oxides in the initial soil with respect to P sorption, obtained from the desorption isotherm, was 0.46, which is in good agreement with α_{max} values reported in sorption studies of van der Zee et al. (1988) and Freese et al. (1992).
- Based on the desorption isotherm and a critical P concentration in soil solution where plant uptake of P can just be maintained, it was calculated that in the long-term 65% of P_{ox} in the initial soil may be removed by plant uptake.
- Continuous cropping of grass without external P addition under greenhouse conditions caused a fast and relatively large decrease of the P concentration in soil solution. Thus, mining soil P, as proposed by van der Zee et al. (1992) and Chardon et al. (1996b), may be an effective management strategy to decrease the risk of P leaching from our P-enriched soil. This result should be tested further under practical field conditions.
- Measuring the P concentration in a solution standardized with respect to the $CaCl_2$ concentration leads to results that are easier to interpret in this pot experiment, where results of the 5-cm treatment were compared to those of the 10-cm treatment, than using 1:2 (w/v) water extracts.

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6

Phosphorus desorption dynamics in soil and the link to a dynamic concept of bioavailability

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J. Environ. Qual., accepted

Abstract

Soils under intensive livestock farming and heavily fertilized with animal manure may have elevated soil phosphorus (P) contents. We determined P desorption kinetics in batch experiments using soils from a pot experiment where grass was cropped on a P rich noncalcareous sandy soil without P addition, to lower the soil P content. A diffusion model was used to describe P desorption kinetics from a spherical aggregate. The model was calibrated with data from the batch experiments. Simulation results show that in the pot experiment, P desorption from the solid phase of the inner layers was initially far from equilibrium with the rest of the aggregate, but desorption came closer to equilibrium as the soil P content decreased further. A simple tool is presented, referred to as the dynamic bioavailability index (DBI), to determine whether kinetics of P desorption limits plant uptake. This tool is the dimensionless ratio of the modeled maximal diffusive flux from soil aggregates to solution and the plant uptake rate measured in the pot experiment. The DBI was initially much larger than one; the maximal possible P desorption rate exceeded the uptake rate, so uptake was not limited by desorption. The DBI stabilized at a value somewhat larger than one after a while, due to soil transport limitations. This decrease coincided with a large decrease of the P content in the grass to a value (far) below what is considered as optimal; the supply rate of P from soil to the root cannot meet the demand needed for an optimal P uptake. The DBI could be seen as a promising onset to a new dynamic approach of bioavailability.

Introduction

In areas with intensive livestock farming, soils are often enriched with phosphorus (P) as a result of decades of P addition, via animal manure, exceeding P removal in harvested crops (e.g., Breeuwsma et al., 1995; Pautler and Sims, 2000). In the Netherlands, intensive livestock farming takes place mainly on noncalcareous sandy soils. In soils treated with large amounts of animal manure, P mainly accumulates in the inorganic form (Sharpley et al., 1984; Koopmans et al., 2003). Amorphous Al- and Fe-(hydr)oxides are the main reactive solid phases in noncalcareous sandy soils (Beek, 1979). The overall reaction of inorganic P with Al- and Fe-(hydr)oxides can be divided into a fast reversible adsorption reaction at surface sites with a reaction time of <1 d and a slow one, that is, (reactive) diffusion through the solid phase or through micropores of these metal-(hydr)oxides possibly followed by precipitation and/or adsorption inside the aggregates (van Riemsdijk and Lyklema, 1980b; Barrow, 1983; van Riemsdijk et al., 1984a; Madrid and De Arambarri, 1985). The total pool of sorbed P in noncalcareous sandy soils has been interpreted to be the sum of reversibly adsorbed P and quasi-irreversibly bound P (van der Zee et al., 1987; van der Zee and van Riemsdijk, 1988). Filter paper strips impregnated with iron oxide have been proposed to determine the amount of reversibly adsorbed P (FeO-P) (van der Zee et al., 1987). The acid ammonium oxalate extraction method of Schwertmann (1964) has been used to determine both the total pool of sorbed P (P_{ox}) as well as amorphous (hydr)oxides of Al and Fe ($[Al+Fe]_{ox}$). The sum of these metal-(hydr)oxides determines the total sorption capacity of inorganic P in noncalcareous sandy soils (Beek, 1979; van der Zee and van Riemsdijk, 1988). The reversibility of the overall reaction of P with the solid phase of the soil is of both agricultural and environmental interest. Because of the often limited availability of P for plant uptake in soils with a low input of P, a better understanding of the desorption kinetics of P from soil may help maintaining an optimal soil fertility for crop production. On the other hand, in areas with intensive livestock farming, where soils have been enriched with P, accumulation of P can lead to saturation of the soil with P and environmental problems such as eutrophication of surface waters resulting from (subsurface) leaching of soil solution with a high P concentration (e.g., Breeuwsma et al., 1995; Sims et al., 1998; Schoumans and Groenendijk, 2000).

Upon the removal of P from soil solution by plant uptake, a fast initial desorption reaction for P adsorbed to surface sites of Al- and Fe-(hydr)oxides is expected (van der Zee et al., 1987). The decrease of P adsorbed to surface sites may be replenished by desorption of P bound inside Al- and Fe-(hydr)oxides followed by diffusion of P to the outer layers of the aggregates (Barrow, 1983). Because intra-aggregate diffusion is slow, this P becomes available again only in the long-term. The importance of intra-aggregate diffusion as the rate-limiting step in the mass transfer of reactive solutes between sorption sites inside porous sorbents and bulk solution was also demonstrated for various metals (Trivedi and Axe, 2000; Lin and Wu, 2001) and organic compounds (Wu and Gschwend, 1986; Rijnaarts et al., 1990). Therefore, this mechanism may be very important in controlling the bioavailability and transport of various reactive solutes in soils. Intra-aggregate diffusion should be considered if realistic models are to be used to model long-term (de)sorption processes of reactive solutes in soil.

Quantitative information about the reversibility of the overall reaction of P in P-enriched soils in the long-term is scarce. A desorption isotherm, describing the long-term equilibrium relationship between P in soil solution and the total pool of sorbed P, can be used to estimate the total amount of P available for plant uptake and leaching. However, these relationships are difficult to determine experimentally, because of the slow desorption kinetics and other more practical problems (van der Zee et al., 1987; Freese et al., 1995). Furthermore, in the field kinetic factors may lead to a lower availability of P than would be estimated from the equilibrium desorption isotherm. Knowledge about the equilibrium situation is nevertheless required before one can do a useful analysis of the P desorption kinetics. Koopmans et al. (2004) recently determined a desorption isotherm using a long-term pot experiment, where grass was cropped on a P rich noncalcareous sandy soil without P addition as a means to lower the amount of P sorbed to the soil. The total pool of sorbed P, estimated by P_{ox}, appeared to be close to equilibrium with P in 1:10 (w/v) 0.01 M $CaCl_2$ extracts used to simulate conditions in the soil solution (McDowell and Sharpley, 2001). The Langmuir equation gave a very good description of the obtained relationship. These $CaCl_2$ extracts were obtained from soil samples taken at various stages of the pot experiment using 2 h of very vigorous shaking (Houba et al., 1986). The vigor of shaking in batch systems is very important in the mass transfer of reactive solutes between sorption sites inside porous sorbents and bulk solution; at very vigorous shaking, only the reaction of the solute may be the rate-limiting step (Ogwada and Sparks, 1986a, 1986b). This may for instance be due to abrasion of soil aggregates leading to (much) shorter diffusion distances causing an increase of the mass transfer rate of the reactive solute, resulting in a faster establishment of equilibrium. This mechanism may have been responsible for the apparent equilibrium of P desorption in the $CaCl_2$ extracts obtained from the soils of the pot experiment of

Koopmans et al. (2004). This hypothesis is supported by results of van Erp et al. (1998); at an extraction time longer than 2 h, the P concentration measured in 1:10 (w/v) 0.01 M $CaCl_2$ extracts determined according to Houba et al. (1986) did not further increase, indicating that equilibrium was reached. The apparent equilibrium of the P desorption isotherm cannot be used to determine whether the desorption processes of P from Al- and Fe-(hydr)oxides inside intact soil aggregates were near equilibrium during the growth of plants that continuously remove P from the soil solution. This requires a dynamic modeling approach of the P desorption kinetics for conditions where the soil aggregates are not degraded by vigorous shaking during the measurement of P desorption. Therefore, we decided to determine P desorption kinetics in batch experiments under more mild shaking conditions using some of the soils that were used to determine the equilibrium desorption isotherm in the pot experiment. For the modeling of the data, we used the simplifying assumption that the soil consists of a collection of spherical aggregates of equal size and composition. The reactive diffusive transport of P in the soil aggregates is calculated with the additional assumption that the diffusion in the soil aggregates is the rate-limiting step. The Langmuir equation is used to calculate the buffering behavior of P sorbed to the solid phase and the (local) solution in the micropores. In studies of Wu and Gschwend (1986), Rijnaarts et al. (1990), and Lin and Wu (2001), a similar modeling approach was used to simulate (de)sorption processes of reactive solutes in porous sorbents. The diffusion model was calibrated with the data from the batch experiments. The calibrated model was then used to simulate the distribution of P inside the soil aggregates during plant growth in the pot experiment using some simplifying assumptions. Whether or not kinetic factors may limit the bioavailability of P for plant uptake can be estimated using a dimensionless ratio of the maximal diffusive flux from the soil aggregates to the soil solution, which can be calculated with the model, and the flux that is required to obtain an optimal P content in the growing plants in the same units. This dimensionless ratio, which we will refer to as the dynamic bioavailability index (DBI), is expected to change during the long-term pot experiment. The same ratio can also be calculated by using the measured rate of plant uptake of P at a certain stage in the pot experiment instead of the flux that is required to obtain an optimal P content in the growing plants. Furthermore, the diffusion model is used to gain more insight in the 1:10 (w/v) 0.01 M $CaCl_2$ method (Houba et al., 1986), which is a procedure to analyze the P status of agricultural soils.

