

# Temperature and wetting effects on phosphate sorption by soil

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## 1. Summary

Early in the growing season phosphate (P) shortages are not uncommon in agricultural practice. Low temperatures may play a role. Temperature affects P adsorption and desorption and microbial activity. Many researchers studied P-sorption while microbial activity was inhibited. In this research this was not the case. P dynamics related to sorption were studied at three different temperatures. Soils were incubated field moist for 39 days and subsequently a desorption experiment was carried out. A P desorption experiment was carried out by introducing Pi papers which act as a P sink. The desorption experiment was carried out at three temperatures as well and in duplicate. During incubation 0.01M CaCl<sub>2</sub> and Olsen extractions were performed to study P dynamics.

P-CaCl<sub>2</sub> decreased strongly during incubation until equilibrium was reached. Soil incubated at higher temperatures reached equilibrium earlier than soils incubated at lower temperatures. These effects are probably caused by microbial activity. There was a large discrepancy between P-CaCl<sub>2</sub> equilibrium value and P-CaCl<sub>2</sub> extracted from dry soil. The equilibrium value was 40-90% lower than P-CaCl<sub>2</sub> from dry soil.

Cumulative desorbed P by Pi papers was higher at 20°C compared to 13°C and 4°C, but this trend was rarely significant. During the desorption experiment P in solution was very difficult to measure due to dilution of the small samples. When the desorption experiment was finished P in solution could be measured easily because the larger samples didn't need dilution. In only two soils P in solution after desorption was significantly higher at 20°C compared to 4°C. In all other soils no significant differences caused by temperature were observed.

P in solution after desorption was also compared to P-CaCl<sub>2</sub> after incubation. In some soils P concentrations hardly changed, while in other soils P concentrations decreased strongly. These observed differences could be expressed by calculating the buffer potential for each soil with the data obtained. Small changes in solution during desorption were reflected by high buffer potentials, whereas large changes were reflected by low buffer potentials.

Addition of P, either inorganic or as manure, did not have significant effects on amounts of P desorbed by five Ppi papers from the soil, neither on P concentrations in solution after desorption.



## 2. Introduction

Phosphorus (P) is an essential nutrient. Early in the growing season phosphate shortages are common in agricultural practice. Low temperatures may play a key role here. Soil temperatures are relatively low compared to above-soil temperatures early in the growing season. Therefore plant roots grow slower than above-soil plant parts. The root system will be relatively small and therefore might be unable to provide sufficient nutrients. Low temperatures can also affect processes involved with phosphate bioavailability, like precipitation, dissolution, adsorption, desorption and microbial activity

Adsorption and desorption rates are known to be affected by temperature (Gardner and Jones, 1973; Barrow and Shaw, 1975; Barrow, 1979; Doula *et al.*, 1996). Rates of both processes increase with increasing temperatures. The equilibrium between adsorbed P and soluble P shifts due to speed changes induced by temperature changes. Increased temperatures favor higher concentrations of P in solution. Researchers studying temperature effects on adsorption and desorption made sure microbial activity was inhibited by adding chloroform or toluene to the soil. In reality microbial activity is present in soils and growth of micro organisms is affected by temperature as well. Inhibition of microbial activity while studying temperature effects on bio availability of P will cease to mimic what really happens in soils.

Above mentioned researchers did their experiments on adsorption and desorption by changing P concentrations in solution and studying any changes in solution. Changes in concentrations were introduced by either adding P or dilution of the P solution. P desorption is often studied by introducing a P sink, which strongly adsorbs P. The sink mimics the P uptake behavior of a plant root. A method commonly used is the Pi paper method, as proposed by Van der Zee *et al.* (1987). P sorbed to the Pi paper is assumed to have been desorbed from the soil. This is supported by the low concentrations in solution during desorption. Studies using this technique generally do not apply any inhibition of microbial activity. Micro organisms therefore can still grow and take up P.

The goal of this research is to study the effects of temperature on phosphate sorption during incubation and subsequent desorption. Research questions are:

What is the effect of temperature on P in moist soil?

- Does phosphate extracted by 0.01M CaCl<sub>2</sub> increase or decrease during incubation due to temperature differences?

What is the effect of temperature on P desorption with Pi papers subsequent to incubation?

- Do differences exist between amounts sorbed by Pi papers at different temperatures?
- Are there differences between phosphate in solution during and after P desorption at different temperatures?
- What are the differences between phosphate extracted by 0.01M CaCl<sub>2</sub> during and after incubation compared to phosphate in solution during and after desorption and does temperature affect these differences?

To study temperature effects on soil and its processes, soil is incubated at field capacity at three different temperatures for 39 days. P concentration in solution was measured with a 0.01M CaCl<sub>2</sub> extraction performed with field moist soil. After incubation temperature effects on P desorption were studied. Desorption of P from soil was done by applying the technique as proposed by Van der Zee *et al.* (1987) and adapted by Van Rotterdam-Los (2010). This desorption experiment was carried out at three different temperatures as well.

### 3. Theory

#### 3.1. Background

Phosphorus (P) is an essential element for plants to grow, next to other macro nutrients like nitrogen (N) and potassium (K). Phosphorus is taken up in the form of dissolved orthophosphate. When phosphorus is strongly bound to the soil, available phosphate for plants can be limited and thus the growth rate of plants. In order to improve nutrient levels farmers use fertilizers. Organic fertilizers are mainly animal manure, sometimes mixed with straw, and crop residues. Inorganic fertilizers might be rock phosphate or artificial fertilizers. Rock phosphate is used as a slow release fertilizer and provides also phosphorus on a longer term. In the Netherlands rock phosphate is not used much; artificial fertilizer P is used commonly.

Since the early 1950s animal agriculture has strongly intensified with high surpluses of manure as a result (Hoffland *et al.*, 2006). To get rid of this manure, farmers added much more manure to their soils than needed for fertilization. In the 1950s policymakers in Europe and the Netherlands were focused on increasing agricultural production. In the 1960s and 1970s it became clear that such a strong intensification of animal agriculture was not environmentally sustainable. The high surpluses of manure caused a build-up of nutrients in soils. For phosphorus this means that P saturation of soils has increased over the years. High degrees of P saturation ultimately enhance phosphorus losses to surface water causing eutrophication. Eutrophication of surface water often results in enhanced growth of algae and macrophytes.

In 1984 the first measures were taken to stop further growing of animal agriculture. Also limits were implemented for manure application and later, in 1990, these application limits were lowered. Restrictions were set on the moment of manure application: application during the winter season was not allowed anymore.

Application rates for phosphorus were set by focusing on equilibrium fertilization (Van der Molen *et al.*, 1998). This term is used to define the supply of fertilizers needed for crop uptake and also compensates for agriculturally inevitable losses and environmentally acceptable losses. Agriculturally inevitable losses of phosphorus are losses mainly through irreversible sorption and (sub)surface runoff, while maintaining good agricultural practice. They are quantified at 25-75 kg P<sub>2</sub>O<sub>5</sub>/ha/yr. Environmentally acceptable losses are nutrient losses that do not harm quality standards for both groundwater and surface water. They are based on average precipitation and quality standards, and are quantified at 1 kg P<sub>2</sub>O<sub>5</sub>/ha/yr. Model calculations for sandy soils in the Netherlands indicate that a phosphorus surplus of 10 kg P<sub>2</sub>O<sub>5</sub>/ha/yr will not further increase the P losses for the next few decades (Van der Molen *et al.*, 1998).

In 1998 MINAS (Mineral Accounting System) was implemented in order to try to solve the remaining nutrient surpluses. In this system all incoming and outgoing nutrients at a farm should be accounted. The difference between inputs and outputs should not exceed certain 'acceptable', so-called levy-free surplus levels. MINAS was based on equilibrium fertilization and the levy-free surpluses coincide with the previous mentioned phosphorus surpluses. The EU however was not satisfied with the Dutch measures. The measures did not comply totally with the EU regulations and they were not strict enough. For

example, the EU regulations prescribe that nutrient balances are calculated at crop (or field) level, while in MINAS nutrient balances were calculated at farm level which allowed movement of nutrients within the farm and between fields. Also the EU regulations did not allow for surpluses on the nutrient balance, while MINAS did with its levy-free surpluses. In 2003, after several additional measures the Dutch government was forced by EU to leave MINAS (Hoffland *et al.*, 2006).

In 2006 a system of application limits was implemented. The application limits again are based on agricultural needs and environmentally acceptable losses. Also the phosphorus state of soils is taken into account. Application limits are visible in table 1 and 2. For grassland and arable land application limits are based on the PAL value and the  $P_w$  value of the soil respectively. The values for 2010-2015 are planned values. The goal is to fully implement equilibrium fertilization in 2015 and the target application limits for grassland and arable land are 90 and 60 kg  $P_2O_5$ /ha/yr respectively (Chardon *et al.*, 2007).

**Table 1: Application limits (kg  $P_2O_5$ /ha/yr) for grassland (Ministry of Agriculture, Nature and Food Quality 2009).**

PAL value	2006	2007	2008	2009	2010	2011	2012	2015
<27	110	105	100	100	100	100	100	100
27-50	110	105	100	100	95	95	95	95
>50	110	105	100	100	90	90	85	85

**Table 2: Application limits (kg  $P_2O_5$ /ha/yr) for arable land (Ministry of Agriculture, Nature and Food Quality 2009).**

$P_w$ value	2006	2007	2008	2009	2010	2011	2012	2013
<36	95	90	85	85	85	85	85	85
36-55	95	90	85	85	80	75	70	65
>55	95	90	85	85	75	70	65	55

### 3.2. Phosphorus pools and processes in soil

In soil there are three major pools of phosphorus: P-soil, P-solution and P in biomass. Phosphorus in P-soil exists as mineral P, sorbed P and organic P. Phosphorus in solution exists as orthophosphate and dissolved organic phosphorus (DOP). P in biomass consists of phosphorus in living plants and (micro) organisms. Upon death, P in biomass is considered as organic P (in P-soil).

Phosphorus originates from weathering of soil minerals. Apatite is the primary mineral and in unweathered or slightly weathered soils it is the dominant P mineral (Pierzinsky *et al.*, 2005). Apatites can be described with the general formula  $Ca_{10}(PO_4)_6X_2$ , where X represents anions like  $F^-$ ,  $Cl^-$ ,  $OH^-$  or  $CO_3^{2-}$ . In increasingly weathered soils calcium (Ca) leach from the soil, pH decreases and iron (Fe) and aluminum (Al) dissolve from the mineral phase. Secondary minerals are formed by reactions between soluble P and Ca,

Fe and Al. In soils with higher pH and consequently Ca being the dominant cation, mainly Ca-phosphate minerals will precipitate. In more acidic soils with lower pH and Fe and Al being the dominant cations, mainly Al- and Fe-phosphates will precipitate (Pierzynski *et al.*, 2005)].

Weathering of soils will also cause formation of Fe- and Al-oxides, which play a key role in phosphate sorption. Examples of Fe- and Al-oxides are gibbsite, goethite and hydrous ferric oxide (HFO). The charge of these Fe- and Al-oxides is dependent on soil pH. At low pH values protonation of the Fe- and Al-oxides will be larger and thus the net charge of the Fe- and Al-oxides will be more positive. Increase of pH will cause lower protonation and thus lower charge on the Fe and Al oxides. PZC is referred to as the point of zero charge. For gibbsite, goethite and HFO the values of PZC are 10, 9 and 8 respectively (Hiemstra and Van Riemsdijk, 2003). At common pH values in soils Fe- and Al-oxides are positively charged. Negatively charged phosphate species will thus react with the Fe- and Al-oxides and adsorb to them. During phosphate sorption ligand exchange takes place between ligands on the surface of Fe- and Al-oxides and phosphate. After ligand exchange innersphere complexes have formed between Fe- and Al-oxides and phosphate. A bidentate binding is formed in which part of the charge of the phosphate anion is transferred to the oxide surface. This binding becomes stronger when charge differences between the oxide surface and the phosphate ion are larger. Other negatively charged species are also able to sorb to Fe- and Al-oxides via ligand exchange. Examples are anions, like sulfate and carbonate, and organic acids, like oxalate and citrate (Hinsinger, 2001). These species can compete with phosphate for surface sites on Fe- and Al-oxides available for sorption.

Organic P in soils originates from decomposed plant and animal residue. Organic P constitutes 29% - 65% of total soil P (Harrison, 1987). Up to 50% of organic P exists as inositol phosphates. Other organic P forms are nucleic acid, sugar phosphates and phospholipids. Through mineralization by micro organisms organic P can be transformed to inorganic P and released into the soil solution. Phosphorus mineralization is controlled by the C:P ratios of the organic matter and micro organisms. At low C:P ratios in organic matter (<200:1) there is usually more P in the organic matter than the decomposing micro organisms can consume and the excess P is then released into the soil solution (P-solution). At high C:P ratios in organic matter (>300:1) all P in organic matter is consumed by the micro organisms and nothing is released into soil solution (Pierzynski *et al.*, 2005). It is possible that the micro organisms will use additionally required P from the soil solution. This is called immobilization. Organic P can be adsorbed to Fe- and Al-oxides (Celi *et al.*, 1999). Also organic P competes with inorganic P for sorption sites on Fe- and Al-oxides. Increased levels of organic P may cause desorption of inorganic P (Berg and Joern, 2006).

