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THE POTENTIAL  
OF SOILS  
TO SUPPLY  
**PHOSPHORUS**  
AND **POTASSIUM**  
PROCESSES AND PREDICTIONS

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*Debby van Rotterdam - Los*

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**THE POTENTIAL OF SOILS TO SUPPLY  
PHOSPHORUS AND POTASSIUM**  
*processes and predictions*

**A.M.D. van Rotterdam- Los**

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PHOSPHORUS AND POTASSIUM**  
*processes and predictions*

**A.M.D. van Rotterdam- Los**

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## ABSTRACT

Nutrient management in agriculture faces many and diverse challenges. These include the excessive use of fertilizer in many first world countries, the depletion of nutrients from soils in parts of sub-Saharan Africa, the increasing demand for agricultural products, and the diminishing, non-renewable phosphorus reserves. One step in the process of optimizing nutrient management is predicting the nutrient status of a soil accurately. As a basis for this optimization this thesis describes a methodology to improve the choice of soil tests and interpretation of the results for phosphorus (P) and potassium (K).

The first step to derive this methodology for P, was to understand the dominant soil processes involved in the translocation of P from soil particles to the plant and the corresponding reaction rates. Experiments were performed wherein the continuous removal of P by a crop was mimicked using an artificial sink. In the experimental setup as used in our study, P uptake by the sink was found to be slower than the release rate by the soil. The desorption rate of the soil was high enough to buffer the P concentration in solution ( $C_p$ ) to a degree that kept this concentration in equilibrium with the soil during the experiment. As a result of this equilibrium, the soil P supply could be described using a soil specific sorption isotherm, relating  $C_p$  and the reversibly adsorbed P ( $Q_p$ ) replenishing  $C_p$ .

In the second step the gained insight, was used to derive a combination of standard soil tests that accurately predict the soil P supply potential. It was found that a minimum of two parameters is needed; a measure for the reversibly adsorbed P ( $Q_p$ , e.g. P-Olsen, PAL) and a measure for  $C_p$  (e.g. P-CaCl<sub>2</sub>). The measure for  $C_p$  is an indication of the rate with which P can be removed from the soil. The ratio  $Q_p$  over  $C_p$  is an indication of the capacity of the soil to buffer  $C_p$ . To increase the accuracy of this prediction a measure for the capacity of the soil to adsorb P, i.e. reactive surface area (e.g. Fe<sub>ox</sub> and Al<sub>ox</sub>) of the soil must also be taken into account. In addition, to be able to extend the prediction to an amount of P that exceeds the amount of reversibly adsorbed P, a measure for the total amount of P must be included (e.g. P<sub>ox</sub>).

In the third step it was verified that the same processes that determine the soil P supply potential to an artificial sink are applicable for a growing crop. In addition, it was found that the combination of soil tests that was needed to describe P supply to an artificial sink can also be used to predict the supply of P to a growing crop.

In order to gain a more comprehensive understanding and prediction of the dynamic soil K supply potential a pot experiment was conducted in which the changes in different soil K fractions during uptake by growing grass were studied. To predict the availability of soil K in the short term, a measure for readily exchangeable K ( $K_{exch}$ ) appears to be sufficient for all soils. For longer timescales a distinction must be made between soils that can and cannot buffer this  $K_{exch}$ . For the soils in this study a distinction based on soil texture is sufficient. In sandy soils  $K_{exch}$  was not buffered. In the silt and clay soils  $K_{exch}$  was buffered. The absolute contribution of this buffering will depend on the type of crop but an estimation may be based on the ratio of a measure for the amount of K buffering  $K_{exch}$  over a measure for  $K_{exch}$ .

The research described in this thesis has resulted in a well founded and generally applicable methodology for predicting the potential of soils to supply the nutrients P and K that can be implemented in routine soil laboratories. Results from field trials in the Netherlands show that predicting P uptake by grass is much more accurate when based on the methodology derived in this study compared to the current approach. It thus offers a basis for optimizing nutrient management strategies.

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*Chapter 1*

**GENERAL INTRODUCTION**

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## **BACKGROUND**

Traditionally nutrient management in agriculture focuses on supplying enough nutrients to a soil to attain a soil nutrient status that is sufficient to obtain optimal growth and quality of a crop. In parts of Europe and North America fertilizer strategies have increased the nutrient status of soils to levels that are excessive in terms of requirement for crops and (potentially) pose a threat to surface- and groundwater (Breeuwsma et al. 1995; Sharpley et al. 1994; Sims et al. 1998). In sharp contrast with the build up of nutrients in soils in Europe and N-America, soil fertility in Sub-Saharan Africa has been depleted by agricultural practice (Sanchez 2002). In addition, there is an increasing strain on agricultural production due to the combination of a growing world population, increasing demand for meat and for biofuels (Khan and Hanjra 2009). As a consequence this increases the demand for the diminishing, non-renewable P reserves (Cordell et al. 2009). All these issues make it increasingly important to optimize nutrient management. One step in this process is to predict the nutrient status, and especially P status, of a soil accurately.

In agricultural practice nutrient management strategies are, a.o. based on fertilizer recommendations. These are derived from the nutrient status of the soil and crop characteristics. The nutrient status of the soil is assessed in routine soil laboratories and is generally performed using a soil test, which must meet the criteria of being cheap, fast, applicable to a wide range of soil types, and be low labor intensive. The choice of soil test may vary widely between countries and laboratories (Allen et al. 1994 ; Neyroud and Lischer 2003). Translation to fertilizer recommendations is based on extensive pot experiments and- or field trials in which a soil test result is coupled to crop response. These experiments often took place several decades ago on representative soils using representative crops. Despite the considerable variation in the original correlations these have subsequently been extrapolated to more general relationships. A single soil test approximates a certain fraction of the nutrient of interest in the soil at a certain moment in time. Although this static approach to the soil's fertility greatly oversimplifies the dynamic processes that determine the actual soil nutrient supply potential, it is very widely used due to its simplicity and cost- labor effectiveness. Trying to approximate the dynamic processes is much more accurate but is also more laborious to execute and complicated to understand. It would be a step forward in optimizing nutrient management if routine soil laboratories could accurately predict the potential of a soil to supply nutrients. This can be achieved by incorporating the processes that determine the soil nutrient supply potential in the choice of soil tests and interpretation of the results.

## **SITUATION IN THE NETHERLANDS**

As described by Kuypers (1968), farms in the Netherlands originally produced both food and livestock, in which the primary function of the cattle was to produce manure for the land. Farmers practiced crop rotation and applied a fallow year in which the soil would be intensively fertilized. In the course of the 19<sup>th</sup> century farmers on clay soils managed to avoid the fallow year by increasing the addition of green manure during crop intervals and using more effective ways of extinguishing weed. Artificial fertilizer was introduced around 1880-1890. Its use gradually became common practice and apart from considerable increases in crop yields, the fallow year disappeared completely and it became possible to cultivate less fertile soils by adding fertilizer. After the second world war, agricultural production intensified due to stimulation by the Common Agricultural Practice (CAP) incentive of the EU, the relatively low prices of inorganic fertilizers and concentrates, and the structural implementation of machinery (Van der Stelt 2007; van Keulen et al. 2000). On the previously unfertile sandy soils, agriculture shifted towards intensive livestock farming. Import of cheap fodder resulted in manure production often exceeding crop requirements (Breeuwsma et al.

1995). Since then, these sandy soils in the flat lowland area of The Netherlands and Belgium have received the highest national phosphorus (P) surpluses within Europe resulting in a P build-up in the soil profile and subsequent P leaching (De Smet et al. 1996). In 1956 (Van der Paauw) already found that leaching from soils well supplied with P could be very high. Also on clay soils with a large P fixing capacity large P losses may occur through cracks in the soil in summer and through water flow shortly after P application (Chardon and Schoumans 2007).

Since the adverse effects of excessive fertilization became clear the EU has imposed a number of policies and measures to limit the environmental burden of agricultural production (Oenema 2004). An example is the EU water framework directive that requires all inland and coastal waters in EU member states to reach a good ecological status by 2015. As discharges from industry and wastewater treatment plants have sharply decreased from the 1980's onwards the discharges of N and P from agriculture have become increasingly important (Oenema et al. 2005). In 2000 the average P application in the Netherlands was 125 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup> but in 2009 the Dutch government restricted this to 100 kg ha<sup>-1</sup> on grassland and 85 kg ha<sup>-1</sup> on arable land. It is intended to further restrict this application to approximate removal by the crop towards 2015. Within the agricultural community this has led to doubts as to whether optimum crop yields can still be obtained and an adequate soil fertility status maintained. As a result, P is becoming increasingly important in the overall nutrient management strategies. For environmental purposes, there is increasing demand for identifying agricultural areas for which the contribution to the overall loading of adjacent water bodies is relatively large, i.e. critical source areas (Chardon and Van Faassen 1999). As P is commonly the limiting nutrient in surface- and groundwater the identification of these critical areas is mainly based on P. Thus, to prevent further uploading of P in soils and to meet crop P requirement with minimum amounts of P fertilizer application, it is increasingly important to accurately determine the soil P supply potential. With the increasing awareness of the adverse effects of excessive fertilizer application, a more accurate prediction of the supply potential of the other main nutrients (nitrogen (N) and potassium (K)) is also desirable.

## **PREDICTING SOIL NUTRIENT SUPPLY POTENTIAL**

The transfer of nutrients from soil to crop roots or to the surrounding environment is based on a number of interacting processes that involve the removal of the nutrient from the soil solution, the transfer of the nutrient through the soil solution, and the release of the nutrient from the soil matrix to the soil solution. To determine the overall transfer of nutrients from soil to roots, several mechanistic models have been developed that combine supply, transport, and uptake (Barber 1995; Jungk and Claassen 1997; Tinker and Nye 2000). The distribution of the nutrients over the soil and soil solution and the relative importance of supply, transport, and uptake on the overall transfer from soil to root vary per nutrient. For P and K uptake exceeds the amount transported to the root through the water flux (mass flow) because the concentration in solution is too low to supply the crop with sufficient nutrients (Barber et al. 1963). This results in a concentration gradient from the root to the bulk soil triggering the additional release of P and K from the soil matrix. For P and K this diffusive transport is more important than transport by mass flow. For P and K it is therefore important to understand the distribution between the soil solid phase and the soil solution.

In 1860 it was already recognized that the uptake of nutrients by plants takes place through the soil solution phase. In terms of soil fertility Mulder (1860) formulated that not the total amount of a specific nutrient present in the soil is important for plant growth but the availability of this nutrient. He defined available as the amount of nutrient that can be dissolved. Since then the

basic concept has been developed that the soil P supply potential is a function of P intensity, P quantity and soil P buffer power. In which intensity ( $I_p$ ) represents the P concentration in solution, P quantity ( $Q_p$ ) is the reversibly adsorbed P and the buffer power (BP) is the capacity of the soil to maintain  $I_p$  upon addition or removal of P from the soil. As suggested by Schofield (1955), and affirmed as such by Barrow (1967), the availability of soil P to growing plants can be described by the combination of  $I_p$  and BP. BP is also the dominant factor determining the diffusivity in soils (Jungk and Claassen 1997). Since then numerous studies have described the uptake of P by a growing plant using a combination of  $I_p$ ,  $Q_p$  and BP e.g. (Bolland et al. 1994; Holford 1988; Holford 1997; Holford and Mattingly 1979). Several studies find that crop response is solely related to a measure for P intensity, but that to predict fertilizer requirement the soil P buffer power must be included (Dear et al. 1992; Moody et al. 1988; Quintero et al. 2003).

In contrast to the concept that the soil P supply potential can be approximated by a combination of  $I_p$ ,  $Q_p$  and BP, routine soil laboratories generally assess this supply potential using a single soil test per nutrient, possibly incorporating other general soil characteristics when translating the soil test result into a fertilizer recommendation. In the past this rough approximation was sufficient as the excessive use of fertilizer was only considered to have economical consequences. The environmental implications were not generally acknowledged. The fundamental problem in determining the nutrient status of a soil using a single soil test is that it is only to a very limited degree based on the dynamic processes that determine the soil P supply potential (Mengel 1982). A single soil test may be an indicator of either P intensity or P quantity, or a complicated mixture of both factors but cannot be an indicator of the relationship between intensity and quantity, i.e. the soil's buffer power (Holford and Mattingly 1976). Incorporation of the BP however is not straightforward as it can be derived from the change in  $Q_p$  and the change in  $I_p$  upon addition or removal of P to the soil after a short equilibration time (Beckett and White 1964).

## SOIL TESTS IN THE NETHERLANDS

Together with the realization that crop yields increase with fertilizer application, farmers wanted to know the nutrient status of their soil (Vermeulen 1970). To meet this demand routine soil laboratories were established. In the Netherlands soil testing started in 1927 by investigating the calcium carbonate and humus content in sandy soil in the first commercial soil testing laboratory now known as "Bedrijfs laboratorium voor grond en gewas". In 1930 this was followed by P and K measurements. From 1937 onwards clay soils were also investigated. Once acquainted with soil investigation the farmers desired more extensive information. Eventually, this resulted in an extensive soil testing program in which the soil nutrient status was assessed using 11 different soil chemical extraction methods (Van Erp 2002).

When specific soil tests for P were first developed, soil P supply potential was known to be a function of  $I_p$ ,  $Q_p$  and BP (Van der Paauw et al. 1971). Based on this knowledge DeVries et al. (1937, as described in Van der Paauw et al. 1971) assessed the P status by using a combination of  $Q_p$  and  $I_p$ . In which  $Q_p$  was approximated using a weak acid extraction and  $I_p$  was approximated using a water extraction. Instead of using this concept as a whole, extensive field- and pot experiments performed around 1930 – 1940 resulted in the decision to use a single extraction measure approximating  $I_p$  for arable land and an extraction measure approximating  $Q_p$  for grassland (Van der Paauw et al. 1971). For grassland the soil test for P was initially a citric acid extraction. In 1958 this method was replaced by an acid ammonium lactate extraction (PAL) for analytical- technical reasons. This replacement was not founded on a recalibration based on field experiments but the translation was based on the graphical relations between the citric acid and the AL extraction taking OM and

lime content into account (Ehlert and Van Wijk 1998). In 1968 a water extraction (Pw) replaced the PAL method in peat- and sandy soils, and in 1970 the Pw method was introduced for all arable soils. This introduction was based on closer relationships between Pw values and crop response compared to PAL. Furthermore, Pw values were found to be independent of other soil characteristics as OM- and calcium carbonate content, phosphate fixing capacity, textural class, pH, and geographic origin. For soils rich in Fe ( $\text{Fe}_2\text{O}_3 > 10\%$ ) the relationship was less pronounced (Henkens 1973; Paauw et al. 1971).

For potassium (K) the translation of soil test result to fertilizer recommendation is not straightforward. The soil test value is used to calculate a K-number. This calculation depends on soil type and land use and may include organic matter content, clay content, and pH which has been derived by improving the explained variance in the relationship between crop response and soil test result. Subsequently, the recommended amount of fertilizer again depends on soil type and land use, and again organic matter content and clay content may be included in the calculation.

At present soil testing laboratories are keen to implement a multi-nutrient extraction method for economical and environmental (less waste) reasons. The 0.01M  $\text{CaCl}_2$  extraction has been suggested to approximate the bioavailable fraction of nutrients in soil (Houba et al. 1996; Houba and Novozamsky 1998). The soil is extracted with a solution which has more or less the same ionic strength as the average salt concentration in the soil solution of agricultural soils. Various nutrients and metals can be measured in the extract that allowing the consideration of relationships between them during interpretation of the data. The relationship between crop response and P- $\text{CaCl}_2$  has been described in several different studies and the explained variance is quite variable (e.g.  $r^2$  between P- $\text{CaCl}_2$  and ryegrass lies between 0.43 and 0.81 in 3 studies considering a wide range of soils; (Arrobas et al. 1995; Humphreys et al. 2001; Simonis and Setatou 1996). Although the  $\text{CaCl}_2$  extraction method may be useful as a basis, it is not sufficient for deriving a generally applicable fertilizer recommendation.

## **THIS THESIS**

### ***Main objectives***

To be able to meet the environmental constraints that are being set to nutrient management in agriculture, there is a growing need to increase the accuracy with which the potential of a soil to supply nutrients can be predicted. There is a gap between the extensive knowledge on nutrient availability in the scientific community and the simplistic and empirical approach generally adopted by routine soil testing laboratories. In practice however, nutrient management strategies are based on the latter. The aim of the research presented in this thesis is to establish an accurate prediction of the potential of a soil to supply nutrients based on the dynamic processes that determine this supply. To be widely applicable in nutrient management strategies this prediction should preferably be based on a (combination) of standard soil tests that can be measured routinely in soil laboratories. Because of the increasing importance of P in nutrient management strategies we mainly focus on this nutrient. A similar approach chosen for P is also applied for K.

### ***Outline***

In chapter 2 the soil P supply potential is studied from a soil chemical point of view. This is approached in laboratory experiments by simplifying the system by mimicking the removal of P by plants using an artificial sink in the form of Fe-oxide coated filter paper strips (Pi-paper). Because P transfer from soil to an artificial sink is sensitive to the chosen experimental setup, chapter

2 consists of a methodological study to understand the processes that occur in the Pi-paper-solution-soil system. Transfer of P from soil to the added strong sorbent is not instantaneous but is a function of the desorption characteristics of the soil and the adsorption characteristics of the sorbent. After establishing the characteristics of the Pi-paper artificial sink, insight in the transfer from soil to Pi-paper is gained by comparing the experimentally determined P transfer with P transfer that is modeled. The model calculations are based on the adsorption characteristics of the Pi-paper and the measured P concentration in solution.

In chapter 3 a methodology is derived for predicting the soil P supply potential using a combination of soil tests. This was approached by modeling the soil P desorption and the decrease in the P concentration in solution during continuous desorption to an artificial P sink. The model is based on the Langmuir sorption isotherm in which the two soil specific parameters are calculated *a priori* based on data derived from diverse standard soil tests.

In order to ultimately translate the gained insights into fertilizer recommendations, the processes that determine the soil P supply potential to an artificial sink and the combination of soil tests that is needed to describe and predict this supply potential are verified in pot experiments with grass in chapter 4. For this purpose, the initial and change in P concentration in the soil solution is measured in situ in combination with the change in P-CaCl<sub>2</sub>, reversibly adsorbed P, and P uptake during the intensive growth of ryegrass. In addition, an assessment is made of when the soil P supply potential is sufficient to meet crop demand and when it becomes limiting.

Chapter 5 aims at gaining a more comprehensive understanding and prediction of the dynamic soil K supply potential. This is approached by studying the release of soil K in a dilution experiment and during K uptake by a growing crop. For this purpose, the initial and change in K concentration in the soil solution is monitored in combination with the change in K-CaCl<sub>2</sub>, exchangeable K, non-exchangeable K, and K uptake during the intensive growth of ryegrass in a pot experiment in the greenhouse. Insight in the change in these soil fractions and availability to the grass is used to assess a possible combination of standard soil tests that would be practically feasible in to measure on a routine basis and together give a good description of the soil K supply potential for plant uptake.

In chapter 6 the results of this research are discussed and the implications of the results are put into a broader perspective. Both the dynamic processes that determine the soil nutrient supply potential and the use of soil tests in predicting this supply potential will be discussed, including the potential and implementation of the methodologies that have been derived in our study. The implications of our results for fertilizer recommendations in the Netherlands are discussed as well as the implications for nutrient management in general.



*Chapter 2*

**PHOSPHORUS REMOVAL FROM SOIL  
USING FE OXIDE-IMPREGNATED PAPER:  
PROCESSES AND APPLICATIONS**

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## ABSTRACT

Fe oxide-impregnated paper (Pi-paper) is used as an artificial phosphorus (P) sink to study P availability in soils and runoff. Pi-papers were introduced as they would mimic P uptake by plant roots by decreasing the P concentration in solution to negligibly low levels and thus enhancing P desorption from the soils solid phase. The rate of transfer of P from soil to Pi-paper would thus be limited by the soil P desorption rate. The maximum desorption rate is indeed achieved when the original method is used in which (at least) four Pi-papers per gram soil are placed in a soil suspension (soil- solution ratio of  $0.025 \text{ kg L}^{-1}$ ). In several studies this method has however been adapted depending on the research question of interest without investigating the effect of this adaptation to the processes involved in the transfer of P from soil to Pi-paper. The aim of this study is to improve our understanding of the processes that occur in the Pi-paper – solution – soil system and so to extend the theoretical basis of this method. Insight is gained in these processes by comparing the experimentally determined P transfer from soil to Pi-paper with P transfer that is modeled based on the measured P concentration in solution and the (kinetic) Langmuir equation of the Pi-paper. P adsorption by a Pi-paper from standard solutions is not instantaneous but can be described with a kinetic Langmuir equation that is a characteristic of the Pi-paper. Over time, the Pi-paper reaches equilibrium with the solution, and the kinetic Langmuir equation can be rewritten to a Langmuir equation. Regardless if there is equilibrium or not, P adsorption to the Pi-paper is a function of the P concentration in solution.

By adding Pi-paper to a soil suspension, a re-distribution of P takes place between the reactive surface area of the soil and the new reactive surface area of the Pi-paper that initially contains no adsorbed phosphate. As opposed to the original method where the desorption rate was limiting the overall P transfer, the adsorption rate to the Pi-paper is limiting when one Pi-paper per gram soil is placed in a soil suspension (soil- solution ratio of  $0.1 \text{ kg L}^{-1}$ ). In this situation, the P concentration in solution is found to be in equilibrium with the soil's solid phase. With increasing contact time ( $> \sim 24$  hours) the whole system approaches equilibrium. With each successive Pi-paper newly added, more P is removed from the soil system and the decrease of P in solution will be governed by the soil P desorption isotherm.

Varying the number of Pi-papers and the soil to solution ratio thus has a large effect on the transfer rate between soil and Pi-paper and if either the soil desorption rate, the Pi-paper adsorption rate or a combination limits this transfer rate. With increased insight in the P transfer between soil and Pi-paper sink, it becomes possible to tailor the experimental design to help answer the research question one is interested in.

## INTRODUCTION

The availability of soil Phosphorus (P) in terms of soil fertility is and has been studied extensively. Most commonly, soil P availability is approximated using one of the numerous (P selective) extraction methods which result in the size of a certain soil P fraction at a certain point in time. To meet the increasing demand to combine soil fertility and environmental goals, there is a growing need to extend this knowledge with the availability of soil P over time. For this reason, several methods have been proposed which establish a continuous desorption of soil P over time. The simplest and most commonly used method is shaking a certain amount of soil with a P free solution at varying soil-solution ratios (Barrow, 1979; Barrow and Shaw, 1979) or by percolating soil columns with a P free solution (Sawhney, 1977). Both methods result in relatively small amounts of P desorbed as the P concentration in solution is generally low, and the amount of P replenishing this P concentration is thus also relatively low (Freese et al., 1995). Desorption can be enhanced by adding materials that bind P, i.e. artificial P sinks. Similar to plant roots and algal uptake these artificial sinks adsorb P from solution and thus result in an additional replenishment of P from the solid phase to the solution. Amer et al. (1955) first introduced a P sink in the form of anion-exchange resin. This resin is however not specific for P and difficult to separate from the soil. A methodological improvement was found by using anion exchange resin membranes (Cooperband and Logan, 1994). Van der Zee et al. (1987) proposed to use Fe oxide impregnated filter paper (Pi-paper) which was found to sorb P selectively and strongly. For the assessment of long-term P desorption kinetics, dialysis membrane tubes filled with hydrous ferric oxide have been proposed by Freese et al. (1995).

The advantages of the Pi-paper method, in which Pi-papers are used to remove P from a soil suspension, is the simplicity and accuracy of the method (Menon et al., 1989), an easy preparation of the Pi-papers, applicability to all soil types, and that the Pi-paper is a strong P sink (Van der Zee et al., 1987). The exact nature and properties of the Pi-papers depend on the procedure of preparation (Chardon et al., 1996; Lin et al., 1991). A drawback of the method is the adhesion of soil particles to the Pi-paper that may lead to an overestimation of desorbable P (Lookman et al., 1995; Perrott and Wise, 1993). This has however been proposed to be minimized by using filter paper with small pore size, placing the paper in a fixed position (Myers et al., 1995), by using a background electrolyte, e.g. 0.01M CaCl<sub>2</sub>, by removing the soil particles using an air-brush (Chardon et al., 1996), and by placing the paper in a protective mesh (Chardon, 2008).

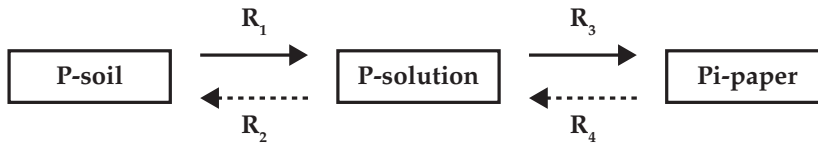
In numerous studies the Pi method has been used to study both plant availability and water quality. Most commonly Pi-papers are placed in a soil suspension (Van der Zee et al., 1987) or agricultural runoff (Sharpley, 1993) for a certain period of time (usually 16-20 hours). Good results have been found when this value is correlated with plant P uptake (Lin et al., 1991; Menon et al., 1997; Menon et al., 1989; Sharpley, 1991) or with algal available P (Sharpley, 1993). The Pi-paper has also been used to study P diffusion by embedding a Pi-paper in a soil column or in-situ for a certain period of time (Menon et al., 1990; Saarela, 1992). This P diffusion parameter was correlated with the grain yield of barley and oats (Saarela, 1992) and with rice dry matter yield grown in flooded conditions (Shekiffu and Semoka, 2007).

These examples show the potential in possible parameters that may be obtained using the Pi-paper method; from soil P desorption rate constant used to model P transport from soil to groundwater (Van der Zee et al., 1987) to diffusion rate coefficients to study P availability to plants (Saarela, 1992). These different parameters may be obtained by simply adapting the experimental setup by changing the ratio between soil, solution, and number of Pi-papers. By varying the contact time between soil and Pi-papers, the P release over time may also be studied (McDowell and Sharpley,

2003). The method may thus offer a large flexibility in answering the broad range in P related questions concerning soil fertility and environmental issues which comprehend a large variation in the amount of P removed from the soil system over a wide range in time. The aim of this paper is to improve our understanding of the processes that occur in the soil – solution – Pi-paper system and so to extend the theoretical basis for the use of this method.

## THEORY AND DATA INTERPRETATION

The iron (hydr)oxide on the Pi-paper is able to strongly bind phosphate. Placing a Pi-paper in a soil suspension will thus result in a re-distribution of P between the reactive surface area of the soil and the reactive surface area introduced by the Pi-paper. This transfer of P from soil to the added strong sorbent is not instantaneous but will be a function of either the desorption kinetics of the soil, the adsorption kinetics of the Pi-paper or a combination of both. It is necessary to know which of these regimes determines the transfer of P from soil to sorbent and how this changes as a function of the experimental setup, in order to be able to design an experiment that can fulfill its intended purpose.



**Figure 1:** shows a schematic presentation of a system containing soil, solution and a Pi-paper. The arrows indicate the adsorption and desorption processes with corresponding rates ( $R$ )

Figure 1 shows a schematic presentation of a system containing soil, solution and a Pi-paper. The arrows indicate the adsorption and desorption processes with corresponding rates ( $R$ ). When the transfer of P from soil to Pi-paper sorbent is limited by the desorption kinetics of the soil ( $R_1$ ), the P concentration in solution should be low enough to suppress the backward adsorption reaction rate ( $R_2$ ) to the extent that it becomes negligible compared to the desorption reaction rate ( $R_1$ ). In contrast, when the transfer is limited by the adsorption kinetics of the Pi-paper ( $R_3$ ), the P concentration in solution can be in continuous equilibrium with the soil while the sink (Pi-paper) is not yet in equilibrium with the solution. Under these conditions, the P concentration in solution is a function of the P desorption isotherm of the soil, which is also the case when full equilibrium between soil, solution, and Pi-paper is established. The adsorption kinetics of P by the Pi-paper ( $R_3$ ) may be derived from a series of adsorption experiments using standard solutions (without soil) containing a range of P concentrations while measuring the concentration as a function of time. Due to the similarity between the reactive surface area of the soil and the Pi-paper, adsorption from a standard P solution to a Pi-paper can be described using the same simple non-electrostatic kinetic Langmuir equation as has been used before to describe P desorption kinetics from a soil (Van der Zee et al., 1987). The net rate of adsorption  $dQ/dt$  is the difference between the rates of adsorption ( $R_3$ ) and desorption ( $R_4$ ) and can be given as:

**Equation 1**

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

in which  $C$  is the concentration in solution ( $\mu\text{mol L}^{-1}$ ),  $Q_{\max}$  is the adsorption maximum of the Pi-paper ( $\mu\text{mol}$ ),  $Q$  is the amount of P bound to the Pi-paper at a certain moment in time ( $\mu\text{mol}$ ),  $k_a$  is the adsorption rate constant ( $\text{L } \mu\text{mol}^{-1} \text{ hr}^{-1}$ ), and  $k_d$  the desorption rate constant ( $\text{hr}^{-1}$ ). The parameters  $k_a$ ,  $k_d$ , and  $Q_{\max}$  are characteristics of the Pi-paper under the chosen standard conditions of the experiment and are determined by fitting the equation to the data. When equilibrium is attained ( $dQ/dt = 0$ ), this equation results in the Langmuir equation with a binding constant  $K = k_a/k_d$ . The kinetic Langmuir equation (eq [1]) is a rather simple approach of the kinetic behavior because actually the Fe-oxide surface is charged and therefore P adsorption is determined by electrostatics (Hiemstra and Van Riemsdijk, 1996) which are not considered in the present approach. Although the experiments with soil and Pi-paper are also done in background electrolyte solution (0.01 M  $\text{CaCl}_2$ ), the conditions for systems with and without soil can differ (e.g. presence of DOC) and this may affect the adsorption behavior, as will be discussed later in the paper.

The experimental setup will determine whether the desorption rate from the soil ( $R_1$ ) or the adsorption rate to the Pi-paper ( $R_3$ ) or a combination of both are rate-limiting in the overall P transfer. A system in which the soil desorption rate ( $R_1$ ) controls the transfer of P from soil to Pi-paper will occur at a low ratio of soil over Pi-paper because this will lead to very low P solution concentrations. This is supposedly achieved provided at least four (Van der Zee et al. 1987) or five (Lin et al., 1991; Van der Zee et al., 1987) Pi-papers are used per gram soil in a system with a soil to solution ratio (SSR) of 1g per 40 mL or 0.025  $\text{kg L}^{-1}$ . In such an experimental setup, the maximum desorption is achieved in a minimum amount of time. The disadvantage of this setup is that the amount of desorbed P is relatively large compared to for instance the P loss to runoff water or P uptake by a crop over a growing season. Moreover, no information is obtained on the change in P release over time in such experiments. With the intention to study P loss to runoff water, McDowell and Sharpley (2003) adapted the method by increasing the SSR from 0.025 to 0.2  $\text{kg L}^{-1}$  and replacing one Pi-paper strip after different time intervals to investigate P release over time. Decreasing the number of Pi-papers per gram soil and increasing the SSR may result in a situation in which P transfer is no longer solely limited by soil P desorption kinetics ( $R_1 \gg R_2$ ) but may be limited by the combination of desorption kinetics of the soil ( $R_1$ ) and adsorption kinetics of the Pi-paper ( $R_3$ ) or even solely by the Pi-paper adsorption kinetics, i.e. the rate of adsorption of P to the Pi-paper may become smaller than the rate of desorption from the soil ( $R_3 < R_1$ ).

The P transfer from soil to the Pi-paper can be modeled using the calibrated kinetic Langmuir equation (eq.[1]), if the P concentration in the soil solution during extraction is known (Fig.1). A specific experiment can be designed in which a Pi-paper is placed in a soil suspension and is replaced by a new Pi-paper at certain time intervals. Each time the Pi-paper is replaced, the solution concentration as well as the amount of P bound by the Pi-paper is measured. Based on the experimentally measured P concentrations in solution, the amount of P adsorbed by the paper can be calculated by numerical integration of the kinetic Langmuir equation. The modeling result can be compared with the experimental data. In the calculation, the concentration is assumed to decrease linearly from the concentration as measured when the Pi-paper is placed in the soil suspension to the concentration when it is removed. For the first data point, the initial P concentration in

solution at zero extraction time ( $C_{ini}$ ) is set equal to the equilibrium P concentration in a 0.01M  $CaCl_2$  extract.

## **MATERIALS AND METHODS**

### ***Preparation Pi-papers***

Pi-papers were prepared by impregnating filter paper (Whatman number 50) with Fe by fluently moving the filter paper through an  $FeCl_3$  solution (0.4M) for 30 seconds and air dried for 1 hour. Subsequently, the papers were fluently moved through a 5% ammonia solution for 30 seconds, rinsed well by immersing the paper several times in demineralized water (Van der Zee et al., 1987). After air drying, the paper is cut into strips of two by ten centimeters.

### ***P adsorption to a Pi-paper from a standard solution***

P uptake kinetics of the Pi-paper is investigated by placing a Pi-paper in a 0.01 M  $CaCl_2$  solution with P concentration of 0, 1.3, 6.5, 13, 26, or 52  $\mu mol L^{-1}$  and shaken end- over- end at 6 RPM. The concentration range is chosen to resemble the concentration range in Dutch agricultural soils in the presence of a Pi-paper. The experiment is performed using a volume of both 250 and 500 mL. A Pi-paper is placed in each of the 12 containers and after 1, 5, 24, and 96 hours, the P concentration in solution is measured. The amount of P adsorbed by the Pi-paper is calculated from the decrease in P concentration in solution corrected for the removal of P from the system during sampling.

### ***P adsorption to a Pi-paper from a soil suspension***

Soil samples were collected from the plough layer (0-20 cm) of ten agricultural sites in the Netherlands in 1994 (Van Erp, 2002). The sites were chosen to represent a wide range of soil types and P-status. The clay content was determined using the sieve and pipet technique (NEN 5753, (Houba et al., 1997), the  $CaCO_3$  content using the volumetric method (NEN 5757, (Houba et al., 1997), and the soil organic carbon content (SOC) using the sulfochromic oxidation (Walinga et al., 1992). The pH-KCl was determined in a 1: 5 (volume fraction) suspension of 1 M potassium chloride solution (ISO 10390). The P-status of the soils was characterized using 0.01M  $CaCl_2$  with a soil solution ratio of 0.10  $kg L^{-1}$  (P- $CaCl_2$ ) (Houba and Temminghoff, 1999; Houba et al., 2000). For the desorption experiment one strip of Pi-paper was brought in contact with a suspension of 4 g soil and 40 mL 0.01M  $CaCl_2$ . The Pi-paper strip was fixed in a holder that was attached to the top of a 50 mL polypropylene tube (greiner) and the tube was gently shaken continuously end- over- end at 6 RPM. Continuous desorption was ensured by replacing the Pi-paper after 1, 2, 4, 8, 24, 48, 78, 145, 221, 337, and 481 hours (11 times in ~ 20 days). Each experiment was done in duplicate. To minimize the effect of the adhesion of soil particles filter paper with small pores (Whatman 50) was used and the paper was thoroughly rinsed with distilled water to remove adhered soil particles. The P was desorbed by shaking the paper for two hours with 20 mL 0.2M  $H_2SO_4$  solution. At each time step, a sample (1 mL) of the solution was taken after centrifugation and the P-concentration in solution was measured.

To check what determines the P concentration in solution during desorption an additional experiment was performed in which the P concentration was measured twice: once in the solution directly after the Pi-paper was removed and once when the soil was allowed to (re-)equilibrate with the soil for half an hour after the Pi-paper was removed. For this experiment, executed in duplicate, a Pi-paper was placed in the soil suspension of the ten soils (4 gram soil in 40 mL 0.01M  $CaCl_2$ ) for either 1, 4, 8, 24, or 72 hours.

### Effect of number of Pi-papers and soil to solution ratio on P adsorption

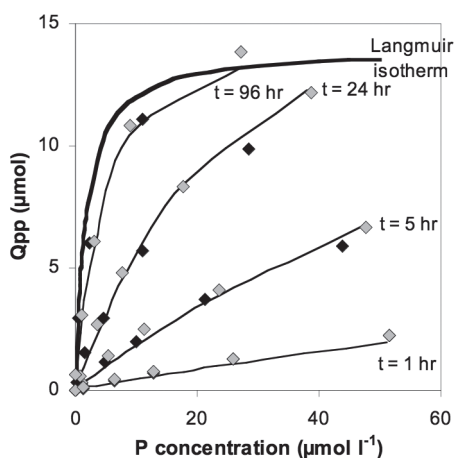
The effect of replacing the Pi-paper over 24 hours was investigated by gently shaking a Pi-paper in a soil suspension and removing this Pi-paper either once or four times over 24 hours. In the latter the Pi-paper is replaced by a fresh Pi-paper after 1, 4, and 8 hours. In both setups the P concentration in solution is measured after 1, 4, 8, and 24 hours. In addition, the influence of the soil to solution ratio is investigated by varying this ratio to result in 0.2, 0.1, 0.05, and 0.025 kg L<sup>-1</sup>. Two soils (1 and 9) were used for both experiments. These two soils differ in the sense that one has a high P-CaCl<sub>2</sub> and relatively low soil P buffer power and the other soil has a low P-CaCl<sub>2</sub> and a relatively high soil P buffer power.

P was measured spectrophotometrically with a segmented flow analyzer (Skalar) equipped with a 32 bits AD-converter.

## RESULTS AND DISCUSSION

### P adsorption to a Pi-paper from a standard solution

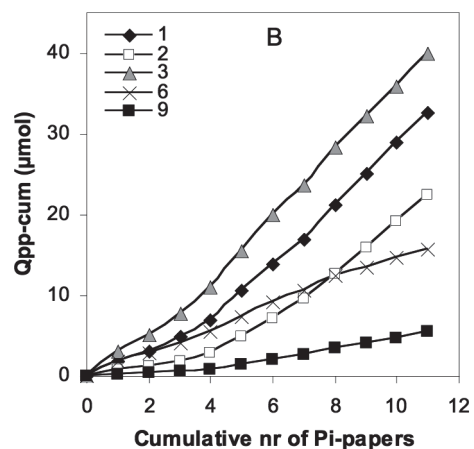
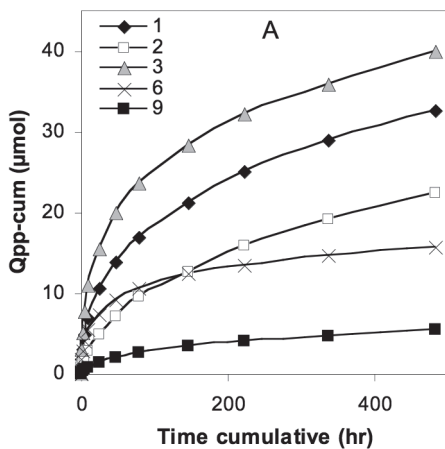
As shown in Figure 2, P adsorption to one Pi-paper ( $Q$ ) from a standard solution is not instantaneous but continues over time and approaches equilibrium after approximately 100 hours. The pH during the adsorption experiment is 5.9 +/- 0.1. Previous studies have also found that P adsorption to a Pi-paper is not instantaneous. Van der Zee et al. (1987) found P adsorption from a standard solution to approach a maximum after approximately 15 hours. Figure 2 shows that P adsorption by a Pi-paper over time can be described well with the kinetic Langmuir equation (Eq.[1]). The parameters of the kinetic Langmuir equation, which have been derived from fitting the equation to the data, are  $Q_{\max} = 15 \mu\text{mol P per Pi-paper}$ ,  $k_a = 0.003 \text{ L } \mu\text{mol}^{-1} \text{ hr}^{-1}$ , and  $k_d = 0.005 \text{ hr}^{-1}$ . As follows from the above described Langmuir model (eq.[1]) the rate of adsorption ( $dQ/dt$ ) depends on the concentration in solution. The adsorption at equilibrium is also determined by the concentration in solution.



**Figure 2** The relationship between the P concentration in solution and the amount of P adsorbed to a single Pi-paper from standard P solutions in 0.01M CaCl<sub>2</sub> over time. The grey diamonds are data points that represent the P adsorption from a volume of 500 ml and the dark diamonds from 250 ml. The lines represent the data fitted using a kinetic Langmuir equation (eq.[1]). The thick line is the corresponding equilibrium Langmuir equation. The parameters of the kinetic Langmuir equation are a  $Q_{\max}$  of 15  $\mu\text{mol P per Pi-paper}$ ,  $k_a$  of 0.003  $\text{l } \mu\text{mol}^{-1} \text{ hr}^{-1}$ , and a  $k_d$  of 0.005  $\text{hr}^{-1}$ .

**Table 1:** General soil properties.

| Soil | Clay (%) | SOC (%) | CaCO <sub>3</sub> (%) | pH-KCl | P-CaCl <sub>2</sub> (μmol kg <sup>-1</sup> ) |
|------|----------|---------|-----------------------|--------|--|
| 1    | 4        | 2.2     | -                     | 6.2    | 429  |
| 2    | 4        | 3.1     | -                     | 4.6    | 98   |
| 3    | 5        | 3.5     | -                     | 5.6    | 886  |
| 4    | 2        | 1.0     | 0.5                   | 7.0    | 344  |
| 5    | 3        | 1.3     | -                     | 4.8    | 82   |
| 6    | 14       | 2.1     | 1.2                   | 6.8    | 430  |
| 7    | 25       | 8.3     | -                     | 4.5    | 19   |
| 8    | 28       | 14.0    | -                     | 5.2    | 104  |
| 9    | 23       | 1.6     | 8.3                   | 7.4    | 22   |
| 10   | 52       | 3.3     | 0.3                   | 6.7    | 27   |



**Figure 3:** Cumulative amount of P adsorbed to 11 Pi-papers versus the cumulative amount of time the Pi-papers have been in contact with a soil suspension (A) and versus the cumulative number of successive Pi-papers (B) for five representative soils.

## P adsorption to a Pi-paper from a soil suspension

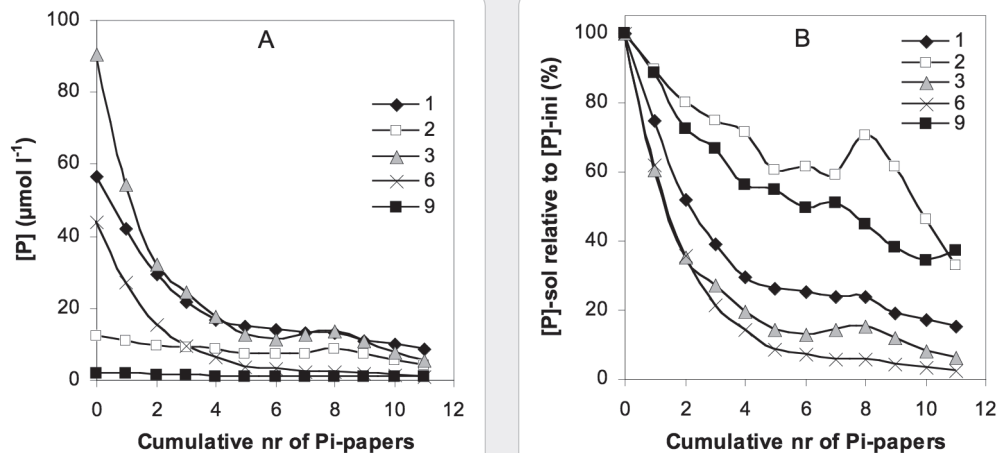
### Cumulative P adsorption

As illustrated by the data in Table 1, the soils were chosen to represent a large variation in general soil properties and P-status. This variation also results in a large variation in cumulative P



adsorption to the Pi-papers between soils. The amount of P removed by the first Pi-paper (placed in the soil suspension for 1 hour) ranges between 0.2 and 3.1  $\mu\text{mol P}$ . The cumulative amount of P removed by 11 successive Pi-papers (cumulative amount of time is 480 hours) ranges between 5.4 and 40  $\mu\text{mol P}$ .

The cumulative amount of P extracted by the Pi papers from the system ( $Q_{cum}$ ) is found by summing the amount adsorbed on the individual Pi-papers. This  $Q_{cum}$  has been plotted for 5 different soils as a function of the cumulative amount of time the successive Pi-papers have been in contact with the soil suspension (Fig.3a) and versus the cumulative number of successive Pi-papers (Fig.3b). Figures 3a and 3b give a quite different impression of the desorption of soil P. When displayed versus cumulative reaction time, the desorption rate seems to slow down over time. This image conforms to the general perception of soil P desorption kinetics (Lookman et al., 1995; Torrent et al., 1992; Van der Zee et al., 1987). When displayed versus the cumulative number of Pi-papers, the cumulative desorption of soil P seems to occur in two phases. In the first phase, the amount adsorbed per Pi-paper is relatively low, as the contact time is relatively short. This gradually changes into the second phase in which, despite the increasing contact time between soil and Pi-paper, the amount adsorbed to each successive Pi-paper becomes approximately constant.  $Q_{cum}$  appears to be linearly related with the cumulative number of Pi-papers although the slope is quite different for the different soils. This may indicate that in this second phase the P adsorption to a Pi-paper is not a function of time but of the frequency with which the Pi-paper is replaced. In that case, neither the desorption kinetics of the soil nor the adsorption kinetics of the Pi-paper are relevant.



