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The pH dependence of phosphate sorption and desorption in Swedish agricultural soils.

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Abstract

A number of previous studies have reported the existence of a minimum in phosphate solubility between pH 5.5 and 7 in non-calcareous soils. Different hypotheses have been forwarded to explain this phenomenon. In this study, ten soil samples with varying textures and phosphorus status were subjected to batch experiments in which dissolved phosphate was measured as a function of pH and phosphate load. Soil samples with more than 20 % clay all had a minimum phosphate solubility between pH 6 and 7, whereas for samples with < 10 % clay, no such minimum was observed. Further experiments involving additions of phosphate and arsenate showed an increasing adsorption of these anions with decreasing pH also below pH 6 in clay soils, suggesting that the pH dependence on adsorption and desorption in short-term experiments was not the same. Kinetic experiments showed that the increased phosphate desorption at lower pH values in non-calcareous clay soils was a quick process, which is consistent with adsorption/desorption being the most important mechanism governing the retention and release of inorganic P. Moreover, by comparing extraction results with batch experiment results for samples from a long-term fertility experiment, it was concluded that more than 60 % of the accumulated phosphate was occluded, i.e. not reactive within six days. Additional evidence for an important role of occluded phosphate comes from an analysis of the Freundlich sorption isotherms for the studied soils. It is hypothesized that interlayered hydroxy-Al and hydroxy-Fe polymers in clay minerals may be important for P dynamics in clay soils by trapping some of the P in an occluded form. The results also suggest that improved knowledge on the speciation and dynamics of phosphorus in soils is required for consistent mechanistically based modelling of phosphate sorption/desorption reactions.

Keywords: phosphate, arsenate, desorption, fertility experiment, clay soils, sorption

1. Introduction

Desorption of initially bound phosphate from soil components is important both for the plant availability of this nutrient and for predictions of P leaching (see, e.g. Hartikainen et al., 2010). In agricultural soils, the pH value may fluctuate with time due to harvest and/or to management practices such as liming. Because the pH affects $\text{PO}_4\text{-P}$ sorption / desorption to soil components (see, e.g. Haynes, 1982), prediction of the pH effect is important for correct estimates of $\text{PO}_4\text{-P}$ solubility in a soil subject to pH changes.

The processes governing the sorption and desorption of $\text{PO}_4\text{-P}$ in soils are several. Adsorption to the surfaces of iron(III) and aluminium (hydr)oxides is known to be important. In addition, $\text{PO}_4\text{-P}$ may be adsorbed also to hydroxy-Al polymers in clay minerals (Karathanasis and Shumaker, 2009) and to carbonate minerals (Yagi and Fukushi, 2011). Because $\text{PO}_4\text{-P}$ adsorption increases with decreasing pH, these adsorption processes would often be expected to be more influential at low pH (Goldberg and Sposito, 1984), resulting in a “positive” pH dependence (i.e. increased $\text{PO}_4\text{-P}$ solubility at higher pH), provided that adsorption is fully reversible within the time scale of interest.

Precipitation of $\text{PO}_4\text{-P}$ with Ca is expected at higher pH. A number of Ca-P minerals may form, such as amorphous calcium phosphate (ACP), octacalcium phosphate (OCP) and apatite (hydroxyapatite, HAp, or fluorapatite, FAp). Precipitation/dissolution of these minerals will cause a “negative” pH dependence (increased $\text{PO}_4\text{-P}$ solubility at lower pH) (Hesterberg, 2010).

At high $\text{PO}_4\text{-P}$ loads (e.g., in heavily fertilized soils) and at low pH there may be precipitation also with Al^{3+} and Fe^{3+} , resulting in mineral phases such as variscite, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ (Veith and Sposito, 1977), and strengite, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (Nriagu, 1972).

Often, it is assumed that the solubility of $\text{PO}_4\text{-P}$ increases with increasing pH in the low to medium pH range, because of sorption/desorption processes involving iron/aluminium (hydr)oxides (e.g., Goldberg and Sposito, 1984)

However, much previous research on the pH dependence of $\text{PO}_4\text{-P}$ solubility in soils shows a more complicated picture. Murrmann and Peech (1969) performed batch titrations for two soils and found decreasing $\text{PO}_4\text{-P}$ solubility with increasing pH until about pH 5.5 to 6, at which pH minimum solubility occurred. At higher pH, $\text{PO}_4\text{-P}$ was more increasingly dissolved again. At very high pH, however, ($> 8\text{-}9$) $\text{PO}_4\text{-P}$ solubility decreased due to Ca-P mineral precipitation. Haynes (1982) provided references to a number of other early studies with the same general results, i.e. a minimum P solubility between pH 5 and 6. More recently, Hartikainen and Simojoki (1997), Devau et al. (2011) and Weng et al. (2011) presented results of a similar kind, although for some soils minimum P solubility was found at even higher pH values (> 6).

Different reasons have been forward to explain this behaviour. Harsh and Doner (1985) hypothesized, based on their studies with $\text{PO}_4\text{-P}$ sorption onto hydroxy-Al-interlayered montmorillonite, that increasing pH led to an increased stability of the hydroxy-Al interlayers, and therefore to an increased $\text{PO}_4\text{-P}$ sorption. Hartikainen and Simojoki (1997) attributed the increased $\text{PO}_4\text{-P}$ solubility at low pH to the dissolution of Ca-P minerals such as apatite, which are known to exist also in acid soils (Beauchemin et al., 2003). This

hypothesis was based on the observation that acidification led to a decrease in the acid-soluble P fraction, which is often believed to constitute mainly of Ca-P minerals. By contrast, Devau et al. (2011) hypothesized that the “negative” pH dependence at low pH was due to the intrinsic $\text{PO}_4\text{-P}$ sorption properties of the illite edge sites they believed were important for $\text{PO}_4\text{-P}$ sorption in these soils. Earlier work by Edzwald et al. (1976) and Manning and Goldberg (1996) showed that illite displays a marked P sorption maximum at around pH 6. Weng et al. (2011) attributed their results to synergistic effects of Ca^{2+} adsorption to oxides and showed that a surface complexation model would predict a minimum in P solubility near pH 7 under the conditions of their study (these authors used 0.01 M CaCl_2 background electrolyte, which might have affected the results and interpretations).

