# Phytoextraction of phosphorus-enriched grassland soils

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# Phytoextraction of Phosphorus-Enriched Grassland Soils

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High soil P contents in agricultural soils in the Netherlands cause excessive losses of P to surface waters. The reductions in P application rates in the present manure policy are not sufficient to reach surface water quality standards resulting from the European Water Framework Directive in 2015. Accordingly, additional measures are necessary to reduce P loading to surface water. Greenhouse experiments showed that a rapid reduction in soluble P and readily available soil P can be obtained by zero P application. However, field data confirming these findings are scarce. In 2002 a phytoextraction experiment started on four grasslands sites on sand, peat, and clay soils. The phytoextraction (mining) plots receive no P and 300 kg N ha$^{-1}$ yr$^{-1}$ and the grass is removed by mowing. The experiment showed that zero P application, over a period of 5 yr, led to a strong (30–90%) reduction in P concentrations in soil solution in the upper soil layer (0–0.05 m). The reduction in concentrations declined with depth. Mining also resulted in a decline in P pools in the soil solid phase. The largest decline (10–60%) was found in weakly bound P pools (water extractable P; $P_w$, and ammonium lactate extractable P; P-AL), whereas reductions in more strongly bound P forms were relatively small. It may be concluded that phytoextraction appears an effective method of reducing soil P concentrations in the uppermost soil layers in a couple of years and prolonged mining may thus be effective in reducing leaching and runoff of P.

Loss of P from agricultural soils has become the most important factor that determines the surface water quality in the Netherlands. In 1985, 80% of the P load to surface water was due to drainage of industrial and communal wastewater. In 2000, the P losses by industry and communities had decreased by 80 to 90%, but diffuse losses from agricultural areas hardly decreased (RIVM, 2002). To improve the quality of surface water and groundwater, the Dutch government implemented a manure policy in the 1990s. Despite this, the accumulation of P in soils still continues. Calculations showed that more than 50% of Dutch agricultural soils are highly enriched with P (Schoumans, 2004). Recently, a Dutch manure and fertilizer policy has been adapted, and the application standard of P will be gradually decreased until equilibrium between P application and plant offtake (i.e., equilibrium fertilization) is reached in 2015. Equilibrium fertilization will stop the ongoing enrichment of the soil with P and is a prerequisite to improve surface water quality. However, these reductions in P application rates are most probably not sufficient to reach surface water quality standards of the European Water Framework Directive (WFD) in 2015 in all areas sensitive to P leaching and P runoff in the Netherlands, due to the large amounts of P accumulated in Dutch agricultural soils. Accordingly, additional measures have to be considered to further reduce P loading to surface water (e.g., Chardon and Koopmans, 2005; Kronvang et al., 2005). Phytoextraction of soil P by crop harvesting without P application (i.e., P mining) has been suggested as a promising method to reduce the risk of P leaching to surface waters within a reasonable amount of time (Van der Zee et al., 1992; Chardon et al., 1996; Delorme et al., 2000; Koopmans et al., 2004; Sharma and Sahi, 2005; Sharma et al., 2007). Phytoextraction has gained worldwide attention as an environmentally-friendly and cost-effective technique to remove heavy metals from contaminated soils (Zhao et al., 2003; Koopmans et al., 2007). Mining of P enriched soils has been mainly limited to greenhouse experiments, which have shown a rapid reduction of the P concentrations in soil solution and readily available soil P on zero P application (Pothuluri et al., 1991; Delgado and Torrent, 1997; Yli-Halla et al., 2002; Koopmans et al., 2004). However, field data confirming these findings are scarce. Sharpley et al. (2009) found a 83% lower amount of total P in runoff from a plot where no P was

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**Abbreviations:** BP, buffer power; DPS, degree of phosphorus saturation; MRP, molybdate reactive phosphorus; MUP, molybdate unreactive phosphorous; $P_w$, water-extractable P; P-AL, ammonium lactate extractable P; $P_{ox}$, oxalate extractable P; $Fe_{ox}$, oxalate extractable Fe; $Al_{ox}$, oxalate extractable Al.

applied during 5 yr of a corn–soybean rotation, compared with a treatment where litter was applied to meet crop N requirements (40–116 kg P ha$^{-1}$ yr$^{-1}$). Over the same period, however, average Mehlich-3 P in the surface soil (0–0.05 m depth) showed no consistent overall change with different litter treatments. Watson et al. (2007) found no change in Olsen P after 5 yr with no P application on grazed grassland soil. However, these authors estimated that only 8.4 kg P ha$^{-1}$ yr$^{-1}$ were removed, mainly via animal live-weight gain.

Although quantitative information on the long-term effects of P-mining is limited, P-mining is often recommended as a best management practice (BMP) for soils with high P test values (Walker, 2005). Phosphorus fertilization recommendation in many countries advice to withheld P for several years when soil P test values are high (Tunney et al., 1997). In practice such BMP's are often neglected in areas suffering from a surplus of animal manure, like the Netherlands.

The aim of this study is to find evidence for the effectiveness of P mining to reduce the risk of P losses to surface waters under field conditions. For this purpose, changes in different soil P pools in four grassland sites at zero P application were quantified over a period of 5 yr. The sites were located on three major Dutch soil types (noncalcareous sand, clay, and peat soils). Results were compared to adjacent plots receiving either equilibrium fertilization or P surpluses representative of present Dutch grassland management (9–18 kg P ha$^{-1}$ yr$^{-1}$). The outcome of this study can be used to evaluate whether mining may be a feasible option to reduce the risk of P losses from P enriched soils.

## Material and Methods

### Experimental Sites

In 1996, a field experiment started on four grassland sites on noncalcareous sand (two sites), clay, and peat soils in the southern and central part of the Netherlands (Table 1). Annual precipitation at the sites was approximately 750 mm and the mean annual temperature was 10°C. The swards on the trial fields on clay and sand were dominated (about 90%) by *Lolium perenne* L. (LP). On the peat soil the sward was on average 35% LP, 20% *Poa trivialis*, 15% *Agrostis stolonifera* L., 5% *Poa annua* L., 10% *Alopecurus geniculatus* L., 10% herbs, and 5% other grasses. There was no change in botanic composition during the experiment. The experiment consisted originally of six treatments: three P surpluses (i.e., 0, 9, and 18 kg P ha$^{-1}$ yr$^{-1}$) in combination with two N surpluses (i.e., 180 and 300 kg N ha$^{-1}$ yr$^{-1}$). In 2002, the experimental design was expanded with a P mining experiment. The treatments were not replicated. The plots were rectangular in shape with an area of 350 m$^2$. The location of the P mining plots adjacent to the plots receiving P has given us the opportunity to compare the effect of P mining with balanced or regular fertilization. Changes in different P pools in both the soil solution and the soil solid phase were monitored during the field experiment in four treatments: the P mining treatment (S0), the treatments receiving a N surplus of 180 kg N ha$^{-1}$ yr$^{-1}$ and a P surplus of 0

(P0) or 9 kg P ha$^{-1}$ yr$^{-1}$ (P9), and at the plot with an N surplus of 300 kg N ha$^{-1}$ yr$^{-1}$ and a P surplus of 18 kg P ha$^{-1}$ yr$^{-1}$ (P18). In this paper, the results of those four plots are presented.

