Increasing soil organic carbon content can enhance the long-term availability of phosphorus in agricultural soils

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Running title: impact of organic C on long-term P availability

Abstract

The stocks of phosphorus (P) in soil resulting from decades of over-fertilisation can be used as a long-term source of P provided that crop P bioavailability is ensured. This study was set-up to identify to what extent soil organic matter (SOM) affects the long-term availability of these stocks, the premise being that OM may limit irreversible P fixation in soil by blocking P sorption sites on sesquioxides. An ensemble of 42 agricultural soils, composed from experimentally amended soils (field and incubation trials) and soils with contrasting properties, was subjected to 288 days of P depletion with anion exchange membranes as a P sink; this method was previously shown to yield P pools with agronomic significance. Cumulative P desorption data were fitted with a two-pool kinetic desorption model, yielding estimates for a fast (labile) and total desorbable P pool. On average, 42% of oxalate extractable P (P_{ox}) associated with poorly crystalline iron (Fe) and aluminium (Al) (oxy)hydroxides (Fe_{ox} and Al_{ox}) was desorbable and 25% of that fraction (i.e. 11% of P_{ox}) was labile. That labile P pool matched well with the 24h isotopically exchangeable P (E value) in these soils (R^2=0.74). Both the fast and total desorbable fraction of P_{ox} were larger at higher degrees of phosphorus saturation (DPS). In soils with a low DPS (< 0.30), the labile fraction of P_{ox} increased as the ratio of soil organic carbon (SOC) to Fe_{ox}+Al_{ox} increased (R^2 = 0.70; $p<0.001$), but soils with a higher DPS did not exhibit that trend. These results adhere to soil chemical views that enhanced SOM contents reduce fixation of P by competitive sorption and prevention of P diffusion into micropores. No such effects occur in more P saturated soils, probably because orthophosphate sorption and electrostatic effects outcompete effective SOM sorption. The findings suggest that simultaneous application of OM with P fertilisers could keep P better available on the long-term, but that this OM application does not affect P fixation when soils are excessively dosed with P.

Keywords

ageing, availability, desorption, long-term, organic matter, phosphorus

Highlights

- Long-term availability of P in soil was assessed in contrasting soils in a P depletion experiment
- A high ratio of organic C to Fe and Al in soil enhances the P fraction that is readily available
- The positive effect of organic matter on soil P availability is only found at low soil P saturation
- Residual P in European soils can sustain adequate P for crops for 5-55 years depending on the soil

1. Introduction

Decades of excessive use of phosphorus (P) fertilisers in agriculture have led to the build-up of large soil P reserves in arable soils (Sattari et al. 2012). This historical over-fertilisation contrasts with the impending scarcity of natural mineral P resources (Cordell et al. 2009) and has led to losses of P to the natural environment (Vanden Nest et al. 2015). To reduce the negative consequences of such unsustainable P use, fertilisation policies in some regions advocate a negative annual P balance on agricultural soils, thereby mining residual P from the soil (Manure Action Plan 2015). This mining of legacy P is only possible and justified if a high bioavailability to crops is ensured and current crop production levels can be maintained. However, it is well known that historically added P in soil has a reduced availability compared to that of a within-season P application due to the acknowledged ageing processes of P in soil (Frossard et al. 1994). An accurate evaluation of the remaining, *long-term* availability of the legacy P in soil (i.e. several years after application) is, therefore, needed.

The dynamics of P in acid to neutral arable soils are largely controlled by its interactions with iron (Fe) and aluminium (Al) (oxy)hydroxides (Frossard et al. 1995; Antelo et al. 2007). These interactions are generally divided into fast and slow sorption reactions. Upon addition of P to soils, a fast initial removal of a large fraction of P from the soil solution is consistently followed by a long period of slow decrease of solution P (Fardeau et al. 1991; Strauss et al. 1997; Warrinnier et al. 2018). These reaction kinetics are characterised by a continuum in reaction rates because of the vast heterogeneity in sorption sites of Fe and Al oxides (Warrinnier et al. 2018), but the description is often reduced to a simplified two pool system (Barrow 1983; Lookman et al. 1995). In this two pool system, the fast pool is assumed to be orthophosphate (PO_4) immobilised by a complexation reaction to the surface sites of Fe and Al (oxy)hydroxides, in particular as a bidentate surface complex (Parfitt et al. 1975; Barrow 2017). The adsorption reaches equilibrium within hours to days (Barrow 1983; McGechan and Lewis 2002). The desorption reaction from the fast pool is slower than the adsorption (Barrow 1983), but the reversibility of the reaction makes this pool the most relevant to crops as it replenishes the P in solution (Smolders et al. 2020). The second, slow pool consists of soil P that is not immediately buffering the solution P. The initial, fast surface-based sorption reaction establishes a diffusion gradient towards the interior of the (oxy)hydroxides (McLaughlin et al. 2011). This can either be into micropores (Madrid and De Arambarri 1985) or into the lattice of (oxy)hydroxides via solid-state diffusion (Barrow 1983); both pathways are used to denote the P *ageing* that yields the slow P pool. Furthermore, also precipitation of P with Fe, Al or calcium (Ca) ions, at the mineral surface or inside of micropores, can contribute to slow removal of P from solution (Van Riemsdijk and Lyklema 1980), and evidently decreases P availability. This P aged in amorphous minerals (Torrent et al. 1992; Wang et al. 2013), which are represented by acid oxalate-extractable Fe and Al, is not irreversibly lost and can become available after prolonged desorption times, such as during a P depletion scenario (Lookman et al. 1995; Koopmans et al. 2004; Smolders et al. 2020). However, ageing yields a hysteresis effect: desorption curves of P do not retrace the paths of adsorption (Ryden and Syers 1977; Barrow 1979). This leads to higher critical soil P values (i.e. the P required to obtain 95% relative yield) in P depleting scenarios compared to the period of P reserve build-up (Smolders et al. 2020).

Amorphous Fe and Al (oxy)hydroxides are not only effective adsorbents of phosphates, but also of other oxyanions and of soil organic matter (SOM), i.e. humates and fulvates. This association protects the SOM both physically and biologically, often resulting in elevated organic carbon (OC) contents in soils with a large sorption capacity (Kaiser and Guggenberger 2003). Due to this comparable sorption characteristic, SOM and P can compete for sorption sites, potentially leading to an increase in P availability with increasing SOM content. In short-term experiments, Antelo et al. (2007) observed that the adsorption of P on goethite indeed decreased upon amendment with humic acids (HA), whether they were simultaneously or consecutively added. Weng et al. (2008) found an even stronger effect when using fulvic acids (FA). Several other studies with low molecular weight organic anions such as oxalate (Violante et al. 1991) and citrate (de Souza et al. 2014) also observed increased P availability, although less pronounced compared to HA and FA. These examples all refer to short-term effects of SOM on P availability, and thereby mainly concern P present in the fast pool. In addition, OM sorption to Fe oxides can lead to a strong reduction in specific surface area due to a decrease in microporosity (Kaiser and Guggenberger 2003; Eusterhues et al. 2005). Large SOM molecules (e.g. 1-7 nm for HA and FA; Weng et al. 2008) can spread out over the sorption surface, thereby shielding micropores from P and, potentially, decreasing P ageing. This latter aspect has, to the best of our knowledge, never been explored in detail.

In agronomic terms, a positive effect of SOM on the long-term availability of P would imply that soils with a history of organic fertilisation could be mined to a further extent than those fertilised with mineral P fertilisers at equivalent total P input. This would not only be useful information for contemporary mining projects, but also advocate a shift towards more organic farming practices in the future instead of the conventional use of finite mineral P resources. As there is still considerable room for improvement when it comes to the reuse of organic waste streams, this could be a step from a linear P utilisation system towards a closed P cycle and, consequently, global phosphorus security (Cordell et al. 2011; Ott and Rechberger 2012; Glæsner et al. 2019). So far, long-term field trials have not conclusively shown higher fertiliser use efficiencies of organic compared to mineral fertiliser treatments. However, most long-term trials with organic fertilisers have been designed to compare N use efficiency or C storage and typically have equivalent doses of N or OC, not P. As a result, large variations in soil P within such trials impede a proper comparison of the availability of P among fertiliser treatments.

Taken together, the better use of the legacy P in soil requires improved knowledge of the role of SOM on the long-term availability of residual soil P. Such information is critical to identify the most sustainable fertilisation strategies. This study was set up to address this issue, hypothesizing that P is more reversibly bound when the SOM content is larger, all other factors being constant. Such a study requires arable soils with long-term aged P, i.e. that is present in soil over several years of applications. As a strategy to overcome the drawback that no field trials with factorial SOMxP combinations exist, we used a weight of evidence approach, combining experimentally amended soils with soils of a survey. An ensemble of 42 agricultural topsoils was composed from soils (i) with contrasting soil properties (n=20), (ii) subjected to long-term mineral and organic fertiliser applications in the field (n=14) and (iii) submitted to short-term laboratory incubations (n=8). The long-term P availability was tested by chemical mining of P during 288 days using an established protocol. As the focus of this study was on the effect of SOM on the ageing of P in soils, the mining experiment was performed under abiotic conditions by chloroform addition, limiting the contribution of organic P mineralisation to long-term P availability.

2. Materials and Methods

2.1 Soils and soil treatments

The set of soils used in this study was composed of 42 soils and soil treatments, originating from 24 different sampling sites (Table 1). Soils 1-20 were sampled from across the UK by Rothamsted Research and were selected for their adequate level of available P (Olsen P index ≥ 3 according to Defra (2010); Olsen et al. (1954)) in combination with a wide range in soil properties of interest, such as SOM content and oxalate-extractable Fe and Al. The remaining 22 soil samples came from four locations, i.e. 14 from field trials at two locations and 8 from a laboratory experiment based on samples of two locations. Soils 21.X-22.X (Table 2), with X referring to the treatment, comprise 14 samples collected from two long-term field trials in Melle (BE) and Zürich (CH). Both trials are randomised complete block experiments with different mineral and organic fertiliser treatments. Seven treatments per soil were selected for this study to investigate the effect of fertilisation history on the long-term availability of P in soil. Although the trials had been set up to study soil organic carbon (SOC) storage, it was endeavoured to select treatments that received a comparable P dose over the years. The trial in Melle started in 2005 and was sampled after 8 years, in 2012. The selected treatments included: a control with no fertiliser (#21.1), mineral NPK fertiliser (#21.2), cattle slurry (#21.3), farmyard manure (#21.4), farm compost with a high (#21.5) and a low (#21.6) C:N ratio and vegetable, fruit and garden waste (VFG) compost (#21.7). The second field trial, the Zürich Organic Fertilisation Experiment (ZOFE), started in 1949 and was sampled in 2019, after 70 years of continuous organic and/or mineral fertilisation. A control with no fertiliser (#22.1), mineral NPK fertiliser at a low (#22.2) and high (#22.3) P dose, manure with PK (#22.4), only compost (#22.5) and compost supplemented with PK (#22.6), and peat with PK (#22.7) were selected. Selected soil properties for all treatments are presented in Table 2; more information on the design, fertiliser additions and crop rotations can be found in Vanden Nest et al. (2014) and Oberholzer et al. (2014). Finally, Soils 23.X-24.X were collected from two low P arable soils from Grignon (FR) and Gembloux (BE); both were subjected to an incubation trial prior to the start of the P desorption experiment (with X referring to the treatment; Table 2). In this trial, they were amended with 100 mg P kg^{-1} as KH_2PO_4 and dried maize at a rate of 3 g C kg^{-1} in a full factorial design. The resulting four treatments per soil were incubated for 6 months in a dark 20°C climate room at 20% gravimetric water content to allow ageing of the freshly applied P. Soils were regularly aerated and gently mixed to avoid anaerobic conditions. All soils were air-dried, sieved <2 mm and stored dry prior to the start of the mining experiment.