The purpose of this work was to increase the understanding of the factors determining pH dependence of $\text{PO}_4\text{-P}$ adsorption/desorption of soils. This was done by performing batch equilibrations on a number of soils with different characteristics, by studying the response of pH-dependent $\text{PO}_4\text{-P}$ solubility to P additions in the form of long-term fertilization or short-term $\text{PO}_4\text{-P}$ additions on the laboratory, and by comparing the observed $\text{PO}_4\text{-P}$ adsorption/desorption patterns with those of a similar anion, arsenate (AsO_4). As $\text{PO}_4\text{-P}$ and AsO_4 show similar (although not entirely identical) adsorption patterns on iron and aluminium (hydr)oxides (e.g., Antelo et al., 2005), and as As is normally preserved in its pentavalent state in batch equilibrations with surface soils (Gustafsson, 2006), AsO_4 might be used as an analogue to $\text{PO}_4\text{-P}$. This is useful particularly as many natural soils contain only a very small amount of initially sorbed As.

2. Materials and methods

2.1 Soils

Seven of the soils used in this study were collected from long-term fertility experiments in Sweden (Table 1; Carlgren and Mattsson, 2001). Samples were collected from the treatments that had received no mineral fertilizer since the starting year of the experiments (1956 in Fjärdingslöv, Orup and Örja, 1963 in Kungsängen and Fors, and 1966 in Vreta Kloster and Högåsa). In addition, two soils were collected from a catchment in S.E. Sweden subject to environmental monitoring of nutrient losses (E21:2, E21:24), and one more soil was collected from a field developed in postglacial clay north of Stockholm (Broknäs). A soil sample was collected also from a plot at Kungsängen that had been treated with 30 kg P ha⁻¹ and 80 kg K ha⁻¹ annually, in addition to replacement with mineral fertilizer. The mineralogy of the soils from the fertility experiments is well studied and has been reported in a number of earlier publications (Kirchmann, 1991; Kirchmann and Eriksson, 1993; Andrist-Rangel et al., 2006).

The soils were air-dried and when needed, they were homogenized gently in a mortar. The soils were characterized by oxalate extraction according to the procedure of van Reeuwijk (1995), and by ascorbic-acid-extractable Fe according to Kostka and Luther (1994). The concentration of Fe and Al in these extracts were determined by using ICP-OES (VarianVista-PRO Simultaneous ICP-OES with a SPS-5 autosampler), and the PO₄-P concentration in the oxalate extract was determined colorimetrically using the method of Wolf and Baker (1990). Oxalate-extractable As was measured with ICP-OES, but was below the detection limit for the method used, and is therefore not reported. PO₄-P was determined also after acid ammonium lactate (AL) extraction (Egnér et al., 1960), a method that is routinely used in Sweden for assessing the concentration of plant-available P. The particle size distribution was measured by the pipette method or by wet sieving for particles larger than 0.06 mm diameter. The total C content was analysed using a

LECO CHN 932 analyzer. For selected extracts from the Kungsängen samples, the total organic carbon (TOC) concentration was determined using a Shimadzu TOC-5000 Analyzer.

2.2 Batch experiments

In all experiments, 2 g air-dried soil was mixed with 30 cm³ solution in a polypropylene centrifuge tube with a screw cap. The solution that was added to the soil always contained 0.01 M NaNO₃. Varying concentrations of acid (as HNO₃), base (as NaOH) was added to different centrifuge tubes to produce a range of pH values. To a number of samples from the Kungsängen soil, different concentrations (50, 133, 200 and 300 µM) of PO₄-P (as NaH₂PO₄) were added. To the Broknäs A and E21:2 samples, 50 µM of AsO₄ (as Na₂HAsO₄) was added in separate series, to study the pH dependence of AsO₄ sorption onto these soils. In another set of experiments, different concentrations of PO₄-P were added to study PO₄-P sorption as a function of the equilibrium PO₄-P concentration in solution. This was done for all soils except Kungsängen. The additions made corresponded to 0, 0.15, 0.3, 0.6, 1.05, 1.5, 2.25, 3 and 4.5 mmol P kg⁻¹ dry soil. Other conditions were identical as in the pH-dependence experiments.

After 6 days of gentle shaking at room temperature, the suspension in the tube was centrifuged. The pH of the supernatant was then measured with a Radiometer combination glass electrode. The remaining supernatant solution was filtered through a 0.2 µm single-use filter (Acrodisc PF) prior to the analysis of PO₄-P (colorimetrically using a Tecator Aquatec 5400 spectrophotometer with flow injection analysis), and of Ca, Mg, Al and As (ICP-OES as above). Preliminary studies showed that no PO₄-P or AsO₄ was adsorbed by the centrifuge tubes or by the filters used.

For the Kungsängen A3 soil, an experiment was also performed to study the desorption rate of PO₄-P in acid soil extracts. The general outline of this experiment was the same as above (with acid additions of 15 and 60 mmol H⁺ kg⁻¹ soil), and duplicate samples were collected after 2 h, 1 d, 3 d and 6 d of shaking

2.3. Speciation modelling

The results were processed using the geochemical code Visual MINTEQ (Gustafsson, 2011) to obtain free ion activities and to calculate saturation indices of different minerals that might precipitate (Table 2). We used the standard thermodynamic database for aqueous speciation calculations, which mostly relies on the NIST critical stability constants database (Smith et al., 2003). To calculate the Al^{3+} activity from measured total dissolved Al, we considered the presence of dissolved organic matter (DOM), which is important for Al speciation. This was done using the Stockholm Humic Model, SHM (Gustafsson, 2001) with generic complexation constants and using the assumption that the concentration of fulvic acid equalled $1.65 \times \text{DOC}$ (Sjöstedt et al., 2010). At $\text{pH} > 5$ however, the calculated Al^{3+} activity was usually higher than the one calculated from the solubility of “soil” $\text{Al}(\text{OH})_3(\text{s})$ (Gustafsson et al., 2001), and then the Al^{3+} activity was instead fixed by the solubility of $\text{Al}(\text{OH})_3(\text{s})$, in agreement with procedures used for lake water (Sjöstedt et al., 2010).