### Agricultural Management and Soil Sampling

All plots with a P surplus (i.e., 0, 9, and 18 kg P ha$^{-1}$ yr$^{-1}$) received the same amount of P in cattle (*Bos taurus*) slurry, supplying P approximately equal to the P offtake (approx. 40 kg P ha$^{-1}$ yr$^{-1}$). The P surpluses (i.e., 9 and 18 kg P ha$^{-1}$ yr$^{-1}$) were obtained by additions of P given as triple superphosphate except for the site at Heino where Gafsa rock phosphate was used. Half of the cattle slurry and the triple superphosphate was applied in early spring and the rest before the fourth cutting in summer (June or July). Cattle slurry was shallow injected in vertical slots up to 0.05 to 0.06 m deep. Spacing between slots was 0.2 m. On peat soil cattle slurry was band spread by trailing feet also 0.2 m apart. The N surpluses were expressed as effective N. Effective N was calculated according to Dutch fertilizer recommendations for grassland (Anonymous, 2002). The efficacy of the mineral N and organic N from cattle slurry within this system was calculated based on N use efficiencies of 76 and 24%, respectively. Mineral N was applied as ammonium nitrate limestone at the same time as cattle slurry was applied. The P mining plots received no P and accordingly N was added as 300 kg N ha$^{-1}$ yr$^{-1}$ of ammonium nitrate limestone (27% N) because slurry, which contains P, could not be used. At the Heino site grass-clover (*Trifolium repens* L.) was used to provide N.

All P surplus sites underwent several harvest cycles and were alternately cut for silage and grazed which is common practice on dairy farms in the Netherlands. The P mining plots were not grazed, but grass was removed by cutting five to seven times each year. The grass yields of the plots were measured repeatedly. Immediately before each harvest cycle, four strips of 5 by 1.5 m were cut from each plot with a trial harvester (Haldrup), weighed, sampled, and analyzed. The grass from the trial harvest before a grazing cycle was returned to the plot as fodder. The P offtake during the season was calculated as the sum of the P removed in the silage cuts and the net P uptake in the animals (heifers). For the purpose of the latter the animals were weighed at least twice during the season. The animals were only fed on grass from the plots.

At each plot, soil samples were collected in late winter (before fertilization, generally in March), early spring (approximately 1 mo after fertilization, generally in April/May), and in late autumn (November/December) at depths of 0 to 0.05, 0.05 to 0.1, 0.1 to 0.2, and 0.2 to 0.3 m. To obtain a soil sample that represents the average properties of the plot, each plot was divided in 20 squares of equal size. In each square, two sampling points were randomly selected. The 40 subsamples were bulked for chemical analysis. In the period between sampling and centrifugation, field-moist samples were stored at 1.5°C. Soil solution samples were obtained by centrifugation of field-moist samples at 7000 rpm (8890 g) for 20 min. Centrifugation was performed within 1 d of sampling. After centrifugation, the soil solution samples were filtered through a 0.2-μm filter, and analyzed within 24 h. The remaining part of the soil samples collected in spring and

**Table 1. Characteristics of the four experimental sites.**

| Site | Soil type layer | Groundwater level | | Characteristics of the topsoil (0–0.3 m) | | |
|---|---|---|---|---|---|---|
| | | MHG† | MLG† | C | pH-KCl | CaCO$_3$ |
| | | —————m————— | | g kg$^{-1}$ | | g kg$^{-1}$ |
| Heino (Hn) | Sand | 0.4 | 1.00 | 16–25 | 5.3–5.9 | 0 |
| Cranendonck (Cr) | Sand | 0.7 | 1.35 | 21–25 | 5.4–5.7 | 0 |
| Waiboerhoeve (Wb) | Clay | 0.4 | 1.50 | 18–38 | 6.9–7.2 | 70 |
| Zegveld (Zg) | Peat | 0.14 | 0.40 | 235–274 | 4.9–5.3 | 0 |

† Mean highest ground water level (MHG) and mean lowest ground water level (MLG) in centimeters from soil surface.

autumn were air-dried, sieved through a 2-mm sieve, and stored until further analysis. Bulk density was measured by sampling undisturbed soil samples in 0.01 m$^3$ steel rings.

## Chemical Analysis

Total N and P contents of the grass and animal manure were determined by digestion with a mixture of sulfuric acid, salicylic acid, hydrogen peroxide, and selenium (Novozamsky et al., 1983, 1984). The N and P concentrations in the digests of animal manure and the N concentrations in the digests of the grass were determined spectrophotometrically by using a Segmented Flow Analyzer. The N concentrations were measured by means of the indophenol blue method (Novozamsky et al., 1974), whereas the P concentrations were measured according to the molybdenum blue method (Murphy and Riley, 1962). To measure the P concentrations in the grass digests, however, an inductively coupled plasma atomic emission spectrometer (ICP–AES) was used.

The soil samples were analyzed for pH-KCl, CaCO$_3$, and carbon content as loss on ignition by standard analytical procedures (Houba et al., 1997). Soil solution samples were analyzed for total P and molybdate reactive phosphorus (MRP). Total P was measured using an ICP–AES (Vista Pro, Varian), and MRP according to Murphy and Riley (1962) by using a Segmented Flow Analyzer (Skalar, SK12). Molybdate unreactive phosphorus (MUP) was calculated as the difference between total P and MRP. Soil samples collected in autumn were analyzed for $P_w$, P-AL, $P_{ox}$, $Al_{ox}$, and $Fe_{ox}$, and the total P content. The $P_w$ was determined by extraction with water at a soil-to-solution ratio of 1:60 (v/v) (Sissingh, 1971); P-AL by extraction with a 0.1 mol L$^{-1}$ ammonium lactate/0.4 mol L$^{-1}$ acetic acid solution (Egnér et al., 1960); $P_{ox}$, $Al_{ox}$ and $Fe_{ox}$ by extraction with acid ammonium oxalate (Schwertmann, 1964), and the total P content by destruction with Fleischmann acid (Houba et al., 1997). The $P_w$ and P-AL extractions were also performed on the soil samples taken in spring. In the Netherlands, $P_w$ and P-AL are used as soil tests for P fertilizer recommendation for arable land and grassland, respectively. Due to the dilution effect of the relatively wide soil-to-solution ratio of the extract, $P_w$ can be interpreted as the sum of P in soil solution and a small part of the reversibly bound P, whereas P-AL extracts both reversibly bound P plus a part of the quasi irreversibly bound P; $P_{ox}$ is used as a measure of the total amount of reversibly and quasi irreversibly bound P (Schoumans and Groenendijk, 2000; Koopmans et al., 2004). In autumn 2001, the pool of reversibly sorbed P ($P_i$) in soils was characterized. The $P_i$ was determined in a 0.01 mol L$^{-1}$ CaCl$_2$ soil suspension (1:40 w/v) by extraction with Fe oxide-impregnated paper for a total period of 144 h based on the method described by Van der Zee

