



WAGENINGEN  
UNIVERSITY & RESEARCH

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

Journal of Environmental Quality

Koopmans, G.F.; Chardon, W.J.; Ehlert, P.A.I.; Dolfing, J.; Suurs, R.A.A. et al

<https://doi.org/10.2134/jeq2004.0965>

This publication is made publicly available in the institutional repository of Wageningen University and Research, under the terms of article 25fa of the Dutch Copyright Act, also known as the Amendment Taverne. This has been done with explicit consent by the author.

Article 25fa states that the author of a short scientific work funded either wholly or partially by Dutch public funds is entitled to make that work publicly available for no consideration following a reasonable period of time after the work was first published, provided that clear reference is made to the source of the first publication of the work.

This publication is distributed under The Association of Universities in the Netherlands (VSNU) 'Article 25fa implementation' project. In this project research outputs of researchers employed by Dutch Universities that comply with the legal requirements of Article 25fa of the Dutch Copyright Act are distributed online and free of cost or other barriers in institutional repositories. Research outputs are distributed six months after their first online publication in the original published version and with proper attribution to the source of the original publication.

You are permitted to download and use the publication for personal purposes. All rights remain with the author(s) and / or copyright owner(s) of this work. Any use of the publication or parts of it other than authorised under article 25fa of the Dutch Copyright act is prohibited. Wageningen University & Research and the author(s) of this publication shall not be held responsible or liable for any damages resulting from your (re)use of this publication.

For questions regarding the public availability of this publication please contact [openscience.library@wur.nl](mailto:openscience.library@wur.nl)

# Phosphorus Availability for Plant Uptake in a Phosphorus-Enriched Noncalcareous Sandy Soil

G. F. Koopmans,\* W. J. Chardon, P. A. I. Ehlert, J. Dolfing, R. A. A. Suurs, O. Oenema, and W. H. van Riemsdijk

## ABSTRACT

Mining soil phosphorus (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<sub>2</sub> extracts and acid ammonium oxalate (P<sub>ox</sub>), 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<sub>ox</sub> 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<sub>ox</sub> 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<sub>2</sub> extracts was much larger than the relative decrease of P<sub>ox</sub>. Mining soil P decreased the P concentration in soil solution effectively and, therefore, risk of P leaching from our P-enriched soil.

**I**N AREAS WITH intensive livestock farming, the soil 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<sup>-1</sup> 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<sup>-</sup> or H<sub>2</sub>O 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 phosphorus (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)ox-

G.F. Koopmans, W.J. Chardon, P.A.I. Ehlert, J. Dolfing, R.A.A. Suurs, and O. Oenema, Alterra, Wageningen University and Research Centre (WUR), P.O. Box 47, 6700 AA, Wageningen, the Netherlands. W.H. van Riemsdijk, Department of Soil Quality, Wageningen University, WUR, P.O. Box 8005, 6700 EC, Wageningen, the Netherlands. Received 25 June 2003. \*Corresponding author (gerwin.koopmans@wur.nl).

Published in J. Environ. Qual. 33:965–975 (2004).  
© ASA, CSSA, SSSA  
677 S. Segoe Rd., Madison, WI 53711 USA

**Abbreviations:** FeO-P, phosphorus extractable with a filter paper strip impregnated with iron oxide; P<sub>AL</sub>, phosphorus extractable with acetic acid and ammonium lactate; P<sub>ox</sub>, ammonium oxalate-extractable phosphorus; P<sub>w</sub>, water-extractable phosphorus.

ides 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 phosphorus ( $P_{ox}$ ), 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., 1995). 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 turn, 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 iso-

therm, 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<sub>2</sub> 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<sub>2</sub> extracts. Furthermore, reversibly adsorbed P and the total pool of sorbed P were estimated. In the Netherlands, water-extractable phosphorus ( $P_w$ ) and phosphorus 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  $P_w$  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<sup>-1</sup> yr<sup>-1</sup> (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<sup>-1</sup> yr<sup>-1</sup>. 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<sup>2</sup>. 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<sub>4</sub>NO<sub>3</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 50 mg K as K<sub>2</sub>SO<sub>4</sub>, 75 mg Mg as MgSO<sub>4</sub>·7H<sub>2</sub>O, 4.5 mg Cu as CuSO<sub>4</sub>·5H<sub>2</sub>O, and 0.5 mg B as Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O. 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<sub>4</sub>·7H<sub>2</sub>O, 4 mg Fe as FeEDTA, 4 mg Mo as Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, and Mn as a 1% (w/v) MnSO<sub>4</sub>·4H<sub>2</sub>O 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<sub>4</sub>·H<sub>2</sub>O 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 two 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 homoge-

nized. 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<sup>-1</sup> 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<sub>2</sub>SO<sub>4</sub>, and inorganic P measured after digestion of soil with 0.5 M H<sub>2</sub>SO<sub>4</sub> (Kuo, 1996). Total P was measured after soil digestion with Fleischmann acid (a 1:1 [v/v] mixture of concentrated HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) (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<sub>2</sub> extracts (Houba et al., 1986; reciprocal 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 × 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 reciprocally 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<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> 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<sub>3</sub> solution for 5 min and neutralized in 2.7 M NH<sub>4</sub>OH 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<sub>2</sub> at 4 rotations per minute (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<sub>2</sub>SO<sub>4</sub> 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 P<sub>w</sub> (water-extractable P at a soil to solution ratio of 1:60 [v/v]) (Sissingh, 1971) and P<sub>AL</sub> (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