Materials and methods

Summary of the pot experiment

Koopmans et al. (2004) performed a pot experiment where ryegrass (*Lolium perenne* L.) was cropped over 978 d on a P rich loamy noncalcareous sandy soil without P addition. The soil was sampled from the tillage layer (0-30 cm) of a plot from a long-term field experiment and received large applications of pig slurry in the past (see Del Castilho et al. [1993]). The pot experiment was performed in a greenhouse. There were two treatments: in a pot with a volume of 2.5 L, soil was placed in a layer of either 5 or 10 cm thickness. To prevent N and K limitation of plant growth, N and K were regularly added. Grass was harvested 31 times, at an interval of 19 to 47 d. Dry weight and total P content of the harvested grass were determined. At various stages of the pot experiment, soil of two pots per treatment (duplicate pots) was destructively sampled (22, 41, 88, 151, 236, 319, 692, and 978 d). Soil was dried at 40°C and passed through a 2-mm sieve. For an extensive description of the setup of the pot experiment, see Koopmans et al. (2004). The pH and organic matter content were determined according to Houba et al. (1997). Phosphorus in soil solution was estimated using 1:10 (w/v) 0.01 M $CaCl_2$ extracts (Houba et al., 1986). The $CaCl_2$ extracts were shaken on a reciprocating shaker at 165 strikes per minute (spm). After centrifugation (1800 x g), P was measured colorimetrically (Murphy and Riley, 1962). Reversibly adsorbed P was estimated using a modified FeO strip method of van der Zee et al. (1987); see Koopmans et al. (2004) for details. The total pool of sorbed P was estimated using the acid ammonium oxalate extraction method of Schwertmann (1964). Concentrations of P, Al, and Fe were measured using inductively coupled plasma atomic emission spectroscopy.

Phosphorus desorption kinetics

The initial soil and soils from the 5- and 10-cm treatments of the pot experiment sampled after 151 and 978 d of plant uptake of P were used. For the soils sampled after 151 and 978 d, the soil of only one of the duplicate pots was used. Soil was incubated in duplicate with 0.01 M $CaCl_2$ at soil to solution ratios of 1:10, 1:50, 1:100, 1:500, and 1:1000 (w/v). To prevent biological activity, 0.5 mL of a 2% (w/v) sodium azide (NaN_3) solution was added. Soil suspensions were shaken in a relatively mild motion on a reciprocating shaker at 75 spm for 3, 24, 48, 96, and 408 h. After filtration over a 0.45 μm filter, P was measured colorimetrically (Murphy and Riley, 1962).

Model

The numerical model was developed by Chardon and de Willigen (1997). The soil is assumed to consist of a collection of spherical aggregates of equal size and composition. Linquist et al. (1997) demonstrated the importance of the size of soil aggregates for P sorption. To represent the soil, the model uses one spherical aggregate divided into 50 concentric parts of equal mass. Sorption sites are distributed uniformly through the aggregate. Sorption or desorption of P occurs instantaneously according to the Langmuir equation:

$$Q = \frac{Q_{max} \times K \times C}{1 + K \times C} \qquad [6.1]$$

where Q is the amount of P sorbed to the soil (mg P kg^{-1}), Q_{max} is the sorption maximum (mg P kg^{-1}), K is a constant describing the affinity of the soil for P (L mg^{-1}), and C is the P concentration (mg P L^{-1}). Intra-aggregate diffusion of P is considered as the rate-limiting step in P desorption. Transport of P within the aggregate is caused by diffusion described by Fick's first law:

$$F = -D_e \times \frac{dC}{dr} \qquad [6.2]$$

where F is the flux of solute (mg P dm^{-2} s^{-1}), D_e is the diffusion coefficient of P in water corrected for the volume of the micropores within the aggregate (dm^2 s^{-1}), and r the radial coordinate (dm). The effective diffusion coefficient D_e is assumed to decrease with the volume of water-filled micropores according to:

$$D_e = \theta^3 \times D \qquad [6.3]$$

where θ is the water-filled pore volume fraction of the aggregate (-) and D is the diffusion coefficient of P in free water (dm^2 s^{-1}). Furthermore, there is no external limitation in the mass transfer of P from the aggregate to the bulk solution. Under static conditions in batch experiments, diffusion of P through a nonturbulent external film of water adhering to and surrounding porous sorbents may be the rate-limiting step in the mass transfer of reactive solutes. However, under nonstatic conditions resulting from shaking, the effect of film diffusion as the rate-limiting step may be strongly decreased (Ogwada and Sparks, 1986a, 1986b; Rijnaarts et al., 1990). Table 6.1 shows the parameters used in the model. The values of Q_{max} and K used in the model were derived from the desorption isotherm determined in the pot experiment.

Table 6.1. Parameter values used in the diffusion model.

Parameter	Values
ρ†	2.5 kg L^{-1}
Radius	1 mm
D†	0.5 $dm^2\ s^{-1}$
θ‡	0.035
Q_{max}§	951 mg P kg^{-1}
K§	16.4 L mg^{-1}

†Values of ρ and D were taken from Chardon and de Willigen (1997).
‡The pore volume fraction of the spherical aggregate was used as a fitting parameter.
§Values of Q_{max} and K were obtained from the Langmuir equation fitted to the isotherm that was determined in the pot experiment of Koopmans et al. (2004).

For the total amount of P initially present in the aggregate, we used the sum of the total pool of sorbed P and P desorbed in the $CaCl_2$ extract of the initial soil. The total pool of sorbed P was calculated from the Langmuir equation determined in the pot experiment where the measured P concentration in the $CaCl_2$ extract of the initial soil was used as an input variable. The initial distribution of the total amount of P over the solution in the micropores and the solid phase of the aggregate was calculated from the mass balance:

$$T = g \times Q + v \times C \qquad [6.4]$$

where T is the total amount of P initially present (mg P), g is the weight of the aggregate (kg), and v is the volume of the micropores (L). The Langmuir equation can be substituted for Q in the mass balance (van Noordwijk et al., 1990), after which Eq. [6.4] can be solved analytically for C (see Koopmans et al. [2002]). Subsequently, the initial P concentration in the micropores and the corresponding amount of P sorbed to the solid phase was calculated.

The ratio α between P_{ox} and $[Al+Fe]_{ox}$ (both expressed in mmol kg^{-1}) is a measure of the degree of P saturation of a soil with respect to its content of amorphous Al- and Fe-(hydr)oxides (van der Zee and van Riemsdijk, 1988). The α of the initial soil was 0.42, which is close to the α_{max} of 0.46 derived from the Langmuir equation determined in the pot experiment (Koopmans et al., 2004). The Al- and Fe-(hydr)oxides of the initial soil were thus nearly saturated with P, indicating that the P initially present was distributed uniformly through the aggregate.

In the model, P desorption with time can be simulated by the presence of an external solution surrounding the aggregate with an initially zero P concentration. The soil to solution ratio of the external solution can be varied. The data from the batch experiments, where the kinetics of P desorption from the initial soil were determined, was used to calibrate the model using the pore volume fraction of the aggregate as a fitting parameter. Plant uptake of P measured in the 5- and 10-cm treatments of the pot experiment was simulated to determine whether P desorption from Al- and Fe-(hydr)oxides inside soil aggregates reached equilibrium. Phosphorus desorbed to the soil solution was removed in the model with a rate according to the measured plant uptake of P. Soil solution was simulated by the addition of an external solution with a soil to solution ratio of 1:0.3 (w/v), which may be representative for conditions in the soil. To calculate the maximal P desorption rate, the P concentration in an external solution with a soil to solution ratio of 1:0.3 (w/v) was maintained at zero to facilitate continuous maximal P desorption. To simulate the results of the batch experiments and to calculate the maximal P desorption rate for the soils sampled after 151 and 978 d of plant uptake of P, the same procedures were followed as described above for an aggregate after 151 and 978 d of simulation of plant uptake.

Results and discussion

Pot experiment

Table 6.2 shows some results of soil extractable P obtained in the pot experiment of Koopmans et al. (2004). In the soils of the 5- and 10-cm treatments, the P concentration in the 1:10 (w/v) 0.01 M $CaCl_2$ extracts measured according to Houba et al. (1986) had decreased by 93 and 91% after 978 d of continuous cropping of grass. The amount of P extractable with an FeO strip decreased by 83 and 72%, respectively. The relative decrease of P_{ox} was much smaller; P_{ox} decreased by 48 and 32% in the soils of the 5- and 10-cm treatments, respectively. The $[Al+Fe]_{ox}$ content remained relatively constant as expected. The ratio α between P_{ox} and $[Al+Fe]_{ox}$ of the initial soil was 0.42 and decreased with time to 0.23 and 0.28, respectively.

Table 6.2. Selected characteristics and soil extractable P from the initial soil and soils of the 5- and 10-cm treatments.†

	5 cm						10 cm					
Time	pH (H_2O)	Organic matter	$[Al+Fe]_{ox}$	1:10 (w/v) 0.01 M $CaCl_2$	FeO-P	P_{ox}	pH (H_2O)	Organic matter	$[Al+Fe]_{ox}$	1:10 (w/v) 0.01 M $CaCl_2$	FeO-P	P_{ox}
d		%	mmol kg^{-1}	mg P L^{-1}	mg P kg^{-1}	mg P kg^{-1}		%	mmol kg^{-1}	mg P L^{-1}	mg P kg^{-1}	mg P kg^{-1}
0	5.18	3.41	69.0	0.84	49.2	896	5.18	3.41	69.0	0.84	49.2	896
151	4.93 ± 0.04	2.59 ± 0.76	68.7 ± 1.4	0.35 ± 0.03	32.2 ± 1.0	814 ± 3	5.26 ± 0.08	3.89 ± 0.13	68.1 ± 0.8	0.46 ± 0.01	34.6 ± 1.3	847 ± 4
978	6.07 ± 0.20	5.12 ± 0.10	65.1 ± 3.3	0.06 ± 0.00	8.5 ± 0.5	468 ± 24	5.83 ± 0.08	4.22 ± 0.10	69.8 ± 2.1	0.07 ± 0.01	13.6 ± 1.2	611 ± 39

†Values are averages of duplicate pots ± standard deviations. Data were taken from Koopmans et al. (2004).

Phosphorus desorption isotherm and desorption kinetics

Figure 6.1 shows the desorption isotherm using the soils from the pot experiment, where the uptake of P by the growing plants leads to P desorption. The isotherm was constructed by plotting P_{ox} of the initial soil and the soils of the 5- and 10-cm treatments after various periods of plant growth against P measured in 1:10 (w/v) 0.01 M $CaCl_2$ extracts. The Langmuir equation fitted very well to these data points. The $CaCl_2$ extracts were obtained after 2 h of very vigorous shaking. The vigor of shaking in batch systems is very important in the mass transfer of reactive solutes between sorption sites inside porous sorbents and bulk solution (Ogwada and Sparks, 1986a, 1986b). This was also demonstrated in a P sorption study of Barrow and Shaw (1979b); vigorous shaking caused abrasion of soil particles leading to the exposure of new surface sites and greater P sorption. Vigorous shaking thus leads to shorter diffusion distances causing an increase of P (de)sorption rates, resulting in a faster establishment of equilibrium. Vigorous shaking during the $CaCl_2$ extraction may thus have caused the equilibrium of the desorption isotherm. The fact that equilibrium may have been reached in the $CaCl_2$ extracts is thus not necessarily indicative that P desorption from Al- and Fe-(hydr)oxides inside intact soil aggregates was near equilibrium. The situation prevailing in the soil will be later analyzed using the diffusion model. Furthermore, Fig. 6.1 shows the results of the batch experiments where the kinetics of P desorption were determined. Similar to the isotherm, P_{ox} was plotted against P desorbed in 1:10 (w/v) 0.01 M $CaCl_2$ extracts as a function of time. To prevent abrasion of soil aggregates, we chose a relatively mild shaking method in the batch experiments. Under these shaking conditions, intra-aggregate diffusion may be expected to act as the rate-limiting step in P desorption. Thus, the most important experimental difference between the data points used to construct the isotherm and the data points representing the results of the batch experiments is the vigor of shaking. The kinetics of P desorption is most clearly visible for a higher P concentration in the $CaCl_2$ extracts, where the equilibrium isotherm is approached only for the batch experiment with the longest duration (408 h). However, at a low P concentration, kinetic effects are hardly visible.