et al. (1987) and Menon et al. (1989). The total binding capacity of the soil for P was calculated from the amounts of $Al_{ox}$ and $Fe_{ox}$ assuming a binding capacity of 0.5 mol P per mol $Al_{ox}$ or $Fe_{ox}$. The degree of phosphorus saturation (DPS) was calculated as $P_{ox}/[0.5 (Al+Fe)_{ox}]$ (molar values) (Schoumans and Groenendijk, 2000). The buffer power (BP (L kg$^{-1}$) of a soil is defined as the ratio between sorbed P and P dissolved in soil solution at equilibrium (Holford, 1980; Ehlert et al., 2003) corresponding to a point on the soil's P sorption isotherm. For calculating BP, we used $P_i$ as an estimate of sorbed P (Van Noordwijk et al., 1990) and MRP concentrations in the centrifuged soil solution as an estimate of dissolved P. Both values were determined in the 0- to 0.5-m layer of soil samples taken in autumn 2001 at the start of the P mining period.

## Soil Characteristics

The two sandy sites are located on noncalcareous loamy sands with carbon contents in the topsoil (0–0.30 m) of 16 to 25 g C kg$^{-1}$ (Table 1). The sandy site at Cranendonck is well-drained and can be classified as a Typic Quartzipsamment. The sandy soil at Heino has a somewhat higher groundwater table in winter and is classified as a Typic Plagganthreps. The clay soil is classified as an Oxyaquic Udifluvent, and is formed on a slightly calcareous (70 g kg$^{-1}$ lime) marine clay (Table 1). The texture ranges from light clay to clay loam. The site is moderately well drained. The peat site (Hydric Haplofibrist) is poorly drained, and consists of a clayey peat topsoil overlying eutrophic to mesothropic peat. Soil P status in the upper 0.1 m ($P_w$ and P-AL) of all sites is considered as moderate to high (Table 2). In the peat and the clay soil, $P_w$ and P-AL rapidly decreased with depth, whereas they remain high throughout the upper 0.3 m of the soil profile at the sandy sites. The same distribution of P with depth is found for the stronger bound P forms like $P_{ox}$ and total P (Table 2). The DPS is highest at the sandy site at Heino (depth weighted average 0.6) and lowest at the peat site in Zegveld (0.15).

## Statistical Analyses

The treatment effects on average P concentrations and P pools over the period 2002–2006 were analyzed with ANOVA. The analyses included interactions between soil type, surpluses, and soil layer. The initial P concentration or P content measured in respectively spring 2002 and autumn 2001 was taken into account as covariate. The MRP and MUP concentrations in the soil solution were log transformed to avoid non-normal distributions of residues. Significant differences between treatments were based on LSD at a significance level of 5%. The

**Table 2. Phosphorus pools, degree of phosphorus saturation (DPS), and bulk density in autumn 2001 before the start of the P mining experiments.**

| Site | Depth | $P_w$ | $P_i$ | P-AL | $P_{ox}$ | Total P | DPS† | Bulk density |
|---|---|---|---|---|---|---|---|---|
| | m | | | —mg kg⁻¹— | | | | kg m⁻³ |
| Heino | | | | | | | | |
| | 0–0.05 | 11 | 89 | 146 | 606 | 719 | 0.63 | 1174 |
| | 0.05–0.1 | 6 | 77 | 150 | 592 | 633 | 0.53 | 1454 |
| | 0.1–0.2 | 8 | 68 | 172 | 618 | 694 | 0.59 | 1442 |
| | 0.2–0.3 | 8 | 62 | 162 | 517 | 645 | 0.62 | 1463 |
| Cranendonck | | | | | | | | |
| | 0–0.05 | 10 | 88 | 141 | 622 | 716 | 0.48 | 1132 |
| | 0.05–0.1 | 7 | 66 | 132 | 646 | 667 | 0.45 | 1430 |
| | 0.1–0.2 | 6 | 55 | 138 | 599 | 639 | 0.43 | 1448 |
| | 0.2–0.3 | 7 | 51 | 143 | 566 | 623 | 0.44 | 1399 |
| Waiboerhoeve | | | | | | | | |
| | 0–0.05 | 25 | 99 | 214 | 586 | 1031 | 0.50 | 1101 |
| | 0.05–0.1 | 7 | 24 | 74 | 323 | 655 | 0.25 | 1389 |
| | 0.1–0.2 | 4 | 12 | 44 | 248 | 528 | 0.19 | 1361 |
| | 0.2–0.3 | 3 | 13 | 35 | 229 | 511 | 0.18 | 1322 |
| Zegveld | | | | | | | | |
| | 0–0.05 | 13 | 213 | 157 | 932 | 2710 | 0.15 | 355 |
| | 0.05–0.1 | 3 | 111 | 86 | 1301 | 2082 | 0.22 | 510 |
| | 0.1–0.2 | 4 | 44 | 40 | 1028 | 1614 | 0.14 | 447 |
| | 0.2–0.3 | 17 | 37 | 20 | 803 | 1386 | 0.11 | 282 |

† Calculated as $P_{ox}/[0.5 (Al+Fe)_{ox}]$ (molar values).

relationship between MRP concentrations and soil P status in autumn, before the test year and P surplus of the test year was analyzed per location by multiple linear regression. All statistical analyses were performed using Genstat 10.2 (http://www.vsni.co.uk/). Soil P status was determined as $P_w$ or P-AL.

## Results and Discussion

### Phosphorus Uptake and Surplus

Mining led to an average P offtake of 28 to 40 kg P ha⁻¹ yr⁻¹ (Table 3). The P removal declined at most sites during the field experiments, from an average of 38 kg P ha⁻¹ yr⁻¹ in 2002 to 29 kg P ha⁻¹ yr⁻¹ in 2006, except for the sandy site at Heino. The decline in P removal at the peat and clay sites is caused by a decline in P content of the grass, from approximately 3.4 g kg⁻¹ in 2002 to 2.5 g kg⁻¹ in 2006 (Table 4). At the sandy site at Cranendonck, the P content of the grass hardly changed with time, but the dry matter production showed a declining trend (Table 4). At the sandy site at Heino, the P offtake increased from 24 kg P ha⁻¹ yr⁻¹ in 2002 to 36 kg P ha⁻¹ yr⁻¹ in 2006, due to an increase in dry matter production. The P content of the grass remained constant with an average of 3.9 g kg⁻¹ (Table 4). The increase in dry matter production at Heino is most probably due to a limited N supply by the soil and a poor initial N-fixing capacity of the clover at the beginning of the field experiment. This problem of poor growth through N limitation was not found at the P mining plots at the other sites, where mineral N-fertilizer was used (300 kg ha⁻¹ yr⁻¹).