Organic P can also exist as dissolved organic phosphorus (DOP). This can form a major part of total dissolved P (Chardon *et al.*, 1997). DOP is part of dissolved organic matter (DOM). DOM is operationally defined as the organic molecules able to pass through a filter with pore size 0.45 µm. DOM consists of hydrophobic and hydrophilic (Hy) compounds. Hydrophobic DOM can be subdivided in humic acids (HA) and fulvic acids (FA). DOP consists of Hy and FA compounds (Ros *et al.*, 2010). Due to different origins

of Hy, HA and FA DOM these compounds can be ranged from more to less susceptible to mineralization in this order: Hy, FA and HA (Hiemstra and Van Riemsdijk, 2003 and Jandl and Sollins, 1997).

Dissolved inorganic phosphate in soil solution is called orthophosphate. The speciation depends on solution pH, caused by protonation of the phosphate ion. The dissociation of orthophosphoric acid is characterized by three pK values, shown in Figure 1. At common pH values in soil (4-9; worldwide)  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  are the dominant orthophosphate species.

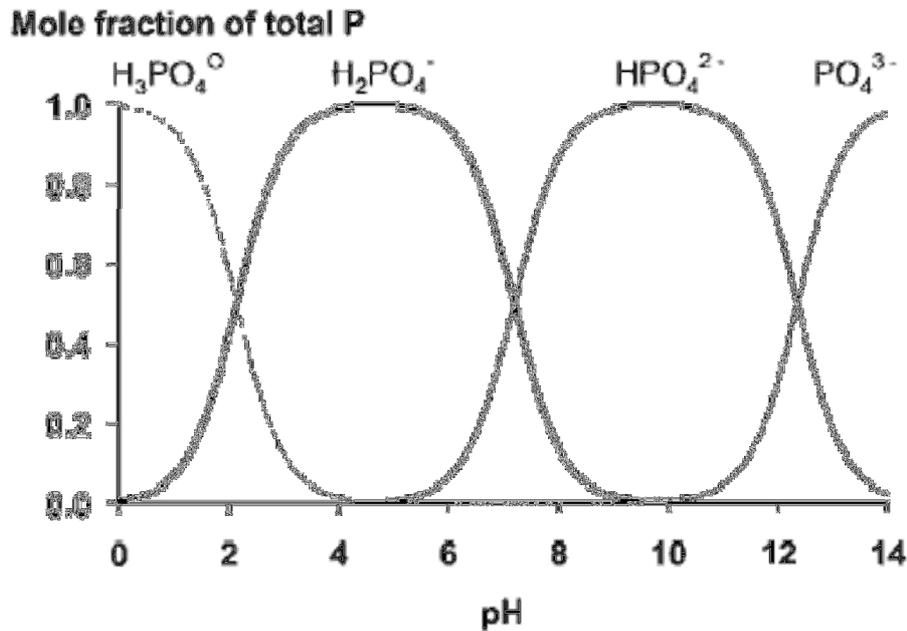


Figure 1: Speciation of orthophosphate in solution as a function of pH. In: Hinsinger (2001)

Phosphate in soil solution is called P intensity or P availability. It is directly available for plant uptake. Labile phosphate is called P quantity or available P and refers to the amount of phosphate that will be taken up by a crop during its growing period. It consists of reversibly sorbed phosphate and possibly mineral phosphorus (precipitates) as well.

### 3.3. Modeling sorbed P

Changes of P amounts sorbed to the soil depend on both adsorption and desorption. This is shown in equation 1 (Van der Zee *et al.*, 1987).

$$\frac{dQ}{dt} = k_a C(Q_{\max} - Q) - k_d Q \quad (1)$$

Sorption depends on sorbed amount (Q) relative to the maximum possible ( $Q_{\max}$ ) and concentration in soil solution (C). The adsorption rate constant ( $k_a$ ) determines the speed of the sorption reaction. Desorption on the other hand depends on sorbed amount (Q), while the desorption rate constant ( $k_d$ ) determines the reaction speed.

At equilibrium, when adsorption and desorption are equal,  $dQ/dt = 0$ , equation 1 reduces to the well-known Langmuir equation, see equation 2.

$$Q = Q_{\max} \frac{KC}{(1 + KC)} \quad (2)$$

The binding constant (K) is determined by both adsorption and desorption rate constants (equation 3).

$$K = \frac{k_a}{k_d} \quad (3)$$

An example isotherm resulting from the Langmuir equation is shown in Figure 2. The buffer potential (BP) of a soil is defined as the slope of the sorption isotherm. It can be calculated by differentiating the Langmuir equation to C, see equation 4 (Van Rotterdam-Los, 2010).

$$BP = \frac{dQ}{dC} = \frac{Q_{\max} K}{(1 + KC)^2} \quad (4)$$

At low amounts sorbed (Q) concentrations in solution (C) increase slowly with increasing amounts sorbed, this behavior is associated with high buffer potential. When amounts sorbed are approaching maximum sorption ( $Q_{\max}$ ), concentrations in solution increase fast with increasing amounts sorbed. In this situation the buffer potential is low, see figure 2.

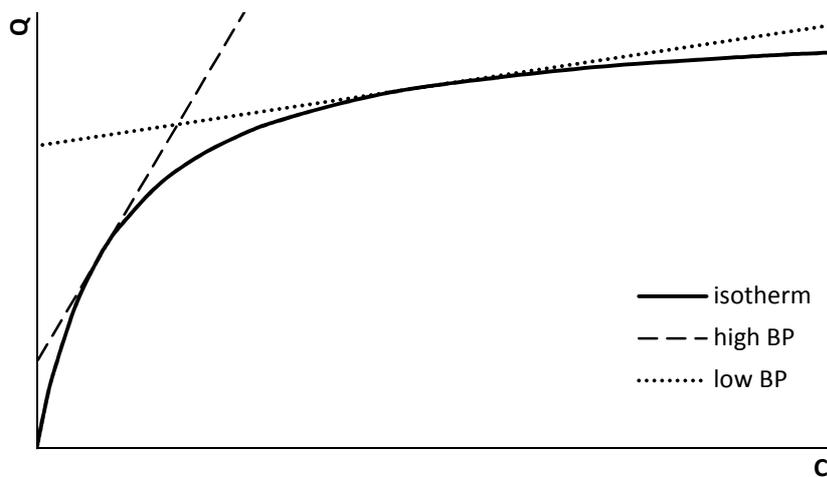
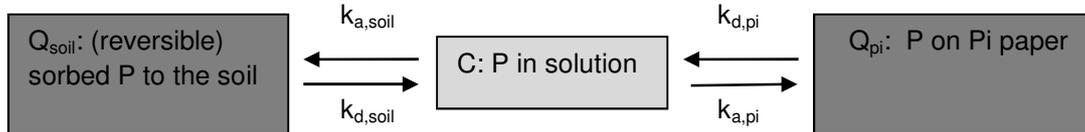


Figure 2: Sorption isotherm resulting from a Langmuir equation. The dashed and dotted lines show situations of high and low buffer potential (BP) respectively.

### 3.4. Measuring P desorption from soil

When measuring P desorption from soils a P sink can be used. Filter papers impregnated with an iron oxide (goethite), called Pi paper, can serve as a P sink. In a system of soil with solution a Pi paper is introduced as a P sink. After introduction of the Pi paper P is redistributed between soil, solution and Pi paper. P desorbed from the soil into solution will be sorbed to the Pi paper. Adsorption and desorption kinetics of both soil and Pi paper play a role. The situation is schematically shown in figure 3 (Van Rotterdam-Los (2010).

When  $k_{d,soil}$  is smaller than  $k_{a,pi}$  desorption kinetics will be limiting and nearly all P in solution will be sorbed to the pi paper. When  $k_{d,soil}$  is larger than  $k_{a,pi}$  pi paper adsorption kinetics will be limiting. Part of the P desorbed from soil will not be sorbed to the pi paper and will thus stay in solution. In that situation  $Q_{soil}$  and P in solution can be in equilibrium while  $Q_{pi}$  and P in solution are not in equilibrium. P in solution will be a function of  $Q_{soil}$ . It is also possible that both  $Q_{soil}$  and  $Q_{pi}$  are at equilibrium with P in solution. In that case P in solution is a function of  $Q_{soil}$  as well.



**Figure 3:** Description of situation during P desorption with an active P-sink (Pi paper). Three pools of P are present: (reversible) sorbed P to the soil, P in solution and P sorbed to the Pi paper. P moves from soil to solution and back and from solution to Pi paper and back with respective rate constants:  $k_{d,soil}$ ,  $k_{a,soil}$ ,  $k_{a,pi}$  and  $k_{d,pi}$

Because concentrations P in solution are generally very low it can be assumed that all  $Q_{pi}$  originates from  $Q_{soil}$ . In that case  $Q_{soil}$  can be described as shown in equation 5.

$$Q_{soil} = Q_0 - Q_{pi} \quad (5)$$

$Q_0$  is the initial amount of reversible sorbed P to the soil. It can be estimated by several extraction methods like Olsen, acid ammonium lactate (PAL) or acid ammonium oxalate ( $P_{ox}$ ). Different extraction methods have a different strength of extraction. Clearly this affects the approximated sorbed P ( $Q_{soil}$ ) when calculated with equation 4. Approximation of  $Q_0$  with a strong extraction method will result in a larger calculated  $Q_{soil}$  compared to a weaker extraction method (Van Rotterdam-Los, 2010).

### 3.5. Temperature effect on sorption rate constant

In general rate constants are affected by temperature: increased temperatures will cause rate constants to increase. This effect can be described with the Arrhenius equation, see equation 6.

$$k = A \cdot e^{\left(\frac{-E_A}{RT}\right)} \quad (6)$$

The value of rate constant ( $k$ ) is a function of temperature ( $T$ ), the gas constant ( $R$ ), activation energy ( $E_A$ ) and a frequency factor ( $A$ ).

Equation 6 can be rewritten to:

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \quad (7)$$

From equation 7 can be seen that  $\ln(k)$  will have a linear relationship with  $1/T$ .

## 4. Materials and Methods

### 4.1. Preparation

#### Soils

The soils used in this research are all originating from the Netherlands. Soils with different properties like clay percentage, pH and phosphate status were selected. The soils had a pH range from 4 to 7. Finally the P-status of the soil was investigated. Based on several properties like 0.01M CaCl<sub>2</sub> extracted P, buffer capacity and the P saturation a selection of soils was chosen. Table 3 gives an overview of properties of the selected soils.

In this experiment Fe-coated quartz was used as a soil as well. The quartz itself is considered to be inert with respect to phosphate. On the other hand phosphate has a high affinity to the goethite coating. This is considered to be the only reactive compound in this sand. The Fe-coated quartz will therefore represent the temperature dependency of phosphate reactivity with goethite.

**Table 3: Properties of the soils used in the adsorption and desorption experiment.**

soil	clay (<2µm) %	OM %C	CaCO <sub>3</sub> %	pH (CaCl <sub>2</sub> )	(Fe+Al) <sub>ox</sub> mmol/kg	P <sub>ox</sub> mmol/kg	P-CaCl <sub>2</sub> µmol/kg	P-Olsen mmol/kg
1	13.0	2.7	0	4.2	109.6	9.2	6	0.78
2	2.0	1	0.53	6.5	13.2	10.1	268	1.57
3	9.0	1.5	0	5.0	59.3	8.6	19	0.52
4	26.0	1.8	2.76	7.2	97.1	14.0	23	2.28
5	28.0	4.1	0	6.4	156.0	24.0	58	1.85

### 4.2. Incubation and sorption experiment

The soils are exposed to different treatments concerning both temperature and P addition. A scheme of the treatments is given in table 4. The soils were prepared in batches of 1.5 kg and depending on the treatment P was added as inorganic P in solution (P) or as manure (M). The addition of inorganic P is 0.5 mmol P/kg soil. This equals the amount of 100 kg P<sub>2</sub>O<sub>5</sub>/ha and it corresponds to the maximum P addition allowed to apply to a grassland during a year. P was added in a solution and soils were brought to field capacity. When phosphate was added as manure, 50 gram of manure was added and the rest of moisture was added as water to reach field capacity. The application was 0.05 kg manure with 0.02 mol P/kg manure (average measured by BLGG) to 1.5 kg soil, which makes a total of 0.7 mmol P/kg soil. The soils were mixed well and 200 to 250 grams of the moist soil was put in plastic containers.