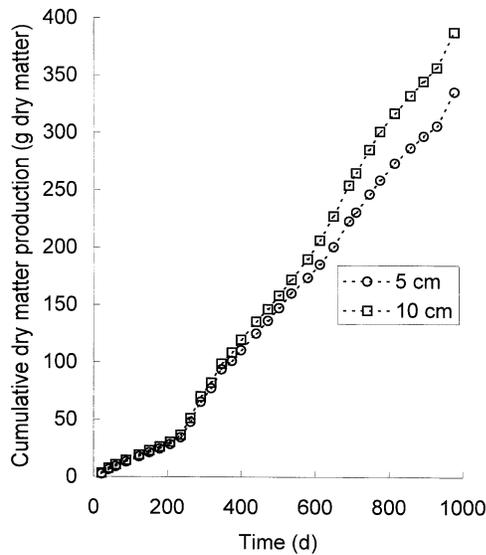


Fig. 1. Cumulative dry matter production in the 5- and 10-cm treatments.

function of time in the 5- and 10-cm treatments was lower than in the remaining part (Fig. 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<sup>-1</sup> of soil, corresponding to 36 and 29% of P<sub>ox</sub> in the initial soil, respectively (Fig. 2 and Table 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 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. 2 and Table 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

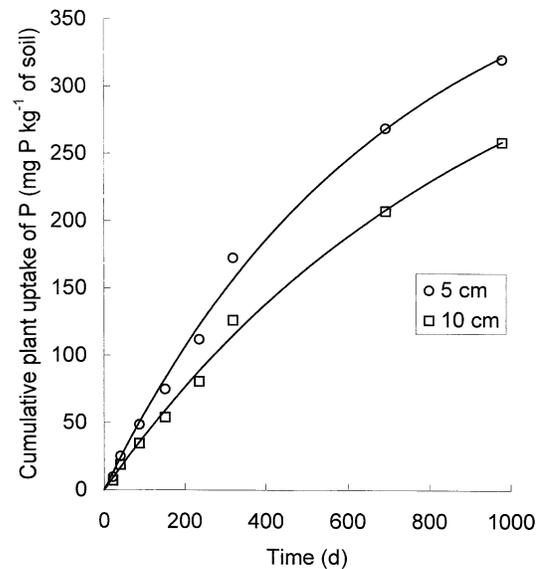


Fig. 2. Cumulative plant uptake of P from the soils of the 5- and 10-cm treatments. To guide the eye, lines, fitted to the data using an exponential curve, have been added.

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 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 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 of >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. 1).

Table 1. Selected characteristics of the soils of the 5- and 10-cm treatments.†

Time d	5 cm						10 cm					
	pH (H <sub>2</sub> O)	Organic matter %	(Al + Fe) <sub>ox</sub> mmol kg <sup>-1</sup>	P <sub>ox</sub> mg P kg <sup>-1</sup>	Organic P mg P kg <sup>-1</sup>	Total P mg P kg <sup>-1</sup>	pH (H <sub>2</sub> O)	Organic matter %	(Al + Fe) <sub>ox</sub> mmol kg <sup>-1</sup>	P <sub>ox</sub> mg P kg <sup>-1</sup>	Organic P mg P kg <sup>-1</sup>	Total P mg P kg <sup>-1</sup>
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 2. Nitrogen and P contents of the harvested grass† and N to P ratio‡ of the 5- and 10-cm treatments.**

Time	5 cm			10 cm		
	N	P	N to P ratio	N	P	N to P ratio
d	g kg <sup>-1</sup> of dry matter			g kg <sup>-1</sup> 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 1). The pH showed an irregular increase during the pot experiment. The N fertilizer applied during the pot experiment was equally divided between NH<sub>4</sub>NO<sub>3</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O. Thus, three-fourths of the N applied was in the form of NO<sub>3</sub><sup>-</sup>, suggesting that N may have been mainly taken up as NO<sub>3</sub><sup>-</sup>. Uptake of excess anions over cations may have been compensated for by root excretion of OH<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>, leading to an increase of the rhizosphere pH (Hinsinger, 2001). Denitrification of some of the NO<sub>3</sub><sup>-</sup> 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 1). The (Al + Fe)<sub>ox</sub> content remained relatively constant as expected (Table 1). In the soils of the 5- and 10-cm treatments, P<sub>ox</sub> decreased with time by 48 and 32%, respectively (Table 1). The decrease of P<sub>ox</sub> in the soils of both treatments was larger than the cumulative plant uptake of P (Fig. 2). This may, in part, be explained by the buildup of a P pool contained in root residues. The ratio between P<sub>ox</sub> and (Al + Fe)<sub>ox</sub> (both expressed in mmol kg<sup>-1</sup>), 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 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 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 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