The P offtake of the plots with a surplus of 0 kg P ha⁻¹ yr⁻¹ was close to P offtake on the mining plots (Table 3). For the plots with surpluses of 9 and 18 kg P ha⁻¹ yr⁻¹, the P offtake was higher (Table

**Table 3. Average P offtake and P surplus (2002–2006) at the mining plots and the surplus plots.**

| | P offtake | | | | P surplus | | | |
|---|---|---|---|---|---|---|---|---|
| | Hn | Cr | Wb | Zg | Hn | Cr | Wb | Zg |
| | | | | —kg P ha⁻¹ yr⁻¹— | | | | |
| Mining | 32 | 35 | 40 | 28 | −32 | −35 | −40 | −28 |
| N180-P0 | 31 | 33 | 37 | 34 | 5 | 4 | 8 | 7 |
| N180-P9 | 32 | 37 | 38 | 37 | 13 | 12 | 16 | 13 |
| N300-P18 | 36 | 46 | 48 | 44 | 21 | 17 | 22 | 19 |

3). The average P surplus of the surplus plots was generally higher than planned (up to 8 kg P ha⁻¹ yr⁻¹) over the period 2002–2006 (Table 3), due to the fact that the dry matter production of the grass was lower than expected in the dry summers of 2003 and 2006 (Table 4). Most of the P was applied before grass mowing. Obviously, the P application rate could not be corrected when the grass was not mowed because of poor growth.

### Effects of Mining on Soil Phosphorus Pools

In (heavily) fertilized soils, the pools of $P_{ox}$ and total P in the topsoil are relatively large compared to the yearly P offtake. For example, $P_{ox}$ in the upper 0.1 m ranged from 498 kg P ha⁻¹ at Zegveld to 814 kg P ha⁻¹ at Cranendonck, whereas total P ranged from 882 kg P ha⁻¹ at Heino to 1099 kg P ha⁻¹ at Waardenburg. The P offtake by the grass (28–40 kg P ha⁻¹ yr⁻¹) will thus have a limited effect on these soil P pools in the short term. The relationship between the MRP concentration in soil solution and the amount of reversibly sorbed P can typically be described using a Langmuir equation (Van der Zee et al., 1988). This equation indicates a nonlinear asymptotic relationship between P in soil solution and reversibly sorbed P. Accordingly, a small decline in the amount of sorbed P will lead to a large decrease in soil solution P at high DPS (Koopmans et al., 2001, 2004). Indeed, mining resulted in a rapid decline of MRP concentrations in soil solution compared to the plots receiving zero (not shown) and positive P surpluses. At all mining plots the first signs of a decline in MRP concentrations were found in the 0- to 0.05-m soil layer. In the deeper soil layers, the decline started later and was less pronounced (Fig. 1). The fastest response was found in the 0- to 0.05-m soil layer at the clay site where MRP concentrations at the end of the first growing season was already considerably lower than on the plots receiving a positive P surplus (S9) (Fig. 2). At the sandy sites, differences in MRP concentrations between the mining plots (P0) and the plots receiving a positive P surplus (S9) emerged in the second growing season, whereas effects on the peat site were not found before 2004 (Fig. 2). The response of MRP concentrations in the soil solution on P mining is expected to be related to the buffer power (BP) of the soil. P offtake by plants is expected to have a smaller effect on MRP concentrations in soil solution at a high BP. The BP of the soils increased in the order: clay soil (0.08) < sandy soil at Heino (0.13) < sandy soil at Cranendonck (0.16) < peat soil (1.39). Thus, BP could explain the different effects of P mining on MRP in soil solution at the four sites (Fig. 2).

Not only MRP concentrations but also MUP concentrations declined on zero P application. However, the decline in MUP

**Table 4. Dry matter production (DM) and P content of the grass during the mining experiment.**

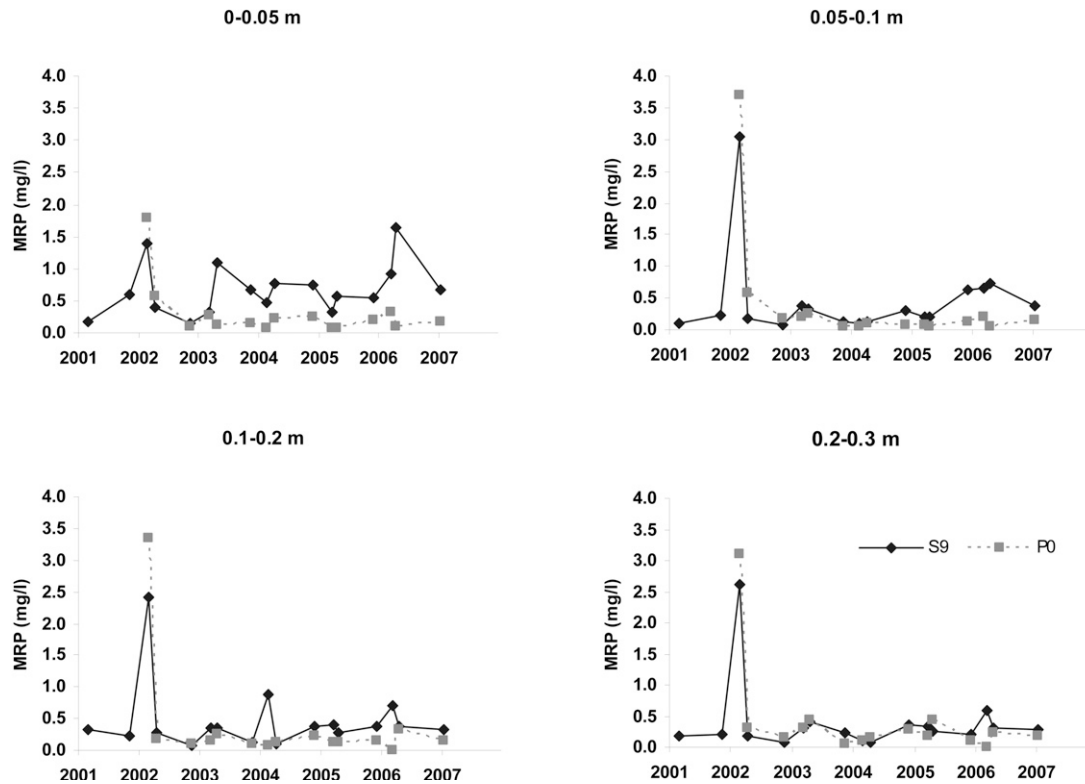| Site | DM, Mg ha⁻¹ yr⁻¹ | | | | | P content , g kg⁻¹ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2002 | 2003 | 2004 | 2005 | 2006 | 2002 | 2003 | 2004 | 2005 | 2006 |
| Heino | 6.5 | 5.4 | 8.0 | 13.6 | 9.8 | 3.9 | 4.0 | 4.0 | 3.7 | 3.8 |
| Cranendonck | 14.7 | 10.6 | 11.5 | 14.6 | 7.8 | 2.8 | 2.9 | 3.1 | 3.0 | 3.0 |
| Waiboerhoeve | 13.8 | 12.2 | 13.6 | 12.7 | 12.2 | 3.5 | 3.5 | 3.5 | 3.0 | 2.5 |
| Zegveld | 11.9 | 9.7 | 11.6 | 11.0 | 9.4 | 3.3 | 2.5 | 2.4 | 2.2 | 2.6 |