The sorption experiment lasted for 39 days. After 1, 7, 14, 21 and 38 days of incubation measurements were carried out to check the nutrient status of the soils. Shaking of the soil solutions for the 0.01M CaCl<sub>2</sub>, P-Olsen and PAL extractions was done at the chosen temperatures (4 °C, 13 °C and 20 °C). Filtration, centrifugation and addition of the final reagents (in the case of P-Olsen extraction) were done at 20 °C due to practical limitations. But as these time steps take little time the temperature effects likely will be

small. Because field moist soil was used instead of dry soil which is normally used for these extractions, additional calculations were made to make corrections for the water content. The amount of water added at the start is known and therefore the water content of the soil. To correct for the water content, extra soil was sampled. Afterwards the sampled amount of dry weight soil was calculated.

**Table 4: Different treatments of temperature and P addition of the soils. Crosses indicate which combination of soil-temperature and P addition have been carried out. Concerning the P addition the following abbreviations are used: nP: no P addition; P: inorganic P added as solution; M: P added as manure.**

temperature	4°C			13°C			20°C		
	no P	inorganic P	P as manure	no P	inorganic P	P as manure	no P	inorganic P	P as manure
soil	(nP)	(P)	(M)	(nP)	(P)	(M)	(nP)	(P)	(M)
1	x	x	x	x	x	x	x	x	x
2	x			x			x		
3	x	x		x	x		x	x	
4	x	x	x	x	x	x	x	x	x
5	x	x		x	x		x	x	
quartz		x	x		x	x		x	x

### 0.01M CaCl<sub>2</sub>

An extraction with 0.01M CaCl<sub>2</sub> is used to get an indication of the ‘available’ phosphate in the soil solution. The ionic strength of the extraction solution is constant due to the 0.01M CaCl<sub>2</sub>. This method is a measure for P intensity. In this extraction 3 grams of dry soil is shaken with 30 mL 0.01M CaCl<sub>2</sub> for 2 hours. The solution was filtered (0.45µm) and the filtrate was spectrophotometrically analyzed for P-PO<sub>4</sub> with a Skalar segmented flow analyzer. The detection limit was 0.02 mg P-PO<sub>4</sub>/L.

### Olsen’s method

With the extraction method according to Olsen (Olsen et al., 1954) the pH is increased to 8.5 and therefore mainly P sorbed to Fe- and Al-oxides is measured. P-Olsen is an estimation of P availability. In the extraction 2.5 grams of dry soil is shaken with 50 mL 0.5M NaHCO<sub>3</sub> (at pH 8.5) for 30 minutes. Then the extract is centrifuged, and 4.5 mL of the centrifugate is brought to pH 5 by adding 0.5 mL 12M H<sub>2</sub>SO<sub>4</sub>. This is mixed well and 1 mL is diluted five times to make a final volume of 5 mL. The final solution was spectrophotometrically analyzed for P-PO<sub>4</sub> with a Skalar segmented flow analyzer. The detection limit was 0.02 mg P-PO<sub>4</sub>/L.

### PAL extraction

A PAL extraction, ammonium lactate and acetic acid buffered at pH 3.75, is an estimation of available P during a growing season. The low pH will dissolve P bound to Calcium (Ca). At the same time the acetic acid competes with phosphate for adsorption sites at the Fe- and Al-oxides and part of the P adsorbed to Fe- and Al-oxides will desorb. Thus P bound to Ca and part of the P adsorbed to Fe- and Al-oxides is measured with this extraction. PAL is an estimation of P availability. In the PAL extraction 2.5 grams of soil is shaken with 50 mL of PAL extraction solution for 4 hours. The solution was filtered

and the filtrate was spectrophotometrically analyzed for total nitrogen and total phosphorus with a Skalar segmented flow analyzer. The detection limit was 1.00 mg P-PO<sub>4</sub>/L.

### 4.3. Desorption experiment

#### Pi paper preparation

After the incubation a desorption experiment was carried out to determine the amount of phosphate available to plants. This was done with so called Pi papers. The method is developed by Van der Zee et al. (1987) and adapted by Van Rotterdam-Los (2010).

The Pi papers serve as an artificial P sink and are prepared by impregnating filter paper with Fe-hydroxide. The filter papers were moved through a solution of 0.37M FeCl<sub>3</sub> for five minutes and then left to dry for an hour. Next the filter papers were moved through a 5% (w/v) ammonia solution for 60 seconds and subsequently the papers were rinsed very well with demineralized water. The filter papers were again left to dry. Finally they were cut into pieces with a size of 2 x 10 centimeters.

#### Experimental setup

For the desorption experiment four grams of soil was put in a container (greiner tube) together with 40 mL 0.01M CaCl<sub>2</sub> and gently shaken (around 4 RPM) end-over-end. In the suspension one Pi paper was attached to a holder which was attached to the lid of the container. The Pi paper was replaced after 2, 4, 8, 24 and 48 hours and subsequently rinsed very well with demineralized water to ensure no soil was attached to it anymore. P was desorbed from the Pi papers by adding 20 mL 0.1M H<sub>2</sub>SO<sub>4</sub> and shaking this for at least 2 hours. In this solution P was measured spectrophotometrically with ICP-AES. The detection limit was 0.02 mg P/L.

After 48 hours the suspension of 0.01M CaCl<sub>2</sub> and soil was centrifuged at 3000 RPM. The centrifugate was analyzed for P-PO<sub>4</sub> spectrophotometrically with a Skalar segmented flow analyzer. The detection limit was 0.02 mg P-PO<sub>4</sub>/L.

The desorption experiment was carried out in duplicate. The replacing and analyzing of the Pi papers was carried out exactly the same in the second series. The second series differed from the first in the fact that at all time steps the suspension of 0.01M CaCl<sub>2</sub> and soil was centrifuged (first at 3000 RPM and later at 2000 RPM, because some bottles broke) and a small subsample (1 mL) was taken, diluted and analyzed spectrophotometrically for P-PO<sub>4</sub> with a Skalar segmented flow analyzer. The detection limit was 0.02 mg P-PO<sub>4</sub>/L. The sample was not filtrated, because it was too small. During careful sampling from the centrifugate no floating particles were sampled.

### 4.4. Soil-solution-ratio

In the experiments performed in this research moist soils were sampled for extraction. Therefore already water is in the soil and if not corrected for during sampling, the intended soil-solution-ratio (SSR) is not reached. The 0.01M CaCl<sub>2</sub> extraction carried out several times during incubation has an intended SSR of 0.1. Before incubation a known amount of water was added to the dry soils to bring them to field capacity. When

sampling these soils for extraction more than the subscribed 4 grams of soil was sampled to correct for added water in the soil. Despite this, SSR was not exactly 0.1 in almost all cases. An overview of average SSR during P-CaCl<sub>2</sub> measured during incubation is shown in table 5.

Soils 1, 2, 3 and quartz have SSR's that are close to 0.1. Soils 4 and 5 have too low SSR's. Low SSR during 0.01M CaCl<sub>2</sub> extraction lead to increased extracted phosphate from the soil (Van Rotterdam-Los, 2010).

**Table 5: Average SSR during P-CaCl<sub>2</sub> extractions during incubation per soil. Errors show standard deviations.**

soil	SSR
1	0.097 ± 0.015
2	0.10 ± 0.0038
3	0.098 ± 0.0050
4	0.089 ± 0.0048
5	0.090 ± 0.0066
qtz	0.10 ± 0.0081

## 5. Results & Discussion

### 5.1. Incubation

#### P extracted with 0.01M CaCl<sub>2</sub>

Extraction of soil with 0.01M CaCl<sub>2</sub> (P-CaCl<sub>2</sub>) shows a decrease over the duration of the incubation. For example in soil 3 without added P (further referenced to as soil 3nP) P-CaCl<sub>2</sub> decreases from 25-40 μmol P/kg after one day of incubation to around 5 μmol/kg or less after 38 days of incubation (see figure 4). This is a decrease of 80-90% between day 1 and day 38, regardless of temperature.

No initial measurement at the start of the incubation (t=0) has been carried out.

Therefore results of an extraction at 20°C with 0.01M CaCl<sub>2</sub> on dry soil will be used as an estimate for t=0, similar to the approach used by Van Rotterdam-Los (2010) to estimate the initial P concentration in solution for a desorption experiment. These extractions on dry soil have been carried out in another research using these soils. For Fe-coated quartz no value for P-CaCl<sub>2</sub> in dry soil is known, because it was not measured.

For soil 3 P-CaCl<sub>2</sub> from dry soil is reported a value of 19 μmol/kg (see table 3). This is lower than the value measured after one day of incubation: 29 μmol/kg for soil 3nP, measured at 20°C. In nearly all soils P-CaCl<sub>2</sub> from dry soil underestimates available phosphate compared to P-CaCl<sub>2</sub> from moist soil. Measuring P-CaCl<sub>2</sub> from dry soil might thus not give a good indication of available phosphate. For comparison, P-CaCl<sub>2</sub> results after 1 day of incubation are shown in table 6. For all soils except soils 2, higher values have been observed after 1 day incubation compared to P-CaCl<sub>2</sub> from dry soil.

Between day 1 and day 38 the rate of decrease of extracted P is affected by temperature. At 20°C the rate of decrease is much more rapid; P-CaCl<sub>2</sub> reaches values below 5 μmol P/kg already after 14 days of incubation, a decrease of 89%. The soil reaches then a point of equilibrium as P-CaCl<sub>2</sub> decreases no further and stays roughly equal during the remainder of the incubation. At 13°C this equilibrium point, also at 5 μmol P/kg (-93%), is reached after 21 days of incubation. P-CaCl<sub>2</sub> incubated at 4°C decreases slower compared to both incubation at 20°C and 13°C. Only after 38 days of incubation P-CaCl<sub>2</sub> at 4°C reaches a value of 5 μmol P/kg (-81%). As no further

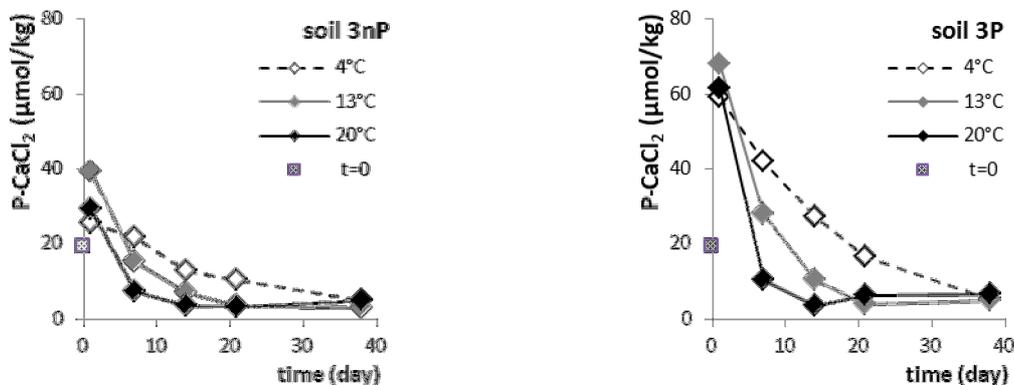


Figure 4: P-CaCl<sub>2</sub> from soil 3 without P addition (3nP) and with P addition (3P) at three temperatures during incubation.

measurements were done, it can only be assumed that soil incubated at 4 °C has reached equilibrium, similar to the soils incubated at 20 °C and 13 °C.

The observed effects observed are most likely caused by microbial activity. Upon 'rewetting' of the dry soil at the start of the incubation inactive micro organisms became active again. The rewetting of soil also causes nutrients, present in the soil, to become soluble again and thus available for uptake. This is the reason of the increased P-CaCl<sub>2</sub> after one day. Uptake of P by micro organisms is relatively high shortly after rewetting. During incubation the P uptake rate slows down until it reaches a situation of apparent equilibrium. Equilibrium between microbial uptake of P and available P, through dissolution and desorption, has been reached.

Inorganic P has been added to soil 3P at the start of incubation (t=0). Compared to soil 3nP, to which no P was added, P-CaCl<sub>2</sub> in soil 3P was about two times higher after one day of incubation, see figure 4. A strong decrease of P-CaCl<sub>2</sub> was observed during 38 days in incubation in soil 3P, similar to soil 3nP. After 38 days virtually nothing of the added P could be measured by CaCl<sub>2</sub>-extraction. P-CaCl<sub>2</sub> after 38 days was nearly equal in soil 3P and soil 3nP. All P added at the start of incubation was adsorbed by the soil. The equilibrium value is the same for both treatments.

Similar to soil 3nP, also in soil 3P temperature had a clear effect on rates of decreasing P-CaCl<sub>2</sub> concentrations. After 14 days P-CaCl<sub>2</sub> at 20 °C reached a value already of less than 5 µmol P/kg, similar to the observations done at soil 3nP. After 21 days soil 3P at 13 °C reaches equilibrium and only after 38 days soil 3P at 4 °C reaches equilibrium. P-CaCl<sub>2</sub> concentrations drop from around 60 µmol P/kg to 5 µmol P/kg, a decrease of 90% or more.