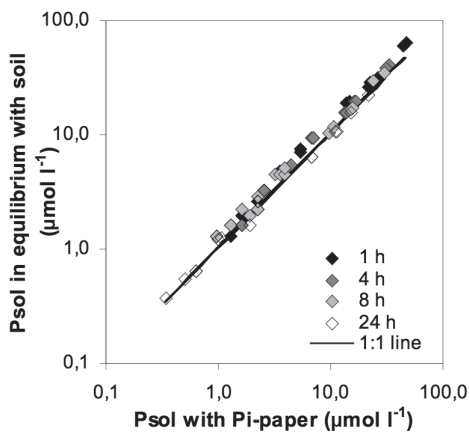
**Figure 4:** P concentration in solution (A) and P concentration in solution relative to the initial P concentration (B) versus the cumulative number of successive Pi-papers for five representative soils. The initial P concentration in solution is assumed equal to P-CaCl<sub>2</sub>.

### P concentration in solution

The change in P concentration in solution ( $P_{\text{sol}}$ ) was monitored by measuring  $P_{\text{sol}}$  each time a Pi-paper was replaced. For all soils,  $P_{\text{sol}}$  is assumed to increase “instantaneously” to a concentration that is equal to  $P\text{-CaCl}_2$  ( $C_{\text{ini}}$ ) after which  $P_{\text{sol}}$  decreases due to the removal of P from the solution by the Pi-papers (Fig.4). Because  $P_{\text{sol}}$  is relatively low, a small contamination of the sample may lead to a relatively large error in the measured value. This was probably the case for soil 2 at the eighth and ninth Pi-paper (Fig.4b). The soils show a large variation in the absolute (Fig.4a) as well as in the relative (Fig.4b) decrease in  $P_{\text{sol}}$ . However, for none of the soils the Pi-paper is able to reduce  $P_{\text{sol}}$  to approximate zero, and in all systems  $P_{\text{sol}}$  is thus buffered to a certain extent by the soil. This indicates that the rate of desorption from the soil ( $R_2$ ) is relatively high compared to the rate of adsorption to the Pi-paper ( $R_3$ ). In addition, each Pi-paper removes (much) more P than is present in solution when the Pi-paper is placed in the soil suspension. Again, this shows that buffering of P by the soil during desorption is very important for the total amount of P removed by the Pi-paper.

The relative decrease (Fig.4b) in  $P_{\text{sol}}$  is not a function of the initial concentration ( $C_{\text{ini}}$ ). The relative decrease expresses the differences in soil P buffer power of the soils. For a soil with a large buffer power (e.g. soil 2), the concentration decreases between 10% compared to  $C_{\text{ini}}$  after 1 Pi-paper and 76% after 11 Pi-papers. For a soil with a relatively small buffer power (e.g. soil 6), the concentration decreases between 38% after one Pi-paper and 98% after 11 Pi-papers.

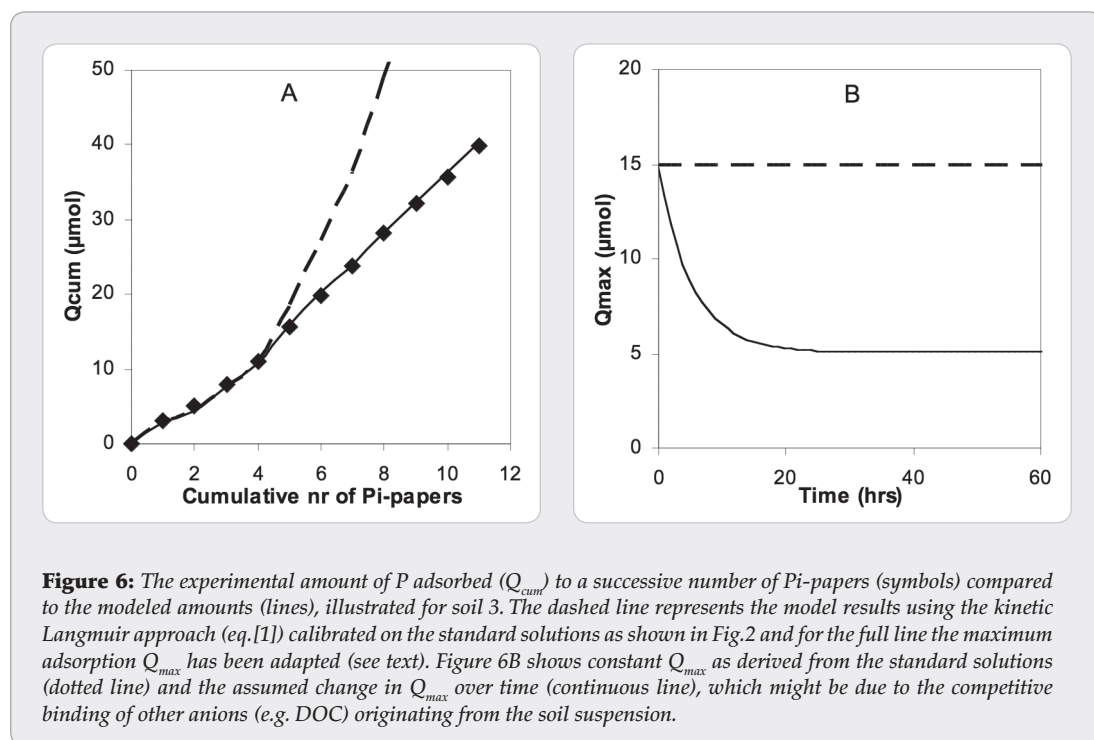
The P concentration in solution during desorption might be determined solely by Pi-paper adsorption kinetics ( $R_3$ ) or by a combination of both Pi-paper adsorption kinetics ( $R_3$ ) and soil P desorption kinetics ( $R_4$ ). Therefore, an additional experiment was performed in which  $P_{\text{sol}}$  was measured twice: once in the solution directly after the Pi-paper was removed and once when the soil was allowed to (re-)equilibrate with the solution for half an hour after removal of the Pi-paper. Figure 5 shows that  $P_{\text{sol}}$  measured directly after the Pi-paper is removed and after the soil – solution is allowed to re-equilibrate are approximately equal. During a continuous removal of soil P by a Pi-paper,  $P_{\text{sol}}$  thus remains approximately in equilibrium with the soil. The soil P desorption rate is thus fast enough to keep up with the adsorption rate of the Pi-paper ( $R_1 > R_3$ ). As a result,



**Figure 5:** Comparison between the P concentration in solution measured after removal of a Pi-paper and a re-equilibration time of 0.5 hours and the P concentration in solution measured directly after interaction with a Pi-paper for either 1, 4, 8, or 24 hours.

the transfer rate of P from soil to Pi-paper is limited by the Pi-paper adsorption kinetics. During the second phase of the desorption experiment, the solution is in equilibrium with both the soil and with the Pi-paper.

The above shows that in all stages of the experiment,  $P_{\text{sol}}$  is governed by the P desorption isotherm of the soil. In the first stage this is due to a higher rate of desorption from the soil than the adsorption by the paper ( $R_1 > R_3$ ) and in the second stage equilibrium is reached between both adsorption phases, i.e. soil and Pi-paper. It implies that one is able to follow the change in the equilibrium concentration as a function of the change of the loading of P in the soil. Initially, a relatively rapid decrease in  $P_{\text{sol}}$  is found, which levels off with continuous P removal from the soil. After approximately five papers, the decrease of the solution concentration is relatively small on a linear scale. This behavior is typical for a high affinity isotherm, i.e. relatively large changes in the concentration at high loading and small changes when this loading decreases.



**Figure 6:** The experimental amount of P adsorbed ( $Q_{\text{cum}}$ ) to a successive number of Pi-papers (symbols) compared to the modeled amounts (lines), illustrated for soil 3. The dashed line represents the model results using the kinetic Langmuir approach (eq.[1]) calibrated on the standard solutions as shown in Fig.2 and for the full line the maximum adsorption  $Q_{\text{max}}$  has been adapted (see text). Figure 6B shows constant  $Q_{\text{max}}$  as derived from the standard solutions (dotted line) and the assumed change in  $Q_{\text{max}}$  over time (continuous line), which might be due to the competitive binding of other anions (e.g. DOC) originating from the soil suspension.

### Predicting P adsorption to a Pi-paper from a soil suspension

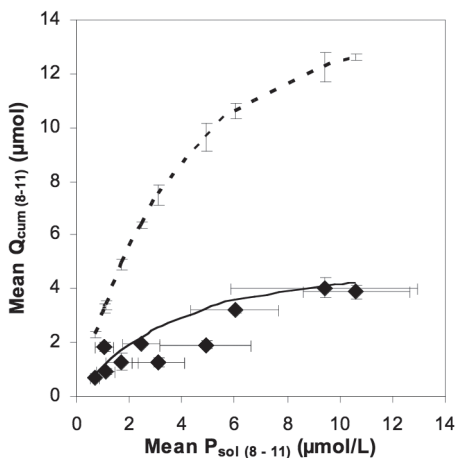
To obtain more information on P transfer from soil to Pi-paper, the cumulative amount of P extracted by the paper,  $Q_{\text{cum}}$ , has been modeled with the kinetic Langmuir approach (Eq.[1]) as described in the section on theory and data interpretation. The calculated amount of P removed by the paper is found based on the P concentration as measured at each successive replacement of the Pi-paper and the (kinetic) P adsorption isotherm of the Pi-paper.

Figure 6 shows the modeled  $Q_{\text{cum}}$  (dashed line) compared to the experimental data (symbols) for a representative soil (soil 3). For the first four Pi-papers, the calculated  $Q_{\text{cum}}$  is generally in good agreement with the measurements. This shows that on the short term the adsorption rate

of P to each successive Pi-paper is correctly predicted based on the P concentration in solution (eq.[1]) at which the soil buffers the solution. Note that the parameterization of the Langmuir kinetic equation of the Pi-paper is done independently by calibration in standard solutions (0.01 M CaCl<sub>2</sub>).

In contrast with the good agreement between the modeling and the experimental data collected for relatively short contact times (<8 hours), the calculations increasingly overestimate the experimental data when the contact time increases (Fig.6a, dashed line). For the last four Pi-papers in the soil suspension the contact time ranged between 67 and 144 hours and full equilibrium is obtained for both the paper and the soil. The data can be understood (full line, Fig.6) if we assume in the modeling that the Pi-paper adsorption isotherm belonging to this measured equilibrium has a much lower apparent adsorption maximum ( $Q'_{max}$ ) than the maximum derived from P adsorption from standard solutions (Fig.2). The adsorption isotherm of the Pi-paper thus changes due to a change in  $Q_{max}$  when a Pi-paper is placed in a standard solution compared to when it is placed in a soil suspension. A possible explanation for this apparent decrease in  $Q_{max}$  may be the presence of other anions that are present in the soil suspension and compete with phosphate for the Pi-paper binding sites. The most likely competing anions will be DOC in the soil solution and more specifically the presence of humic or fulvic acids (Antelo et al., 2007). Both humic and fulvic acids strongly bind to iron-oxides (Weng et al., 2007; Weng et al., 2006) and will compete with phosphate for the binding sites which can qualitatively explain the observed decrease in P binding. In model systems Borggaard et al. (2005) found that humic acid have only a limited influence on P adsorption by iron oxides. On the contrary, Antelo et al (2007) found soil humic acid (SHA) to decrease P adsorption to goethite up to 45%. The concentrations of both P and DOC in the Antelo study were comparable to the concentrations found in this study whereas Borggaard et al. used higher P and lower DOC concentrations.

The hypothesis that the adsorption maximum of P to the Pi-paper is affected by competition with humic and fulvic acids may be incorporated in the model by assuming that the adsorption of these molecules is also time dependent, i.e. adsorption increases over time until a certain maximum adsorption is reached. As a result, the corresponding adsorption maximum for P ( $Q_{max}$ ) will



**Figure 7:** The average amount of P adsorbed to each of the Pi-papers nr. 8-11 (contact time 67 – 144 hours) and the corresponding average P concentration in solution for 10 soils as measured (symbols). The lines represent the Langmuir isotherm of the Pi-papers present in a synthetic 0.01 M CaCl<sub>2</sub> solution (upper line) and the actual Langmuir isotherm when the paper is in contact with a soil, which leads to a reduction of the maximum adsorption ( $Q_{max}$ ), e.g. due to competitive binding of anions originating from the soil, like DOC

decrease at an increase in contact time due to the increased effect of competition over time. This is sketched in Figure 6b in which  $Q_{\max}$  is allowed to gradually decrease from 15  $\mu\text{mol}$  to 5  $\mu\text{mol}$  per paper strip during the first 28 hours. Adapting  $Q_{\max}$  in this way highly increases the accuracy of the model predictions as shown by the full line compared to the dotted line in Figure 6a and figure 7. The change in effective  $Q_{\max}$  is adapted equally for all soils. For the first 4 Pi-papers, the maximum contact time is four hours. Although the effective adsorption maximum is strongly decreased in the first hours of contact (Fig.6b), the decrease in effective  $Q_{\max}$  hardly affects the calculated P adsorption. The reason is that the Pi-paper is not strongly loaded at short times of contact as shown in Figure 2 resulting in a good agreement between modeled and measured  $Q_{\text{cum}}$  in the first stage of our experiments. We finally note that despite the change in effective  $Q'_{\max}$  the amount of P adsorbed by the Pi-paper in a soil suspension remains a function of the adsorption isotherm of the Pi-paper although this isotherm deviates from the isotherm found by the adsorption of P from standard solutions.

### **Considerations concerning the experimental setup**

As described in the Theory and data interpretation section, P transfer from soil to Pi-paper can be limited by soil P desorption kinetics ( $R_1$ ), Pi-paper adsorption kinetics ( $R_3$ ) or a combination of both, or equilibrium can be reached depending on the experimental setup. Below, the effect of the number of Pi-papers, the choice of the soil to solution ratio (SSR), and the effect of the reaction time on the transfer of P from soil to Pi-paper will be discussed.

With an increasing number of Pi-papers per gram of soil the P concentration in solution will decrease. According to the model (Fig.1), this will increase the desorption rate until the P transfer from soil to Pi-paper becomes the limited rate ( $R_1$ ). This effect is comparable to the effect of the increase of the weight of anion exchange resin per gram soil on  $P_{\text{sol}}$  (Barrow and Shaw, 1977). The limiting case when P transfer is kinetically controlled by soil desorption kinetics ( $R_3 > R_1$ ) has been found to occur when at least four (Van der Zee et al. 1987) or five (Lin et al., 1991; Van der Zee et al., 1987) Pi-papers per gram soil are used. In that situation, the highest desorption rate is reached resulting in a maximum P desorption in a minimum of time. In contrast, equilibrium between  $P_{\text{sol}}$  and soil is reached ( $R_1 = R_2$ ) when one Pi-paper per four grams of soil is used (this study). P transfer is (kinetically) controlled by Pi-paper adsorption, and the rate of P removal ( $R_3$ ) depends on the P concentration in solution. This concentration is controlled by the equilibrium with the soil and depends on the experimental setup, e.g. the SSR, and the soil P buffer power. In conclusion, the total amount of P removed by a single Pi-paper will depend on the SSR, reaction time, and the P-buffering.

The influence of the SSR on the P-removal was studied in an additional experiment (Table 2). One Pi-paper was added to 40 ml 0.01M  $\text{CaCl}_2$  and 1, 2, 4, and 8 gram soil resulting in a SSR of 0.025, 0.05, 0.1 and 0.2  $\text{kg L}^{-1}$ . With a decreasing amount of soil in the system,  $P_{\text{sol}}$  decreases. The lower  $P_{\text{sol}}$  results in a lower cumulative amount of P adsorbed per Pi-paper when expressed in  $\mu\text{mol P}$  adsorbed. However, when  $Q_{\text{cum}}$  is expressed per mass unit soil ( $\mu\text{mol kg}^{-1}$ ) more soil P is adsorbed per Pi-paper. This difference is related to the soil P buffer power, i.e. the sorption isotherm of the soil. In the extreme of an infinite buffering,  $P_{\text{sol}}$  would not change with SSR and therefore also the rate of adsorption to the Pi-paper would not change. Because in that situation the amount of soil in the system does vary, this results in a variable amount of P adsorbed by the Pi-paper if expressed per mass soil. As a result, varying the SSR results in a difference in the rate with which the soil moves down its desorption isotherm. The data in Table 2 show that with a smaller amount of soil per Pi-paper (lower SSR), more soil P is removed per Pi-paper and as a consequence, the

**Table 2:** Effect of Soil Solution ration (SSR) on the cumulative amount of P adsorbed ( $Q_{cum}$ ) and the P concentration in solution ( $P_{sol}$ ) when a Pi-paper is replaced four times over 24 hours.

| Time (hr) | soil | SSR = 0.2 kg L <sup>-1</sup>         |                               |                                     | SSR = 0.1 kg L <sup>-1</sup>         |                               |                                     |
|-----------|------|--------------------------------------|-------------------------------|-------------------------------------|--------------------------------------|-------------------------------|-------------------------------------|
|           |      | $P_{sol}$ ( $\mu\text{mol L}^{-1}$ ) | $Q_{cum}$ ( $\mu\text{mol}$ ) | $Q_{cum}$ ( $\text{mmol kg}^{-1}$ ) | $P_{sol}$ ( $\mu\text{mol L}^{-1}$ ) | $Q_{cum}$ ( $\mu\text{mol}$ ) | $Q_{cum}$ ( $\text{mmol kg}^{-1}$ ) |
| 0         | 1    | 78                                   |                               |                                     | 58                                   |                               |                                     |
| 1         |      | 54                                   | 3.6                           | 0.4                                 | 38                                   | 2.7                           | 0.7                                 |
| 4         |      | 38                                   | 6.6                           | 0.8                                 | 26                                   | 4.3                           | 1.1                                 |
| 8         |      | 32                                   | 9.9                           | 1.2                                 | 18                                   | 6.4                           | 1.6                                 |
| 24        |      | 23                                   | 15.7                          | 2.0                                 | 21                                   | 10.1                          | 2.5                                 |
| 0         | 9    | 3.1                                  |                               |                                     | 1.8                                  |                               |                                     |
| 1         |      | 2.6                                  |                               |                                     | 1.4                                  | 0.3                           | 0.07                                |
| 4         |      | 2.3                                  | 0.5                           | 0.06                                | 1.3                                  | 0.5                           | 0.1                                 |
| 8         |      | 2.0                                  | 1.0                           | 0.1                                 | 1.4                                  | 0.8                           | 0.2                                 |
| 24        |      | 2.0                                  | 2.0                           | 0.3                                 | 0.9                                  | 1.5                           | 0.4                                 |
| Time (hr) | soil | SSR = 0.05 kg L <sup>-1</sup>        |                               |                                     | SSR = 0.025 kg L <sup>-1</sup>       |                               |                                     |
|           |      | $P_{sol}$ ( $\mu\text{mol L}^{-1}$ ) | $Q_{cum}$ ( $\mu\text{mol}$ ) | $Q_{cum}$ ( $\text{mmol kg}^{-1}$ ) | $P_{sol}$ ( $\mu\text{mol L}^{-1}$ ) | $Q_{cum}$ ( $\mu\text{mol}$ ) | $Q_{cum}$ ( $\text{mmol kg}^{-1}$ ) |
| 0         | 1    | 40                                   |                               |                                     | 32                                   |                               |                                     |
| 1         |      | 22                                   | 1.9                           | 1.0                                 | 16                                   |                               |                                     |
| 4         |      | 17                                   | 3.2                           | 1.6                                 | 12                                   | 1.7                           | 1.7                                 |
| 8         |      | 14                                   | 5.2                           | 2.6                                 | 8                                    | 2.7                           | 2.7                                 |
| 24        |      | 15                                   | 8.2                           | 4.1                                 | 5                                    | 4.5                           | 4.5                                 |
| 0         | 9    | 1.5                                  |                               |                                     | 1.3                                  |                               |                                     |
| 1         |      | 1.4                                  | 0.4                           | 0.2                                 | 1.0                                  | 0.3                           | 0.3                                 |
| 4         |      | 1.7                                  | 0.6                           | 0.3                                 | 0.7                                  | 0.4                           | 0.4                                 |
| 8         |      | 0.9                                  | 0.8                           | 0.4                                 | 1.0                                  | 0.6                           | 0.6                                 |
| 24        |      | 1.6                                  | 1.2                           | 0.6                                 | 0.5                                  | 0.8                           | 0.8                                 |

difference in buffer power between soils becomes more pronounced. In the system described by McDowell and Sharpley (2003) having a SSR=0.2 kg L<sup>-1</sup> and one Pi-paper, the amount of P removed from the soil will be smaller compared to SSR =0.1 kg L<sup>-1</sup> (this study).

When P transfer is limited by the Pi-paper adsorption rate ( $R_1 > R_3$ ), the frequency with which the Pi-paper is removed will theoretically have little effect on the amount desorbed as long as the P loading of the Pi-paper is low. This is confirmed in an additional experiment in which the amount of P adsorbed to one Pi-paper replaced after 24 hours is slightly lower but comparable to the cumulative amount of P adsorbed to 4 successive Pi-papers over the same period of time

**Table 3:** The time-dependent change of the P concentration in solution ( $[P]_{\text{sol}}$ ) and the cumulative adsorption by Pi-paper ( $Q_{\text{cum}}$ ) using two different soils (SSR= 0.1 kg/L) and a replacement of Pi-paper(s) either once or four times during the course of the experiment. In case of 1 replacement,  $[P]_{\text{sol}}$  is measured but the Pi-paper was not replaced.

| Time | Soil | 4 replacements                                |                                      | 1 replacement                                 |                                      |
|------|------|---|--------------------------------------|---|--------------------------------------|
|      |      | $[P]_{\text{sol}}$ ( $\mu\text{mol L}^{-1}$ ) | $Q_{\text{cum}}$ ( $\mu\text{mol}$ ) | $[P]_{\text{sol}}$ ( $\mu\text{mol L}^{-1}$ ) | $Q_{\text{cum}}$ ( $\mu\text{mol}$ ) |
| 0    | 1    | 58  | 0.0                                  | 58  |                                      |
| 1    | 1    | 38  | 2.7                                  | 30  |                                      |
| 4    | 1    | 26  | 4.3                                  | 32  |                                      |
| 8    | 1    | 18  | 6.4                                  | 28  |                                      |
| 24   | 1    | 21  | 10.1                                 | 31  | 9.2                                  |
| 0    | 9    | 1.8   | 0.0                                  | 1.8   |                                      |
| 1    | 9    | 1.4   | 0.3                                  | 1.3   |                                      |
| 4    | 9    | 1.3   | 0.5                                  | 1.5   |                                      |
| 8    | 9    | 1.4   | 0.8                                  | 1.6   |                                      |
| 24   | 9    | 0.9   | 1.5                                  | 1.3   | 1.1                                  |

(Table 3).  $P_{\text{sol}}$  measured in both setups after 1, 4, 8, and 24 hours, show similar results;  $P_{\text{sol}}$  is only slightly higher when the Pi-paper is replaced once compared to when it is replaced four times. At low loading of the paper ( $Q \ll Q_{\text{max}}$ ) the desorption rate from the paper ( $R_4$ ) is negligible compared to the adsorption rate ( $R_3$ ) as follows from eq.[1]. In this limiting case of eq.[1], the rate is only determined by the concentration in solution,  $Q'_{\text{max}}$  and  $k_a$ . The P transfer will no longer be independent of this replacement frequency when the total system reaches equilibrium ( $t > 24$  hours). In that case, the frequency of replacement of the Pi-paper determines the amount of P removed from the soil because the rate of adsorption ( $R_3$ ) is not the relevant factor.

## 5. CONCLUSIONS

Placing a Pi-paper in a soil suspension results in a re-distribution of P between the reactive surface area of the soil and the new, empty reactive surface area of the Pi-paper. Adsorption of P to a Pi-paper from a standard solution is not instantaneous but time dependent. The Pi-paper adsorption kinetics can be described by a kinetic Langmuir equation until equilibrium is reached and the equation reduces to the Langmuir isotherm of the Pi-paper. When placing a Pi-paper in a soil suspension, transfer of P from soil to the Pi-paper depends on the experimental setup and may be limited by the soil P desorption kinetics ( $R_1$ ), Pi-paper adsorption kinetics ( $R_3$ ) or both. When one Pi-paper is placed in a soil suspension of 4 gram soil and 40 ml electrolyte solution, the transfer rate from soil to Pi-paper is limited by P adsorption kinetics of the Pi-paper ( $R_3$ ) on short timescales ( $t < 24$  hours). With longer timescales ( $t \sim 24$  hours), the soil - solution - Pi-paper system approaches full equilibrium. At equilibrium less P is removed by the Pi-paper than expected from P adsorption to a Pi-paper from a standard solution. This is proposed to be caused by the competition of P with other negatively charged ions in the soil (e.g. humic and fulvic acids) for the same sorption sites on the Pi-paper. This effect is approximately equal for all soils and is

expressed by a reduction in the effective maximum adsorption by a factor three. Nonetheless, the amount of P removed by each Pi-paper continues to be a function of the P concentration in solution. The P concentration is in equilibrium with the soil and therefore a function of the P-desorption isotherm of the soil, regardless if equilibrium is attained or not. Transfer of P from soil to Pi-paper is initially a function of the initial P concentration in solution but with continuous P removal becomes a function of the capacity of the soil to buffer this concentration, i.e. the soil P buffer power. Varying the number of Pi-papers and the SSR will have a large effect on the transfer rate between soil and Pi-paper and on what factors may limit this transfer rate. The method thus offers a large flexibility in answering a broad range in P-related questions concerning soil fertility and environmental issues which encompasses a large variation in the amount of P removed from the soil system over a wide range in time.



*Chapter 3*

**INTEGRATING SOIL PHOSPHORUS  
SUPPLY POTENTIAL AND STANDARD  
SOIL TESTS**

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## ABSTRACT

To make it possible that nutrient management is optimized to include both agronomic and environmental goals, there is a growing need to increase the accuracy with which routine laboratories assess the phosphorus (P) status of a soil. In this study this is approached by integrating the dynamic soil P supply potential and the static P status of a soil. This integration is achieved by modeling the soil P supply potential during the continuous removal of P by an artificial P sink (Fe oxide-impregnated paper). The soil P supply potential is described with a Langmuir isotherm and in the model the two parameters of this isotherm are calculated *a priori* from standard soil tests. To be able to predict the P desorption isotherm a minimum of two parameters is needed; a measure for P quantity (e.g. P-Olsen, PAL) and a measure for P intensity (e.g. P CaCl<sub>2</sub>). The accuracy of this prediction increases for soils with increasing soil P buffer power, i.e. with decreasing P saturation of the reactive surface area associated with the readily desorbable P. To increase the accuracy of this prediction for soils that don't have a high soil P buffer power, a measure for the reactive surface area (e.g. Fe<sub>ox</sub> and Al<sub>ox</sub>) of the soil must also be taken into account. In addition, to be able to extend the prediction of the soil P supply potential to an amount of P exceeding the amount of readily desorbable P a measure for the total amount of P must be included.

## INTRODUCTION

There is a large discrepancy between the way the P supply potential of a soil is approached in routine soil laboratories and the current knowledge within the scientific community. In routine soil laboratories the P supply potential is generally assessed using a single soil test, which must meet the criteria of being cheap, fast, applicable to a wide range of soil types, and be low labor intensive. A wide variety in P extraction methods have been developed that may differ largely with respect to the amount of P extracted for a given soil sample (Kuo 1996). Different laboratories and countries show a large variation in their choice of soil test (Neyroud and Lischer 2003). This indicates the lack of consensus in predicting the soil P supply potential based on a single soil test. The agronomical relevance of the chosen soil test has been deduced from correlations between soil test results and crop response determined from pot experiments and- or field trials which have often taken place several decades ago. These correlations often show a considerable variation, implying that the fitted relationship is not very reliable.

In 1920 Hoagland et al. already stated that progress in the study of soil nutrient availability for plants would depend on the increased knowledge of the soil solution. Elaborating hereon Smethurst (2000) concluded that knowledge of both the P concentration in the soil solution and components of P supply could lead to more widely applicable methods of P analyses. The main nutrient bioavailability models are indeed based on the concentration in solution, its buffering behavior and the effective diffusion coefficient (Barber 1995; Tinker and Nye 2000). Intensity is defined as (a measure for) the P concentration in the soil solution. The buffer power is defined as the ability of the soil to maintain the P intensity upon addition or removal of P. The soil P that is associated with this buffering is defined as the P quantity. From a crop perspective P quantity may be defined as the amount of P that will replenish the soil solution and be taken up by the crop during its life cycle (Holford 1997). From a soil chemical perspective P quantity may be defined as the total desorbable amount of P consisting of both a fast and a slow desorbing pool (Lookman et al. 1995). Desorption of P may also be considered to occur from a continuum of phases instead of from distinct phases (Frossard et al. 2000; McDowell and Sharpley 2003; Koopmans et al. 2004).

In many places of the world a net excess in P application has resulted in agricultural fields being a (potential) source of pollution of surface and ground water. As P is often the limiting nutrient in these water bodies there is a growing need to optimize soil P management in order to achieve both agronomic and environmental goals (Sharpley et al. 1994). This results in the need to increase the accuracy with which routine soil laboratories predict the soil P supply potential. The soil P supply potential is governed by intensity, quantity, and buffer power, either singly or in combination, depending on the relative variations of these factors in the soil and a single soil test result is a rather poor approximation (Moody et al. 1988). P intensity, P quantity, and buffer power are integrated in a soil specific sorption isotherm. The buffer power combines the soils P intensity and P quantity as it is directly related to the slope of this isotherm (Barrow 1967). A single soil test may be an indicator of either P intensity or P quantity, or a complicated mixture of both factors but cannot be an indicator of the relationship between intensity and quantity. Several researchers have suggested that it is necessary to include the soil P buffer power, in order to enhance the predictive value of a single soil test (Holford 1997; Frossard et al. 2000; Ehlert 2003). The increased accuracy in predicting soil P supply potential may also be facilitated by using improved soil testing methods that are more based on the mechanisms that control nutrient availability to plants than presently used methods (Skogley 1994; Morel et al. 2000).

In this paper the challenge to increase the accuracy with which routine soil laboratories can predict the soil P supply potential is approached by integrating the P supply potential of a soil

and standard soil tests that can be measured in a routine way. This is achieved by modeling soil P desorption and the decrease in the P concentration in solution during continuous desorption to an artificial P sink, using the Langmuir sorption isotherm of which the parameters are related to data derived from standard soil tests. In this way a combination of soil tests can be deduced that are minimally needed to give an accurate prediction of the soil P supply potential. The artificial P sink used in this study is Fe oxide-impregnated paper.

## **MATERIALS AND METHODS**

Soil samples were collected from the plough layer (0-20cm) of 17 agricultural sites in the Netherlands in 2004. The sites were chosen to represent a wide range of soil types and P-status (Van Erp 2002). The clay content was determined using the sieve and pipet technique (NEN 5753), the CaCO<sub>3</sub> content using the volumetric method (NEN 5757), and the organic carbon content using the sulfochromic oxidation (ISO 14235). The pH-KCl was determined in a 1: 5 (volume fraction) suspension of 1 M potassium chloride solution (ISO 10390). The P-status of the soils was characterized using the following extraction methods: 0.01M CaCl<sub>2</sub> (P-CaCl<sub>2</sub>) (Houba and Temminghoff 1999; Houba et al. 2000), acid ammonium oxalate (Pox, Fe-ox, and Al-ox), (Schwertmann 1964), 0.5M NaHCO<sub>3</sub> (P-Olsen, Olsen et al. (1954), and acid ammonium lactate (PAL, Egnér et al. (1960).

Desorption behavior was studied by the continuous removal of P using Fe oxide-impregnated filter paper (Pi-paper) as an artificial P sink (Van der Zee et al., 1987) and replacing the Pi paper at set time intervals (Van Rotterdam et al. 2009). This P sink can be used to study both the short- and long term desorption (Menon et al. 1997) as it binds P strongly and the soil suspension is not strongly altered by the presence of the Pi-paper. Furthermore this method offers the possibility of monitoring the P concentration in the solution when the ratio between paper, soil, and solution is well chosen (Van Rotterdam et al. 2009). A drawback of the method is the adhesion of soil particles to the Pi-paper that may lead to an overestimation of desorbable P (Perrott and Wise 1993; Lookman et al. 1995). This effect can however be minimized by using filter paper with a small pore size, placing the paper in a fixed position (Myers et al. 1995), by using a background electrolyte, e.g. 0.01M CaCl<sub>2</sub>, and by removing the soil particles using an air-brush (Chardon et al. 1996). These precautions were all taken into account.

The Pi paper was prepared according to (Van der Zee et al., 1987). Soil P desorption was studied using the method described in Van Rotterdam et al. (2009). In short, a strip of Pi paper (2 x 10 cm) was brought in contact with a suspension of 4 g soil and 40 ml 0.01M CaCl<sub>2</sub> by attaching the strip to a holder that was attached to the top of a 50 ml polypropylene tube (greiner) and gently shaken continuously end- over- end at 6 RPM. Continuous desorption was ensured by replacing the Pi-paper after 2, 4, 8, 24, 48, 78, 145, 221, 337, and 481 hours (10 times in ~ 20 days). After the Pi-paper was removed from the soil suspension, P was dissolved by shaking the paper for two hours with 20 ml 0.2M H<sub>2</sub>SO<sub>4</sub> solution. In the suspension the P-concentration in solution was measured after each of the first five Pi-papers were replaced and after the last (tenth) Pi-paper was removed. Directly after each of these Pi-papers was removed the suspension was centrifuged and a sample (1 ml) of the solution was taken and analyzed for P. In calculating the P desorption from the soil the withdrawal of solution was corrected for. P was measured spectrophotometrically with a segmented flow analyzer (Skalar) equipped with a 32 bits AD-converter. The detection limit was 0.32 μmol L<sup>-1</sup> (10 μg L<sup>-1</sup>).

## DATA INTERPRETATION

Fe oxide-impregnated paper (Pi-paper) is used as an artificial P sink to study P availability in soils and runoff. Adding Pi-paper to a soil suspension results in the transfer of P from the soil, through the solution, to the Pi-paper. The processes that occur during this transfer from soil to Pi-paper and the characteristics of the P sink have been described in a previous paper (Van Rotterdam et al. 2009). In the experimental setup as used in this study, the transfer rate of P from soil to Pi-paper was solely determined by P adsorption to the Pi-paper; i.e. P adsorption to the Pi-paper is rate limiting when the contact time between soil and Pi-paper is relatively short (<~24 hours). Despite the presence of the strong P sink adsorbing P from the solution, the desorption rate of the soil was high enough to buffer the concentration in the solution to a degree that the concentration in solution remained in equilibrium with the soil. P adsorption to the Pi-paper could be described well with the kinetic Langmuir equation (Van der Zee et al. 1987):

**Equation 1**

$$\frac{dQ_{Pi}}{dt} = k_a C(Q_{max,Pi} - Q_{Pi}) - k_d Q_{Pi}$$

In which  $Q_{Pi}$  is the amount of P bound to the Pi-paper at a certain moment in time ( $\mu\text{mol}$ ),  $C$  is the concentration in solution ( $\mu\text{mol l}^{-1}$ ),  $Q_{max,Pi}$  is the adsorption maximum of the Pi-paper ( $\mu\text{mol}$ ),  $k_a$  is the adsorption rate constant ( $\text{l } \mu\text{mol}^{-1} \text{ hr}^{-1}$ ), and  $k_d$  the desorption rate constant ( $\text{hr}^{-1}$ ). With increasing contact time (>24 hours) between soil and Pi-paper the soil, solution, Pi-paper system reaches full equilibrium. When equilibrium is attained equation 1 results in the Langmuir equation of the Pi-paper. The parameters  $k_a$ ,  $k_d$ , and  $Q_{max,Pi}$  are characteristics of the Pi-paper under the chosen standard conditions of the experiment and were determined from adsorption experiments in standard solutions containing a range in P concentrations. However, when a Pi-paper is placed in a soil suspension, as opposed to when it is placed in a standard solution,  $Q_{max,Pi}$  for P is not constant but was found to decrease gradually from 15 to 5  $\mu\text{mol P}$  per Pi-paper over approximately 28 hours. This is supposedly caused by competition with other negatively charged ions in the soil (e.g. humic and fulvic acids) for the Pi-paper sorption sites (Van Rotterdam et al. 2009). Overall, the (rate of) P adsorption to a Pi-paper is continuously a function of the saturation of the Pi-paper adsorption sites and the prevailing P concentration in solution ( $C$ ), in which  $C$  is determined by the soil.

This previous study focused on understanding the processes that determine the transfer of P from soil to Pi-paper by modeling this transfer based on adsorption (kinetics) to the Pi-paper. The soil P supply potential was incorporated in the model through the measured P concentration in solution. In this study we focus on understanding and predicting the soil P supply potential. As  $C$  was found to be in equilibrium with the soil during the desorption experiment the decrease in  $C$  will be governed by the P desorption isotherm of the soil. Soil P desorption may thus be calculated using a sorption isotherm for which we will use the simple well known Langmuir isotherm:

Equation 2

$$Q = \frac{Q_{\max} KC}{1 + KC}$$

In which  $Q$  is the amount of P bound to the soil at a certain concentration in solution ( $\text{mmol kg}^{-1}$ ),  $C$  is the concentration in solution ( $\mu\text{mol l}^{-1}$ ),  $Q_{\max}$  is the adsorption maximum of the soil ( $\text{mmol kg}^{-1}$ ),  $K$  is an effective soil P affinity constant ( $\text{l } \mu\text{mol}^{-1}$ ). In both equations 1 and 2,  $C$  is the same P concentration in solution and thus links soil P desorption to P adsorption (kinetics) to the Pi-paper.

The transfer of P from soil to Pi-paper is modeled using both the adsorption (kinetics) to the Pi-paper (Eq. 1) and the soil P desorption using the Langmuir isotherm of the soil (Eq. 2). Adsorption to the Pi-paper is calculated by numerical integration of the kinetic Langmuir equation of the Pi-paper (Eq. 1). The concentration in solution is used as an input parameter in this equation and is calculated from the desorption isotherm of the soil (Eq. 2). During the transfer of P from soil to the Pi-paper the actual amount of P adsorbed to the soil at a certain moment in time ( $Q_t$ ) determines the P concentration in solution (equilibrium), which in turn determines (the rate) of P adsorption to the Pi-paper. During the desorption experiment ten successive Pi-papers are used to remove soil P and the cumulative amount of P transferred from soil to the cumulative number of Pi-papers ( $Q_{\text{cum}}$ ) is calculated by adding the calculated amount of P transferred from the soil to each successive Pi-paper over the period of time each Pi-paper was in the soil suspension in the experiment.

To be able to model the transfer of P from soil to Pi-paper the parameters that determine the adsorption to the Pi-paper and the parameters that determine the desorption from the soil must be known. The parameters of equation 1 have been investigated and described by Van Rotterdam et al. (2009). The parameters that determine the desorption of the soil will be investigated here. This is approached by relating the parameters in the Langmuir sorption isotherm of the soil (Eq. 2) to data derived from standard soil tests. The Langmuir isotherm has two soil specific parameters; the soil P adsorption maximum ( $Q_{\max}$ ) and the affinity constant ( $K$ ), which together determine the form and scale of the isotherm. Different approaches can be chosen to determine  $Q_{\max}$  and  $K$ : they may be assumed equal for all soils, or they may be fitted to the data, or they may be calculated *a priori* using data derived from standard soil tests. In this study the latter approach is chosen. An advantage of calculating  $Q_{\max}$  and  $K$  in this way is that the point of departure ( $t=0$ ) of the modeled and measured isotherm are equal.

The P adsorption maximum ( $Q_{\max}$ ) may be related to the reactive surface area of the soil and may be approximated by a fraction of  $(\text{Fe}+\text{Al})_{\text{ox}}$  (Van der Zee et al. 1987):

Equation 3

$$Q_{\max} = \beta(\text{Fe} + \text{Al})_{\text{ox}}$$

In which  $\beta$  is a proportionality parameter and  $(\text{Fe}+\text{Al})_{\text{ox}}$  is the amorphous Fe and Al content as approximated by the amount of Fe and Al extracted in an acid ammonium oxalate extract. The

affinity constant can be calculated by rewriting the Langmuir isotherm (Eq. 2):

Equation 4

$$K = \frac{Q_0}{Q_{\max} - Q_0} - \frac{1}{C}$$

In which  $Q_{\max}$  is the soil P adsorption maximum ( $\text{mmol kg}^{-1}$ ),  $Q_0$  is the initial amount of reversibly adsorbed P to the soil ( $\text{mmol kg}^{-1}$ ) and  $C_0$  is the initial P concentration in solution ( $\mu\text{mol l}^{-1}$ ). Apart from deriving  $Q_{\max}$  from  $(\text{Fe}+\text{Al})_{\text{ox}}$ ,  $Q_0$  may be derived from a measure representing P quantity, and  $C_0$  from a measure representing P intensity. It should not be a surprise that the estimated value of K is not the same for all soils. The effective affinity of the soil for P and thus also C are influenced by pH, ionic strength, Ca concentration and presence of competing ions (e.g. humic and fulvic acids) (Barrow et al. 1980; Rietra et al. 2001; Antelo et al. 2005, Weng et al. 2006, 2007). Performing the desorption experiments in a matrix of 0.01M  $\text{CaCl}_2$  has the advantage that the ionic strength and Ca level are imposed and thereby increasing the comparability between soils (Houba et al. 1996). In similar experiments P- $\text{CaCl}_2$  was found to be a good indicator for  $C_0$  (Van Rotterdam et al. 2009). The choice for  $Q_0$  is less straight forward and different possibilities will be examined.

**Table 1:** General soil characteristics and P extractability.

| Soil | Clay % | OS % | $\text{CaCO}_3$ % | pH-KCl | $[\text{Al}+\text{Fe}]_{\text{ox}}$ $\text{mmol kg}^{-1}$ | P- $\text{CaCl}_2$ $\mu\text{mol kg}^{-1}$ | P-Olsen $\text{mmol kg}^{-1}$ | PAL $\text{mmol kg}^{-1}$ | Pox $\text{mmol kg}^{-1}$ |
|------|--------|------|-------------------|--------|---|--|-------------------------------|---------------------------|---------------------------|
| 1    | 7      | 2.2  | -                 | 5      | 81  | 246  | 2.9                           | 7.0                       | 23                        |
| 2    | 4      | 4.4  | -                 | 6      | 71  | 646  | 5.0                           | 25                        | 48                        |
| 3    | 4      | 4.2  | -                 | 5.5    | 92  | 58   | 4.7                           | 12                        | 26                        |
| 4    | 8      | 3.7  | -                 | 5.6    | 361   | 35   | 1.6                           | 3.7                       | 38                        |
| 5    | 5      | 4.6  | -                 | 5.4    | 70  | 809  | 4.5                           | 20                        | 39                        |
| 6    | 2      | 0.6  | 0.6               | 6.7    | 12  | 161  | 1.3                           | 5.3                       | 6.0                       |
| 7    | 3      | 3    | -                 | 5.1    | 65  | 162  | 3.0                           | 9.6                       | 20                        |
| 8    | 11     | 0.9  | -                 | 5.5    | 69  | 163  | 1.8                           | 6.4                       | 15                        |
| 9    | 21     | 4.9  | -                 | 4.2    | 239   | 77   | 2.7                           | 5.5                       | 35                        |
| 10   | 14     | 4    | 1.7               | 6.9    | 34  | 39   | 0.9                           | 3.2                       | 8.0                       |
| 11   | 25     | 15.4 | -                 | 5.3    | 307   | 22   | 1.5                           | 4.0                       | 36                        |
| 12   | 7      | 1.2  | 1.7               | 7.5    | 50  | 115  | 1.8                           | 7.0                       | 11                        |
| 13   | 28     | 18.8 | -                 | 4.7    | 233   | 19   | 1.0                           | 3.0                       | 21                        |
| 14   | 23     | 3.1  | 6.5               | 7.1    | 106   | 26   | 1.4                           | 6.1                       | 15                        |
| 15   | 26     | 1.8  | 2.8               | 7.3    | 97  | 45   | 1.6                           | 4.1                       | 14                        |
| 16   | 3      | 0.6  | 0.7               | 7.2    | 13  | 209  | 1.7                           | 6.6                       | 7.8                       |
| 17   | 52     | 4.6  | -                 | 6      | 282   | 19   | 1.5                           | 2.6                       | 22                        |

## RESULTS AND DISCUSSION

### General soil characteristics

The 17 soils show a large variation in clay content, organic C content, pH, and  $(\text{Fe}+\text{Al})_{\text{ox}}$  content (Table 1). All soils contain no or a low  $\text{CaCO}_3$  content except soil 9 which contains ~7%  $\text{CaCO}_3$ . The 17 soils also show a large variation in P extractability (Table 1). The P- $\text{CaCl}_2$ , which is a measure for the P-intensity (Moody et al. 1988; Hinsinger 2001), varied between 0.02 and 0.8 mmol P per kg soil. Pox, PAL, as well as P-Olsen have been proposed as measures for the P quantity. Pox, is the strongest extraction method of the three (6 - 48 mmol P  $\text{kg}^{-1}$ ) followed by PAL (3 - 25 mmol P  $\text{kg}^{-1}$ ) and P-Olsen (0.9 - 5 mmol P  $\text{kg}^{-1}$ ). These three extraction methods are not or poorly correlated to P- $\text{CaCl}_2$ . Only PAL and P- $\text{CaCl}_2$  seem to be correlated due to two soils which both have a high P- $\text{CaCl}_2$  and high PAL. Without these two soils the correlation coefficient decreases from 0.79 to 0.2. Overall the soils show a range in P intensity as well as in P quantity.