Fig. 1. Molybdate reactive phosphorus (MRP) concentrations in the soil solution at the sandy site at Heino, for 0 to 0.05, 0.05 to 0.1, 0.1 to 0.2 and 0.2 to 0.3 m depth at a P surplus of 9 kg P ha⁻¹ yr⁻¹ (S9) and zero P application (P0).

concentrations was generally less pronounced than the decline in MRP concentrations (Fig. 3). The concentration of MUP is often assumed to represent organic P (e.g., Chardon et al., 1997; Koopmans et al., 2006), although polyphosphates and inorganic P bound to colloids can contribute to MUP as well (Haygarth and Sharpley, 2000). Concentrations of MUP in soil solution depend on the input of organic P from animal manure, mineralization of organic P compounds in the soil, and conversion of MUP to MRP by soil microorganisms (Chardon et al., 1997; Leinweber et al., 1997; Richardson et al., 2001; Koopmans et al., 2003). The mining plots did not receive animal manure since 2002, whereas at the sites with a zero P surplus or positive P surpluses 58 to 100% of the P was applied in the form of cattle slurry, resulting in a lower input of MUP into the soil solution of the mining plots compared to the other plots. Also, the lower MUP concentrations of the mining plots can be a result of a reduced supply of P to the grass causing a reduced input of MUP due to turnover of roots and possibly a stimulation of soil microbial conversion of MUP to MRP (Turner et al., 2005).

Both MRP and MUP concentrations in the soil solution varied considerably within and between the years (Fig. 1, 2,

and 3). The MRP and MUP concentrations showed a strong seasonal fluctuation at the fertilized plots. The highest concentrations were generally found after fertilization in early spring. The fluctuations in concentrations were less pronounced at the mining plots. Considerable variation in concentrations was also found between the individual years. For example, concentrations of MRP and MUP in 2002 were extremely low at most sites, whereas considerably higher concentrations of both fractions were observed in 2003, 2005, and 2006. The variation in the measured MRP and MUP concentrations may be caused by several factors, such as differences in soil water content, temperature, and P uptake rates by the grass before soil sampling. For example, 2001 and 2002 were extremely wet with an annual precipitation surplus of 956 and 924 mm, respectively, whereas 2003 was much drier than average (i.e., a precipitation surplus of 631 mm). In wet years, higher leaching losses, higher P uptake rates and dilution of the soil solution lead to lower soil solution concentrations of MRP and MUP, whereas the opposite will occur in dry years (cf. variation in offtake at mining plots). Moreover, wetting and drying cycles may strongly influence the concentrations of MUP and MRP. Rewetting may lead to higher
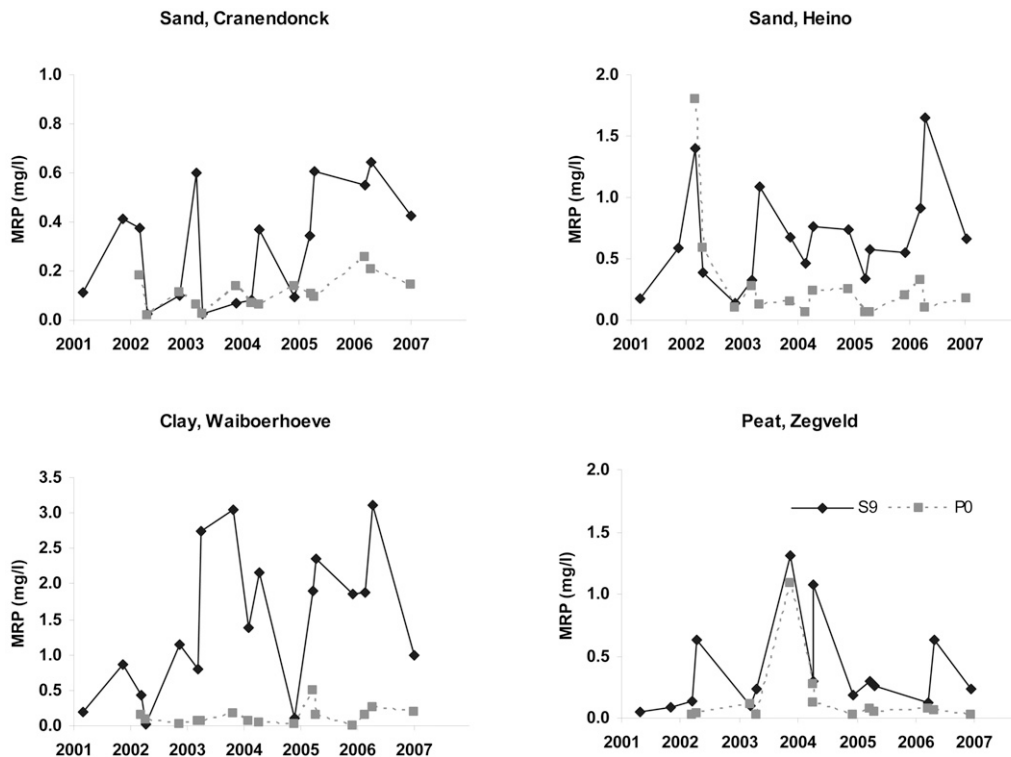
**Fig. 2. Molybdate reactive phosphorus (MRP) concentrations in the soil solution at a depth of 0 to 0.05 m for the sandy sites at Cranendonck and Heino, the clay site and the peat site at a P surplus of 9 kg P ha$^{-1}$ yr$^{-1}$ (S9) and zero P application (P0).**
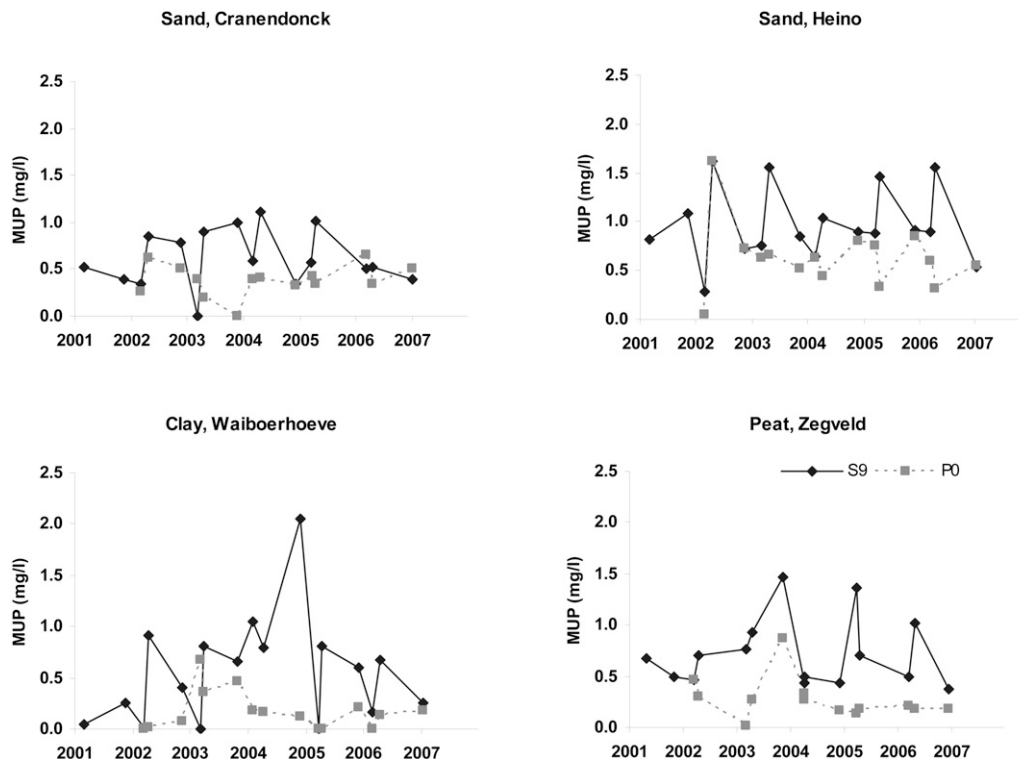