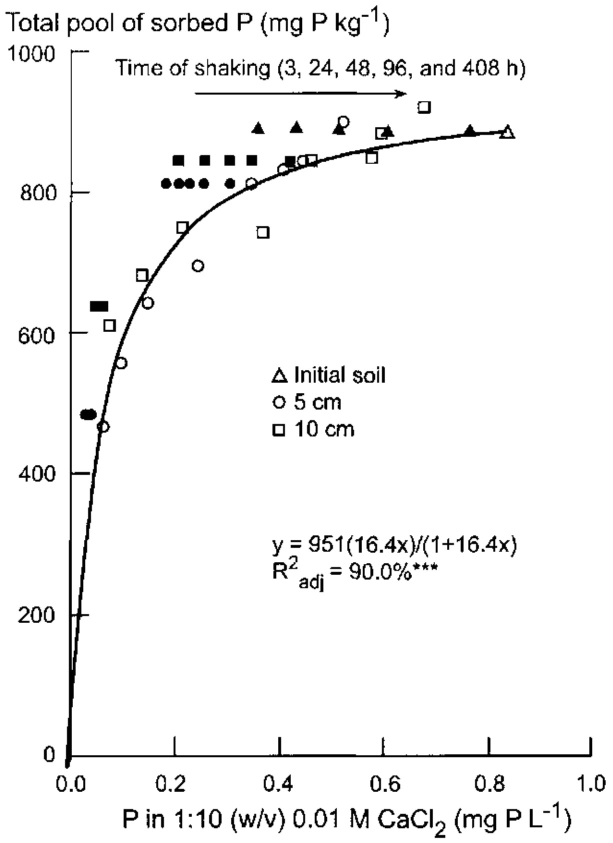

Figure 6.1. Desorption isotherm of the soils of the pot experiment (Koopmans et al., 2004) describing the relationship between the P concentration measured in 1:10 (w/v) 0.01 M $CaCl_2$ extracts (vigorous shaking) and the total pool of sorbed P (open symbols). The Langmuir equation was fitted to the data. Furthermore, the total pool of sorbed P is plotted against the P concentration as a function of time measured in 1:10 (w/v) 0.01 M $CaCl_2$ extracts obtained under mild shaking conditions in the batch experiments (closed symbols).

In Fig. 6.2, experimental and model results are shown for the P desorption kinetics of the initial soil at varying soil to solution ratios, whereas Fig. 6.3 shows results of the 1:10 (w/v) 0.01 M $CaCl_2$ extracts obtained from the soils taken from the pot experiment after plant uptake of P for 151 and 978 d. The model was calibrated with the pore volume fraction of the aggregate as a fitting parameter to predict the data presented in Fig. 6.2. We assumed a uniform radius of the soil aggregates of 1 mm, because the soil was sieved through a 2-mm sieve. The model describes the increase in the P concentration with time, using a radius of 1.0 mm and a fitted pore volume fraction of 0.035, quite well for the 1:10, 1:50, and 1:100 (w/v) 0.01 M $CaCl_2$ extracts obtained from the initial soil. For the soil to solution ratios of 1:500 and 1:1000 (w/v), the model predictions are less accurate. The model gives a reasonable prediction of the P concentration in the 1:10 (w/v) 0.01 M $CaCl_2$ extracts obtained from the soils of the 5- and 10-cm treatments sampled after 151 and 978 d of plant uptake of P.

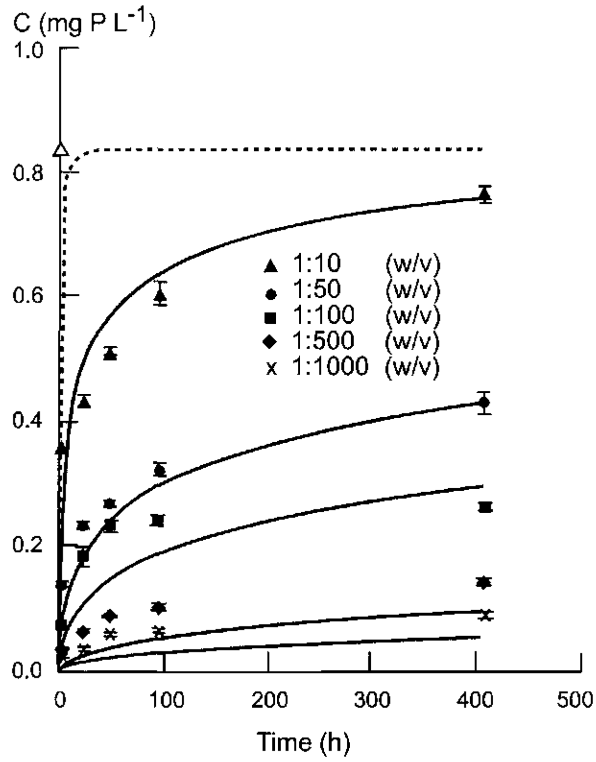

Figure 6.2. Measured (symbols) and predicted P concentrations (lines) in 0.01 M $CaCl_2$ extracts with varying soil to solution ratios as a function of time at a fitted pore volume fraction of 0.035. The $CaCl_2$ extracts were obtained from the initial soil under mild shaking conditions in the batch experiments. The open triangle represents the P concentration measured in the 1:10 (w/v) 0.01 M $CaCl_2$ extract with vigorous shaking. The dotted line represents the predicted P concentration at a soil to solution ratio of 1:10 (w/v) whereby the radius of the spherical aggregate was set at 0.1 mm.

Figure 6.4 shows the simulation of the P concentration in the micropores of the 50 concentric parts of the aggregate representing the initial soil incubated at a soil to solution ratio of 1:10 (w/v) as a function of time for relatively mild shaking conditions. The P concentration in the outer layers of the aggregate shows a fast decrease, due to an initially high P desorption rate. After 41 h, the P concentration in the outer layer decreased by 42%. This can be explained by the initially large difference between the P concentration in the outer layer of the aggregate and the P concentration in the external solution, which is the driving force of the P efflux; after 0.1 h, the P concentration in the outer layer is 25 times larger than the P concentration in the external solution (results not shown). Initially, P desorption from the solid phase of the inner layers is thus far from equilibrium with the rest of the aggregate. The concentration gradient at the interface between the outer layer of the aggregate and the external solution decreases with time. Desorption of P comes closer to equilibrium, because the concentration gradient along the radius of the aggregate is relatively small. This results in a low P flux from the aggregate to the external solution. However, there is still a concentration gradient along the radius of the aggregate, which reaches equilibrium only very slowly. After 10 000 h, equilibrium is clearly reached, because there is no concentration gradient anymore in the system. The model shows that after 10 000 h, the same P concentration is reached in the external solution (results not shown) as was obtained for 2 h of vigorous shaking (Fig. 6.2), which was shown to lead to almost equilibrium (van Erp et al., 1998).

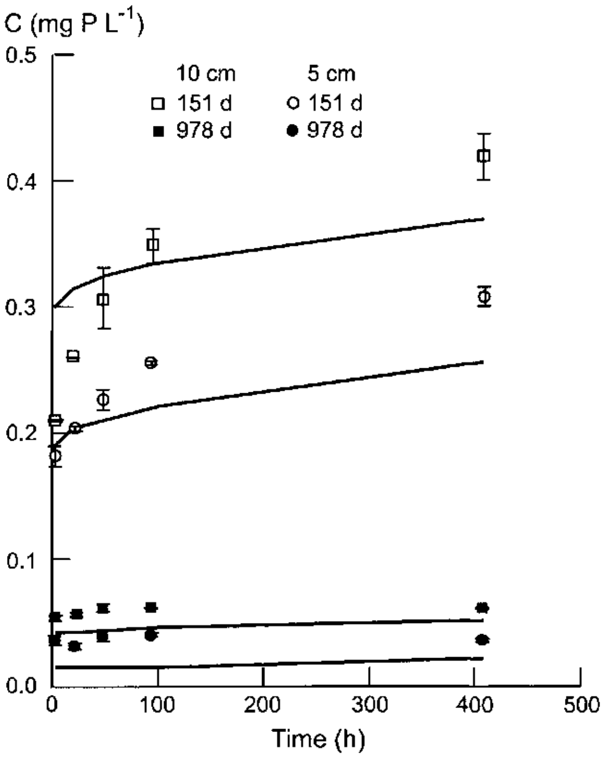

Figure 6.3. Measured (symbols) and predicted P concentrations (lines) in 1:10 (w/v) 0.01 M $CaCl_2$ extracts as a function of time. The $CaCl_2$ extracts were obtained from the soils of the 5- and 10-cm treatments sampled after 151 and 978 d of plant uptake of P in the batch experiments.

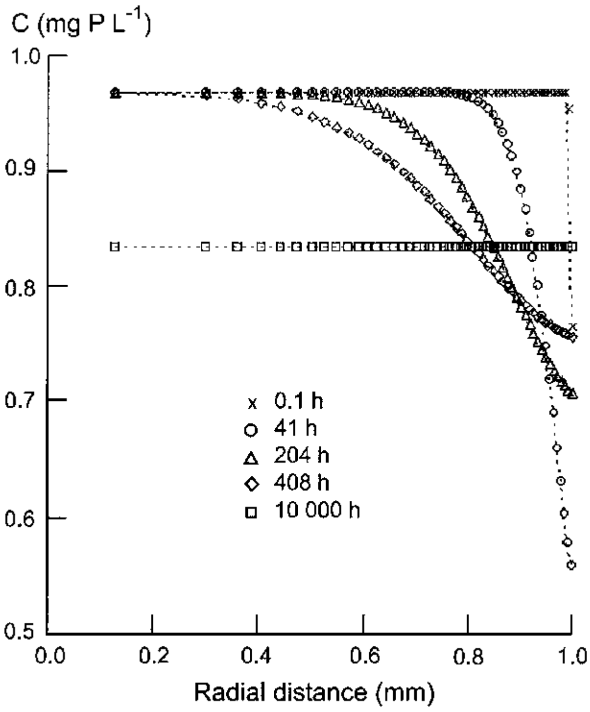

Figure 6.4. Profile of the P concentration along the radius of the spherical aggregate simulated for P desorption from the initial soil to an external solution with a soil to solution ratio of 1:10 (w/v) (x = 0 mm corresponds with the centre of the spherical aggregate).