2.4. Freundlich sorption modelling

The particular form of the Freundlich equation that has been most often used in studies of $\text{PO}_4\text{-P}$ sorption to soils was originally suggested by Fitter & Sutton (1975):

$$n_{\text{sorb}} = K_{\text{F}} \cdot c^m - n_{\text{init}} \quad (1)$$

where n_{sorb} and n_{init} denote $\text{PO}_4\text{-P}$ sorbed in the experiment and initially bound $\text{PO}_4\text{-P}$, respectively (mol kg^{-1}), c is the dissolved $\text{PO}_4\text{-P}$ concentration (mol L^{-1}), whereas K_{F} and m are coefficients that need to be optimized, and where m is expected to be < 1 . After logarithmic transformation, equation 1 can be written as:

$$\log n = \log K_{\text{F}} + m \cdot \log c \quad (2)$$

where $n = n_{\text{sorb}} + n_{\text{init}}$ as above. This means that the Freundlich equation implies a linear relationship between $\log n$ and $\log c$, where the slope is m and the intercept is $\log K_F$. A problem when all three parameters K_F , m and n_{init} are optimized at the same time, is that the fit is quite sensitive to very small differences in the data (see, e.g., Peltovuori, 2007). Moreover, the value of n_{init} found in this way is expected to be larger than the “real” n_{init} , as the Freundlich equation is not expected to hold at very low values of c . To prevent this, it is beneficial if n_{init} can be determined through extraction, or if m can be fixed at some realistic value.

In several studies it has been shown that m has been of the same magnitude in different soils. Barrow (1978) suggested the use of $m = 0.4$, whereas Tolner & Füleky (1995) recommended $m = 0.33$. They showed that this is fairly consistent with results from isotopically exchanged P, since the n_{init} which was found with $m = 0.33$ was similar in magnitude to the isotope value. In our study we employed an m value of 0.35 as a compromise. The exact value of m (0.33, 0.35 or 0.4) did not influence the conclusions.

3. Results

3.1. pH dependence of $\text{PO}_4\text{-P}$ solubility

The solubility of $\text{PO}_4\text{-P}$ as a function of pH was different in the nine soils (Fig. 1). To assist in the interpretation of the data, second-order polynomials were fitted to the data sets of Fig. 1 (see Table S1). In the investigated clay soils, a minimum in $\text{PO}_4\text{-P}$ solubility was observed between pH 6 and pH 7. The minimum pH value was calculated from the point where the first derivative of the fitted second-order polynomial was equal to 0 (see results in Table S1). No such minimum was found for the three sandy soils, in which the $\text{PO}_4\text{-P}$ solubility increased monotonically with increasing pH. For soils with intermediate texture, the Orup soil had a well-defined minimum in $\text{PO}_4\text{-P}$ solubility at pH 5.9, whereas

a minimum could not be defined for Fjärdingslöv within the pH range of the observations (Table S1); however, from visual inspection of the data of Fig. 1 it seems probable that there might be a minimum between pH 6.5 and 7 in this soil. The Fors soil, which was the only calcareous soil studied, had a minimum $\text{PO}_4\text{-P}$ solubility at pH 7.5 (i.e. the highest recorded). Below this pH value, the $\text{PO}_4\text{-P}$ solubility increased rapidly with decreasing pH, in a manner distinctly different from the other soils.

Speciation modelling revealed that the Fors soil extracts remained slightly supersaturated with respect to model hydroxyapatite on acidification (Fig. S1, Supporting Information). For other soils, there was no indication of equilibrium with respect to any Ca phosphate, see three examples in Fig. S1. This suggests that the Fors soil contained reactive Ca phosphate (possibly hydroxyapatite or fluorapatite) that dissolved readily, thus determining the pH dependence of the $\text{PO}_4\text{-P}$ solubility for this soil, whereas for other soils Ca-P dissolution was probably less important. The presence of reactive Ca phosphates in the Fors soil was suggested also by Börling et al. (2001) when they compared results from P_{AL} and Olsen-P extractions.

3.2. Fertilization effect on pH-dependent $\text{PO}_4\text{-P}$ sorption and desorption

After long-term fertilization at the Kungsängen site, the solubility of $\text{PO}_4\text{-P}$ increased considerably (Fig. 2; A3 = unfertilized, D3 = fertilized with 30 kg P ha⁻¹ annually). Similar to the A3 sample, the fertilized D3 sample still displayed increasing $\text{PO}_4\text{-P}$ solubility with lower pH at pH < 6.8. However, on a log-log scale the pH dependence was flattened considerably.

In additional experiments, various additions of $\text{PO}_4\text{-P}$ were made to both the A3 and D3 soils. Laboratory additions of between 2.66 and 4 mmol kg^{-1} to the A3 sample resulted in similar dissolved $\text{PO}_4\text{-P}$ concentrations as in the D3 sample. This can be compared to the difference in extractable P values between the two soils (Table 1). The difference in oxalate-extractable P (10.5 mmol kg^{-1}) was clearly much larger, which may suggest that a considerable proportion of the accumulated P in this pool was not soluble in a short term. For P_{AL} the difference (2.1 mmol kg^{-1}) was much more in agreement with the values obtained from $\text{PO}_4\text{-P}$ additions.