**Fig. 3. Molybdate unreactive phosphorus (MUP) concentrations in the soil solution at a depth of 0 to 0.05 m for the sandy sites at Cranendonck and Heino, the clay site and the peat site at a P surplus of 9 kg P ha$^{-1}$ yr$^{-1}$ (S9) and zero P application (P0)**

soil solution concentrations of MRP and MUP, due to the exposure of new desorption sites, mineralization of organic P, and release of MUP from soil microbial biomass (Chepkwony et al., 2001; Turner and Haygarth, 2001; Koopmans et al., 2006). Finally, statistical analyses of the MRP concentrations in the plots receiving surplus P showed a significant correlation (t < 0.001)
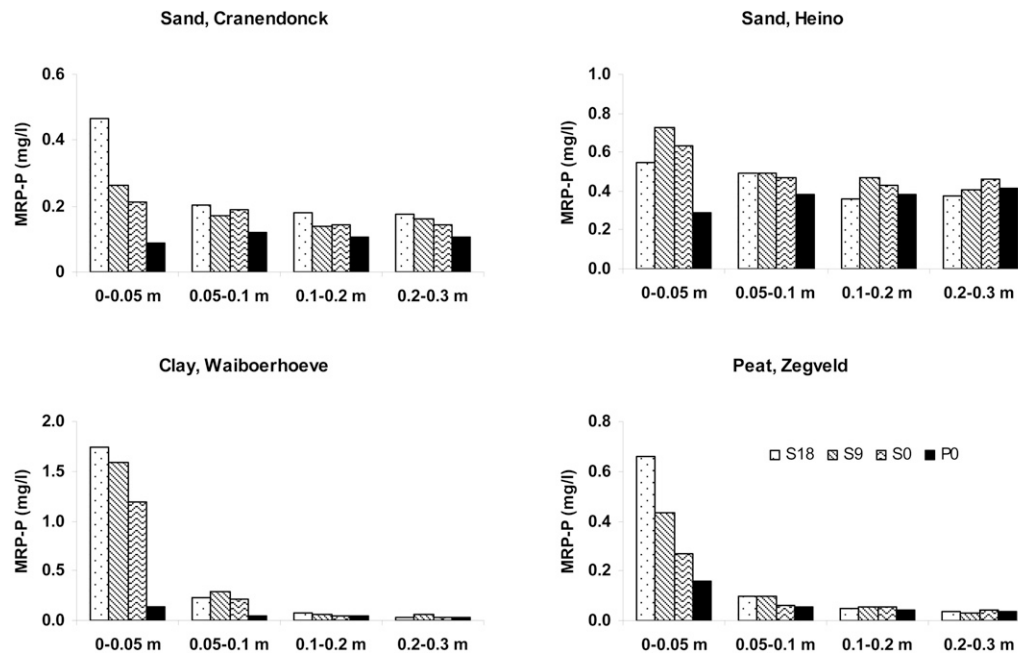
**Fig. 4. Average concentration of molybdate reactive phosphorus (MRP) in soil solution over the period 2002 to 2006 at P surpluses of 18 (S18), 9(S9) and 0(S0) kg P ha⁻¹ yr⁻¹ and zero P application (P0). Note differences in scale on *y* axis.**

between the actual P surplus of a given year and the observed MRP concentrations in autumn. Variation in MRP and MUP concentrations may also be caused by spatial variability, despite the fact that subsamples were collected on 40 well distributed sites across the plot (see Material and Methods).

The high temporal variation in the MRP and MUP concentrations in soil solution makes it difficult to estimate the annual change in P concentrations on mining. Instead, average concentrations over the period 2002–2006 at the mining plots were compared with the plots receiving zero or positive P surpluses to make an estimate of the impact of mining. In the 0- to 0.05-m soil layer, the differences in MRP concentrations between the mining sites and the surplus sites ranged from 58% at the sandy site at Heino to more than 90% at the clay site compared to respectively a zero P surplus and the largest corresponding P surplus (Fig. 4). At 0.05 to 0.1 m depth, the differences in MRP concentrations ranged from 20 to 85% but differences were only significant for the clay soil and the sandy soil in Heino. In deeper layers, the differences became even less prominent. The reduction in the average MRP concentration over the upper 0.2 m ranged from 25 to 50% in the sand and peat soils to 86% in the clay soil. Gallet et al. (2003) reported a reduction of MRP concentrations in the soil solution of 60% in the upper 0.2 m of arable land during a 9-yr P mining experiment. Similarly, Stroia et al. (2007) found reductions in MRP concentrations of 47 and 70% in the upper 0.2 m of grassland following 7 yr of P mining with P removal rates of respectively 26 and 37 kg P ha⁻¹ yr⁻¹. The reduction found in our study may be lower than in the studies of Gallet et al. (2003) and Stroia et al. (2007) due to the shorter time span (5 yr). Moreover, in this study, average reduction percentages were used due to the high temporal variation in the MRP concentrations in soil solution. These reduction percentages were based on the average concentrations in the period

2002–2006 at the mining plots compared to the plots receiving zero or positive P surpluses. The difference in MRP concentrations between the P mining and the surplus plots increased over the period 2002–2006, and our estimates thus underestimate the decline in concentrations after 5 yr of mining.

The reduction in MUP concentrations was on average smaller than in MRP concentrations, and ranged from 25 to 39% at the sandy soil in Heino to 61 to 76% in the clay soil at a depth of at 0 to 0.05 m (Fig. 5). At 0.05 to 0.1 m depth, the decline in MUP ranged between 15 to 60%, but changes were only significant in the sandy soil at Heino.