**Table 3. Soil extractable P in the 5- and 10-cm treatments.†**

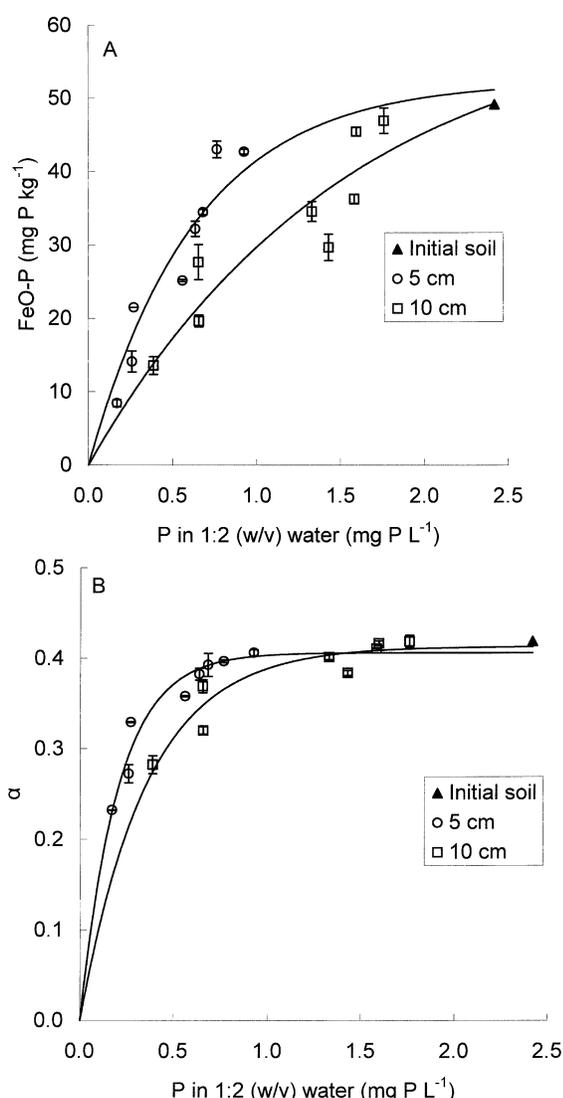
Time	5 cm					10 cm				
	1:2 (w/v) Water	1:10 (w/v) 0.01 M CaCl <sub>2</sub>	P <sub>w</sub>	FeO-P	P <sub>AL</sub>	1:2 (w/v) Water	1:10 (w/v) 0.01 M CaCl <sub>2</sub>	P <sub>w</sub>	FeO-P	P <sub>AL</sub>
d	mg P L <sup>-1</sup>		mg P kg <sup>-1</sup>			mg P L <sup>-1</sup>		mg P kg <sup>-1</sup>		
0 (t0)	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.

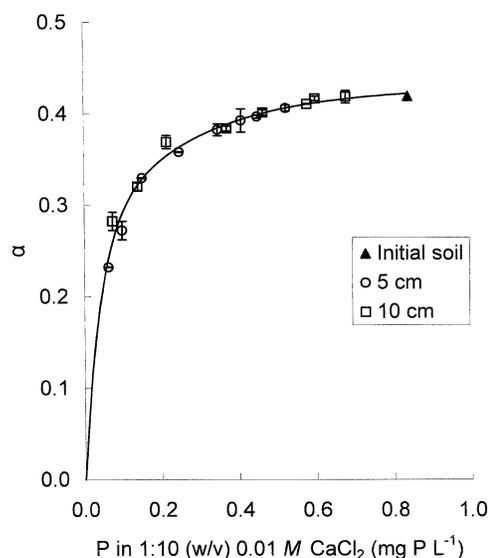
§ After 968 d of incubation, soil was sampled (t9) and the P concentration in 1:10 (w/v) 0.01 M CaCl<sub>2</sub> extracts and P<sub>w</sub> were measured.

§ Not determined.