We used the model to see how much abrasion of soil aggregates is needed in order to reproduce the results of 1:10 (w/v) 0.01 M $CaCl_2$-extractable P from the initial soil with vigorous shaking. We again simulated P desorption to an external solution with a soil to solution ratio of 1:10 (w/v) for 408 h. Instead of a 1-mm radius of the aggregate, we now used a radius of 0.1 mm, supposing that vigorous shaking caused a ten times reduction of the size of the soil aggregates. Desorption of P after 2 h was now close to equilibrium as the P concentration in the external solution amounted to 84% of the P concentration in the $CaCl_2$ extract measured with vigorous shaking (Fig. 6.2). This suggests that the soil aggregates were relatively unstable.

Dynamic simulation of the behavior of phosphorus in soil aggregates in the pot experiment

Figure 6.5 shows the simulation of the P concentration and the corresponding amount of P sorbed to the solid phase of the 50 concentric parts of the aggregate as a function of time, resulting from plant uptake of P measured in the 5-cm treatment. Simulation of the behavior of P in soil aggregates of the 10-cm treatment shows similar results (results not shown). The P concentration in the outer layers of the aggregate shows a fast decrease, due to an initially high P desorption rate. After 1000 h, the P concentration in the outer layer had decreased by 60%. As discussed above, this can be explained by the initially large concentration gradient at the interface between the outer layer of the aggregate and the external solution, which is stimulated by plant uptake of P from the soil solution. After 0.1 h, the P concentration in the outer layer is 1.5 times larger than the P concentration in the external solution (results not shown). The concentration gradient decreases with time; from 1000 h onward, the P concentration in the outer layer of the aggregate almost equals the P concentration in the external solution, resulting in lower P efflux. Nevertheless, in the initial stage of the pot experiment, the soil can easily meet the demand of the plant due to uptake of P. This will be demonstrated later using the diffusion model. In the initial stage of the simulation, the relative decrease of the amount of P sorbed to the solid phase of the outer layers of the aggregate is much smaller than what is observed for the P concentration. This is easily explained by the fact that initially the soil is nearly saturated with P, implicating that the slope of the isotherm is rather small, leading to a large response of the P concentration upon a relatively small decrease of the amount of sorbed P (Fig. 6.1 and Table 6.2). The initial fast decrease of the P concentration in the outer layers of the aggregate is only slowly replenished by P desorbed from the solid phase of the inner layers, due to slow intra-aggregate diffusion, resulting in a very steep concentration gradient along the radius of the aggregate. Desorption of P from the solid phase of the inner layers is thus far from equilibrium with the rest of the aggregate. The concentration gradient clearly becomes much less steep with time in both treatments. Apparently, desorption of P inside the aggregate comes closer to equilibrium as the soil P content is further lowered by plant uptake. This explains why kinetic effects on P desorption in the 1:10 (w/v) 0.01 M $CaCl_2$ extracts obtained from the soils of the 5- and 10-cm treatments taken from the pot experiment after plant uptake of P for 978 d are hardly visible for relatively mild shaking conditions in the batch experiments (Fig. 6.1).

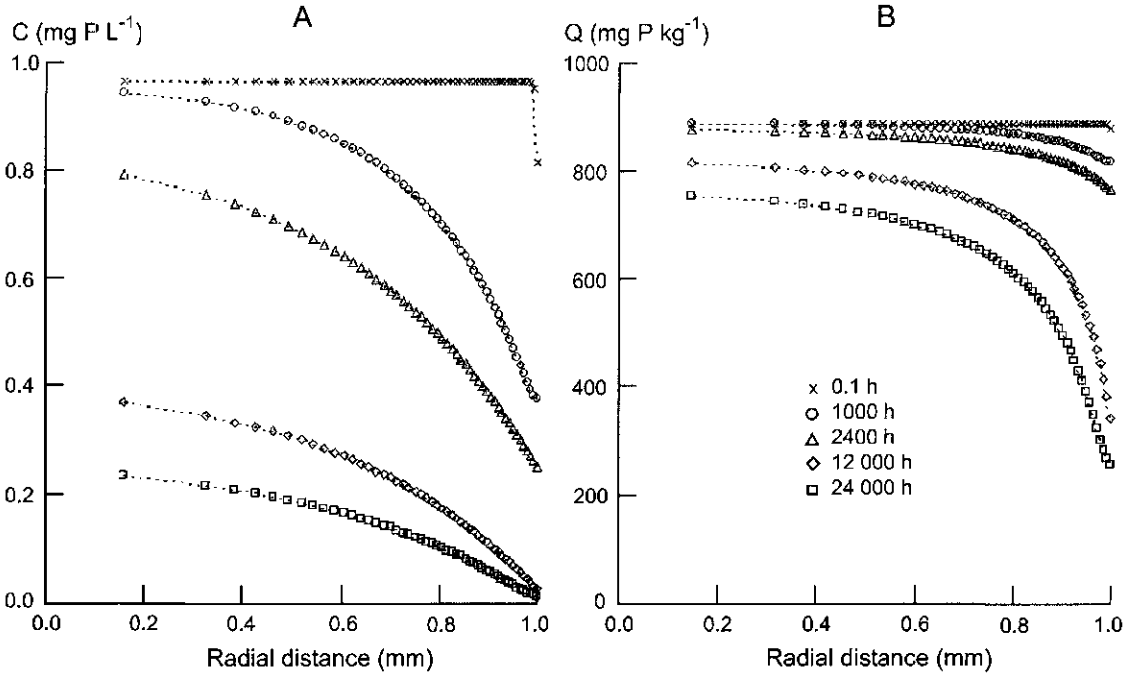

Figure 6.5. Profile of the P concentration (A) and the amount of P sorbed to the solid phase (B) along the radius of the spherical aggregate simulated for the measured plant uptake of P in the 5-cm treatment (x = 0 mm corresponds with the centre of the spherical aggregate).

Dynamic bioavailability index

Soil analysis is commonly used as a means to estimate the bioavailability of elements for plants or other organisms. Relationships between the measured concentration in a certain extract and the yield of plants growing in the field can be established by comparing both sets of data. Such relationships are widely used as a basis for fertilizer recommendations (Tunney et al., 1997). Plant growth is a dynamic process, and for an optimal growth, a certain flux of a given nutrient at the interface between the soil solution and the root is needed to satisfy the demand of the growing plant. Whether or not the soil can provide for the needs of the plant depends on the amount of the nutrient present in soil, on plant factors, and on physical and chemical soil characteristics determining the supply (van Noordwijk et al., 1990; Jungk and Claassen, 1997; Hinsinger, 2001). One often simplifies the bioavailability concept by considering that a certain fraction of the total amount of an element is bioavailable. However, this notion of bioavailability is rather static, and we propose here to use instead a dynamic concept of bioavailability that still can be applied in a rather simple way. The plant requirement can be derived by measuring the uptake under conditions that are considered optimal for plant growth in a pot or field experiment, or from literature data on the plant uptake rate of a nutrient. One can then calculate the average supply rate expressed as amount of the nutrient per unit of weight of soil per unit of time that has to be delivered by the soil in order to be able to satisfy the demand. The challenge is then to be able to estimate the potential of a given soil to fulfill this using data that can be readily collected in routine soil analysis in combination with some modeling of physical, chemical, and biological processes governing the rate of release of the nutrient from the soil and the rate of transport to the root. One can then estimate to what extent bioavailability may be limiting plant growth and, if so, what action needs to be taken to optimize the situation. This approach was used before by van Noordwijk et al. (1990) in order to develop a mechanistic model of P transport in the soil to calculate the so-called Pw value required for an optimal P uptake by crops within a growing season on the basis of plant and root density data and some physical and chemical soil characteristics. In the Netherlands, Pw (water-extractable P at a soil to solution ratio of 1:60 [v/v]) (Sissingh, 1971) is used in agricultural practice as a soil test for P fertilizer recommendations of arable land. In the approach of van Noordwijk et al. (1990), however, the emphasis was put on P transport from the soil to the root, the desorption itself being assumed to occur instantaneously. In the approach presented here, we will use the diffusion model in order to develop a simple tool that can be used to determine to what extent P desorption kinetics may be limiting plant uptake of P. This approach is based on what we will call the DBI. This DBI is analogous to the dimensionless Damköhler number, which is used in the chemical engineering literature to determine the rate-limiting step in reactive flow, that is, flow accompanied by a chemical reaction, in chemical reactors and bioreactors (van 't Riet and Tramper, 1991). The Damköhler number relates the rate of the reaction with the physical transport rate of the reactant. The DBI is the ratio of the maximal desorption rate of a given nutrient from the soil divided by the plant uptake rate, both expressed in the same units. For the plant uptake rate, one can either use a constant value related to optimal plant growth as discussed above, or the actual plant uptake rate measured in a pot or field experiment. The ratio can both be larger or smaller than one when a constant optimal plant uptake rate is used in the calculation of the index. When the index is much larger than one, the kinetics of desorption is most likely not limiting optimal plant growth for the nutrient considered, whereas values smaller than one are indicative that optimal plant uptake will not be reached unless corrective action is taken. Using the actual plant uptake rate to calculate the dynamic bioavailability index is expected to lead to values larger than or equal to one. When the kinetics of P desorption is limiting plant growth, the maximal desorption rate and the actual plant uptake rate are expected to be rather similar. However, this situation will apply only for an infinitely high root density where all soil aggregates are in direct contact with the plant root (van

Noordwijk et al., 1990). The calculated maximal desorption rate will not be reached for soil aggregates that are not in direct contact with the roots, due to transport limitations in the soil matrix. This may cause the buildup of a concentration gradient towards the root limiting further P desorption (Jungk and Claassen, 1997). Even at a dense rooting, like in pot experiments, the volume of soil that is in direct contact with the plant root is relatively small (Geelhoed et al., 1997). For a finite root density, one may thus expect that the actual plant uptake rate is consistently lower than the maximal possible desorption rate. The difference between the maximal possible desorption rate and actual uptake rate is the amount remaining in the soil, due to transport limitations in the soil between aggregates (van Noordwijk et al., 1990). The extent to which the maximal desorption kinetics and the actual plant uptake approach each other is thus a function of root density, but also of physical characteristics, like the water content and tortuosity of the soil, determining the rate of transport in the soil (Jungk and Claassen, 1997).