All 42 soils and soil treatments were characterised. The SOC and soil N content were determined by dry combustion after acidification of dry soil samples with 10% HCl to remove inorganic C, and subsequent measurement of released CO_2 and N_2 with an elemental analyser (EA1108, Thermo Scientific). Oxalate P (P_{ox}), associated with amorphous Fe (Fe_{ox}) and Al (Al_{ox}) oxyhydroxides, was determined by the acid oxalate extraction method of Schwertmann (1964): air-dried soil was extracted for 2 h with a mixture of ammonium oxalate and oxalic acid at pH 3 in the dark. After filtration over 0.45 µm (Chromafil Xtra, PET -45/25), the extracts were analysed for P, Fe and Al with ICP-OES (Thermo Scientific iCap 7000). These oxalate-extractable elements were used to determine the degree of phosphorus saturation (DPS)

$$DPS\ (mol\ mol^{-1}) = \frac{P_{ox}\ (mol\ kg^{-1})}{0.5\cdot(Fe_{ox}\ (mol\ kg^{-1}) + Al_{ox}\ (mol\ kg^{-1}))} \qquad \text{(Equation 1)}$$

and the degree of carbon saturation (DCS)

$$DCS\ (mol\ mol^{-1}) = \frac{SOC\ (mol\ kg^{-1})}{0.5\cdot(Fe_{ox}\ (mol\ kg^{-1}) + Al_{ox}\ (mol\ kg^{-1}))} \qquad \text{(Equation 2)}$$

Furthermore, the isotopically exchangeable P or the E_{24h} value (Equation 3) was determined as an estimate of the readily available P (Maertens et al. 2004). In short, soils pre-equilibrated in 5 mM $CaCl_2$ at a 1:10 soil solution ratio were spiked with 30 kBq ^{32}P g^{-1}. After 24h of isotope dilution, the ^{31}P concentration ($^{31}P_{sol}$) and remaining ^{32}P activity concentration ($^{32}P_{sol}$) in solution were measured in 0.45 µm filtrates with malachite green and liquid scintillation counting (Perkin Elmer, Tri-carb 2800 TR Liquid Scintillation Analyzer), respectively.

$$E_{24h}\ (mg\ P\ kg^{-1}) = {}^{31}P_{sol}\ (mg\ P\ kg^{-1}) \cdot \frac{{}^{32}P_{added}\ (Bq\ kg^{-1})}{{}^{32}P_{sol}\ (Bq\ kg^{-1})} \qquad \text{(Equation 3)}$$

2.2 Selection of the P desorption method

Prior to the start of the mining experiment, three desorption methods were tested on two soils with contrasting P availability, and evaluated for ease of use and ability to keep the P desorption rate as high as possible. All three desorption methods followed the zero P sink principle, adding a binding surface for P to the solution phase of a soil extract to keep the P concentration in solution close to zero. The methods tested were 1) dialysis bags filled with hydrous ferric oxide (HFO) in suspension (Lookman et al. 1995), 2) iron oxide impregnated filter papers (P_i papers), separated from the soil by nylon mesh bags

(Van der Zee et al. 1987), and 3) anion exchange membranes (AEMs) in bicarbonate form (Kouno et al. 1995). The amount of desorbed P followed the order P_i paper > AEMs ≥ HFO bags in both soils. However, based on the brown colour of blank papers, part of the desorbed P in the P_i paper method was attributed to colloids that migrated through the nylon mesh. For the AEMs, little Fe and Al was measured in the extracts: taking into account the DPS of the soils, the contribution of colloidal P was estimated to be less than 1% of the desorbed P. Furthermore, a comparison between colorimetric and ICP-OES measurements confirmed that all desorbed P was inorganic. Because of this, and their superiority in ease of use over the HFO bags which readily break upon longer shaking times, the AEMs were selected as a P sink for the mining experiment.

2.3 Chemical mining

The 42 soils and soil treatments were subjected to 288 days of P mining using AEMs as a zero P sink. Three weeks prior to the start of the experiment, 30 g air dry soil was wetted to approximately field capacity for each sample and pre-incubated in a dark 20°C climate room. Soils were regularly aerated and gently mixed to avoid anaerobic conditions. At day 0 of the mining, the equivalent of 2.5 g dry soil was weighed into 50 mL polypropylene tubes (Sarstedt) with 4 replicates per sample. To this soil, 40 mL of milliQ water was added, as well as a few drops of chloroform ($CHCl_3$) to limit the contribution of organic P mineralisation to P mining during the experiment. Suspensions were mounted on an end-over-end shaker (30 rpm) in a dark 20°C climate room. After shaking for 2 h, the pH was measured. Subsequently, two AEM strips of 6 cm^2 (551642S, VWR Chemicals) in bicarbonate form were added to the suspensions as a P sink. The tubes were sampled every two weeks, with a higher sampling frequency during the first four weeks of the experiment (on day 1, 3, 7, 12, 20 and 28) to capture the fast dynamics expected in this initial phase. Sampling consisted of taking out the AEMs with tweezers while making sure to remove as little soil as possible, rinsing with milliQ water and eluting the adsorbed P overnight in 20 mL 0.5M HCl. The AEMs were immediately replaced with fresh ones that had been conditioned overnight in 0.5M $NaHCO_3$. For quality control, 3 fresh blanks (milliQ water) and reference samples (KH_2PO_4 solution of 8 mg P L^{-1}) were included at every sampling time. Desorbed P was quantified colorimetrically with the malachite green method of Ohno and Zibilske (1991). Absorbance of the coloured complex was measured at 630 nm, using a Perkin Elmer Lambda 25 spectrophotometer. Standard series were prepared in the same matrix as the samples, i.e. 0.5M HCl, to account for the effect of acidity on colour formation. The AEMs proved to be a suitable zero P sink: reference samples consistently yielded >90% recovery of P in solution, averaging at 98%, while blank samples always remained below the detection limit of the malachite green method (i.e. 8 μg L^{-1}). Every other sampling time up until day 98, the pH of two out of four replicates was measured to keep track of potential changes induced by desorption of bicarbonate from the AEMs.

2.4 Data analysis

The results of the chemical mining were described by fitting a serial two-pool model to the data of cumulative P desorption over time (Lookman et al. 1995; Smolders et al. 2020). As Figure 1 shows, the fast desorbable P pool (Q_1, mg P kg^{-1}) is in direct contact with the soil solution and is replenished by desorption/migration of P from the slow pool (Q_2, mg P kg^{-1}). When assuming first order kinetics for both desorption reactions, the equation describing cumulative P desorption under zero P sink conditions (Q_{des}, mg P kg^{-1}) reads:

$$Q_{des}\,(t) = \left(Q_1 - \frac{k_2}{k_1 - k_2} Q_2\right)\left(1 - e^{-k_1 t}\right) + \left(\frac{k_1}{k_1 - k_2} Q_2\right)\left(1 - e^{-k_2 t}\right) \qquad \text{(Equation 4)}$$

with the desorption rate constants k_1 and k_2 in day^{-1}. Generally, it is assumed that all oxalate-extractable P is desorbable at prolonged desorption times, i.e. $Q_1 + Q_2 = P_{ox}$, turning Equation 4 into a 3-parameter model (Lookman et al. 1995; Smolders et al. 2020). However, the P_{ox} is likely an overestimation of the truly desorbable P pool, and making this assumption has a considerable impact on the estimation of Q_1

and both desorption rate constants (k_1 and k_2). For this reason, an alternative version of the model was tested, in which no such assumptions about the P_{ox} pool were made, and Q_2 was simply estimated as an additional, fourth parameter. For both models (3 and 4 parameters), fitting was done by nonlinear regression in JMP Pro 15 (SAS, Cary, NC, USA) by minimising the sum of squared errors (SSE) between modelled and measured data, using all four replicates per soil. For the samples from the field and incubation trials, all treatments were fitted together to avoid overfitting: only the size of Q_1 and Q_2 was allowed to vary between treatments, while the desorption rate constants k_1 and k_2 were assumed to be constant for all soil samples from the same location.

The two models were compared for their adequacy to describe cumulative P desorption by means of two criteria, i.e. (1) the root mean squared error (RMSE; (Goos 2011)), which is a measure of the misfit between modelled and measured values

$$RMSE = \sqrt{\frac{SSE}{N-n_p}} \qquad \text{(Equation 5)}$$

with N the number of data points and n_p the number of parameters to be estimated (i.e. 3 or 4); and (2) Akaike's Information Criterion (AIC)

$$AIC = N \cdot ln\left(\frac{SSE}{N}\right) + 2 \cdot n_p \qquad \text{(Equation 6)}$$

which also penalises the models for increasing the number of parameters to get a better fit. The AIC can, thus, be used to justify the addition of the fourth parameter. Both criteria should be as low as possible.

The fast Q_1, slow Q_2 and total desorbable P pool ($Q_1 + Q_2$) estimated by model fitting were normalised to permit comparison between soils with a different P content, thereby indicating the relative desorbability of P in the soils. It was opted to perform this normalisation per unit of P_{ox}, and not total P, as this pool is deemed the most relevant with respect to soil P dynamics. Desorbable P pools, fractions and their desorption rate constants were correlated to the selected set of soil properties presented in Table 1 and 2. For this correlation analysis, a subset of 37 soils and soil treatments was used. The four samples of the +P treatments from the incubation trial were omitted as it became clear during mining that the P did not have enough time to age properly, yielding faster P desorption than observed in the field soils (see Section 3.4). Additionally, Soil 6 was excluded as it consistently appeared to be an outlier in a preliminary correlation analysis including all soils. Its low concentrations in Fe and Al (oxy)hydroxides and high calcite content (8.1% inorganic C; data not shown) likely cause its long-term P availability to be controlled by reactions with $CaCO_3$ rather than Fe and Al (oxy)hydroxides (Frossard et al. 1995). Moreover, it is well-known that the acid oxalate extraction is not well-suited for such calcareous soils, likely resulting in spurious values for P_{ox}, DPS and DCS for this soil (Guo and Yost 1999). For k_1 and k_2, only one treatment was included per soil from the field or incubation trials to avoid overrepresentation, as these parameters were kept constant among treatments during fitting; the same applies to soil texture as this was only determined once per soil. Simple linear regression was performed to assess the relationship between desorbable P fractions Q_1 (%) and Q_1+Q_2 (%) (response variables) and the most well-correlated soil properties resulting from the correlation analysis, i.e. the DPS and DCS (predictors). The coefficient of determination (R^2), quantifying the proportion of variation that is explained by the regression, is presented as a measure for the goodness of fit. Residuals were visually inspected for heteroscedasticity and their distribution was tested to be normal based on histogram analysis (Welham et al. 2014). Prior to correlation and regression analysis, the soil properties of interest were inspected for normality. Properties with a skewness coefficient exceeding the threshold of -1 or 1, i.e. the SOC content, DCS and all oxalate-extractable elements, were $\log_{10}$ transformed (Webster 2001). All statistical analyses were performed using JMP Pro 15.

