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Koopmans, G.F.; Zeeuw, M.E.; Chardon, W.J.; Dolfing, J.

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## SELECTIVE EXTRACTION OF LABILE PHOSPHORUS USING DIALYSIS MEMBRANE TUBES FILLED WITH HYDROUS IRON HYDROXIDE

G.F. Koopmans, M.E. van der Zeeuw, W.J. Chardon, and J. Dolfing

Leaching of phosphorus (P) can be a serious problem in P-enriched sandy soils. Techniques that 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  $\text{CaCl}_2$  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  $Q_0$  and  $k_d$  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. (Soil Science 2001;166:475-483)

**Key words:** P-depletion, phosphorus extractability, infinite sink.

**I**N 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 P<sub>w</sub> (water extractable P with a soil: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 groundwater 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 groundwater exceeds the surface water limit of 0.15 mg total P L<sup>-1</sup> in an estimated 50% of Dutch sandy soils, 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

Alterra, Wageningen University and Research Center, P.O. Box 47, 6700 AA, Wageningen, The Netherlands. G.F. Koopmans is corresponding author. E-mail: g.f.koopmans@alterra.wag-ur.nl

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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. (1995) 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  $\text{CaCl}_2$ -based methods and the ammonium-oxalate-based P saturation index (*PSI*). Water and  $\text{CaCl}_2$  extractable P represent the more labile P forms in soil, whereas stable P is included in ammonium-oxalate but not in water and  $\text{CaCl}_2$  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 Castillo 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  $\text{ha}^{-1}$  was applied annually during a period of 10 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 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  $\text{CaCO}_3$ . 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

TABLE 1  
Selected physical and chemical characteristics of the soils (analytical means of P-ox with sample sd)

Soils	% Clay (0–2 $\mu\text{m}$ )	% Silt (2–50 $\mu\text{m}$ )	% Sand (50–2000 $\mu\text{m}$ )	Texture class	pH-KCl	Organic matter (%)	P-ox (mg P $\text{kg}^{-1}$ )	Total P (mg P $\text{kg}^{-1}$ )
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

Fleischmann acid (a 1:1 v:v mixture of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ).

#### *Preparation of Hydrous Fe-(Hydr)oxide*

The HFO suspension was prepared according to the method of Freese et al. (1995). One hundred grams of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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 ( $\text{pH}_0$ ) of HFO, thus facilitating flocculation (Schwertmann and Cornell, 1991). The HFO suspension was centrifuged (10 min at 670 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  $300 \mu\text{S cm}^{-1}$  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).

#### *P Depletion Experiment*

Dialysis membrane tubes (Visking, size 3, diameter 15.9 mm, approximate pore size 2.5 to 5.0 nm, membrane thickness 3  $\mu\text{m}$ ) 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  $\text{CaCl}_2$  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  $\text{H}_2\text{SO}_4$  in order to measure P and Fe. Standard P calibration solutions were adjusted to the same background Fe and  $\text{H}_2\text{SO}_4$  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 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  $\mu\text{m}$ ), and P was measured colorimetrically (Murphy and Riley, 1962).

#### *Standard P Solution Experiment*

The effectiveness of the DMT-HFO for uptake of P from solution was studied by determination of the  $k_s$  value (Eq. (1)). A DMT-HFO was shaken with 125 mL of 5 mg P  $\text{L}^{-1}$  standard P solution ( $\text{KH}_2\text{PO}_4$ ) in 0.01 M  $\text{CaCl}_2$  (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  $\text{FeCl}_3$  solution for 5 min and neutralized in 2.7 M  $\text{NH}_4\text{OH}$  for 45 s. One FeO strip in a fixed position was shaken end-over-end with 40 mL of 5 mg P  $\text{L}^{-1}$  standard P solution in 0.01 M  $\text{CaCl}_2$  (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:

$$\ln C(t) = \ln C_0 - k_s * t \quad (1)$$

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

#### *Langmuir Adsorption Isotherm*

Two grams of soil were suspended in 40 mL 0.005 M  $\text{CaCl}_2$  in a 100-mL glass jar and in 10 different initial P concentrations using  $\text{KH}_2\text{PO}_4$ , which ranged from 0 to 50 mg P  $\text{L}^{-1}$ . 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  $\text{CaCl}_2$  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:

$$Q = \frac{v * \Delta C}{w} + Q_0 \quad (2)$$

where  $Q$  is the amount of P adsorbed (mg P kg<sup>-1</sup>),  $v$  is the volume of solution used (L),  $\Delta C$  is the difference between the initial and the equilibrium P concentration (mg P L<sup>-1</sup>),  $w$  is weight of soil used (kg), and  $Q_0$  is the amount of P initially adsorbed (mg P kg<sup>-1</sup>). Results were fitted to the Langmuir adsorption isotherm:

$$Q = \frac{Q_{\max} * K * C}{1 + K * C} \quad (3)$$

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

#### P Extraction Methods

The extractability of P from the depleted soil samples was characterized using four extraction methods denoted as P-1:2, P-CaCl<sub>2</sub>, 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 g), supernatants were filtered (0.45  $\mu$ m), and P was determined in the filtrates. Calcium chloride extractable P (P-CaCl<sub>2</sub>) was determined in 0.01 M CaCl<sub>2</sub> according to Houba et al. (1986). The CaCl<sub>2</sub> 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<sub>2</sub>, and Pw extracts, P was measured colorimetrically (Murphy and Riley, 1962). Amounts of ammonium-oxalate extractable P, Fe, and Al were determined by the method of Schwertmann (1964). Extracts were shaken on a reciprocating shaker at 165 spm. Phosphorus, Fe, and Al were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The PSI was calculated according to:

$$PSI = \frac{P\text{-ox}}{[Fe + Al]\text{-ox}} \quad (4)$$

where P-ox and [Fe+Al]-ox are the amounts of ammonium-oxalate extractable P, Fe, and Al (mmol kg<sup>-1</sup>).

#### 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:

$$\frac{dQ}{dt} = k_a * C * (Q_{\max} - Q) - k_d * Q \quad (5)$$

where  $k_a$  is an adsorption constant (L mg<sup>-1</sup> h<sup>-1</sup>), and  $k_d$  is a desorption constant (h<sup>-1</sup>). At equilibrium ( $dQ/dt = 0$ ), Eq. (5) reduces to the Langmuir isotherm where  $K = k_a/k_d$  (Eq. (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<sup>-1</sup> at  $t > 0$  h, Eq. (5) becomes:

$$\frac{dQ}{dt} = -k_d * Q \quad (6)$$

Integration of Eq. (6) gives:

$$Q(t) = Q_0 * \exp(-k_d * t) \quad (7)$$

where  $Q(t)$  is the amount of P adsorbed in time (mg P kg<sup>-1</sup>). Substitution of  $Q(t) = Q_0 - Q_S(t)$  in Eq. (7) gives:

$$Q_S(t) = Q_0 * [1 - \exp(-k_d * t)] \quad (8)$$

where  $Q_S(t)$  is the amount of P desorbed in time (mg P kg<sup>-1</sup>). 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 build-up of a P concentration during their experiment was negligible ( $< 0.02$  mg P L<sup>-1</sup>), 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. (8). The error in  $Q_0$  was obtained by inserting a constant P concentration during the P depletion experiment in the Langmuir isotherm (Eq. (3)). The error in  $k_d$  was calculated by (van der Zee et al., 1987):

$$\text{error } k_d = k_a * C \quad (9)$$

where  $C$  is a constant P concentration.

## RESULTS AND DISCUSSION

#### P Desorption

Application of the DMT-HFO method removed relatively small amounts of P from either soil compared with the large amounts of P-ox initially present. Desorption of P was greatest in the Har 11 soil (Fig. 1). After 960 h, 13% of P-ox

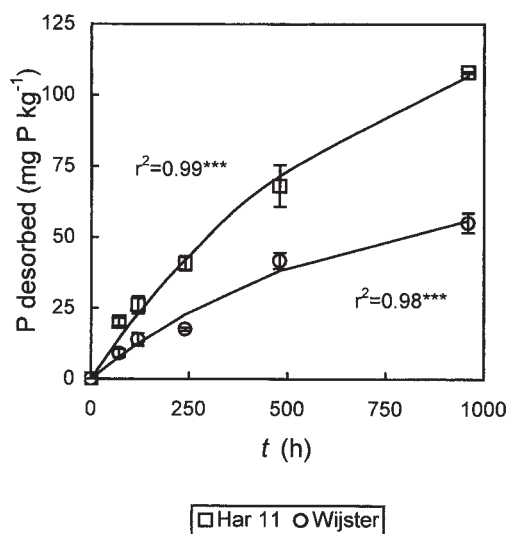


Fig. 1. Experimental and modeled P desorption results of Har 11 and Wijster soils (average values with sample sd; the symbol \*\*\* indicates significance at the 0.001 level).