The temperature effect is visible in all soils. Graphs for all soils are shown in Appendix I; all concentrations of P-CaCl<sub>2</sub> during incubation are given in Appendix II. The effects are not in all soils as clear as in soil 3nP. This might be caused by low P-CaCl<sub>2</sub> values (soil 1) or by P saturation (soil 2). Values for P-CaCl<sub>2</sub> in soil 1 are mostly below the detection limit. Any trends in soil 1 are therefore difficult to distinguish and uncertain.

**Table 6: P-CaCl<sub>2</sub> extracted from dry soil compared to P-CaCl<sub>2</sub> after one day of incubation (no P addition and at 20 °C) and to P-CaCl<sub>2</sub> at equilibrium**

Soil		P-CaCl <sub>2</sub> (dry soil) (µmol/kg)	P-CaCl <sub>2</sub> (after 1 day) (µmol/kg)	P-CaCl <sub>2</sub> (equilibrium) (µmol/kg)
1	nP	6	11	2.6 ± 1.1
	P			4.7 ± 1.4
	M			4.0 ± 1.2
2	nP	268	249	144 ± 8.8
3	nP	19	29	3.1 ± 0.26
	P			3.9 ± 0.70
4	nP	23	48	13.7 ± 2.8
	P			13.8 ± 1.4
	M			13.9 ± 3.0
5	nP	58	69	20.0 ± 1.8
	P			15.1 ± 0.67

In Fe-coated quartz with inorganic P (quartzP) added no temperature effects are observed, see figure 5. Also P-CaCl<sub>2</sub> stays pretty much equal throughout the incubation, at a value of about 115-125 μmol P/kg. In this Fe-coated quartz soil almost no micro organisms will be present. Therefore no uptake can take place and logically only small temperature effects are observed. P-CaCl<sub>2</sub> decreases slightly during the incubation. In Fe-coated quartz with P added as manure (quartzM) micro organisms are introduced through manure. As expected in this soil both P-CaCl<sub>2</sub> decrease and temperature effects during incubation are observed. Both effects (decrease of P-CaCl<sub>2</sub> and the temperature effect) point towards P uptake by micro organisms. At 20°C and 13°C P-CaCl<sub>2</sub> decreases from 120 to 60 μmol P/kg and from 145 to 90 μmol P/kg between day 1 and day 38 respectively. At 4°C a strange and unexpected trend of constant to slightly increasing P-CaCl<sub>2</sub> values is observed between day 1 and day 38. The values measured after 7 days at 20°C and after 21 days at 13°C might be false. When these values are left out, the trends at both temperatures show a smooth decreasing curve. Deviations might be caused by the spatial variation of manure.

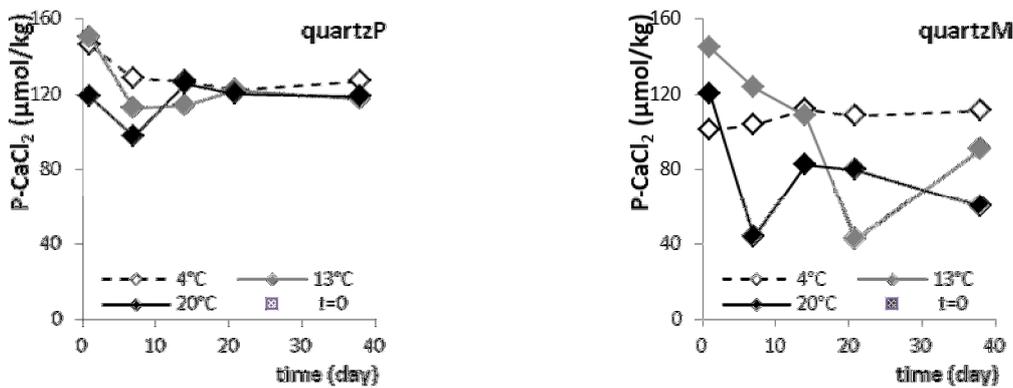


Figure 5: P-CaCl<sub>2</sub> from Fe-coated quartz with inorganic P added (quartzP) and with P added as manure (quartzM) at three temperatures during incubation. No value for t=0 is measured.

Values for the observed equilibrium are shown in table 6. Equilibrium values were calculated as the average of the three lowest values measured across three temperatures per treatment. The standard deviation is calculated with the same previously mentioned lowest values. The average was not calculated by taking the values measured after 38 days, because it was not sure all soils reached the equilibrium yet, which was especially the case for soils incubated at 4°C. In soil 5 significant differences were observed between addition of P and no addition of P. With inorganic P added the equilibrium was lower compared to the treatment where no P was added. In all other soils no significant differences were observed between treatments with no P added, inorganic P added and P added as manure. P addition did not have an effect on P-CaCl<sub>2</sub> after 38 days of incubation.

Differences between P-CaCl<sub>2</sub> extracted from dry soil and P-CaCl<sub>2</sub> extracted from field moist soil after 38 days of incubation are large. From the results shown it can be concluded that P-CaCl<sub>2</sub> extracted from dry soil is higher than P-CaCl<sub>2</sub> extracted after 38 days of incubation. P-CaCl<sub>2</sub> extracted from dry soil is between 1.7 and 6.1 times higher than the equilibrium values, for the soils shown. Therefore the use of P-CaCl<sub>2</sub> extracted

from dry soil is not suitable as an estimate for the initial value for a desorption experiment. Instead the lower values measured after 38 days of incubation will be used.

### P extracted with Olsen's method

During incubation phosphate extracted with Olsen method (P-Olsen) decreases in all soils. Figures showing trends of P-Olsen during the incubation are shown in Appendix XI. The observed decreases are probably an effect of microbial uptake of P, similar to the decreases of P-CaCl<sub>2</sub>. Due to uptake of P from the soil solution the equilibrium between P sorbed to Fe- and Al-oxides and P in solution shifts. Therefore P desorbs from the soil towards soil solution where it can be taken up, this is reflected by lowering of P sorbed to Fe- and Al-oxides, i.e. P-Olsen. This is supported by observed effects in Fe-coated quartz, see figure 6. In Fe-coated quartz where only inorganic P was added a slight decrease of P-Olsen during incubation was observed. In Fe-coated quartz with P added as manure, and thus more micro organisms, the decrease of P-Olsen was much larger. Uptake of P by micro organisms from the soil solution causes P to desorb from the soil and thus a decrease of P-Olsen.

The Olsen-extractions have been carried out at the respective incubation temperature. Though, at lower temperatures than the standard 20°C the Olsen extraction itself is slow as well compared to extraction at 20°C. Therefore results obtained at different extraction temperatures cannot be compared.

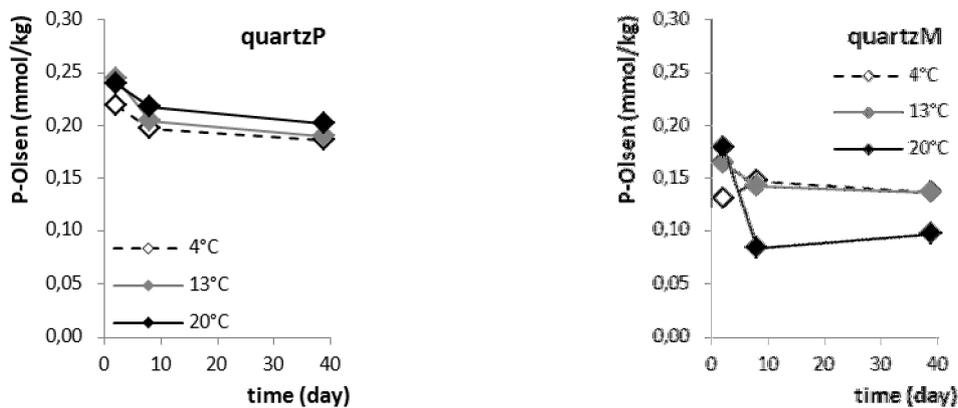


Figure 6: P-Olsen from Fe-coated quartz during incubation. Treatments with inorganic P added (quartz) and P added as manure (quartzM) are shown in the left-hand side and right-hand side graph respectively.

## 5.2. Desorption

### P in solution

During the desorption experiment, after each replacement of Pi papers, small samples were taken of the 0.01M CaCl<sub>2</sub> solution in which P desorption by means of a Pi paper took place. The P concentration in this solution was measured. Only in soil 3 temperature did have a significant effect on P in solution (P<sub>sol</sub>) after 48 hours of desorption with five Pi papers, see figure 7. In both treatments (3nP and 3P) P in solution was significantly higher at 20°C compared to 4°C. In the other soils, except 4nP and 5P, P in solution was higher at 20°C than at 4°C but not significantly.

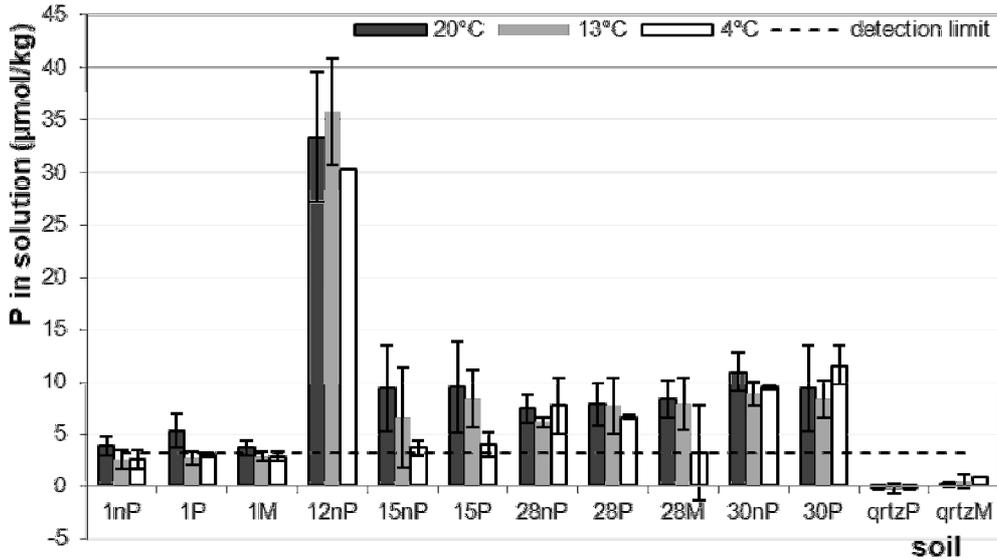


Figure 7: Average P in solution ( $\mu\text{mol P/kg}$ ) after 48 hours of desorption with five Pi papers during two duplicate experiments at three temperatures. Error bars show the standard deviation.

In none of the soils P in solution after 48 hours of desorption was significantly higher in soils to which inorganic P was added compared to soils to which no P was added. Differences between addition of inorganic P and addition of P as manure could not be studied in soil 1 and Fe-coated quartz due to values below the detection limit. In soil 4 differences between addition of inorganic P and P added as manure were not significant.

The concentrations measured in the small samples (1 mL) taken at mid-experiment time steps showed values below the detection limit for almost all soils. This is probably due to strong dilution of the small sample taken. In soil 1 and Fe-coated quartz values measured after 48 hours of desorption were also below the detection limit.

### Comparing P in solution after desorption and P-CaCl<sub>2</sub>

During the incubation experiment, before desorption, extractions with 0.01M CaCl<sub>2</sub> and a 1:10 soil-to-solution-ratio (SSR) were performed. The desorption experiment with Pi

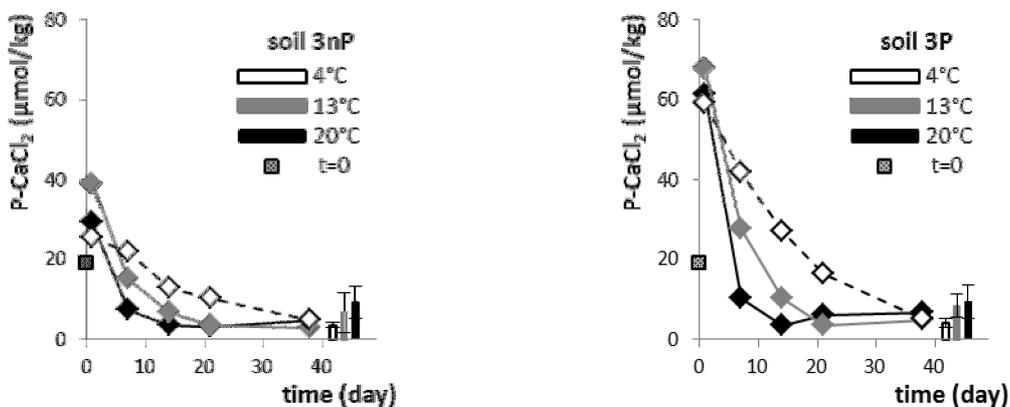


Figure 8: Comparison of P-CaCl<sub>2</sub> during incubation (lines) to average P in solution after 48 hours of desorption (bars) for soil 3, with (3P) and without added P (3nP). Error bars show the standard deviation.

papers was carried out in a 0.01M CaCl<sub>2</sub> solution and a SSR of 1:10. The results of both P-CaCl<sub>2</sub> and P in solution after 48 hours of desorption in soil 3 are shown in figure 8 and table 7 and can be compared.