Moreover, the pH dependence of dissolved $\text{PO}_4\text{-P}$ was not the same in the D3 sample with no P added, as in the A3 samples with P added on the laboratory. As Fig. 2 shows, the D3 sample had a minimum $\text{PO}_4\text{-P}$ solubility between pH 6.5 and 7, whereas in the A3 sample with P addition, dissolved $\text{PO}_4\text{-P}$ was lowest at low pH, below pH 5. In other words, the pH-dependent P solubility patterns was not the same in a soil subjected to long-term P fertilization in the field (D3) as in a low-P soil treated with P in a 6-d experiment (A3). Thus the pH-dependent solubility of P was different depending on whether the P was fresh, i.e. added on the laboratory, or if the P originated from long-term fertilization in the field.

Further evidence for this comes from comparing the pH-dependent solubility of initial $\text{PO}_4\text{-P}$ with that of AsO_4 added on the laboratory. Such data are available for two of the clay soils (Fig. 3). These data show an increased sorption with decreasing pH for AsO_4 , which contrasts with the minimum solubility at pH 6 or higher as observed for initially bound P. Because the content of initially sorbed AsO_4 was negligibly small, dissolved AsO_4 was only affected by the extent of AsO_4 sorption after 6 d of reaction. A possible

reason for these observations may be that a large part of the initially bound soil P is occluded, i.e. not immediately reactive, and that part of this occluded P can be mobilized at low pH. This is being discussed further below.

There were no evidence for a significant role of Ca phosphates for the P dynamics at the Kungsängen site, as most samples were undersaturated with respect to hydroxyapatite and increasingly so with decreasing pH (Fig. 4). Nevertheless, some fertilized samples at the higher pH end were supersaturated, which indicates a potential for apatite-like Ca phosphates to form. However, the formation of reactive Ca phosphates should have caused some samples to remain close to the solubility line of hydroxyapatite on acidification (e.g., as for the Fors site), but this was not the case. Instead, speciation modelling suggests a significant role of Al phosphates in retaining P at high fertilization levels and at $\text{pH} < 6.5$ (Fig. 4). Most samples subjected to P additions either in the field or at the laboratory were supersaturated with respect to variscite. Some samples were also close to saturation with amorphous Al phosphate at low pH. This agrees with Pierzynski et al. (1990) and Hetrick and Schwab (1992), who suggested a significant role of Al phosphates in acidic and excessively fertilized soils.

The reasons for the increased solubility of initial $\text{PO}_4\text{-P}$ with decreasing pH may be both desorption from (hydr)oxide surfaces and weathering (e.g. of apatite-like compounds). Desorption from (hydr)oxide surfaces is expected to be reversible, i.e. if pH was increased again the $\text{PO}_4\text{-P}$ would readsorb. Weathering, however, is normally expected to be irreversible. To cast further light on the type of mechanism involved, batch experiments were carried out for different times (ranging from 2 h to 6 d) and after two different acid additions. In these experiments, the pH value was initially low and was then increasing,

most probably as a result of weathering of silicate minerals in the sample (Fig. 5). Dissolved $\text{PO}_4\text{-P}$ was initially very high and then decreased, apparently as a result of the pH increase. This experiment was repeated also for another clay soil (E21:2), with the same general result (data not shown). This behaviour is consistent with sorption/desorption processes governing the $\text{PO}_4\text{-P}$ solubility, as adsorption/desorption reactions would be expected to take place quickly. Kinetically constrained weathering of P-containing minerals seems a less likely explanation to the observed trends, since slow weathering would be expected to cause a progressively increasing $\text{PO}_4\text{-P}$ dissolution with time. However, these very simple experiments are only indicative, and more direct methods would be needed to more firmly establish the mechanism(s) governing P dissolution/desorption patterns in these soils.

3.3. Results from Freundlich sorption modelling

Under the conditions of the sorption isotherm experiment, the pH values were practically constant as a function of P addition, and the difference recorded was < 0.2 units (Table 3). The fits to the Freundlich equation were usually better than $r^2 > 0.98$ and visual inspection of the plots confirms that the fits are generally quite good (Fig. 6). As could be expected, the fitted Freundlich coefficients K_F were fairly well correlated with the sum of oxalate-extractable Fe and Al ($r^2 = 0.70$).

The values of n_{init} obtained can be compared to the extraction results in Table 1. Usually, the modelled n_{init} values were close to the ones obtained with the P_{AL} extraction method, whereas they were considerably lower than the oxalate-extractable values. A significant exception is the Fors soil, in which P_{AL} was much higher than the modelled

n_{init} . This is most likely caused by accumulation of reactive Ca phosphate in this soil, which is partly dissolved during the P_{AL} extraction.

These observations suggest that the oxalate-extractable P pool, at least in these soils, represent a pool of P that is reactive only to a minor extent within a time period of six days. Apparently, the P_{AL} -extractable value is a better representation of this fast-reacting pool in the non-calcareous soils.

4. Discussion

This study confirms a number of earlier studies showing that the pH-dependent solubility of initially bound $\text{PO}_4\text{-P}$ often displays a minimum between pH 6 and pH 7 (e.g., Muurman and Peech, 1967; Devau et al., 2011; Weng et al., 2011). Our data for ten different soils suggest that this is the case for clay soils, whereas for sandy soils such a minimum solubility was not observed except possibly at much lower pH (< 5). Of the seven additional soils studied by Devau et al. (2011) and Weng et al. (2011), only one soil (no. 18 of Weng et al., 2011) contradicts this pattern.

By contrast, laboratory P additions made to an initially P-depleted soil (Kungsängen A3), and AsO_4 adsorption studies on two of the other clay soils of this study, showed markedly different pH-dependent patterns of dissolved $\text{PO}_4\text{-P}$ or As. Thus, the results for systems in which P or As was added are in much better agreement with the commonly perceived view that anion adsorption increases with decreasing pH.

These contradicting patterns suggest that it might be risky to put too much emphasis on P desorption patterns when calibrating surface complexation models aimed at properly

describe P sorption/desorption in soils. Without further refinement, such models would not be consistent, i.e. they would predict the same pH dependence of P *adsorption* as for P *desorption*, which is not observed in the short-term laboratory experiments used for optimizing the models. What, then, is causing the different patterns between P sorption and desorption?