### Cumulative P desorption versus standard soil tests

The large variation in soil properties and P extractability between the soils, results in a large variation in both the cumulative soil P desorption and in the absolute and relative decrease in the P concentration in solution (C) during the experiment using ten successive Pi-papers (Table

**Table 2:** Cumulative soil P desorption to ten successive Pi-papers and the corresponding P concentration in solution at the moment the first five and the last Pi-paper were removed from the soil suspension. The P concentration before the first Pi-paper is placed in the soil suspension is assumed to equal the P concentration in a 0.01M  $\text{CaCl}_2$  extract. The P concentration was not measured at Pi-paper 6 to 9.

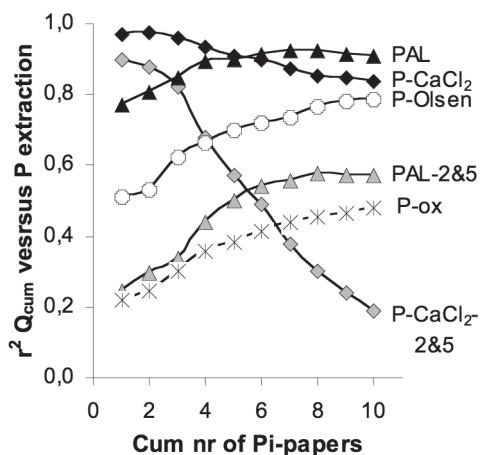
| Soil | Qpp-cum (mmol $\text{kg}^{-1}$ ) |     |     |     |     |     |     |     |     |     | P-CC | C ( $\mu\text{mol l}^{-1}$ ) |     |     |     |     |     |
|------|----------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------------------------------|-----|-----|-----|-----|-----|
|      | 1                                | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  |      | 0                            | 1   | 2   | 3   | 4   | 5   |
| 1    | 0.3                              | 0.5 | 0.8 | 1.2 | 1.6 | 1.9 | 2.3 | 2.7 | 3.2 | 3.6 | 25   | 11                           | 7.1 | 5.5 | 3.1 | 3.1 | 1.1 |
| 2    | 0.7                              | 1.2 | 1.8 | 3.2 | 4.1 | 5.0 | 6.2 | 7.1 | 7.9 | 8.9 | 65   | 31                           | 22  | 15  | 9.1 | 7.1 | 4.3 |
| 3    | 0.1                              | 0.2 | 0.4 | 0.8 | 1.2 | 1.6 | 2.1 | 2.7 | 3.3 | 3.9 | 5.8  | 4.8                          | 4.3 | 3.5 | 3.3 | 3.7 | 2.0 |
| 4    | 0.1                              | 0.2 | 0.3 | 0.6 | 0.8 | 1.0 | 1.4 | 1.7 | 2.0 | 2.4 | 3.6  | 3.4                          | 2.9 | 2.4 | 1.5 | 2.0 | 0.7 |
| 5    | 0.9                              | 1.4 | 2.0 | 3.1 | 4.0 | 4.7 | 5.6 | 6.4 | 7.5 | 8.6 | 81   | 33                           | 21  | 13  | 6.9 | 4.9 | 2.6 |
| 6    | 0.2                              | 0.3 | 0.4 | 0.6 | 0.7 | 0.9 | 1.1 | 1.2 | 1.4 | 1.6 | 16   | 5.4                          | 3.6 | 2.4 | 1.5 | 1.6 | 0.6 |
| 7    | 0.3                              | 0.4 | 0.7 | 1.2 | 1.7 | 2.0 | 2.5 | 3.1 | 3.6 | 4.1 | 17   | 8.8                          | 6.2 | 4.7 | 3.5 | 3.1 | 1.3 |
| 8    | 0.3                              | 0.5 | 0.7 | 1.1 | 1.4 | 1.6 | 2.0 | 2.3 | 2.8 | 3.2 | 16   | 7.5                          | 4.8 | 3.2 | 2.0 | 1.6 | 0.6 |
| 9    | 0.1                              | 0.2 | 0.4 | 0.8 | 1.1 | 1.4 | 1.8 | 2.1 | 2.5 | 2.9 | 7.7  | 5.4                          | 4.3 | 3.4 | 2.5 | 2.0 | 0.9 |
| 10   | 0.1                              | 0.2 | 0.2 | 0.4 | 0.5 | 0.6 | 0.8 | 0.9 | 1.0 | 1.1 | 3.9  | 2.6                          | 2.2 | 1.7 | 1.3 | 1.2 | 0.4 |
| 11   | 0.1                              | 0.1 | 0.2 | 0.4 | 0.6 | 0.9 | 1.2 | 1.5 | 1.9 | 2.2 | 2.3  | 2.6                          | 2.1 | 1.8 | 1.4 | 1.5 | 0.8 |
| 12   | 0.2                              | 0.3 | 0.4 | 0.8 | 1.0 | 1.2 | 1.6 | 1.8 | 2.1 | 2.4 | 12   | 6.1                          | 4.6 | 3.5 | 2.0 | 1.8 | 0.6 |
| 13   | 0.0                              | 0.1 | 0.1 | 0.3 | 0.5 | 0.6 | 0.8 | 1.0 | 1.3 | 1.6 | 1.9  | 2.4                          | 2.0 | 1.7 | 1.1 | 1.3 | 0.6 |
| 14   | 0.1                              | 0.2 | 0.3 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 | 2.6  | 2.7                          | 2.2 | 1.8 | 1.6 | 1.3 | 0.6 |
| 15   | 0.1                              | 0.2 | 0.3 | 0.6 | 0.9 | 1.1 | 1.4 | 1.7 | 1.9 | 2.2 | 4.5  | 3.5                          | 3.0 | 2.7 | 1.7 | 1.7 | 0.5 |
| 16   | 0.2                              | 0.3 | 0.4 | 0.7 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 | 1.7 | 21   | 7.3                          | 4.2 | 2.7 | 1.7 | 1.7 | 0.8 |
| 17   | 0.1                              | 0.1 | 0.2 | 0.5 | 0.7 | 0.9 | 1.2 | 1.4 | 1.7 | 2.0 | 1.9  | 2.2                          | 2.1 | 1.9 | 1.2 | 1.3 | 0.5 |



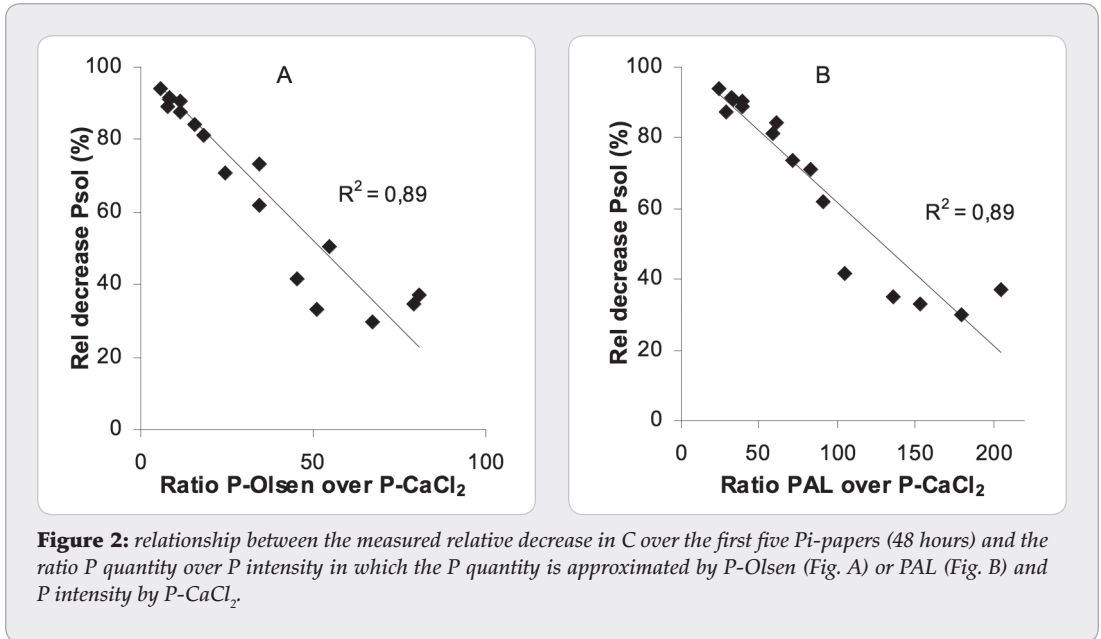
2). All soils buffer C because each Pi-paper removes more P than can be accounted for by the corresponding drop in concentration. The amount of P adsorbed to the first Pi-paper (contact time of 2 hours) ranges between 0.02 and 0.9 mmol kg<sup>-1</sup> and is comparable with the range in P intensity approximated by P-CaCl<sub>2</sub>. Over 10 successive Pi-papers (20 days) the cumulative amount of P transferred from soil to sink ( $Q_{cum}$ ) has increased and, depending on the soil, ranges between 8 – 100 times the amount of P extracted with the P-CaCl<sub>2</sub> method.  $Q_{cum}$  is comparable to or somewhat larger than the measure for P quantity as approximated by P-Olsen (0.8 – 1.9 times), and smaller compared to both PAL (0.3 – 0.8 times) and Pox (0.06 – 0.3 times).

In Figure 1 the change in correlation coefficient between the cumulative amount of P transferred from soil to Pi-paper ( $Q_{cum}$ ) and different soil tests of the 17 soils with cumulative number of Pi-papers are shown. In the short term  $Q_{cum}$  is related to the P intensity, here approximated with P-CaCl<sub>2</sub>. Despite the fact that  $Q_{cum}$  exceeds the amount of P extracted in a CaCl<sub>2</sub> extract already after the first Pi-paper (2 hours) the correlation between  $Q_{cum}$  and P-CaCl<sub>2</sub> is high ( $r^2 > 0.9$ ) for the first 5 Pi-papers (cumulative amount of time 48 hours). This shows that the predictive value of P-CaCl<sub>2</sub> may extend to the potential supply of a larger amount of P than is associated with this measure for P intensity. This may hold when considering a large range in P-CaCl<sub>2</sub>, however when the two soils (soil 2 and 5) with the highest P-CaCl<sub>2</sub> are excluded from the relationship the correlation decreases more rapidly ( $r^2 < 0.8$  after 3 Pi-papers). With continuous P desorption the correlation between P intensity and  $Q_{cum}$  decreases due to the difference between soils in their potential to buffer C during the continuous removal of P from the soil, i.e. the soil P buffer power. The predictive value of P intensity extends to a larger amount of potentially available soil P for soils with a high buffer power.

With continuous desorption  $Q_{cum}$  is increasingly related to a measure for P quantity as shown by the positive trend in increasing correlation with increasing number of Pi-papers (Fig. 1). Of the three selective extractions that may represent (part of) the P quantity PAL is best related to  $Q_{cum}$  followed by P-Olsen and Pox. For PAL, similarly to P-CaCl<sub>2</sub>, two soils (soil 2 and 5) have relatively high values with respect to the other soils. Excluding these two soils results in an overall lower correlation of PAL with  $Q_{cum}$  and the order in which the soil tests are correlated with  $Q_{cum}$



**Figure 1:** The correlation coefficient between a single test result and the available P during the desorption experiment as a function of the cumulative number of Pi-papers. Each correlation coefficient is calculated from the relationship between the soil test results of the initial soils and the cumulative amount of P transferred from soil to each successive Pi-paper. The soil tests are: P-CaCl<sub>2</sub> (diamonds), P-Olsen (circles), PAL (triangles), and Pox (double crosses). Two additional lines are shown for P-CaCl<sub>2</sub> and PAL in which the two soils with high P-CaCl<sub>2</sub> and high PAL (soil 2 and 5) are left out of the calculation (grey symbols instead of dark symbols).



changes to the highest correlation with P-Olsen, followed by PAL, and Pox. The change in correlation between single soil tests and C during the experiment shows a comparable trend; an initially high correlation with P-CaCl<sub>2</sub> but a decrease in this correlation with increasing desorption and an increasing correlation with a measure for P quantity.

A single soil test that is a measure for P intensity may thus give information on the initial soil P supply potential, and a single soil test that is a measure for P quantity may thus give information on the amount of P that can potentially desorb over a certain period of time. However, no information can be deduced concerning the change in supply potential during the removal of P from a soil. As described in the section concerning data interpretation and in accordance with the nutrient availability models (Barber 1995; Tinker and Nye 2000), the transfer rate of P from soil to sink is continuously a function of the prevailing P concentration in solution. The change in soil P supply potential is thus related to the capacity of the soil to buffer the concentration. The measured decrease in C after five Pi-papers relative to C<sub>0</sub> shows a high correlation with the ratio of a measure for P quantity over a measure for P intensity in which P intensity is approximated by P-CaCl<sub>2</sub> and P quantity by either P-Olsen ( $r^2 = 0.89$ ) or PAL ( $r^2 = 0.89$ , Fig. 2). For the ratio PAL over P-CaCl<sub>2</sub> soil 9 is discarded from the correlation because it contains a high CaCO<sub>3</sub> content (7%) and P adsorbed to CaCO<sub>3</sub> and Ca-P precipitate in the soil will dissolve at the pH in the PAL extract (Guidry and Mackenzie 2003) but will not contribute to P desorption at the pH level of the soil under natural conditions. For soils with a high CaCO<sub>3</sub> content PAL may thus give an overestimation of the P-quantity.

A combination of two soil tests, one representing a measure for the P intensity and another a measure for the P quantity, not only provides information concerning the initial supply potential and the amount reversibly adsorbed P, but through the ratio Q<sub>0</sub> over C<sub>0</sub> also provides an indication for the relative change in supply potential during continuous desorption. This may thus result in a first step in predicting the soil P supply potential. To be able to make a well considered decision

concerning the combination of soil tests that is needed to predict soil P supply potential with the desired accuracy, the absolute soil P supply potential will be considered in more detail.

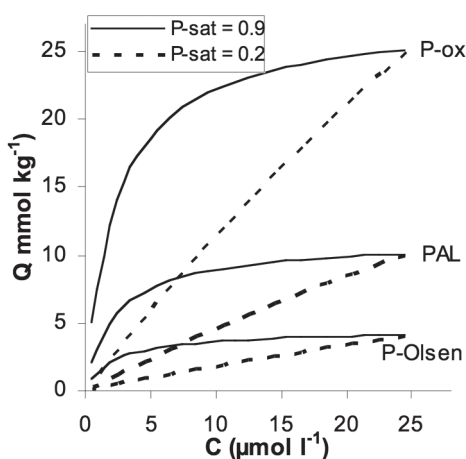
### Modeling soil P desorption

The soil P supply potential is measured by continuously removing P from a soil suspension using a successive number of Pi-papers. As the transfer of P from soil to Pi-paper is continuously a function of C, and C was found to continuously approximate equilibrium with the soil, the soil P supply potential is determined by the desorption isotherm of the soil. By combining the P adsorption (kinetics) to the Pi-paper (Eq. 1) and soil P desorption based on the Langmuir sorption isotherm (Eq. 2) the measured decrease in C and the corresponding cumulative P transfer to the ten successive Pi-papers can thus be modeled. The parameters of the adsorption (kinetics) to the Pi-paper are taken from a previous study (Van Rotterdam et al. 2009) in which  $k_a$  is  $0.003 \text{ l } \mu\text{mol}^{-1} \text{ hr}^{-1}$ ,  $k_d$  is  $0.005 \text{ hr}^{-1}$ , while  $Q_{\text{max,Pi}}$  for P is not constant but decreases gradually from 15 to  $5 \mu\text{mol P}$  per Pi-paper over approximately 28 hours.

To be able to derive a combination of (static) easy to measure soil tests that together are (minimally) needed to predict the (dynamic) soil P supply potential, the two parameters of the Langmuir equation are calculated *a priori* from standard soil tests. Which combination of soil tests gives the best results is decided by comparing the modeled results to the measured soil P supply potential using the Pi-papers.  $Q_{\text{max}}$  can be related to  $(\text{Fe}+\text{Al})_{\text{ox}}$  through a proportionality parameter  $\beta$  (Eq. 3) and K will be calculated from a combination of  $Q_{\text{max}}$ , a measure for P quantity ( $Q_0$ ) and a measure for P intensity ( $C_0$ , Eq. 4). When  $C_0$  is approximated by the P concentration in a  $\text{CaCl}_2$  extract and taking  $Q_{\text{max}}$  proportional to the  $(\text{Fe}+\text{Al})_{\text{ox}}$  content, the proportionality parameter ( $\beta$ , Eq. 3) and  $Q_0$  (Eq. 4) are the two variables that may be varied to calculate  $Q_{\text{max}}$  and K and thus the shape and scale of the desorption isotherm.

### Choice of $Q_0$ and $\beta$

The shape of the Langmuir isotherm may be divided into three regions. At low P saturation ( $Q_0/Q_{\text{max}}$  is much smaller than 1) the isotherm is linear and C decreases linearly with Q. With increasing



**Figure 3:** Hypothetical desorption curves in which  $Q_0$  is approximated by either P-Olsen, PAL, or Pox at a P-saturation (ratio  $Q_0$  over  $Q_{\text{max}}$ ) of either 0.9 (continuous lines) or 0.2 (dotted lines).

P-saturation the desorption isotherm becomes increasingly nonlinear. This continues until  $Q$  approaches  $Q_{\max}$  and the isotherm becomes linear again as the surface is saturated with P and an addition of P only results in an increase in C and in a negligible change in Q. At a low P saturation the Langmuir desorption isotherm approximates a linear relationship and the slope approximates the ratio Q over C. The ratio Q over C is in this case a measure for the soil P buffer power. When a soil is in this linear part of the isotherm at the start of the desorption experiment the choice of the extraction measure approximating  $Q_0$  has a large effect on the slope of the isotherm and thus on the calculated soil P buffer power as is illustrated in Figure 3. With increasing strength of the extractant approximating  $Q_0$ , the initial slope will thus be steeper corresponding with a larger soil P buffer power.

With increasing P-saturation the desorption isotherm becomes increasingly nonlinear and the slope of the isotherm (ratio dQ over dC) increasingly deviates from the ratio Q over C. In this case the buffer power (BP) is calculated by differentiating the Langmuir isotherm to C:

**Equation 5**

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

The buffer power decreases with an increase of the relative saturation of the soil ( $Q/Q_{\max}$ ) and is close to zero when the adsorption maximum is approached. In the nonlinear part of the isotherm there is thus a combined effect of the choice of  $Q_0$  and  $\beta$  to approximate K and  $Q_{\max}$  on the shape of the isotherm. The three investigated soil tests that may approximate P quantity (P-Olsen, PAL, and Pox), show quite a different range in amount of P extracted from the 17 soils. Pox is assumed to approximate the total inorganic P content (Van der Zee and Van Riemsdijk 1988), P-Olsen is assumed to approximate the readily desorbable P and PAL approximates a P fraction intermediate between P-Olsen and Pox. When approximating  $Q_0$  by either P-Olsen, PAL, or Pox but keeping K and the P-saturation equal by adapting  $\beta$ , the shape of the isotherm is steeper, i.e. the ratio dQ over dC increases, with increasing strength of the extractant (Fig. 3). When the desorption isotherm is nonlinear the buffer power is thus a function of both  $Q_{\max}$  and K which may be derived from the combination  $(Fe+Al)_{ox}$ ,  $\beta$ ,  $Q_0$  and  $C_0$ .

As the three measures for P quantity extract different fractions of P, a different proportion of the reactive surface area is associated with this fraction. The choice of  $\beta$  will thus differ with the chosen measure for  $Q_0$ . The sorption maximum associated with both P adsorption ( $Q_{\max}$ ) and total P sorption (sum of  $Q_{\max}$  and the maximal sorption due to slow reactions) have been shown to be related to the  $(Fe+Al)_{ox}$  content. The adsorption maximum of the readily desorbable P fraction ( $Q_{\max}$ ) was found to be approximated by 0.135 times  $(Fe+Al)_{ox}$  for noncalcareous acid soils that were pre-saturated with P (Van der Zee et al. 1988). The total sorption maximum associated with the total inorganic P content is related to  $(Fe+Al)_{ox}$  through a proportionality parameter  $\alpha_m$ , which was found to be 0.63 +/- 0.14 for 84 Dutch topsoils after equilibrium was approached at a P concentration of 5 mmol l<sup>-1</sup> (Van der Zee and Van Riemsdijk 1988).

In this study  $\beta$  is adapted with the chosen measure for  $Q_0$  and is assumed equal for all soils. When P-Olsen is used to approximate the readily desorbable P,  $\beta$  is assumed to be equal to 0.135. Similarly, when Pox is used to approximate the total inorganic P content (Van der Zee and Van Riemsdijk 1988),  $\beta$  ( $\alpha_m$ ) is assumed to be equal to 0.63. PAL approximates a P fraction intermediate

between P-Olsen and Pox and  $\beta$  is assumed to equal an intermediate value of 0.5. For soil 2  $\beta$  must be adapted to a larger value (0.7) when  $Q_0$  is approximated by Pox because otherwise  $Q_0$  exceeds  $Q_{\max}$  and K cannot be calculated. Overall the extractant chosen to approximate  $Q_0$  and the corresponding  $\beta$ , has a large effect on both the scale and shape of the calculated desorption isotherm.

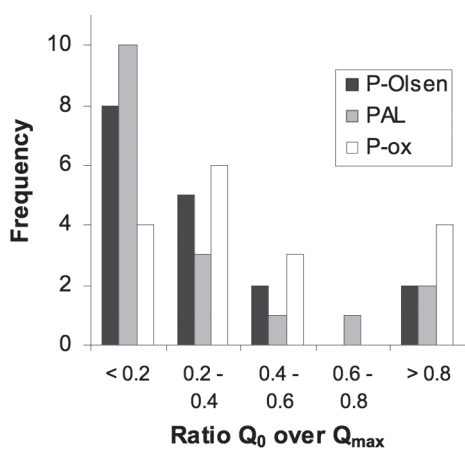
### Modeling P transfer from soil to Pi-paper for the 17 soils

Because the soil was found to continuously be in close equilibrium with the soil solution (Van Rotterdam et al. 2009), measuring the amount of P adsorbed to each successive Pi-paper and the corresponding P concentration in solution during the desorption experiment gives an impression of the shape of the desorption isotherm. As these measurements do not provide a fixed point of departure at  $t=0$  the choice of  $C_0$  and  $Q_0$  in the calculations are also used as a point of departure

**Table 3:** Calculated parameters of the Langmuir equation (Equation 2), in which  $Q_{\max}$  is calculated using equation 3 and K using equation 4, with varying choice for  $Q_0$  and  $\beta$ .

| Soil   | $Q_0 = \text{P-Olsen}, \beta = 0.135$ |                             |                  | $Q_0 = \text{PAL}, \beta = 0.55$    |                             |                  | $Q_0 = \text{Pox}, \beta = 0.63^*$  |                             |                  |
|--------|---------------------------------------|-----------------------------|------------------|-------------------------------------|-----------------------------|------------------|-------------------------------------|-----------------------------|------------------|
|        | $Q_{\max}$<br>mmol kg <sup>-1</sup>   | K<br>l $\mu\text{mol}^{-1}$ | $Q_0 / Q_{\max}$ | $Q_{\max}$<br>mmol kg <sup>-1</sup> | K<br>l $\mu\text{mol}^{-1}$ | $Q_0 / Q_{\max}$ | $Q_{\max}$<br>mmol kg <sup>-1</sup> | K<br>l $\mu\text{mol}^{-1}$ | $Q_0 / Q_{\max}$ |
| 1      | 11                                    | 0.01                        | 0.26             | 41                                  | 0.01                        | 0.17             | 51                                  | 0.03                        | 0.44             |
| 2      | 10                                    | 0.02                        | 0.52             | 36                                  | 0.04                        | 0.71             | 50                                  | 0.44                        | 0.97             |
| 3      | 12                                    | 0.10                        | 0.38             | 46                                  | 0.06                        | 0.26             | 58                                  | 0.14                        | 0.45             |
| 4      | 49                                    | 0.01                        | 0.03             | 180                                 | 0.01                        | 0.02             | 227                                 | 0.06                        | 0.17             |
| 5      | 9                                     | 0.01                        | 0.47             | 35                                  | 0.02                        | 0.56             | 44                                  | 0.09                        | 0.88             |
| 6      | 2                                     | 0.26                        | 0.81             | 6                                   | 0.46                        | 0.88             | 8                                   | 0.24                        | 0.8              |
| 7      | 9                                     | 0.03                        | 0.34             | 33                                  | 0.03                        | 0.30             | 41                                  | 0.06                        | 0.49             |
| 8      | 9                                     | 0.02                        | 0.20             | 35                                  | 0.01                        | 0.18             | 44                                  | 0.03                        | 0.34             |
| 9      | 32                                    | 0.01                        | 0.08             | 119                                 | 0.01                        | 0.05             | 150                                 | 0.04                        | 0.23             |
| 10     | 5                                     | 0.07                        | 0.21             | 17                                  | 0.06                        | 0.19             | 21                                  | 0.15                        | 0.37             |
| 11     | 41                                    | 0.02                        | 0.04             | 154                                 | 0.01                        | 0.03             | 193                                 | 0.10                        | 0.19             |
| 12     | 7                                     | 0.03                        | 0.26             | 25                                  | 0.03                        | 0.28             | 31                                  | 0.04                        | 0.34             |
| 13     | 31                                    | 0.02                        | 0.03             | 117                                 | 0.01                        | 0.03             | 147                                 | 0.09                        | 0.14             |
| 14     | 14                                    | 0.04                        | 0.10             | 53                                  | 0.05                        | 0.11             | 67                                  | 0.11                        | 0.22             |
| 15     | 13                                    | 0.03                        | 0.12             | 49                                  | 0.02                        | 0.08             | 61                                  | 0.07                        | 0.23             |
| 16     | 2                                     | 0.63                        | 0.93             | 7                                   | 2.35                        | 0.98             | 9                                   | 0.54                        | 0.92             |
| 17     | 38                                    | 0.02                        | 0.04             | 141                                 | 0.01                        | 0.02             | 178                                 | 0.07                        | 0.12             |
| Min    | 2                                     | 0.01                        | 0.03             | 6                                   | 0.01                        | 0.02             | 8                                   | 0.03                        | 0.12             |
| Max    | 49                                    | 0.63                        | 0.93             | 180                                 | 2.35                        | 0.98             | 227                                 | 0.54                        | 0.97             |
| Avg    | 17                                    | 0.08                        | 0.21             | 64                                  | 0.19                        | 0.20             | 81                                  | 0.14                        | 0.37             |
| Median | 11                                    | 0.02                        | 0.20             | 41                                  | 0.02                        | 0.17             | 51                                  | 0.09                        | 0.34             |

\* Except for soil 2 which  $\beta$  is 0.7 instead of 0.63, see text



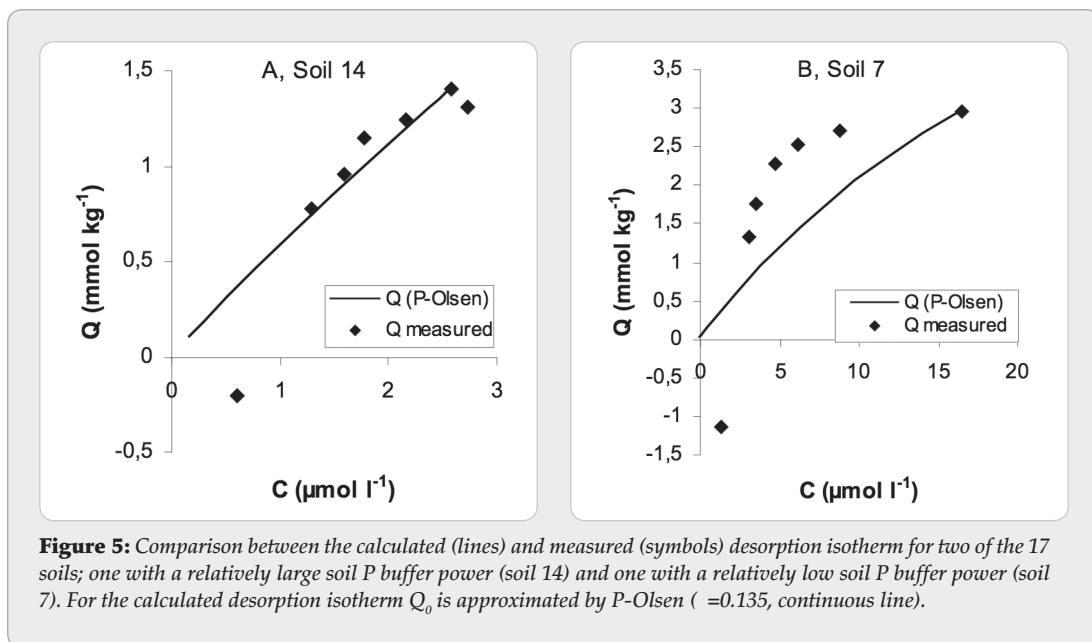
**Figure 4:** Frequency distribution of the calculated ratio  $Q_0$  over  $Q_{max}$  when  $Q_0$  is approximated by P-Olsen (black bars), PAL (grey bars), or Pox (white bars).

for the measured desorption isotherm. In this way the initial scale of the measured and calculated desorption isotherm are equal.

As shown in Table 3, approximating  $Q_0$  by P-Olsen, PAL, or Pox in combination with a corresponding fixed  $\beta$ , results in a large variation in the calculated  $Q_{max}$  and K for the 17 soils. The P-saturation, as approximated by the ratio  $Q_0$  over  $Q_{max}$  largely determines where the initial soil sample is situated on its isotherm. Figure 4 shows the frequency distribution of the calculated ratio  $Q_0$  over  $Q_{max}$  when  $Q_0$  is approximated by P-Olsen ( $\beta=0.135$ ), PAL ( $\beta=0.5$ ), or Pox ( $\beta=0.63$ ). This frequency distribution shows that (almost) half the soils show a P-saturation that is lower than 0.2 when  $Q_0$  is approximated by either P-Olsen (8 soils) or PAL (10 soils). Consequently, this approach results in a linear desorption isotherm for these soils. A high P-saturation ( $\geq 0.8$ ), resulting in a (highly) nonlinear desorption isotherm, is only found for two of the 17 soils when  $Q_0$  is approximated by P-Olsen or PAL. When  $Q_0$  is approximated by Pox four of the 17 soils have a P-saturation  $\geq 0.8$  (Table 3). Overall, the calculations show a tendency towards a more linear desorption isotherm for the majority of the soils. This is contrary to what is generally found and is also contrary to the measured desorption curves which are all to a varying degree nonlinear.

Despite this discrepancy between the shape of the calculated and measured isotherms, the overall best fit is found when  $Q_0$  is approximated by P-Olsen,  $Q_{max}$  by 0.135 times  $(Fe+Al)_{ox}$  and  $C_0$  by P-CaCl<sub>2</sub>. With increasing strength of the extractant approximating  $Q_0$  the slope of the isotherm increases, provided that the P-saturation is equal for the different measures for  $Q_0$  (Fig. 3). As a result the calculated desorption isotherm is too steep compared to the measurements when  $Q_0$  is approximated by either PAL ( $\beta=0.5$ ) or Pox ( $\beta=0.63$ ). This results in a (strong) overestimation of the potential desorbable soil P and an underestimation of the decrease in C. The soils for which the calculated initial P-saturation is relatively high ( $> \sim 0.8$ ) form an exception as the calculated desorption isotherm is strongly nonlinear and is generally in good agreement with the measured desorption isotherm.

In the following discussion we will focus on the calculations based on P-Olsen as this measure for  $Q_0$  resulted in the best prediction of the desorption isotherm of the 17 soils. The ratio of  $Q_0$  (mmol kg<sup>-1</sup>) over  $C_0$  ( $\mu\text{mol l}^{-1}$ ), which is easy to measure with two simple extractions, can be used to give

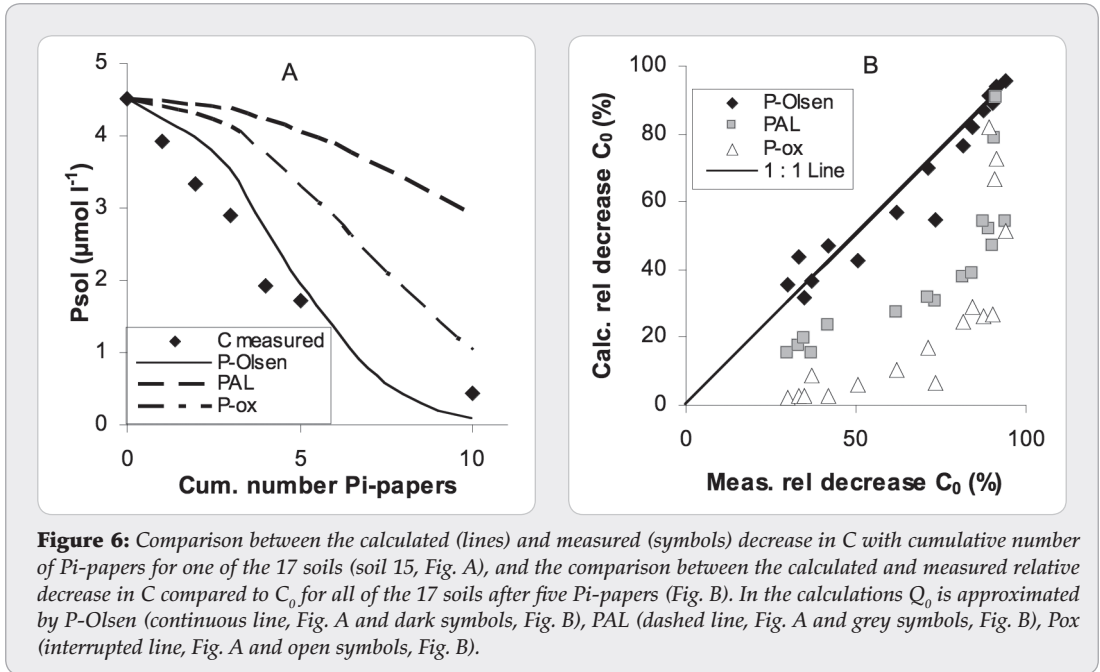


an indication of the initial soil P buffer power. For the soils that show a large soil P buffer power (ratio  $Q_0$  over  $C_0 > 40$ ,  $n = 6$ ), the calculated desorption isotherms are in good agreement with the measurements for the first five Pi-papers. An example of this good agreement is shown in Figure 5A for soil 14. Due to the large buffer power, these soils show an approximately linear desorption isotherm for the first five Pi-papers. However, contrary to the calculations, the P concentration after the tenth Pi-paper was removed is higher than expected from the linear desorption isotherm. The P concentration in solution was not measured for Pi-paper 6-9.

For the soils with a low soil P buffer power (ratio  $Q_0$  over  $C_0 < 40$ ,  $n=11$ ), the measured desorption isotherm is nonlinear. As mentioned before this nonlinear behavior is only found for the calculated desorption isotherm of two of these soils when  $Q_0$  is approximated by P-Olsen. For the other nine soils the shape of the calculated desorption isotherm is too linear in comparison with the measured desorption isotherm. An example of the discrepancy between the calculated and measured shape of the isotherm is shown in Figure 5B for soil 7. Similar to the soils with high buffer power, the P concentration after the tenth Pi-paper was removed is also higher than expected from the calculated desorption isotherm.

During the desorption experiment  $Q_{cum}$  exceeds the amount of P extracted with P-Olsen between the fifth and the tenth Pi-paper for all soils except for soil 3. When P-Olsen is depleted in the calculations this results in a decrease in C to very low values and a subsequent diminution in P transfer from soil to Pi-paper. The measurements however show that C is buffered at a higher concentration than expected from the calculations. In none of the soils where  $Q_{cum}$  exceeds P-Olsen does the measured C decrease to zero and the measurements also show a continuous desorption of P from the soil. Below a certain concentration the soil has a large capacity to buffer this concentration. The readily desorbable P approximated by P-Olsen must thus be replenished from a larger reservoir of soil P.

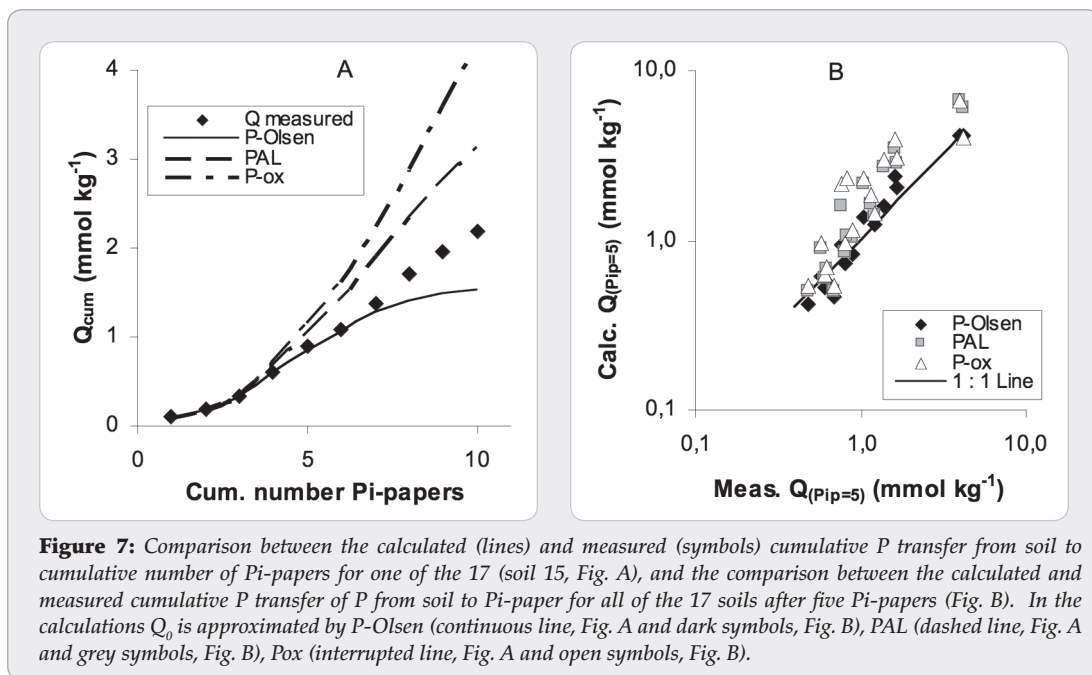
Predicting the soil P desorption isotherm comprises the prediction of both the cumulative transfer



of P from soil to Pi-paper and the decrease in C during the desorption experiment. In agreement with the best prediction of the desorption isotherm, the best prediction of both  $Q_{cum}$  and of the decrease in C for the first five Pi-papers is found when  $Q_0$  is approximated by P-Olsen,  $Q_{max}$  by 0.135 times (Fe+Al)<sub>ox</sub> and  $C_0$  by P-CaCl<sub>2</sub> compared to when  $Q_0$  is approximated by either PAL ( $\beta=0.5$ ), or Pox ( $\beta=0.63$ ). Figure 6 shows that there is a relatively good agreement between the measured and calculated decrease in C after five Pi-papers when  $Q_0$  is approximated by P-Olsen. This is illustrated for one of the 17 soils (soil 15) in Figure 6A and for all 17 soils in Figure 6B. It must be noted that the relative decrease in C is related to the ratio  $Q_0$  over  $C_0$  when  $Q_0$  is approximated by both P-Olsen and PAL (Fig. 2). Despite this good correlative relationship shown in Figure 2, using PAL leads to a strong underestimation of the absolute decrease in C due to an overestimation of the slope of the isotherm (Fig. 7). Figure 7 shows the relatively good agreement between the measured and calculated cumulative P transfer when  $Q_0$  is approximated by P-Olsen. Similar to Figure 6, this is illustrated for one of the 17 soils (soil 15) in Figure 7A and for all 17 soils in Figure 7B. As mentioned before, when  $Q_0$  is depleted this leads to an overestimation of the decrease in C (Fig. 6A) and a resulting underestimation of  $Q_{cum}$  (Fig. 7A). When considering the removal of an amount of P from a soil that exceeds P-Olsen of that soil, e.g. several cropping seasons, the replenishment of the readily reversible P from a larger P fraction must be considered. This larger P fraction might be approximated by Pox.

From a practical point of view the (Fe+Al)<sub>ox</sub> content is a relatively stable soil parameter and under normal soil management would only have to be measured once every 5 to 10 years. The rate with which the P specific soil tests change in the field will increase from Pox to P-Olsen to P-CaCl<sub>2</sub>. This will thus result in an increase in frequency with which these measures can be measured that increases from Pox to P-Olsen to P-CaCl<sub>2</sub>.





## CONCLUSIONS

The soil P supply potential can be predicted with various degrees of accuracy. To be able to make any prediction of the soil P supply potential a minimum of two parameters is needed; a measure for P quantity and a measure for P intensity. The accuracy of this prediction increases for soils with increasing soil P buffer power, i.e. with decreasing P saturation of the reactive surface area associated with the readily desorbable P. To increase the accuracy of this prediction for soils that don't have a high soil P buffer power, a measure for the reactive surface area of the soil must also be taken into account. In addition, to be able to extend the prediction of the soil P supply potential to an amount of P exceeding the amount of readily desorbable P a measure for the total amount of P must be included.

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*Chapter 4*

**SOIL P SUPPLY POTENTIAL: COMBINING  
ARTIFICIAL P SINK, RYEGRASS, AND  
STANDARD SOIL TESTS**

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## ABSTRACT

In practice phosphorus (P) fertilizer recommendations are based on interpreting the results of a single soil test. With the growing need to optimize fertilizer recommendation to encompass both agricultural and environmental aims there is also a growing need to increase the accuracy with which the soils P supply potential can be predicted. Both the choice of soil test and the interpretation of the results, offers room for improvement. In this study this is approached by studying the dynamic processes that determine the soil P supply potential and use this as a base to derive a combination of soil tests that can be used as a sound basis for future fertilizer recommendations.

In two dynamic approaches the soil P supply potential was investigated by the continuous removal of P from the soil by using an artificial P sink in the form of Fe oxide-impregnated papers (Pi-paper) and by growing ryegrass pot experiments. P uptake by both the artificial sink and the grass are continuously a function of the prevailing P concentration in solution (C) which is a function of the initial P concentration and the soil's capacity to buffer this concentration. This buffering was found to be relatively fast, resulting in equilibrium between the reversibly adsorbed P (Q) and the P concentration in the soil solution (C) as described in a soil specific desorption isotherm. The measured change in Q and C showed a comparable desorption isotherm as a result of the removal of P from the soil by an artificial sink and by uptake by ryegrass. The soil chemical processes involved in the transfer of P from soil to a Pi-paper sink were thus comparable to those involved in the transfer to the growing grass.

To evaluate if supply can meet demand, a deviation is made between soils with a P intensity that is high enough to sustain a flux to the root that is sufficiently high to meet demand and soils for which this intensity is too low, or becomes too low during the growing season to sustain this flux. In the pot experiments a P-CaCl<sub>2</sub> of ~ 100 μmol kg<sup>-1</sup> was found to be high enough to sustain a sufficiently high flux to the roots to meet demand. Environmental conditions and N fertilization did not seem to affect this value. The rate of change in P intensity due to P uptake, i.e. the soil P buffer power, could be approximated by the ratio of a measure for Q (P-Olsen or PAL) over a measure for C (P-CaCl<sub>2</sub>). P-CaCl<sub>2</sub> was found to strongly decrease during the experiments when the ratio of a measure for P quantity over P-CaCl<sub>2</sub> was lower than a certain critical level. These critical levels will deviate in the field situation due to e.g. differences in temperature and moisture level, rooting intensity, and when other crops are considered. Nevertheless the same principles are expected to apply for the field situation and the same concept can thus be used to derive a judgment of the P status and to derive a fertilizer advice that is appropriate for the field situation.

## INTRODUCTION

From both an agricultural and an environmental point of view different approaches have been used to understand the soil P supply potential. The two main approaches have been: (1) a static approach (basis of most fertilizer recommendations), and (2) a dynamic approach. In the static approach the P status of the soil at a certain point in time is established. This is commonly measured by means of standard soil tests. In routine laboratories these tests usually are extraction methods that extract a certain soil P fraction at a certain moment in time. In the dynamic approach soil P is assessed in terms of fluxes instead of pools. This is a more realistic approach as the transfer of P from soil to a sink, e.g. a plant root is the result of a combination of complex and interacting dynamic processes. The availability of soil P is the result of the rate with which P is removed from the soil system by the ad- or absorbing medium, the rate with which P is transported to this sink, and the rate with which P is released from the soil matrix. With continuous desorption P is removed from a continuum of phases (Frossard et al. 2000; Koopmans et al. 2004a). These may consist of reversibly adsorbed P to variably charged Fe- and Al (hydr-) oxides, partly directly soluble Fe-, Al-, and Ca- phosphate minerals, and of organic P forms that can readily be mineralized (Brady and Weil 2002). The dynamic processes involved in the transfer of P from soil to sink may be studied by the removal of P by growing crops. In order to gain insight in these processes the system may also be simplified compared to the growing crop by using an artificial P sink under standardized laboratory conditions.

Although the static approach greatly oversimplifies the concept of soil P supply potential it is very widely used due to its simplicity and cost- and labor effectiveness. On the other hand the dynamic approach is much more accurate but also more complicated to understand and laborious to execute. Due to the increased awareness (and legislation) that the excessive use of fertilizer, and especially P, leads to environmental problems routine soil laboratories are challenged to increase the accuracy of the fertilizer recommendations. To be able to achieve this more accurate prediction the soil test(s) must be based on the factors and processes that control nutrient availability (Mengel 1982; Skogley 1994). The objective of the present work is to couple the dynamic to the static approach to find a more mechanistic based combination of soil tests that together may form a solid basis for fertilizer recommendations and environmental studies concerning P. In a previous study the soil P supply potential was studied by mimicking the continuous removal of P by a crop using an artificial P sink. This soil P supply potential was subsequently predicted using a combination of soil tests. To be able to incorporate the gained insights into fertilizer recommendations, the processes that determine the soil P supply potential to an artificial sink and the combination of soil tests that is needed to describe and predict this supply potential is verified in pot experiments with grass. In addition, an assessment is made of when the soil P supply potential is sufficient to meet crop demand and when it becomes limiting.