From figure 8 can be seen that adding a Pi paper to the solution hardly changes the P in solution in soil 3nP. The concentrations of P in solution measured after 48 hours of desorption with five Pi papers do not significantly differ from P-CaCl<sub>2</sub> measured after 38 days of incubation. For soil 3P a very similar result is observed. P in solution in soil 3P does not significantly differ from P in solution in soil 3nP.

Table 7: P-CaCl<sub>2</sub> extracted from dry soil compared to P-CaCl<sub>2</sub> at equilibrium and to P in solution after 48 hours of desorption.

Soil		P-CaCl <sub>2</sub> (dry soil)	P-CaCl <sub>2</sub> (equilibrium)	P in solution after 48 hours of desorption
		( $\mu\text{mol/kg}$ )	( $\mu\text{mol/kg}$ )	( $\mu\text{mol/kg}$ )
1	nP	6	2.6 ± 1.1	3.9 ± 0.93
	P		4.7 ± 1.4	5.4 ± 1.6
	M		4.0 ± 1.2	3.8 ± 0.74
2	nP	268	144 ± 8.8	33 ± 5.4
	P		3.1 ± 0.26	9.3 ± 3.9
3	nP	19	3.9 ± 0.70	9.5 ± 4.2
	P		14 ± 2.8	7.5 ± 1.3
	M		14 ± 1.4	8.2 ± 2.2
4	nP	23	14 ± 3.0	8.6 ± 1.8
	P		20 ± 1.8	11 ± 1.8
	M		15 ± 0.67	9.7 ± 0.22

In soil 2nP a completely different result is observed, see figure 9. The introduction of Pi papers in soil 2nP changed P in solution strongly. While P-CaCl<sub>2</sub> after 38 days of incubation varied between 155 and 195  $\mu\text{mol/kg}$ , P in solution after 48 hours of desorption was only 30-40  $\mu\text{mol/kg}$ . This change of P in solution means the P properties of soil 2 have moved with respect to the adsorption isotherm. The soil has moved to a position in the steeper (left side) part of the isotherm (figure 2). The buffer potential of soil 2 has increased. Relative to the other soils P concentrations in soil 2 after desorption are still high.

In Fe-coated quartz all P in solution has been sorbed by the Pi papers, see figure 9. The goethite on both the quartz and the Pi papers sorbs P very strongly and causes that no P

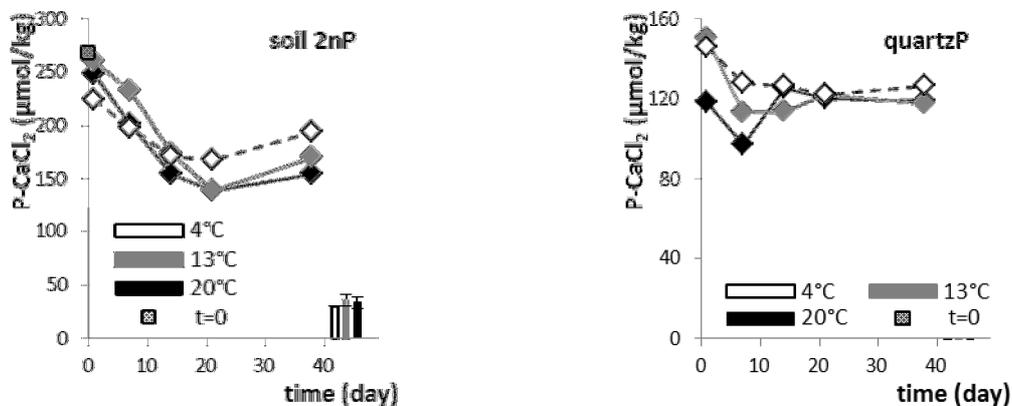


Figure 9: Comparison of P-CaCl<sub>2</sub> during incubation (lines) to average P in solution after 48 hours of desorption (bars) for soil 2, without added P (2nP) and Fe-coated quartz with added inorganic P (quartzP). Error bars show the standard deviation.

is present in solution anymore.

Figures showing comparisons between P-CaCl<sub>2</sub> during incubation and P in solution after desorption for all soils are shown in Appendix III.

### P desorbed from the soil by Pi papers

After five Pi papers had been replaced, cumulative desorbed P by Pi papers ( $Q_{cum}$ ) was highest at 20°C in all soils (see figure 10). Though,  $Q_{cum}$  at 20°C is significantly higher compared to  $Q_{cum}$  at both 4°C and 13°C in only a few soils, namely soils 3nP, 4nP and 4P. In soils 1nP and 3P significant differences were present between  $Q_{cum}$  at 20°C and 4°C, and in soil 5nP a significant difference between 20°C and 13°C was observed.

After five replacements of Pi papers  $Q_{cum}$  at 20°C was significantly higher compared to  $Q_{cum}$  at 13°C and 4°C, see figure 11. In soil 3 with added P (3P)  $Q_{cum}$  increases with

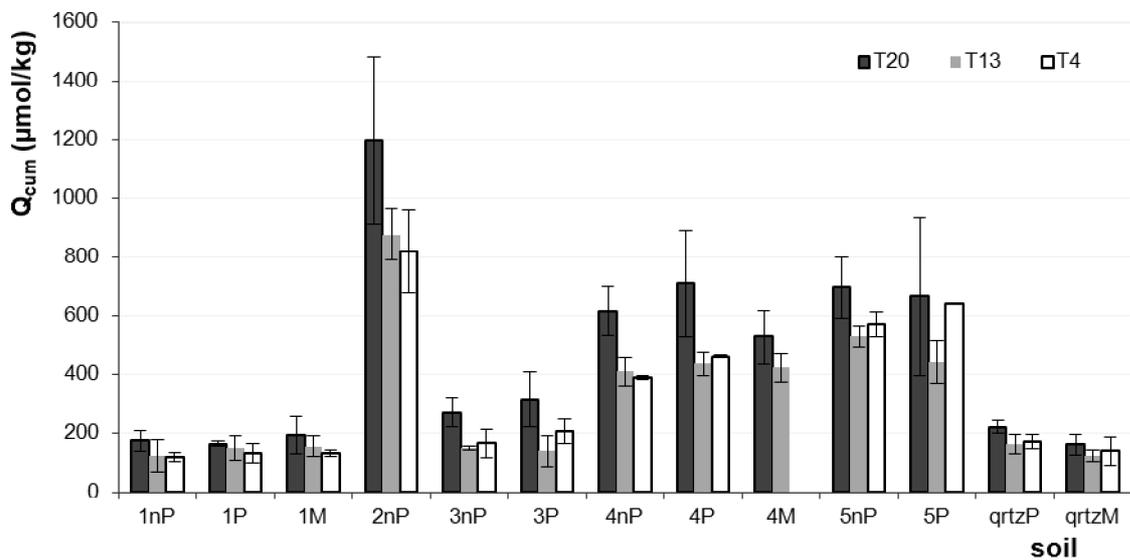


Figure 10: Average cumulative desorbed P by 5 Pi papers (µmol) during two duplicate experiments at three temperatures. Error bars show the standard deviation.

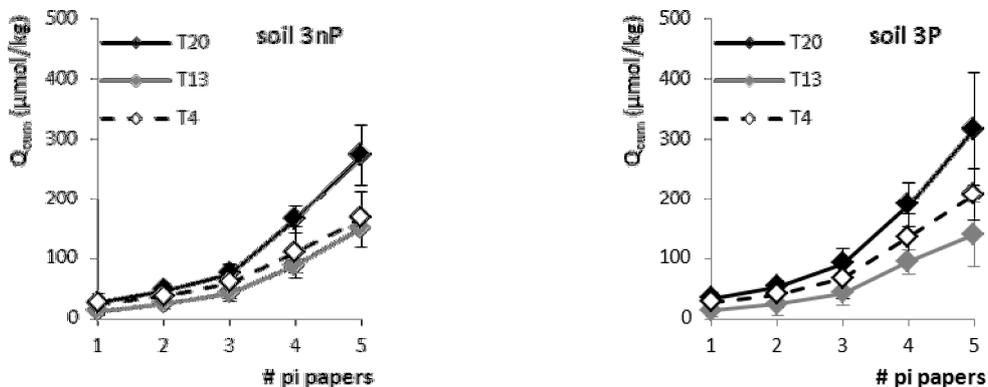


Figure 11: Trends of average cumulative desorbed P by Pi papers (µmol) during two duplicate experiments at three temperatures for soil 3 without added P (3nP) and with added P (3P). Error bars show the standard deviation.

increasing temperatures. These differences are not significant though, since standard deviations increase with increased numbers of replaced pi papers. No significant differences of  $Q_{cum}$  between soils without added P and with added P were observed.

A gradual increase of P sorbed to the Pi papers is observed at the first three Pi papers. After the third Pi papers the figures show straight lines, meaning that equal amounts of P sorbed at the fourth and fifth Pi paper. This indicates that  $CaCl_2$  solution was not at equilibrium with the Pi papers until the third Pi paper was replaced.

Similar results were observed in the other soils. Figures showing cumulative desorbed P by Pi papers of the other soils are listed in Appendix IV. Values corresponding to these results are given in Appendix V.

P desorbed by Fe-coated quartz shows rather different trends, see figure 12. Fe-coated quartz shows a straight line throughout the desorption experiment. At all Pi papers, except the first, equal amounts of P were sorbed. To the first Pi paper between 120 and 170  $\mu\text{mol P/kg}$  was adsorbed, opposed to only 4 to 18  $\mu\text{mol P/kg}$  to the rest of the Pi papers. The large amount of P adsorbed to the first Pi paper is largely due to adsorption of P from solution. After the incubation experiment P- $CaCl_2$  was about 120  $\mu\text{mol P/kg}$  soil in Fe-coated quartz with added inorganic P. The desorption experiment was carried out with 4 grams of Fe-coated quartz. All of the P in solution was adsorbed by the Pi papers plus a small amount of P which was desorbed from Fe-coated quartz.

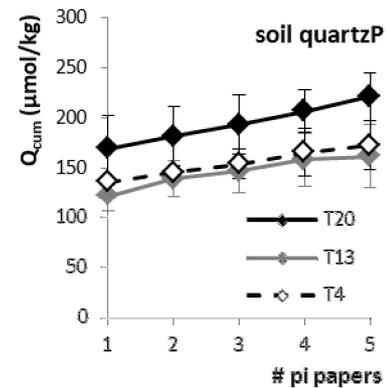


Figure 12: Trends of average cumulative desorbed P by Pi papers during two duplicate experiments at three temperatures for Fe-coated quartz with added P (quartzP). Error bars show the standard deviation.

At the start of the incubation experiment 500  $\mu\text{mol P/kg}$  soil was added. Around 25-34% of this P was extractable with 0.01M  $CaCl_2$  (paragraph 5.1) and was sorbed easily by the first Pi paper. After 48 hours of desorption with five Pi papers 163 to 222  $\mu\text{mol P/kg}$  has been desorbed, which is 35-44% of total P in Fe-coated quartz.

At the end of the incubation experiment PAL was measured for all soils. In table 8 a comparison is shown between cumulative P desorbed by five Pi papers and PAL after 39 days of incubation for all soils at 20°C. For soils 1 to 5 between 7.5% and 14.2% of PAL is removed by desorption with Pi papers. For Fe-coated quartz more P was removed by Pi papers

Table 8: Average cumulative desorbed P by five Pi papers compared to PAL after 39 days of incubation.

Soil		$Q_{cum}$ ( $\mu\text{mol/kg}$ )	PAL ( $\mu\text{mol/kg}$ )	$Q_{cum}/PAL$ (%)
1	nP	174	1570	11.1
	M	164	1930	8.50
	P	194	1860	10.4
2	nP	1198	11000	10.9
	P	317	3420	9.30
3	nP	273	3650	7.50
	P	317	3420	9.30
	M	528	5270	10.0
4	nP	615	5340	11.5
	P	710	5010	14.2
	M	528	5270	10.0
5	nP	697	8560	8.14
	P	666	6390	10.4
	M	161	120	134
quartz	P	222	190	117
	M	161	120	134

than was measured by PAL after incubation. Only 38% of inorganic P added to Fe-coated quartz (quartzP) was measured by PAL.

### 5.3. Buffer Potential

In paragraph 2.3 buffer potential was introduced, which is a means of expressing the effect of P desorption from the soil on P in solution. In order to calculate the buffer potential of the soils, equation 4 will be adapted to:

$$BP = \frac{\Delta Q}{\Delta C} \quad (8)$$

$\Delta C$  is the change in P in solution. This value will be calculated as the difference between P-CaCl<sub>2</sub> after 38 days of incubation and P in solution after desorption with five Pi papers.  $\Delta Q$  is the change in P sorbed to the soil and is thus equal to  $Q_{cum}$  after five Pi papers. In table 9 the calculated buffer potentials are shown per treatment.