To start with, the kinetic experiments for the Kungsängen soil suggest that the contrasting patterns are not likely caused by weathering of P-containing minerals, as P was dissolved very quickly in acid conditions and after a short reaction time, and as a fraction of it was readsorbed when the pH increased due to other processes. Instead, the quick reactions lead us to hypothesize that the reactions that govern the solubility of $\text{PO}_4\text{-P}$ are dominated by sorption/desorption.

An analysis of the extraction data for P, and of the results from the sorption experiment, provides further clues as to what might be happening. The sorption isotherm experiment indicated that only a relatively small fraction of the oxalate-extractable P was reactive within a six-day period. This agrees with the observations of Peltovuori et al. (2002), who attributed this to the dissolution of significant quantities of calcium phosphate minerals into the oxalate extract. This almost certainly is an important process in the Fors soil, but there is no evidence for this being an important process in the other soils of this study.

Another possible process is that the non-reactive part of the oxalate-extractable P pool represents an ‘occluded’ P phase. The data from Kungsängen suggest that although this pool may not be reactive in short-term equilibrations, it is dynamic in the long run. As Table 1 shows, oxalate-extractable P had increased by $10.5 \text{ mmol kg}^{-1}$ relative to that of

the unfertilized plot after 45 years of fertilization. Only 20 % of this was in an AL-extractable form (and hence reactive in short-term laboratory experiments). This result can be compared to the study of Börling et al. (2004), who reported results for Kungsängen and for eight other Swedish soil fertility experiments with similar P fertilization levels. According to Börling et al. (2004), oxalate-extractable P had, on average, increased by 9.3 mmol kg⁻¹, of which 37.5 % was extractable by AL. Considering that the AL-extractable pool is of similar magnitude as the fast-reacting pool in laboratory experiments, this implies that most of the accumulated P was in an ‘occluded’ phase, not immediately available for solubilization.

These observations show that it might be necessary to properly account for the slow-reacting pool in laboratory procedures and models that aim to properly describe the long-term response of soils to P fertilization, including the risk for P leaching.

We hypothesize, on the basis of our results, that hydroxy-Al and/or hydroxy-Fe interlayers of clay minerals may be important P sorbents, at least in clay soils. The P associated with these interlayers may to a large extent be ‘occluded’, i.e. trapped inside the clay minerals. On acidification, interlayers will start to dissolve which will (i) reduce the total amount of the sorbent, leading to desorption of P bound to these interlayers, and (ii) expose previously inaccessible interlayer hydroxy-Al or Fe, to which both P and As can (re)adsorb (and initially bound P desorb). When the pH is increased again, new interlayers are formed, and some of the adsorbed P and As will be trapped, i.e. occluded. These factors taken together may account for the contrasting pH dependences of P/As sorption and desorption in the batch experiments. To test this and other hypotheses, the identity and dynamics of soil P pools need to be much better characterized through e.g. X-ray

absorption spectroscopy (e.g. Beauchemin et al., 2003) and nuclear magnetic resonance (NMR) spectroscopy (Lookman et al., 1997). The dynamics of these pools should be studied in well-designed laboratory experiments. Until more detailed information of this kind is available, the calibration of mechanistically based surface complexation models for P sorption/desorption will remain difficult and to some extent speculative.

5. Conclusions

- (i) Batch experiments conducted for ten Swedish agricultural soils showed different pH dependences of $\text{PO}_4\text{-P}$ desorption; soil texture appeared to be significant in this regard. For soils with a high clay content, there was a minimum $\text{PO}_4\text{-P}$ solubility between pH 6 and 7. For sandy soils, such a minimum solubility was not observed.
- (ii) Experiments with an initially P-depleted clay soil showed that the pH dependence of soluble $\text{PO}_4\text{-P}$ changed when P had been added to the soil. Under these conditions, the least P was dissolved at very low pH. Similar results were obtained when AsO_4 , a $\text{PO}_4\text{-P}$ analogue, was added to two of the other clay soils. Thus, pH-dependence of soluble $\text{PO}_4\text{-P}$ may be different depending on whether it is adsorbed or desorbed.
- (iii) Sorption experiments showed that the initial pool of reactive $\text{PO}_4\text{-P}$ on the soil particle surfaces was more accurately estimated by acid lactate extraction than by oxalate extraction. In addition, results from long-term fertility experiments show that a large part (> 60 %) of the accumulated P was in a phase not

recovered by acid lactate and thus probably not reactive in short-term laboratory experiments

- (iv) The results show that attempts to model P adsorption/desorption in agricultural clay soils need to be able to account for the different behaviour of phosphate during sorption and desorption as well as the different dynamics of surface-reactive and occluded phosphate.

6. Acknowledgements

Kristina Dahlman, Nils Henoeh, Katja Larholt, Jimmy Stensson and Nicholas Zmijewski are acknowledged for sampling the Kungsängen soil samples and for carrying out some of the batch experiments for this soil. Thanks also to Stefan Andersson for providing us with some of the other samples, and to Christina Öhman, Inger Juremalm and Magnus Mörtz for laboratory analyses. This study was supported by Swedish Farmers' Foundation for Agricultural Research.

References

- Andrist-Rangel, Y., Simonsson, M., Andersson, S., Öborn, I., Hillier, S., 2006. Mineralogical budgeting of potassium in soil: A basis for understanding standard measures of potassium. *Journal of Plant Nutrition and Soil Science* 169, 605-615.
- Antelo, J., Avena, M., Fiol, S., Lopez, R., Arce, F., 2005. Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite-water interface. *Journal of Colloid and Interface Science* 285, 475-486.
- Barrow, N.J., 1978. The description of phosphate adsorption curves. *Journal of Soil Science* 29, 447-462.