The effects of mining on the P pools in the soil solid phase may be expected to be much smaller, due to the large amount of P bound to the solid phase of our soils. The strongest effects may be expected on the relatively small and weakly bound P pools ($P_w$ and P-AL). The $P_w$ showed a similar but slightly smaller response on P mining than MRP concentrations in soil solution (Fig. 6). The $P_w$ values (0–0.05 m) declined immediately on zero P application in the clay soil and showed a slower response in the sandy soils (Fig. 6). The peat soil showed the slowest response, and lower $P_w$ values in the peat soil were found from the end of 2003 onward (Fig. 6). Mining resulted in a reduction in average $P_w$ values over the period 2002–2006 of 60 to 70% in the 0- to 0.05-m soil layer of the clay soil and of 20 to 30% in the peat and sandy soils (Fig. 6). In the deeper soil layers, the decline was smaller and generally not significant, except for the clay soil where $P_w$ declined by 50% (results not shown).

A somewhat slower decline with time was found for P-AL at the mined plots, compared to $P_w$ and MRP concentrations, in particular in the sandy soils. The average P-AL in the mined plots declined by 50 to 60% in the 0- to 0.05-m layer of the clay soil, by 20 to 50% in the peat soil, and by 10 to 40% in the sandy soils (Fig. 7). Similar to $P_w$, the decline in P-AL at
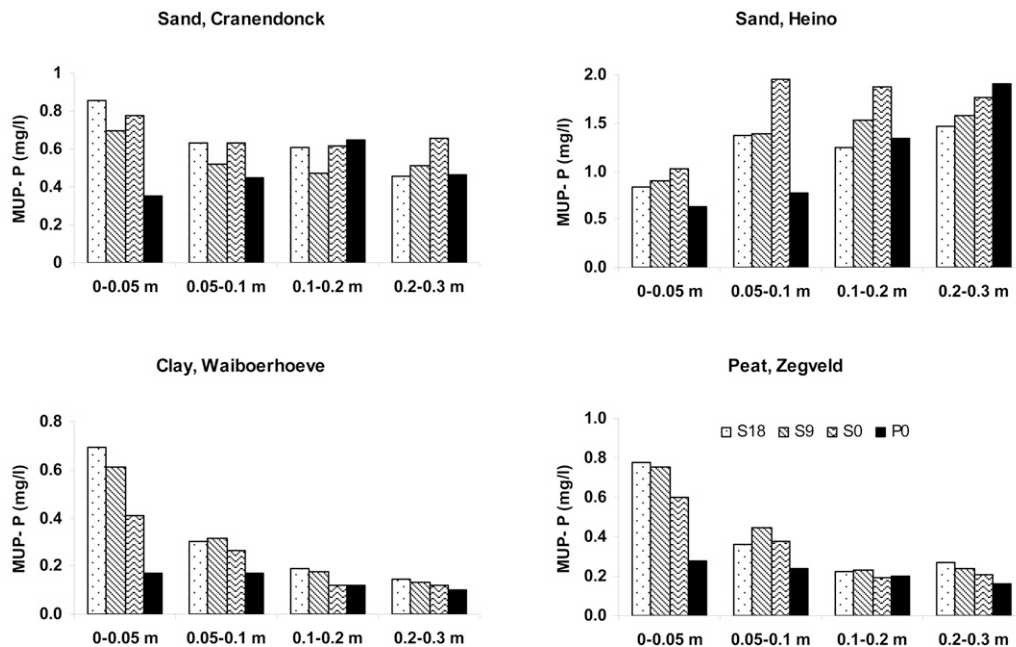
**Fig. 5. Average concentration of molybdate unreactive phosphorus (MUP) in soil solution over the period 2002 to 2006 at P surpluses of 18 (S18), 9(S9) and 0(S0) kg P ha⁻¹ yr⁻¹ and zero P application (P0). Note differences in scale on _y_ axis.**

the mined plots was smaller in the deeper soil layers. Significantly lower P-AL values were found for the clay soil up to a depth of 0.2 m. In the other soils, P-AL values in the mined plots were not significantly lower than on the plots receiving a zero P surplus, but values were lower compared to the plots that received surpluses of 9 or 18 kg P ha⁻¹ yr⁻¹. The observed reductions in P-AL values in the upper 0.05 m of the soil are quite comparable to reductions found in the topsoil (0–0.05 m) of other Dutch grassland sites where mining occurred (Van Dijk et al., 2003).

During the 5-yr experiment $P_{ox}$ and total P started to decline at the mined plots, in particular in the upper 0.05 m of the soil. However, in most soils changes were too small to lead to significant differences in average values over the first 5 yr of mining. An exception was the clay soil, where both average $P_{ox}$ and total P were significantly lower than on the fertilized plots, up to a depth of 0.2 m (results not shown).

## Practical Implications

In this study the effect of mining soil P due to P offtake by grass was studied on soils with moderate to high P contents in the topsoil. Mining resulted in a rapid decline in MRP and MUP concentrations in soil solutions in the upper 0.05 m of the soil, but the effect was less pronounced at lower depths. Mining resulted in significantly smaller weakly bound soil P pools ($P_w$, P-AL). Stronger bound P pools ($P_{ox}$) also started to decline in the uppermost soil layers. The decline in MRP concentrations may be expected to slow down due to the nonlinear relationship between the amount of reversibly sorbed P and MRP concentrations in soil solution. This relationship indicates that at lower amounts of sorbed P more P has to be removed to reach a given decline in P concentrations compared to the start of the mining experiment (c.f. Koopmans et al., 2004). More-

over, the mining plots (except for the plot at Heino) showed a declining trend in P offtake indicating that mining will become less effective in the forthcoming years due to a decline in P contents in the grass and a decline in dry matter production. For an optimal nutritional value of grass to serve as feed for high yielding dairy cows, it should not contain less than 3 g P kg⁻¹ of dry matter, if grass is the only component of the diet (Valk et al., 1999). However, the P content of the grass harvested from the clay and peat sites dropped below 3 g kg⁻¹ of dry matter at the end of the mining experiment (Table 4), indicating that the grass had a poorer nutritional value. Thus, additional P supply may be needed in the future, if this grass would be used as the sole component of the diet for high yielding dairy cows. This will lead to additional costs for the farmer.