We used the DBI to determine whether or not P desorption kinetics limited the bioavailability of P for plant uptake in the pot experiment during some time. The index was calculated as the ratio of the simulated maximal flux from the aggregate to the soil solution and the measured plant uptake rate (Table 6.3). Figure 6.6 shows the simulated maximal P desorption rate and actual plant uptake rate measured in the 10-cm treatment as a function of time; the results of the 5-cm treatment give a similar picture (results not shown). The maximal P desorption rate shows a fast decrease with time. This can be explained by the decrease of the concentration gradient between the outer layer of the aggregate and the external solution, which is the driving force of the P efflux. The measured plant uptake rate shows an irregular but much slower decrease. In the period between 0 and 236 d, the DBI is much larger than one (Fig. 6.6), since the maximal possible P desorption rate is much larger than the measured plant uptake rate, which may result in a buildup of P in soil solution causing an increased risk of P leaching. This high value of the DBI was caused by the large amount of desorbable P in the soil we used. The P content measured in the grass harvested in the period between 0 and 236 d is (much) larger than what may be considered as optimal (4 g P kg^{-1} of dry matter) in conventional agricultural practice in the Netherlands (Agterberg and Henkens, 1995). Apparently, plant uptake of P is initially not limited by P desorption, but is governed by other factors like biological constraints in the uptake of P by the root (Jungk and Claassen, 1997). The curves for the variation of the maximal desorption rate and the actual plant uptake rate approach each other after a while and run parallel in the later stage of the pot experiment. The curve for the P content of the harvested grass and that of the calculated maximal desorption rate show interestingly a high similarity as a function of time (Fig. 6.6). The DBI fluctuates around a constant value of two after 236 d, so the measured plant uptake rate is half of the maximal possible desorption rate in this period. During the pot experiment, not all soil aggregates may have been in direct contact with the roots, which explains why the DBI stabilizes at a value somewhat larger than one, due to additional transport limitations, as discussed above. The decrease of the DBI to a value of around two coincides with a large decrease of the P content in the harvested grass to a value (far) below 3 g P kg^{-1} of dry matter (Table 6.3). For an optimal nutritional value of grass to serve as feed for high yielding dairy cows, it should not contain less than 3 g P kg^{-1} of dry matter if grass is the only component of the diet (Valk et al., 1999). This implies that the grass harvested in the period between 236 and 978 d would have too little nutritional value. Apparently, the supply rate of P from soil to the root in this period cannot meet the demand needed for an optimal P uptake by the grass. Corrective action like the application of P fertilizer thus seems to be necessary in order to restore the optimal plant uptake rate.

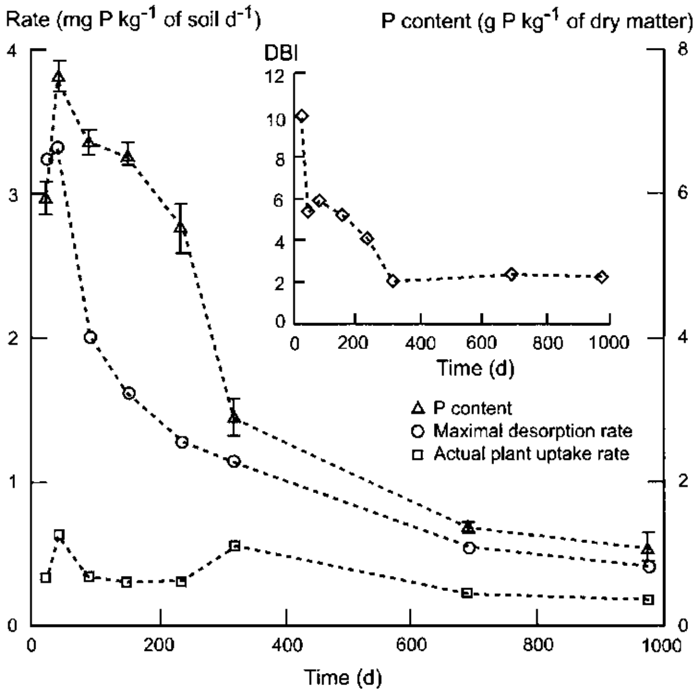

Figure 6.6. Simulated maximal P desorption rate from the spherical aggregate and the actual plant uptake rate measured and the P content measured in the grass harvested in the 10-cm treatment as a function of time. The inserted figure shows the dynamic bioavailability index (DBI) as a function of time.

Table 6.3. Phosphorus content of the harvested grass†, the plant uptake rate of P, the calculated maximal P desorption rate from the spherical aggregate, and the dimensionless dynamic bioavailability index (DBI)‡.

	5 cm				10 cm			
Time	P content	Plant uptake rate	Maximal P desorption rate	DBI	P content	Plant uptake rate	Maximal P desorption rate	DBI
d	g P kg^{-1} of dry matter	mg P kg^{-1} of soil d^{-1}			g P kg^{-1} of dry matter	mg P kg^{-1} of soil d^{-1}		
22	5.93±0.33	0.43	3.23	7.4	5.94±0.23	0.32	3.23	10.1
41	6.81±0.32	0.82	3.22	3.9	7.61±0.21	0.62	3.29	5.3
88	5.80±0.15	0.50	1.92	3.8	6.70±0.16	0.34	2.01	5.9
151	5.32±0.16	0.42	1.51	3.6	6.54±0.17	0.31	1.62	5.2
236	4.61±0.25	0.44	1.15	2.7	5.52±0.34	0.31	1.27	4.0
319	2.34±0.12	0.73	0.97	1.3	2.87±0.27	0.55	1.14	2.1
692	1.09±0.08	0.26	0.51	2.0	1.34±0.07	0.22	0.54	2.5
978	0.75±0.03	0.18	0.41	2.3	1.09±0.19	0.18	0.41	2.3

†Values are averages ± standard deviations. Data were taken from Koopmans et al. (2004).

‡The DBI was calculated as the ratio of the maximal P desorption rate and the measured plant uptake rate of P.

To apply this dynamic concept of bioavailability in the field, one needs to account for the lower root density and a less optimal water content. Both factors would lower the bioavailability of P for a given soil compared to the pot experiment. The dimensionless bioavailability index needed for optimal plant growth may thus be higher than two. However, the plant can explore a larger volume of soil in the field than in those of the 5- or 10-cm treatments used in the pot experiment. This leads to a lowering of the desorption rate from the aggregates per unit of weight of soil that is required for an optimal plant growth, which improves the bioavailability situation. How these two opposing effects work out in practice with respect to the application of the proposed bioavailability index requires more research. The concept presented here could be seen as a promising onset that needs to be developed further.

Conclusions

- In a previous study, an equilibrium desorption isotherm was determined in a pot experiment where grass was cropped on a P rich noncalcareous sandy soil without P addition. In the batch experiments, using soils from the pot experiment, kinetics of P desorption was clearly visible for relatively high P concentrations in the 1:10 (w/v) 0.01 M $CaCl_2$ extracts. The equilibrium isotherm was approached only for the batch experiment with the longest duration. At a low P concentration, kinetic effects were hardly visible.
- A diffusion model, where the Langmuir equation derived from the equilibrium isotherm was used to calculate the buffering behavior of P, gave a good description of the P concentration in 0.01 M $CaCl_2$ extracts obtained from the initial soil and gave reasonable descriptions for the soils from the 5- and 10-cm treatments that were collected after various times of plant uptake of P.
- According to the results of the diffusion model, P desorption from the solid phase of the inner layers was far from equilibrium with the rest of the aggregate during the growth of plants in the initial stage of the pot experiment. However, the transport inside the aggregate became extremely slow as the soil P content was further lowered by plant uptake. This explains why kinetic effects on P desorption in the 1:10 (w/v) 0.01 M $CaCl_2$ extracts obtained from the soils sampled after long-term plant uptake under relatively mild shaking conditions were hardly visible.
- A simple tool is presented, referred to as the DBI, used to determine whether kinetics of P desorption is expected to limit plant uptake. This

tool is the dimensionless ratio of the maximal diffusive flux from soil aggregates to solution, calculated with the model, and the plant uptake rate measured in the pot experiment. Based on the DBI, P uptake in the initial stage of the pot experiment was not limited by P desorption. However, with time, the supply rate of P from soil to the root cannot meet the demand needed for an optimal P uptake anymore. The concept presented here could be seen as a promising onset to a new dynamic approach of bioavailability.

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Summary and conclusions

Introduction

Phosphorus (P) is an essential nutrient for plant growth. In highly weathered tropical soils, but also in many soils in temperate areas which have not received P fertilizers, P is present in relatively short supply, leading to limitation of plant growth. To overcome P deficiency, application of P fertilizer is needed. However, in soils under areas with intensive livestock farming, P contents have often increased as a result of heavy applications of animal manure for decades. In this case, the total P input has by far exceeded P removal in harvested crops. Soil P accumulation can increase the potential for P loss to surface waters, contributing to P enrichment of surface waters and eutrophication.

n the Netherlands, intensive livestock farming is mainly located on noncalcareous sandy soils. In general, the sorption capacity of these soils for P is limited, and as a result, P can be transported to ground water via leaching, especially in flat areas with shallow ground water tables. Mining soil P (i.e., harvesting P taken up from the soil by a crop grown without external P addition, followed by the off-site removal of the above ground plant parts) has been proposed as a possible remediation strategy to decrease the risk of P leaching. However, quantitative information is scarce on the long-term change in soil P after P application has ceased. To fully evaluate the potential of mining soil P, quantitative information is needed on changes in different soil P pools induced by mining soil P. Another important issue is the extent to which uptake of P from P-enriched soil may be considered as an equilibrium desorption reaction. In the case of equilibrium, a desorption isotherm, describing the long-term equilibrium relationship between P in soil solution and the total pool of reversibly sorbed P, can in principle be used to estimate the total amount of P available for uptake and leaching. However, in the case of disequilibrium, kinetics of P desorption from the solid phase to the soil solution determines the availability of P for uptake and leaching. The general objective of the present study was to gain knowledge on the speciation and desorption kinetics of P in P-enriched noncalcareous sandy soils, with special emphasis on the analysis of soil samples at varying stages of P depletion.