Finally, to assess the effect of fertilisation history on the long-term availability P in soil, the treatments in the field trials were corrected for dissimilar P doses received over the years. These had resulted in varying final DPS values, which might confound effects due to organic amendments. To overcome this, 95% prediction intervals (PI) were constructed for the desorbable P fractions in the different treatments; these were based on the relation with the DPS that was established by regression analysis on the other soils (but including only the control and mineral treatment for the Melle and Zürich soil themselves). The labile and total desorbable P fractions in the treated soils from the field were then compared with these PIs to assess the effect of fertilisation type.

3. Results

3.1 Soil properties

Properties of the selected soils spanned a range that was wide though relevant for Western-European agriculture (Table 1 and 2). The pH ranged from 4.4 to 7.4 and the SOC content from 0.9 to 5.0 %. The P_{ox} ranged between 200-1800 mg P kg^{-1} and constituted, on average, 60% of the total soil P. These concentrations corresponded to DPS values (in mol mol^{-1}) between 0.19 and 0.56 (with the exception of one outlier with DPS=1.00) and DCS values (in mol mol^{-1}) between 14 and 88. In the field trials, SOC increased from 0.9% to values up to 1.3% upon organic fertilisation. The strongest build-up was observed for compost and peat, despite similar OC inputs compared to manure and cattle slurry. This can be explained by the higher degree of decomposition of the organic matter in the former inputs, making it more stable and, therefore, less prone to further degradation. The organic fertilisation consistently increased soil pH compared to mineral fertilisation and the control soil; this has been observed many times before and is attributed to decarboxylation of organic matter (Yan et al. 1996; Cai et al. 2020; Nobile et al. 2020). The repeated administration of different doses of P over the years resulted in significant differences in P_{ox}: in the Melle trial, P_{ox} differed up to 15% compared to the mineral treatment, while in the longer trial Zürich, differences in P_{ox} among treatments were up to 70%. In the incubation trials, amendment with dried maize increased the SOC content with 0.1% (GE-P) to 0.4% (GR-P). The P dose added in the experiment was completely recovered by the P_{ox} of the soils, and 60-75% of this dose was still present in the E_{24h} value.

3.2 P desorption kinetics

For 288 days, 42 soils and soil treatments were mined for P in a long-term desorption experiment. Replicability was adequate, with an average relative standard deviation of 3% between replicates. Addition of the bicarbonate-conditioned membranes shifted soil pH towards neutrality compared to the initial pH: mean shifts (final-initial) were 0.8 pH units, with a maximum increase of 1.6 for an acid soil and maximum decrease of 1.1 for a calcareous soil. During the course of the mining experiment, an unforeseen temperature spike occurred due to a climate room error, resulting in solution temperatures of ± 50°C for several hours. This event significantly increased the rate of P desorption compared to the previous period and occurred between day 56-70 for Soils 1-20 and day 42-56 for Soils 21-42 (examples in Figure 2). Despite this significant increase, leaving out the data points of these days resulted in only a negligible change in model parameters. It was, therefore, decided to include all results as measured.

After 288 days, between 60-340 mg P kg^{-1} was mined from the soils, corresponding to 13-63% of P_{ox} and 8-42% of total P. For all soils, cumulatively mined P (examples in Figure 2) distinctively showed a short initial phase of fast desorption, followed by a long period of slow desorption which could be well described by the simple two-pool model of Equation 4. Including Q_2 as a fourth parameter, instead of assuming that $Q_1+Q_2=P_{ox}$, improved both the RMSE and AIC of the model fits (Figure S1 in Supporting Information, SI). The 4-parameter version of the model in Equation 4 was, therefore, selected for further data analysis in this study. Fitting this model to the data yielded estimates of pool sizes and reaction rate constants for a fast (Q_1) and slow (Q_2) desorbable P pool, with their sum (Q_1+Q_2) being defined as the total desorbable P of a soil (Table 3; results per soil in Table S1). The fitted half-lives of the Q_1 pool were 1-6 days. Corresponding values of the slow Q_2 pool were a factor 30-180 larger, averaging at 200 days. The total desorbable P ranged between 23-67% of P_{ox} among soils, with a mean of 42% (Figure 3), and was significantly lower than P_{ox} for all soils. The labile Q_1 pool was, on average, only 25% of the corresponding Q_1+Q_2 pools. Its size ranged between 13-142 mg P kg^{-1} depending on the soil, and markedly agreed with the 24h isotopically exchangeable P or E_{24h} values (Figure 4).

3.3 Soil properties affecting long-term P availability

The correlations between kinetic parameters and soil properties are presented in Table S2. As expected, both the fast Q_1 and slow Q_2 pool were positively correlated with P_{ox} in absolute terms. The DPS most significantly explained the kinetic P fractions, i.e. Q_1/P_{ox} and $(Q_1+Q_2)/P_{ox}$. Figure 5 shows that, both the Q_1 and Q_1+Q_2 fractions increased with increasing DPS. The grey data point in frame B corresponds to Soil 17 (Weston), a high pH soil with only little P_{ox}. The pH decrease induced by adding bicarbonate conditioned AEMs potentially caused the gradual dissolution of Ca-phosphates, resulting in a considerable overestimation of the total desorbable P fraction. The labile P fraction was not correlated to the SOC content, while the total desorbable P fraction was even negatively correlated to $\log_{10}$(SOC) ($r = -0.54$; $p < 0.001$). However, when the SOC content was expressed relative to binding sites, i.e. as DCS, significant relations were revealed. Indeed, it is not the SOC *content* but rather its *ratio* to binding sites that can impact P availability. Figure 6 shows that the labile Q_1 fraction of a soil increased with increasing $\log_{10}$(DCS). Interestingly, this effect was only observed in soils with a relatively low DPS and not in the more P saturated soils. The DPS threshold was set at 0.30, though in reality it would obviously be a gradual transition. Importantly, within the group of low DPS ($n = 17$), an increased Q_1 fraction was unrelated to an increased DPS ($R^2 = 0.05$; $p = 0.37$) and was, therefore, fully attributed to the positive impact of the DCS ($R^2 = 0.70$; $p < 0.001$). On the contrary, for the more P saturated soils (DPS > 0.30; $n = 20$), the DPS remained the main soil characteristic explaining the variability in the labile Q_1 fraction ($R^2 =$

0.62; p<0.001). It is important to note that all these observations also hold when including only one treatment per soil from the field and incubation trials.

3.4 Fertilisation history affecting long-term P availability

In the field trials of Melle and Zürich, mineral and organic fertilisers were applied for 8 and 70 years respectively, resulting in DCS values ranging between 26-37 mol mol^{-1} and 21-32 mol mol^{-1}. The long-term character of the trials provided enough time for the ageing of added P, so that these differences between treatments were translated to considerable differences in long-term P availability. However, different P doses over the years also resulted in varying final DPS values, ranging between 0.41-0.47 (Melle) and 0.26-0.43 (Zürich). As shown in Figure 5, an increase in DPS generally results in an increase in labile and total desorbable P fraction, which might confound effects due to organic amendments. To overcome this, measured fractions were compared with prediction intervals that were constructed based on the linear regression between labile (for high DPS soils) or total desorbable P fractions, and the DPS. That regression used all soils excluding the treatments of the field trials, but including the Control, Mineral (Melle) and Mineral high (Zürich). Treatments for which the marker does not overlap with the corresponding PI in Figure 8 have a higher or lower labile or total desorbable P fraction than expected for their DPS.

Figure 8 shows the lack of a general, unidirectional effect of organic fertilisers on P desorption compared to mineral fertilisers. The labile P fraction was unaffected by addition of farmyard manure or cattle slurry compared to the mineral treatment when taking into account the difference in DPS. However, compost and peat application lowered the labile P fraction compared to the other treatments. This effect was most clear in the 70-year long Zürich field trial: both compost treatments as well as the peat treatment had a P availability that was lower than predicted for their respective DPS. For the Melle trial, this effect was less clear, likely because of the shorter term character of the trial as well as the fact that all treatments were above their predicted range. Similar trends were observed for the total desorbable P fraction.

For the two soils from the incubation trial, differences in desorbable P fractions between treatments were small and rarely significant (results in SI, Figure S2). For both the Grignon and the Gembloux soil, about 90% of the (nominal) 100 mg P kg^{-1} that was applied could still be found in the Q_1+Q_2 pool after 6 months incubation. On average, 67% was even still present in the fast desorbable pool. The unexpected differences in both soils between the treatments without P application (Control and Control + OM) were likely caused by the addition of some P with the OM amendment (estimated at 16 mg P kg^{-1} in total, i.e. inorganic and organic P), even though this was not reflected in the P_{ox} of the treatments.

4. Discussion

4.1 Long-term availability of P in soil

The long-term availability of P in soil was evaluated by quantifying fast and total desorbable P fractions in soils with contrasting properties. In earlier studies using a similar zero P sink and two-pool kinetic desorption model (Equation 4), it was typically assumed that all P_{ox} is desorbable at prolonged desorption times (Lookman et al. 1995; Smolders et al. 2020). However, in this study, with much longer desorption times compared to these other studies (288 vs 66-77 days), it was chosen not to make this assumption, as it was found to overestimate the size of the Q_1 pool and underestimate its desorption rate constant. This decision was supported by the lower AIC values obtained when fitting the 4-parameter model, and substantiated by the observation that the resulting total desorbable P pool was significantly smaller than P_{ox} for all soils. In fact, our results suggest that, on average, more than half of P_{ox} could not become available in the long-term. Similarly, in a biological mining experiment by Koopmans et al. (2004), a maximum of 65% of P_{ox} could be removed by plants. The low availability of the remainder of the P_{ox} can likely be attributed to precipitation of P in micropores of poorly crystalline Fe and Al (oxy)hydroxides, surface precipitation of P with dissolved Fe, Al or Ca ions (Warrinnier et al. 2018) or solid state diffusion (Barrow 1983). Additionally, part of the fraction of P_{ox} observed to be unavailable in our study is likely P in organic form. This is partially included in oxalate extractions (on average 15% of P_{ox} in this study) but its contribution to the P mining potential is not accounted for in our mining experiment because organic P mineralisation was halted through the addition of chloroform.