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. (1995), 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 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. (3)), was lower than the affinity of the Wijster soil (Table 3). These findings are in agreement with the observation that P desorption was greatest in the Har 11 soil.

#### Characterization of P Extractability

Soil P depletion obtained by the DMT-HFO method resulted in a large decrease of water and  $\text{CaCl}_2$  extractable P in both soils. The decrease of water and  $\text{CaCl}_2$  extractable P was largest in the depleted Har 11 soil samples because of the larger amount of P desorbed (Table 2 and Fig. 1). On

TABLE 2  
Amounts of P extracted from depleted Har 11 and Wijster soil samples using 4 extraction methods (analytical means with sample sd), and P concentrations in suspension (average values with sample sd)

Incubation periods (h)	Har 11					Wijster				
	P-1:2 (mg P kg <sup>-1</sup> )	P-CaCl <sub>2</sub> (mg P kg <sup>-1</sup> )	P <sub>w</sub> (mg P kg <sup>-1</sup> )	<i>PSI</i> <sup>†</sup>	P concentration (mg P L <sup>-1</sup> )	P-1:2 (mg P kg <sup>-1</sup> )	P-CaCl <sub>2</sub> (mg P kg <sup>-1</sup> )	P <sub>w</sub> (mg P kg <sup>-1</sup> )	<i>PSI</i>	P concentration (mg P L <sup>-1</sup> )
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 (0.9)	0.40 (0.010)	0.45 (0.02)	0.99 (0.05)	2.4 (0.07)	16.9 (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)	15.9 (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

<sup>†</sup>*PSI* calculated as  $\text{P-ox}/[\text{Fe}+\text{Al}]\text{-ox}$  (Eq. (4)); nd, not determined.



TABLE 3

Estimated constants of the Langmuir adsorption isotherm ( $Q_{\max}$  and  $K$ ) (Eq. (3)) and of Eq. (8) ( $Q_0$  and  $k_d$ ) with se of the constants, and the calculated errors in  $Q_0$  (Eq. (3)) and  $k_d$  (Eq. (9)) in Har 11 and Wijster soils

Soils	$Q_{\max}$ (mg P kg <sup>-1</sup> )	$K$ (L mg <sup>-1</sup> )	$Q_0$ (mg P kg <sup>-1</sup> )	Error $Q_0$ (mg P kg <sup>-1</sup> )	$k_d$ (h <sup>-1</sup> )	Error $k_d$ (h <sup>-1</sup> )
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 (0.0005)	0.006

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<sub>2</sub> 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<sub>2</sub> extractable P, are readily removed. The more stable P, which is included in P-ox but not in water and CaCl<sub>2</sub> 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 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).

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. 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. 3). Other methods to determine a P saturation degree, e.g., 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

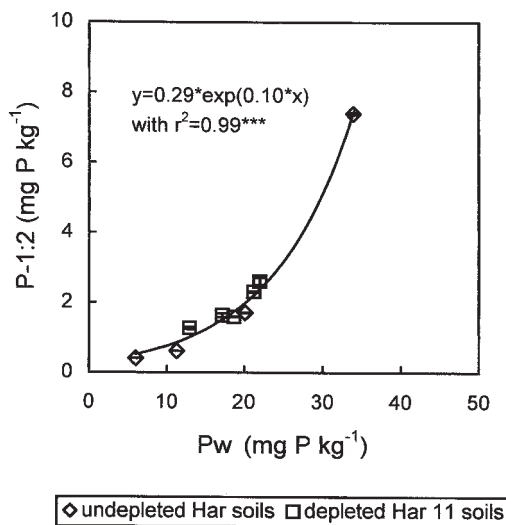


Fig. 2. P-1:2 plotted against Pw in the undepleted Har 1, Har 7, Har 9, Har 11 and the depleted Har 11 soil samples (analytical means, sample sd of P-1:2 falls within symbols; the symbol \*\*\* indicates significance at the 0.001 level).