In soil 1 many values were below the detection limit. The inaccuracy of these values caused about half of the  $\Delta C$  values to be less than zero, resulting in negative buffer potentials. The lack of changes in P concentrations due to P desorption by pi papers shows that the buffer potential of soil 1 is high. Although  $Q_{cum}$  was largest in soil 2 compared to the other soils, the buffer potential is very low because the lowering of P in solution due to P desorption by pi papers is spectacular. In soil 3P in solution after desorption was often higher than P-CaCl<sub>2</sub> after 38 days of incubation, resulting in  $\Delta C$  being below zero. Contrary to soil 1, this was not caused by values being near or below the detection limit. Thus there can be concluded that  $\Delta C$  was not affected by P desorption by pi papers. This is supported by the standard deviations shown in figure 7 (soil 3nP) which show that P-CaCl<sub>2</sub> after incubation and P in solution after desorption did not differ significantly. The conclusion should be that soil 3 has a large buffer potential. Two of the six treatments of soil 3 show this. Soils 3nP and 3P at 4°C have buffer potentials of 0.58 L/kg, and 0.72 L/kg respectively. Soil 4 shows buffer potentials between 0.11 L/kg and 0.69 L/kg. Soil 5 shows buffer potentials between 0.12 L/kg and 0.43 L/kg. As expected Fe-coated quartz has a very low buffer power. Similar to soil 2 the lowering of P in solution due to P desorption was very large.

Table 9: Calculated buffer potentials per P addition and temperature.

soil		buffer potential (L/kg)		
		4 °C	13 °C	20 °C
1	nP	-0.37	1.04	-1.09
	P	0.54	0.17	-0.39
	M	0.14	0.25	-2.08
2	nP	0.02	0.03	0.04
3	nP	0.58	-0.16	-0.25
	P	0.72	-0.15	-0.45
4	nP	0.11	0.37	0.29
	P	0.11	0.39	0.47
	M	-*	0.69	-*
5	nP	0.15	0.12	0.33
	P	0.13	0.23	0.43
quartz	P	0.01	0.01	0.01
	M	0.01	0.01	0.01

\* no values could be calculated due to missing data caused by broken bottles

In soils 2nP, 4P, 5P and quartzP and quartzM an increasing buffer potential with increasing temperatures was observed.

For comparison buffer potentials are recalculated. Instead of P-CaCl<sub>2</sub> after 38 days of incubation, P-CaCl<sub>2</sub> extracted from dry soil is used to calculate ΔC. The recalculated buffer potentials are shown in table 10.

The recalculated values should be compared with the buffer potentials from the respective soils with no added P (nP) and incubated and desorbed at 20 °C. There can be concluded that with this method the calculated buffer potentials are lower. Buffer potentials using P-CaCl<sub>2</sub> after incubation are up to a factor 5.5 higher compared to P-CaCl<sub>2</sub> using dry soil. P-CaCl<sub>2</sub> from dry soil is not a good means to measure soil buffer potentials. Buffer potentials calculated from P-CaCl<sub>2</sub> from dry soil are too low and indicate more available P than measured after 38 days in the incubation experiment.

**Table 10: Buffer potentials calculated using P-CaCl<sub>2</sub> extracted from dry soil, P in solution at 20 °C and Q<sub>cum</sub> at 20 °C.**

soil	recalculated buffer potential (L/kg)
1	0.33
2	0.02
3	0.11
4	0.16
5	0.06

## 6. Conclusions

P-CaCl<sub>2</sub> measured during incubation at field moist levels gradually reaches equilibrium. Temperature affects the rate with which P-CaCl<sub>2</sub> decreases towards the equilibrium during incubation. At 20 °C the equilibrium was reached after two to three weeks of incubation, while at 4 °C the equilibrium was reached at the end of the incubation (38 days). Decreasing amounts of P-CaCl<sub>2</sub>, decreasing amounts of P sorbed to Fe- and Al-oxides and the temperature effects indicate that the observed equilibrium is the result of microbial activity during incubation

Cumulative P desorbed from soil by Pi papers is highest at 20 °C in all soils, although only in a very few soils significantly. Temperature does not have a clear effect on P in solution after desorption. In some soils concentrations were at or below the detection limit, which made it difficult to draw conclusions. In a few soils large differences were observed between P-CaCl<sub>2</sub> after incubation and P in solution after desorption.

These differences can be expressed by a soil property called buffer potential. For five treatments which consisted of different soils and P additions, the buffer potential increased with increasing temperatures. Calculation of the buffer potential was hampered in case of several soils by values near or below the detection limit.

Often soil extractions are performed on dry soil. Large discrepancies exist between P-CaCl<sub>2</sub> measured with dry soil and P-CaCl<sub>2</sub> measured after one day of incubation or after prolonged incubation allowing the soil to reach equilibrium. Therefore using P-CaCl<sub>2</sub> is not a good means to calculate soil buffer potentials.

From the results of this research can be concluded that additions of P, either inorganic or organic, did not have significant effects on amounts of P desorbed by 5 Pi papers from the soils, neither on P concentrations in solution after desorption. Most of the added P will be adsorbed and will be made available on the long term by desorption. This means that the buffer potentials of these soils are fairly high. Regarding P properties, the soils are still at the steep part of the adsorption isotherm. Additions of P did not change this position much, and thus had not much effect on the directly available P. On the long term though, it surely added to available P.



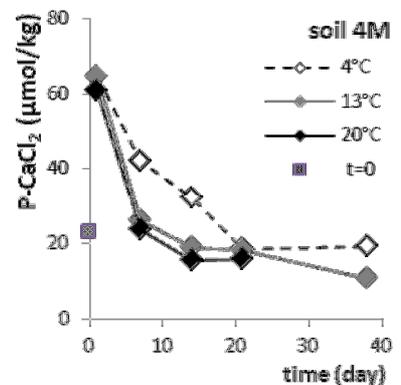
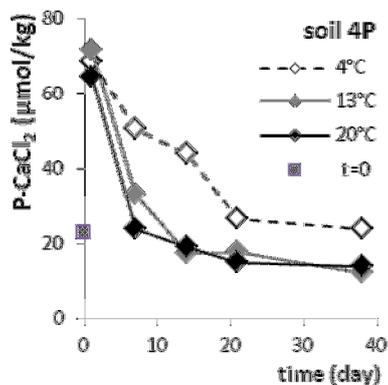
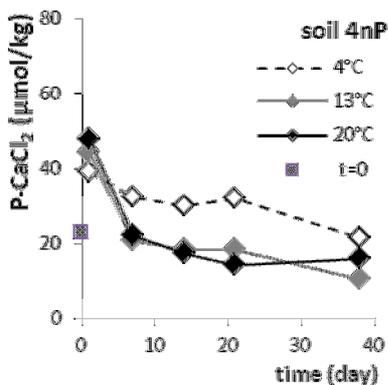
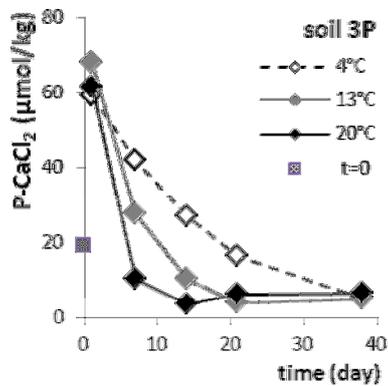
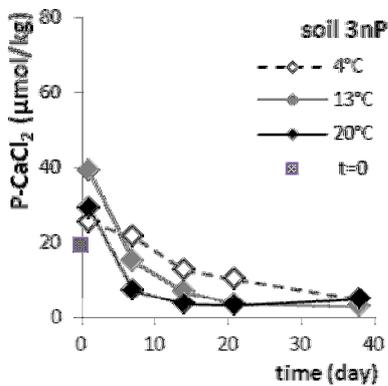
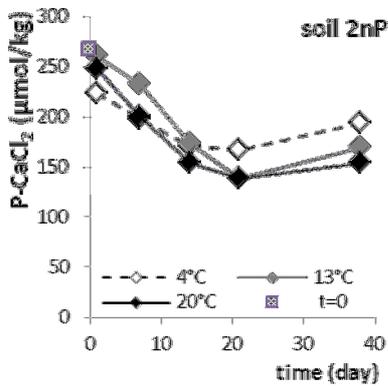
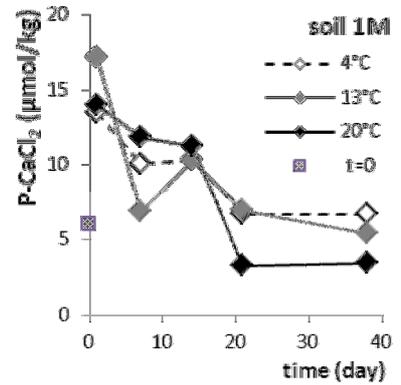
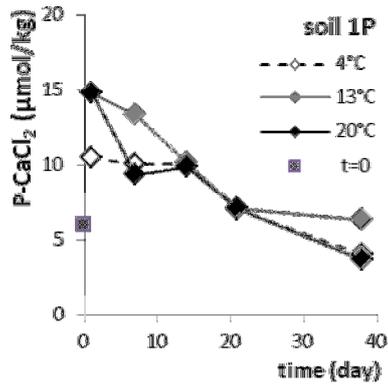
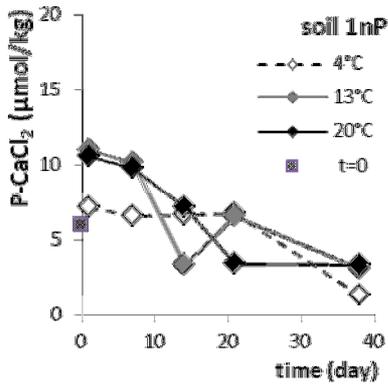
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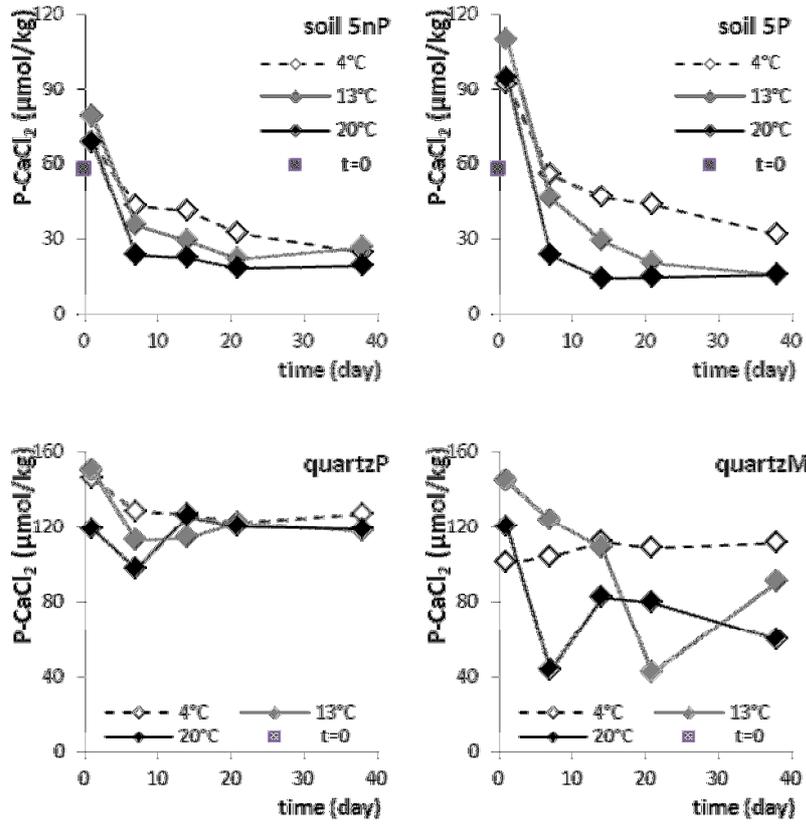
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## Appendices