The sizes of the labile Q_1 pools corresponded with findings in earlier papers using a similar method and model, both in absolute terms and relative to the P_{ox} (Lookman et al. 1995; Smolders et al. 2020), and were comparable to fast desorbable P pools determined in a flow-through reactor P release experiment (Frossard et al. 2014). The ranges observed in our study, equivalent to 50-550 kg P ha^{-1} in an arable topsoil (0-30 cm), could support plant growth for 5-55 years when assuming uptake rates as defined by Sattari et al. (2012) for Western Europe. Interestingly, Q_1 pool sizes markedly agreed with the 24h isotopically exchangeable P or E_{24h} values. Diffusion and crop uptake modelling recently highlighted that the P fluxes in soil highly depend on the magnitude of the Q_1 pool (Smolders et al. 2020). Along the same lines, E values determined at different exchange times, ranging from 1 minute (Sen Tran et al. 1988; Lemming et al. 2019) over several days (Warrinnier et al. 2018; Braun et al. 2019) to weeks (Frossard et al. 1994), have also been used to predict soil P bioavailability across different soils. Though it is striking to note that Q_1 and E_{24h} values could be interchanged as the index of soil P bioavailability.

4.2 Effect of SOC on long-term P availability

Correlation analysis suggested that the DPS and DCS of a soil are the most important characteristics explaining the variability in the labile Q_1 fraction (Q_1/P_{ox}). The positive relation between DPS and the kinetic P fractions has been observed before (Kuo 1988; Lookman et al. 1995) and is rather obvious: when soil sorption sites become saturated (i.e. high DPS), the fraction of adsorbed P that is weakly bound becomes larger. Similarly, Braun et al. (2019) observed that a higher recovery of a radioactive ^{33}P spike was obtained by common single-step extractions for soils with a higher DPS, confirming that P remains better available in such soils. This observation goes hand in hand with an increase in desorption rate constants with increasing DPS: at high P saturation, generally associated with smaller concentrations of Fe and Al oxides, both the fast and slow desorbable P pool are, on average, “faster”.

The hypothesised positive effect of the DCS on the labile Q_1 fraction (Q_1/P_{ox}) was only observed in soils that were not too saturated with P; in those soils, it even outweighed the effect of the DPS. It is hypothesized that, at low DPS, when only a small fraction of surface sorption sites is occupied by P, adsorbed SOM molecules can spread out over the surface of Fe and Al (oxy)hydroxides, bind with multiple functional groups and cover micropores. This can prevent diffusion of P into the pores, leading to less ageing (or a higher Q_1 fraction of the P_{ox}) at higher DCS. In contrast, at high DPS, when a large fraction of sorption sites on the surface is occupied by anionic phosphates, adsorbed P effectively competes with SOM, possibly forcing the adsorbed SOM molecules to be oriented in an extended, rather than spread out, conformation with respect to the sorption surface. Because of this, the adsorbed SOM cannot cover micropores, thereby allowing P to enter them and become less available. A high DCS is, in this case, not effective in reducing ageing and thus improving the lability of soil P. This hypothesis, illustrated in Figure 7, is supported by the observation of Kaiser and Guggenberger (2003) that SOM occupied a larger fraction of the sorption surface per molecule C at lower SOC surface loadings compared to higher loadings. In a later study, they confirmed with Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT) that at small surface concentrations of OM, most carboxylate groups at the surface of goethite were complexed, while this proportion decreased when OM surface concentrations increased (Kaiser and Guggenberger 2007). This resulted in a transition from tight OM surface coatings to bulky accumulations of OM upon higher surface loadings, as was confirmed with

Scanning Electron Microscopy (SEM). Comparable changes in arrangement at the surface of minerals were also observed for organic polymers (Theng 2012).

This positive effect of an increased DCS on the long-term availability of P in low DPS soils could also explain observations in previous field trials on soils with a marginal initial P availability. In several such trials in Madagascar (Andriamananjara et al. 2018; Andriamananjara et al. 2019) and Kenya (Otinga et al. 2013), a significant positive effect of farmyard manure on grain yield and/or P uptake was observed for rice, Bambara groundnut and maize when mineral P fertiliser was combined with farmyard manure compared to application of mineral P only (all treatments received adequate N and K), but this only became visible after several growing seasons. In hindsight, this delayed effect could be explained by the observations in our study: P added as or together with farmyard manure remains better available over the years compared to purely mineral P at the same rate of application due to a decrease in ageing at increased DCS.

The effect of SOC on the total desorbable P fraction is, compared to the labile P fraction, less straightforward and, more importantly, less relevant for actual field situations. Not only will mining of residual P in reality not be performed to such an extent, but also the SOC content would change over such periods of time as are necessary to perform complete mining; the size of the total desorbable P pool in the soils from this study would be enough to sustain crop growth for 23-170 years.

4.3 Effect of fertiliser type on long-term P availability

The soils from the field trials included in this study allow to investigate the experimental effect of fertiliser strategy on long-term P availability. There was no consistent effect of organic fertilisers on P desorption compared to mineral fertilisers, which contrasts our starting hypothesis as well as observations in field trials on soils with low P availability. However, as both soils had a high DPS at the start of the trials (Melle = 42%; Zürich = 35%), these findings are in line with the general observation that the DCS has no effect on P desorption at larger soil DPS. A focussed screening of the effect of fertiliser type on the long-term availability of P in low DPS soils is still required to confirm the mechanism proposed in this research, and may be the subject of future studies.

The data in this study suggest that, in high DPS soils, manure does not increase the long-term availability of P compared to other fertilisers, as has been suggested before for the concerning field trials (Vanden Nest et al. 2016; Warrinnier et al. 2018). In contrast, the availability of P in soils fertilised with manure (and by extension cattle slurry) is in line with that of mineral fertilisation when corrected for the DPS. Rather, compost and peat applications decreased the labile P fraction compared to other fertilisers and, consequently, have a negative impact on the mining potential of legacy P from arable soils. This negative effect of compost and peat on long-term P availability is somewhat surprising but has been observed before in other studies (Vanden Nest et al. 2016; Glæsner et al. 2019; Lemming et al. 2019). It was suggested that this is the result of the formation of complexes between P and the stable OC compounds from the fertiliser, rendering the P less labile. It is speculated that compost and peat, being in a further state of degradation, contain more of such stable OC compounds than e.g. cattle slurry and farmyard manure (Leytem et al. 2005; Vanden Nest et al. 2016). Furthermore, it has also been shown with solid-state ^{31}P NMR analysis that compost can contain scarcely soluble Ca-P compounds such as apatites, which would imply that part of administered P is already less available at the start (Frossard et al. 2002; Glæsner et al. 2019).

5. Conclusion

In the light of recently communicated intentions by some European regions to start the mining of residual P from heavily P loaded agricultural soils, the long-term availability of P was assessed in a chemical mining experiment using anion exchange membranes as a zero P sink. Fast and total desorbable P were estimated by fitting a two-pool model to data of cumulative P desorption. It was shown that, despite ageing processes, a considerable fraction of residual P can still become available during a P depletion scenario, although not the whole P_{ox} pool as has been assumed until now. As hypothesised, this remaining availability was larger at large OC/(Fe+Al) ratios (DCS), but only under conditions of low P saturation. As a mechanism, it was hypothesised that SOM molecules can effectively prevent diffusion of P into micropores of soil reactive minerals by spreading out over the sorption surface, thereby reducing P ageing. In more P saturated soils, such as are prevalent in Western Europe, the lack of available sorption sites likely hinders spreading out of the SOM by competitive and electrostatic effects of sorbed P. Translated to the field, our results suggest that application of organic fertilisers could be beneficial in terms of availability during the period of build-up, provided that the soil does not become too saturated with P. A comparison between different organic fertilisers pleaded in favour of farmyard manure over compost as the latter was found to decrease the labile P fraction. However, further research is required to elucidate the mechanisms behind this.

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Conflict of Interest

None of the authors declare a conflict of interest.

Data Availability Statement

Most data generated for this study are presented in the manuscript or the Supporting Information. Data that are not shown can be made available upon request to the corresponding author.

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Table 1: Selected properties of the soils collected across the UK (Rothamsted Research), the mineral treatments of the soils from the field trials in Melle (#21.2; Table 2) and Zürich (#22.3; Table 2) and the control treatments for the incubation trial (#23.1 and #24.1; Table 2).

Soils		**General soil properties**			**Soil phosphorus**			**Binding properties**			
#	name	texture	pH_{CaCl2}	OC	E_{24h}	P_{ox}	P_{tot}	Fe_{ox}	Al_{ox}	DPS	DCS
				(%)	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mol mol^{-1})	(mol mol^{-1})
1	Longclose	clay loam	4.7	4.0	70	880	1420	9130	1900	0.24	29
2	Duchy	silt loam	6.0	3.3	54	1180	1730	8710	5840	0.20	15
3	School Field	clay loam	5.5	3.9	86	770	1270	6760	1470	0.28	37
4	Gays Farm	loam	5.2	3.5	78	810	1280	6200	1710	0.30	33
5	Horsey Park	clay loam	5.3	5.0	36	790	1330	9890	1830	0.21	34
6	Plumpton	silty clay loam	7.4	2.3	75	680	1470	1120	640	1.00	87
7	Boxworth	clay	7.4	1.7	50	350	820	1570	1010	0.34	43
8	Vale Farm	sandy loam	5.9	1.3	73	450	630	3850	530	0.33	25
9	Morton Morrel	clay	5.8	3.8	94	450	840	4640	1250	0.22	49
10	Kingston Maurward	silt loam	5.8	1.6	90	590	930	3490	1140	0.36	25
11	Conygre	sandy loam	5.5	1.9	50	310	520	1340	310	0.56	88
12	TSB	loam	5.4	3.3	15	890	1420	8490	4070	0.19	18
13	Llanon	loam	5.6	3.1	53	820	1310	6360	2010	0.28	27
14	Cardigan	loam	5.5	2.5	50	780	1160	7350	2610	0.22	18
15	Harper Adams	sandy clay loam	5.6	2.0	67	420	620	3540	770	0.29	36
16	Broadmead	clay	7.3	2.6	44	410	930	4480	1110	0.22	36
17	Weston	clay loam	7.3	1.5	57	210	520	2200	710	0.20	38
18	Inschfield	sandy loam	6.0	4.7	80	1790	2950	13110	9420	0.20	14
19	Barnfield 85	silty clay loam	5.4	2.6	79	500	930	4190	1070	0.28	38
20	Barnfield 86	silty clay loam	6.0	2.8	154	660	1390	2360	1030	0.53	58
21	Melle (#21.2)	silt loam	5.5	0.9	69	360	550	2070	510	0.42	28
22	Zürich (#22.3)	sandy loam	4.8	0.9	43	400	650	2420	790	0.35	21
23	Grignon (#23.1)	loam	6.7	1.2	33	230	590	1100	730	0.31	43
24	Gembloux (#24.1)	silt loam	5.5	0.9	29	250	500	2550	640	0.23	22
Min		-	4.7	0.9	15	210	500	1100	310	0.19	14
Median		-	5.7	2.5	67	500	930	3850	1070	0.28	34
Max		-	7.4	5.0	154	1790	2950	13110	9420	1.00	88

Soil texture: laser diffraction analysis (performed by NRM laboratories; Bracknell, UK); pH: 10 mM $CaCl_2$ at a 1:5 soil solution ratio; Total P: 0.5 M H_2SO_4 extraction on 550°C muffled soils (Saunders and Williams 1955), measured colorimetrically with malachite green. The DPS and DCS are the degree of P (Equation 1) and C (Equation 2) saturation, respectively.