Major research findings

A recent approach to characterize P-enriched agricultural soils involves the application of split-line models to determine a soil P threshold (change point or break point) in soil P quantity-intensity (q-i) relationships. Thresholds define a critical level in soil P quantity or soil extractable P above which a soil exhibits an increased risk for P loss. Thresholds can thus be used for the identification of problem soils. In Chapter 2, effects of methodology, soil chemical characteristics, and soil P levels on the variation in soil P q-i relationships were explored using a simple modeling exercise (based on Langmuir adsorption theory) along with data from literature. Soil P q-i relationships highly depend upon the soil to solution ratio, used to assess the P intensity parameter, the adsorption capacity (Q_{max}) and the binding strength (K) of the soil, and the total range in soil extractable P. This, in turn, affects the calculation of a threshold in soil extractable P. Because of the sensitivity of calculated thresholds to methodological and soil chemical conditions, the use of this approach in the risk assessment of P loss from agricultural soils must be done with great care.

In agricultural soils treated with large amounts of animal manure over long periods, increased inorganic and organic P contents can be expected. However, little information exists on changes of inorganic and organic P fractions and the distribution of P among the various P compounds in these soils. In Chapter 3, the speciation of P was characterized in both NaOH-Na_2EDTA and 1:5 (w/v) water extracts by using both classical wet chemical analysis and solution ^{31}P nuclear magnetic resonance (NMR) spectroscopy. These soils were sampled from the top 5 cm of grassland sites which had been treated for a period of 11 years with either no fertilizer (control), N fertilizer (no P application), N-P-K fertilizer, or different animal manures. Concentrations of inorganic P were highly elevated in the NaOH-Na_2EDTA extracts of the soils amended with N-P-K and animal manures, while organic P increased only in the soil treated with pig slurry. Water-extractable P showed similar trends. Orthophosphate monoesters were the main organic P compounds in all soils, as indicated by ^{31}P NMR. Long-term application of large amounts of P fertilizer and animal manures on grassland caused an accumulation of inorganic P in the topsoil, which may result in an increase of the risk of inorganic P leaching from the topsoil to the subsoil.

In Chapter 4, two P-enriched soils were incubated with dialysis membrane tubes filled with hydrous Fe-(hydr)oxide (DMT-HFO) to create soil samples at varying stages of P depletion. Various extraction methods were used to characterize the change in different soil P pools. Total amounts of P removed from these soils by the DMT-HFO technique were relatively small compared with the large initial amounts of ammonium oxalate-extractable P (P_{ox}) in the two P-enriched soils. The relative decrease of the amounts of P extractable with water (1:2 [w/v] and 1:60 [v/v]) and 0.01 M $CaCl_2$ (1:10 [w/v]) was much larger than the relative decrease of P_{ox}. Therefore, the desorption and subsequent removal of a relatively small amount of P from soil may cause a significant decrease of the soil potential to release dissolved P. Furthermore, the suitability of the DMT-HFO to act as an 'infinite' P sink for P desorption was evaluated. Desorption results were described with a simple kinetic Langmuir equation. The uncertainty of the estimated k_d (desorption constant) and Q_0 (amount of P initially adsorbed) parameters was calculated. Although the model fit was good for both soils, errors in k_d and Q_0 were relatively large. Therefore, the DMT-HFO method could not be used to determine the desorption constants of the soils. Values of k_d and Q_0 obtained by this method should not be used in modeling studies.

In Chapter 5, the method of cropping grass was used to deplete a P-enriched soil in a long-term greenhouse pot experiment. The availability of soil P for uptake by plants and the effectiveness of mining soil P to decrease P in different pools were assessed. Phosphorus in the soil solution and the total pool of sorbed P were estimated using 1:10 (w/v) 0.01 M $CaCl_2$ extracts and P_{ox}, respectively. Using these data for soil samples at varying stages of P depletion, an equilibrium desorption isotherm was constructed. The Langmuir equation gave a very good description of the isotherm. In the long-term, 65% of P_{ox} in the initial soil can be removed through P uptake by plants, as was calculated from the Langmuir equation and a critical P concentration in soil solution at which P uptake can just be maintained. Thus, P_{ox} may be largely plant available. From the strong nonlinearity of the desorption isotherm, it can be understood why the relative decrease of the P concentration in the $CaCl_2$ extracts was much larger than the relative decrease of P_{ox}. These results are in agreement with those obtained from the laboratory experiment, where the change in different soil P pools was characterized after removal of P from two P-enriched soils by an artificial P sink (Chapter 4). Mining soil P decreased the P concentration in soil solution effectively and, therefore, the risk of P leaching from the P-enriched soil.

In the soils of the pot experiment collected after various times of plant growth, the total pool of sorbed P seemed to be close to equilibrium with P in the $CaCl_2$ extracts. Vigorous shaking of these extracts, causing abrasion of soil aggregates and leading to a faster establishment of equilibrium, may have caused the apparent equilibrium of P desorption. Therefore, this result could not be used to determine whether P desorption from Al- and Fe-(hydr)oxides inside intact soil aggregates was near equilibrium during plant growth in the pot experiment. This requires a dynamic modeling approach of desorption kinetics for conditions where soil aggregates are not degraded by vigorous shaking. In Chapter 6, the initial soil and some P-depleted soils were used to determine the P desorption kinetics in batch experiments under relatively mild shaking conditions. Kinetic effects were clearly visible for relatively higher P concentrations in the 1:10 (w/v) 0.01 M $CaCl_2$ extracts. The equilibrium desorption isotherm was approached only for the batch experiment with the longest duration of shaking. At a low P concentration, kinetic effects were hardly visible. A diffusion model was used to simulate the P desorption kinetics from a spherical aggregate. The Langmuir equation, derived from the desorption isotherm, was used to calculate P buffering during transport of P through the aggregate to the soil solution. The model was calibrated with data from the batch experiments. According to the model, in the initial stage of the pot experiment, P desorption from the solid phase of the inner layers was far from equilibrium with the rest of the aggregate, but desorption came closer to equilibrium as the soil P content decreased by plant uptake. This explains why kinetic effects on P desorption in the $CaCl_2$ extracts of the soils subjected to desorption via uptake over a long time were hardly visible under relatively mild shaking conditions.

Availability of soil P for uptake by plants is usually assessed by the use of extraction methods. However, this notion of bioavailability is rather static. For an optimal growth, a certain flux of a given nutrient at the interface between the soil solution and the root is needed to satisfy the demand of the growing plant. Whether or not the soil can provide for the needs of the plant depends on the amount of the nutrient present in soil, on plant factors, and on physical and chemical soil characteristics determining the supply. Also in Chapter 6, a dynamic concept was proposed to interpret the bioavailability of P based on the kinetics of desorption. This concept, referred to as the dynamic bioavailability index (DBI), is the dimensionless ratio of the maximal diffusive flux of P from soil aggregates to the soil solution, calculated with the model, and the rate of uptake required to obtain an optimal P content in the growing plants. For the pot experiment, the DBI was calculated by using the measured rate of uptake. Initially, the DBI was much larger than one: the maximal possible desorption rate exceeded the uptake rate, so P uptake was not limited by P desorption. After a certain period, the DBI stabilized at a value somewhat larger than one, due to transport limitations in the soil matrix. This decrease coincided with a large decrease of the P content in the grass to a value (far) below what is considered as optimal: the supply rate of P from soil to the root could not meet the demand needed for an optimal P uptake anymore.

Conclusions

- Soil P q-i relationships are highly dependent upon experimental conditions, soil chemical characteristics, and soil extractable P. This, in turn, affects the calculation of a threshold in soil extractable P. Use of thresholds in risk assessment of P loss from agricultural soils must be done with great care.
- Phosphorus accumulated mainly in the inorganic form in the top 5 cm of grassland soils, exposed to long-term applications of large amounts of either N-P-K fertilizer or different animal manures; this was shown using 0.25 M NaOH-0.05 M Na_2EDTA and 1:5 (w/v) water extracts. Orthophosphate monoesters were the main organic P compounds extracted. Thus, risk of P loss from the top 5 cm to the subsoil was mainly related to inorganic P.
- Removal of a relatively small amount of P from P-enriched soils by an artificial P sink resulted in a relatively large decrease of 1:2 (w/v) and 1:60 (v/v) water- and 1:10 (w/v) 0.01 M $CaCl_2$-extractable P. In contrast, the relative decrease of P_{ox} was much smaller. Risk of P leaching from these P-enriched soils may already decrease upon the removal of only a relatively small amount of P from soil.
- In the pot experiment, the total pool of P sorbed to the solid phase (P_{ox}) seemed to be in equilibrium with the P concentration in 1:10 (w/v) 0.01 M $CaCl_2$ extracts. Using these data for soil samples at varying stages of P depletion, equilibrium desorption isotherm was constructed. Based on the desorption isotherm and a critical P concentration in soil solution where uptake of P can just be maintained, 65% of P_{ox} in the initial soil was estimated to be available for uptake in the long-term.
- Continuous cropping of grass without external P addition under greenhouse conditions caused a fast and relatively large decrease of the P concentration in the 1:10 (w/v) 0.01 M $CaCl_2$ extracts. This suggests that mining soil P may be an effective remediation strategy to decrease the risk of P leaching from P-enriched soils. However, this suggestion has to be confirmed in the field.
- In the batch experiments, where kinetics of P desorption was determined in 1:10 (w/v) 0.01 M $CaCl_2$ extracts obtained from soils of the pot experiment under relatively mild shaking conditions, kinetic effects were clearly visible for relatively high P concentrations in the $CaCl_2$ extracts. The equilibrium isotherm was approached only for the batch experiment with the longest duration. At a low P concentration, kinetic effects were hardly visible. Therefore, a low P concentration in

the soil solution as obtained by mining soil P is expected to remain relatively constant.

- According to the results of the diffusion model, P desorption from the solid phase of the inner layers of a spherical aggregate was far from equilibrium with the rest of the aggregate during the growth of plants in the initial stage of the pot experiment. However, the transport inside the aggregate became extremely slow as the soil P content was further lowered by plant uptake. This explains why kinetic effects on P desorption in the $CaCl_2$ extracts obtained from the soils sampled after long-term plant uptake under relatively mild shaking conditions were hardly visible.
- A simple tool, referred to as the DBI, was used to determine whether kinetics of P desorption are expected to limit uptake. Based on the DBI, P uptake in the initial stage of the pot experiment was not limited by P desorption. However, with time, the supply rate of P from soil to the root could not meet the demand needed for an optimal P uptake anymore. The concept presented here could be seen as a promising onset to a new dynamic approach of bioavailability.