Appendix I. Trends of P-CaCl<sub>2</sub> during incubation



Temperature and wetting effects on phosphate sorption by soil



**Appendix II. Values of P-CaCl<sub>2</sub> during incubation (μmol/kg)**

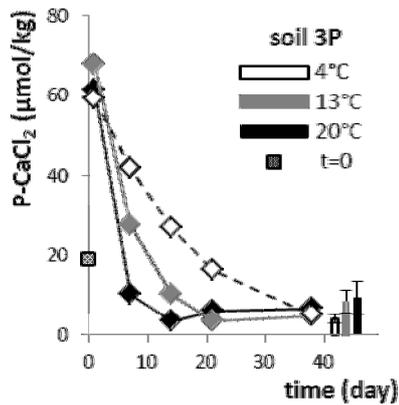
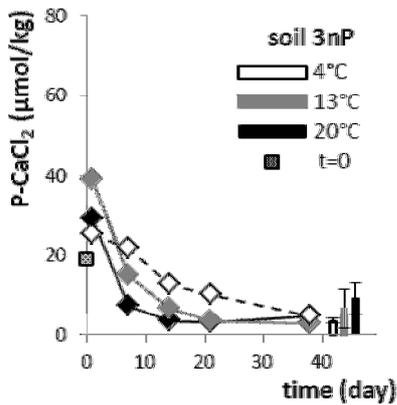
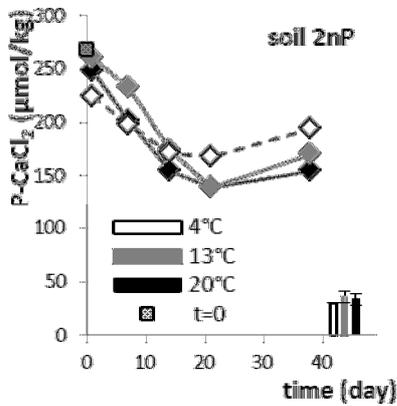
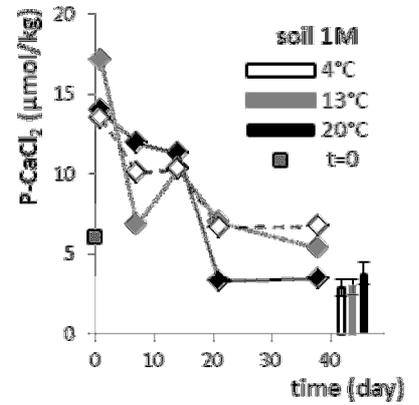
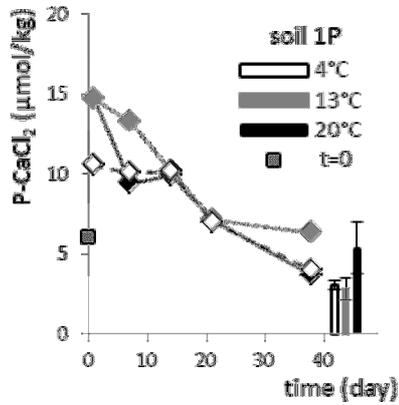
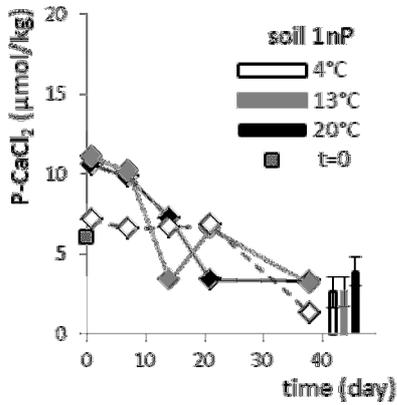
soil	temperature (°C)	time (day)				
		1	7	14	21	38
1nP	4	7.14	6.55	6.67	6.79	1.31
	13	11.0	10.2	3.36	6.59	3.09
	20	10.6	9.84	7.21	3.39	3.30
1P	4	10.5	10.1	10.2	6.96	4.03
	13	14.8	13.3	10.2	7.10	6.29
	20	14.7	9.41	9.89	7.12	3.71
1M	4	13.5	10.1	10.4	6.67	6.70
	13	17.1	6.81	10.4	6.93	5.38
	20	14.0	11.9	11.3	3.26	3.45
2nP	4	225	198	172	168	194
	13	261	233	174	139	170
	20	249	201	154	139	155
3nP	4	25.4	21.7	12.7	10.3	4.82
	13	39.2	15.1	6.75	3.38	2.86
	20	29.1	7.25	3.36	3.09	4.95
3P	4	59.1	41.9	27.0	16.5	5.20
	13	67.9	27.5	10.1	3.62	4.69
	20	61.4	10.1	3.38	6.21	6.65
4nP	4	39.4	32.4	30.0	32.2	21.5
	13	44.5	20.7	18.5	18.3	10.6
	20	47.7	22.1	17.3	14.5	16.0
4P	4	68.7	50.7	44.1	26.6	24.0
	13	71.7	33.3	17.6	17.9	12.3
	20	64.5	24.1	19.1	15.0	14.0
4M	4	64.4	42.1	32.0	18.4	19.0
	13	64.5	25.8	18.9	18.2	10.5
	20	60.8	23.5	15.4	15.9	
5nP	4	68.6	42.8	40.8	32.2	24.7
	13	78.9	35.5	29.0	21.9	26.9
	20	68.8	23.5	22.7	18.4	19.6
5P	4	92.3	55.9	46.5	43.7	31.8
	13	110	46.2	29.0	20.7	16.1
	20	94.9	23.7	14.4	15.1	15.7
qtzP	4	146	128	127	122	127
	13	150	113	114	122	118
	20	119	97.5	126	120	119
qtzM	4	101	104	112	109	111
	13	145	124	109	42.7	90.6
	20	120	43.9	82.4	79.7	60.4

\* broken bottle

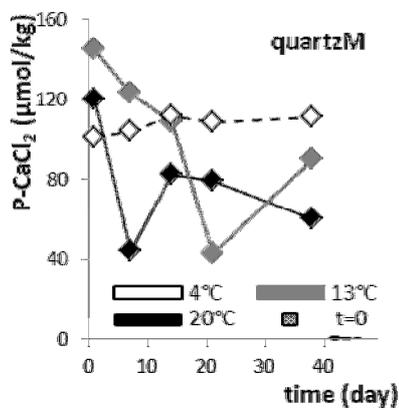
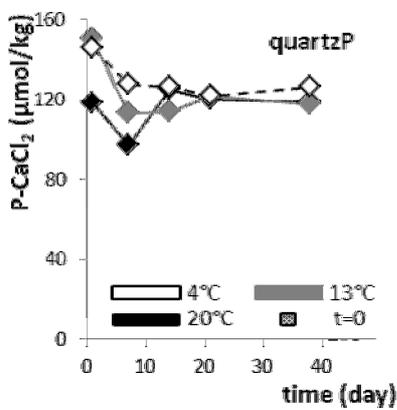
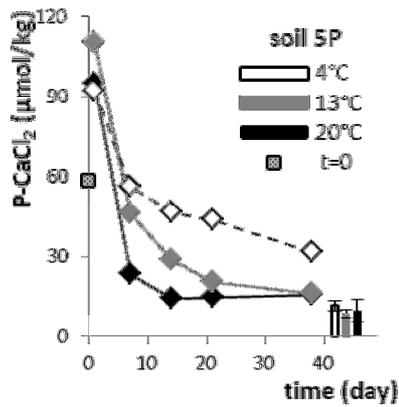
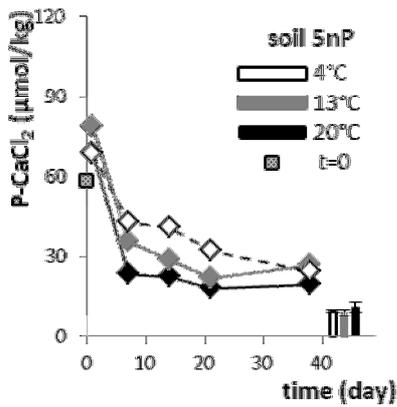
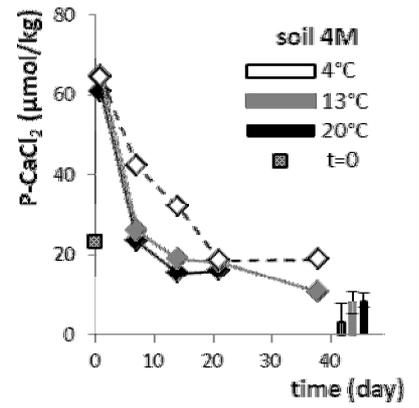
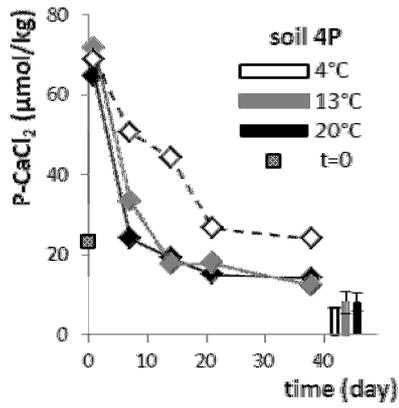
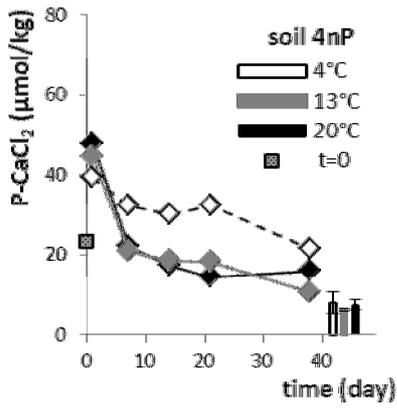


**Appendix III. P-CaCl<sub>2</sub> during incubation compared to average P in solution after desorption**

Error bars show the standard deviation

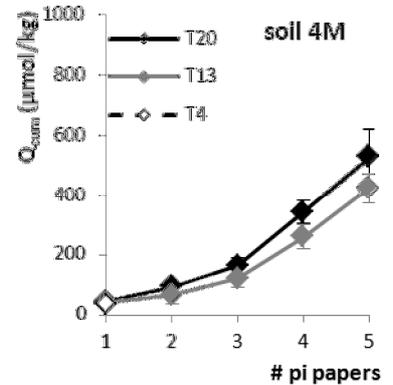
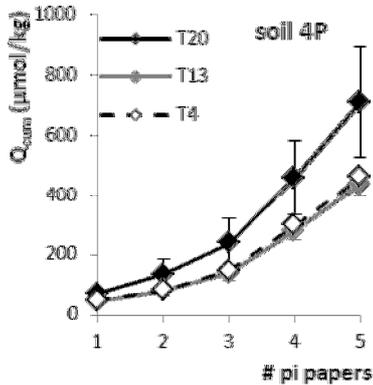
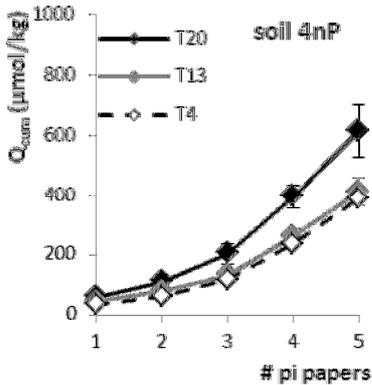
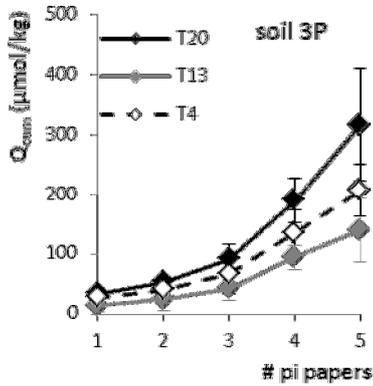
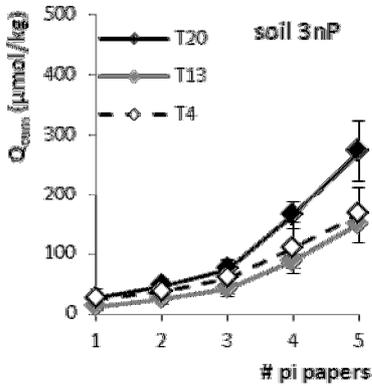
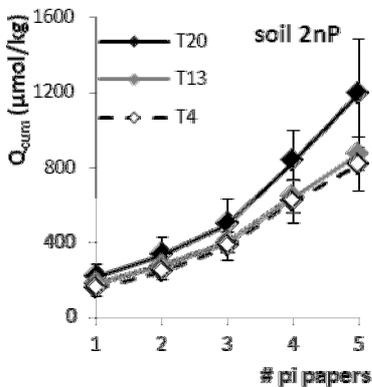
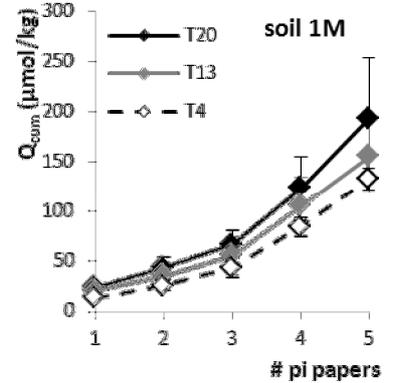
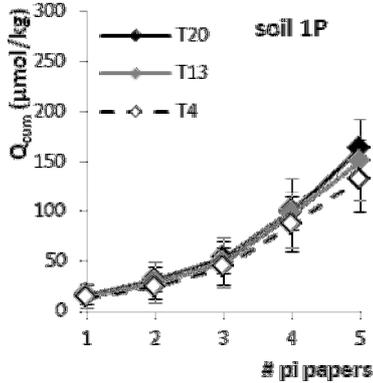
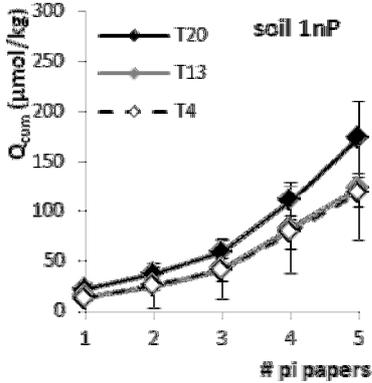