**Fig. 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) phosphorus extractable with a filter paper strip impregnated with iron oxide (FeO-P) and (B)  $\alpha$ , which was calculated as  $P_{ox}/(Al + Fe)_{ox}$  [with  $P_{ox}$  and  $(Al + Fe)_{ox}$  in mmol kg<sup>-1</sup>]. To guide the eye, lines, fitted to the data using an exponential curve, have been added.

desorption of P decreases with an increase of the Ca concentration in solution (Barrow and Shaw, 1979; Koopmans et al., 2001; Rieta et al., 2001). The difference between the curves with FeO-P (Fig. 3A) and  $\alpha$  (Fig. 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



**Fig. 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<sub>2</sub> extracts and  $\alpha$ , which was calculated as  $P_{ox}/(Al + Fe)_{ox}$  [with  $P_{ox}$  and  $(Al + Fe)_{ox}$  in mmol kg<sup>-1</sup>]. To guide the eye, a line, fitted to the data using a double exponential curve, has been added.

experiment may be explained by (temporal) fluctuations of the Ca concentration.

Figure 4 shows the relationship between the P concentration in the 1:10 (w/v) 0.01 M CaCl<sub>2</sub> extracts and  $\alpha$ . In this case, the salt level and Ca concentration is dominated by the 0.01 M CaCl<sub>2</sub> 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<sub>2</sub> extracts were shaken for 2 h. In principle, it is questionable whether the P concentration measured

**Table 4.** Elemental composition of 1:2 (w/v) water extracts. Results were obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis.

Treatment	Time	Al	Ca	Cu	Fe	K	Mg	Mn	Na	N-NH <sub>4</sub>	N-NO <sub>3</sub>	P	S
		mmol L <sup>-1</sup>											
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

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<sub>2</sub> extracts did not increase further, 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<sub>2</sub> extracts obtained from these soils remained relatively constant (t8 and t9 in Table 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.

### Phosphorus Desorption Isotherm

We derived a desorption isotherm that describes the long-term equilibrium relationship between the P concentration in the CaCl<sub>2</sub> extracts and the total pool of P sorbed to the solid phase of the soils of the 5- and 10-cm treatments (Fig. 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<sub>2</sub> 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<sub>2</sub> 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

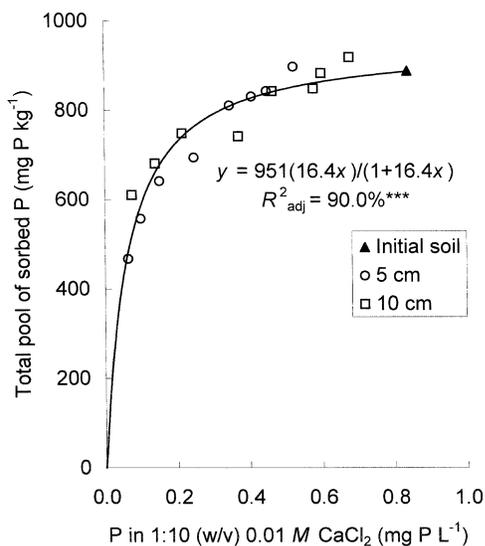


Fig. 5. The desorption isotherm for the soils of the 5- and 10-cm treatments describing the relationship between the P concentration in 1:10 (w/v) 0.01 M CaCl<sub>2</sub> extracts and the total pool of sorbed P ( $P_{ox}$  corrected for the amount of P in the CaCl<sub>2</sub> extracts). The Langmuir equation was fitted to the data.

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. 4, the data points in Fig. 5 show more variation around the fitted curve. This may be due to small variation in the measured  $(Al + Fe)_{ox}$  contents (Table 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., 1995). 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<sub>2</sub> 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. 2 and Table 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. 6:

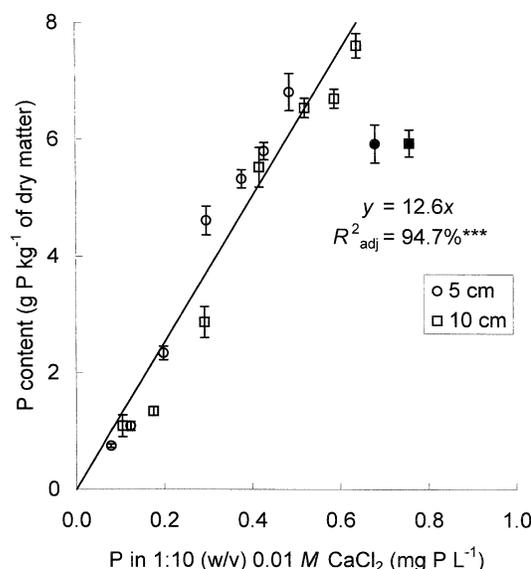


Fig. 6. Relationship for the soils of the 5- and 10-cm treatments between the average P concentration, calculated from the P concentration measured in 1:10 (w/v) 0.01 M CaCl<sub>2</sub> extracts at two subsequent sampling points, and the P content of the grass harvested since the previous sampling point. The filled symbols of the 5- and 10-cm treatments, representing the average P concentration in the CaCl<sub>2</sub> 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.