Samenvatting en conclusies

Inleiding

Fosfor (P) is een essentieel nutriënt voor plantengroei. In verweerde tropische gronden, maar ook in veel gronden in gematigde gebieden die niet zijn bemest, is de beschikbaarheid van P voor plantenopname vaak te laag voor optimale groei. Het toedienen van P in kunstmest of dierlijke mest is dan noodzakelijk om het gebrek aan P in de grond op te heffen. Het P-gehalte van intensief gebruikte landbouwgronden in West-Europa en delen van de Verenigde Staten met intensieve veehouderij is vaak hoog omdat gedurende lange tijd hoeveelheden kunstmest en dierlijke mest werden toegediend die de afvoer van P met het gewas in ruime mate overschreden. De ophoping van P in de bodem leidt tot grotere verliezen van P naar het grond- en oppervlaktewater. Verrijking van het oppervlaktewater met P leidt tot ongewenste eutrofiëring.

De intensieve veehouderij komt in Nederland voornamelijk voor op kalkarme zandgronden. Het vermogen van deze gronden om P te binden is beperkt. Hierdoor spoelt P relatief gemakkelijk uit naar het grond- en oppervlaktewater. Dit gebeurt vooral in vlakke gebieden met ondiepe grondwaterstanden en met een intensief afwateringsstelsel. Uitmijnen, het onttrekken van P aan de grond door middel van het oogsten en afvoeren van een gewas zonder P-bemesting, is mogelijk een maatregel om het risico van P-uitspoeling uit dergelijke gronden te verminderen. Er bestaat echter weinig kwantitatieve informatie over veranderingen op de lange termijn in de totale hoeveelheid P in de grond en de verdeling daarvan over de verschillende vormen van P (speciatie) nadat het toedienen van P is gestopt. Deze informatie is noodzakelijk om de mogelijkheden van uitmijnen goed te kunnen beoordelen. Een andere belangrijke vraag is of de opnamesnelheid van P door planten uit het bodemvocht van een met P verrijkte grond in evenwicht is met de desorptiesnelheid van P dat gebonden is aan de vaste fase van de bodem. De relatie tussen de P-concentratie in het bodemvocht en de totale hoeveelheid gebonden P wordt met een zogenaamde desorptie-isotherm beschreven. In het geval van evenwicht kan een dergelijke isotherm worden gebruikt om de totale hoeveelheid P te schatten die beschikbaar is voor opname door planten en uitspoeling. Als de desorptiereactie daarentegen niet beschouwd mag worden als een evenwichtsreactie, dan wordt de beschikbaarheid van P bepaald door de desorptiesnelheid (kinetiek). Het doel van deze studie is om informatie te verkrijgen over de speciatie en desorptiekinetiek van P bij het uitmijnen van bemeste kalkarme zandgronden.

Belangrijke onderzoeksresultaten

Een benadering in recente literatuur om met P verrijkte landbouwgronden te karakteriseren is het afleiden van een drempelwaarde voor de hoeveelheid P in de bodem waarboven het risico van het optreden van P-verliezen fors toeneemt. Deze drempelwaarde kan worden gebruikt voor het identificeren van gronden die een mogelijk probleem vormen voor de kwaliteit van het oppervlaktewater. Voor het afleiden van deze drempelwaarde wordt gebruik gemaakt van een zogenaamde gebroken-lijn model die de relatie beschrijft tussen een kwantiteit (hoeveelheid) aan P in de bodem en intensiteit (concentratie) aan P in het bodemvocht, de zogenaamde kwantiteit-intensiteit relaties. In Hoofdstuk 2 zijn de effecten onderzocht van extractiemethoden, bodemchemische eigenschappen en het P-gehalte van de grond op de variatie van kwantiteit-intensiteit relaties en de drempelwaarde. Hierbij is gebruik gemaakt van een eenvoudig Langmuir-model en van data uit de literatuur. Kwantiteit-intensiteit relaties worden in sterke mate beïnvloed door de verhouding tussen de hoeveelheid grond en het volume van de extractievloeistof bij het vaststellen van de P-intensiteit. Daarnaast spelen de adsorptiecapaciteit (Q_{max}) en de bindingssterkte (K) van de grond en de hoeveelheid P die geëxtraheerd kan worden een belangrijke rol. De berekende drempelwaarde wordt hierdoor beïnvloed. Vanwege de gevoeligheid van drempelwaarden voor de gebruikte methoden en bodemchemische condities is deze benadering voor het beoordelen van het risico van P-uitspoeling alleen zinvol indien de condities waaronder drempelwaarden worden afgeleid worden gestandaardiseerd.

In landbouwgronden waaraan gedurende lange tijd grote hoeveelheden dierlijke mest zijn toegediend worden (sterk) verhoogde gehalten aan anorganisch en organisch P verwacht. Er is echter weinig informatie voorhanden over de speciatie van P in dergelijke gronden. In Hoofdstuk 3 is de speciatie van P gekarakteriseerd met behulp van klassieke nat-chemische analysemethoden en ^{31}P kernmagnetische resonantiespectrometrie (NMR) in extracten met zowel NaOH-Na_2EDTA als water (1:5 [g/v]). De grondmonsters waren afkomstig van de bovenste 5 cm van verschillende veldjes op grasland die gedurende een periode van 11 jaren waren behandeld zonder kunstmest (controle), N-kunstmest (zonder P), N-P-K-kunstmest of verschillende soorten dierlijke mest. Orthofosfaat-monoesterverbindingen waren in de extracten van alle grondmonsters kwantitatief gezien de belangrijkste organische P-vormen (NMR-analyse). De anorganisch P-concentraties in de NaOH-Na_2EDTA-extracten van de gronden die waren behandeld met N-P-K-kunstmest en verschillende soorten dierlijke mest waren in sterke mate verhoogd, terwijl de organisch P-concentratie alleen toenam bij de grond die behandeld was met varkensdrijfmest. Eenzelfde trend was zichtbaar in de resultaten van het met water geëxtraheerde P. Toediening van P via kunstmest en dierlijke mest aan grasland leidt dus voornamelijk tot ophoping van anorganisch P in de bovengrond (0-5 cm). Hierdoor neemt het risico van het uitspoelen van anorganisch P uit de bovengrond naar dieper gelegen bodemlagen toe.

In Hoofdstuk 4 zijn in een schudexperiment twee met P verrijkte grondmonsters geïncubeerd met dialysemembraanzakjes die gevuld waren met een waterige Fe-(hydr)oxide-suspensie (DMT-HFO). Hierdoor desorbeert P van de grond naar de schudoplossing en wordt het gedesorbeerde P door de DMT-HFO opgenomen. Op deze wijze zijn grondmonsters in verschillende stadia van uitmijning gecreëerd. De hoeveelheden P die werden opgenomen door de DMT-HFO waren relatief klein ten opzichte van de totale hoeveelheden anorganisch P in de twee oorspronkelijke grondmonsters. De totale hoeveelheid anorganisch gebonden P is geschat met zure ammoniumoxalaatoplossing (P_{ox}). Vervolgens zijn extractiemethoden met een verschillende sterkte gebruikt om de speciatie van P in de grondmonsters in verschillende stadia van uitmijning te karakteriseren. De relatieve afname van de hoeveelheden P die werden geëxtraheerd met water (1:2 [g/v] en 1:60 [v/v]) en 0.01 M $CaCl_2$ (1:10 [g/v]) was veel groter dan de afname van P_{ox}. Bij een relatief geringe afname van de totale hoeveelheid gebonden P in de grond vindt een veel grotere daling plaats van de P-concentratie in het bodemvocht ten gevolge van het sterke niet-lineaire karakter van de relatie tussen de hoeveelheid gebonden P in de grond en de P-concentratie in het bodemvocht bij evenwicht (ad- of desorptie-isotherm). In Hoofdstuk 4 is ook de geschiktheid onderzocht van de DMT-HFO-techniek om als een oneindige P-sink te functioneren voor P-desorptie. De resultaten van de desorptie van P zijn beschreven met een eenvoudige kinetische Langmuir-vergelijking. De onzekerheid is berekend van de geschatte parameters k_d (desorptieconstante) en Q_0 (initiële hoeveelheid geadsorbeerd P). Alhoewel het model voor beide gronden een goede beschrijving gaf van de resultaten was de onzekerheid in k_d en Q_0 relatief groot. De DMT-HFO-techniek kan dus niet worden gebruikt om deze constanten te schatten. Waarden van k_d en Q_0 die zijn verkregen met deze methode kunnen niet gebruikt worden in modelstudies.

In Hoofdstuk 5 is gras gebruikt om een met P verrijkte grond uit te mijnen in een potproef. Deze potproef is uitgevoerd in een kas over een relatief lange periode (978 dagen), waardoor grondmonsters zijn gecreëerd in verschillende stadia van uitmijning. De beschikbaarheid van P in de grond voor opname door planten is onderzocht evenals de afname van de hoeveelheid P en de veranderingen in de speciatie van P. Fosfor in het bodemvocht en de totale hoeveelheid gebonden P zijn geschat met behulp van respectievelijk $CaCl_2$-extractie en de P_{ox}-methode. Met behulp van deze data is een desorptie-isotherm geconstrueerd die goed kan worden beschreven met de Langmuir-vergelijking. Op basis van een P-concentratie in het bodemvocht waar planten nog net in staat zijn om P op te nemen kon met deze vergelijking berekend worden dat op de lange termijn 65% van de oorspronkelijke hoeveelheid P_{ox} uit de grond kan worden opgenomen; P_{ox} blijkt dus grotendeels beschikbaar voor plantenopname. De relatieve afname van de P-concentratie in de $CaCl_2$-extracten is evenwel veel groter dan de afname van P_{ox}. Dit wordt veroorzaakt door de sterke niet-lineariteit van de desorptie-isotherm. Deze resultaten zijn in overeenstemming met die van het schudexperiment waar P door middel van een kunstmatige sink is onttrokken aan de grond (Hoofdstuk 4). Uitmijnen verlaagt de P-concentratie in het bodemvocht dus relatief snel en hierdoor eveneens het risico van P-uitspoeling.