## MATERIALS AND METHODS

### *Soil analyses*

Soil samples were collected from the plough layer (0-20cm) of ten agricultural sites in the Netherlands in 2004. The sites were chosen in a previous study (Van Erp 2002) and represent a wide range in soil type and P-status. The soils in this study are taken from the same fields as the soils used in the Van Rotterdam et al. (2009a) study but the sampling took place some 10 years later with common agricultural practice going on in the meantime. The clay content was determined using the sieve and pipet technique (NEN 5753), the CaCO<sub>3</sub> content using the volumetric method

(NEN 5757), and the organic carbon content using the sulfochromic oxidation (ISO 14235). The pH-KCl was determined in a 1: 5 (volume fraction) suspension of 1 M potassium chloride solution (ISO 10390). The P-status of the soils was characterized with the following extraction methods: 0.01M CaCl<sub>2</sub> (P-CaCl<sub>2</sub>) (Houba and Temminghoff 1999; Houba et al. 2000), acid ammonium oxalate (P-ox, Fe-ox, and Al-ox), (Schwertmann 1964), 0.5M NaHCO<sub>3</sub> (P-Olsen) (Olsen et al. 1954), and acid ammonium lactate (PAL) (Egnér et al. 1960).

Soil P supply potential of the 10 soils was studied using Fe oxide impregnated filter paper (Pi-paper), that is a strong artificial sink for P (Van der Zee et al. 1987), using the method described in Van Rotterdam et al. (2009b). In short a strip of Pi-paper (2 x 10 cm) was brought into contact with a soil suspension by attaching the strip to a holder that was attached to the top of a 50 ml polypropylene (greiner) tube containing 4 g soil and 40 ml 0.01M CaCl<sub>2</sub>. The tubes were gently shaken continuously end- over- end at 6 RPM. In order to assure continuous desorption the Pi-paper was replaced ten times at set time intervals by a new Pi-paper (2, 4, 8, 24, 48, 78, 145, 221, 337, 481 hours). After each Pi-paper was removed from the soil suspension it was thoroughly washed with demineralized water using an air brush (Chardon et al. 1996) and subsequently extracted with 20 ml 0.2M H<sub>2</sub>SO<sub>4</sub> to determine the amount of P adsorbed to the Pi-paper. To determine the P concentration in solution a sample was taken from the soil solution after centrifugation of the suspension directly after each of the first 5 and tenth Pi-paper were removed. Each experiment was performed in duplicate. P was measured spectrophotometrically with a segmented flow analyzer (Skalar) equipped with a 32 bits AD-converter.

### **Pot experiments**

In two pot experiment continuous P removal from the soil was studied by following the P uptake of grass during 6 weeks using the same ten Dutch agricultural soils as used in the above described Pi-paper desorption experiment. The first experiment was conducted in January and February 2006 using soil nr 2, 3, 4, 9, and 10 and the second was conducted in August and September 2006 using soil nr 1, 2, 5, 6, 7, and 8. In this way each experiment contained a combination of soils with a large variation in both general soil properties and P level. To be able to compare the experiments soil 2 was used in both pot experiments.

Depending on the soil pots were filled with 5 to 7 kg of soil that was brought to field capacity of the soil with nutrient solution and water. The pots (Mitscherlich) had a diameter of 20 cm and a height of 22 cm. In experiment 1 500 ml nutrient solution was added containing 5 mmol l<sup>-1</sup> CaCl<sub>2</sub>, 5 mmol l<sup>-1</sup> KNO<sub>3</sub>, 2.5 mmol l<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub>, 2.5 mmol l<sup>-1</sup> MgSO<sub>4</sub>. In experiment 2 400 ml nutrient solution was added containing 2.5 mmol l<sup>-1</sup> CaCl<sub>2</sub>, 12.5 mmol l<sup>-1</sup> KNO<sub>3</sub>, 20 mmol l<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub>, 2.5 mmol l<sup>-1</sup> MgSO<sub>4</sub>. The trace elements Fe, B, Mn, Zn, Cu, and Mo were added in both experiments. The soils were allowed to incubate for two weeks before 4 gram of grass seeds were sown on each pot. The weight loss due to evapo-transpiration was noted daily and compensated for using demineralized water. During the 6 weeks of growth per soil a duplicate set of separate pots were harvested at three time steps; 2, 4, and 6 weeks after sowing. From each pot grass was harvested and soil samples were taken. In experiment 1 the roots were also sampled at each time step by cautiously separating the roots from the soil by extensively washing the soil. Shoots and roots were dried at 70°C before the dry weight production was measured. Total P content of both the dried shoots and roots was measured by digestion with H<sub>2</sub>SO<sub>4</sub>, salicylic acid, hydrogen peroxide, and selenium (Novozamsky et al. 1983). Soil was dried at 40°C and sieved over 2 mm. In addition to the initial soils the selective P extractions were also performed at different time steps (2, 4, and 6 weeks after sowing). P-CaCl<sub>2</sub> was measured at each time step. P-Olsen and PAL were measured

after 2 and 6 weeks.

In separate pots the soil solution was sampled twice a week using rhizon soil moisture samplers (rhizons, Rhizosphere products) during the 6 weeks from sowing. The rhizons used in this study are thin polyethersulfone (PES) membranes of 10 cm length and a diameter of 2.5 mm and a pore size of  $<0.2 \mu\text{m}$ . The rhizons were placed horizontally at  $\sim 5$  cm from the top of the pot and connected to a 10 ml syringe through PVC/PE extension tubing. Soil solution was sampled by creating an under pressure using the syringe. All samples were acidified with  $10 \mu\text{l}$  5M HCl before the P concentration was measured. The pH was measured on a non acidified sub-sample. P was measured spectrophotometrically with a segmented flow analyzer (Skalar).

## RESULTS AND DISCUSSION

The results and discussion will be divided into three parts. In the first part the general results of the pot- and desorption experiments will be presented and placed into the perspective of a field situation, more specifically the situation in The Netherlands. In the second part the processes involved in the translocation of P from soil to both the growing grass and to the artificial Pi-paper sink will be compared and discussed. In the third part these processes will be translated to a combination of soil tests that together may give a prediction of the availability of soil P to a growing crop.

### *Pot- and desorption experiments in perspective*

#### *General soil properties*

The 10 soils show a large variation in the soil properties clay content, organic C content, and pH-KCl (Table 1). All soils contain no or a low ( $<1.7\%$ )  $\text{CaCO}_3$  content except soil 9 which contains  $7\%$   $\text{CaCO}_3$ . The 10 soils also show a large variation in P extractability both in P- $\text{CaCl}_2$ , which is a measure of the P intensity (Moody et al. 1988; Smethurst 2000) and in the measures representing P quantity which are P-Olsen, PAL, and P-ox (Table 1).

**Table 1:** General soil properties.

| Soil | Clay % | OC % | $\text{CaCO}_3$ % | pH-KCl | Fe-ox $\text{mmol kg}^{-1}$ | Al-ox $\text{mmol kg}^{-1}$ | P- $\text{CaCl}_2$ $\mu\text{mol kg}^{-1}$ | P-Olsen $\text{mmol kg}^{-1}$ | PAL $\text{mmol kg}^{-1}$ | P-ox $\text{mmol kg}^{-1}$ | Pss $\mu\text{mol l}^{-1}$ |
|------|--------|------|-------------------|--------|-----------------------------|-----------------------------|--|-------------------------------|---------------------------|----------------------------|----------------------------|
| 1    | 4      | 4    | -                 | 6      | 13                          | 58                          | 646  | 4.1                           | 25.4                      | 48                         | 103                        |
| 2    | 2      | 4    | -                 | 5.5    | 20                          | 72                          | 58   | 3.8                           | 11.9                      | 26                         | 4.3                        |
| 3    | 3      | 5    | -                 | 5.4    | 35                          | 35                          | 809  | 3.9                           | 19.6                      | 39                         | 147                        |
| 4    | 2      | 1    | 0.6               | 6.7    | 9                           | 3                           | 161  | 1.3                           | 5.3                       | 6                          | 51                         |
| 5    | 3      | 3    | -                 | 5.1    | 17                          | 48                          | 162  | 2.9                           | 9.6                       | 20                         | 25                         |
| 6    | 7      | 4    | 1.7               | 6.9    | 24                          | 10                          | 39   | 1.0                           | 3.2                       | 8                          | 5.9                        |
| 7    | 36     | 15   | -                 | 5.3    | 264                         | 43                          | 22   | 1.2                           | 4.0                       | 36                         | 1.8                        |
| 8    | 22     | 19   | -                 | 4.7    | 174                         | 59                          | 19   | 0.9                           | 3.0                       | 21                         | 1.2                        |
| 9    | 21     | 3    | 6.5               | 7.1    | 86                          | 20                          | 26   | 1.5                           | 6.1                       | 15                         | 4.7                        |
| 10   | 53     | 5    | -                 | 6      | 219                         | 63                          | 19   | 1.5                           | 2.6                       | 22                         | -                          |

**Table 2:** Plant characteristics 2, 4, and 6 weeks after sowing. In experiment 2 the total P uptake needed to calculate P uptake by mass flow is calculated from the linear relationship between P uptake in shoots and total uptake in experiment 1. In experiment 2 the roots were not sampled

| Exp | Soil nr | 2             |    |    | 4                                   |     |     | 6                                   |     |     | 2                         |      |     | 4 |  |  | 6 |  |  |
|-----|---------|---------------|----|----|-------------------------------------|-----|-----|-------------------------------------|-----|-----|---------------------------|------|-----|---|--|--|---|--|--|
|     |         | DW Shoots (g) |    |    | [P] shoots (mg kg <sup>-1</sup> dw) |     |     | PU shoots (mmol pot <sup>-1</sup> ) |     |     | P uptake by mass flow (%) |      |     |   |  |  |   |  |  |
| 1   | 2       | 2             | 7  | 13 | 6,6                                 | 4,4 | 3,4 | 0,4                                 | 1,0 | 1,5 | 1,7                       | 2,3  | 3,2 |   |  |  |   |  |  |
| 1   | 3       | 2             | 7  | 15 | 8,7                                 | 7,1 | 4,9 | 0,5                                 | 1,6 | 2,4 | 27                        | 35   | 31  |   |  |  |   |  |  |
| 1   | 4       | 2             | 7  | 14 | 6,8                                 | 5,1 | 3,8 | 0,5                                 | 1,2 | 1,7 | 4,5                       | 7,6  | 6,3 |   |  |  |   |  |  |
| 1   | 9       | 2             | 6  | 13 | 5,2                                 | 3,6 | 2,3 | 0,3                                 | 0,7 | 0,9 | 1,3                       | 2,0  | 2,5 |   |  |  |   |  |  |
| 1   | 10      | 1             | 5  | 12 | 4,4                                 | 3,4 | 2,4 | 0,2                                 | 0,6 | 0,9 | 0,0                       | 1,0  | 1,2 |   |  |  |   |  |  |
| 2   | 1       |               | 17 | 26 |                                     | 5,9 | 6,5 |                                     | 3,3 | 5,4 |                           | 12,0 | 8,5 |   |  |  |   |  |  |
| 2   | 2       |               | 17 | 24 |                                     | 4,2 | 4,1 |                                     | 2,3 | 3,2 |                           | 2,7  | 2,7 |   |  |  |   |  |  |
| 2   | 5       |               | 17 | 25 |                                     | 5,8 | 6,0 |                                     | 3,1 | 4,7 |                           | 5,8  | 4,5 |   |  |  |   |  |  |
| 2   | 6       |               | 17 | 25 |                                     | 3,4 | 2,9 |                                     | 1,8 | 2,3 |                           | 2,3  | 2,3 |   |  |  |   |  |  |
| 2   | 7       |               | 17 | 25 |                                     | 3,4 | 3,2 |                                     | 1,8 | 2,6 |                           | 0,6  | 0,6 |   |  |  |   |  |  |
| 2   | 8       |               | 17 | 27 |                                     | 2,8 | 2,4 |                                     | 1,5 | 2,0 |                           | 0,6  | 0,6 |   |  |  |   |  |  |

### Pot- and desorption experiments in perspective

The two pot experiments show a large difference in dryweight production of grass between the experiments whilst the difference in dryweight production between soils within an experiment is small (Table 2). The difference between experiments is mainly caused by the much lower light intensity in experiment 1 as it was conducted in winter compared to experiment 2, conducted in autumn. In addition to the lower light intensity N fertilization was also lower (5 mmol pot<sup>-1</sup> which coincides with ~ 22 kg N ha<sup>-1</sup>) in the first experiment compared to the second (21 mmol pot<sup>-1</sup> which coincides with 94 kg ha<sup>-1</sup>) which will also affect the dryweight production as grass is sensitive to N fertilization. When the dryweight production is expressed as ton dryweight per hectare the first experiment shows a yield of 4.3 +/- 0.4 ton ha<sup>-1</sup> and the second experiment 8.1 +/- 0.3 ton ha<sup>-1</sup> six weeks after sowing. For comparison the average first grass cutting in The Netherlands, grown for 6 to 10 weeks, has a yield of 1 – 2 ton ha<sup>-1</sup> when the pasture is used for grazing and a yield of 3 – 4 ton ha<sup>-1</sup> when the pasture is intensively managed. In the pot experiment the growth rate is higher compared to the field situation as the conditions are optimized as much as possible in the greenhouse concerning moisture, temperature, and light and also the plant density is higher.

The combination of relatively low N fertilization and the relatively large dryweight production compared to the field situation in the first pot experiment results in an N concentration in the shoots that decreases below the target value for the N concentration in ryegrass used in Dutch fertilizer recommendations (30 g kg<sup>-1</sup> dryweight) between 4 and 6 weeks after sowing for 4 of the 5 soils (not for soil 10). For this reason the N fertilization was increased in the second experiment. This resulted in an N concentration that was higher or approximately equal to this target value during the 6 weeks of growth despite the higher dryweight production.

In the first experiment the root dryweight production was measured at every time step and the root length was measured after the third time step (6 weeks). The root length was linearly related to the root dryweight production ( $r^2=0.97$ ,  $n=10$ ). The results also show a linear relationship



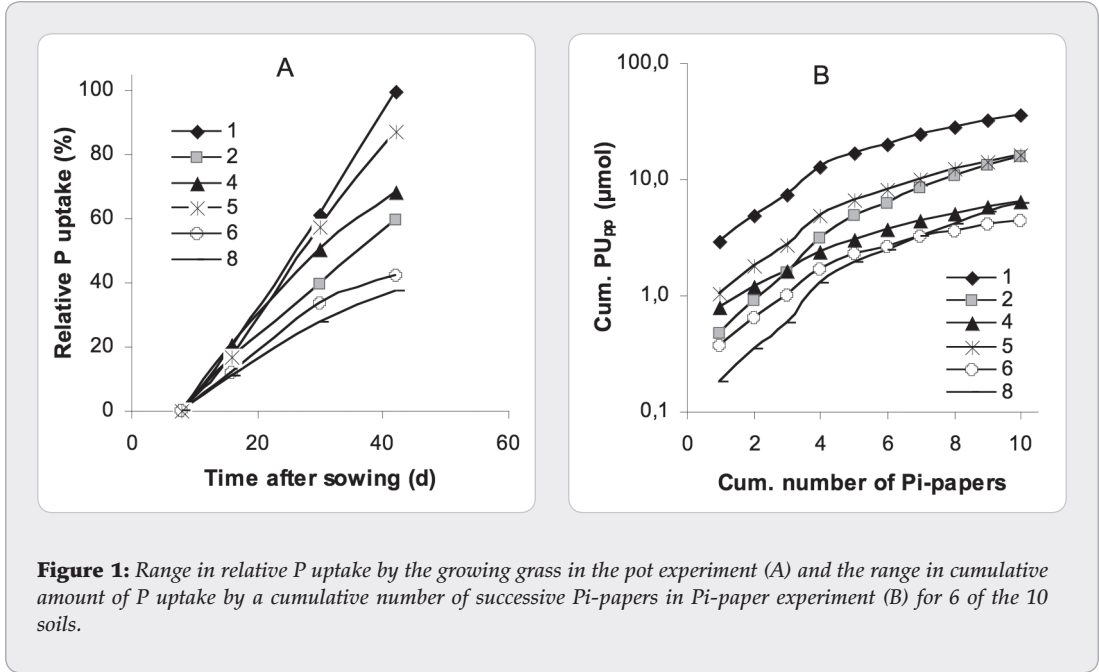
between dryweight shoots and dryweight roots 2, 4, and 6 weeks after sowing ( $r^2 = 0.97$ ,  $n=27$  excluding soil 3, 4, and 10 after 6 weeks). After 6 weeks soil 3, 4, and 10 deviate from this linear relationship because soil 3 and 4 have a higher root-shoot ratio probably due to N limitation and soil 10 has a lower root-shoot ratio probably due to relatively high N availability. At approximately equal growth conditions there is thus a linear relationship between root and shoot dryweight production. Extrapolating this linear relationship to experiment 2 shows that the higher light intensity and N fertilization in experiment 2 not only leads to a larger dryweight production of the shoots but also of the roots.

Of old, the target value of the P concentration in grass in Dutch fertilizer recommendations is 4 g P kg<sup>-1</sup> dryweight. To meet nutritional values for grass that is used for feed for dairy cows, for which grass is the main component of the diet, it should contain a minimum P concentration of 2.8 g P kg<sup>-1</sup> dryweight (Valk and Sebek 1999). For five (soil 6, 7, 8, 9, and 10) of the 10 soils the P concentration is lower than the target value after 4 weeks and after 6 weeks this is also the case for two more soils (soil 2 experiment 1 and soil 4). For soil 8, 9, and 10 the P concentration even decreases below the minimum nutritional value of 2.8 g kg<sup>-1</sup> dryweight for dairy cows between 4 and 6 weeks (Table 2).

The variation in P concentration in the shoots and the relatively small variation in dryweight results in a variation in the amount of P removed by the growing grass both between the two experiments and within each experiment (Table 2). The average P uptake by grass in the field may be calculated from the average P content (4.2 g kg<sup>-1</sup> dryweight for the years 1997 to 1999, data from soil testing laboratory Bgg, The Netherlands) and the average dryweight production (3 tons ha<sup>-1</sup>) and thus results in an average P removal of ~13 kg ha<sup>-1</sup> for the first cut of an intensively mowed grassland. In the first experiment the P removal (9 – 24 kg ha<sup>-1</sup>) is of the same order of magnitude but in the second experiment the grass removes more P (20 – 53 kg ha<sup>-1</sup>) from the soil in the same period of time. Overall the dryweight production and P removal show that the first experiment may be compared with the first cut of an intensively mowed pasture and that for the second experiment this is approximately twice as high.

To compare all soils from both pot experiments P uptake is first made relative to the P uptake from soil 2 in each of the two pot experiments as soil 2 is used in both experiments. Secondly P uptake is expressed relative to the maximum uptake measured in order to scale P uptake from the different soils to 100%. Figure 1a illustrates the variation in this relative P uptake for 6 of the 10 soils.

The large variation in soil properties and P extractability of the ten soils comes to expression in the Pi-paper desorption experiment through the large variation in both the cumulative amount of P transferred from each soil to the 10 successive Pi-papers and through the corresponding change in P concentration in solution measured as each successive Pi-paper was removed from the soil suspension (Table 3). The variation in cumulative P adsorption to each Pi-paper is illustrated in Figure 1b for 6 of the 10 soils. To put the Pi-paper desorption experiment into perspective the cumulative amount of P adsorbed to the successive number of Pi-papers can also be compared with the average P removal in the field. When assuming a bulk density of 1.4 kg l<sup>-1</sup> and a rooting depth of 10 cm the cumulative amount of P adsorbed by the Pi-papers can be expressed in kg P per ha soil. The 10 soils show a large variation in the amount of P adsorbed to the successive number of Pi-papers and when expressed in kg ha<sup>-1</sup> this amount is relatively large compared to P uptake in the field and P uptake in the pot experiment (Table 3). The amount of P adsorbed by the first Pi-paper is 5 kg ha<sup>-1</sup> (median value for the 10 soils, range 2 – 40 kg ha<sup>-1</sup>) and after the third Pi-paper the median cumulative amount of P adsorbed (15 kg ha<sup>-1</sup>, range 7 – 95 kg ha<sup>-1</sup>) is equal to the average amount of P removed by the grass during the first cut of intensively mowed



**Table 3:** Desorption properties of the soil to 10 successive Pi-papers, after 1 (= 2h), 5 (= 48h), and 10 (= 481h) Pi-papers.

| Soil | P desorbed mmol kg <sup>-1</sup> |       |        | P desorbed kg ha <sup>-1</sup> |       |        | [P] in solution µmol l <sup>-1</sup> |       |        | %       |
|------|----------------------------------|-------|--------|--------------------------------|-------|--------|--------------------------------------|-------|--------|---------|
|      | T=2h                             | T=48h | T=481h | T=2h                           | T=48h | T=481h | T=0h                                 | T=48h | T=481h |         |
|      | 1                                | 5     | 10     | 1                              | 5     | 10     | Ini                                  | 5     | 10     | 0 – 48h |
| 1    | 0.73                             | 4.1   | 8.9    | 34                             | 193   | 413    | 65                                   | 7.1   | 4.3    | 89      |
| 2    | 0.12                             | 1.2   | 3.9    | 5                              | 56    | 182    | 5.8                                  | 3.7   | 2.0    | 37      |
| 3    | 0.85                             | 4.0   | 8.6    | 40                             | 185   | 398    | 81                                   | 4.9   | 2.6    | 94      |
| 4    | 0.20                             | 0.8   | 1.6    | 9                              | 35    | 74     | 16                                   | 1.5   | 0.6    | 91      |
| 5    | 0.26                             | 1.7   | 4.1    | 12                             | 77    | 191    | 16                                   | 3.1   | 1.3    | 81      |
| 6    | 0.09                             | 0.6   | 1.1    | 4                              | 27    | 51     | 3.9                                  | 1.1   | 0.4    | 71      |
| 7    | 0.07                             | 0.6   | 2.1    | 3                              | 28    | 100    | 2.2                                  | 1.6   |        | 30      |
| 8    | 0.05                             | 0.5   | 1.5    | 2                              | 22    | 72     | 1.9                                  | 1.3   | 0.7    | 33      |
| 9    | 0.09                             | 0.6   | 1.6    | 4                              | 29    | 75     | 2.6                                  | 1.3   | 0.6    | 50      |
| 10   | 0.08                             | 0.7   | 2.0    | 4                              | 32    | 94     | 1.9                                  | 1.3   | 0.5    | 35      |

grassland. The amount of P removed from the soil by 10 successive Pi-papers is large compared to the amount of P removed by grass in the field (range 51 – 413 kg ha<sup>-1</sup>). The cumulative amount of P adsorbed by a successive number of Pi-papers thus shows a large variation between soils and depending on the number of Pi-papers may be quite large compared to the amount of P removed

by growing grass both in the field as in the pot experiment.

### ***P uptake by the growing grass***

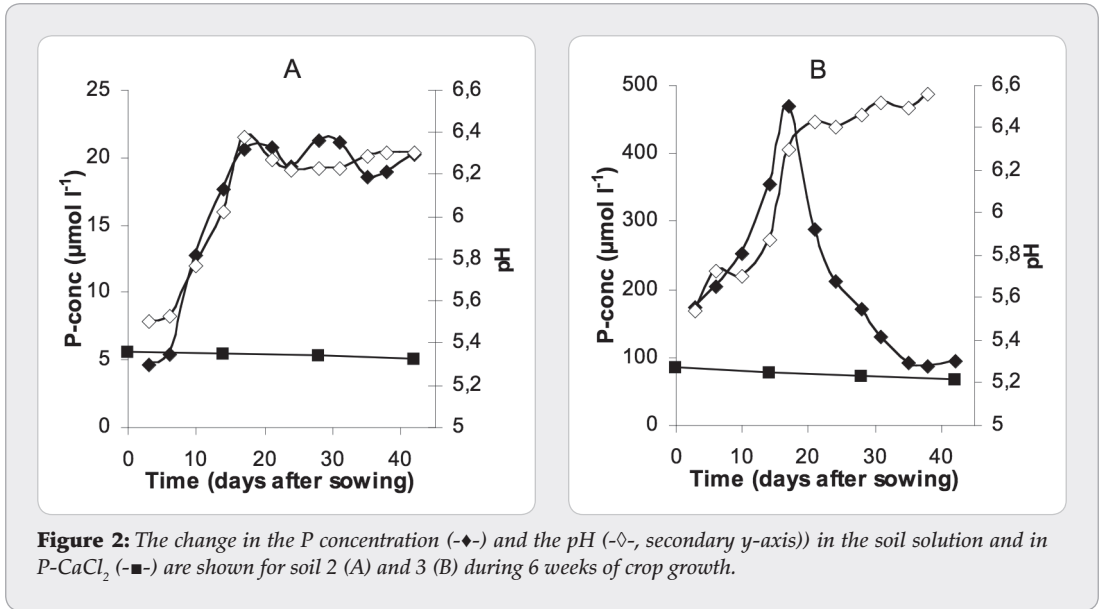
For plants P uptake varies with plant species, variety, temperature, plant age, root age, plant nutrient status, and nutrient concentration at the root surface. The main mechanisms regulating P uptake are the rate of P absorption per unit root and the size of the root system and for ryegrass both mechanisms have been found to be important (Föhse et al. 1988). The resulting effect on the potential P uptake from a soil is shown by the difference in P uptake between the two experiments (Table 2). The P uptake from soil 2 which was used in both experiments is, similar to the difference in dryweight production, approximately twice as high in the second experiment compared to the first experiment after 6 weeks. The P concentration in the shoots is also higher in the second experiment compared to the first experiment. The higher P uptake in combination with a higher P concentration indicates that a larger amount of soil is exploited for P and this is in agreement with the above described relationship between dryweight production of the shoots and roots. In this way the dryweight production of grass, which is related to environmental conditions (e.g. light and temperature) and N fertilization, determines the absolute P removal from one soil. Within each experiment and when comparing all soils by calculating the P uptake relative to soil 2 there is a large variation in relative P uptake between all soils and this difference increases over time (Figure 1a). This indicates that the environmental conditions and N fertilization affect the maximum P uptake, but the P uptake relative to this maximum is mainly determined by the soil P supply potential of the different soils.

### ***P concentration in soil solution and P-CaCl<sub>2</sub> during grass growth***

In both pot experiments the P concentration and the pH in the soil solution were monitored twice a week using rhizons. P-CaCl<sub>2</sub> was measured in the initial soil, at sowing, and 2, 4, and 6 weeks after sowing. The 10 soils show a large variation in P concentration in the soil solution (P<sub>ss</sub>), with concentrations at the time of sowing ranging between 1.3 (soil 8) and 150 (soil 3)  $\mu\text{mol l}^{-1}$  (Table 1). This range corresponds with the range found in Dutch agricultural soils (Chardon and Van Faassen 1999). At the time of sowing the P concentration in the CaCl<sub>2</sub> extract ( $\mu\text{mol l}^{-1}$ , Table 1) is linearly related to the P<sub>ss</sub> ( $r^2 = 0.93$ ) and is of the same order of magnitude. Because of the large dilution in the CaCl<sub>2</sub> extract (soil: solution ratio of 1: 10) compared to the situation in the pot experiments this shows that the soil has a large capacity to buffer the concentration in solution. It also implies that the environment in the CaCl<sub>2</sub> extract is comparable to the environment in the soil solution of the pot experiment.

Contrary to the expected decrease upon removal of P by the growing plant, P<sub>ss</sub> increased in the first two weeks after sowing for all soils. This increase varies between 1.6 and 6 times the initial P concentration and coincides with an increase in the pH of the soil solution (0.4 – 1.1 pH units) for nine of the 10 soils. An example for two soils (soil 2 and 3) is shown in Figure 2. In soil 9 no pH increase is observed because of pH buffering due to the presence of CaCO<sub>3</sub>.

The pH increase is related to the anion / cation balance in plants which results in a net efflux of OH<sup>-</sup> ions when NO<sub>3</sub><sup>-</sup> is the main N species in the soil solution (Gahoonia et al. 1992) as was the case in these experiments. The interaction between P<sub>ss</sub> and pH is complex but in general metal (hydr-)oxides become less positively charged with increasing pH resulting in a decrease in P adsorption and an increase in P<sub>ss</sub> (Antelo et al. 2005; Geelhoed et al. 1997a; 1997b). The effect of increasing P concentration may be amplified when Ca that would co-adsorb or co-precipitate with P is removed by uptake by the crop (Rietra et al. 2001). After approximately two weeks P<sub>ss</sub>

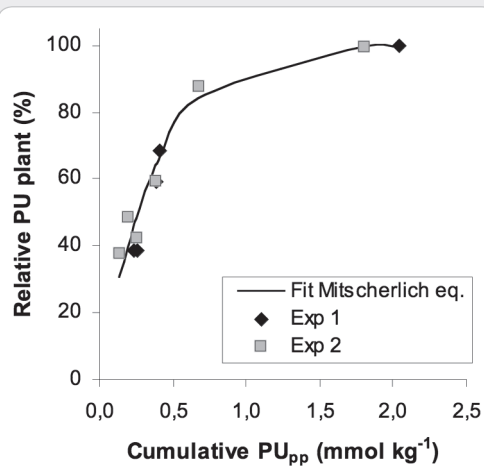


starts to decrease due to the continuous P uptake by the growing grass (Figure 2). The Pss as measured with the rhizons is thus very sensitive to changes in the soil environment probably as a result that the soil solution sample is extracted from a very restricted volume of soil comparable to the rhizosphere.

The large fluctuations found for Pss are not apparent in the CaCl<sub>2</sub> extract (Figure 2). The reason for this is that contrary to Pss the soil sample used for the CaCl<sub>2</sub> extraction is a mixed sample taken from a relatively large amount of soil that contains both rhizosphere and bulk soil. Furthermore the salt level and the Ca-concentration, which both affect the P adsorption (Antelo et al. 2005; Barrow et al. 1980; Rietra et al. 2001), are imposed in the extract and are variable in the soil solution. P-CaCl<sub>2</sub> may thus be a more robust measure for the P intensity of the soil than Pss as it is related to the initial Pss but is less prone to fluctuations.

### **Comparison between P transfer from soil to Pi-paper and from soil to growing grass**

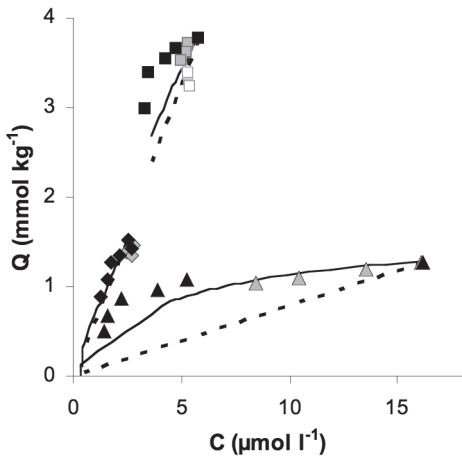
As was shown above P uptake by the growing grass ( $PU_{\text{grass}}$ ) in the pot experiments during 6 weeks may be compared with the first cut in an intensively mowed pasture (first experiment) or with twice this amount (second experiment). In the desorption experiment the soil P removal rate was much faster as the cumulative amount of P adsorbed to a successive number of Pi-papers (for convenience abbreviated as  $PU_{\text{pp}}$ ) was comparable to the first cut in an intensively mowed pasture after 3 Pi-papers (8 hours), or to approximately twice this amount after 5 Pi-papers (48 hours) and showed a large variation between soils. The faster soil P removal rate per kg soil in the desorption experiment compared to the pot experiment is because the Pi-paper sink is in maximal contact with the soil due to both the low soil-solution ratio (1 g per 10 ml or 0.01 kg l<sup>-1</sup>) and that the whole system is slowly but continuously shaken. In contrast there is a relatively small contact area between sink and soil in the pot experiment due to a relatively small fraction of the soil pore space that is occupied by roots, a high soil-solution ratio (5.9 kg l<sup>-1</sup> for sandy soils and 3.8 kg l<sup>-1</sup> for clay soils), and the low effective diffusion coefficient of P in soil.



**Figure 3:** The relationship between the relative P uptake by ryegrass after 6 weeks and the cumulative amount of P adsorbed by three successive Pi-papers ( $t=8$  hours). To compare all soils to each other P uptake is first made relative to the P uptake from soil 2 in each of the two pot experiments as soil 2 is used in both experiments. Secondly P uptake is expressed relative to the maximum in order to scale P uptake from the different soils to 100%. Data from the first pot experiment is depicted with the dark diamonds and from the second experiment with grey squares. A Mitscherlich equation is fitted to all data points.

Despite this difference in contact area and contact time between the soil and either the Pi-papers or the grass there is a close relationship between the relative  $PU_{grass}$  after 6 weeks and  $PU_{pp}$  by three cumulative Pi-papers ( $t = 8$  hours,  $n=10$ ), as shown in Figure 3. This relationship between  $PU_{grass}$  and  $PU_{pp}$  is curvilinear towards a maximum and can be described well with a Mitscherlich equation. This maximum in  $PU_{grass}$  for soils with a high soil P supply potential is determined by environmental conditions (e.g. light and temperature) and N fertilization. The difference in relative  $PU_{grass}$  between the ten soils is a function of the soil P supply potential and the close relationship with  $PU_{pp}$  (3 Pi-papers) indicates that the same processes involved in the transfer of P from soil to the artificial Pi-paper sink are also involved in the transfer of P from soil to the growing grass in the pot experiment.

The transfer of P from soil to roots is mainly determined by P diffusion (Barber et al. 1963; Bouldin 1961; Lewis and Quirk 1967). When neglecting P uptake by root interception, P uptake by diffusion in these pot experiments can be calculated by subtracting P uptake by mass flow from the total P uptake. P uptake by mass flow is calculated from the transpiration data and the measured P concentration in the soil solution. With the exception of soil 3, P uptake by mass flow in these experiments ranges between 0.6 to 8.5 % of the total P uptake (Table 2). This is comparable to the range of 0.01 - 4% found by various authors as described in (Jungk and Claassen 1997; Lambers et al. 1998). For soil 3 an exceptionally high value of approximately 30% of P uptake by mass flow is found. This may be explained by the combination of the extra investment in roots shown by the relatively high root-shoot ratio and the very high P concentration in the soil solution for this soil. For all soils the transport of P from the soil to the root is governed by diffusion, and the replenishment of the soil solution from the soils solid phase is thus important during crop growth. In the main nutrient bioavailability models the transfer of P from soil to root is based on the P concentration at the root surface which is calculated from the P concentration in solution, the soil P buffer power and the effective diffusion coefficient (Barber 1995; Jungk and Claassen 1997; Tinker and Nye 2000). Similar to the soil P supply potential to the Pi-paper sink, the soil P supply potential to the growing grass is a function of the initial P concentration in solution and the soils capacity to buffer this concentration.

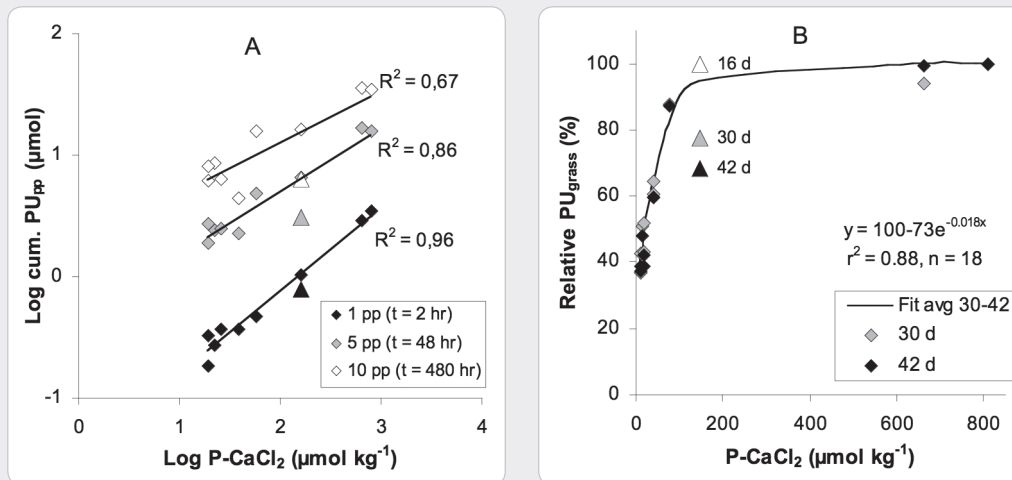


**Figure 4:** Desorption isotherm of three of the ten soils measured in the Pi-paper desorption experiment (dark symbols), first pot experiment (grey symbols), and the second pot experiment (open symbols), and calculated based on the Langmuir isotherm of which the parameters are approximated by a combination of soil tests (line) and calculated based on a linear isotherm (dotted line). The three soils are soil 2 (squares), soil 4 (triangles), and soil 9 (diamonds).  $Q_0$  and  $C_0$  are approximated by respectively P-Olsen and P-CaCl<sub>2</sub> of the initial soil

The initial flux of P from soil to sink (Pi-paper or plant roots) depends on the distribution of P in the initial soil. During P removal from the soil, the relationship between the decrease in P that is reversibly adsorbed P to the reactive surface sites ( $Q$ ) regulates the replenishment of the solution and the decrease in the P concentration in solution ( $C$ ). In the experimental setup used in this study, P desorption from the soil is faster than P adsorption to each successive Pi-paper (Van Rotterdam et al. 2009b). The P concentration in solution therefore remains in equilibrium with  $Q$ . The decrease in  $C$  is dictated by  $Q$  as described by a soil specific desorption isotherm. The desorption isotherm derived using the successive Pi-papers to remove P from the soil, is illustrated in Figure 4 for 3 of the 10 soils (soil 2, 4, and 9). In this figure the desorption isotherm as measured in the pot experiments is also shown for the same three soils. For both the desorption- and pot experiments the initial  $Q$  ( $Q_0$ ) at the start of the experiments is assumed to be approximated by P-Olsen and the decrease in  $Q_0$  is calculated by subtracting either  $PU_{pp}$  or  $PU_{grass}$ . For both experiments the initial  $C$  ( $C_0$ ) is approximated by P-CaCl<sub>2</sub>. The solution matrix in the desorption experiments was 0.01M CaCl<sub>2</sub> with a soil solution ratio of 0.1 kg L<sup>-1</sup>. To be able to compare both experiments the decrease in  $C$  is approximated by the measured decrease in P-CaCl<sub>2</sub> during the pot experiments. In the pot experiments P-CaCl<sub>2</sub> was also found to be a more robust measure for the P intensity than P<sub>ss</sub> (Figure 2). The lines in the figure will be discussed in a later section. Comparing the results of the desorption and the pot experiment shows a roughly comparable desorption isotherm and shows that the pot experiment corresponds with only a small part of the desorption isotherm as determined in the Pi-paper experiment. Overall the soil chemical processes involved in the transfer of P from soil to a Pi-paper sink are comparable to those involved in the P transfer from soil to growing grass in a pot experiment. The distribution of P in the initial soil and knowledge of the desorption isotherm together determine the soil P supply potential of a soil.

### **Coupling P transfer from soil to sink to standard soil tests**

To be able to use the insights from the Pi-paper desorption and pot experiment on a more routine basis the soil P supply potential will be coupled to a combination of soil tests that can be readily determined and together may form a solid basis for fertilizer recommendations and environmental



**Figure 5:** Relationship between the cumulative P uptake (to 1, 5, and 10 Pi-papers) and P-CaCl<sub>2</sub> (Figure A) and between the relative P uptake by ryegrass (4 and 6 weeks after sowing) and P-CaCl<sub>2</sub> (Figure B). In Figure B a Mitscherlich equation is fit to the data:  $y = 100 - 73e^{-0.018x}$ ,  $n = 18$  as soil 4 is excluded from the calculation, see text. The relative P uptake from soil 4 after 2 (open symbol), 4 (grey symbol) and 6 weeks (dark symbol) is indicated with triangles instead of diamonds.

studies concerning P.

As shown in the previous section a measure for the P intensity, e.g. P-CaCl<sub>2</sub> will only be predictive for the initial transfer rate of P from soil to P sink and with continuous desorption this predictive value will decrease due to the difference in soil P buffer power (BP) between the soils. This is illustrated in Figure 5a in which the correlation coefficient between PU<sub>pp</sub> and P-CaCl<sub>2</sub> decreases from 0.96 after the first Pi-paper to 0.86 after the fifth (~ growing season) to 0.67 after the tenth Pi-paper. The effect of the difference in BP between the soils is illustrated for soil 4 (indicated with triangles in Figure 5a) which has a relatively small BP as shown by the large decrease in P concentration in solution after 5 and 10 Pi-papers (Table 3) and the flat initial desorption isotherm (Figure 4). With continuous desorption this results in a lower PU<sub>pp</sub> than expected from the initial P-CaCl<sub>2</sub>. In the pot experiment the relative P uptake after 2, 4, and 6 weeks is also related to P-CaCl<sub>2</sub> of the initial soil and the relationship is approximately equal after 4 and 6 weeks (Figure 5b). Comparable to the relationship between PU<sub>grass</sub> and PU<sub>pp</sub> (Figure 3) the relationship between PU<sub>grass</sub> and P-CaCl<sub>2</sub> is curvilinear towards a maximum and can be described with a Mitscherlich equation. In the calculation of this Mitscherlich equation soil 4 (indicated with triangles in Figure 5b) is omitted because, similar to the results in the desorption experiment, soil 4 shows a relatively large decrease in P-CaCl<sub>2</sub> during the 6 weeks of growth also resulting in a lower PU<sub>grass</sub> than expected from the initial P-CaCl<sub>2</sub>. In addition to a measure for P intensity a measure for the soils capacity to buffer this intensity is needed.

The soil P buffer power of a soil is directly related to the slope of the desorption isotherm (ratio dQ over dC) (Barrow 1967). In the most simple approach the initial BP can be approximated by the ratio Q over C which is a linear approximation of the slope of the desorption isotherm. In Figure 4 the linear desorption isotherm based on the ratio P-Olsen over P-CaCl<sub>2</sub> is shown by

the dotted line. When assuming a Langmuir isotherm the accuracy of approximation of the BP by the ratio Q over C is high for soils that contain a low P-saturation (= ratio Q over  $Q_{\max}$ ) as the Langmuir isotherm is linear at low P-saturation and the corresponding slope is indeed equal to the ratio Q over C. With increasing P-saturation the isotherm becomes increasingly nonlinear and approximating the slope with the ratio Q over C is increasingly erroneous. Incorporating a measure for the soil's adsorption maximum ( $Q_{\max}$ ) was found to increase the accuracy of predicting the relative decrease in C during a Pi-paper desorption experiment (Van Rotterdam et al. 2009a) in which  $Q_{\max}$  was approximated by a fraction of the  $(\text{Fe}+\text{Al})_{\text{ox}}$  content. The Langmuir desorption isotherm may be calculated *a priori* from a combination of soil test results of the initial soil by approximating  $Q_0$  by P-Olsen,  $C_0$  by P-CaCl<sub>2</sub>,  $Q_{\max}$  by a fraction of the  $(\text{Fe}+\text{Al})_{\text{ox}}$  content and the affinity constant K by a combination of  $Q_0$ ,  $C_0$ , and  $Q_{\max}$  (for the exact calculations see Van Rotterdam et al. (2009a)). The thus calculated Langmuir isotherm is shown in Figure 4 (continuous line) for three of the ten soils. For the soils with a low initial P-saturation the thus calculated Langmuir isotherm is approximately equal to a linear desorption isotherm based solely on  $Q_0$  and  $C_0$  (soil 2 and 9 in Figure 4). Soils with a high initial P-saturation (also indicated by a low ratio  $Q_0$  over  $C_0$ , e.g. soil 4 in Figure 4) indeed show an increased accuracy in predicting the desorption isotherm when incorporating a measure for  $Q_{\max}$  in the calculations.

In the Pi-paper desorption experiment the variation in BP between soils is shown by the difference in the relative decrease in P concentration in solution compared to the initial P concentration and ranges between 30% (large BP) and 94% (small BP, Table 2) after 5 Pi-papers. As was also shown in Van Rotterdam et al. (2009a) the relative decrease in C after 5 Pi-papers during the desorption experiment is indeed related to the ratio P-Olsen over P-CaCl<sub>2</sub> ( $r^2 = 0.87$ ) and the ratio PAL over P-CaCl<sub>2</sub> ( $r^2 = 0.90$ ). Because soil 9 contains ~7% CaCO<sub>3</sub> the acid PAL extraction will overestimate P availability due to the dissolution of Ca-phosphates and this soil is thus excluded from the correlations involving PAL. For the correlations involving P-Olsen all soils are considered.