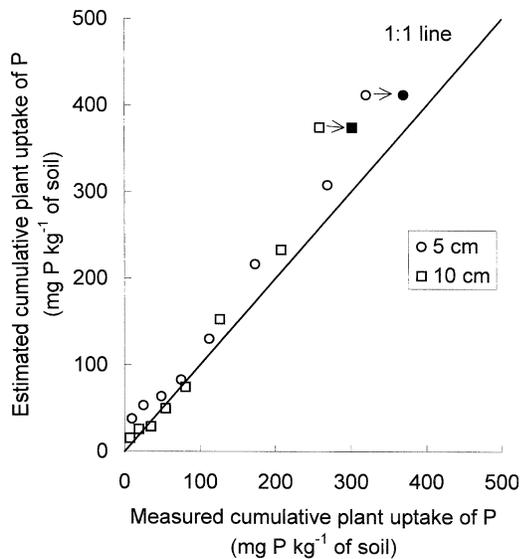


Fig. 7. Relationship between the measured and estimated cumulative plant uptake of P. In the filled symbols of the 5- and 10-cm treatments, representing the cumulative plant uptake of P at t8, P measured in root residues was included.

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  $\text{CaCl}_2$  extracts of soils sampled at two subsequent sampling points. As follows from Fig. 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.

### Maximum of the Desorption Isotherm

In Fig. 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  $951 \pm 23 \text{ mg P kg}^{-1}$  (mean  $\pm$  standard error). We estimated the maximum saturation factor  $\alpha_{\max}$  of the amorphous Al- and Fe-(hydr)oxides with respect to P sorption by calculating the ratio between  $F_{\max}$  and  $(\text{Al} + \text{Fe})_{\text{ox}}$  (both expressed in  $\text{mmol kg}^{-1}$ ). For  $(\text{Al} + \text{Fe})_{\text{ox}}$ , we used the average  $(\text{Al} + \text{Fe})_{\text{ox}}$  content of the initial soil and the soils sampled during the pot experiment (Table 1). The estimated  $\alpha_{\max}$  is 0.46, whereas the  $\alpha$  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  $\alpha_{\max}$ , which was obtained from the desorption isotherm, is in very good agreement with values of  $\alpha_{\max}$  reported in sorption studies of van der Zee et al. (1988) and Freese et al. (1992), who found  $\alpha_{\max}$  values of around 0.4. However, somewhat higher  $\alpha_{\max}$  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) can be used to estimate the cumulative plant uptake of P. The P concentration measured in the  $\text{CaCl}_2$  extracts (Table 3) was used as an input variable in the equation given in Fig. 5 to calculate the total pool of sorbed P. Subsequently, the sum of the total pool of sorbed P and P in the  $\text{CaCl}_2$  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 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 toward the 1:1 line.

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  $0.03 \text{ mg P L}^{-1}$  where plant uptake of P can just be maintained. Based on the desorption isotherm of Fig. 5, the total pool of sorbed P corresponding to a P concentration of  $0.03 \text{ mg P L}^{-1}$  in the  $\text{CaCl}_2$  extracts, calculated from the Langmuir equation, is  $314 \text{ mg P kg}^{-1}$ . This suggests that plant uptake can remove  $582 \text{ mg P kg}^{-1}$  from soil in the long-term, representing 65% of  $\text{P}_{\text{ox}}$  in the initial soil (Table 1). Thus,  $\text{P}_{\text{ox}}$  may be largely available for plant uptake in the long-term. This is in agreement with results of Lookman et al. (1995) and Guo and Yost (1999). In a long-term desorption study of Lookman et al. (1995), 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  $\text{P}_{\text{ox}}$  was desorbed. Based on their model results of the long-term P desorption kinetics, all  $\text{P}_{\text{ox}}$  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,  $\text{P}_{\text{ox}}$  was also largely available for plant uptake.

### Practical Implications

The relative decrease of the P concentration in the  $\text{CaCl}_2$  extracts was much larger than the relative decrease of  $\text{P}_{\text{ox}}$  after 978 d of continuous cropping under greenhouse conditions. The P concentration in the  $\text{CaCl}_2$  extracts and  $\text{P}_{\text{ox}}$  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 (Tables 1 and 3).

This is due to the strong nonlinearity of the desorption isotherm (Fig. 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<sub>2</sub> 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. 6). In conventional agricultural practice in the Netherlands, the P content of grass is approximately 4 g kg<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> of dry matter (Table 2), implying 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<sup>-1</sup> in the dry matter requires a P concentration in a CaCl<sub>2</sub> extract of 0.24 mg L<sup>-1</sup> (calculated from the equation given in Fig. 6). This P concentration is 71% lower than the initial P concentration (Table 3). From the Langmuir equation given in Fig. 5, it can be calculated that a P concentration of 0.24 mg P L<sup>-1</sup> in a CaCl<sub>2</sub> extract can already be reached when only 15% of P<sub>ox</sub> in the initial soil has been mined (Table 1).