De totale hoeveelheid gebonden P in de grondmonsters van de potproef na verschillende perioden van plantengroei lijkt ogenschijnlijk in evenwicht met de P-concentratie in de $CaCl_2$-extracten. Dit wordt vermoedelijk veroorzaakt door krachtig schudden van deze extracten waardoor bodemaggregaten kapotgaan en het evenwicht zich snel instelt. Hierdoor was het niet mogelijk om te bepalen of gedurende de groei van planten in de potproef de desorptie van P binnen intacte bodemaggregaten (bijna) in evenwicht was. Dit vereist een dynamische en modelmatige benadering met als randvoorwaarde dat bodemaggregaten niet kapotgaan door krachtig schudden. In Hoofdstuk 6 zijn de oorspronkelijke grond en enkele uitgemijnde grondmonsters van de potproef gebruikt om de P-desorptiekinetiek vast te stellen in schudexperimenten waarbij een relatief milde schudmethode is gebruikt. Kinetische effecten waren duidelijk zichtbaar bij hogere P-concentraties in de $CaCl_2$-extracten. De desorptie-isotherm (evenwicht) werd alleen benaderd door het schudexperiment met de langste duur. Kinetische effecten waren nauwelijks zichtbaar bij een lagere P-concentratie. Vervolgens is een diffusiemodel gebruikt om de kinetiek van P-desorptie in een bolvormig aggregaat te voorspellen. De Langmuir-vergelijking voor de desorptie-isotherm is gebruikt om het bufferende vermogen van de grond gedurende het transport van P door het aggregaat naar het bodemvocht te berekenen. Het model is gekalibreerd met de data van de schudexperimenten. Volgens de voorspellingen van het model was de desorptie van P in de binnenste lagen van het aggregaat niet in evenwicht met die in de rest van het aggregaat. De desorptie van P kwam dichterbij evenwicht naarmate het P-gehalte van de grond afnam door opname in het gras. Dit verklaart waarom er in de $CaCl_2$-extracten van grondmonsters die langdurig waren uitgemijnd nauwelijks kinetische effecten op P-desorptie zichtbaar waren.

De beschikbaarheid van P in de bodem voor opname door planten wordt doorgaans bepaald door middel van extractiemethoden. Deze interpretatie van de biobeschikbaarheid van P houdt echter weinig rekening met de desorptiekinetiek van P. Voor een optimale groei is er een bepaalde transportsnelheid nodig van een nutriënt van de grond naar de plantenwortels. Of de grond al dan niet kan voorzien in de behoefte van de plant aan een specifiek nutriënt hangt af van de hoeveelheid nutriënt in de grond, plantenfactoren en fysische en chemische bodemkarakteristieken die de snelheid bepalen waarmee de grond het desbetreffende nutriënt kan leveren. In Hoofdstuk 6 is een concept voorgesteld om de biobeschikbaarheid van P te interpreteren op basis van de desorptiekinetiek. De dynamische biobeschikbaarheidsindex (DBI) is de dimensieloze verhouding tussen de maximale transportsnelheid van P vanuit de bodemaggregaten naar het bodemvocht, zoals berekend met het model, en de opnamesnelheid die nodig is om een optimaal P-gehalte te verkrijgen in de groeiende planten. In Hoofdstuk 6 is de DBI berekend op basis van de in de potproef gemeten opnamesnelheid van P door het gras. De waarde van de DBI was in het begin van de potproef veel groter dan één: de maximale desorptiesnelheid was dus hoger dan de opnamesnelheid, waardoor de opname van P door het gras niet werd beperkt door P-desorptie. De DBI stabiliseerde na een zekere periode op een lagere waarde die hoger was dan één als gevolg van beperkt transport van P door de bodemmatrix. De afname van de DBI viel samen met een afname van het P-gehalte in het gras tot beneden de waarde die wordt beschouwd als optimaal. De snelheid waarmee de grond P kon leveren voor opname door de plantenwortels kon dus niet langer meer in de behoefte voorzien voor een optimaal P-gehalte.

Conclusies

- Kwantiteit-intensiteit relaties zijn in sterke mate afhankelijk van experimentele condities, bodemchemische karakteristieken en de hoeveelheid P die geëxtraheerd kan worden uit de grond. Dit beïnvloedt de uit deze relaties afgeleide drempelwaarden die worden gebruikt voor het beoordelen van het risico van P-verliezen uit met P verrijkte gronden. Deze benadering is alleen zinvol indien de condities waaronder drempelwaarden worden afgeleid worden gestandaardiseerd.

- Het toedienen van grote hoeveelheden P via kunstmest of dierlijke mest aan grasland leidt tot ophoping van P in voornamelijk anorganische vorm in de bovenste 5 cm van de bodem. Orthofosfaat-monoesterverbindingen waren kwantitatief gezien de belangrijkste geëxtraheerde organische vormen van P. Verliezen van P vanuit de bovenste 5 cm van de bodem naar dieper gelegen bodemlagen vinden naar verwachting vooral plaats in de vorm van anorganisch P.
- Bij een relatief geringe afname van de totale hoeveelheid gebonden P in de grond vindt een veel grotere daling plaats van de P-concentratie in het bodemvocht ten gevolge van het sterke niet-lineaire karakter van de relatie tussen de hoeveelheid gebonden P in de grond en de P-concentratie in het bodemvocht bij evenwicht (ad- of desorptie-isotherm). Het risico van P-uitspoeling neemt dus al af als een relatief kleine hoeveelheid P wordt onttrokken aan de grond.
- Op basis van data voor de P-concentratie in het bodemvocht en de totale hoeveelheid gebonden P is een desorptie-isotherm geconstrueerd die goed kan worden beschreven met de Langmuir-vergelijking. Op de lange termijn kan 65% van de oorspronkelijke hoeveelheid P_{ox} uit de bodem worden opgenomen, zoals werd berekend met deze vergelijking en een P-concentratie in het bodemvocht waar planten nog net in staat zijn om P op te nemen; P_{ox} blijkt dus grotendeels beschikbaar voor plantenopname.
- Het telen van gras zonder het toedienen van P in de kas leidde tot een snelle en relatieve grote afname van de P-concentratie in een $CaCl_2$-extract. Uitmijnen kan dus een effectieve strategie zijn om het risico van het optreden van P-uitspoeling uit de bovenste bodemlaag van met P verrijkte gronden te verminderen, maar moet nog worden getest onder veldomstandigheden.
- Bij hoge P-concentraties waren kinetische effecten op de desorptie van P in de $CaCl_2$-extracten onder milde schudcondities duidelijk zichtbaar. De desorptie-isotherm (evenwicht) werd alleen benaderd door het schudexperiment met de langste duur. Kinetische effecten waren nauwelijks zichtbaar bij een lagere P-concentratie. De binnen een relatief korte periode door uitmijnen verkregen lage P-concentratie in het bodemvocht zal naar verwachting nauwelijks toenemen in de tijd.
- Uit modelberekeningen blijkt dat de desorptie van P in de binnenste lagen van het aggregaat aanvankelijk niet in evenwicht was met die in de rest van het aggregaat. Transport van P in bodemaggregaten verloopt zeer traag. Dit verklaart waarom er nauwelijks kinetische

effecten zichtbaar waren op P-desorptie in de $CaCl_2$-extracten van de grondmonsters die langdurig waren uitgemijnd in de potproef.

- Een dynamische biobeschikbaarheidsindex (DBI) is afgeleid om na te gaan of de P-desorptiekinetiek de opname van P door het gras in de potproef beperkte. De opname van P werd aanvankelijk niet beperkt door P-desorptie. Na verloop van tijd kan de grond echter onvoldoende snel P leveren voor een optimale opname door de plant. Het gepresenteerde concept kan worden gezien als een aanzet tot een nieuwe dynamische benadering van biobeschikbaarheid.

Nawoord

Na bijna zes jaar zwoegen is mijn proefschrift vrijwel af en moet ik alleen mijn nawoord nog schrijven. Sinds het begin van mijn aanstelling als Assistent in Opleiding (AiO) heb ik gedacht aan dit moment, maar nu het zover is valt het mij niet mee om de juiste woorden te vinden. In een nawoord worden vaak de mensen bedankt die hebben bijgedragen aan het tot stand komen van het proefschrift. Minder plezierige ervaringen worden vaak vergeten. Het begin van mijn promotieonderzoek verliep echter nogal moeizaam, mede als gevolg van een reorganisatie en de toen aanstaande sluiting van de vestiging van het Instituut voor Agrobiologisch en Bodemvruchtbaarheidsonderzoek (AB-DLO) te Haren, waar ik was gestationeerd. Als gevolg hiervan moest een deel van het personeel naar Wageningen verhuizen, waaronder ikzelf. Voor een AiO, die aan het begin staat van een promotieonderzoek, is een dergelijke werksituatie verre van optimaal. Na de verhuizing en de uiteindelijke fusie van een klein deel van het AB, het Staring Centrum en het Instituut voor Bos- en Natuuronderzoek tot Alterra, ontstond er een enthousiaste groep mensen waarin ik mij de afgelopen jaren thuis heb gevoeld en met veel plezier heb gewerkt.

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Levensloop

Gerwin Ferdinand Koopmans werd geboren op 18 juni 1972 te Gorredijk (Fryslân). Na de HAVO in Drachten (Drachtster Lyceum) begon hij in 1989 aan een HBO-studie Milieukunde aan het Prof. H.C. van Hall Instituut te Groningen. Hij rondde zijn studie af (afstudeerrichting Natuurbeheer) in 1993, met een afstudeeronderwerp over de ecotoxicologische effecten van hoge gehalten aan zware metalen (cadmium en zink) in de bodem op de samenstelling en het functioneren van een bodemvoedselweb in de Brabantse Kempen, bij het (toenmalige) Instituut voor Bodemvruchtbaarheid te Haren. Hierna ging hij Milieubiologie studeren aan de Rijksuniversiteit Groningen (RUG). Hij voerde zijn eerste doctoraalonderwerp uit bij de vakgroep Microbiologie (werkgroep Microbiële Ecologie) met als onderwerp de dynamiek van organische zwavelverbindingen in microbiële matten. Vervolgens woonde hij enige tijd te Rio de Janeiro (Brazilië), waar hij zijn tweede doctoraalonderwerp uitvoerde bij het Laboratório de Radioisótopos Eduardo Penna Franca van het Instituto de Biofisica Carlos Chagas Filho (Universidade Federal do Rio de Janeiro), met als onderwerp: polycyclische aromatische koolwaterstoffen in het Paraíba do Sul-Guandu riviersysteem. In 1996 ontving hij zijn bul van de RUG. In 1998 werd hij aangesteld als Assistent in Opleiding (AiO) bij de sectie Bodemkwaliteit van Wageningen Universiteit, en gestationeerd bij het Instituut voor Agrobiologisch en Bodemvruchtbaarheidsonderzoek (AB-DLO) te Haren. Het betrof een promotieonderzoek naar fosfor in zwaar bemeste landbouwgronden, waarvan de resultaten zijn weergegeven in dit proefschrift. Na het opheffen van de vestiging van het AB te Haren verhuisde hij in 1998 naar de vestiging te Wageningen. In 2000 fuseerden een klein deel van het AB, het Staring Centrum en het Instituut voor Bos- en Natuuronderzoek tot Alterra, waar hij momenteel werkt bij het Centrum Bodem als wetenschappelijk onderzoeker op het gebied van de dynamiek van nutriënten in de bodem. Hij woont samen met Marike Broos in Wageningen en is sinds 2 juli 2003 vader van een tweeling, Ferre en Jord.

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