In the pot experiment the decrease in P intensity can be shown by the P concentration in solution (Pss) and by P-CaCl<sub>2</sub>. The decrease in Pss is difficult to quantify because Pss first increases corresponding with an increase in pH and at the point the concentration starts to decrease the concentration may not have reached a maximum (Figure 2). As a rough indication the decrease in Pss is quantified as the relative decrease between the P concentration 6 weeks after sowing and the maximum P concentration which, depending on the soil, occurs around 2 weeks after sowing. The thus calculated decrease in Pss varies between 5 and 85 %. Comparable to the relative decrease in C in the Pi-paper experiment this decrease in Pss in the pot experiment is also linearly related to the ratio P-Olsen over P-CaCl<sub>2</sub> ( $r^2 = 0.55$ ) and the ratio PAL over P-CaCl<sub>2</sub> ( $r^2 = 0.69$ , excluding soil 9). As described above P-CaCl<sub>2</sub> is a more robust measure for the P intensity in the pot experiment than Pss. The decrease in P-CaCl<sub>2</sub> relative to P-CaCl<sub>2</sub> at sowing varies between 0 and 50%. Again this decrease is linearly related to the ratio P-Olsen over P-CaCl<sub>2</sub> ( $r^2 = 0.94$ ) and the ratio PAL over P-CaCl<sub>2</sub> ( $r^2 = 0.59$ , excluding soil 9) but only when omitting soil 1, 3, and 5. These soils are omitted because P uptake by the grass has reached a maximum for these soils and P-CaCl<sub>2</sub> thus decreases less than expected from the ratio Q over C.

Overall the ratio P-Olsen over P-CaCl<sub>2</sub> and the ratio PAL over P-CaCl<sub>2</sub> give a rough indication for the relative decrease in C during both the transfer of P from soil to Pi-paper and from soil to growing grass. The ratio Q over C is thus a measure for the change in P availability during continuous desorption.

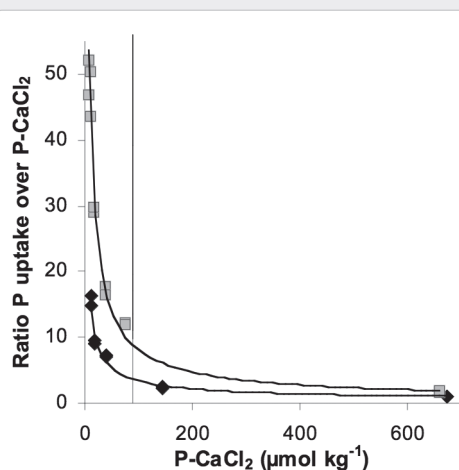


### **P supply versus demand**

In practice a single soil test result is generally used to deduce the soil P status and compare this status with a critical soil P level associated with a certain crop. The critical soil P level is defined as the P level of a soil that ensures that per unit root, supply meets demand throughout the growing season (Van Noordwijk et al. 1990). Based on the previous sections this results in a division between soils with a P intensity that is sufficiently high to sustain a flux to the root that is sufficiently high to meet demand for good quality grass (with a sufficient P concentration in the grass) and soils for which this intensity is too low, or becomes too low during the growing season to sustain this flux. In the following it will be evaluated when the soil P supply potential can meet demand for ryegrass based (among others) on the results of the two pot experiments.

The soil P intensity level that is sufficient to meet demand during a growing season is specific to the plant species in question and can be derived from soils with a high soil P buffer power (Föhse et al. 1988). From the relationship between  $PU_{\text{grass}}$  and  $P\text{-CaCl}_2$ , the  $P\text{-CaCl}_2$  at which 90% of the relative P uptake is achieved is calculated using the Mitscherlich equation (Figure 5b) and is found to occur at a  $P\text{-CaCl}_2$  of  $110 \mu\text{mol kg}^{-1}$ . Environmental conditions and N fertilization do not seem to affect this value of  $110 \mu\text{mol kg}^{-1}$  as data from both experiments show comparable results. These results are in agreement with Bolland and Guthridge (2007) who also found that N fertilization did not affect the level of applied P to achieve 90% of the maximum P uptake. In addition Dear et al. (1992) found the critical soil P concentration ( $P\text{-CaCl}_2$ ) to be comparable between the field and a pot experiment for subterranean clover. This suggests that soil P supply meets the P demand of ryegrass as long as the  $P\text{-CaCl}_2$  of the soil is maintained above a value of  $\sim 110 \mu\text{mol kg}^{-1}$ .

This is also shown by comparing the amount of P in a  $P\text{-CaCl}_2$  extract with the amount of P taken up by the growing grass in the pot experiments. Because  $P\text{-CaCl}_2$  is a measure for the P intensity the contribution of  $P\text{-CaCl}_2$  in replenishing the soil solution during P uptake by a growing crop is assumed to be small. However, comparing the amount of P taken up by the grass after 6 weeks with the amount of P extracted using the  $\text{CaCl}_2$  method shows that in soils with a high P intensity the crop may take up a comparable amount as extracted with  $P\text{-CaCl}_2$  when expressed per kg soil (0.6 times  $P\text{-CaCl}_2$  in soil 3 experiment 1 and 1.3 times  $P\text{-CaCl}_2$  in soil 1 experiment 2). A comparable

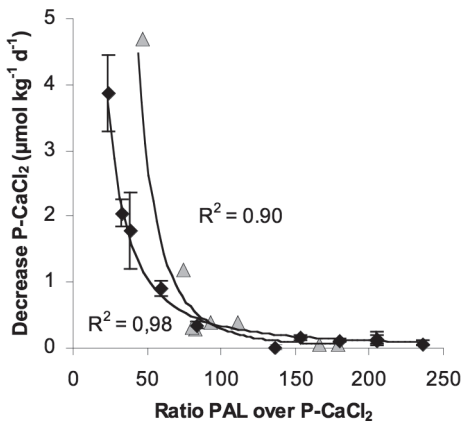


**Figure 6:** The ratio P uptake by ryegrass after 6 weeks over  $P\text{-CaCl}_2$  as a function of  $P\text{-CaCl}_2$ . Experiment 1, diamonds and experiment 2, squares. A line at  $P\text{-CaCl}_2$  equals  $90 \mu\text{mol kg}^{-1}$  is also shown.

result was found by Hylander et al. (1995) for fertilized soils. For soils with a low P intensity the amount taken up by the crop far exceeds the amount extracted with P-CaCl<sub>2</sub> (16 times in soil 10, experiment 1, and ~50 times in soils 7 and 8 experiment 2). Figure 6 shows that the ratio P uptake by grass over P-CaCl<sub>2</sub> is related to the initial P-CaCl<sub>2</sub> and can be described using a power function ( $r^2=0.988$  experiment 1 and  $r^2=0.994$  experiment 2). The point at which the ratio P uptake over P-CaCl<sub>2</sub> starts to rapidly increase is graphically derived to be at P-CaCl<sub>2</sub> below ~100  $\mu\text{mol kg}^{-1}$  for both experiments. Overall P quantity becomes increasingly important in replenishing the soil solution with decreasing P intensity, especially below a P-CaCl<sub>2</sub> of ~100  $\mu\text{mol kg}^{-1}$ .

Whether or not this flux is maintained depends on the buffer power of the soil. The absolute decrease rate of P-CaCl<sub>2</sub> during the pot experiments is calculated by the slope of the linear regression of P-CaCl<sub>2</sub> over time, measured at sowing and 2, 4, and 6 weeks after sowing. The rate of decrease in P-CaCl<sub>2</sub> is significant (slope  $\neq 0$ ,  $P \leq 0.05$ ) for 7 of the 10 soils. For soil 2, 9, and 10 the decrease in P-CaCl<sub>2</sub> during the 6 weeks of the experiment is not significant. The decrease in P-CaCl<sub>2</sub> over time is related to the ratio  $Q_0$  over  $C_0$  as shown by the relationship between this decrease and the ratio PAL over P-CaCl<sub>2</sub> in Figure 7 and can be described using a power function ( $r^2=0.98$  excluding soil 10). The decrease in P-CaCl<sub>2</sub> over time rapidly increases when the ratio PAL over P-CaCl<sub>2</sub> decreases below a ratio of ~100 as is graphically derived from Figure 7. The ratio P-Olsen over P-CaCl<sub>2</sub> shows a similar relationship ( $r^2 = 0.95$ ) and a rapid increase in the rate of decrease in P-CaCl<sub>2</sub> at a ratio of ~30. These results are based on P uptake on a relatively short time scale. The effect of P uptake on P-CaCl<sub>2</sub> can be studied for a much longer time-scale using the data from a pot experiment described by Koopmans et al. (2004b) where P is mined in a greenhouse pot experiment from a P enriched non-calcareous sandy soil by P uptake and removal by grass in 31 successive harvests during a 978 day period. At nine time steps the soil was sampled and P-CaCl<sub>2</sub> and PAL were determined. The data from this mining experiment show the same trend: a rapid increase in the decrease in P-CaCl<sub>2</sub> over time when the ratio PAL over P-CaCl<sub>2</sub> drops below a ratio of ~100 (Figure 7).

Based on the results of P uptake by ryegrass in the two pot experiments soils with a P-CaCl<sub>2</sub> that is maintained above 100  $\mu\text{mol kg}^{-1}$  is high enough to sustain a sufficiently high flux to the roots. Data



**Figure 7:** The relationship between the decrease in P-CaCl<sub>2</sub> and the ratio PAL over P-CaCl<sub>2</sub> during P uptake by growing grass during 6 weeks in a pot experiment (diamonds) and in a mining experiment (triangles, Koopmans et al. 2004).

from the two pot experiments and from a long term mining experiment (Koopmans et al. 2004b) show that the absolute decrease in P-CaCl<sub>2</sub> over time during grass growth increases strongly when the ratio PAL over P-CaCl<sub>2</sub> decreases below ~100 or when the ratio P-Olsen over P-CaCl<sub>2</sub> decreases below ~30. These values will be different for the field situation due to e.g. differences in temperature and moisture level, rooting density, and when other crops are considered. Nevertheless the same principles are expected to apply for the field situation and the same concept can thus be used to derive a judgment of the P status and to derive a fertilizer advice that is appropriate for the field situation.

## CONCLUSIONS

Comparing two pot experiments to a Pi-paper desorption experiment showed that the same soil chemical processes involved in the transfer of P from soil to the artificial Pi-paper sink under standardized conditions in the laboratory were also involved in the transfer of P from soil to the roots of growing ryegrass. For ryegrass the maximum P uptake was determined by environmental conditions (e.g. temperature and light intensity) and N fertilization but the P uptake relative to this maximum was mainly determined by the soil P supply potential of the different soils. The transfer flux of P from soil to either the Pi-paper or roots was a function of the prevailing P intensity and was thus a function of the initial P intensity and the soils capacity to buffer this intensity. The buffer power is directly related to the slope of the desorption isotherm. To be able to make a prediction of the soil P supply potential on a routine basis both the initial P intensity and the desorption isotherm must be approximated by a combination of standard soil tests. As an indicator for the initial P intensity P-CaCl<sub>2</sub> was found to be a more robust measure than the P concentration in solution as it was related to the initial P concentration in solution but was less prone to fluctuations. The buffer power as measured by the relative decrease in P intensity during both the Pi-paper desorption experiment and the pot experiments could be approximated by the ratio of a measure for the P quantity (e.g. P-Olsen or PAL) over a measure for the P intensity (P-CaCl<sub>2</sub>) both measured in the initial soil provided the isotherm is still in its linear part. In case of a non linear isotherm also information on the P adsorption maximum, or in other words on the amount of reactive surface sites is required.

These results may be used to couple soil P supply potential to crop demand during a growing season. Soils may thus be divided into soils with a P intensity that is high enough to sustain a flux to the root that is sufficiently high to meet demand during a growing season and soils for which this intensity is too low, or becomes too low during the growing season to sustain this flux. In the pot experiments a P-CaCl<sub>2</sub> of ~ 100 μmol kg<sup>-1</sup> was found to be high enough to sustain a sufficiently high flux to the roots to meet demand. In addition P-CaCl<sub>2</sub> was found to strongly decrease during the experiments when the ratio PAL over P-CaCl<sub>2</sub> was lower than ~100 or when the ratio P-Olsen over P-CaCl<sub>2</sub> was lower than ~30. These values will deviate in the field situation due to e.g. differences in temperature and moisture level, rooting intensity, and when other crops are considered. They however do illustrate the soil chemical concept of using a combination of two standard soil tests to estimate the soil P supply potential during continuous removal of soil P.

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*Chapter 5*

**THE POTENTIAL OF SOILS  
TO SUPPLY POTASSIUM DURING UPTAKE  
BY RYEGRASS**

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## ABSTRACT

To gain a more comprehensive understanding and prediction of the dynamic soil K supply potential, the changes in soil K fractions during K uptake by a growing crop have been studied. For this purpose, the initial and change in K concentration in the soil solution ( $K_{ss}$ ) measured *in situ* was monitored in combination with the change in K-CaCl<sub>2</sub> exchangeable K ( $K_{exch}$ ), non-exchangeable K ( $K_{nexch}$ ), and K uptake during the intensive growth of ryegrass in a pot experiment in the greenhouse. The soils show a variation in affinity for K between soil groups of different texture, as expressed by the soil K exchange coefficient. This affects the distribution of the directly available K fraction over  $K_{ss}$  and  $K_{exch}$ . Contrary to expectations, this does not affect the availability of  $K_{exch}$  for the growing grass. The difference in  $K_{ss}$  between soil groups of different texture is compensated for by the difference in soil K buffer power. This results in an approximately equal availability of  $K_{exch}$  as K uptake shows a close relationship with the readily available K fraction ( $K_{ss} + K_{exch}$ ). To predict the availability of soil K on the short term a measure for this readily available K appears to be sufficient for all soils. For longer timescales a distinction must be made between soils that can and cannot buffer this readily available K. For the soils in this study a distinction based on soil texture is sufficient but for soils of widely varying origin the clay mineralogy must also be considered. Although the contribution of  $K_{nexch}$  to the total soil K supply potential is generally accepted, in our relatively short experiment (6 weeks)  $K_{nexch}$  is only found to contribute for the silt and clay soils and not for the sandy soils. For sandy soils the soil K supply potential is thus solely determined by the readily available K. For silt and clay soils the soil K supply potential is determined by both  $K_{exch}$  and  $K_{nexch}$ . The absolute contribution of  $K_{nexch}$  in these soils will depend on the type of crop but an estimation may be based on the ratio of a measure for  $K_{nexch}$  over a measure for  $K_{exch}$ .

## INTRODUCTION

Potassium (K) is an essential nutrient for plant growth and in this context K supply potential of soils has been studied extensively. To be able to understand and predict soil K supply potential both the distribution of K in the soil and the release (rate) upon removal of K from the soil must be understood. The distribution of K in the soil can be divided into K in the soil solution ( $K_{ss}$ ), exchangeable K ( $K_{exch}$ ), non-exchangeable K ( $K_{nexch}$ ), and structural K in K bearing minerals ( $K_{min}$ ) (Barber 1995; Sparks and Huang 1985).  $K_{exch}$  are ions that are adsorbed by outer-sphere surface complexes or are adsorbed in the diffuse ion swarm and are predominantly bound by electrostatic binding mainly to clay minerals and organic matter (Sposito 1989). The preference for binding K is relatively high compared to an ion like sodium and is similar to that of ammonium.  $K_{nexch}$  is strongly bound in cavities between two opposing siloxane planes in 2:1 clay minerals e.g. illite (Sposito 1989) and involves dehydration of the adsorbing ion. This K is generally referred to as non-exchangeable since most other cations have no affinity for this configuration (Ca, Mg, and Na). Although most soil K (~90%) is present as  $K_{min}$  (Sharpley 1989) the release rate due to weathering is generally too small to meet crop demand (Pal et al. 2001).

In routine soil laboratories the soil K supply potential is often based on the approximation of  $K_{nexch}$ ,  $K_{exch}$ , or  $K_{ss}$ , using selective extractions. The most commonly used extractant is a 1M  $NH_4OAc$  extraction (McLean and Watson 1985) which assesses the readily available K ( $K_{exch} + K_{ss}$ ). Several other methods extracting a similar fraction are in use, e.g. 0.1M HCl, ammonium lactate/acetic acid (Egnér et al. 1960), 0.1M  $BaCl_2$  (Gillman 1979). A slightly weaker extraction method is 0.01M  $CaCl_2$  (Houba et al. 2000). This method has the advantage of being a multi-nutrient extraction method. The 0.01M  $CaCl_2$  extraction has been suggested to approximate the bioavailable fraction of nutrients in soil (Houba et al. 1996; Houba and Novozamsky 1998) as the extract has more or less the same ionic strength as the average salt concentration in the soil solution of agriculturally used soils.

For the supply of K to a growing crop the roots take up K from the soil solution. Because the amount of K in the soil solution is relatively small compared to K uptake by a crop,  $K_{ss}$  is subsequently replenished or buffered by cation exchange. This forms the basis for calculating K uptake by a growing crop in the main nutrient bioavailability models (Barber 1995; Tinker and Nye 2000). In accordance herewith, the critical soil K value for  $K_{ss}$  below which plants respond to K fertilization, was found to be a function of the soil K buffer power in pot experiments (Mengel and Busch 1982) and in field experiments (Schneider et al. 2003). In these studies  $K_{ss}$  was assumed to be replenished from  $K_{exch}$  and the buffer power was derived from the relationship between  $K_{exch}$  and  $K_{ss}$  in exchange isotherms ( $BP_{exch}$ ). In the nutrient bioavailability models  $BP_{exch}$  is approximated by the ratio  $K_{exch}$  over  $K_{ss}$  as the initial isotherm is assumed to be linear (Barber 1995; Silberbush and Barber 1983; Tinker and Nye 2000).

$K_{nexch}$  has frequently been found to contribute substantially to K uptake by crops e.g. (Cox et al. 1999; Hoagland and Martin 1933; Mengel and Uhlenbecker 1993) in which case the total soil K buffer power ( $BP_{tot}$ ) is a combination of buffering from  $K_{exch}$  ( $BP_{exch}$ ) and buffering from  $K_{nexch}$  ( $BP_{nexch}$ ) (Schneider 1997; Wang et al. 2004). In soils low in  $K_{exch}$  the  $BP_{tot}$  may even be dominated by  $BP_{nexch}$  (Wang et al. 2004). The contribution of  $BP_{nexch}$  to the total soil K buffer potential can be assessed separately to the contribution of  $BP_{exch}$  or in combination. The  $BP_{exch}$  is generally derived from the relationship between  $K_{exch}$  and  $K_{ss}$  in exchange isotherms for which equilibrium is assumed, indicating that this buffering is fast. The availability of the  $K_{nexch}$  has been found to be related to the release rate, which depends on the type of K-bearing minerals, and the level of depletion of  $K_{ss}$  (Martin and Sparks 1985). A measure for the release dynamics of  $K_{nexch}$  has been

found to be an indicator for K uptake by itself (Mengel and Uhlenbecker 1993; Singh et al. 1983) or in combination with  $K_{\text{exch}}$  (Nair et al. 1997; Schmitz and Pratt 1953).

Instead of approximating the soil K supply potential by a combination of a measure for the readily available K and the soil K buffer power ( $BP_{\text{tot}}$  or  $BP_{\text{exch}}$  or  $BP_{\text{nexch}}$ ), the contribution of  $K_{\text{nexch}}$  has also been incorporated directly by replacing the standard soil test that approximates the readily available K by a stronger extractant that approximates both  $K_{\text{exch}}$  and  $K_{\text{nexch}}$  e.g. by sodium tetraphenyl-boron ( $\text{NaBPh}_4$ , (Smith and Scott 1966), boiling 1M  $\text{HNO}_3$ , or concentrated  $\text{H}_2\text{SO}_4$  (Hunter and Pratt 1957). The procedures that simultaneously extract  $K_{\text{exch}}$  and  $K_{\text{nexch}}$  have been found to give a better prediction of plant available K than a measure for  $K_{\text{exch}}$  (Cox et al. 1999; Hunter and Pratt 1957; Mengel and Uhlenbecker 1993). This approach however ignores the dynamic processes behind the transfer of K from soil to plant root.

The actual soil K supply potential is determined by a combination of interacting processes in which the replenishment of the soil solution may comprise both buffering from  $K_{\text{exch}}$  and buffering from  $K_{\text{nexch}}$ . These contributions may be assessed by the associated quantities of K or to their release dynamics. From the above it follows that there is a large variation in possible approximations of the total K supply potential of a soil. In practice however nutrient management strategies are generally based on a single soil test, in most cases approximating  $K_{\text{exch}}$  (McLean and Watson 1985).

The aim of this paper is to gain a more comprehensive understanding and prediction of the dynamic soil K supply potential. This is approached by studying the concentration and amount of K in solution in a dilution experiment in which the soil solution composition is mimicked by using a 0.01M  $\text{CaCl}_2$  matrix. In addition, the initial and change in: (i) K concentration in the soil solution ( $K_{\text{ss}}$ ) measured in situ, (ii) K extracted using a standard 0.01M  $\text{CaCl}_2$  method, (iii) exchangeable K ( $K_{\text{exch}}$ ), (iv) non-exchangeable K ( $K_{\text{nexch}}$ ), and (v) K uptake are studied during the intensive growth of ryegrass in a pot experiment in the greenhouse. Insight in the change in these soil fractions and availability to the grass is used to assess a possible combination of standard soil tests that are practically feasible to measure in routine soil laboratories and together give a good description of the soil K supply potential.

## **MATERIALS AND METHODS**

Soil samples were collected in 1990 from the plough layer (0-20 cm) of 15 Dutch agricultural soils. The sites were chosen in a previous study and represent the variation in Dutch agricultural soils except peat soils (Van Erp 2002b). The clay content was determined using the sieve and pipet technique (NEN 5753), the  $\text{CaCO}_3$  content using the volumetric method (NEN 5757), and the organic carbon content using the sulfochromic oxidation (ISO 14235). Acid ammonium oxalate extractable Fe and Al ( $\text{Fe}_{\text{ox}}$  and  $\text{Al}_{\text{ox}}$ ) were determined according to (Schwertmann 1964). The size and saturation ratio of the CEC was determined using an un-buffered  $\text{BaCl}_2$  method (Gillman 1979) and modified according to (Van Erp 2002a). The K-status of the soils was characterized with the following extraction methods: 0.01M  $\text{CaCl}_2$  (Houba et al. 2000), 0.1M  $\text{BaCl}_2$  (Gillman 1979; Van Erp 2002a), and 3M  $\text{H}_2\text{SO}_4$  (Hunter and Pratt 1957).

### ***Dilution experiment***

To gain some understanding in the distribution of K over the soils exchange sites and the soil solution and the change in this distribution during K removal a dilution experiment is performed under standardized conditions in the laboratory. The matrix is 0.01M  $\text{CaCl}_2$  as this mimics the composition of the soil solution of agricultural soils. In the experiments the soil- solution ratio (SSR) is varied from, 1, 0.1, 0.02, and 0.01  $\text{kg l}^{-1}$ . This is performed for 9 of the 15 soils (soil nr 1,



3, 5, and 10-15). After centrifugation the extract is filtered and the K concentration in solution is measured by flame atomic emission spectrometry (AES).

### Pot experiment

In a pot experiment continuous K removal from the soil was studied by following the K uptake by Ryegrass and the change in  $K_{ss}$ ,  $K_{exch}$  and  $K_{nexch}$  during 6 weeks using 15 Dutch agricultural soils. The pot experiment was designed to investigate K availability and therefore all nutrients were added except K. The pots, which contained approximately 1 kg of soil, were incubated at field capacity for a week before the grass seeds were sown. There were four series performed in duplicate: in three of these series grass was grown for either 2, 4, or 6 weeks and in the fourth no grass was sown (blank). The grass was full grown after 4 weeks and to ascertain continuous removal of K between 4 and 6 weeks the grass was cut after 4 weeks in the pots that were grown for 6 weeks.

At each time step dry weight, and nutrient content of both the shoots and roots was determined. Shoots and roots were dried at 70°C before the dry weight production was measured. Total K content of both the dried shoots and roots was measured by digestion with  $H_2SO_4$ , salicylic acid, hydrogen peroxide, and selenium (Novozamsky et al. 1983). Soils were dried at 40°C and sieved over 2 mm. Of the initial soil, at sowing and at each time step in both the pots with and without plants K, Mg, Na, P, N and S were measured in a standard 0.01M  $CaCl_2$  extract (Houba et al. 2000) and exchangeable K, Ca, Mg and Na were measured in a 0.1M  $BaCl_2$  extract.

In separate series pots the soil solution was sampled twice a week using rhizon soil moisture samplers (rhizons, Rhizosphere products) during the 6 weeks from sowing. The rhizons used in this study are thin polyethersulfone (PES) membranes of 10 cm length and a diameter of 2.5 mm

**Table 1:** Some general soil characteristics of the 15 soils

| Soil | < 2 $\mu m$<br>% | Textural<br>group | Org C<br>% | $CaCO_3$<br>% | pH- $CaCl_2$ | pH-KCl | Fe-ox<br>mmol $kg^{-1}$ | Al-ox<br>mmol $kg^{-1}$ | CEC- $BaCl_2$<br>cmol $kg^{-1}$ |
|------|------------------|-------------------|------------|---------------|--------------|--------|-------------------------|-------------------------|---------------------------------|
| 1    | 0,9              | Sand              | 1,0        | 0,5           | 6,5          | 7,0    | 9                       | 4                       | 4,5                             |
| 2    | 1,7              | Sand              | 3,8        | -             | 4,5          | 4,2    | 29                      | 55                      | 3,5                             |
| 3    | 2,0              | Sand              | 0,6        | 0,7           | 6,8          | 7,2    | 10                      | 3                       | 3,2                             |
| 4    | 5,0              | Sand              | 1,0        | -             | 6            | 6,0    | 31                      | 24                      | 3,6                             |
| 5    | 5,4              | Sand              | 2,2        | -             | 5,2          | 5,0    | 48                      | 33                      | 5,1                             |
| 6    | 6,4              | Sand              | 3,7        | -             | 5,6          | 5,6    | 342                     | 19                      | 14                              |
| 7    | 10               | Silt              | 3,3        | -             | 5,6          | 5,5    | 93                      | 33                      | 12                              |
| 8    | 11               | Silt              | 0,9        | -             | 5,7          | 5,5    | 50                      | 19                      | 5,8                             |
| 9    | 17               | Silt              | 1,6        | -             | 6,3          | 6,0    | 42                      | 30                      | 12                              |
| 10   | 22               | Clay              | 2,3        | 1,9           | 6,9          | 7,0    | 45                      | 27                      | 25                              |
| 11   | 27               | Clay              | 14         | -             | 5,5          | 5,2    | 132                     | 58                      | 33                              |
| 12   | 28               | Clay              | 3,3        | -             | 4,5          | 4,1    | 114                     | 21                      | 17                              |
| 13   | 30               | Clay              | 8,3        | -             | 4,9          | 4,5    | 252                     | 46                      | 25                              |
| 14   | 42               | Clay              | 3,1        | 0,8           | 7,3          | 7,0    | 114                     | 41                      | 40                              |
| 15   | 46               | Clay              | 1,9        | 3,5           | 7,5          | 7,3    | 163                     | 43                      | 35                              |

and a pore size of  $<0.2 \mu\text{m}$ . The rhizons were placed horizontally approximately halfway each pot and connected to a 10 ml syringe through PVC/PE extension tubing. Soil solution was sampled by creating an under pressure using the syringe. The soil solution was monitored over time by extracting an *in situ* soil solution sample twice a week. Rhizons were placed in pots with plants and in pots without plants. The concentration of K, Ca, Mg, Na, S, P, and N in the soil solution was monitored in all these pots.  $K_{ss}$  is measured by sampling the soil solution in-situ during the pot experiment by means of rhizon samplers,  $K_{exch}$  is approximated by subtracting  $K_{ss}$  from K extracted with 0.1M  $\text{BaCl}_2$  ( $K\text{-BaCl}_2$ ), after  $K_{ss}$  is converted to the same unit.  $K_{nexch}$  is approximated by subtracting  $K\text{-BaCl}_2$  from K extracted with 3M  $\text{H}_2\text{SO}_4$ . In this way the amount of K extracted with 3 M  $\text{H}_2\text{SO}_4$  is the sum of  $K_{ss}$ ,  $K_{exch}$ , and  $K_{nexch}$  and in the following it is assumed to approximate the total amount of soil K available for the growing grass ( $K_{TA}$ ). The amount of K extracted in a standard 0.01M  $\text{CaCl}_2$  extract (SSR 0.1  $\text{kg l}^{-1}$ ) is referred to as  $K\text{-CaCl}_2$  and exists of  $K_{ss}$  and part of  $K_{exch}$  (Van Erp et al. 1998).

## RESULTS AND DISCUSSION

### Initial soil K status

The soils represent a wide range in general soil properties (Table 1); e.g. in clay content (0.9–46%), pH  $\text{CaCl}_2$  (4.5–7.5) and org C content (0.6–14%). CEC is correlated to clay content ( $r^2=0.87$ ). The soils also show a large variation in amount of soil K and the distribution of this K over the different K fractions (Table 2). This is shown by the large variation in  $K_{ss}$  (0.07–13  $\text{mmol l}^{-1}$  or 0.02–2.7  $\text{mmol kg}^{-1}$ ),  $K\text{-CaCl}_2$  (0.6–9  $\text{mmol kg}^{-1}$ ),  $K_{exch}$  (1.2–21  $\text{mmol kg}^{-1}$ ),  $K_{nexch}$  (0.1–33  $\text{mmol kg}^{-1}$ ), and in  $K_{TA}$  (1.7–47  $\text{mmol kg}^{-1}$ ). When the 15 soils are divided into three groups of different texture (sand  $n=6$ , silt  $n=3$ , and clay soils  $n=6$ ) a difference in the average  $K_{TA}$  and the average distribution of this K over  $K_{nexch}$ ,  $K_{exch}$ , and  $K_{ss}$  is observed (Fig.1). The amount of  $K_{TA}$  shows an increasing trend with increasing clay content of the textural soil groups. This is mainly the result of an increase in  $K_{nexch}$  and to a smaller extent to a decrease in  $K_{ss}$ . Because K “fixing” clay minerals, mainly illite, are generally (dominant) present in Dutch agricultural soils (Kuipers 1984) an increase in clay content thus corresponds with an overall increase in the soil’s capacity to very strongly bind K, approximated by  $K_{nexch}$ .

### Exchange of K

The behavior of K can only be understood in relation to the other main cations; Ca, Mg, and Na. We will only consider the exchange of K by Ca, as Ca is the main cation in solution and on the exchange complex for all soils. The (Gaines-Thomas) exchange coefficient, based on the reaction in which Ca on the exchange complex is exchanged by K ( $K_{K/Ca}$ ) can be calculated from the measured data:

Equation 1

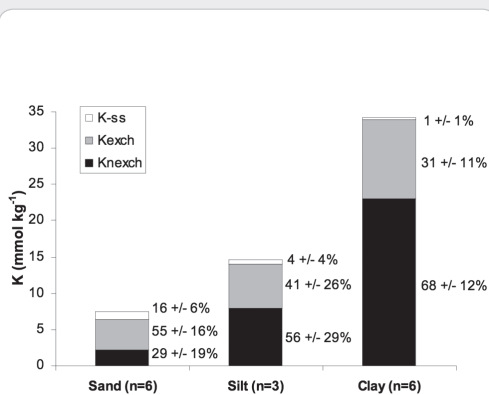
$$K_{K/Ca} = \frac{\beta_K \times [\text{Ca}]^{0.5}}{\beta_{Ca}^{0.5} \times [\text{K}]}$$

**Table 2:** K distribution of the initial soils approximated using different selective K extraction methods

| Soil | K-H <sub>2</sub> SO <sub>4</sub><br>mmol kg <sup>-1</sup> | K-BaCl <sub>2</sub><br>mmol kg <sup>-1</sup> | K-CaCl <sub>2</sub><br>mmol kg <sup>-1</sup> | K-ss<br>mmol l <sup>-1</sup> | K <sub>exch</sub> *<br>mmol kg <sup>-1</sup> | K <sub>exch</sub> **<br>mmol kg <sup>-1</sup> | β <sub>K</sub><br>% |
|------|---|--|--|------------------------------|--|---|---------------------|
| 1    | 5,8   | 3,7  | 2,5  | 7,0                          | 2,1  | 2,6   | 8,2                 |
| 2    | 1,7   | 1,6  | 1,1  | 2,4                          | 0,1  | 1,2   | 4,6                 |
| 3    | 6,5   | 3,0  | 2,4  | 6,3                          | 3,5  | 2,1   | 9,4                 |
| 4    | 8,3   | 4,5  | 3,1  | 6,4                          | 3,8  | 3,7   | 13                  |
| 5    | 15  | 13   | 9,1  | 13                           | 2,1  | 11  | 26                  |
| 6    | 7,5   | 6,1  | 4,1  | 4,4                          | 1,4  | 5,2   | 4,4                 |
| 7    | 18  | 13   | 7,2  | 8,1                          | 5,1  | 12  | 11                  |
| 8    | 10  | 4,9  | 2,1  | 2,0                          | 5,3  | 4,7   | 8,4                 |
| 9    | 16  | 2,1  | 0,7  | 0,4                          | 13   | 2,0   | 1,8                 |
| 10   | 47  | 14   | 5,5  | 1,2                          | 33   | 14  | 5,6                 |
| 11   | 28  | 13   | 5,5  | 1,6                          | 16   | 12  | 3,8                 |
| 12   | 46  | 22   | 11   | 3,1                          | 23   | 21  | 13                  |
| 13   | 27  | 6,1  | 2,1  | 0,5                          | 20   | 5,9   | 2,4                 |
| 14   | 17  | 4,3  | 0,6  | 0,07                         | 12   | 4,3   | 1,1                 |
| 15   | 41  | 8,5  | 2,0  | 0,3                          | 33   | 8,4   | 2,4                 |

\* Calculated by subtracting K-BaCl<sub>2</sub> from K-H<sub>2</sub>SO<sub>4</sub>

\*\* Calculated by subtracting K<sub>ss</sub> (expressed in mmol kg<sup>-1</sup>) from K-BaCl<sub>2</sub>



**Figure 1:** Total available amount of soil K and the distribution of this K over the soil K fractions K<sub>exch</sub>, K<sub>exch</sub> and K<sub>ss</sub> for the 15 soils divided into three groups of different texture (sand, silt, and clay).

The equivalent fractions of K and Ca ( $\beta_K$  and  $\beta_{Ca}$ ) are the charge fractions of exchange sites occupied by K or Ca respectively and are calculated from the measured CEC and exchangeable cations using the  $BaCl_2$  method. The activity of K ( $[K]$ ) and Ca ( $[Ca]$ ) in the soil solution are calculated from the concentration measured *in situ* in the soil solution using the Davies equation in which the ionic strength of the soil solution ( $I_{ss}$ ) is calculated using the Debye-Hückel equation. Because all main cat- and anions are measured in the soil solution except  $Cl^-$ , the  $Cl^-$  concentration is calculated from the Ca concentration.

**Table 3:** The composition of the soil solution and exchange complex for K and Ca at the start of the pot experiment (before sowing) and the selectivity coefficient calculated from this data, Apart from the range in values for all 15 soils a distinction is made for soil groups of different texture.

|                              |                                    | Range |   |      | Sand (n=6) |     |      | Silt (n=3) |     |      | Clay (n=6) |     |      |
|------------------------------|------------------------------------|-------|---|------|------------|-----|------|------------|-----|------|------------|-----|------|
|                              |                                    | Min   |   | Max  | Avg        |     | SD   | Avg        |     | SD   | Avg        |     | SD   |
| <b>Soil Solution</b>         |                                    |       |   |      |            |     |      |            |     |      |            |     |      |
| K                            | mmol l <sup>-1</sup>               | 0,07  | - | 13   | 6,5        | +/- | 3    | 3,5        | +/- | 4    | 1,1        | +/- | 1,1  |
| Ca                           | mmol l <sup>-1</sup>               | 5,50  | - | 31   | 15         | +/- | 4    | 24         | +/- | 6    | 6,5        | +/- | 1,4  |
| [K]                          | mmol l <sup>-1</sup>               | 0,06  | - | 10   | 5          | +/- | 3    | 3          | +/- | 3    | 1,0        | +/- | 1,0  |
| [Ca]                         | mmol l <sup>-1</sup>               | 2,5   | - | 11   | 5,7        | +/- | 1,5  | 10         | +/- | 2    | 3,3        | +/- | 0,5  |
| I                            | mmol l <sup>-1</sup>               | 22    | - | 131  | 88         | +/- | 10   | 109        | +/- | 25   | 33         | +/- | 10   |
| [Ca] <sup>0.5</sup> /[K]     | -                                  | 0,2   | - | 29   | 0,6        | +/- | 0,3  | 3,7        | +/- | 4,3  | 7          | +/- | 11   |
| <b>Exchange complex</b>      |                                    |       |   |      |            |     |      |            |     |      |            |     |      |
| K-X                          | cmol <sup>+</sup> kg <sup>-1</sup> | 0,12  | - | 2,1  | 0,5        | +/- | 0,4  | 0,6        | +/- | 0,5  | 1,1        | +/- | 0,6  |
| Ca-X                         | cmol <sup>+</sup> kg <sup>-1</sup> | 2,6   | - | 45   | 5          | +/- | 3    | 10         | +/- | 3    | 29         | +/- | 12   |
| $\beta_K$                    | -                                  | 0,009 | - | 0,19 | 0,08       | +/- | 0,06 | 0,05       | +/- | 0,03 | 0,04       | +/- | 0,04 |
| $\beta_{Ca}$                 | -                                  | 0,58  | - | 0,93 | 0,8        | +/- | 0,1  | 0,81       | +/- | 0,08 | 0,8        | +/- | 0,1  |
| CEC                          | cmol <sup>+</sup> kg <sup>-1</sup> | 3     | - | 40   | 5          | +/- | 4    | 10         | +/- | 3    | 30         | +/- | 10   |
| $\beta_K / \beta_{Ca}^{0.5}$ | -                                  | 0,01  | - | 0,24 | 0,10       | +/- | 0,08 | 0,06       | +/- | 0,04 | 0,05       | +/- | 0,04 |
| <b>Exchange coefficient</b>  |                                    |       |   |      |            |     |      |            |     |      |            |     |      |
| $K_{K/Ca}$                   | -                                  | 0,026 | - | 0,27 | 0,04       | +/- | 0,01 | 0,11       | +/- | 0,06 | 0,13       | +/- | 0,08 |

Table 3 shows the main results of the soil solution and exchange complex for K and Ca for the 15 soils at the start of the pot experiment (before the seeds were sown). Again the soils are separated into three categories based on their texture: sand soils (n=6), silt soils (n=3) and clay soils (n=6). Following from the large variation in clay content there is a large variation in CEC between the 15 soils (Table 1).  $Ca_{exch}$  shows a close correlation with CEC ( $r^2 = 0.96$ ) as Ca is the main cation on the exchange complex for all soils ( $\beta_{Ca}$  is  $0.8^+ / 0.1$ ). Despite the increase in capacity to electrostatically bind K with increasing CEC, there is no clear increase in  $K_{exch}$  with either CEC or clay content. As the range in  $\beta_{Ca}$  is relatively small between the soils the ratio of  $\beta_K$  over  $\beta_{Ca}^{0.5}$  is mainly determined by  $\beta_K$ .

The soils show an overall large variation in  $K_{ss}$ . With increasing clay content of the three textural soil groups  $K_{ss}$  shows a decreasing trend (Fig.1). The Ca concentration ( $Ca_{ss}$ ) and ionic strength of

the soil solution ( $I_{ss}$ ) show a smaller variation between the soils, but comparable to  $K_{ss}$ , both  $Ca_{ss}$  and  $I_{ss}$  are also lower in clay soils compared to the sand and silt soils. Solely based on the addition of the nutrient solution an average  $I_{ss}$  of  $57 \pm 17$  mmol l<sup>-1</sup> and  $Ca_{ss}$  of  $10 \pm 3$  mmol l<sup>-1</sup> is expected. In the sandy and silt soils both  $I_{ss}$  and  $Ca_{ss}$  are higher (on average 95 and 18 mmol l<sup>-1</sup> respectively) than would be expected from the addition of the nutrient solution. On the contrary, both  $I_{ss}$  and  $Ca_{ss}$  are smaller (on average 33 and 6 mmol l<sup>-1</sup> respectively) than expected from the addition of the nutrient solution as a result of the large binding capacity in the clay soils. As the range in [Ca] in the soil solution is relatively small between the soils, the variation in the ratio of [Ca]<sup>0.5</sup> over [K] is mainly determined by the variation in [K]

Data of the soil solution and the exchangeable fractions are combined to calculate  $K_{K/Ca}$  (Table 3). The calculated  $K_{K/Ca}$  ranges between 0.026 and 0.27. The calculated  $K_{K/Ca}$  shows a variation of a factor 10 between the soils, but is smaller when distinguishing between soil groups of different texture. In accordance with the relatively low ratio of [Ca]<sup>0.5</sup> over [K] in the sandy soils compared to the silt and clay soils, the exchange coefficient is also lower in the sandy soils compared to the silt and clay soils.  $K_{exch}$  in the silt and clay soils is bound more strongly compared to the sandy soils. The difference may be explained by the different kinds of K adsorption sites in 2:1 clay minerals (Bolt and Sumner 1963). For soils low in clay and silt a relatively large portion of  $K_{exch}$  may be adsorbed on planar positions in soils. In contrast, a relatively large portion of  $K_{exch}$  may be adsorbed to edge and interlattice positions in silt and clay rich soils. In addition, the stronger binding of K in silt and clay soils compared to sandy soils may also be affected by the larger relative contribution of SOM to the CEC (calculated according to (Weng et al. 2001) in sandy soils compared to silt and clay soils as SOM has a lower selectivity for K compared to clay. Németh et al. (1970) found that the difference in affinity for K between the soil groups of different texture could not be explained by clay mineralogy.

The range in  $K_{K/Ca}$  found in this study is rather low compared to values found in literature. In a literature overview by Bruggenwert and Kamphorst (1982) the exchange coefficient found for several soils varies between 0.6 and 3.3 and approximates on average 1.4. Lower values for  $K_{K/Ca}$  have been found, for instance Thabet and Selim (1996) reported an average  $K_{K/Ca}$  of 0.21 and Robbins and Carter (1983) reported a range in  $K_{K/Ca}$  of 0.15–0.53 for eight soils. Comparing selectivity coefficients from different studies is not straightforward as  $K_{K/Ca}$  depends on  $\beta_K$  on  $I_{ss}$ , and the method of determination and calculation may vary per study. One of the studies (Ehlers et al. 1967), described in Bruggenwert and Kamphorst (1982), shows a huge increase in  $K_{K/Ca}$  (0.75 to 200000), with decreasing  $\beta_K$ , i.e. a large increase in the soil's affinity for K with decreasing equivalent fraction of K on the exchange complex.

In our experiments, the low  $K_{K/Ca}$  compared to values in literature may result from the relatively high measured  $K_{ss}$ . Especially when considering that all nutrients were added to the soil at the start of the pot experiment except K. For one soil (soil 4)  $K_{ss}$  is higher than  $Ca_{ss}$ . For the other soils  $Ca_{ss}$  is on average four times higher than  $K_{ss}$ . For comparison,  $Ca_{ss}$  is usually 10 times higher than  $K_{ss}$  in Ca dominated soils (Németh et al. 1970).