- Beauchemin, S., Hesterberg, D., Chou, J., Beauchemin, M., Simard, R.R., Sayers, D.E., 2003. Speciation of phosphorus in phosphorus-enriched agricultural soils using X-ray absorption near-edge structure spectroscopy and chemical fractionation. *Journal of Environmental Quality* 32, 1809-1819.
- Börling, K., Ottabbong, E., Berberis, E., 2001. Phosphorus sorption in relation to soil properties in some cultivated Swedish soils. *Nutrient Cycling in Agroecosystems* 59, 39-46.
- Börling, K., Ottabbong, E., Berberis, E., 2004. Soil variables for predicting potential phosphorus release in Swedish noncalcareous soils. *Journal of Environmental Quality* 33, 99-106.
- Carlgren, K., Mattsson, L., 2001. Swedish soil fertility experiments. *Acta Agriculturae Scandinavica B* 51, 49-76.
- Christoffersen, M.R., Christoffersen, J., Kibalczyk, W., 1990. Apparent solubilities of two amorphous calcium phosphates and of octacalcium phosphate in the temperature range 30-42°C. *Journal of Crystal Growth* 106, 349-354.
- Devau, N., Hinsinger, P., Le Cadre, E., Colomb, B., Gérard, F., 2011. Fertilization and pH effects on processes and mechanisms controlling dissolved inorganic phosphorus in soils. *Geochimica et Cosmochimica Acta* 75, 2980-2996.
- Edzward, J.K., Toensing, D.C., Leung, M.C.Y., 1976. Phosphate adsorption reactions with clay minerals. *Environmental Science and Technology* 10, 485-490.
- Egnér, H., Riehm, H., Domingo, W.R., 1960. Untersuchung über die chemische Bodenanalyse als Grundlage für die Beurteilung des Nährstoffzustandes der Böden. 2. Chemische Extraktionsmethoden zur Phosphor und Kaliumbestimmung. *Ann. R. Agric. Coll. Swed.* 26, 199-215.
- Fitter, A.H., Sutton, C.D., 1975. The use of the Freundlich isotherm for soil phosphate sorption data. *Journal of Soil Science* 26, 241-246.
- Goldberg, S., Sposito, G., 1984. A chemical model of phosphate adsorption by soils. 1. Reference oxide minerals. *Soil Science Society of America Journal* 48, 772-778.
- Gustafsson, J.P., 2001. Modelling competitive anion adsorption on oxide minerals and an allophane-containing soil. *European Journal of Soil Science* 52, 639-653.
- Gustafsson, J.P., 2006. Arsenate adsorption to soils: modelling the competition from humic substances. *Geoderma* 136, 320-330.
- Gustafsson, J.P., 2011. Visual MINTEQ, ver. 3.0. Available at:
<http://www2.lwr.kth.se/English/OurSoftware/vminteq/index.html>.

- Gustafsson, J.P., Berggren, D., Simonsson, M., Zysset, M., Mulder, J., 2001. Aluminium solubility mechanisms in moderately acid Bs horizons of podzolised soils. *European Journal of Soil Science* 52, 655-666.
- Harsh, J.B., Doner, H.E., 1985. The nature and stability of aluminum hydroxide precipitated on Wyoming montmorillonite. *Geoderma* 36, 45-56.
- Hartikainen, H., Simojoki, A., 1997. Changes in solid- and solution-phase phosphorus in soils on acidification. *European Journal of Soil Science* 48, 493-498.
- Hartikainen, H., Rasa, K., Withers, J.A., 2010. Phosphorus exchange properties of European soils and sediments derived from them. *European Journal of Soil Science* 61, 1033-1042.
- Haynes, R.J., 1982. Effects of liming on phosphate availability in soils. *Plant Soil* 68, 289-308.
- Hesterberg, D., 2010. Macroscale chemical properties and X-ray absorption spectroscopy of soil phosphorus. In: Singh, B., Gräfe, M. (Eds.), *Synchrotron-based techniques in soils and sediments. Developments in Soil Science*, Vol. 34. Elsevier, Burlington, MA., pp. 313-356.
- Hetrick, J.A., Schwab, A.P., 1992. Changes in aluminium and phosphorus solubilities in response to long-term fertilization. *Soil Science Society of America Journal* 56, 755-761.
- Karathanasis, A.D., Shumaker, P.J., 2009. Organic and inorganic phosphate interactions with soil hydroxy-interlayered minerals. *Journal of Soils and Sediments* 9, 501-510.
- Kirchmann, H., 1991. Properties and classification of soils of the Swedish long-term fertility experiments: 1. Sites at Fors and Kungsängen. *Acta Agriculturae Scandinavica* 41, 227-242.
- Kirchmann, H., Eriksson, J., 1993. Properties and classification of soils of the Swedish long-term fertility experiments: 2. Sites and Örja and Orup. *Acta Agriculturae Scandinavica* 43, 193-205.
- Kostka, J.E., Luther, G.W., 1994. Partitioning and speciation of solid-phase iron in saltmarsh sediments. *Geochimica et Cosmochimica Acta* 58, 1701-1710.
- Lagno, F., Demopoulos, G.P., 2006. The stability of hydrated aluminium phosphate, $\text{AlPO}_4 \cdot 1.5\text{H}_2\text{O}$. *Environmental Technology* 27, 1217-1224.
- Lindsay, W.L., 1979. *Chemical equilibria in soils*. John Wiley & Sons, New York.
- Lookman, R., Grobet, P., Merckx, R., van Riemsdijk, W.H., 1997. Application of ^{31}P and ^{27}Al MAS NMR for phosphate speciation studies in soil and aluminium hydroxides: Promises and constraints. *Geoderma* 80, 369-388.