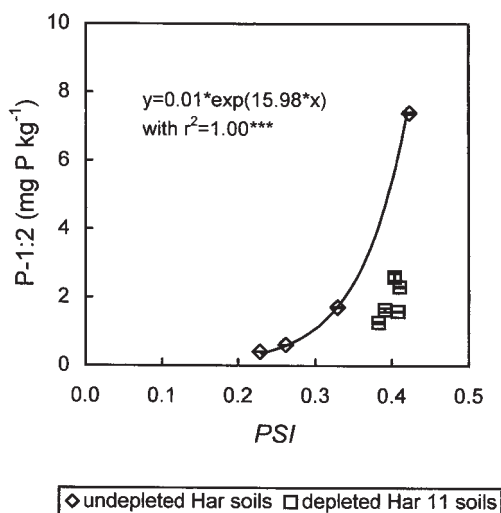


Fig. 3. P-1:2 plotted against PSI in the undepleted Har 1, Har 7, Har 9, Har 11 and the depleted Har 11 soil samples (analytical means, sample sd of P-1:2 falls within symbols; the symbol \*\*\* indicates significance at the 0.001 level).

depleted by plant uptake. The trend, as observed in Fig. 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).

In summary, although total amounts of P removed from soil were relatively small, amounts of water and  $\text{CaCl}_2$  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  $\text{CaCl}_2$  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. (8) to model the P desorption results of both soils (Fig. 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 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  $0.2 \text{ h}^{-1}$  (sample sd =  $0.08 \text{ h}^{-1}$ ). 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 2). The build-up 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. (3)) (Table 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. (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 3).

Low effectiveness of the DMT-HFO for uptake of desorbed P from solution leads to the build-up 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 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  $0.07 \pm 0.001 \text{ h}^{-1}$  ( $\pm$  standard error, se) and corresponds well with results of Freese et al. (1995). We estimated a  $k_s$  value of  $0.09 \text{ h}^{-1}$  from their results. However, the  $k_s$  value of FeO-paper was much higher:  $0.54 \pm 0.100 \text{ h}^{-1}$ . 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.

In summary, since the DMT-HFO functioned as a sink for P, we succeeded in decreasing amounts of water and  $\text{CaCl}_2$  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. (1995). We are currently working on an im-



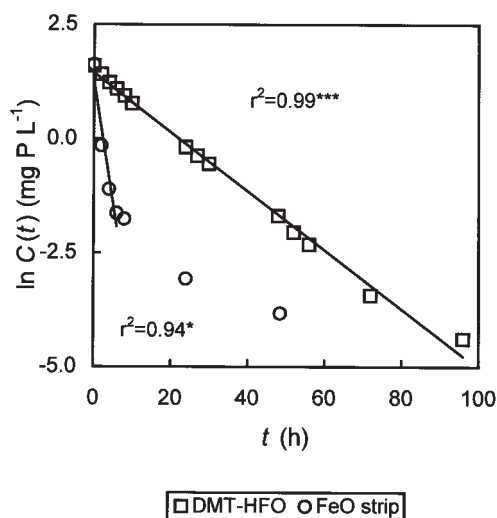


Fig. 4. P concentration decrease in a standard P solution ( $5 \text{ mg P L}^{-1}$  and  $0.01 \text{ M CaCl}_2$ ) incubated with a DMT-HFO or an FeO strip (the symbols \* and \*\*\* indicate significance at the 0.05 and 0.001 levels, respectively).

proved 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  $\text{CaCl}_2$  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  $\text{CaCl}_2$  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 build-up 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.

### ABBREVIATIONS

DMT-HFO	dialysis membrane tube filled with hydrous Fe-(hydr)oxide
EC	electrical conductivity

opm	oscillations per minute
P	phosphorus
P-1:2	amount of P desorbed in a 1:2 w:v water extract
P- $\text{CaCl}_2$	amount of P desorbed in $0.01 \text{ M CaCl}_2$
P-ox	ammonium-oxalate extractable P
<i>PSI</i>	phosphorus saturation index
Pw	amount of P desorbed in a 1:60 v:v water extract
rpm	rotations per minute
spm	strokes per minute
sd	standard deviation
se	standard error

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### APPENDIX

List of symbols used in this article:

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

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