The value of  $K_{ss}$  is found to be very susceptible to the method of determination. This is shown by comparing  $K_{ss}$  measured *in situ* in the pot experiment with the K concentration measured at different soil solution ratio's in the dilution experiment (Table 4). The soil- solution ratio (SSR) affects the K concentration in solution, and this effect is particularly large for the sandy soils. When comparing  $K_{ss}$  (SSR in the pots is 3–7 kg l<sup>-1</sup>) with the K concentration at the SSR of 1 kg l<sup>-1</sup>, it is equal ( $1.0 \pm 0.3$ ) for the clay soils (n=6) but for the sandy soils (n=3)  $K_{ss}$  is 3-4 times higher. With decreasing SSR (0.1–0.01 kg l<sup>-1</sup>) this difference largely increases for the sandy soils;  $K_{ss}$  is 16-26

**Table 4:** K concentration in solution ( $\text{mmol l}^{-1}$ ) measured at the start of the pot experiment ( $K_{ss}$ ) and in a dilution experiment with varying soil- solution ratio (1, 0,1, 0,02, 0,01  $\text{kg l}^{-1}$ ) in a matrix of 0,01M  $\text{CaCl}_2$ . Soil 1, 3, and 5 are sandy soils and soil 10 to 15 are clay soils. In the pot experiment the SSR varies between 3 and 7 depending on the soil.

| Soil | K concentration in solution $\text{mmol l}^{-1}$ |   |      |      |      | Amount of K extracted $\text{mmol kg}^{-1}$ |   |      |      |      |                 |
|------|--|---|------|------|------|---|---|------|------|------|-----------------|
|      | $K_{ss}$   | Soil- solution ratio ( $\text{kg l}^{-1}$ ) |      |      |      | $K_{ss}$                                    | Soil- solution ratio ( $\text{kg l}^{-1}$ ) |      |      |      | $\text{BaCl}_2$ |
|      |  | 1   | 0,1  | 0,02 | 0,01 |   | 1   | 0,1  | 0,02 | 0,01 |                 |
| 1    | 7,0  | 1,7   | 0,28 | 0,06 | 0,03 | 1,1   | 1,7   | 2,8  | 3,1  | 3,0  | 3,7             |
| 3    | 6,3  | 1,6   | 0,24 | 0,05 | 0,03 | 0,90  | 1,6   | 2,4  | 2,6  | 2,8  | 3,0             |
| 5    | 12,6   | 4,5   | 0,79 | 0,19 | 0,11 | 2,7   | 4,5   | 7,9  | 9,7  | 10,8 | 13              |
| 10   | 1,2  | 1,3   | 0,53 | 0,17 | 0,11 | 0,24  | 1,3   | 5,3  | 8,7  | 10,8 | 14              |
| 11   | 1,6  | 1,0   | 0,59 | 0,18 | 0,11 | 0,56  | 1,0   | 5,9  | 9,2  | 11,4 | 13              |
| 12   | 3,1  | 3,4   | 1,21 | 0,32 | 0,19 | 0,67  | 3,4   | 12,1 | 16,2 | 19,4 | 22              |
| 13   | 0,5  | 0,5   | 0,22 | 0,07 | 0,05 | 0,14  | 0,48  | 2,2  | 3,5  | 4,6  | 6,1             |
| 14   | 0,07   | 0,12  | 0,09 | 0,04 | 0,03 | 0,02  | 0,12  | 0,87 | 2,0  | 3,1  | 4,3             |
| 15   | 0,3  | 0,4   | 0,23 | 0,10 | 0,07 | 0,09  | 0,35  | 2,3  | 5,1  | 6,7  | 8,5             |

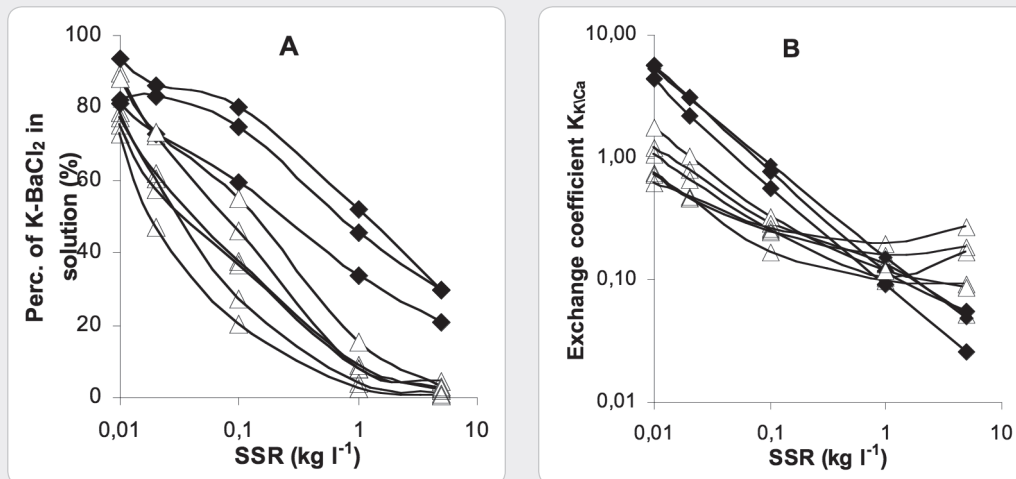
times higher compared to the K concentration in the soil suspension at a SSR 0.1  $\text{kg l}^{-1}$ . For the clay soils  $K_{ss}$  is also higher compared to the K concentration in the soil suspensions at 0.1  $\text{kg l}^{-1}$  but this difference is much smaller. The sandy soils show an especially low capacity to buffer the K concentration in solution upon dilution, both in an absolute sense and compared to the clay soils.

This large difference in the capacity to buffer  $K_{ss}$  between soils of different texture can be explained by the soil's affinity for K as shown by the percentage of readily available K (approximated by K-BaCl<sub>2</sub>) that is in the soil solution (Fig.2a). Over the entire range in SSR the percentage of readily available K in solution is higher in the sandy soils compared to the clay soils. This difference is increasingly pronounced at higher SSR. In the pot experiment 20-30% of K-BaCl<sub>2</sub> is in the soil solution in the sandy soils, whilst in the clay soils this is only 0.5-4%. With increasing SSR an increasing percentage of K-BaCl<sub>2</sub> is dissolved. K-BaCl<sub>2</sub> extracts both  $K_{ss}$  and  $K_{exch}$ .

$K_{ss}$  is often assessed using water soluble K at SSR of 0.5 or 0.1  $\text{kg l}^{-1}$ . The large effect of the SSR on the K concentration in solution found in the dilution experiment (Table 4) will be even more pronounced when water is used as a matrix instead of 0.01M  $\text{CaCl}_2$ . In the 0.01M  $\text{CaCl}_2$  matrix exchange of K by the added Ca enhances dissolution of K. In a water extract the K concentration is much lower compared to  $K_{ss}$  and the soil K buffer power will be an important factor determining the measured K concentration in solution.

The capacity of the soil to buffer  $K_{ss}$  has a large effect on the calculated  $K_{K/Ca}$  (Fig.2b). As a result of the very low capacity of sandy soils to buffer the K concentration in solution, the calculated  $K_{K/Ca}$  increases rapidly when the activity in solution is derived from an experimental setup with a SSR smaller than that in the field. This may explain the low  $K_{K/Ca}$  in this study compared to values in literature. For instance in a study using the same and similar soils, the calculated  $K_{K/Ca}$  was much higher (range between 3.4 and 17) when the concentration was measured in a 0.01M  $\text{CaCl}_2$  extract at a SSR of 0.1  $\text{kg l}^{-1}$  (Van Erp 2002b).

The affinity for K increases from organic matter to clay to high affinity sites on the clay. For the



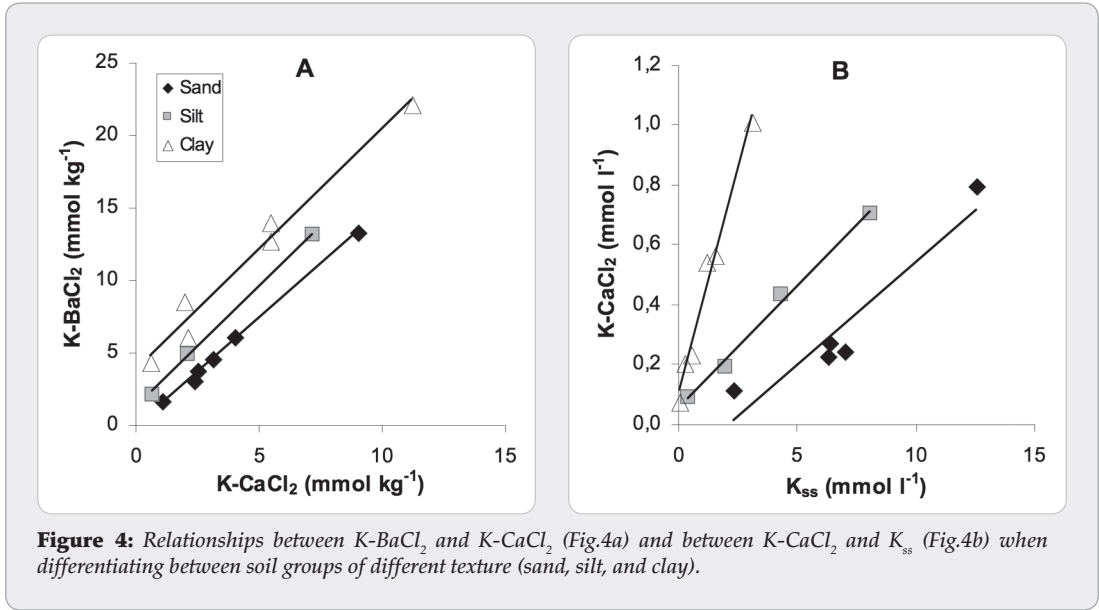
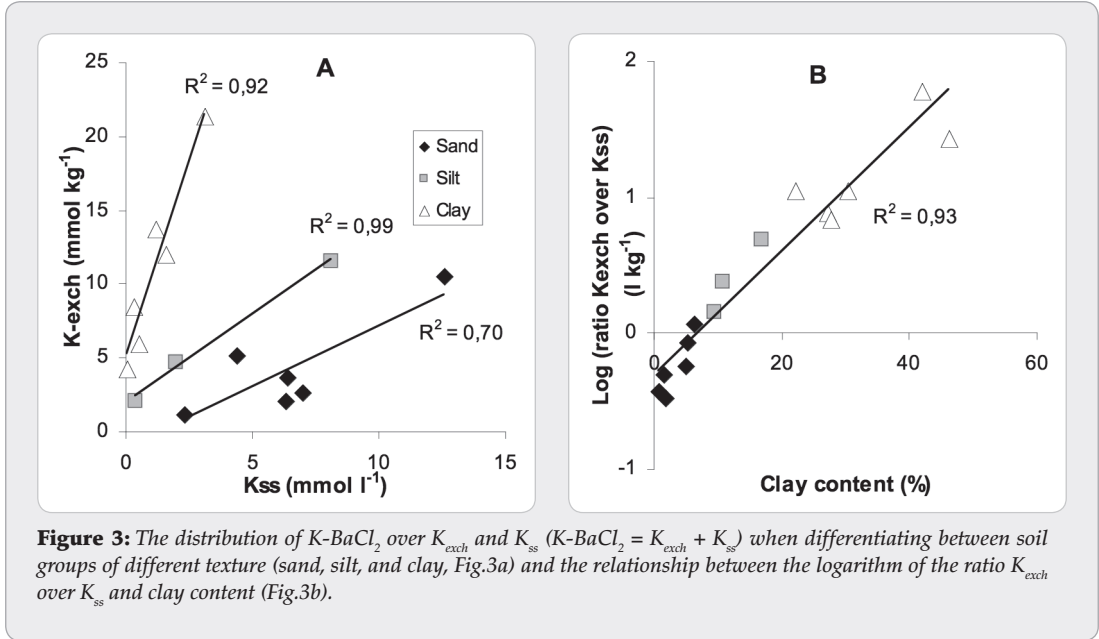
**Figure 2:** The percentage of K-BaCl<sub>2</sub> in solution (Fig.2a) and the logarithm of the exchange coefficient  $K_{K/Ca}$  (Fig.2b) as a function of the logarithm of the soil- solution ratio. The soil- solution ratio of 5 corresponds with the K and Ca concentration as measured in situ at the start of the pot experiment. The diamonds are the 3 sandy soils and the triangles the 6 clay soils used in the dilution experiment.

clay soils the calculated  $K_{K/Ca}$  also increases upon dilution but as a result of the larger capacity to buffer the concentration in solution this increase is less pronounced than for the sandy soils. As discussed above,  $K_{K/Ca}$  is lower for sandy soils compared to clay soils when the data from the soil solution is used, which is conform expectations. When the data from the dilution experiment is used to determine the concentrations in solution, no difference in  $K_{K/Ca}$  is found between sandy and clay soils at a SSR of 1, but at lower SSR  $K_{K/Ca}$  is increasingly higher compared to  $K_{K/Ca}$  in the clay soils. Adapting the SSR and matrix to measure the concentrations of the main cations in solution may thus lead to large errors when calculating  $K_{K/Ca}$ .

### Indicators for soil K status

The affinity of the soil for K, as expressed by the selectivity coefficient, determines the distribution of K over  $K_{exch}$  and  $K_{ss}$ . As expected, there is no overall relationship between  $K_{exch}$  and  $K_{ss}$ , but when differentiating between the three soil groups of different texture (sand, silt and clay), three different linear relationships between  $K_{exch}$  and  $K_{ss}$  are found. The slope of these linear relationships increases with increasing clay content (Fig.3a). When considering all soils, the ratio  $K_{exch}$  over  $K_{ss}$  shows a close logarithmic relationship with clay content ( $r^2=0.94$ , Fig.3b). In agreement with the results of the calculated  $K_{K/Ca}$ , the relationship between  $K_{exch}$  and  $K_{ss}$  shows a stronger binding of K with increasing clay content. Németh et al. (1970) also found different relationships between  $K_{exch}$  and  $K_{ss}$  when the soils were differentiated according to clay and silt content.

Comparable to the results found by van Erp et al. (1998), figure 4a shows that K-CaCl<sub>2</sub> extracts a certain fraction of  $K_{exch}$ , varying between 50–80% on sandy soils and 20–50% on clay soils. Despite this difference in the fraction of  $K_{exch}$  extracted by K-CaCl<sub>2</sub>, there is an overall rather good relationship between K-CaCl<sub>2</sub> and K-BaCl<sub>2</sub> ( $r^2=0.85$ ). In accordance with the difference in preference for K, this relationship is even better ( $r^2>0.98$ ) when distinguishing between soil groups



of different texture (Fig.4a). Comparable results have been found in several studies, e.g. (Baier and Baierova 1998; Houba et al. 1986). The high correlation coefficient when distinguishing between soil groups of different texture indicates that contrary to the results found by Sharpley (1989), clay mineralogy does not seem important. This may be caused by the general presence (dominance) of illitic clay minerals in Dutch soils whilst the study by Sharpley contained three mineralogical groups



(kaolinite, smectite, and mixed). Comparable to K-BaCl<sub>2</sub>, there is no overall relationship between K-CaCl<sub>2</sub> and K<sub>ss</sub> but when distinguishing between soil groups of different texture, three different linear relationships between K-CaCl<sub>2</sub> and K<sub>ss</sub> are found with an increasing slope with increasing clay content (Fig.4b). Comparable to Fig.3b the logarithm of the ratio K-CaCl<sub>2</sub> over K<sub>ss</sub> is linearly related to clay content ( $r^2=0.92$ ). K-CaCl<sub>2</sub> is not a direct measure for either the K concentration in the soil solution or for the exchangeable amount of K. However, from our experiments it seems possible to translate K-CaCl<sub>2</sub> to a measure for K<sub>exch</sub> or to a measure for K<sub>ss</sub> based on soil texture.

### Crop response

The main results concerning crop response after 2, 4, and 6 weeks of growth are shown in Table 5. During the pot experiment the grass shoots show a large increase in dry weight (dw) production to full grown grass within 4 weeks (2.8–6.7 gram dw). To ascertain continuous removal of K, the grass was cut after 4 weeks and allowed to re-grow between 4 and 6 weeks resulting in a cumulative dw production of 4.2–10.8 gram.

The total (shoots + roots) K uptake by grass varies between 1.4 and 13.2 mmol after 6 weeks for the 15 soils. Although the pot experiment was relatively short, the small pots and optimal growing conditions in the greenhouse resulted in a higher K removal rate than would be achieved in the field in the same period of time. After 2 weeks the range in K uptake by the shoots is relatively small (0.3–1.5 mmol) but in accordance with the large increase in dw production between 2 and 4 weeks there is also a large increase in K uptake (absolute range 1.0–8.8 mmol). This large increase

**Table 5:** Dry weight of the shoots, K concentration, and (total) uptake of the grass during the pot experiment after 2, 4, and 6 weeks.

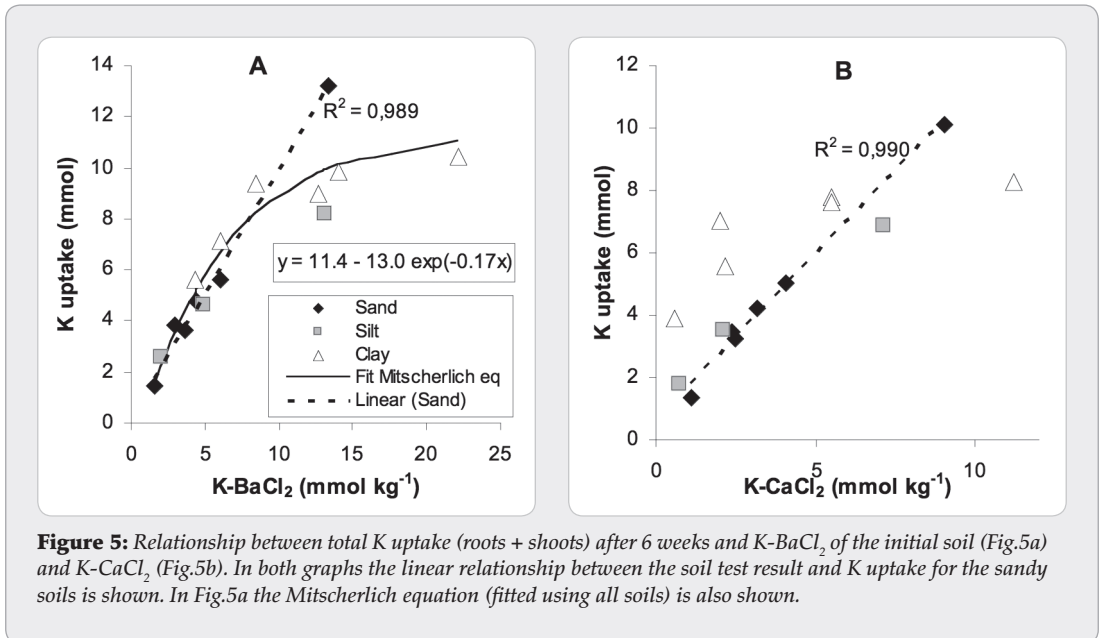
| Soil | DW shoots (g) |      |      | K conc shoots (mol kg <sup>-1</sup> ) |      |      | K uptake Shoots (mmol) |      |      | Total K uptake* (mmol) |      |      |
|------|---------------|------|------|---------------------------------------|------|------|------------------------|------|------|------------------------|------|------|
|      | 2 wk          | 4 wk | 6 wk | 2 wk                                  | 4 wk | 6 wk | 2 wk                   | 4 wk | 6 wk | 2 wk                   | 4 wk | 6 wk |
| 1    | 0,5           | 4,2  | 5,8  | 1,4                                   | 0,60 | 0,47 | 0,6                    | 2,5  | 2,7  | 1,0                    | 3,2  | 3,6  |
| 2    | 0,5           | 3,9  | 5,2  | 1,1                                   | 0,25 | 0,20 | 0,6                    | 1,0  | 1,0  | 0,7                    | 1,3  | 1,4  |
| 3    | 0,4           | 2,8  | 4,2  | 1,5                                   | 0,98 | 0,72 | 0,7                    | 2,7  | 3,0  | 1,0                    | 3,5  | 3,8  |
| 4    | 0,9           | 4,4  | 5,9  | 1,5                                   | 0,77 | 0,62 | 1,4                    | 3,3  | 3,7  | 1,9                    | 4,2  | 4,8  |
| 5    | 0,8           | 6,7  | 10,8 | 1,8                                   | 1,3  | 1,0  | 1,5                    | 8,8  | 11,0 | 1,7                    | 10,1 | 13,2 |
| 6    | 0,6           | 5,2  | 7,1  | 1,6                                   | 0,79 | 0,62 | 1,0                    | 4,1  | 4,4  | 1,2                    | 5,0  | 5,6  |
| 7    | 0,5           | 4,4  | 6,1  | 1,7                                   | 1,2  | 1,0  | 0,9                    | 5,3  | 6,4  | 1,2                    | 6,8  | 8,2  |
| 8    | 0,2           | 3,2  | 5,0  | 1,4                                   | 0,91 | 0,76 | 0,3                    | 3,0  | 3,8  | 0,5                    | 3,5  | 4,6  |
| 9    | 0,6           | 3,3  | 5,8  | 0,9                                   | 0,44 | 0,34 | 0,5                    | 1,4  | 2,0  | 0,6                    | 1,8  | 2,6  |
| 10   | 0,7           | 5,3  | 7,4  | 1,7                                   | 1,2  | 1,0  | 1,2                    | 6,3  | 7,7  | 1,5                    | 7,8  | 9,9  |
| 11   | 0,9           | 6,5  | 9,9  | 1,6                                   | 1,0  | 0,77 | 1,4                    | 6,6  | 7,7  | 1,7                    | 7,6  | 9,0  |
| 12   | 0,8           | 5,1  | 7,3  | 1,7                                   | 1,3  | 1,1  | 1,3                    | 6,5  | 8,0  | 1,8                    | 8,3  | 10,4 |
| 13   | 0,6           | 4,9  | 6,8  | 1,5                                   | 0,94 | 0,80 | 0,9                    | 4,6  | 5,5  | 1,3                    | 5,5  | 7,1  |
| 14   | 0,8           | 6,1  | 9,8  | 1,0                                   | 0,56 | 0,47 | 0,8                    | 3,4  | 4,6  | 1,0                    | 3,9  | 5,6  |
| 15   | 0,6           | 5,3  | 8,3  | 1,6                                   | 1,16 | 0,93 | 1,0                    | 6,1  | 7,7  | 1,2                    | 7,0  | 9,4  |

\* Total K uptake is uptake by roots and shoots.

in K uptake by the shoots does not continue between 4 and 6 weeks; after 6 weeks K uptake increases between 3 and 38% compared to K uptake after 4 weeks. The extent to which the grass continues to remove K between 4 and 6 weeks depends on the soil. For the sandy soils, K uptake increases only between 3 and 11% between 4 and 6 weeks. An exception is soil 5 which increases 25%. This is because the initial amount of readily available K ( $K\text{-BaCl}_2$ ) was high ( $13 \text{ mmol kg}^{-1}$ ) and even after 4 weeks of intensive K uptake by the growing grass the readily available K is still  $3.1 \text{ mmol kg}^{-1}$ . For the silt and clay soils, K uptake increases 16–38% between 4 and 6 weeks. There is an overall large variation in K uptake during the first cutting (4 weeks). The continuation in K uptake towards the following cutting (between 4 and 6 weeks) seems to be affected by the texture of the soil.

### Crop response versus indicators for soil K status

The soil K supply potential as assessed in routine soil laboratories is generally based on a single measure for the readily available soil K ( $K_{ss} + K_{exch}$ ), which in this study is approximated by  $K\text{-BaCl}_2$ . The potential of  $K\text{-CaCl}_2$  (SSR  $0.1 \text{ kg l}^{-1}$ ) is also investigated. The relationship between the total K uptake by the ryegrass (shoots and roots) and  $K\text{-BaCl}_2$  and  $K\text{-CaCl}_2$  after 4 and 6 weeks is shown in Fig.5. When only considering the sandy soils, K uptake by the grass shows a strong linear relationship with both  $K\text{-BaCl}_2$  ( $r^2=0.989$ ) and  $K\text{-CaCl}_2$  ( $r^2=0.997$ ). In general plants have a maximum response above a certain availability parameter that is associated with the prevailing environmental conditions (e.g. light, temperature, fertilization). Due to the relatively large  $K\text{-BaCl}_2$  for soil 5 the grass does not seem to have reached the maximum K uptake. The silt and clay soils show a more curved relationship between K uptake and  $K\text{-BaCl}_2$  or  $K\text{-CaCl}_2$ . For the silt and clay soils a maximum response does seem to have been reached. For  $K\text{-BaCl}_2$  all these relationships fall together and a standard Mitscherlich equation can be fitted through all data points. With continuous cropping however the difference in soil K supply potential between soil groups of



different texture may diminish this overall relationship. There is no overall relationship between K uptake and K-CaCl<sub>2</sub> (Fig.5b). This overall relationship may be achieved when including soil K buffer power, in our study mainly determined by soil texture.

As K is taken up from the soil solution, the flux towards the roots is a function of the concentration in solution. An increase in slope between  $K_{\text{exch}}$  and  $K_{\text{ss}}$  with increasing clay content (Fig.4) implies a decreasing flux towards the roots due to the lower  $K_{\text{ss}}$  at equal  $K_{\text{exch}}$ . However, no relationship between K uptake and  $K_{\text{ss}}$  is found. Although  $K_{\text{ss}}$  is lower in clay soils compared to the sandy soils, the soil K buffer power of the clay soils is much larger compared to the sandy soils (Table 4). As a result K-BaCl<sub>2</sub> is equally available for sand, silt, and clay soils (Fig.5a). Using a measure for  $K_{\text{ss}}$  as an indicator for the soil K supply potential is not warranted if the soil K buffer power is not taken into account. In addition, most methods applied to measure  $K_{\text{ss}}$  alter the SSR from the ratio in the field (which also fluctuates to some extent) and thus indirectly incorporates the soil K buffer power to a certain degree (Table 4).

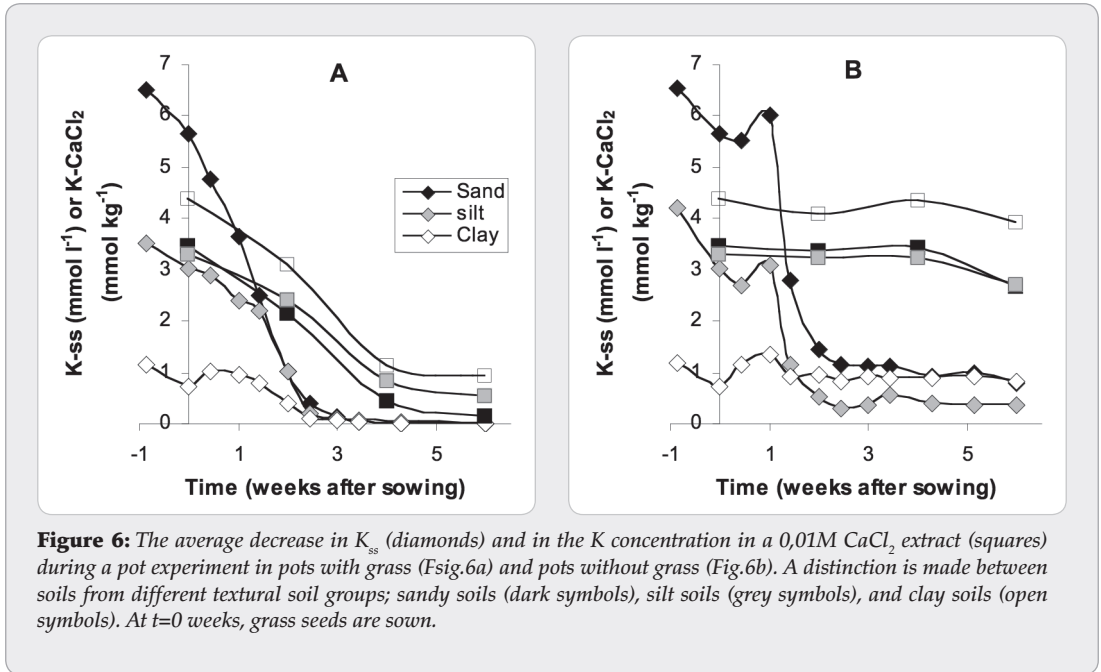
In Dutch agricultural soils the amount of K removed in an average pasture is roughly comparable to the amount of readily available K in the soil (appendix 1). The exchange complex must thus be replenished to maintain readily desorbable K at an adequate level. Ideally an estimation of this replenishment is made in order to minimize excessive fertilizer application. In the pot experiment the grass grown on the silt and clay soils shows a continuous K uptake between 4 and 6 weeks whilst for the sandy soils K uptake seems to have ceased. The change in soil K supply potential during grass growth in the pot experiment and the relative contributions of  $K_{\text{ss}}$ ,  $K_{\text{exch}}$  and  $K_{\text{nexch}}$  will be investigated by studying the change in the different K fractions in more detail.

## ***Change in (measures for) soil K supply potential during grass growth***

### ***K concentration in the soil solution***

Although the soils show a large variation in both the absolute  $K_{\text{ss}}$  and in the amount of K in the soil solution relative to the total amount of available K ( $K_{\text{TA}}$ ) as assessed by K-H<sub>2</sub>SO<sub>4</sub> (0.1 – 25%, Fig.1), all soils show a decrease in  $K_{\text{ss}}$  to negligibly low concentrations within 2.5 to 3 weeks after sowing (~1.5–2 weeks after germination, Fig.6a). It is striking that this strong decrease in  $K_{\text{ss}}$  is not only restricted to the period of removal of these nutrients by the growing grass but, in the sandy and silt soils also decreases in the absence of plants, both in blank pots (without plants) and in the pots with plants before germination. In the blank pots  $K_{\text{ss}}$  does not continue to decrease to negligibly low concentrations as was the case in pots with plants, but stabilizes after ~2.5 weeks (Fig.6b). For soils with high clay content the concentration remains approximately constant over time when K is not removed by the growing crop. A possible explanation for the decrease in the K concentration in the sandy and silt soils in the absence of plants is that the rhizons are placed in the middle of the pots and water is also mostly added to the centre resulting in a dilution effect and more importantly a lowering of the salt level. This may strongly diminish the K concentration around the rhizon. In the clay soils this effect is countered by the much higher soil K buffer power compared to the sandy and silt soils.

The large decrease in  $K_{\text{ss}}$  in sandy soils in the absence of plants is not found in the CaCl<sub>2</sub> extract (Fig.6b). The same trend in the concentration in solution and in the amount extracted with 0.01M CaCl<sub>2</sub> as found for K in pots with and without plants, is also found for all the other measured nutrients (Ca, Mg, Na, NO<sub>3</sub>, NH<sub>4</sub> and S) except for P. The concentration of the nutrients in solution is very susceptible to the salt level of the concentration which is constant in the CaCl<sub>2</sub> extract. The P concentration is hardly affected by changes in the salt level and also dilution will have small



**Figure 6:** The average decrease in  $K_{ss}$  (diamonds) and in the K concentration in a 0,01M  $CaCl_2$  extract (squares) during a pot experiment in pots with grass (Fig.6a) and pots without grass (Fig.6b). A distinction is made between soils from different textural soil groups; sandy soils (dark symbols), silt soils (grey symbols), and clay soils (open symbols). At  $t=0$  weeks, grass seeds are sown.

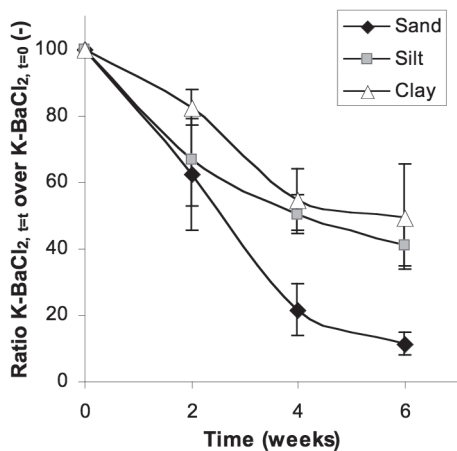
effects due to the very high buffering of the soil for P. The difference in fluctuation between the  $CaCl_2$  extract and the soil solution might also be (partly) explained by the way of sampling. The soil used in the  $CaCl_2$  extract is a mixed sample taken from the whole pot and thus approximates a bulk soil sample. The concentration in solution is sampled by means of a rhizon fixed in a certain position in each pot during the experiment and may thus more approximate the local situation. Additionally, the large dilution (SSR of  $0.1 \text{ kg l}^{-1}$ ) and addition of  $Ca^{2+}$  in the  $CaCl_2$  extract results in a partial desorption of  $K_{exch}$  and consequently in a larger amount of K extracted in the  $CaCl_2$  extract compared to the amount dissolved in the soil solution (2.5–43 times larger, Table 4). The concentration in the  $CaCl_2$  extract will thus be less prone to fluctuations than the concentration in the soil solution.

During the grass growth in the pot experiment all nutrients (except P) show a decrease in their concentration in the soil solution and thus the ionic strength ( $I_{ss}$ ) also decreases. Initially  $I_{ss}$  is higher in the sandy and silt soils compared to the clay soils but these soils also show a stronger decrease in  $I_{ss}$ . Within 4 weeks after germination, this results in a lower  $I_{ss}$  in the sandy and silt soils compared to the clay soils. As  $Ca_{ss}$  is closely related to  $I_{ss}$ , a stronger decrease in  $K_{ss}$  is also expected in the sandy and silt soils compared to the clay soils. This is indeed found for the measured decrease in  $K_{ss}$  after 2 weeks. After 4 weeks however  $K_{ss}$  has strongly decreased (98%/2%) for all soils. This decrease is larger than would be expected based on the exchange with Ca; calculated from the measured decrease in  $Ca_{ss}$  and measured equivalent K and Ca fractions on the CEC. In addition the calculated  $K_{KlCa}$  (based on the K and Ca activities in solution and exchangeable K and Ca fractions measured after 2, 4, and 6 weeks) increases over time during the experiment. As far as  $K_{KlCa}$  can be calculated it increases during 6 weeks to fall within the range as found by Bruggenwert and Kamphorst (1982).  $K_{KlCa}$  is known to increase with decreasing equivalent fraction of K on the CEC (Ehlers et al. 1967 as described in Bruggenwert and Kamphorst 1982). Thus, during K

uptake by the growing grass in the pot experiment the soil increases in affinity for K, resulting in a decrease in K availability.

A decrease in the availability of  $K_{\text{exch}}$  during the removal of K from the soil is contrary to the commonly used simple approach of assuming a linear relationship between  $K_{\text{exch}}$  and  $K_{\text{ss}}$ , i.e. a linear desorption isotherm. In agreement with our results, it has been hypothesized, that a highly nonlinear desorption isotherm occurs due to the rapid decrease in  $K_{\text{ss}}$  in the vicinity of plant roots (Meyer and Jungk 1992). A similar situation may occur in the field with the exception that as K is removed from the dense rooting zone, readily available K from deeper in the soil profile may be transported to this rooting zone.

Apart from the lack of a direct relationship between K uptake by the grass and the initial  $K_{\text{ss}}$ , the strong decrease in  $K_{\text{ss}}$  to negligibly low concentrations within 2.5–3 weeks after sowing also does not seem to affect K uptake. Meyer and Jungk (1992) also found an ongoing cumulative K release despite a steep drop in the K concentration in the percolate solution (>90%) when percolating a soil sample with 0.01M  $\text{CaCl}_2$ . The low  $K_{\text{ss}}$  subsequently initiates the K release from  $K_{\text{exch}}$  and possibly  $K_{\text{nexch}}$ .



**Figure 7:** The relative decrease in  $K\text{-BaCl}_2$  (ratio  $K\text{-BaCl}_2$  measured either after 0, 2, 4, or 6 weeks after sowing over the initial  $K\text{-BaCl}_2$ ) versus time during pot experiment in pots with grass.

### Exchangeable cations

During the 6 weeks of the experiment,  $K\text{-BaCl}_2$  ( $K_{\text{exch}} + K_{\text{ss}}$ ) shows a strong decrease due to K uptake by the growing grass (Fig.7). Overall the largest decrease occurs during the first 4 weeks (decrease of 36 - 93% relative to  $K\text{-BaCl}_2$  at the time of sowing). There is a large difference in initial  $K\text{-BaCl}_2$  when considering all soils without a difference between soil categories of different texture. There is however a difference in the decrease in  $K\text{-BaCl}_2$  between soil categories of different texture (Table 6). The decrease in  $K\text{-BaCl}_2$  is larger for the sandy soils (79  $\pm$  8%, after 4 weeks and 89  $\pm$  4% after 6 weeks) compared to the silt and clay soils during the experiment ((47  $\pm$  8% after 4 weeks and 54  $\pm$  14% after 6 weeks). This is in accordance with results found by Sparks et al. (1980). The availability of  $K\text{-BaCl}_2$  is equal for all soils irrespective of texture, as is illustrated by the close relationship between K uptake and  $K\text{-BaCl}_2$  (Fig.5a) for all soils both after 4 and 6 weeks. The difference in relative decrease in  $K\text{-BaCl}_2$  however indicates that with continuous removal of K by

the growing grass the availability of K will become increasingly different due to the contribution of  $K_{\text{nexch}}$ .

**Contribution of  $K_{\text{exch}}$  and  $K_{\text{nexch}}$  to K uptake**

The contribution of  $K_{\text{nexch}}$  in the soil K supply potential to plants is widely acknowledged e.g. (Cox et al. 1999; Hoagland and Martin 1933; Mengel and Uhlenbecker 1993; Schneider 1997; Wang et al. 2004). The contribution of  $K_{\text{exch}}$  and  $K_{\text{nexch}}$  to the soil K available for the growing grass is assessed by the change in K-BaCl<sub>2</sub> compared to the total K uptake (roots+shoots). A low  $K_{\text{ss}}$  is generally assumed to be the driving force behind release of  $K_{\text{nexch}}$ . As  $K_{\text{ss}}$  shows a rapid decrease within 2,5 weeks after sowing (Fig.6), a potential release of  $K_{\text{nexch}}$  is possible in all soils.

The results however show a marked difference in the relative contribution of  $K_{\text{exch}}$  and  $K_{\text{nexch}}$  between sandy soils and silt and clay soils (Table 6). For the sandy soils the decrease in K-BaCl<sub>2</sub> is equal to the amount of K removed by the plant ( $1.0 \pm 0.05$ ) after both 4 and 6 weeks. This shows that K-BaCl<sub>2</sub>, which comprises of both  $K_{\text{exch}}$  and  $K_{\text{ss}}$  is the only K source for the growing grass during this period, despite the presence of 0.1–3.8 mmol kg<sup>-1</sup>  $K_{\text{nexch}}$  in these soils and the decrease in  $K_{\text{ss}}$  to concentrations below which  $K_{\text{nexch}}$  is known to be released. Thus  $K_{\text{nexch}}$  does not replenish  $K_{\text{exch}}$  and does not participate in the overall soil K supply potential in these sandy soils. As stated before, K uptake stagnates between 4 and 6 weeks in the sandy soils after approximately 80% of

**Table 6:** Total (shoots+roots) K uptake (KU) expressed in mmol K per kg soil after 6 weeks of growth and K-BaCl<sub>2</sub> and K-CaCl<sub>2</sub> at the time of sowing (t=0) and after 2, 4, and 6 weeks of grass growth. The ratio K uptake by the grass over the change in K-BaCl<sub>2</sub> or K-CaCl<sub>2</sub> during the same period of time is also shown. When the decrease in K-BaCl<sub>2</sub> or K-CaCl<sub>2</sub> is equal to K uptake over the same period of time this ratio is 1. When the ratio is greater than 1, K uptake exceeds the corresponding change in K-BaCl<sub>2</sub> or K-CaCl<sub>2</sub>.

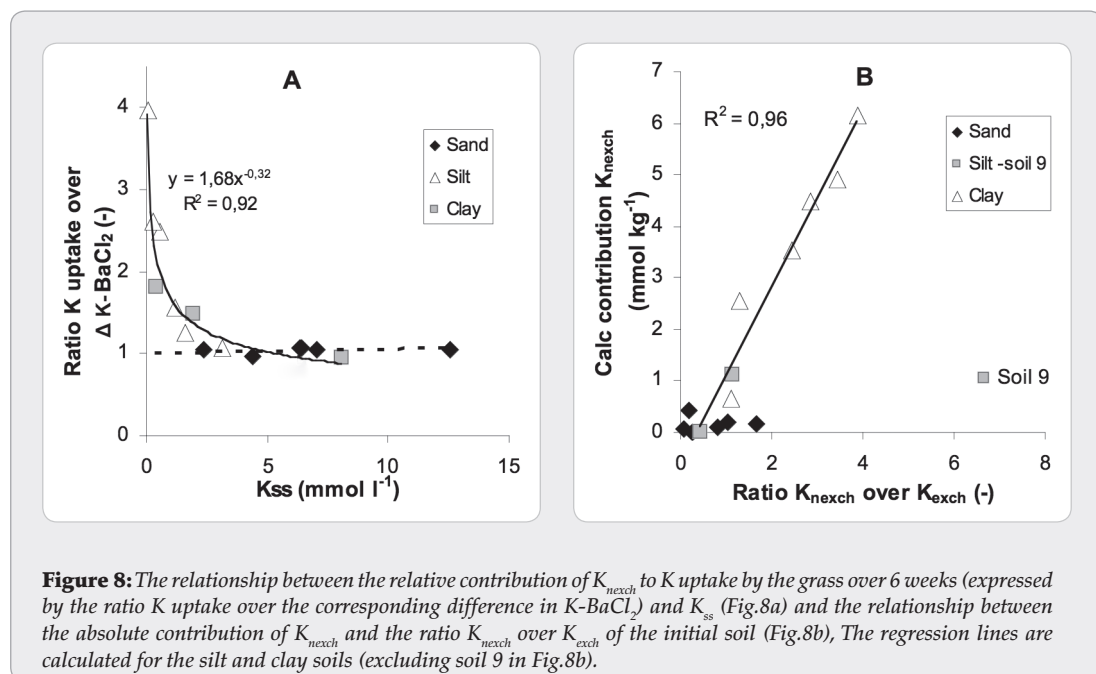
| Soil | K uptake (mmol kg <sup>-1</sup> ) |      | K-BaCl <sub>2</sub> (mmol kg <sup>-1</sup> ) |      |      |      | KU / Δ-BC |     | K-CaCl <sub>2</sub> (mmol kg <sup>-1</sup> ) |     |     |     | KU / Δ-CC |     |
|------|-----------------------------------|------|--|------|------|------|-----------|-----|--|-----|-----|-----|-----------|-----|
|      | 4                                 | 6    | 0  | 2    | 4    | 6    | 4         | 6   | 0  | 2   | 4   | 6   | 4         | 6   |
| 1    | 2,5                               | 2,8  | 2,9  | 1,9  | 0,7  | 0,2  | 1,1       | 1,0 | 2,4  | 1,2 | 0,2 | 0,1 | 1,1       | 1,2 |
| 2    | 1,2                               | 1,3  | 1,4  | 0,5  | 0,09 | 0,1  | 0,9       | 1,0 | 1,1  | 0,3 | 0,0 | 0,0 | 1,1       | 1,2 |
| 3    | 2,6                               | 2,9  | 3,0  | 1,8  | 0,6  | 0,3  | 1,1       | 1,1 | 2,3  | 1,1 | 0,2 | 0,1 | 1,3       | 1,3 |
| 4    | 3,2                               | 3,6  | 4,0  | 2,4  | 0,9  | 0,7  | 1,0       | 1,1 | 2,7  | 1,1 | 0,3 | 0,1 | 1,3       | 1,4 |
| 5    | 8,2                               | 10,7 | 11,3   | 9,6  | 3,1  | 1,0  | 1,0       | 1,0 | 7,9  | 6,5 | 1,4 | 0,2 | 1,2       | 1,4 |
| 6    | 4,7                               | 5,3  | 6,3  | 4,4  | 1,7  | 0,9  | 1,0       | 1,0 | 4,4  | 2,7 | 0,5 | 0,2 | 1,2       | 1,3 |
| 7    | 6,3                               | 7,5  | 12,2   | 6,3  | 5,5  | 4,3  | 0,9       | 0,9 | 7,0  | 5,5 | 1,8 | 1,2 | 1,2       | 1,3 |
| 8    | 2,6                               | 3,5  | 3,9  | 3,1  | 2,2  | 1,6  | 1,5       | 1,5 | 1,9  | 1,3 | 0,5 | 0,3 | 1,9       | 2,2 |
| 9    | 1,7                               | 2,4  | 2,5  | 1,7  | 1,2  | 1,2  | 1,3       | 1,8 | 0,9  | 0,4 | 0,1 | 0,1 | 2,0       | 2,8 |
| 10   | 7,8                               | 9,8  | 13,6   | 11,5 | 7,0  | 7,3  | 1,2       | 1,6 | 5,4  | 3,7 | 1,2 | 1,1 | 1,9       | 2,3 |
| 11   | 10,3                              | 12,2 | 12,3   | 10,2 | 4,7  | 2,7  | 1,3       | 1,3 | 5,6  | 3,8 | 0,7 | 0,2 | 2,1       | 2,2 |
| 12   | 8,4                               | 10,5 | 21,1   | 17,5 | 11,9 | 11,2 | 0,9       | 1,1 | 10,1   | 8,2 | 4,3 | 3,7 | 1,4       | 1,6 |
| 13   | 6,3                               | 8,2  | 5,6  | 4,0  | 3,1  | 2,3  | 2,6       | 2,5 | 2,3  | 1,2 | 0,2 | 0,2 | 3,0       | 3,9 |
| 14   | 4,2                               | 6,0  | 4,5  | 3,8  | 2,9  | 3,0  | 2,6       | 4,0 | 0,7  | 0,4 | 0,1 | 0,1 | 6,3       | 9,7 |
| 15   | 7,5                               | 10,0 | 9,6  | 8,4  | 5,9  | 5,7  | 2,0       | 2,6 | 2,0  | 1,3 | 0,2 | 0,2 | 4,1       | 5,5 |

K-BaCl<sub>2</sub> has been removed. In agreement with the strong increase in the calculated  $K_{K/Ca}$  during grass growth, this indicates that with continuous K removal from the sandy soils it becomes increasingly difficult to remove  $K_{exch}$ . Although K-CaCl<sub>2</sub> extracts a fraction of  $K_{exch}$ , K uptake after 6 weeks exceeds the decrease in K-BaCl<sub>2</sub> (Table 6). K uptake is only slightly higher in the sandy soils (1.3 times), but K uptake can exceed K-CaCl<sub>2</sub> up to 10 times (soil 14). Although the contribution of  $K_{nexch}$  has been found in numerous studies, our results show that this contribution is not found in the investigated sandy soils.

Contrary to the results for the sandy soils, the silt and clay soils do show a contribution of  $K_{nexch}$  to K uptake. Already after 4 weeks  $K_{nexch}$  makes a considerable contribution to the total soil K supply potential; on average K uptake is  $1.6 \pm 0.7$  times larger compared to the change in K-BaCl<sub>2</sub>. The contribution of  $K_{nexch}$  is larger for the clay soils compared to the silt soils and for both the silt and clay soils this contribution of  $K_{nexch}$  increases during the experiment (Table 6). The change in K-BaCl<sub>2</sub> during the removal of K by the growing grass is thus the combined result of the desorption of  $K_{exch}$  and the replenishment of  $K_{exch}$  by  $K_{nexch}$ .

In accordance with the generally assumed relationship between the release of  $K_{nexch}$  and  $K_{ss}$  the relative contribution of  $K_{nexch}$  to K-uptake (expressed as the ratio K uptake over the corresponding change in K-BaCl<sub>2</sub>) indeed shows a close relationship with  $K_{ss}$  in the initial soil ( $r^2=0.92$  following a power function, Fig.8a). There is thus a rapid increase in the contribution of  $K_{nexch}$  with decreasing  $K_{ss}$ . As all soils show a steep decrease in  $K_{ss}$ , the initial  $K_{ss}$  may thus be indicative for the concentration gradient inducing  $K_{nexch}$  release. This may be explained by the diffusion controlled release of  $K_{nexch}$  and thus depends on the prevailing  $K_{ss}$  (Rahmattullah and Mengel 2000, Martin and Sparks 1985).