Table 2: Selected soil properties of the different soil treatments in the field |(#21-22) and incubation (#23-24) trials. The field trials consist of two soils subjected to different organic and mineral fertiliser treatments for 8 (Melle) and 70 (Zürich) years. The incubation trial comprises of two soils subjected to a full factorial amendment with P (+P) and OM (+OM) 6 months prior to the start of the mining.

Soil treatments			**General properties**		**Soil phosphorus**			**Binding properties**			
name	#	treatment	pH_{CaCl2}	OC	E_{24h}	P_{ox}	P_{tot}	Fe_{ox}	Al_{ox}	DPS	DCS
				(%)	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mol mol^{-1})	(mol mol^{-1})
Melle	21.1	Control	5.4	0.9	68	380	600	2260	510	0.41	26
(field trial)	21.2	Mineral	5.5	0.9	69	360	550	2070	520	0.42	28
	21.3	Cattle slurry	5.7	1.1	81	380	590	2210	490	0.43	30
	21.4	Farmyard manure	5.9	1.2	100	420	640	2190	490	0.47	35
	21.5	Compost high C:N	5.7	1.2	71	380	600	2320	510	0.41	33
	21.6	Compost low C:N	5.9	1.2	76	400	610	2220	520	0.44	33
	21.7	VFG compost	6.1	1.3	80	430	670	2290	510	0.46	37
Zürich	22.1	Control	4.6	0.9	25	300	510	2220	750	0.28	22
(field trial)	22.2	Mineral low	4.4	0.9	23	280	540	2230	800	0.26	21
	22.3	Mineral high	4.8	0.9	43	400	650	2420	790	0.35	21
	22.4	Farmyard manure +PK	4.8	1.0	41	400	690	2280	760	0.38	25
	22.5	Compost	6.0	1.3	36	380	650	2310	700	0.37	32
	22.6	Compost +PK	5.7	1.3	46	410	710	2210	690	0.41	32
	22.7	Peat +PK	4.8	1.3	51	480	750	2460	790	0.43	31
Grignon	23.1	Control	6.7	1.2	33	230	590	1100	730	0.32	43
(incubation)	23.2	Control +OM	6.9	1.4	40	220	640	1070	720	0.31	51
	23.3	+P	6.8	1.2	93	330	690	1140	750	0.44	42
	23.4	+P +OM	6.9	1.6	119	330	740	1110	730	0.45	56
Gembloux	24.1	Control	5.5	0.9	29	250	500	2550	640	0.23	22
(incubation)	24.2	Control +OM	5.5	1.1	36	250	510	2440	610	0.24	27
	24.3	+P	5.4	0.9	90	340	590	2450	640	0.33	22
	24.4	+P +OM	5.5	1.0	96	340	610	2460	600	0.33	26

Soil texture: laser diffraction analysis (Beckman Coulter LS13 320); pH: 10 mM $CaCl_2$ at a 1:5 soil solution ratio; Total P: 0.5 M H_2SO_4 extraction on 550°C muffled soils (Saunders and Williams 1955), measured colorimetrically with malachite green. The DPS and DCS are the degree of P (Equation 1) and C (Equation 2) saturation, respectively.

Table 3: Model parameters of the two-pool, four parameter model obtained by fitting Equation 4 to the cumulative P uptake data of the mining experiment. In this model, Q_1 and Q_2 are the fast and slow desorbable P pool, respectively, whereas their sum is defined as the total desorbable P. The minimum, median and maximum comprise all samples from Table 1, i.e. only the Mineral (Melle) and Mineral high (Zürich) treatment for the field trials, and the Control treatments for the incubation trials to avoid over-representation.

	Q_1 pool			**Q_2 pool**			**Desorbable P**
	Size (mg P kg^{-1})	k_1 (day^{-1})	Desorption $t_{1/2}$ (days)	Size (mg P kg^{-1})	k_2 (10^{-2} day^{-1})	Desorption $t_{1/2}$ (days)	Q_1+Q_2 (% of P_{ox})
Min	13	0.12	1.0	44	0.14	69	23
Mean	**59**	**0.28**	**3.0**	**179**	**0.56**	**170**	**42**
Max	142	0.74	6.0	355	1.00	492	67

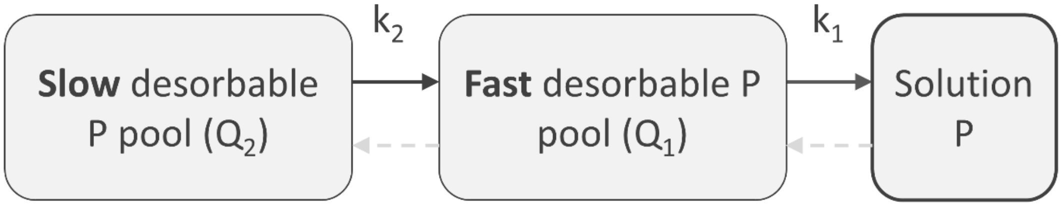

Figure 1: Desorption of P from the slow pool (Q_2) replenishes the fast pool (Q_1), which in turn replenishes the P in solution. Adsorption (dashed grey lines) is suppressed under zero P sink conditions.

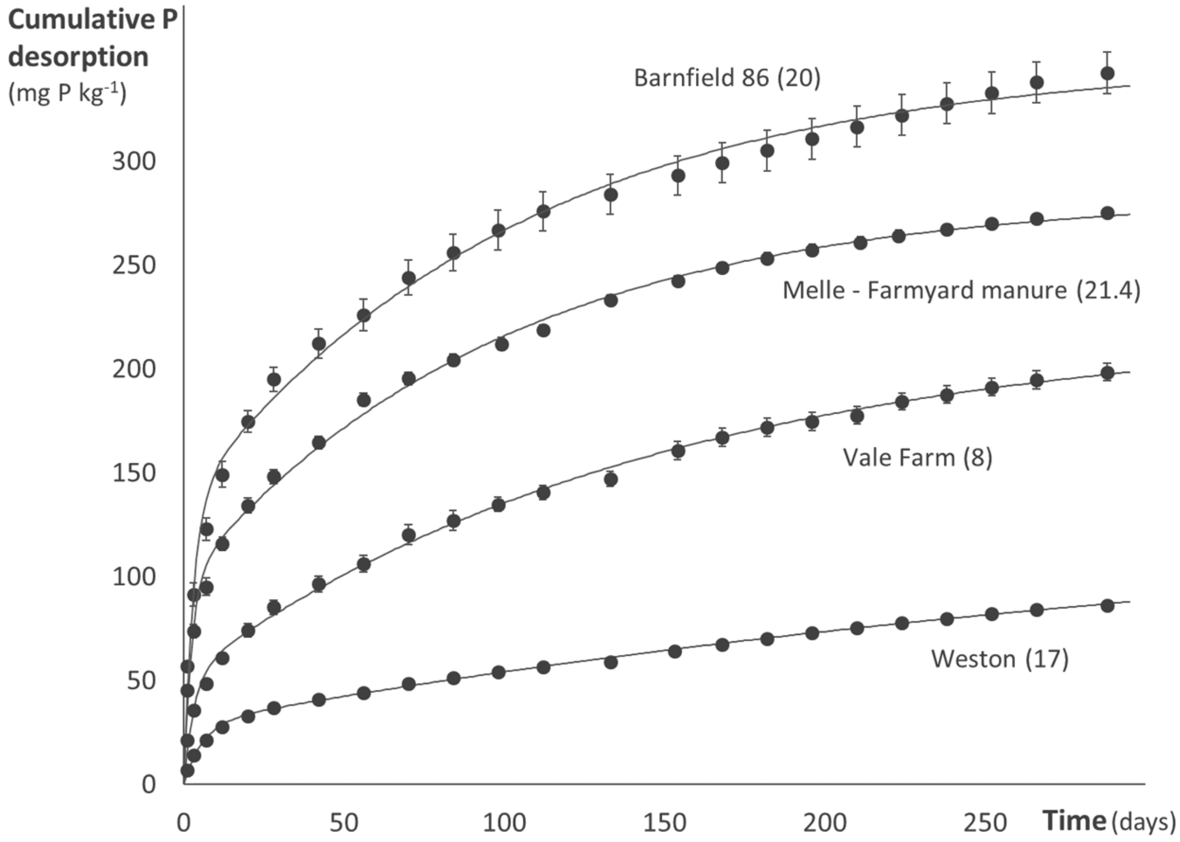

Figure 2: Desorption curves of four different soils. Data points show the average of four replicates with the error bars representing the standard deviation. The curves correspond to the two-pool model (Equation 4) fitted to the data with the four model parameters as shown in Table S1.