Under field conditions, loss of P to surface water can be caused by overland flow, erosion, and leaching (c.f. Haygarth and Sharpley, 2000). The observed decline in MUP and MRP concentrations in soil solution and P pools in the soil solid phase during the first 5 yr of the experiment may be expected to have only a limited impact on the leaching of P to surface water as reductions are mainly limited to the upper 0.05 m of the soil. However, dissolved P in overland flow and discharge of very shallow drained soils will decline rapidly due to lower soil solution concentrations in the uppermost part of the soil, but the loss of sediment bound P will hardly change (Kleinman et al., 2007), as P in solid phase pools showed a relatively small decrease. Moreover, other factors like leaching of P from the subsoil and ditch sediments can impede the immediate translation of improvements on a field scale to effects on the watershed scale (Sharpley et al., 2009). Continuation of the mining experiment will lead to a decline in P concentrations and P pools at greater depth in the root zone. Accordingly, a more pronounced reduction in P losses at the mining sites may be expected in the future.
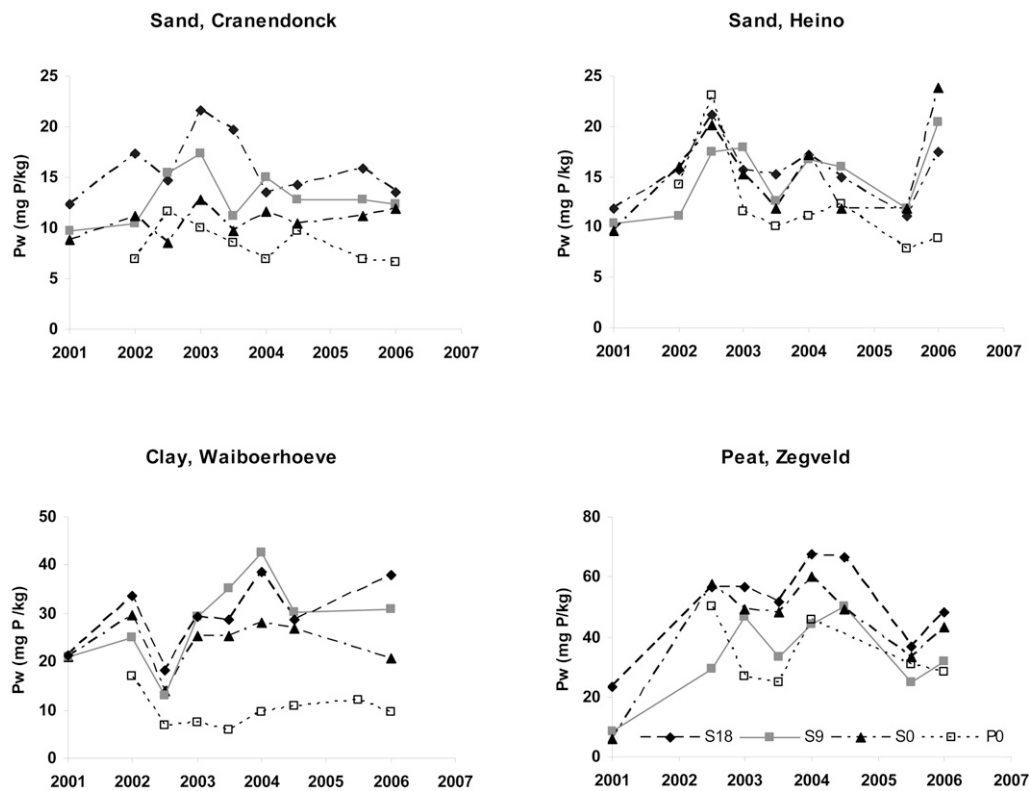
**Sand, Cranendonck**



**Sand, Heino**



**Clay, Waiboerhoeve**



**Peat, Zegveld**



Fig. 6. The $P_w$ values (mg P kg$^{-1}$) as a function of time in the topsoil (0–0.05 m) for the sandy sites at Cranendonck and Heino, the clay site and the peat site at P surpluses of 18 (S18), 9(S9), and 0(S0) kg P ha$^{-1}$ yr$^{-1}$ and zero P application (P0).





**Clay, Waiboerhoeve**



**Peat, Zegveld**



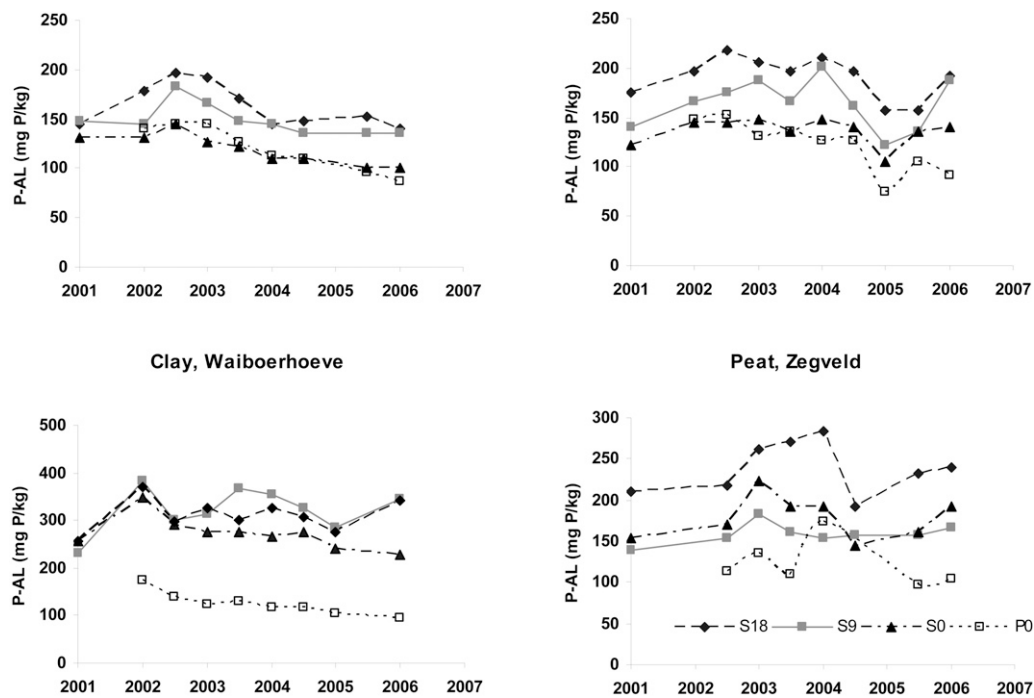Fig. 7. The P-AL values (mg P kg$^{-1}$) as a function of time in the topsoil (0–0.05 m) for the sandy sites at Cranendonck and Heino, the clay site and the peat site at P surpluses of 18 (S18), 9(S9) and 0(S0) kg P ha$^{-1}$ yr$^{-1}$ and zero P application (P0).

Although the effects of mining on P losses to surface waters will become more pronounced when mining is continued for longer time periods, the rate of decline in P concentrations may be expected to slow down when mining is continued over a long-time period.

# Conclusions

Mining soil P by zero P application on non-grazed grassland soils, over a period of 5 yr, led to a strong (30–90%) reduction in both MRP and MUP concentrations in soil solution in the upper soil layer (0–0.05 m) compared to plots receiving P additions. This effect declined with depth and changes were generally not significant in the deeper soil layers ( >0.1 m depth). Mining also led to a decline in P pools in the soil solid phase compared to the fertilized plots. The largest decline was found in $P_w$ (20–60%) and P-AL (10–60%), whereas reductions in P pools that contain more strongly bound P forms, such as $P_{ox}$ and total P, were relatively small. These results confirm earlier greenhouse experiments indicating a rapid decline in soil solution concentrations and a slower decline in absorbed P pools due to the nonlinear behavior of P sorption. The effects of mining on P leaching to surface water may be expected to be small over the (5 yr) period considered, as changes are mainly limited to soil solution in the uppermost soil layers. However, losses of P by overland flow and discharge of very shallow drained soils will decline rapidly. Continued mining will lead to a decline in P losses from the root zone. However, a slow down of the mining process may be expected when P availability starts to limit plant growth.

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