In agreement with conclusions by Rahmattullah and Mengel (2000), our results indicate that this process is only significant for silt and clay soils. The release of  $K_{nexch}$  from silt and clay fractions



should thus be considered when methods are developed for assessing the soil K supply potential for fertilizer recommendations. To be able to incorporate the contribution of  $K_{\text{nexch}}$  on a routine basis, this contribution must be assessed in a cost-effective way. This is approached by coupling the contribution of  $K_{\text{nexch}}$  to standard soil tests. The amount of  $K_{\text{nexch}}$  that participates in the replenishment of  $K_{\text{exch}}$  during the experiment approaches up to  $4 \text{ mmol kg}^{-1}$  after 4 weeks and up to  $6 \text{ mmol kg}^{-1}$  after 6 weeks for the silt and clay soils. This contribution of  $K_{\text{nexch}}$  is not a direct function of the amount of  $K_{\text{nexch}}$  present in the silt and clay soils but is related to the ratio  $K_{\text{nexch}}$  over  $K_{\text{exch}}$  ( $r^2=0.95$  when discarding soil 9, Fig.8b). Comparable to our results, Németh (1975) found that the change in the readily available K fraction, which was a measure for the change in grass yield with continuous cropping, was related to the ratio of a measure for  $K_{\text{nexch}}$  over a measure for readily available K (both assessed by electro ultra-centrifugation. When the amount of  $K_{\text{exch}}$  is large compared to  $K_{\text{nexch}}$  the contribution of  $K_{\text{nexch}}$  is small, and vice versa. For soil 9, the ratio  $K_{\text{nexch}}$  over  $K_{\text{exch}}$  is relatively high (6.7) compared to the other soils as a result of the relatively low  $K_{\text{exch}}$  ( $2 \text{ mmol kg}^{-1}$ ) of this soil. This low  $K_{\text{exch}}$  may presumably cause a relatively small flux of K towards the roots (K uptake is closely related to  $K_{\text{exch}}$ ) causing soil 9 to fall outside the regression line. This implies that to predict the contribution of  $K_{\text{nexch}}$  to the total soil K supply potential  $K_{\text{exch}}$  must exceed a certain minimum level. In addition, the contribution of  $K_{\text{nexch}}$  to the total soil K supply potential will depend on the type of crop, and more specifically on the root properties (Rahmatullah and Mengel 2000).

## CONCLUSIONS

This study investigates the soil K supply potential by studying the contribution over time of  $K_{\text{exch}}$  and  $K_{\text{nexch}}$  to the total K uptake by growing grass in a pot experiment. In addition, the dynamics of the K concentration in solution were measured in a dilution experiment and *in situ* in the pots via a rhizon sampler. Overall, after 6 weeks K uptake shows a close relationship with the directly available K fraction ( $K_{\text{ss}} + K_{\text{exch}}$ ) as approximated by K-BaCl<sub>2</sub>. The soils show a variation in affinity for K between the soil groups of different texture, as expressed by the soil K exchange coefficient. This affects the distribution of the directly available K fraction over  $K_{\text{ss}}$  and  $K_{\text{exch}}$ .  $K_{\text{exch}}$  is closely related to  $K_{\text{ss}}$  only when differentiating between soil groups of different texture. This differentiation must also be made when comparing K-CaCl<sub>2</sub> with K-BaCl<sub>2</sub> and  $K_{\text{ss}}$  as K-CaCl<sub>2</sub> extracts  $K_{\text{ss}}$  and only part of  $K_{\text{exch}}$ . The variation in the distribution of K over  $K_{\text{exch}}$  and  $K_{\text{ss}}$  was expected to influence the availability of K-BaCl<sub>2</sub> as uptake of K by the grass roots occurs from the soil solution. However, no effect of the affinity of the soil for K and the resulting  $K_{\text{ss}}$  is found on the availability of  $K_{\text{exch}}$ . The difference in  $K_{\text{ss}}$  is thus compensated for by the difference in soil K buffer power. In addition,  $K_{\text{ss}}$  is found to rapidly decrease for all soils. This decrease exceeds the expected decrease calculated from the decrease in  $\text{Ca}_{\text{ss}}$  and the exchangeable K and Ca fractions and the exchange coefficient calculated at the start of the experiment. Thus, indicating the increased affinity of the soil for K during K removal by the growing grass. This is also confirmed by the decrease in K availability of  $K_{\text{exch}}$  over time for the sandy soils.

Although the contribution of  $K_{\text{nexch}}$  to the total soil K supply potential is generally accepted, in our experiment this contribution is only found for the silt and clay soils and not for the sandy soils. For the sandy soils the directly available soil K fraction is found to be the only soil K contributing to the overall soil K supply potential, despite the presence of various amounts of  $K_{\text{nexch}}$  and the steep decrease in  $K_{\text{ss}}$ . In the silt and clay soils  $K_{\text{nexch}}$  shows a considerable contribution to K supply to the grass (up to 60%) already after 4 weeks and this contribution increases over time. The relative contribution of  $K_{\text{nexch}}$  compared to K uptake by the grass is inversely related to the initial  $K_{\text{ss}}$ . This



is in agreement with the general assumption that the release of  $K_{\text{nexch}}$  is diffusion controlled and stimulated by a low  $K_{\text{ss}}$ .

To predict the availability of soil K on the short term (growing season) a measure for the readily available K ( $K_{\text{ss}} + K_{\text{exch}}$ ) appears to be sufficient for all soils. When considering a weaker extraction method, e.g. K-CaCl<sub>2</sub>, soil's texture must also be taken into account. For longer timescales a distinction must be made between soils that can and cannot buffer this readily available K. For the soils in this study a distinction based on soil texture was sufficient but for soils with highly varying origin clay mineralogy must also be considered. For sandy soils the soil K supply potential is solely determined by the readily available K. When this K is depleted this will potentially result in K deficiency. For silt and clay soils the soil K supply potential is determined by both  $K_{\text{exch}}$  and  $K_{\text{nexch}}$ . The absolute contribution of  $K_{\text{nexch}}$  in these soils will depend on the type of crop but an estimation may be based on the ratio of a measure for  $K_{\text{nexch}}$  over a measure for  $K_{\text{exch}}$ .

## APPENDIX

To get a rough indication of crop uptake versus  $K_{\text{exch}}$  in the soil, a comparison is made between the removal of K by grass over a year and the K status of a representative set of Dutch agricultural soils. The average yield of grass is approximately 10 to 15 ton  $\text{ha}^{-1}$  in the Netherlands, with an average K concentration of 35,3 kg K  $\text{ton}^{-1}$  dryweight (based on data from '97, '98, '99, Praktijkgids bemesting, 2000). This results in an average removal rate of 3,2 to 4,9 mmol K  $\text{kg}^{-1}$  soil  $\text{yr}^{-1}$  (assuming a 20 cm soil layer and a bulk density of 1,4  $\text{kg m}^{-3}$ ). The K status of Dutch agricultural soils has been analyzed within the Kompas project (K-HCl and K- $\text{CaCl}_2$ ) on 3380 soil samples and within the Copernicus project (K- $\text{BaCl}_2$ , K-HCl, K- $\text{CaCl}_2$ ) on 41 soil samples (Table appendix). The Copernicus soils show that K- $\text{BaCl}_2$  and K-HCl are of the same order of magnitude and linearly related ( $r^2=0,91$ ). Both the Copernicus and Kompas soils show that K- $\text{CaCl}_2$  is on average approximately half of K- $\text{BaCl}_2$  and K-HCl. This is in accordance with the results found in this study and in previous studies e.g. (Van Erp et al. 1998). Combining the uptake data to the amount of K extracted with  $\text{CaCl}_2$ , HCl and  $\text{BaCl}_2$  shows that the average annual removal of K by grass (3,2–4,9 mmol  $\text{kg}^{-1}$ ) is of the same order of magnitude or slightly lower compared to the median amount of K extracted with K-HCl and K- $\text{BaCl}_2$  (4,6 and 4,9 mmol  $\text{kg}^{-1}$  respectively) and slightly higher compared to K- $\text{CaCl}_2$  (2,3 mmol  $\text{kg}^{-1}$ ). This rather rough comparison shows that in Dutch agricultural soils there is a narrow margin between the average amount of K removed by the crop and the amount of K extracted with the most commonly used measures to assess the soil K supply potential. The exchange complex must thus be replenished to maintain readily desorbable K at an adequate level. Ideally an estimation of this replenishment is made in order to minimize excessive fertilizer application.

**Table appendix:** Overview of HCl,  $\text{CaCl}_2$ , and  $\text{BaCl}_2$  extractable K (mmol  $\text{kg}^{-1}$ ) in Dutch agricultural soils, analyzed within the Kompas project ( $n = 3380$ ) and within the Copernicus project ( $n = 41$ ).

|           | Kompas soils |                    | Copernicus soils   |       |                    |
|-----------|--------------|--------------------|--------------------|-------|--------------------|
|           | K-HCl        | K- $\text{CaCl}_2$ | K- $\text{BaCl}_2$ | K-HCl | K- $\text{CaCl}_2$ |
| Median    | 4,6          | 2,3                | 4,9                | 4,0   | 2,5                |
| Min       | 0,5          | 0,3                | 1,2                | 1,2   | 0,6                |
| Max       | 51           | 28                 | 22                 | 17    | 11                 |
| Mean      | 5,9          | 3,1                | 6,6                | 5,3   | 3,2                |
| St. error | 0,1          | 0,04               | 0,4                | 0,5   | 0,7                |

*Chapter 6*  
**GENERAL DISCUSSION**

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The background of the research presented in this thesis is the growing need in the Netherlands to optimize fertilizer recommendations, especially concerning phosphorus (P). This is the result of the increasing awareness and legislation that the excessive use of fertilizers leads to environmental problems for surface and ground water. The issues concerning P management are not restricted to the Netherlands but are widespread and quite diverse. Environmental problems concerning excessive use of fertilizers are widespread in the western world, especially in Europe and North America e.g. (Breeuwsma et al. 1995; Sharpley et al. 1994a; Sims et al. 1998). This not only leads to the need to optimize fertilizer recommendations but also to identify soils that pose a potential risk to the surrounding environment. In other parts of the world, mainly Sub-Saharan Africa, the soils nutrient status has been depleted (Sanchez 2002). In addition, P is a non-renewable resource of which the reserves are rapidly diminishing (Cordell et al. 2009; Smit et al. 2009). For all these issues there is a growing need to increase the accuracy with which the potential of a soil to supply nutrients can be predicted, especially concerning P. The aim of the research presented in this thesis is to establish an accurate prediction of the soil nutrient supply potential based on the dynamic processes that determine this supply. To be widely (economically) applicable in routine soil laboratories this prediction should be based on a (combination) of standard soil tests. Because of the increasing importance of P in nutrient management strategies we mainly focus on this nutrient. A similar approach chosen for P is also applied for potassium (K).

In this chapter the results of our research are discussed and the implications of these results are put into a broader perspective. First the dynamic processes that determine the soil nutrient supply potential will be discussed. The similarities and differences of the potential of a soil to supply P or K will be reflected on briefly. This is followed by a discussion concerning soil tests in general and the potential and implementation of the combination of soil tests that are derived in our study for predicting the soil P and K supply potential. The implications of our results for fertilizer recommendations in the Netherlands will be discussed as well as the implications for nutrient management in general. A short summary and discussion of the research concerning P is also presented in Appendix 1 (in Dutch).

## **DYNAMIC SOIL P AND K SUPPLY POTENTIAL**

### ***Soil P supply potential as determined by an artificial sink***

The overall transfer of nutrients from soil to roots depends on the potential of a soil to supply nutrients and the ability of plants to acquire nutrients. Complex dynamic processes are involved in both the soil supply and root uptake. To be able to study the soil P supply potential, the system is simplified by mimicking the P removal by plants using an artificial sink in the form of Fe-(hydr) oxide coated filter paper strips (Pi-paper) under standardized conditions in the laboratory (Ch.2). P is released from a continuum of phases (Frossard et al. 2000; Koopmans et al. 2004) as P in the soil matrix consists of reversibly adsorbed P to variably charged Fe- and Al (hydr-) oxides, Fe-, Al-, and Ca- phosphate minerals, and organic P forms (Brady and Weil 2002). The continuous release of P from the soil is studied by refreshing the Pi-paper at set time intervals. Both the adsorption of P to the Pi-paper and desorption of P from the soil are not instantaneous. By determining the uptake characteristics of the Pi-paper and measuring the P concentration in solution ( $C_p$ ) during the desorption experiments, the supply characteristics of the soil can be established.

In the chosen experimental setup, the uptake rate of P from the solution is slower than the release rate of P by the soil. The adsorption rate of P to the Pi-paper is a direct function of  $C_p$  and the characteristics of the Pi-paper.  $C_p$  thus directly determines the current soil P supply. The

desorption rate of the soil is high enough to buffer  $C_p$  to a degree that keeps this concentration in equilibrium with the soil during the experiment.  $C_p$  thus depends on the nature and surface area of soil particles, pH, concentration of Fe, Al, and Ca, and the concentration of anions competing for adsorption (Geelhoed et al. 1997; Hinsinger 2001; Holford 1997). Several mechanistic models have been developed which describe the sorption of P by Fe- and Al oxides e.g. (Barrow 1983; Hiemstra and Van Riemsdijk 1996). These models are mechanistically sound but also need a number of specific input parameters. In contrast the more simplistic but generally applied Langmuir and Freundlich sorption isotherms only need two input parameters. The advantage of the Langmuir over the Freundlich isotherm is that it incorporates an adsorption maximum (Olsen and Watanabe 1957). For P the isotherm is generally (strongly) non-linear because with continuous desorption the activation energy with which P is adsorbed to the surface sites increases, and as a result the concentration in solution is increasingly buffered (Barrow and Shaw 1977; Sharpley 1983). Because during the experiment  $C_p$  is in equilibrium with the soil, a soil specific desorption isotherm can be derived. This sorption isotherm thus describes the soil P supply potential.

The release kinetics of P from the soil have been interpreted as consisting of two reactions: an initial fast reaction and a subsequent slow reaction (Barrow 1983; Lookman et al. 1995; Van der Zee and Van Riemsdijk 1986; Van Riemsdijk et al. 1984). The initial fast reaction is ascribed to the reversible sorption of P to surface sites of Al- and Fe (hydr-)oxides which are in direct contact with the aqueous phase. The decrease of P adsorbed to surface sites may be replenished by slow dissolution kinetics or by desorption of P bound inside porous Al- and Fe-(hydr-) oxides. These concepts may be used to understand the soil P supply during continuous removal in the desorption experiments (Ch.3). During the initial part of the desorption experiment (first 5 Pi-papers)  $C_p$  is in equilibrium with reversibly adsorbed P. The change in the initial  $C_p$  depends on where the soil is positioned on its sorption isotherm at the start of the experiment. With continuous desorption (Pi-paper 6 – 10) all soils show that  $C_p$  remains approximately constant. The very substantial capacity to buffer P with continuous desorption is the result of the low  $C_p$  in combination with a relatively (very) large total P content. The level at which the soil buffers  $C_p$  with continuous desorption may depend on the amount of P bound in the larger soil pools, e.g. inside porous Al- and Fe-(hydr-) oxides or present in soil minerals. In our experiments these processes are fast enough to maintain equilibrium between  $C_p$  and the soil's P reserves.

### **Soil P supply potential and growing grass**

The results of the experiments using the artificial P sink are verified in pot experiments using grass (Ch. 4). Apart from the fact that plants have a maximum P uptake which is related to environmental conditions, crop characteristics and fertilization, P uptake relative to this maximum is determined by the soil P supply potential. This relative P uptake is found to be comparable to P uptake by the sink. The change in the (measure for) P concentration in solution is also found to be comparable between pot experiments and artificial sink experiments. Consequently, the change in reversibly adsorbed P ( $Q_p$ ) and the change in a measure for  $C_p$  (P-CaCl<sub>2</sub>), integrated in the soil specific P desorption isotherm as a result of P uptake by the growing grass is found to approximate (part of) the desorption isotherm derived from the desorption experiment using the artificial P sink.

Comparable to plant roots, the Pi-paper removes P from the solution, subsequently initiating the release of P from the soil into the solution. This is in agreement with the main nutrient availability models in which the soil solution plays a key role in calculating the overall P transfer from soil to root. (Barber 1995; Jungk and Claassen 1997; Tinker and Nye 2000). In 1860 (Mulder) saw the importance of the soil solution and concluded that in terms of soil fertility not the amount of

a specific nutrient present in the soil, but the availability of this nutrient is important. Mulder defined available as the amount of nutrient that can become dissolved. In 1920 (Hoagland et al.) stated that further progress in the study of soil fertility would depend on the increased knowledge of the soil solution. Elaborating hereon numerous studies have stressed the importance of the soil solution as a tool in understanding and predicting the soil P status e.g. (Frossard et al. 2000; Morel et al. 2000; Smethurst 2000). In our studies, the concentration in solution, measured *in situ* or by an approximation hereof using a weak extractant has also been essential in understanding the soil P and K supply potential.

Similar to the results from the artificial sink experiments, the P concentration in the (bulk) soil solution is also found to be in equilibrium with P adsorbed to the soil matrix in the pot experiments. That the soil P release kinetics is relatively fast compared to P uptake by the roots, i.e. that P desorption from the soil is not rate limiting during uptake of P by roots is also found by Olsen and Watanabe (1966). The overall rate of transfer of P from soil to root is thus determined by the rate of absorption per unit root. This absorption rate is primarily determined by the absorbing power of the root and the nutrient concentration at its surface (Jungk and Claassen 1997). Uptake increases with root absorbing power until diffusion through the soil becomes limiting (Nye 1966). Plant roots may affect the P concentration in the vicinity of the root by root induced pH changes, or the release of root exudates (rhizosphere processes). The impact and relative contributions depend on plant species, plant nutrient status, and ambient soil conditions (Hinsinger 2001). Other biological factors, e.g. microbial biomass, mycorrhiza, and earthworms, may also affect P availability (Frossard et al. 2000). These mechanisms may play a (major) role in uptake from P deficient soils. In our experiments, using ryegrass and Dutch agricultural soils, we indeed found fluctuations in  $C_p$  which were closely related to changes in pH of the soil solution. On the overall P uptake however, these fluctuations did not seem important.

To determine whether P supply can meet the P demand of a crop, the demand must also be specified. Our pot experiments were performed with grass for which the main mechanisms regulating P uptake at a certain soil P supply potential are both the rate of P absorption per unit root and the size of the root system (Föhse et al. 1988). The plants nutrient requirement differs per development stage of the plant (Jungk and Barber 1975), per type of plant (Föhse et al. 1988) and even per genotype (Nielsen and Schjørring 1983). For crops P requirement can thus be expressed by the size and morphology of the root system and the absorption rate per unit root. The transfer rate of P from a soil to a crop is a function of the rate with which P is removed from the soil solution. During P removal the soil subsequently moves down its desorption isotherm. The extent to which this occurs depends on P requirement of the crop.

### **Phosphate versus potassium**

There are some essential similarities and differences in (predicting) the potential of a soil to supply P or K. For both P and K, diffusion is the main transport mechanism from soil to root as uptake exceeds the amount in solution and a concentration gradient is developed between bulk soil and the soil in the vicinity of roots (rhizosphere). As a result the flux towards the root is a function of water content and the capacity of a soil to buffer the concentration in solution. Assuming that the concentration at the root surface is negligibly low compared to the concentration in the bulk soil, the diffusive flux is directly related to the concentration in the bulk soil. This implies that to determine the nutrient supply potential, knowledge of the concentration in solution is essential. In our experiments this was indeed the case for P (Ch.2-4). P uptake was continuously a function of (a measure for)  $C_p$ . The supply potential could be understood by (a measure for) the initial

concentration in solution and the capacity of the soil to maintain this concentration as can be described using a soil specific sorption isotherm. For all soils the capacity to buffer  $C_p$  is high as a result of the relatively low  $C_p$  compared to the amount of P adsorbed to the soil surface ( $Q_p$ ) buffering this concentration. For K however (Ch.5), the amount of K in solution may be high (up to 43%) relative to the amount of readily exchangeable K ( $K_{exch}$ ). As a result, the capacity of the soil to buffer the K concentration in solution ( $C_k$ ) is relatively low. There is however a marked difference between soil groups of different texture (sand, silt, and clay). Although  $C_k$  is lower in clay soils compared to the sandy soils, the soil K buffer power of the clay soils is much larger compared to the sandy soils. As a result the difference in  $C_k$  between the soil groups of different texture is compensated for by the difference in buffer power and the readily available K ( $K_{exch} + K$  in solution) is equally available for sand, silt, and clay soils (this research). Contrary to the results for P however, K uptake by the grass does not show a direct relationship with  $C_k$ . Soil K supply is a function of  $K_{exch}$ , which is readily available for K uptake. For sandy soils no replenishment of this readily available soil K is found to occur. For the silt and clay soils the readily available K is replenished by soil K that is bound in cavities between two opposing siloxane planes in 2:1 clay minerals ( $K_{nexch}$ ). This replenishment is a function of the ratio  $K_{nexch}$  over  $K_{exch}$ . Similarly the replenishment of readily available soil P is also a function of the ratio of the amount of soil P replenishing the readily available P over the readily available P.

## **PREDICTING SOIL P AND K SUPPLY POTENTIAL BASED ON STANDARD SOIL TESTS**

The main challenge of this research was to derive a combination of soil tests to increase the accuracy with which routine soil laboratories predict soil P and K supply potential and also be economically affordable. Soil tests have been in use for over a century to determine the nutrient status of soils as a basis for nutrient management. The considerations from a routine soil laboratory point of view are that the soil test must ideally be cost- and labor effective, give reproducible results, be applicable to all soils, and nowadays must also produce a minimal amount of waste. A soil test extracts a certain nutrient fraction from the soil which is the result of the interaction between the soil and the extracting solution. Over time, a wide variety of P extraction methods have been developed that may differ largely in respect to the amount of P extracted for a given soil sample (Kuo 1996). Different countries, states, and laboratories show a large variation in their choice of soil test (Allen et al. 1994; Neyroud and Lischer 2003) indicating the lack of consensus concerning the prediction of the soil P supply potential based on a single soil test. Practical issues have often dominated the development and value of most extraction methods. For instance, when the Pw method (P water extraction) was introduced, disturbance in the amount of P extracted due to the presence of colloids was realized, but due to practical considerations the extra steps to counteract this effect have been neglected, leading to a rather ill defined system (Koopmans et al. 2005).

### ***Methodology for predicting soil P supply potential***

In chapter 3 a methodology is derived for predicting soil P supply potential using a combination of soil tests based on the dynamic processes that determine this supply as studied using an artificial P sink (Ch.2) and verified in pot experiments using grass (Ch.4). The integration of soil P supply potential and standard soil tests is approached by modeling the soil P desorption and the decrease in  $C_p$  during continuous removal of P by the artificial sink. The continuous desorption to the sink is predicted using a Langmuir sorption isotherm. The two soil specific parameters of this isotherm are related to data derived from standard soil tests. The soil P supply potential can be predicted

with various degrees of accuracy. To be able to make a prediction of the soil P supply potential a minimum of two parameters is needed; a measure for the reversibly adsorbed P ( $Q_p$ , e.g. P-Olsen, PAL) and a measure for  $C_p$  (e.g. P-CaCl<sub>2</sub>). The measure for  $C_p$  is an indication of the rate with which P can be removed from the soil. The ratio  $Q_p$  over  $C_p$  is an indication of the capacity of the soil to maintain  $C_p$ , and thus the capacity to maintain the flux from the soil to the sink. The accuracy of this prediction increases for soils with increasing buffer power, i.e. with decreasing P saturation of the reactive surface area associated with the readily desorbable P, as in this case the isotherm is indeed linear. To increase the accuracy of this prediction for soils that don't have a high buffer power and the isotherm is thus non-linear, a measure for the reactive surface area (e.g. Fe<sub>ox</sub> and Al<sub>ox</sub>) of the soil must also be taken into account. In addition, to be able to extend the prediction of the soil P supply potential to an amount of P exceeding the amount of readily desorbable P, a measure for the total amount of P must be included (e.g. P<sub>ox</sub>). This total amount indicates the level at which the concentration is highly buffered once the reversibly adsorbed P has been depleted. The fundamental problem in determining the nutrient status of a soil using a single soil test is that it is only to a very limited degree based on the dynamic processes that determine the soil nutrient supply potential (Mengel 1982). A single soil test may be an indicator of either P intensity or P quantity, or a complicated mixture of both factors but cannot be an indicator of the relationship between intensity and quantity, i.e. the soil's buffer power (Holford and Mattingly 1976). It has therefore been suggested that improved soil testing methods should be used which are based more on the mechanisms that control nutrient availability to plants than methods used at present (Morel et al. 2000; Skogley 1994). These methods are however difficult to implement in routine soil laboratories as they are generally more laborious to execute compared to the traditional extraction methods. Calibration with crop response is also lacking. A proposal for increasing the accuracy in predicting soil P supply potential suggests the incorporation of (a measure for) the soil P buffer power (Ehlert 2003; Frossard et al. 2000; Holford 1997). In the derived methodology the buffer power is incorporated. For the simplest approximation only a single additional extraction needs to be performed to get an indication of this buffer power. The advantage of the methodology based on the sorption isotherm is that the user can decide the level of accuracy of the prediction. The sorption isotherm can be used as a simple tool to interpret the results. The derived methodology is based on Dutch agricultural soils. As described in the introduction the issues concerning P are diverse and widespread. Because the methodology is based on the actual processes that determine the dynamic soil P supply potential, the method is also expected to be widely applicable.

### **Methodology for predicting soil K supply potential**

In chapter 5 a prediction of the dynamic soil K supply potential is derived by studying the changes in soil K fractions during K uptake by a growing crop. To predict the availability of soil K on the short term a measure for the readily available K ( $K_{ss} + K_{exch}$ ) appears to be sufficient for all soils. In intensively mowed grassland K removal in a growing season is approximately equal to the amount of readily available K. For longer timescales a distinction must be made between soils that can and cannot buffer this readily available K. For the soils in this study a distinction based on soil texture is sufficient, but for soils of widely varying origin the clay mineralogy must also be considered. For sandy soils the readily available K is not found to be replenished. For these soils the prediction of the soil K supply potential can solely be determined by the readily available K. For silt and clay soils the readily available soil K is replenished. The soil K supply potential is determined by both  $K_{exch}$  and  $K_{nexch}$ . The absolute contribution of  $K_{nexch}$  in these soils will depend on the type of crop but



an estimation may be based on the ratio of a measure for  $K_{\text{nexch}}$  over a measure for  $K_{\text{exch}}$ .

## CaCl<sub>2</sub> METHOD

This PhD research project was originally initiated under the title: "Towards a more mechanistic based fertilizer recommendation based on 0.01M CaCl<sub>2</sub>". The CaCl<sub>2</sub> method indeed is a main thread through this research. It is therefore appropriate to elaborate our findings concerning the interpretation of the results using this extraction method. The 0.01M CaCl<sub>2</sub> extraction method was introduced by Houba et al. (1986) as a promising multi-nutrient extraction method. Details concerning the laboratory procedure have been described in several studies (Houba and Novozamsky 1998; Houba and Temminghoff 1999; Houba et al. 2000; Van Erp et al. 1998). Apart from the economical, operational, and analytical advantages (repeatability and reproducibility (Houba and Novozamsky 1998), there are several theoretical considerations for choosing the 0.01M CaCl<sub>2</sub> method (Houba et al. 1996). The ionic strength of the extractant is low enough to approximate the salt concentration in the soil solution of agricultural soils, but high enough to dictate the ionic strength, and thus enhances the comparability between soils. As Ca<sup>2+</sup> is the main cation on the exchange complex, extraction with CaCl<sub>2</sub> gives information on the other adsorbed cations. Moreover, the pH of the extract solution is unbuffered and therefore reflects the availability of the nutrients at the pH of the soil. Since it is a multi-nutrient extractant, relationships between the different nutrients and measurable dissolved organic carbon fractions can be studied. CaCl<sub>2</sub> is a weak extractant. It is however too simple to assume that, because the extracting solution is comparable to the soil solution with respect to pH and electrolyte concentration, the composition of the extract is equal to the soil solution.

### P-CaCl<sub>2</sub>

The interpretation of P-CaCl<sub>2</sub> can be approached in two ways; the concentration in solution and the amount of P extracted. In terms of the P concentration in solution P-CaCl<sub>2</sub> is of the same order of magnitude and linearly related to the P concentration in the soil solution ( $C_p$ ) measured *in situ* (Ch. 4). This implies that the environment in the CaCl<sub>2</sub> extract is comparable to the environment in the soil solution of the pot experiment. Measuring an approximately equal P concentration at much lower soil to solution ratio (SSR) in the extract (0.1 kg l<sup>-1</sup>) compared to the soil solution (3–7 kg l<sup>-1</sup>) shows the soils large capacity to buffer  $C_p$ . This is caused by the relatively low  $C_p$  compared to the amount of P adsorbed to the soil surface (Q) buffering this concentration. It follows that the amount of P in solution when expressed per kg soil, is much larger in the extract compared to the soil solution. P-CaCl<sub>2</sub> thus mainly consists of P that is weakly adsorbed and which can readily replenish the soil solution. However, compared to the reversibly adsorbed P (approximated by P-Olsen), P-CaCl<sub>2</sub> is much lower (on average P-CaCl<sub>2</sub> extracts approximately 5% of P-Olsen). The previous deals with inorganic dissolved P whilst for peat and calcareous clay soils dissolved organic P should perhaps also be considered (Koopmans et al. 2006). The relative contribution of inorganic and organic P species also depends on soil management (McDowell 2003).

During the pot experiment,  $C_p$  is very sensitive to the change in the composition of the soil solution induced by plant roots. Contrary to these fluctuations, P-CaCl<sub>2</sub> is not sensitive to these changes. The reason for this is that the salt level and the Ca-concentration, which both affect the P adsorption (Antelo et al. 2005; Barrow et al. 1980; Rietra et al. 2001), are imposed in the extract and are variable in the soil solution. P-CaCl<sub>2</sub> may thus be a more robust measure for the P intensity of the soil than C as it is related to the initial C but is less prone to fluctuations.

Despite the fact that P-CaCl<sub>2</sub> is an intensity parameter the amount of P extracted may be as large

as the total amount of P taken up by a crop (when expressed per kg soil) in highly fertilized soils (Hylander et al. 1995), Ch. 4). Generally however, P-CaCl<sub>2</sub> will be (much) smaller compared to the amount taken up by a crop.

In terms of predicting the soil P supply potential, P-CaCl<sub>2</sub> approximates C<sub>p</sub> and thus gives an indication of the size of the potential flux to the roots and thereby of the initial transfer rate of P from soil to plant root. The capacity of the soil to maintain this flux depends on the soil P buffer power. The predictive value of P-CaCl<sub>2</sub> as a measure for the potential flux increases with increasing buffer power of the soil. However, the predictive value of P-CaCl<sub>2</sub> also depends on the situation in the field. The main transfer mechanism of P from soil to root is diffusion, and the effective diffusion coefficient will affect the actual flux. In the pot experiments the grass was watered daily, but in the field soil water content may affect nutrient availability, especially for P and K. In addition the P demand and root system will also affect the actual flux.

### **K-CaCl<sub>2</sub>**

Compared to P-CaCl<sub>2</sub>, K-CaCl<sub>2</sub> is quite different when comparing the amount extracted and the concentration in the extract to the amount of exchangeable K (K<sub>exch</sub>) and the K concentration in the soil solution measured *in situ* (C<sub>K</sub>) during a pot experiment. There is no overall relationship between K-CaCl<sub>2</sub> and C<sub>K</sub>. However, when differentiating between soil groups of different texture, namely sand, silt, and clay soils the soils show three linear relationships between the K concentration in the CaCl<sub>2</sub> extract and C<sub>K</sub>. Because C<sub>K</sub> is relatively large compared to the amount of exchangeable K (K<sub>exch</sub>) that directly buffers this concentration, the K concentration in the extract is lower than C<sub>K</sub>. The capacity of the soil to buffer C<sub>K</sub> in the extract (i.e. the slope) increases with soil groups of increasing clay content. In soils differing greatly in mineralogy this will also play a role (Sharpley 1989) but in the soils used in our studies this was not the case.

Compared to K<sub>exch</sub>, the amount of K extracted with 0.01M CaCl<sub>2</sub> (K-CaCl<sub>2</sub>) is large (on average approximately 50%). The soils show a linear relationship between K<sub>exch</sub> and K-CaCl<sub>2</sub> when differentiating between soil groups of different texture. K-CaCl<sub>2</sub> extracts a certain fraction of K<sub>exch</sub> which is approximately equal for all three soil groups of different texture (approximately equal slopes). However, the amount of K<sub>exch</sub> that is structurally not extracted with K-CaCl<sub>2</sub> (the intercept) increases with soil groups of increasing clay content. This is the result of a combination of the increased presence of high affinity K sorption sites for which K is not exchanged by Ca, and the smaller amount of Ca relative to the CEC for soil groups with increasing texture (Van Erp 2002). K-CaCl<sub>2</sub> not only extracts an intermediate amount of soil K compared to the amount of K in the soil solution and K<sub>exch</sub>, the decrease in K-CaCl<sub>2</sub> also behaves in an intermediate way.

## **APPLICATION OF PROPOSED METHODOLOGY IN ENVIRONMENTAL SOIL TESTING**

The increasing percentage of agricultural soils that have a high nutrient status has initiated the desire to identify soils that pose a potential threat to surrounding water bodies. P can be lost as dissolved P from the top soil through subsurface pathways or as erosion of particulate P. In areas with sloping landscapes erosion is the main cause of P loss to surface waters. In flat regions, e.g. like the Netherlands, transport of dissolved P through the soil profile is dominant in sandy soils, whereas in clay soils incidental losses are dominant (Chardon and Schoumans 2007). Identifying soils that are potential non-point pollution sources involves characterizing and combining both soil P status and hydrological setting. In the U.S.A. a "Phosphorus indexing system" is (being) developed which integrates soil P status, fertilizer management, and transfer factors, e.g. drainage,

runoff, and erosion potential (Lemunyon and Gilbert 1993). The assessment of the soil P status is generally based on soil tests and several methods have been applied or developed as environmental soil tests. This offers new challenges for routine soil laboratories in identifying potential critical source areas (Sims 1993) and monitoring to evaluate management strategies or policies (Fixen and Grove 1990). Adapting soil testing strategies to the requirements of environmental soil testing is however not straightforward as all aspects, from soil sampling to implementation of the results, must be carefully re-examined (Sims 1993). For instance, there is a fundamental difference as agronomic soil testing aims at defining soils with a low P status and environmental soil testing aims at defining soils with a high P status.

In Dutch environmental and manure policies the concept of the degree of P saturation (DPS) was introduced for non-calcareous sandy soils (Van der Zee et al. 1990). This is the ratio of the total amount of soil P (approximated by  $P_{ox}$ ) over the total sorption capacity (approximated by a fraction of  $(Fe_{ox} + Al_{ox})$  times 100%. The critical levels for environmental targets are derived from the degree of P saturation (DPS), in which the critical level has been set at a DPS of 25% above which the soils are defined as being P saturated (Van der Zee et al. 1990). In The Netherlands, and also in the rest of Europe and North America (Beauchemin and Simard 1999) a large percentage of the agricultural soils have a DPS that exceeds 25%, thus posing a threat to the surrounding environment (Breeuwsma et al. 1995; Chardon and Schoumans 2007). Fertilizer application was however never forbidden on soils with a DPS exceeding 25% in The Netherlands because this would lead to friction between manure surplus and manure application and result in large surpluses of manure (Chardon and Schoumans 2007). Model results predict that reducing P input in acid sandy soils in order to reduce P leaching to an environmentally acceptable level, may result in P concentrations below the target value needed for optimal crop yields (Del Campillo et al. 1999). In addition, it may take decades before the P-status of the soil in the P sensitive areas has been reduced to environmentally acceptable levels (Schoumans and Groenendijk 2000). These issues indicate that in the sensitive areas, mainly consisting of noncalcareous sandy soils with intensive livestock farming, the situation is complex. To optimize removal of added P, restrictions may be set on the type of crop, or more specifically the root length density of crops and thereby on the intensity with which the applied P is removed from the soil (Van Noordwijk et al. 1990).

Various studies have shown a correlation between DPS and the P concentration in solution ( $C_p$ , e.g. (Delgado and Torrent 2001; Lookman et al. 1996; Sharpley 1995). The explained variance of this correlation in these various studies however depends on the variation in studied soils and the extractants used to determine the DPS (Beauchemin and Simard 1999). Although DPS and  $C_p$  are related, it is better to approach them as being complementary (Koopmans et al. 2001).

In the Netherlands the soil test in use for arable land is the water extraction ( $P_w$ , (Sissingh 1971) which is also suggested to be applicable for environmental soil testing (Schoumans and Groenendijk 2000). Sharpley (1993a; b) proposed using a simple method using an Fe oxide-impregnated paper (Pi-paper) as proposed by Van der Zee (1987) as an environmental soil test. In the proposed experimental setup this will approximate an intensity parameter (Ch.3). Other measures for the P intensity, e.g. 0.01M  $CaCl_2$  or a water extraction at different soil to solution ratios, have also been shown to be related to P concentration in water leaching from undisturbed soils (Maguire and Sims 2002; McDowell and Sharpley 2001; Turner et al. 2004). This relationship is soil dependant (Turner et al. 2004). Data describing the relationship between a measure for P quantity (standard soil test) and P concentration in drainage waters has been used to determine a change point above which the concentration in solution rapidly increases (McDowell and Sharpley 2001). This change point could be determined using a minimum of 8 samples (McDowell et al.

2001). This would be comparable to determining a desorption isotherm. From the above it is clear that, comparable to soil testing for agricultural purposes, environmental soil testing has also developed different approaches. In principle the same processes occur when P is removed from a soil, either by transfer to the surrounding environment or by uptake by plant roots. When soil P is removed the concentration in solution decreases in equilibrium to the soil's solid phase as described by its soil specific sorption isotherm. This implies that the methodology derived as a basis for predicting the soil P supply potential to a growing crop (Ch.3) will also be applicable as a basis for predicting the potential P loss to the surrounding environment. Using a measure for P intensity as an environmental soil test will provide information on the current potential flux from the soil to the surrounding environment. But will give no information on how this flux will change upon continuous removal. With the additional measurement of a measure for the reversibly adsorbed soil P ( $Q_p$ ) a (rough) approximation of the buffering of the P intensity can be obtained. This would provide information on the capacity of the soil to maintain the P flux from soil to surrounding environment. This can be predicted with much higher accuracy when the P sorption capacity is included. The long-term prediction can be achieved by including a measure for the total P content. The P sorption capacity and total P content can be approximated by  $P_{ox}$ ,  $Fe_{ox}$  and  $Al_{ox}$ . These are also used to derive the DPS. The DPS is a measure for the P-status in the long-term. Insight in the sorption isotherm gives insight into the potential of a soil to release P to the environment in the short term. To gain a comprehensive understanding of the soil P supply potential a measure for the P intensity, P quantity, P sorption capacity and total P content may be combined. These parameters may change in time in the following order:  $Fe_{ox}$  and  $Al_{ox}$ ,  $P_{ox}$  measure for reversibly adsorbed P, P intensity. When determining these parameters this can be taken into account in the frequency with which they are measured. In this way agronomic and environmental soil testing may be combined.

When P is transferred to the surrounding environment by erosion, it may be appropriate to determine these parameters on the soil size fraction prone to be eroded (Maguire et al. 2002). With stricter legislation concerning P application in combination with intensive livestock farming in The Netherlands, fertilizer will be applied as manure or slurry and the use of inorganic fertilizer will be minimal. As dissolved organic P is a function of soil management, it might be useful to measure both the organic and inorganic P-CaCl<sub>2</sub> (McDowell 2003) in order to assess P intensity, especially when the total concentration levels are very low. This is seldom the case in Dutch agricultural soils at present.

## **IMPLICATIONS FOR FERTILIZER RECOMMENDATIONS**

### ***Fertilizer recommendations in general***

Several steps are involved in the process of establishing and implementing fertilizer recommendations. These steps involve: sample collection, sample preparation, soil analyses, interpretation of soil test results, and implementation of results in nutrient management strategies. Sample collection must aim at collecting a representative sample and involves decisions concerning spatial and temporal variation in the field, e.g. distribution of sampling points, sampling depth, time of sampling. Sample preparation involves decisions concerning e.g. drying, sieving, and storage. The interpretation of soil tests in terms of fertilizer recommendations is based on either correlation experiments that determine the relationship between soil test result and crop response, or calibration experiments that determine yield response to fertilizer application at a certain soil test result (Sharpley et al. 1994b). The accuracy decreases when these calibration or

correlative studies are used to predict fertilizer application (Fixen and Grove 1990). As the original relationship between soil test result and crop response is generally not very strong, the choice of response curve has a large effect on the critical soil test result below which crops are predicted to respond to fertilizer application (Mallarino and Blackmer 1992), and fertilizer recommendation (Dahnke and Olson 1990). In addition, poor characterization of climatic conditions during the experiment and of the experimental sites also affect the interpretation of soil test results (Blair and Lefroy 1993). The final decisions when implementing the results in nutrient management strategies depend on economic situation, legislation, experience, manure or fertilizer availability, fertilizer cost etc. Each step introduces a possible contribution to the overall error in predicting the nutrient status and the derived fertilizer recommendation.

In this thesis we have focused on deriving a methodology for increasing the accuracy with which the soil nutrient supply potential can be predicted. With this generally applicable methodology the choice of soil analyses and the interpretation of the soil test results for P and K can be optimized. When implementing the suggested methodology optimization of the other steps must however also be taken into account. In addition, the translation of soil nutrient status to fertilizer recommendation should be adapted per (group of) crop(s). This adaptation must be based on the crops nutrient requirement as expressed by the size and morphology of the root system and the absorption rate per unit root. These crop characteristics, in combination with the effective diffusion coefficient of the nutrient in the soil determine the soil area exploited and thus the relative importance of the readily available nutrients (P in the soil solution and K in the soil solution + exchangeable K) and the P and K replenishing this readily available P and K.

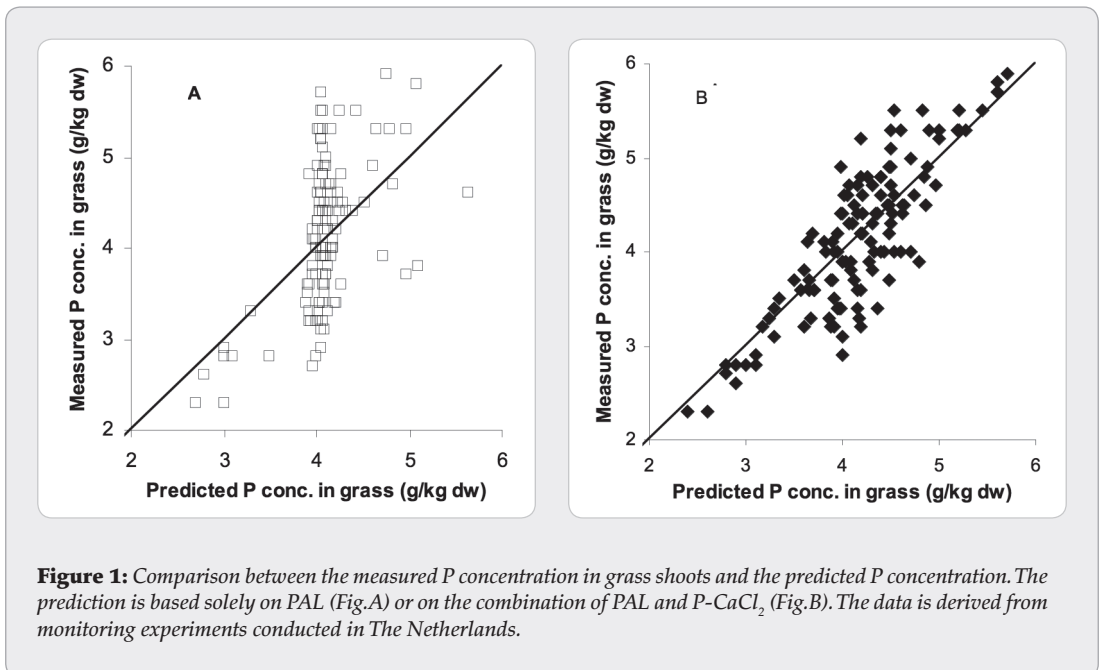
### ***Phosphorus fertilizer recommendations in the Netherlands***

As described in the introduction of this thesis (Ch.1) both the chosen soil test and the method of analysis of this soil test have changed over the years in the Netherlands. The applied soil tests have been developed per nutrient and resulted in 11 different extraction methods for the different nutrients. At present soil testing laboratories are keen to implement a multi-nutrient extraction method for economical and environmental (less waste) reasons. In the Netherlands the 0.01M  $\text{CaCl}_2$  has been suggested to be a good option for its additional analytical advantage, and the advantage of being relatively easy to interpret in soil chemical terms (Houba et al. 1996; Houba and Novozamsky 1998). Changing from one extraction method to another gives rise to problems, as the fertilizer recommendations are based on the relationship between the old soil test results and crop response. This implies that either a new calibration must be performed in field-and/or pot experiments or that the new soil test is correlated to the previous soil test. It is clear that the calibration approach is expensive and laborious and that the correlative approach introduces an additional source of error. In The Netherlands PAL is used for grassland soils and Pw for soils from arable land. There is a poor correlation between P- $\text{CaCl}_2$  and PAL. Although there is a seemingly good correlation between P- $\text{CaCl}_2$  and Pw when considering the entire range in values, this correlation decreases when considering the range that is relevant for fertilizer recommendations (Los et al. 2005). In addition, the relationship between crop response and P- $\text{CaCl}_2$  has been described in several different studies with a substantial variation in the explained variance (Ch.1). In this thesis we have deduced that P- $\text{CaCl}_2$  may be a good basis for fertilizer recommendations though only in combination with a measure for Q. Except at a high P intensity at which it is safe to assume the soil P supply potential is sufficient during the growing season (Ch.3). Because PAL is already in use in the Netherlands this is a logical choice as a measure for Q. It must be noted that in theory this soil test does not give reliable results for calcareous soils. The combination of soil

**Table 1:** Field examples of 5 plots in which the P concentration in grass shoots, PAL, P-CaCl<sub>2</sub>, and the current fertilizer recommendation are compared. The current fertilizer recommendation is solely based on PAL.

| Plot | Valuation        | PAL<br>(mg P <sub>2</sub> O <sub>5</sub> 100g <sup>-1</sup> ) | P-CaCl <sub>2</sub><br>(mg kg <sup>-1</sup> ) | P-conc grass<br>(g P kg <sup>-1</sup> dw) |
|------|------------------|---|---|---|
| 1    | Sufficient       | 35  | 1.0   | 3.1                                       |
| 2    | Sufficient       | 32  | 4.0   | 4.6                                       |
| 3    | Rather low       | 23  | 6.0   | 4.1                                       |
| 4    | Amply sufficient | 41  | 2.0   | 4.2                                       |
| 5    | Rather low       | 19  | 0.24  | 2.7                                       |

tests provides a basis with which fertilizer recommendations can be optimized. The effect of using the combination of a measure for C<sub>p</sub> (P-CaCl<sub>2</sub>) and a measure for Q (PAL) on the eventual fertilizer recommendation has been investigated using field data obtained from monitoring experiments on a large number of fields in The Netherlands (D.W. Bussink, Nutrient management Institute Wageningen, (Hietkamp 2008a; b). Table 1 shows the P concentration in grass shoots, PAL, P-CaCl<sub>2</sub>, and the P-status according to the current fertilizer recommendation for 5 of these plots. The current fertilizer recommendation is solely based on PAL. Plot 1 and 2 are both judged as having a P-status that is 'sufficient'. Despite the equal value for PAL, P-CaCl<sub>2</sub> is four times higher in plot 2 compared to plot 1. The higher P-CaCl<sub>2</sub> indicates the larger availability of PAL and as a result P uptake is also higher on plot 2 compared to plot 1. Plot 3 and 4 receive the



value 'rather low' and 'amply sufficient' based on the current fertilizer recommendation because for plot 3 PAL is half the value of plot 4. However, P-CaCl<sub>2</sub> is three times higher in plot 3 compared to plot 4. This results in an equal P uptake by the grass from both plots. These two examples show that it is not sufficient to predict the soil P supply potential for P uptake by grass based only on PAL, and that the combination of P-CaCl<sub>2</sub> and PAL is much more accurate. This is confirmed by comparing the measured and predicted P concentration in grass for all data from the monitoring experiments (Fig.1).