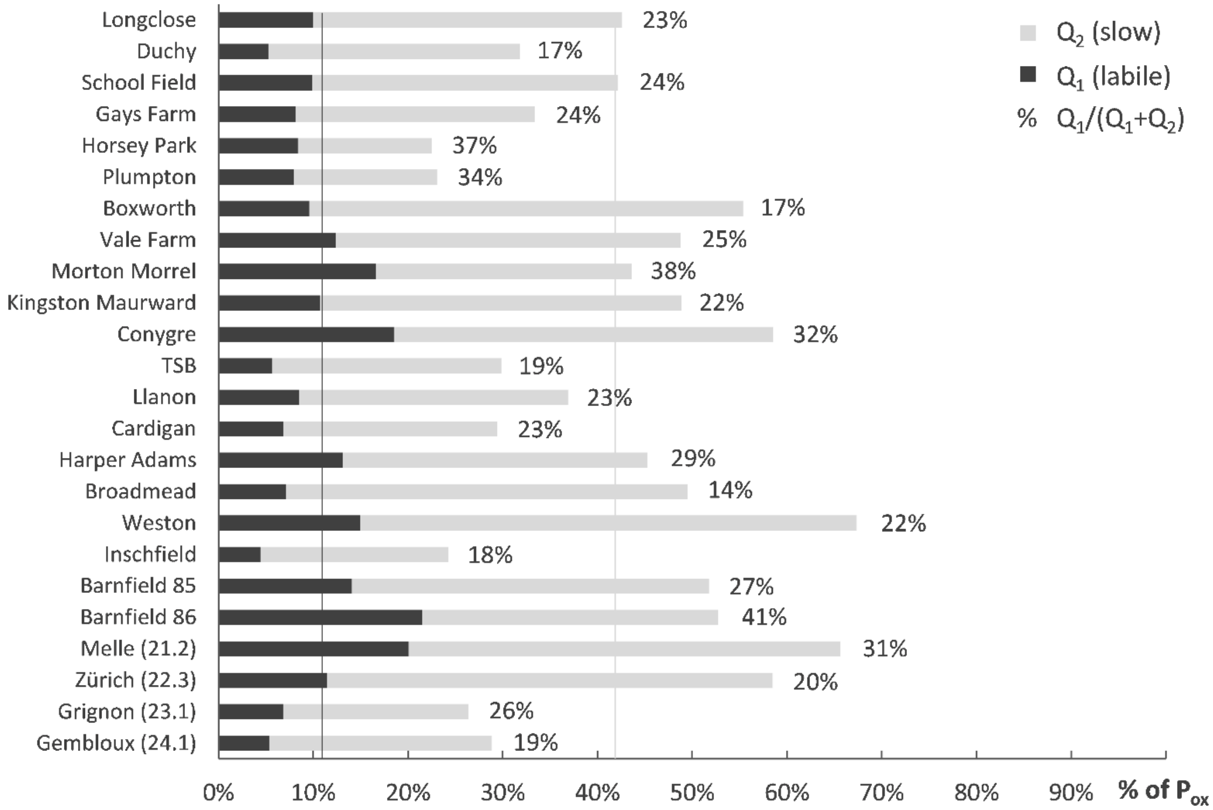

Figure 3: The fast (Q_1, black) and total (Q_1+Q_2, black+grey) desorbable P per soil, expressed as a fraction of the soil's oxalate-extractable P; vertical lines represent the averages of these two pools among soils. For the soils from the field and incubation trials, only the Mineral (Melle), Mineral high (Zürich) and Control (Grignon and Gembloux) treatments are shown.

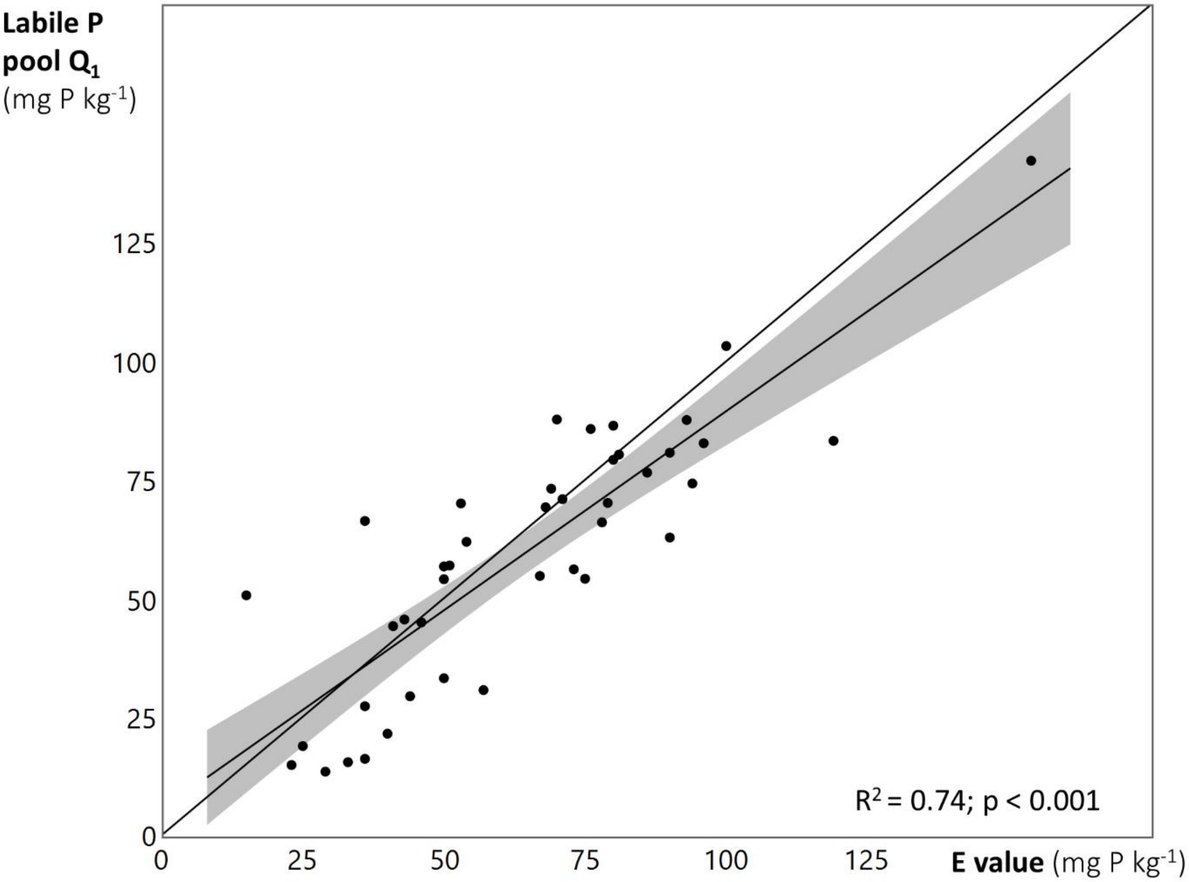

Figure 4: The E_{24h} value (isotopically exchangeable P) corresponds well with the labile P pool Q_1. The pools were significantly correlated and comparable in size; the 1:1 line is shown. The grey area indicates the 95% confidence region for the fitted line.

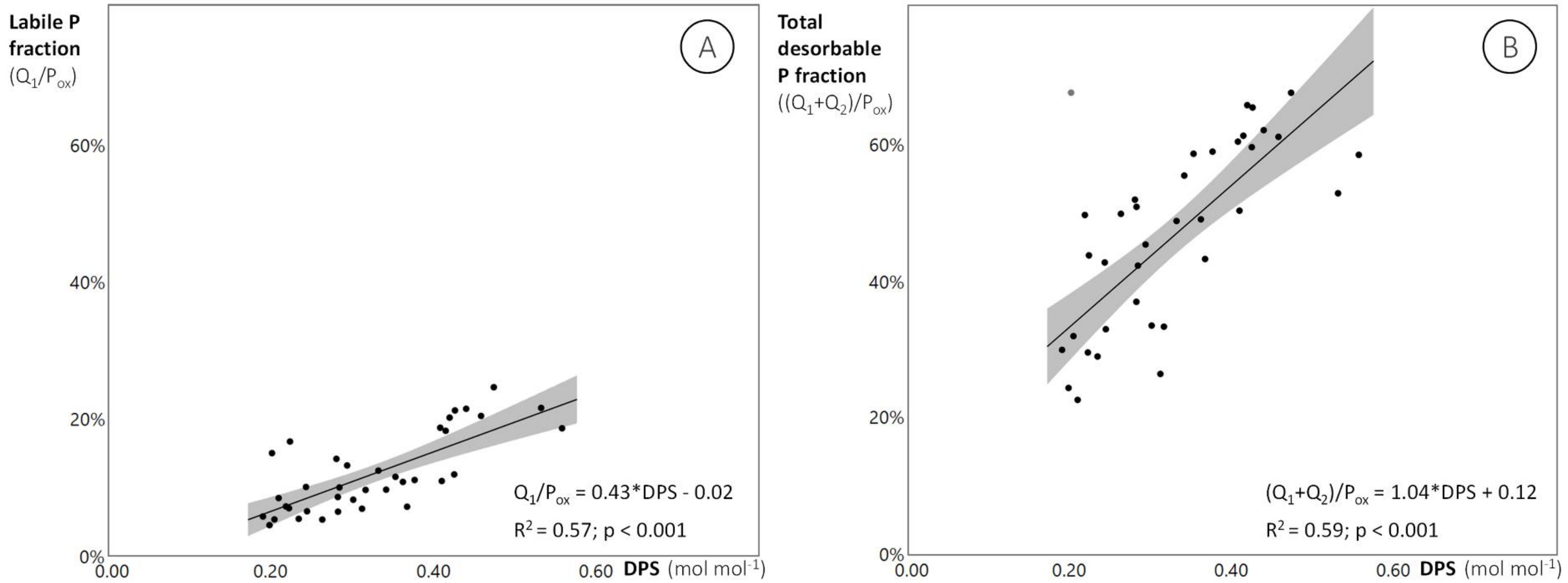

Figure 5: Both the labile (A) and total desorbable (B) fraction of P_{ox} increase with increasing degree of phosphorus saturation (DPS) of the soil; grey areas indicate the 95% confidence region for the fitted line. Including outlying Soil 17 (grey data point in frame B) decreases the R^2 to 0.45 but the significant correlation ($p<0.001$) is maintained.

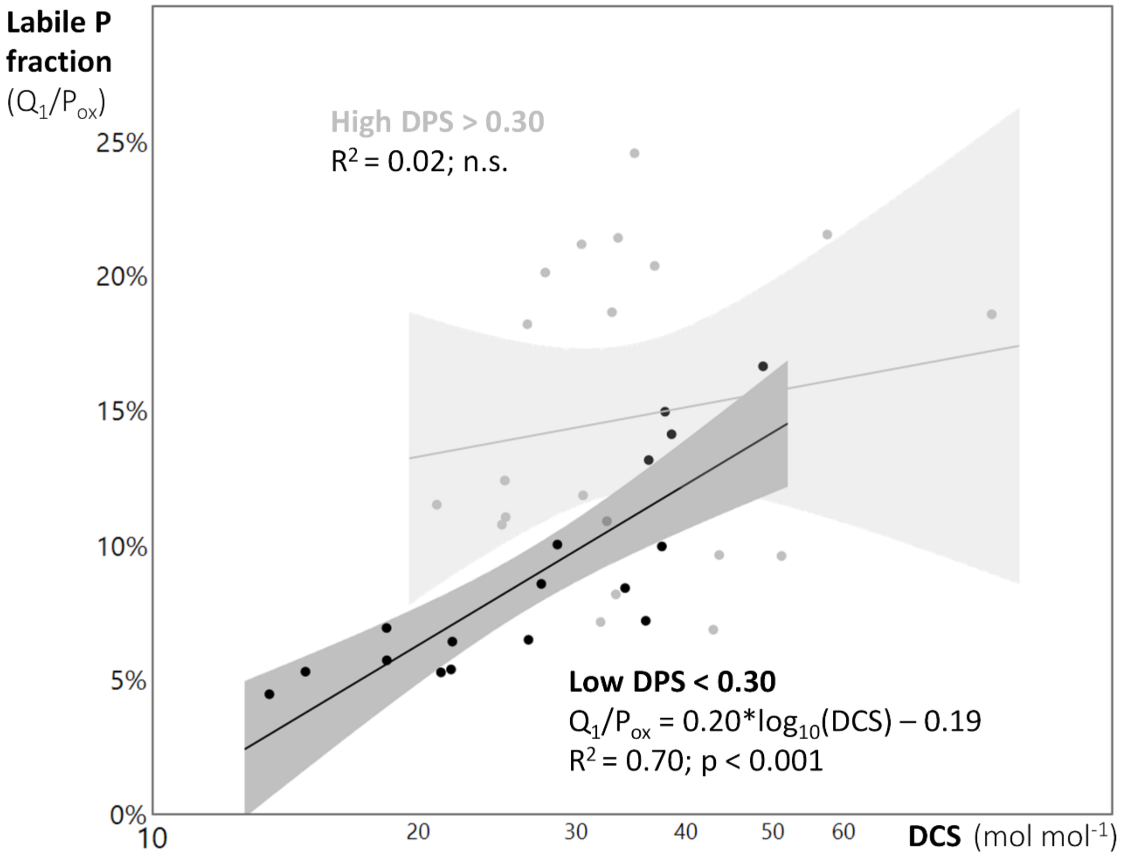

Figure 6: The degree of carbon saturation (DCS) has a positive effect on the labile P fraction (Q_1/P_{ox}), though only in soils with a low degree of phosphorus saturation (DPS < 0.30). The grey areas indicate the 95% confidence region for the regression lines. Note that the DCS is presented on a $\log_{10}$ scale.