In the Netherlands, P<sub>w</sub> and P<sub>AL</sub> 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, P<sub>w</sub> decreased by 85 and 73% whereas P<sub>AL</sub> decreased by 61 and 45%, respectively (Table 3). Due to the dilution effect of the relatively wide soil to solution ratio of P<sub>w</sub> (1:60 [v/v]), P extracted with P<sub>w</sub> can be interpreted as the sum of P in soil solution and part of the reversibly adsorbed P, whereas P<sub>AL</sub> 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), it can be understood why the relative decrease of P<sub>w</sub> was larger than the relative decrease of P<sub>AL</sub>. 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 continu-

ous 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<sub>AL</sub> was 154 and 219 mg P kg<sup>-1</sup>, respectively (Table 3). These P<sub>AL</sub> 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<sup>-1</sup> 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 2). Evidently, the results of this study cannot be directly transferred 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 P<sub>w</sub> was measured. The P<sub>w</sub> did not change as a result of incubation of moist soil sampled at the end of the pot experiment (t8 and t9 in Table 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<sub>2</sub> 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<sub>2</sub> 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  $\alpha_{\max}$  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  $\alpha_{\max}$  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<sub>ox</sub> 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  $\text{CaCl}_2$  concentration leads to results that are easier to interpret in this pot experiment, where results of the 5-cm treatment were compared with those of the 10-cm treatment, than using 1:2 (w/v) water extracts.

### ACKNOWLEDGMENTS

We thank O.F. Schoumans for helpful comments on a previous version of our manuscript. We are further indebted to W. Schuurmans for performing the ICP-AES analyses.