Temperature and wetting effects on phosphate sorption by soil

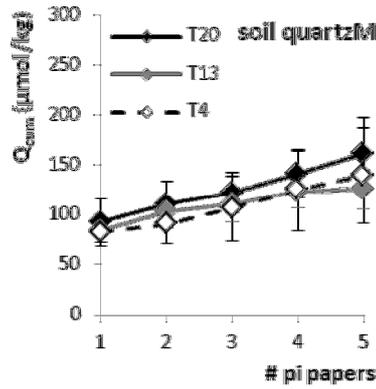
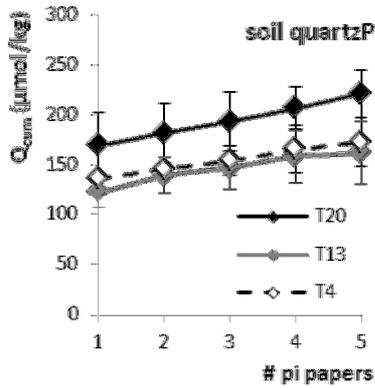
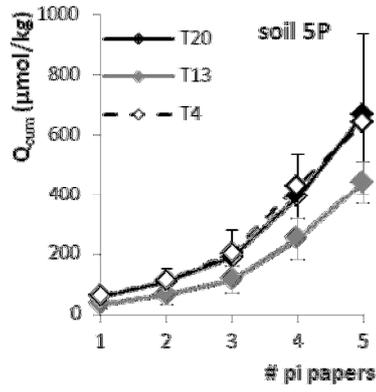
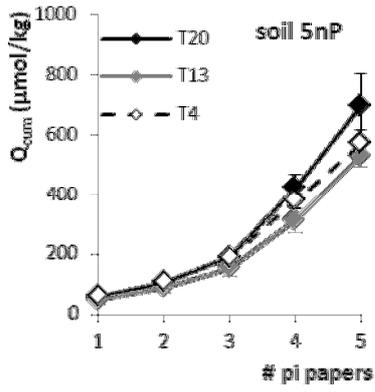


**Appendix IV. Trends of average cumulative desorbed P ( $Q_{cum}$ )**

Error bars show the standard deviation.



## Temperature and wetting effects on phosphate sorption by soil



**Appendix V. Values of average desorbed P and average cumulative P**

Format: average ± standard deviation

Unit: µmol P/kg soil

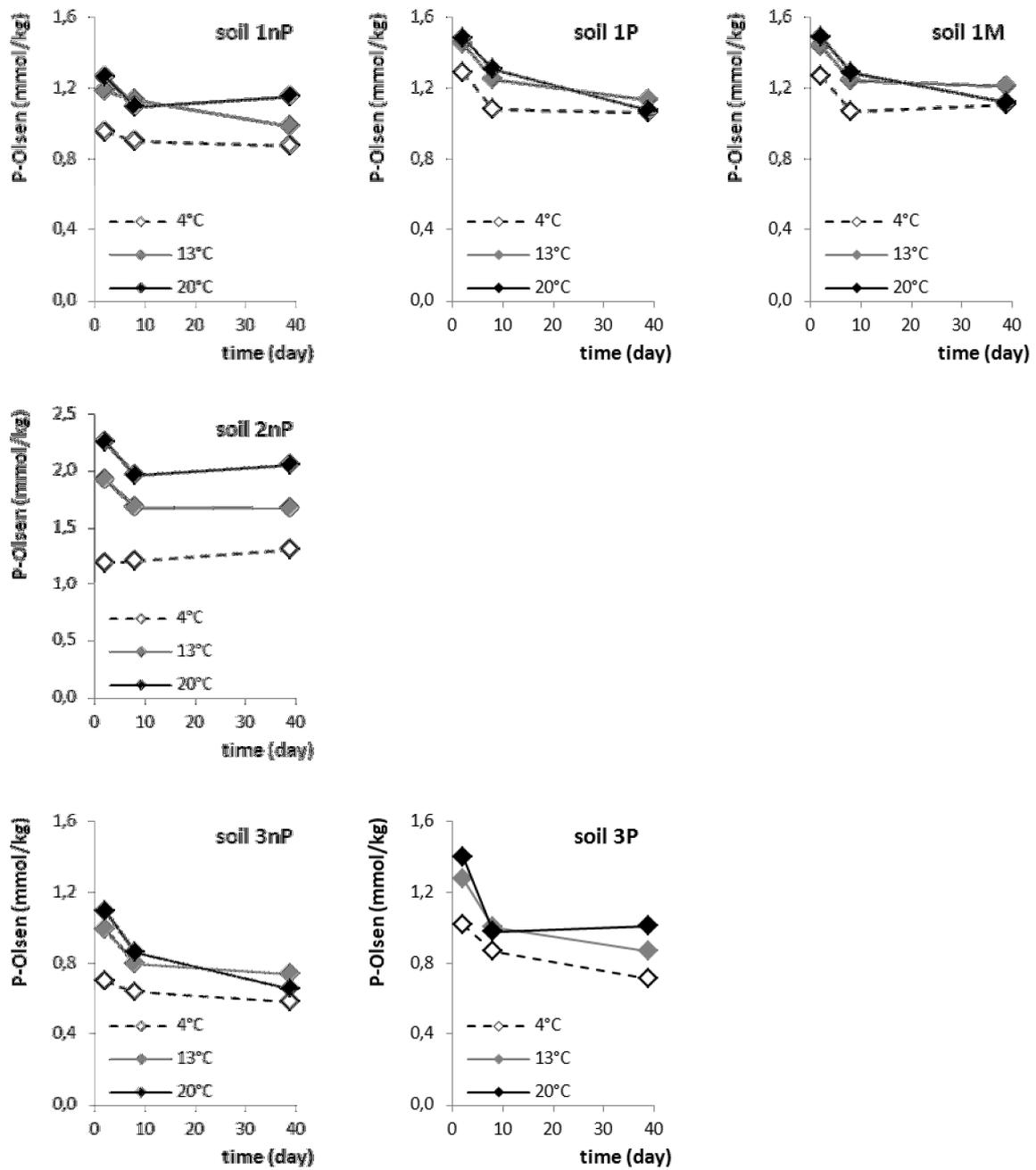
soil	temp (°C)	# pi papers					cumulative by 5 pi papers
		1	2	3	4	5	
1nP	4	13,2 ± 2,77	13,4 ± 2,65	15,3 ± 5,80	37,4 ± 5,28	40,6 ± 1,56	120 ± 14,9
	13	14,91 ± 14,1	10,7 ± 8,22	16,5 ± 7,05	40,1 ± 14,9	42,0 ± 8,28	124 ± 52,6
	20	22,0 ± 5,91	15,5 ± 1,28	22,1 ± 5,79	51,2 ± 6,26	63,5 ± 16,7	174 ± 35,9
1P	4	13,8 ± 6,20	11,1 ± 6,81	19,9 ± 6,02	42,1 ± 8,72	46,4 ± 6,02	133 ± 33,8
	13	15,3 ± 12,4	13,8 ± 8,00	19,8 ± 4,88	49,6 ± 10,1	53,1 ± 5,85	152 ± 41,2
	20	16,6 ± 9,59	15,0 ± 2,65	22,1 ± 3,57	46,9 ± 3,91	63,5 ± 11,9	164 ± 7,79
1M	4	13,9 ± 1,78	11,9 ± 3,45	17,9 ± 5,17	40,9 ± 0,47	48,5 ± 1,40	133 ± 11,3
	13	20,6 ± 6,16	15,0 ± 7,42	20,2 ± 5,6	49,9 ± 10,7	50,0 ± 6,24	156 ± 36,1
	20	24,2 ± 3,50	19,5 ± 7,79	23,0 ± 2,79	57,2 ± 18,1	69,6 ± 28,9	194 ± 61,1
2nP	4	156 ± 42,7	86,9 ± 0,27	137 ± 32,5	241 ± 44,6	200 ± 22,4	821 ± 142
	13	181 ± 42,3	95,4 ± 6,46	123 ± 6,56	248 ± 34,2	230 ± 2,46	877 ± 87,1
	20	217 ± 63,9	116 ± 27,9	164 ± 41,1	338 ± 31,1	361 ± 122	1198 ± 286
3nP	4	25,2 ± 15,6	11,6 ± 5,30	22,4 ± 9,44	50,6 ± 11,4	55,8 ± 5,45	166 ± 47,2
	13	12,8 ± 6,56	12,1 ± 3,22	17,9 ± 0,133	45,4 ± 1,92	61,8 ± 5,02	150 ± 6,5
	20	26,8 ± 2,59	19,4 ± 3,97	28,4 ± 9,27	90,2 ± 7,13	108 ± 26,6	273 ± 49,5
3P	4	27,7 ± 16,3	12,8 ± 6,70	26,4 ± 9,95	68,4 ± 5,47	71,2 ± 4,81	206 ± 43,2
	13	13,7 ± 10,2	10,0 ± 7,27	18,5 ± 3,13	52,1 ± 0,070	45,4 ± 32,0	140 ± 52,4
	20	34,0 ± 6,18	19,4 ± 4,32	38,4 ± 13,5	97,5 ± 13,7	127 ± 55,1	317 ± 92,8
4nP	4	33,7 ± 0,64	26,8 ± 6,65	55,6 ± 1,15	120 ± 0,707	153 ± 4,02	389 ± 8,17
	13	43,3 ± 5,42	34,4 ± 11,5	54,6 ± 2,73	129 ± 8,47	148 ± 19,0	410 ± 47,1
	20	59,5 ± 7,17	50,1 ± 16,0	93,2 ± 12,0	192 ± 3,97	220 ± 47,4	615 ± 86,5
4P	4	48,1 ± 1,44	32,3 ± 9,44	65,49 ± 5,31	152 ± 5,55	162 ± 4,05	460 ± 4,20
	13	42,9 ± 8,9	36,4 ± 9,14	59,2 ± 8,46	141 ± 4,03	157 ± 8,21	437 ± 38,8
	20	69,6 ± 13,0	63,6 ± 40,4	104 ± 30,7	221 ± 40,4	251 ± 59,6	710 ± 184
4M	4	32,5 ± 2,37	10,96	30,5	66,8	68,7	
	13	40,5 ± 11,2	24,1 ± 17,9	56,6 ± 1,60	138 ± 8,97	164 ± 8,24	424 ± 48,0
	20	44,0 ± 1,12	49,7 ± 16,6	70,7 ± 7,96	178 ± 12,9	185 ± 53,2	528 ± 91,8
5nP	4	59,5 ± 7,24	45,4 ± 13,4	84,1 ± 0,10	189 ± 6,55	193 ± 16,9	572 ± 44,0
	13	48,1 ± 14,5	41,4 ± 5,16	62,6 ± 4,89	160 ± 14,6	217 ± 1,53	529 ± 37,6
	20	55,9 ± 6,86	48,0 ± 8,91	84,1 ± 23,0	233 ± 18,9	275 ± 61,8	697 ± 106

## Temperature and wetting effects on phosphate sorption by soil

soil	temp (°C)	# pi papers					cumulative by 5 pi papers
		1	2	3	4	5	
5P	4	60,0 ± 1,55	50,5 ± 3,4	92,2 ± 9,74	225 ± 4,55	214 ± 10,4	641 ± 0,244
	13	33,2 ± 11,7	31,2 ± 20,6	49,8 ± 11,8	136 ± 25,2	192 ± 0,87	441 ± 70,1
	20	58,3 ± 19,1	49,8 ± 26,4	81,0 ± 43,6	203 ± 55,6	275 ± 124	666 ± 268
qtzP	4	136 ± 2,79	9,22 ± 3,85	8,80 ± 7,86	11,5 ± 9,33	7,04 ± 0,768	173 ± 24,6
	13	123 ± 16,1	17,5 ± 1,93	7,41 ± 3,64	11,4 ± 4,67	3,71 ± 5,24	163 ± 31,6
	20	170 ± 33,3	12,1 ± 3,68	11,2 ± 0,151	13,6 ± 8,01	14,5 ± 1,96	222 ± 23,4
qtzM	4	82,1 ± 9,41	8,47 ± 9,71	15,8 ± 13,3	18,5 ± 8,04	14,8 ± 7,34	140 ± 47,8
	13	83,9 ± 12,1	18,8 ± 1,04	7,93 ± 4,27	12,4 ± 0,95	2,58 ± 3,64	126 ± 20,1
	20	92,8 ± 23,7	17,7 ± 0,032	11,6 ± 2,80	18,9 ± 2,88	20,4 ± 12,1	161 ± 35,9

\* broken bottle

Appendix VI. Trends of P-Olsen during incubation



## Temperature and wetting effects on phosphate sorption by soil