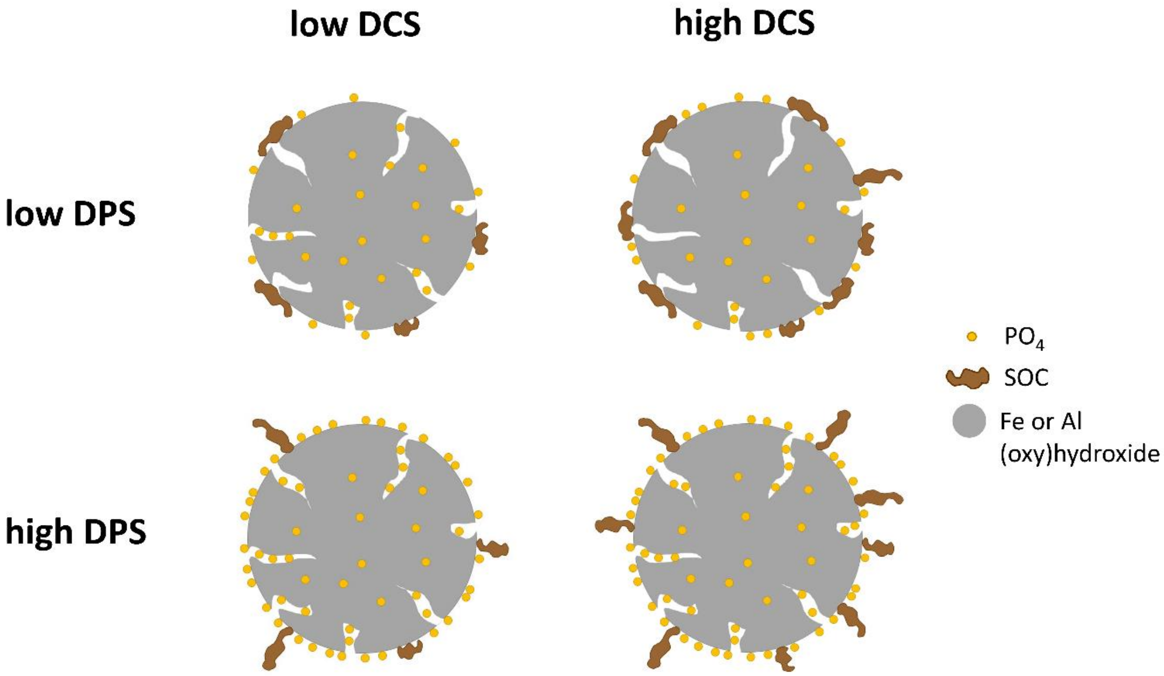

Figure 7: Conceptual figure showing the hypothesised impact of DCS on the long-term availability of P in soils. For soils with a low DPS, increasing the DCS could prevent P from diffusing into the micropores of amorphous and poorly crystalline Fe and Al (oxy)hydroxides, thereby keeping it more available in the labile P pool. In soils with a high DPS, adsorbed P effectively competes with SOM for sorption sites and, thereby, likely hinders spreading out of the latter. In this case, an increasing DCS does not prevent P from becoming less available.

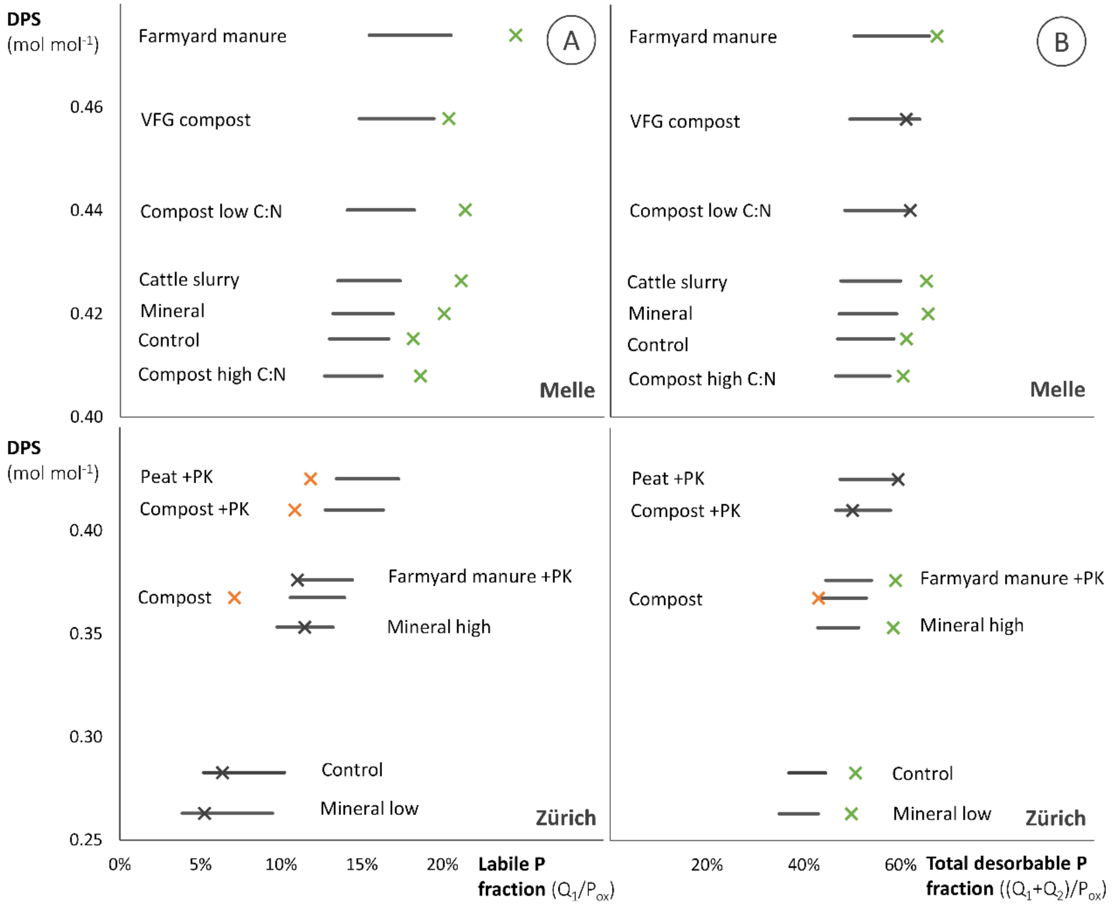

Figure 8: Mining results of the different treatments from the field trials in Melle and Zürich. Cross markers represent the (A) labile (Q_1/P_{ox}) or (B) total desorbable (($Q_1+Q_2)/P_{ox}$) P fraction as determined by fitting Equation 4 to the mining data. Full lines indicate the 95% prediction intervals (PI) based on the correlation between the labile or total desorbable P fraction and the DPS (Figure 5).

Increasing soil organic carbon content can enhance the long-term availability of phosphorus in agricultural soils

Supporting Information

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Running title: impact of organic C on long-term P availability

Numbers of Tables: 2

Numbers of Figures: 2

S1. Two-pool kinetic desorption model

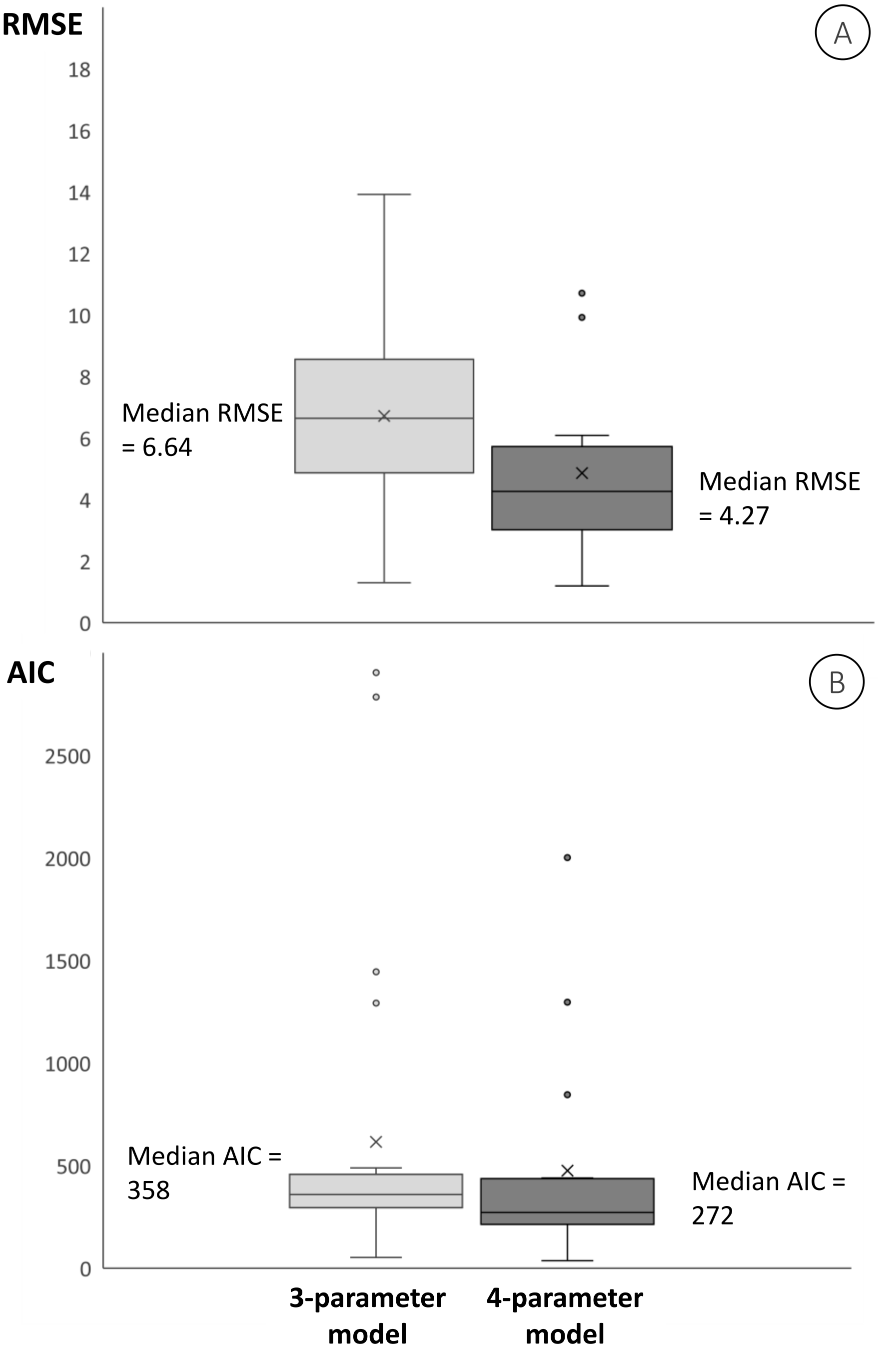

Figure S2: The two-pool kinetic desorption model in Equation 4 has previously been used as a 3-parameter model, with $Q_2 = P_{ox} - Q_1$. In our study, however, it was decided not to make this assumption that all oxalate-extractable P is desorbable at prolonged desorption times, and Q_2 was estimated as a fourth parameter. The lower RMSE and AIC of this 4-parameter version of the model corroborate this decision.