The closer correspondence with the 1: 1 line and less scatter in the data clearly shows the increase in accuracy when applying the combination of soil tests compared to the prediction based solely on PAL. In addition, soils with very low P-status can be pointed out more accurately. For example the P-status of plot 5 (Table 1) is not defined as very low based on PAL, while the measured P concentration of the grass is below the minimum value of 2.8 g P kg<sup>-1</sup> dryweight needed to meet nutritional requirements for cows for which grass is the main diet component (Valk and Sebek 1999). In combination with P-CaCl<sub>2</sub> this could have been predicted. Taking into account P dynamics approximated by two standard soil tests is thus a major improvement regarding the development of accurate fertilizer recommendations. In the Dutch situation the new methodology also has the advantage of being applicable to both grass- and arable land for which at present separate soil tests are used.

## CONCLUSIONS

This thesis presents a thorough approach in which the soil chemical processes that determine the soil P and K supply potential are studied and used to derive a combination of standard soil tests that can be easily implemented in routine soil laboratories. For P the methodology not only provides a tool for routine soil laboratories to increase the accuracy of predicting soil P supply potential but also to identify agricultural areas that are vulnerable to P loss to aquatic ecosystems (critical source areas). In field trials the implementation of the derived methodology has resulted in a large increase in the accuracy with which P uptake by grass can be predicted. Using the methodology in decreasing nutrient status of soils, e.g. when changing use of land from agriculture to a natural situation by mining or when identifying critical source areas additional research is needed.

The approach chosen in this research has resulted in a well grounded and generally applicable methodology for predicting the potential of soils to supply the nutrients P and K.

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*Appendix 1*

**OP WEG NAAR EEN NAUWKEURIGE  
VOORSPELLING VAN DE  
CHEMISCHE BESCHIKBAARHEID VAN  
FOSFAAT IN DE BODEM  
VOORSPELLING VAN FOSFAATOPNAME  
DOOR ENGELS RAAIGRAS**

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**Het nauwkeurig vaststellen van de beschikbaarheid van fosfaat (P) in de bodem is van groot belang om agrarische- en milieudoelstelling te kunnen integreren. Vanuit de bodemchemische processen die de beschikbaarheid van P in de bodem bepalen is daarom een nieuwe methodiek afgeleid. Deze is gebaseerd op een combinatie van minimaal twee parameters die gangbaar zijn binnen het routinematig bodemonderzoek maar tot nu toe los van elkaar werden gebruikt. Met de nieuwe methodiek kan de P-status van een perceel beter worden vastgesteld met als gevolg dat de huidige P-adviezen naar verwachting met zeker 15 kg ha<sup>-1</sup> verlaagd kunnen worden.**

## **ACHTERGROND**

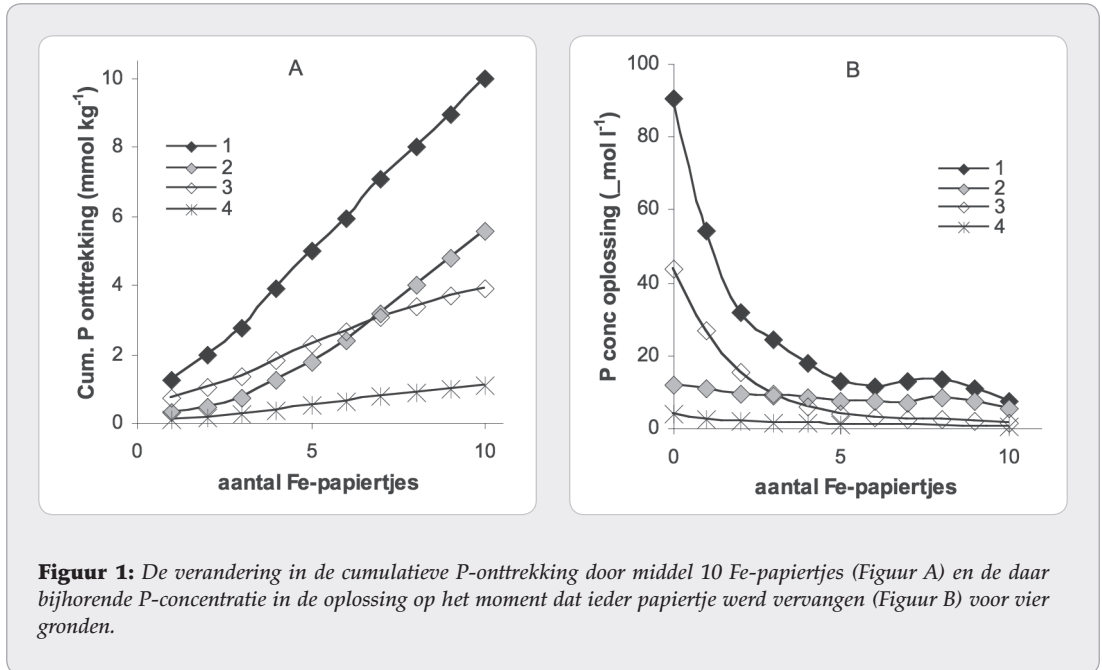
Van oudsher is de landbouwpraktijk erop gericht om gewassen met voldoende fosfaat (P) te voorzien voor een goede groei en gewaskwaliteit. De aanvoer via meststoffen overtrof daarbij veelal de afvoer via het gewas met een ophoping van P in de bodem als gevolg. Dit kan milieukundige risico's inhouden voor het oppervlakte- en of grondwater. Via het stelsel van gebruiksnormen is het P gebruik daarom sterk ingeperkt. Bij de agrarische sector is er nu twijfel of er nog wel optimaal bemest kan worden. Om binnen de P-gebruiksruimte op maat te kunnen bemesten wordt het dus steeds belangrijker om de P-beschikbaarheid op een perceel juist te kunnen voorspellen. Het doel van het hier gepresenteerde onderzoek is om een meer universele en accurate grondslag te ontwikkelen voor het vaststellen van de P-beschikbaarheid in een bodem. Daartoe zijn de dynamische processen die de beschikbaarheid van P bepalen bestudeerd.

## **ROUTINEMATIGE BEPALING VAN DE P-TOESTAND VAN EEN BODEM**

Al in 1860 beschreef Mulder dat niet de totale hoeveelheid van een nutriënt in de bodem relevant was maar de beschikbaarheid van dit nutriënt.<sup>1</sup> Sindsdien zijn er vele methodes ontwikkeld om deze beschikbaarheid te benaderen.<sup>2</sup> Binnen het routinematig bodemonderzoek wordt de P-status momenteel geschat op basis van één bepaalde extractiemethode. De keuze van deze methode is veelal gebaseerd op efficiëntie op zowel uitvoerend als economisch niveau. Om tot een bemestingsadvies te komen zijn de resultaten van zo'n extractie gekoppeld aan gewasrespons in talloze veld- en potproeven. Dit is uitgevoerd voor een aantal gewassen op een aantal representatieve grondsoorten en vervolgens is dit, vaak zwakke correlatief verband (veelal  $r^2 < 0.6$ ), geëxtrapoléerd naar een algemene relatie die regionaal of voor een land werd toegepast. Zowel de keuze van methode als de interpretatie van de resultaten biedt ruimte voor verbetering. Meer kennis van de P-beschikbaarheid is gewenst om tot betere en scherpere adviezen te komen.

## **BESCHIKBAARHEID VAN P IN DE BODEM**

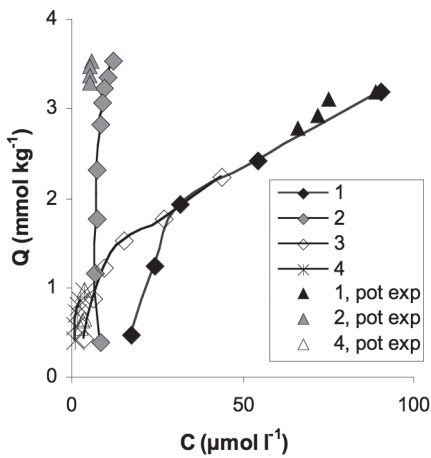
In tegenstelling tot het meten van een zekere P-fractie is de beschikbaarheid van P voor gewas en milieu een dynamisch proces. Deze is onderzocht door experimenten uit te voeren waarbij P aan een grond suspensie werd onttrokken door een relatief sterke P-adsorbent in de vorm van een met ijzer(hydr-)oxide gecoat papiertje (Fe-papiertje).<sup>3</sup> Continue onttrekking werd bewerkstelligd door op gezette tijden het Fe-papiertje te vervangen. Deze methode bootst de gewasonttrekking na onder geconditioneerde omstandigheden. De zo onttrokken hoeveelheid P en het effect hiervan op de P-concentratie in de oplossing zijn elke keer als het Fe-papiertje werd vervangen gemeten. Deze experimenten zijn uitgevoerd op sterk van elkaar verschillende



Figuur 1 laat de cumulatieve P-onttrekking ( $Q_{cum}$ ) door 10 Fe-papierjes zien (Fig.1a) en de daar bijhorende P-concentratie in de oplossing (C) op het moment dat ieder papierje werd vervangen (Fig.1b). De vier gronden vertonen een grote variatie in  $Q_{cum}$  gedurende het experiment. De hoeveelheid P dat door de eerste Fe-papierjes wordt onttrokken is nauw verbonden met de initiële concentratie in de oplossing ( $r^2=0.97$   $n=17$ ).<sup>4</sup> In overeenstemming hiermee is de initiële onttrekking van grond 3 groter dan die van grond 2. Echter, met de voortdurende onttrekking van P gedurende het experiment wordt  $Q_{cum}$  van grond 3 lager dan van grond 2 (Fig 1a). Na twee uur heeft het eerste Fe-papierje uit de verschillende gronden al minstens evenveel P verwijderd als er initieel aan P in de oplossing aanwezig was. Ook in het veld is de P-fractie in de bodemoplossing laag t.o.v. de hoeveelheid die een plant nodig heeft en erg laag t.o.v. de totale hoeveelheid P in de bodem. Tijdens het onttrekken van P aan de bodem moet er dus nalevering plaatsvinden vanuit de vaste fase. De fractie die deze direct beschikbare fractie aanvult is P dat reversibel is gebonden aan het oppervlak van bodemdeeltjes en wordt aangeduid met de term P-kwantiteit (Q). Deze nalevering uit zich in de buffering (weerstand bieden tegen verandering) van C. De mate van buffering varieert echter tussen de gronden (Fig.1b). Zo is bijvoorbeeld het bufferende vermogen (BP) van grond 2 groter dan van grond 3. Ondanks de initieel hogere C van grond 3 in vergelijking met grond 2, resulteert de lagere BP in een sterke daling van C gedurende de onttrekking van P waardoor de beschikbaarheid afneemt. Zoals we net zagen wordt er uiteindelijk minder P aan grond 3 onttrokken dan aan grond 2. De verandering in de hoeveelheid P die kan worden onttrokken gedurende het experiment vertoont een nauwe relatie met de verandering in C.

## SORPTIE-ISOTHERMEN

De desorptie experimenten met de Fe-papiermpjes laat duidelijk zien dat de beschikbaarheid van P in de bodem niet statisch is maar dynamisch en dat deze wordt bepaald door de initiële concentratie in de oplossing, BP en Q. Deze parameters kunnen worden geïntegreerd in een sorptie-isotherm welke de relatie weergeeft tussen Q en C tijdens het onttrekken (of toevoegen) van P aan een bodem. BP is een functie van zowel C als Q en is gerelateerd aan de helling van de sorptie-isotherm.<sup>5</sup> In Figuur 2 staan de desorptie-isothermen weergegeven van dezelfde vier gronden als weergegeven in Figuur 1. Potexperimenten met dezelfde gronden laten zien dat gedurende het onttrekken van P via gras vergelijkbare desorptie-isothermen worden verkregen als met de onttrekking via de Fe-papiermpjes (Fig.2). De dynamische beschikbaarheid van P in een bodem kan dus worden beschreven via de sorptie-isotherm.



**Figuur 2:** De desorptie-isotherm van vier gronden, afgeleid door middel van 10 Fe-papiermpjes die achtereenvolgend in een grondsuspensie zijn geplaatst ( $Q_0$  en  $C_0$  zijn gelijk gesteld aan respectievelijk P-Olsen en P-CaCl<sub>2</sub>). Voor grond 1, 2 en 4 is ook de desorptie-isotherm afgebeeld, afgeleid door middel van het onttrekken van P door gras in een potexperiment.

## SORPTIE-ISOTHERMEN VERSUS ROUTINEMATIG BODEMONDERZOEK

Het kunnen voorspellen van de sorptie-isotherm van een bodem zou overeenkomen met het voorspellen van de P-beschikbaarheid. Een sorptie-isotherm is bodemspecifiek en het bepalen hiervan is arbeidsintensief en duur. Als echter de aanname wordt gedaan dat de helling van de isotherm constant is en door de oorsprong gaat (C is nul bij Q is nul) dan kan deze lineaire sorptie-isotherm worden bepaald door het meten van zowel een maat voor Q als een maat voor C aan het begin van een experiment of groeiseizoen. Deze  $Q_0$  en  $C_0$  kunnen worden benaderd met een extractiemethode.  $C_0$  kan bijvoorbeeld worden benaderd door P-CaCl<sub>2</sub> en  $Q_0$  door P-Olsen of PAL. Behalve dat  $Q_0$  en  $C_0$  een maat zijn voor respectievelijk de initiële hoeveelheid reversibel gebonden P en de concentratie in de bodemoplossing, komt de verhouding  $Q_0$  over  $C_0$  overeen met de helling van de isotherm en is dus een maat voor het vermogen van de grond om C te bufferen (BP). Dit wordt ondersteund door de experimenten met de Fe-papiermpjes waarin de relatieve afname in C een nauw verband laat zien met zowel de verhouding PAL over P-CaCl<sub>2</sub> als de verhouding P-Olsen over P-CaCl<sub>2</sub> ( $r^2=0.89$   $n=17$ ).<sup>4</sup>

Het is duidelijk dat er meerdere kantekeningen zijn te plaatsen bij de aanname van een lineaire sorptie-isotherm. De eerste is dat de sorptie-isotherm van P vaak een kromme is. Hoe dichter

een grond bij zijn adsorptie maximum komt hoe groter de fout bij de aanname van een rechte sorptie-isotherm. Het onttrekken van P leidt dan tot een sterkere daling in C dan je op basis van een lineaire isotherm zou verwachten. De versimpeling heeft dus vooral effect op de nauwkeurigheid van de voorspelling bij gronden met een relatief lage BP, bijvoorbeeld voor de gronden 1 en 3 (Fig.2). Ten tweede is er geen eenduidige methode om  $Q_0$  te bepalen. PAL en P-Olsen bijvoorbeeld extraheren een behoorlijk verschillende hoeveelheid P. Verder zal de aanname dat alleen het reversibel gebonden P de P-concentratie in de bodemoplossing buffert bij langdurige onttrekking niet opgaan. Fosfaat dat deel is van de minerale en organische fase en P dat is gebonden aan oppervlak in bodemdeeltjes kan de reversibel gebonden P aanvullen en zo langer dan verwacht op basis van  $Q_0$  een bepaalde, lage, P-concentratie in de bodemoplossing handhaven.

Bij het meten van één enkele fractie, zoals momenteel normaal is binnen het routinematig bodemonderzoek, kan geen gedetailleerde informatie worden verkregen over de potentiële P-beschikbaarheid als gevolg van het onttrekken of toevoegen van P aan een grond. Zoals hierboven is besproken kan dit inzicht wel worden verkregen met kennis van de grond specifieke sorptie-isotherm. Ondanks de kantekeningen bij de aanname van een lineaire sorptie-isotherm betekent de informatie die kan worden afgeleid uit de combinatie van een maat voor  $Q_0$  en  $C_0$  een sprong voorwaarts in de nauwkeurigheid waarmee de P-beschikbaarheid kan worden voorspeld. De combinatie van deze twee parameters geeft namelijk inzicht in de schaal van de isotherm en door middel van de verhouding Q over C ook in BP. De onnauwkeurigheid die, met name voor gronden met een lage BP, wordt geïntroduceerd door de aanname van een lineaire isotherm kan worden gecorrigeerd door regelmatig grondonderzoek uit te voeren.

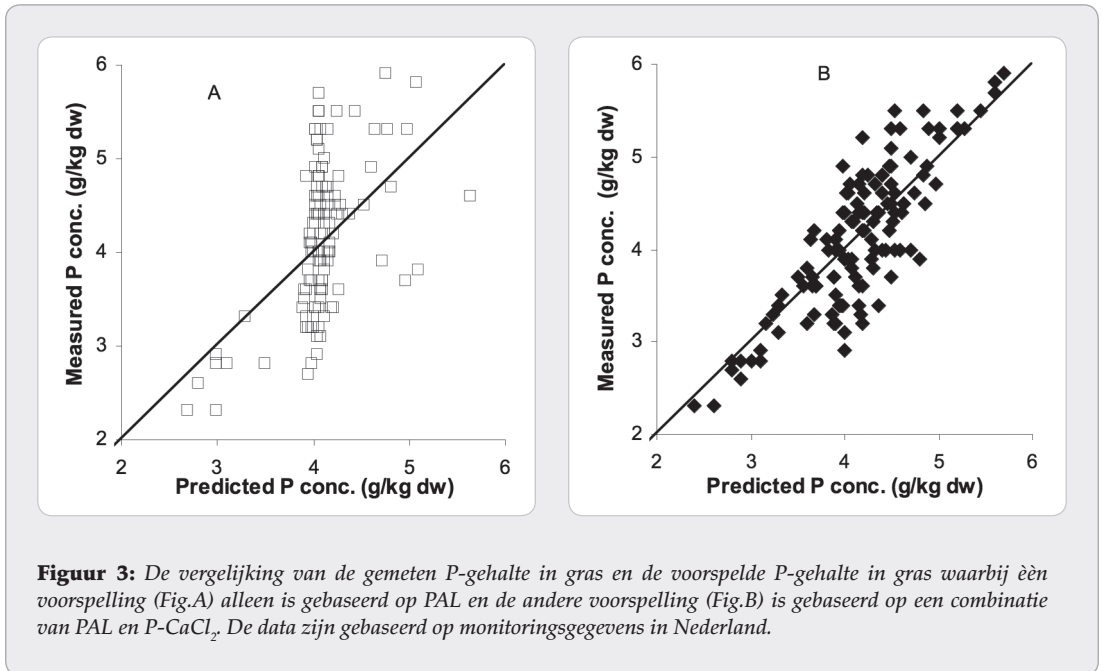
*Tabel 1: Praktijkvoorbeelden waarin het P-gehalte in gras op verschillende percelen met verschillende niveaus voor PAL en P-CaCl<sub>2</sub> worden vergeleken. De waardering is op basis van het huidige bemestingsadvies dat alleen op PAL is gebaseerd.*

| Perceel | waardering     | PAL<br>(mg P <sub>2</sub> O <sub>5</sub> /100g) | P-CaCl <sub>2</sub><br>(mg P/kg) | P-gehalte gras<br>(g P/kg ds) |
|---------|----------------|---|----------------------------------|-------------------------------|
| 1       | Voldoende      | 35  | 1.0                              | 3.1                           |
| 2       | Voldoende      | 32  | 4.0                              | 4.6                           |
| 3       | Vrij laag      | 23  | 6.0                              | 4.1                           |
| 4       | Ruim voldoende | 41  | 2.0                              | 4.2                           |
| 5       | Vrij laag      | 19  | 0.24                             | 2.7                           |

## IMPLICATIES VOOR DE PRAKTIJK

Het effect van het gebruik van de combinatie van een maat voor C (P-CaCl<sub>2</sub>) en een maat voor Q (PAL) op het bemestingsadvies is uitgewerkt voor een set praktijkgegevens die zijn verkregen van monitoringproeven op een groot aantal percelen binnen Nederland. De meerwaarde van een combinatie van PAL en P-CaCl<sub>2</sub> om de beschikbaarheid voor het gewas te bepalen in vergelijking met alleen het gebruik van PAL blijkt uit twee praktijkvoorbeelden voor gras (Tabel 1). De percelen 1 en 2 krijgen de waardering voldoende volgens het huidige bemestingsadvies

welke alleen gebaseerd is op PAL. Ondanks de vergelijkbare waarde voor PAL is P-CaCl<sub>2</sub> voor perceel 2 vier keer zo hoog in vergelijking met perceel 1. De hogere P-CaCl<sub>2</sub> is een indicatie voor de grotere beschikbaarheid van PAL en als gevolg is ook het P-gehalte in het gras hoger op perceel 2 dan op perceel 1. Perceel 3 en 4 krijgen de waardering vrij laag en ruim voldoende volgens het huidige bemestingsadvies. Voor perceel 3 is de waarde van PAL twee keer zo laag maar is P-CaCl<sub>2</sub> drie keer zo hoog in vergelijking met perceel 4. Uiteindelijk resulteert dit in een gelijke P-gehalte van het gewas op beide percelen. Uit beide voorbeelden blijkt dat het P-gehalte in het gewas niet kan worden afgeleid op basis van PAL alleen maar wel op basis van de combinatie van PAL en P-CaCl<sub>2</sub>.



Bij het vergelijken van de gemeten en voorspelde P-gehalte in gras voor alle gegevens uit de monitoringproeven blijkt dat de combinatie PAL en P-CaCl<sub>2</sub> een veel nauwkeurigere voorspelling geeft dan op basis van PAL alleen (Fig.3). Toepassing van deze bevindingen in eerste aangepaste bemestingsadviezen voor grasland laten zien dat de bemesting gemiddeld zo'n 15 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup> omlaag gaat ten opzichte van de huidige adviessystematiek op basis van alleen PAL. Dit werd bevestigd in monitoringproeven in Drenthe en Noord-Brabant.<sup>7</sup> Na verdere toetsing in de praktijk zullen deze gegevens resulteren in een nieuw bemestingsadvies waarbij de nieuwe systematiek voor zowel grasland als bouwland is toe te passen. Verder kan het systeem van reparatiebemesting beter onderbouwd worden. Op grond van Tabel 1 zou bijvoorbeeld reparatiebemesting op basis van PAL op perceel 5 niet nodig zijn, terwijl het gemeten P-gehalte in gras daar wel aanleiding toe geeft en wat in combinatie met P-CaCl<sub>2</sub> wel vastgesteld had kunnen worden. In regio's waar nagedacht wordt over uitmijnen (tbv oppervlaktewater kwaliteit) zouden betere voorspellingen kunnen worden gedaan over wanneer uitmijnen leidt tot risico's voor de gewasopbrengst, of in de situatie van omvorming van



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landbouw naar natuur hoe lang het duurt voordat de beschikbaarheid voldoende is gedaald voor een bepaalde ecologische doelstelling. Zowel de implicaties voor reparatiebemesting als voor uitmijnen vergt nog nader onderzoek.

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## SUMMARY

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## SUMMARY

The excessive use of fertilizers has led, and still leads to, environmental problems for surface and ground water. As a result there is a growing need as well as increasingly strict legislation to optimize fertilizer recommendations in which both crop yields and environmental goals are incorporated. As a basis for this optimization the choice of soil tests and interpretation of the corresponding results can be improved. The main focus of the research presented in this thesis, is to understand the soil chemical processes that determine the potential of a soil to supply phosphorus (P) and potassium (K), in order to derive a combination of standard soil tests that can easily be implemented in routine soil laboratories.

First the dynamic processes that determine the soil P supply potential were studied. To simplify the system, the uptake of P by plants is mimicked in the laboratory using an artificial sink in the form of filter paper strips that have been coated with Fe-oxide (Pi-paper). Because P transfer from the soil to an artificial sink is sensitive to the chosen experimental setup, chapter 2 describes a methodological study to understand the processes that occur in the Pi-paper-solution-soil system. Transfer of P from soil to the added artificial sink is not instantaneous but is a function of the desorption characteristics of the soil and the adsorption characteristics of the sink. By establishing the characteristics of the Pi-paper, insight into the supply characteristics of the soil can be determined. With each successive newly added Pi-paper, more P is removed from the soil system. The rate with which P is removed is a function of the P concentration in solution ( $C_p$ ) and the characteristics of the Pi-paper.  $C_p$  thus determines the current soil P supply directly. In the experimental setup as used in our study, P uptake by the sink is slower than the release rate by the soil. As a result the desorption rate of the soil is high enough to buffer  $C_p$  to a degree that keeps this concentration in equilibrium with the soil during the experiment. The simplest way to describe the supply from soil to sink is through a soil specific sorption isotherm. This describes the relationship between  $C_p$  and the reversibly adsorbed P replenishing  $C_p$ .

In chapter 3 a combination of soil tests is derived for predicting the soil P supply potential based on insight into the processes that determine the transfer of P from soil to artificial sink. This is approached by modeling the soil P desorption and the decrease in  $C_p$  during continuous removal of P by the artificial sink. The release of P from the soil is modeled using a sorption isotherm (Langmuir). The two soil specific parameters of this isotherm are related to data derived from standard soil tests. Depending on the number of soil tests, the soil P supply potential can be predicted in varying degrees of accuracy. A minimum of two parameters is needed; a measure for the reversibly adsorbed P ( $Q_p$ , e.g. P-Olsen, PAL) and a measure for  $C_p$  (e.g. P-CaCl<sub>2</sub>). The measure for  $C_p$  is an indication of the rate with which P can be removed from the soil. The ratio  $Q_p$  over  $C_p$  is an indication of the capacity of the soil to maintain  $C_p$ , and thus the capacity for maintaining the flux from soil to sink. The accuracy of this prediction increases for soils with increasing buffer power. To increase the accuracy of this prediction for soils that don't have a high buffer power (non-linear isotherm), a measure for the capacity of the soil to adsorb P, i.e. reactive surface area (e.g. Fe<sub>ox</sub> and Al<sub>ox</sub>) of the soil must also be taken into account. In addition, to be able to extend the prediction to an amount of P that exceeds the amount of readily desorbable P, a measure for the total amount of P must be included (e.g. P<sub>ox</sub>). This total amount indicates the level at which the concentration is highly buffered once the reversibly adsorbed P has been depleted.

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In chapter 4 it is verified whether the processes that determine the soil P supply potential to an artificial sink and the combination of soil tests that is needed to describe this supply can also be used to predict the supply of P from a soil to a growing crop. For this purpose pot experiments with grass were conducted. Plants have a maximum P uptake which is related to environmental conditions, crop characteristics and fertilization. P uptake relative to this maximum is determined by the soil P supply potential. This relative P uptake is comparable to P uptake by the sink. The change in (measure for)  $C_p$  is also found to be comparable between pot experiments and artificial sink experiments. Consequently, the change in reversibly adsorbed P ( $Q_p$ ) and the change in a measure for  $C_p$  (P-CaCl<sub>2</sub>), integrated in the soil specific P desorption isotherm as a result of P uptake by the growing grass is found to approximate (part of) the desorption isotherm derived from the desorption experiment using the artificial P sink. Similar to the artificial sink, P uptake by crops is a function of  $C_p$  and crop characteristics. During P removal the soil subsequently moves down its desorption isotherm. The extent to which this occurs depends on P requirement of the crop. To be able to predict if the supply is sufficient to meet crop demand the minimal requirement is the combination of a measure for  $C_p$  and a measure for  $Q_p$ . Except at a  $C_p$  above a certain level, at which it is safe to assume a sufficiently high soil P supply during the growing season.

In order to gain a more comprehensive understanding and prediction of the dynamic soil K supply potential a similar approach as used to study P was chosen (Chapter 5). In a pot experiment the changes in different soil K fractions during uptake by growing grass were studied. The soils show a variation in affinity for K between soil groups of different texture. This affects the distribution of the readily available K ( $K_A$ ) over the soil solution and exchange sites. K uptake shows a close relationship with  $K_A$ . This relationship is not affected by the difference in distribution of this K over soil solution and exchange sites. To predict the availability of soil K in the short term, a measure for  $K_A$  appears to be sufficient for all soils. For longer timescales a distinction must be made between soils that can and cannot buffer this  $K_A$ . For the soils in this study a distinction based on soil texture is sufficient, but for soils of widely varying origin the clay mineralogy must also be considered. For sandy soils  $K_A$  is not found to be replenished. For these soils the prediction of the soil K supply potential is solely determined by a measure for  $K_A$ . For silt and clay soils  $K_A$  is replenished by K that is bound in cavities between two opposing siloxane planes in 2:1 clay minerals ( $K_{\text{nexch}}$ ). The absolute contribution of  $K_{\text{nexch}}$  in these soils will depend on the type of crop but an estimation may be based on the ratio of a measure for  $K_{\text{nexch}}$  over a measure for  $K_A$ .

The challenge in our study was to derive an accurate prediction of the potential of a soil to supply P and K. In the chosen approach the dynamic processes that determine this soil P and K supply potential have been studied. Insights into these processes have subsequently been used to derive a combination of soil tests and a basis for interpreting the obtained results. Results from field trials in the Netherlands show that predicting P uptake by grass is much more accurate when based on the methodology derived in this research compared to the current approach and can be used as a basis for optimizing P fertilizer strategies. The methodology also has potential to tackle a broad range of P related questions concerning fertility and environmental issues.

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## **SAMENVATTING**

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## SAMENVATTING

Het overdadig gebruik van (kunst)mest heeft geleid, en leidt nog steeds, tot milieuproblemen voor oppervlakte- en grondwater. Gevolg hiervan is een groeiende behoefte, alsmede een steeds stringenter mestbeleid, om bemestingsadviezen te optimaliseren waarbij zowel de gewasopbrengst als milieudoelstellingen worden verenigd. Om deze optimalisatie te bereiken is het belangrijk de gekozen meetmethodes en de interpretatie van de resultaten die dat oplevert, beter te onderbouwen. Deze dissertatie presenteert resultaten van onderzoek dat zich richt op de vergroting van het inzicht in de chemische processen die de beschikbaarheid van fosfaat (P) en kalium (K) in de bodem bepalen. Deze inzichten zijn vervolgens gebruikt om een combinatie van standaard bodem meetmethodes af te leiden die in routinelaboratoria gebruikt kunnen worden.

Als eerste zijn de dynamische processen die de beschikbaarheid van P in een bodem bepalen bestudeerd. Om het systeem te simplificeren is de opname van P door planten in het laboratorium nagebootst, door gebruik te maken van kunstmatige adsorbent in de vorm van strips van filtreerpapier die met ijzeroxide zijn gecoat (Fe-papier). Omdat de overdracht van P van de bodem naar het Fe-papier gevoelig is voor de experimentele opzet, beschrijft hoofdstuk 2 een methodologische studie die als doel heeft de processen die plaatsvinden in het systeem "bodem –oplossing– Fe-papier" beter te begrijpen. De overdracht van P van bodemdeeltjes naar de kunstmatige sorbent is niet instantaan, maar is een functie van de desorptiekarakteristieken van de bodem en adsorptiekarakteristieken van het Fe-papier. Inzicht in de karakteristieken van het Fe-papier geeft inzicht in het potentieel van een bodem om P te leveren. Met elke verse strip Fe-papier dat achtereenvolgens aan een grondsuspensie wordt toegevoegd, wordt meer P uit de bodem verwijderd. De snelheid waarmee P wordt verwijderd is een functie van de P concentratie in de oplossing ( $C_p$ ) en de karakteristieken van het Fe-papier. In de experimentele opzet die ook in hoofdstuk 3 en 4 wordt gebruikt, is de opname van P door het Fe-papier langzamer dan de snelheid waarmee de bodem P levert. Gevolg hiervan is dat de desorptiesnelheid van de bodem snel genoeg is om  $C_p$  dusdanig te bufferen dat deze tijdens het experiment in evenwicht blijft met de grond. De meest eenvoudige manier om de overdracht van P van de bodem naar het kunstmatige adsorbent te beschrijven is met een grondspecifieke desorptie-isotherm. Deze desorptie-isotherm beschrijft de relatie tussen enerzijds de concentratie van P en anderzijds het aan de bodem reversibel gebonden P ( $Q_p$ ) dat  $C_p$  buffert.

In hoofdstuk 3 is een combinatie van meetmethodes afgeleid die samen de beschikbaarheid van P in de bodem bepalen. Dit is gebaseerd op inzicht in de processen die de overdracht van P van een bodem naar Fe-papier bepalen. In de gekozen aanpak is de desorptie van P van de bodem en de afname in  $C_p$  gemodelleerd tijdens de continue onttrekking van P uit de bodem tijdens het Fe-papier experiment. Voor het modelleren is gebruik gemaakt van een bodemspecifieke desorptie-isotherm (Langmuir) waarvan de twee parameters zijn afgeleid op basis van standaardmeetmethodes. Afhankelijk van het aantal meetmethodes kan de beschikbaarheid van P met verschillende maten van nauwkeurigheid worden voorspeld. Een minimum van twee parameters bleek noodzakelijk; één maat voor de hoeveelheid reversibel gebonden P ( $Q_p$ , bijvoorbeeld P-Olsen of PAL) en één maat voor de concentratie van P ( $C_p$ , bijvoorbeeld P-CaCl<sub>2</sub>). De maat voor  $C_p$  geeft een indicatie voor de snelheid waarmee de bodem P kan leveren. De verhouding tussen  $Q_p$  en  $C_p$  blijkt een indicatie voor de capaciteit van een bodem om  $C_p$  te handhaven, en dus ook een indicatie voor de capaciteit om de flux van bodem



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naar Fe-papier te handhaven. De nauwkeurigheid van deze voorspelling neemt toe met het toenemende vermogen van een bodem om  $C_p$  te kunnen bufferen. Om de nauwkeurigheid van de voorspelling te verhogen voor bodems zonder een groot bufferend vermogen (niet-lineaire isotherm), moet een maat voor de capaciteit van een bodem om P te adsorberen, met andere woorden het reactief oppervlak (bv  $(Fe+Al)_{ox}$ ) ook worden meegenomen in het model. Bovendien moet ook een maat voor de totale hoeveelheid P in de bodem (bv  $P_{ox}$ ) worden meegenomen om de voorspelling uit te breiden voor de situatie waarbij meer P wordt onttrokken dan de hoeveelheid reversibel gebonden P. Deze maat voor totale hoeveelheid P geeft een indicatie voor het niveau waarop  $C_p$  sterk wordt gebufferd wanneer het reversibel gebonden P in de bodem uitgeput raakt.

In hoofdstuk 4 wordt geïntegreerd of de processen die de beschikbaarheid van P voor een kunstmatige sorbent bepalen, en de combinatie van meetmethodes die nodig zijn om deze beschikbaarheid te beschrijven, kunnen worden gebruikt om de beschikbaarheid voor een gewas te voorspellen. Hiervoor zijn potexperimenten met gras uitgevoerd. Planten hebben een maximum P opname die wordt bepaald door milieukundige condities, karakteristieken van de plant en bemesting. Wanneer de P opname in relatieve termen ten opzichte van dit maximum wordt uitgedrukt, dan wordt deze bepaald door de beschikbaarheid van P in de bodem. Deze relatieve opname is vergelijkbaar met de P opname tijdens het experiment waarbij Fe-papier strips worden gebruikt. De verandering in (een maat voor)  $C_p$  is ook vergelijkbaar tussen de pot- en Fe-papier experimenten. De verandering in reversibel gebonden P ( $Q_p$ ) en de verandering in een maat voor  $C_p$  (P-CaCl<sub>2</sub>) kunnen worden geïntegreerd in een desorptie-isotherm. De desorptie-isotherm van welke in de potexperimenten is afgeleid benadert (een gedeelte) van de isotherm welke met de Fe-papier methode is afgeleid. Vergelijkbaar met de kunstmatige adsorbent, is de P opname door het gewas een functie van  $C_p$  en van karakteristieken van het gewas. Tijdens het verwijderen van P uit de bodem veranderen  $C_p$  en  $Q_p$  in overeenstemming met de desorptie-isotherm. De mate waarin dit gebeurt is afhankelijk van de P behoefte van het gewas. Om te kunnen voorspellen of de levering van P uit de bodem kan voldoen aan de behoefte van het gewas, is een combinatie van een maat voor  $C_p$  (bijvoorbeeld P-CaCl<sub>2</sub>) en een maat voor  $Q_p$  (bijvoorbeeld P-olsen of PAL) een minimale vereiste. Een uitzondering is wanneer  $C_p$  boven een niveau is waar het veilig is om aan te nemen dat de P beschikbaarheid voldoende is voor het komende groeiseizoen.

Om tot een beter inzicht, en nauwkeuriger voorspelling, van de dynamische beschikbaarheid van kalium (K) te komen, is een vergelijkbaar onderzoek als voor P uitgevoerd (hoofdstuk 5). De veranderingen in de verschillende K fracties in de bodem zijn bestudeerd tijdens de opname van K door gras in een potexperiment. De resultaten laten zien dat groepen gronden met verschillende textuur variëren in hun affiniteit voor K, en dus ook in de verdeling van het direct beschikbare K ( $K_A$ ) tussen K in de bodemoplossing en uitwisselbaar K. De opname van K door het gras blijkt sterk gerelateerd aan het direct beschikbare K. Echter, deze relatie wordt niet beïnvloed door het verschil in de verdeling van  $K_A$  tussen de bodemoplossing en uitwisselbare plaatsen. Om de beschikbaarheid van K op de korte termijn te kunnen voorspellen is één maat voor  $K_A$  voldoende. Op de langere termijn zal een onderscheid gemaakt moeten worden tussen gronden die  $K_A$  wel en niet bufferen. Voor de gronden in dit onderzoek blijkt een verdeling gebaseerd op textuur voldoende. Voor gronden met een grote variatie in moedermateriaal zal de mineralogie ook meegenomen moeten worden. Voor zandgronden blijkt geen nalevering van

$K_A$  en kan de beschikbaarheid enkel op basis van een maat voor  $K_A$  worden voorspeld. Voor silt- en kleigronden vindt nalevering van  $K_A$  plaats door  $K$  dat is gebonden in de holte tussen twee tegenover elkaar liggende plaatjes in 2:1 kleimineralen ( $K_{\text{nexch}}$ ). De absolute bijdrage van  $K_{\text{nexch}}$  aan de nalevering van  $K_A$  is afhankelijk van het type gewas, maar een schatting kan worden gebaseerd op de verhouding tussen een maat voor  $K_{\text{nexch}}$  en een maat voor  $K_A$ .

In deze dissertatie is een basis gelegd voor een nauwkeurige voorspelling van de beschikbaarheid van P en K in een bodem. In verschillende studies zijn de dynamische processen bestudeerd die de beschikbaarheid van P en K bepalen. Op basis van het verkregen inzicht in deze processen is een combinatie van standaardmeetmethodes afgeleid en zijn handvatten geformuleerd om de resultaten die deze methodes opleveren te interpreteren. Eerste ervaringen uit de praktijk laten zien dat in het veld de voorspelling van de opname van P door gras - op basis van de resultaten van deze dissertatie - veel nauwkeuriger is dan met de meetmethodes die de gebruikelijke aanpak kenmerken. Derhalve vormen de resultaten, zoals beschreven in deze dissertatie, een goede basis om P bemestingsstrategieën te kunnen optimaliseren. Daarnaast geeft de hier beschreven methodiek aanknopingspunten om een breed scala aan P gerelateerde vraagstellingen aan te pakken.



**DANKWOORD**

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## DANKWOORD

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# CURRICULUM VITAE

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Antje Marjorie Deborah (Debby) Los was born on the 18th of May 1977 in Rheden, The Netherlands. She studied analytical chemistry at the College of Technology Arnhem and Nijmegen. In September 1998 she graduated as Bachelor of Science after a period of vocational training in the molecular spectrometry department of Akzo Nobel central research. The following year she worked as a laboratory technician for Unilever central research where she specialized in mass spectrometry. In January 2000 she started a masters degree in environmental geochemistry at the University of Utrecht. During her studies she was a teaching assistant, helped to promote her study, and participated in a scientific cruise in the Mediterranean as laboratory technician. For her masters degree thesis she studied the effect of acidic (volcanic) irrigation water on agricultural soils in the Asembagus area, N-E Java. After graduating in September 2002 she stayed on at the faculty of Geochemistry as research assistant for nearly a year. The research project was to experimentally determine the kinetic parameters of denitrification in estuary sediments. In September 2003 she started her Ph.D. research in the Soil Quality department of Wageningen University. At present she works in the Sustainable Development department of the town council of Nieuwegein as an environmental soil advisor.



## **LIST OF PUBLICATIONS**

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## LIST OF PUBLICATIONS

### ***Publications from Ph.D. research***

Van Rotterdam A.M.D., Temminghoff E.J.M., Schenkeveld W.D.C., Hiemstra T., and Van Riemsdijk W.H. 2009 Phosphorus removal from soil using Fe oxide-impregnated paper: processes and applications. *Geoderma* 151, 282-289.

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# **SENSE EDUCATION CERTIFICATE**

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Netherlands Research School for the  
Socio-Economic and Natural Sciences of the Environment

## CERTIFICATE

The Netherlands Research School for the  
Socio-Economic and Natural Sciences of the Environment  
(SENSE), declares that

*Antje Marjorie Deborah van Rotterdam-Los*

Born on: *18 May 1977* in: *Rheden, The Netherlands*

has successfully fulfilled all requirements of the  
Educational Programme of SENSE.

Place: *Wageningen* Date: *26 February 2010*

the Chairman of the  
SENSE board

Prof. dr. R. Leemans

the SENSE Director  
of Education

Dr. A. van Dommelen



The SENSE Research School declares that Ms. Antje Marjorie Deborah van Rotterdam- Los has successfully fulfilled all requirements of the Educational PhD Programme of SENSE with a work load of 37 ECTS, including the following activities:

**SENSE PhD courses:**

- Environmental Research in Context
- Research Context Activity: "Co-organizing of and presenting in a theme meeting on nitrogen and phosphorus (Oosterbeek, 19 September 2008)"
- Speciation and bioavailability
- Basic and advanced statistics

**Other PhD and MSc courses:**

- Techniques for writing and presenting scientific papers
- Teaching and supervising thesis students
- Chemical interactions soil-water-sediment
- Speciation and transport
- Nutrient management

**Educational Activities:**

- Participating in project guided education (PGO) for first year students

**Oral Presentations:**

- Phosphorus fertilizer recommendations from a soil point of view, 15<sup>th</sup> international plant nutrition colloquium, 14 – 19 September 2005, Beijing, China
- Towards a more mechanistic based fertilizer recommendation for phosphorus, Soil and Water symposium, 7 June 2006, Lunteren, The Netherlands

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