### REFERENCES

- Agterberg, G.C., and P.L.C.M. Henkens. 1995. Basis for phosphate fertilizer recommendations on grassland. (In Dutch.) *Meststoffen 1995*:12–23.
- Barrow, N.J. 1983. A mechanistic model for describing the sorption and desorption of phosphate by soil. *J. Soil Sci.* 34:733–750.
- Barrow, N.J., and T.C. Shaw. 1979. Effects of ionic strength and nature of the cation on desorption of phosphate from soil. *J. Soil Sci.* 30:53–65.
- Beek, J. 1979. Phosphate retention by soil in relation to waste disposal. Ph.D. thesis. Agric. Univ., Wageningen, the Netherlands.
- Bolan, N.S., N.J. Barrow, and A.M. Posner. 1985. Describing the effect of time on sorption of phosphate by iron and aluminium hydroxides. *J. Soil Sci.* 36:187–197.
- Breeuwsma, A. 1973. Adsorption of ions on hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ). Ph.D. thesis. Agric. Univ., Wageningen, the Netherlands.
- Breeuwsma, A., J.G.A. Reijerink, and O.F. Schoumans. 1995. Impact of manure on accumulation and leaching of phosphate in areas of intensive livestock farming. p. 239–249. *In* K. Steele (ed.) *Animal waste and the land-water interface*. CRC Press, Boca Raton, FL.
- Chardon, W.J., R.G. Menon, and S.H. Chien. 1996a. Iron oxide impregnated filter paper (Pi test): A review of its development and methodological research. *Nutr. Cycling Agroecosyst.* 46:41–51.
- Chardon, W.J., O. Oenema, O.F. Schoumans, P.C.M. Boers, B. Fraters, and Y.C.W.M. Geelen. 1996b. Exploration of options for management and restoration of phosphorus leaking agricultural soils. (In Dutch.) Vol. 8. *The Netherlands Integrated Soil Res. Programme*, Wageningen, the Netherlands.
- Del Campillo, M.C., S.E.A.T.M. van der Zee, and W.H. van Riemsdijk. 1996. Systematic bias in measuring intensities by selective extraction of bulked samples. *Commun. Soil Sci. Plant Anal.* 27:1829–1841.
- Del Castilho, P., W.J. Chardon, and W. Salomons. 1993. Influence of cattle-manure slurry application on the solubility of cadmium, copper, and zinc in a manured acidic, loamy-sand soil. *J. Environ. Qual.* 22:689–697.
- Delgado, A., and J. Torrent. 1997. Phosphate-rich soils in the European Union: Estimating total plant-available phosphorus. *Eur. J. Agron.* 6:205–214.
- Egnér, H., H. Riehm, and W.R. Domingo. 1960. Untersuchungen über die chemische Bodenanalyse als Grundlage für die Beurteilung des Nährstoffzustandes der Böden. II. Chemische Extraktionsmethoden zur Phosphor- und Kaliumbestimmung. *Kungliga Lantbrukshögskolans Annaler* 26:199–215.
- Freese, D., R. Lookman, R. Merckx, and W.H. van Riemsdijk. 1995. New method for assessment of long-term phosphate desorption from soils. *Soil Sci. Soc. Am. J.* 59:1295–1300.
- Freese, D., S.E.A.T.M. van der Zee, and W.H. van Riemsdijk. 1992. Comparison of different models for phosphate sorption as a function of the iron and aluminium oxides of soils. *J. Soil Sci.* 43:729–738.
- Geelhoed, J.S., G.R. Findenegg, and W.H. van Riemsdijk. 1997. Availability to plants of phosphate adsorbed on goethite: Experiment and simulation. *Eur. J. Soil Sci.* 48:473–481.
- Guo, F., and R.S. Yost. 1999. Quantifying the available soil phosphorus pool with the acid ammonium oxalate method. *Soil Sci. Soc. Am. J.* 63:651–656.
- Hinsinger, P. 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: A review. *Plant Soil* 237:173–195.
- Houba, V.J.G., W.J. Chardon, and K. Roelse. 1993. Influence of grinding of soil on apparent chemical composition. *Commun. Soil Sci. Plant Anal.* 24:1591–1602.
- Houba, V.J.G., I. Novozamsky, A.W.M. Huybregts, and J.J. van der Lee. 1986. Comparison of soil extractions by 0.01 M  $\text{CaCl}_2$ , by EUF and by some conventional extraction procedures. *Plant Soil* 96:433–437.
- Houba, V.J.G., J.J. van der Lee, and I. Novozamsky. 1997. Soil analysis procedures; Other procedures (soil and plant analysis, Part 5B). Agric. Univ., Wageningen, the Netherlands.
- Koerselman, W., and A.F.M. Meuleman. 1996. The vegetation N:P ratio: A new tool to detect the nature of nutrient limitation. *J. Appl. Ecol.* 33:1441–1450.
- Koopmans, G.F., M.E. van der Zeeuw, P.F.A.M. Römkens, W.J. Chardon, and O. Oenema. 2001. Identification and characterization of phosphorus-rich sandy soils. *Neth. J. Agric. Sci.* 49:369–384.
- Kuo, S. 1996. Phosphorus. p. 869–919. *In* D.L. Sparks (ed.) *Methods of soil analysis*. Part 3. SSSA Book Ser. 5. SSSA, Madison, WI.
- Lookman, R., D. Freese, R. Merckx, K. Vlassak, and W.H. van Riemsdijk. 1995. Long-term kinetics of phosphate release from soil. *Environ. Sci. Technol.* 29:1569–1575.
- Madrid, L., and P. De Arambarri. 1985. Adsorption of phosphate by two iron oxides in relation to their porosity. *J. Soil Sci.* 36:523–530.
- Maguire, R.O., R.H. Foy, J.S. Bailey, and J.T. Sims. 2001. Estimation of the phosphorus sorption capacity of acidic soils in Ireland. *Eur. J. Soil Sci.* 52:479–487.
- McCollum, R.E. 1991. Buildup and decline in soil phosphorus: 30-Year trends on a Typic Umprabuilt. *Agron. J.* 83:77–85.
- McDowell, R.W., and A.N. Sharpley. 2001. Approximating phosphorus release from soils to surface runoff and subsurface drainage. *J. Environ. Qual.* 30:508–520.
- Murphy, J., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27:31–36.
- Pautler, M.C., and J.T. Sims. 2000. Relationships between soil test phosphorus, soluble phosphorus, and phosphorus saturation in Delaware soils. *Soil Sci. Soc. Am. J.* 64:765–773.
- Prins, W.H. 1980. Changes in quantity of mineral nitrogen in three grassland soils as affected by intensity of nitrogen fertilization. *Fert. Res.* 1:51–63.
- Reijerink, J.G.A., and A. Breeuwsma. 1992. Spatial pattern of phosphate saturation in areas with an excess of manure. (In Dutch.) Rep. no. 222. Staring Centre, Wageningen, the Netherlands.
- Rietra, R.P.J.J., T. Hiemstra, and W.H. van Riemsdijk. 2001. Interaction between calcium and phosphate adsorption on goethite. *Environ. Sci. Technol.* 35:3369–3374.
- Ryden, J.C., and J.K. Syers. 1977. Desorption and isotopic exchange relationships of phosphate sorbed by soils and hydrous ferric oxide gel. *J. Soil Sci.* 28:596–609.
- Schoumans, O.F., and P. Groenendijk. 2000. Modeling soil phosphorus levels and phosphorus leaching from agricultural land in the Netherlands. *J. Environ. Qual.* 29:111–116.
- Schwertmann, U. 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. *Z. Pflanzenernähr. Dueng. Bodenkd.* 105:194–202.
- Sharpley, A. 2000. Phosphorus availability. p. D18–D38. *In* M.E. Sumner (ed.) *Handbook of soil science*. CRC Press, Boca Raton, FL.
- Sharpley, A.N., S.C. Chapra, R. Wedepohl, J.T. Sims, T.C. Daniel, and K.R. Reddy. 1994. Managing agricultural phosphorus for protection of surface waters: Issues and options. *J. Environ. Qual.* 23:437–451.
- Šimek, M., and J.E. Cooper. 2002. The influence of soil pH on denitrifi-