S2. Long-term availability of P in soil

Table S4: Model parameters of the two-pool model obtained by fitting Equation 4 to the cumulative P uptake data of the mining experiment. Q_1 and Q_2 are the fast and slow desorbable P pool, respectively, whereas their sum is defined as the total desorbable P. Soils from the field trials and incubation trial are represented by the Mineral (Melle) and Mineral high (Zürich) treatment and the Control treatment (Grignon and Gembloux), respectively.

Soil	**Q_1 pool**			**Q_2 pool**			**Desorbable P**
	Size (mg P kg^{-1})	k_1 (day^{-1})	Desorption $t_{1/2}$ (days)	Size (mg P kg^{-1})	k_2 (10^{-2} day^{-1})	Desorption $t_{1/2}$ (days)	Q_1+Q_2 (% of P_{ox})
Longclose	88	0.32	2.2	287	0.49	141	43
Duchy	62	0.15	4.6	313	0.22	320	32
School Field	77	0.21	3.3	249	0.32	220	42
Gays Farm	66	0.24	2.9	205	0.61	114	33
Horsey Park	66	0.21	3.4	112	0.55	127	23
Plumpton	54	0.15	4.7	103	0.42	135	23
Boxworth	33	0.17	4.1	158	0.18	392	55
Vale Farm	56	0.31	2.3	165	0.68	103	49
Morton Morrel	74	0.27	2.6	121	0.82	85	44
Kingston Maurward	63	0.31	2.2	224	0.56	123	49
Conygre	57	0.51	1.3	122	0.90	77	59
TSB	51	0.15	4.8	215	0.35	198	30
Llanon	70	0.18	3.8	233	0.40	172	37
Cardigan	54	0.22	3.2	177	0.68	102	29
Harper Adams	55	0.35	2.0	134	0.72	97	45
Broadmead	29	0.13	5.2	174	0.14	492	50
Weston	31	0.17	4.0	108	0.26	265	67
Inschfield	79	0.12	6.0	355	0.20	352	24
Barnfield 85	70	0.26	2.7	188	0.47	147	52
Barnfield 86	142	0.33	2.1	207	0.95	73	53
Melle (21.2)	73	0.40	1.7	166	1.00	69	66
Zürich (22.3)	45	0.42	1.6	187	0.77	90	58
Grignon (23.1)	15	0.69	1.0	44	0.86	80	26
Gembloux (24.1)	13	0.50	1.4	59	0.81	86	29
Min	13	0.12	1.0	44	0.14	69	23
Mean	**59**	**0.28**	**3.0**	**179**	**0.56**	**170**	**42**
Max	142	0.74	6.0	355	1.00	492	67

Table S2: Pearson correlation coefficients between kinetic parameters and soil properties; properties with a skewness coefficient > 1 are considered to be lognormal distributed and are transformed prior to analysis. Correlation analysis was performed on 37 soils and soil treatments, excluding calcareous Soil 6 and the +P treatments of the incubation trial. For k_1 and k_2, only the Mineral (Melle), Mineral high (Zürich) and Control (Grignon and Gembloux) treatments were included to avoid overrepresentation; the same applies to soil texture as this was only determined once per soil. Additionally, the correlation coefficients for the two groups of P saturation, i.e. DPS below (n=17) or above (n=20) 0.30, are given separately for the DPS and DCS. Significant correlations are indicated by *p<0.05, **p<0.01 and ***p<0.001. Note that for the slow and total desorbable P pool, the soil of Weston is included, while in Figure 5, it is not. When excluding this soil, correlations with oxalate-extractable elements and derivatives thereof generally become better.

	Labile P pool			**Slow P pool**			**Total desorbable P pool**	
	Q_1 (mg P kg^{-1})	**Q_1/P_{ox}** (%)	**k_1** (day^{-1})	**Q_2** (mg P kg^{-1})	**Q_2/P_{ox}** (%)	**k_2** (day^{-1})	**Q_1+Q_2** (mg P kg^{-1})	**$(Q_1+Q_2)/P_{ox}$** (%)
Normally distributed soil properties								
pH	-0.07	0.10	-0.19	-0.21	-0.04	-0.41	-0.18	0.01
% sand	-0.08	0.02	-0.03	0.03	0.01	-0.09	-0.00	0.02
% silt	0.09	-0.22	0.21	0.04	-0.37	0.19	0.06	-0.36
% clay	0.02	0.22	-0.21	-0.08	0.40	-0.11	-0.07	0.39
DPS	0.43**	0.75***	0.52*	-0.07	0.48**	0.60**	0.09	0.67***
DPS<0.30		0.23			0.32			0.34
DPS>0.30		0.79***			0.35			0.63**
Log_{10} transformed soil properties								
Org C	0.40*	-0.25	-0.64**	0.52***	-0.59***	-0.46*	0.54***	-0.54***
P_{ox}	0.55***	-0.22	-0.60**	0.86***	-0.44**	-0.39	0.85***	-0.41*
Fe_{ox}	0.30	-0.40*	-0.69***	0.67***	-0.50**	-0.49*	0.62***	-0.53***
Al_{ox}	0.14	-0.58***	-0.66***	0.66***	-0.57***	-0.59**	0.56***	-0.66***
$Fe_{ox}+Al_{ox}$	0.24	-0.50**	-0.70***	0.69***	-0.57***	-0.56**	0.62***	-0.62***
DCS	0.17	0.51**	0.36	-0.44**	0.12	0.34	-0.29	0.30
DPS<0.30		0.84***			0.21			0.54*
DPS>0.30		0.16			0.07			-0.21

The most relevant correlations were discussed in the main text. Furthermore, the SOC content was positively correlated with the Q_1 and Q_2 pool (in absolute terms) and decreased with increasing slow and total desorbable P fractions (Q_2/P_{ox} and $(Q_1+Q_2)/P_{ox}$). These correlations are a mere consequence of the fact that both SOC and P_{ox} are associated with Fe and Al (oxy)hydroxides and, therefore, increase together ($R^2=0.60$; $p<0.001$).

S3. The incubation trials

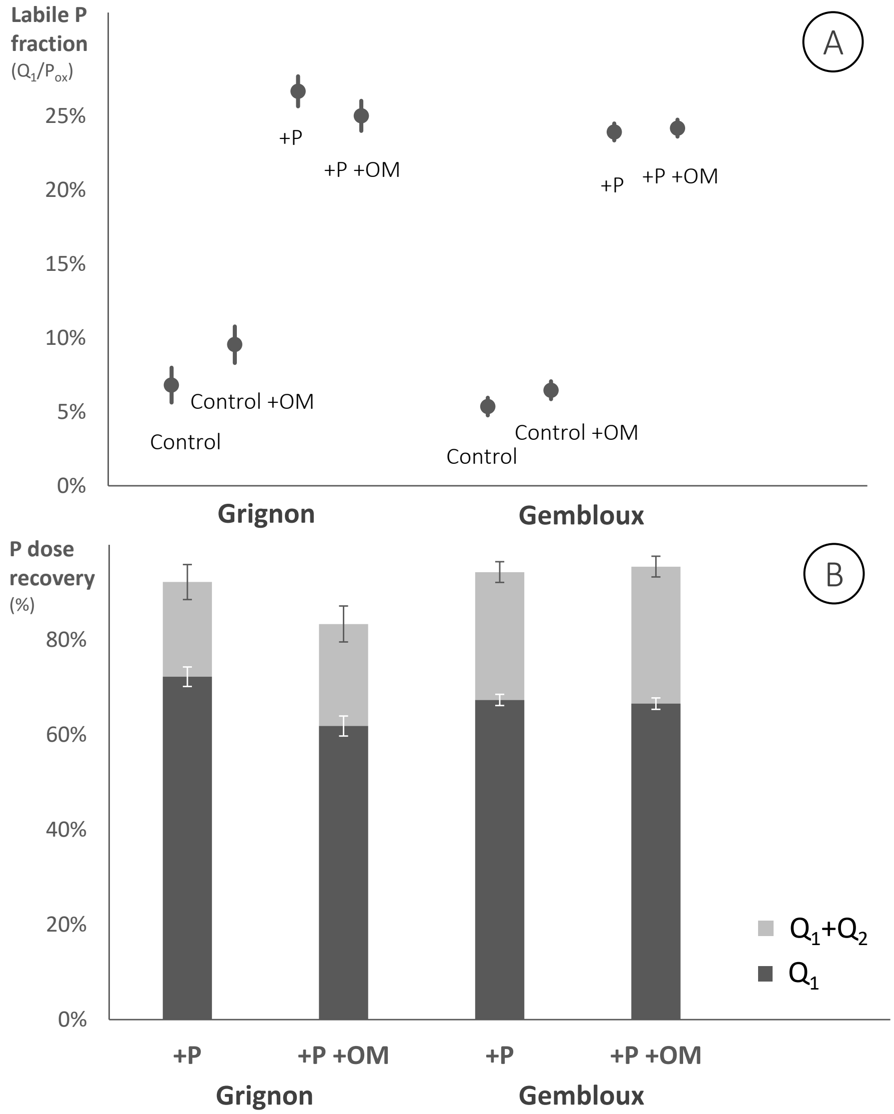

Figure S2: Mining results for the four different treatments from the incubation trial (Soils 23-24). (A) labile P pool (Q_1/P_{ox}) as determined with Equation 4; lines signify the 95% confidence intervals of the estimated parameters. The control treatments were incubated without additional P, but with (Control +OM) and without (Control) OM amendment, while +P and +P +OM received a dose of 100 mg P kg^{-1} at the start of the incubation. (B) Recovery of the nominal P dose in the labile (Q_1) and total desorbable (Q_1+Q_2) P pool of the fertilised treatments. Error bars represent standard deviations.