- Manning, B., Goldberg, S., 1996. Modeling arsenate competitive adsorption on kaolinite, montmorillonite and illite. *Clays and Clay Minerals* 44, 609-623.
- McDowell, H., Gregory, T.M., Brown, W.E., 1977. Solubility of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ in the system $\text{Ca}(\text{OH})_2\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$ at 5, 15, 25, and 37 °C. *Journal of Research of the National Bureau of Standards* 81A, 273–281.
- Murrmann, R.P., Peech, M., 1969. Effect of pH on labile and soluble phosphate in soils. *Soil Science Society of America Proceedings* 33, 205-210.
- Nriagu, J.O., 1972. Solubility equilibrium constant of strengite. *American Journal of Science* 272, 476-484.
- Peltovuori, T., 2007. Sorption of phosphorus in field-moist and air-dried samples from four weakly developed cultivated soil profiles. *European Journal of Soil Science* 58, 8-17.
- Peltovuori, T., Uusitalo, R., Kauppila, T., 2002. Phosphorus reserves and apparent phosphorus saturation in four weakly developed cultivated pedons. *Geoderma* 110, 35-47.
- Pierzynski, G.M., Logan, T.J., Traina, S.J., 1990. Phosphorus chemistry and mineralogy in excessively fertilized soils: Solubility equilibria. *Soil Science Society of America Journal* 54, 1589-1595.
- Sjöstedt, C.S., Gustafsson, J.P., Köhler, S.J., 2010. Chemical equilibrium modeling of organic acids, pH, aluminum and iron in Swedish surface waters. *Environmental Science and Technology* 44, 8587-8593.
- Smith, R.M., Martell, A.E., Motekaitis, R.J., 2003. NIST Critically Selected Stability Constants of Metal Complexes Database. Version 7.0. NIST Standard Reference Database 46. US Department of Commerce, National Institute of Standards and Technology, Gaithersburg.
- Tolner, L., Füleký, G., 1995. Determination of the originally adsorbed soil phosphorus by modified Freundlich isotherm. *Communications of Soil Science and Plant Analysis* 26, 1213-1231.
- Van Reeuwijk, L.P., 1995. Procedures for soil analyses, 5th ed. International Soil Reference and Information Centre: Wageningen, Netherlands.
- Veith, J.A., Sposito, G., 1977. Reactions of aluminosilicates, aluminum hydrous oxides, and aluminum oxide with *o*-phosphate: The formation of x-ray amorphous variscite and montebrasite. *Soil Science Society of America Journal* 41, 870-876.
- Weng, L.P., Vega, F.A., van Riemsdijk, W.H., 2011. Competitive and synergistic effects in pH-dependent phosphate sorption in soils: LCD modeling. *Environmental Science and Technology* 45, 8420-8428.
- Wolf, A.M., Baker, D.E., 1990. Colorimetric method for phosphorus measurement in ammonium oxalate soil extracts. *Communications in Soil Science and Plant Analysis* 21, 2257-2263.

- Woods, T.L., Garrels, R.M., 1987. Thermodynamic values at low temperature for natural inorganic materials. An uncritical summary. Oxford University Press.
- Yagi, S., Fukushi, K., 2011. Phosphate sorption on monohydrocalcite. *Journal of Mineralogical and Petrological Sciences* 106, 109-113.

Fig. 1. pH-dependent $\text{PO}_4\text{-P}$ dissolution from the A horizon of agricultural soils. Upper left: soils with a clay content > 20 %. Upper right: Soils with clay contents ranging from 10 to 20 %. Lower left: Soils with a clay content < 10 %.

Fig. 2. pH-dependent $\text{PO}_4\text{-P}$ dissolution in the Kungsängen soil depending on fertilization level (A3 or D3, see text) or $\text{PO}_4\text{-P}$ additions on the laboratory. Left: Results from all treatments; right: comparison of the A3, 133 μM P treatment with the D3 soil without any P added.

Fig. 3. pH-dependent $\text{PO}_4\text{-P}$ dissolution in the E21:2 (left) and Broknäs A (right) soils, compared to the pH-dependent concentration of dissolved AsO_4 after the addition of 50 μM AsO_4 and equilibration for 6 d.

Fig. 4. Solubility diagrams for the Kungsängen samples. The points represent the calculated solution activities in the batch experiment extracts. The solubility lines are calculated from the data given in Table 2. Data points above the lines indicate supersaturation.

Fig. 5. Dissolved PO₄-P and pH after different time periods in the dissolution rate experiment for the Kungsängen A3 soil. “Low pH” and “Intermediate pH” correspond to samples in which 60 and 15 mmol H⁺ kg⁻¹ soil had been added, respectively.

Fig. 6. Fitted Freundlich sorption isotherms. The points are the measured sorption data corrected for the modeled value of n_{init} (see Table 3), and the lines are the Freundlich model fits.

1 **Table 1**

2 General soil properties of the ten studied sites

Site	Latitude and Longitude	pH(H ₂ O)	Texture	Clay	Organic C (%)	CaCO ₃	Fe _o ^a	Fe _{asc} ^a	Al _o ^a	PO ₄ -P _o ^a	P _{AL} ^a
<i>Fertility experiments</i>											
Fjärdingslöv	54°24'N, 13°14'E	7.3	Sandy loam	17	1.5	0.2	34	6.9	30	1.6	0.5
Fors	60°20'N, 17°29'E	8.2	Silty loam	17	2.1	4.8	26	4.7	32	10.1	4.4
Högåsa	58°30'N, 15°27'E	6.0	Loamy sand	6	1.7	0	48	11	68	8.7	1.2
Kungsängen A3	59°50'N, 17°40'E	7.1	Silty clay	57	2.2	0	155	30	60	12.4	0.8
Kungsängen D3				57	2.3	0	183	34	52	22.9	2.9
Orup	55°49'N, 13°30'E	6.2	Sandy loam	19	1.3	0	45	11	31	2.9	0.6
Vreta Kloster	58°29'N, 13°08'E	6.7	Silty clay	35	1.9	0	24	5.9	62	4.9	1.0
Örja	55°53'N, 12°52'E	5.3	Loam	8	1.9	0	64	19	75	4.4	0.4
<i>Other soils</i>											
Broknäs	59°24'N, 18°18'E	6.7	Silty clay	46	2.1	0	100	26	49	9.4	nd ^b
E21:2	58°26'N, 15°00'E ^c	6.9	Silty clay	44	6.7	0.2	127	30	55	15.6	1.8
E21:24	58°26'N, 15°00'E ^c	5.6	Loamy sand	4	1.2	0	26	8.1	47	7.2	2.0

3 ^a Subscripts refer to results obtained by oxalate extraction (o), ascorbic acid extraction (asc) and acid lactate extraction (AL). See text for details.