- cation: Progress towards the understanding of this interaction over the last 50 years. *Eur. J. Soil Sci.* 53:345–354.
- Sissingh, H.A. 1971. Analytical technique of the Pw method, used for the assessment of the phosphate status of arable soils in the Netherlands. *Plant Soil* 34:483–486.
- Sonneveld, C., J. van den Ende, and S.S. de Bes. 1990. Estimating the chemical compositions of soil solutions by obtaining saturation extracts or specific 1:2 by volume extracts. *Plant Soil* 122:169–175.
- Temminghoff, E.J.M., V.J.G. Houba, W. van Vark, and G.A. Gaikhorst. 2000. Soil and plant analysis; Part 3, plant analysis procedures. Agric. Univ., Wageningen, the Netherlands.
- Tunney, H., A. Breeuwsma, P.J.A. Withers, and P.A.I. Ehlert. 1997. Phosphorus fertilizer strategies: Present and future. p. 177–203. *In* H. Tunney, O.T. Carton, P.C. Brookes, and A.E. Johnston (ed.) Phosphorus loss from soil to water. CABI Publ., Wallingford, UK.
- Valk, H., L.B.J. Sebek, A.Th. van't Klooster, and A.W. Jongbloed. 1999. Clinical effects of feeding low dietary phosphorus levels to high yielding dairy cows. *Vet. Rec.* 145:673–674.
- Van der Zee, S.E.A.T.M., L.G.J. Fokkink, and W.H. van Riemsdijk. 1987. A new technique for assessment of reversibly adsorbed phosphate. *Soil Sci. Soc. Am. J.* 51:599–604.
- Van der Zee, S.E.A.T.M., A. Gjaltema, W.H. van Riemsdijk, and F.A.M. de Haan. 1992. Simulation of phosphate transport in soil columns. II. Simulation results. *Geoderma* 52:111–132.
- Van der Zee, S.E.A.T.M., M.M. Nederlof, W.H. van Riemsdijk, and F.A.M. de Haan. 1988. Spatial variability of phosphate adsorption parameters. *J. Environ. Qual.* 17:682–688.
- Van der Zee, S.E.A.T.M., and W.H. van Riemsdijk. 1988. Model for long-term phosphate reaction kinetics in soil. *J. Environ. Qual.* 17:35–41.
- Van der Zee, S.E.A.T.M., and W.H. van Riemsdijk. 1991. Model for the reaction kinetics of phosphate with oxides and soil. p. 205–239. *In* G.H. Bolt, M.F. de Boedt, M.H.B. Hayes, and M.B. McBride (ed.) Interactions at the soil colloid–soil solution interface. Kluwer Academic Publ., Dordrecht, the Netherlands.
- Van Erp, P.J., V.J.G. Houba, and M.L. van Beusichem. 1998. One hundredth molar calcium chloride extraction procedure. Part I: A review of soil chemical, analytical, and plant nutritional aspects. *Commun. Soil Sci. Plant Anal.* 29:1603–1623.
- Van Noordwijk, M., P. de Willigen, P.A.I. Ehlert, and W.J. Chardon. 1990. A simple model of P uptake by crops as a possible basis for P fertilizer recommendations. *Neth. J. Agric. Sci.* 38:317–332.
- Van Riemsdijk, W.H., L.J.M. Boumans, and F.A.M. de Haan. 1984a. Phosphate sorption by soils: I. A model for phosphate reaction with metal-oxides in soil. *Soil Sci. Soc. Am. J.* 48:537–541.
- Van Riemsdijk, W.H., and F.A.M. de Haan. 1981. Reaction of orthophosphate with a sandy soil at constant supersaturation. *Soil Sci. Soc. Am. J.* 45:261–266.
- Van Riemsdijk, W.H., and J. Lyklema. 1980a. The reaction of phosphate with aluminum hydroxide in relation with phosphate bonding in soils. *Colloids Surf.* 1:33–44.
- Van Riemsdijk, W.H., and J. Lyklema. 1980b. Reaction of phosphate with gibbsite (Al(OH)<sub>3</sub>) beyond the adsorption maximum. *J. Colloid Interface Sci.* 76:55–66.
- Van Riemsdijk, W.H., A.M.A. van der Linden, and L.J.M. Boumans. 1984b. Phosphate sorption by soils: III. The P diffusion-precipitation model tested for three acid sandy soils. *Soil Sci. Soc. Am. J.* 48:545–548.
- Willett, I.R., C.J. Chartres, and T.T. Nguyen. 1988. Migration of phosphate into aggregated particles of ferrihydrite. *J. Soil Sci.* 39:275–282.
- Yli-Halla, M., H. Hartikainen, and P. Väätäinen. 2002. Depletion of soil phosphorus as assessed by several indices of phosphorus supplying power. *Eur. J. Soil Sci.* 53:431–438.