4 ^b Not determined

5 ^cThese coordinates are only approximate, as the exact locations of the sites are confidential.

6

1 **Table 2**

2 Solubility constants and heats of reaction for Ca and Al phosphates used in the speciation calculations

Reaction	$\log K_s$ (25°C) ^a	ΔH_r (kJ/mol) ^a
<i>HAp</i> : $\text{Ca}_5(\text{PO}_4)_3\text{OH}(\text{s}) + \text{H}^+ \Leftrightarrow 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{H}_2\text{O}$	-44.3 ^b	0
<i>OCP</i> : $\text{Ca}_4\text{H}(\text{PO}_4)_3(\text{s}) \Leftrightarrow 4\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{H}^+$	-47.95 ^c	-105 ^c
<i>DCP</i> : $\text{CaHPO}_4(\text{s}) \Leftrightarrow \text{Ca}^{2+} + \text{PO}_4^{3-} + \text{H}^+$	-19.28	31
<i>DCPD</i> : $\text{CaHPO}_4 \times 2\text{H}_2\text{O}(\text{s}) \Leftrightarrow \text{Ca}^{2+} + \text{PO}_4^{3-} + \text{H}^+ + 2\text{H}_2\text{O}$	-19.00	23
<i>ACP2</i> : $\text{Ca}_3(\text{PO}_4)_2(\text{s}) \Leftrightarrow 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	-28.25 ^c	-87 ^c
<i>ACPI</i> : $\text{Ca}_3(\text{PO}_4)_2(\text{s}) \Leftrightarrow 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	-25.5 ^c	-94 ^c
<i>Variscite</i> : $\text{AlPO}_4(\text{s}) \times 2\text{H}_2\text{O}(\text{s}) \Leftrightarrow \text{Al}^{3+} + \text{PO}_4^{3-} + 2\text{H}_2\text{O}$	-22.07 ^d	-9.4 ^e
<i>Hydrated Al phosphate</i> : $\text{AlPO}_4(\text{s}) \times 1.5\text{H}_2\text{O}(\text{s}) \Leftrightarrow \text{Al}^{3+} + \text{PO}_4^{3-} + 1.5\text{H}_2\text{O}$	-20.46 ^f	-9.4 ^e

3 ^a Unless otherwise stated, the values are from Smith et al. (2003).

4 ^b Solubility of HAp at 21°C (McDowell et al., 1977).

5 ^c Calculated from raw data given by Christoffersen et al. (1990)

6 ^d Lindsay (1979)

7 ^e Woods and Garrels (1987)

8 ^f Lagno and Demopoluos (2006)

1 **Table 3**

2 Optimized Freundlich sorption parameters

Soil	Range of pH values after equilibration	K_F^a	m^b	n_{init} (mmol kg ⁻¹)	r^2
Broknäs	6.10 – 6.19	0.162	0.35	1.01	0.997
E21:2	6.66 – 6.75	0.290	0.35	2.28	0.997
E21:24	5.48 – 5.54	0.163	0.35	2.22	0.994
Fjärdingslöv	6.60 – 6.68	0.0779	0.35	0.52	0.978
Fors	7.33 – 7.48	0.0844	0.35	0.76	0.992
Högåsa	5.96 – 6.12	0.171	0.35	1.59	0.990
Örja	5.13 – 5.26	0.306	0.35	1.52	0.998
Orup	5.86 – 5.90	0.0975	0.35	0.62	0.992
Vreta Kloster	6.20 – 6.27	0.129	0.35	0.77	0.983

3 ^aThe K_F value was calculated based on the concentration units mol kg⁻¹ and mol L⁻¹ for n and c , see Equation 1.

4 ^b Fixed at this value, see text.

5

Supporting Information

The pH dependence of phosphate sorption and desorption in Swedish agricultural soils.

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Fig. S1. Solubility diagrams for four samples. The points represent the calculated solution activities in the batch experiment extracts. The solubility lines are calculated from the data given in Table 2. Data points above the lines indicate supersaturation with respect to hydroxyapatite.

Table S1. Fitted second-order polynomials of dissolved $\text{PO}_4\text{-P}$ as a function of pH, and the pH value at minimum $\text{PO}_4\text{-P}$ solubility. Only soils with > 10 % are included in the analysis.

Soil	% clay	Second-order polynomial ^a	r^2	pH at minimum $\text{PO}_4\text{-P}$ solubility
Kungsängen A3	57	$P = 14.04\text{pH}^2 - 179.96\text{pH} + 582.4$	0.89	6.40
Broknäs	46	$P = 7.111\text{pH}^2 - 86.10\text{pH} + 277.0$	0.90	6.05
E21:2	44	$P = 72.82\text{pH}^2 - 955.4\text{pH} + 3158$	0.96	6.56
Vreta Kloster	35	$P = 22.03\text{pH}^2 - 267.4\text{pH} + 831.4$	0.90	6.07
Orup	19	$P = 3.744\text{pH}^2 - 43.89\text{pH} + 145.9$	0.67	5.86
Fors	17	$P = 149.0\text{pH}^2 - 2244\text{pH} + 8502$	0.92	7.53
Fjärdingslöv	17	$P = 5.568\text{pH}^2 - 84.72\text{pH} + 349.1$	0.94	- ^b

^aDissolved P is expressed in $\mu\text{g/l}$

^bNo minimum P solubility was found in the range of pH values analysed