Modelling P Dynamics in soil

- Decomposition and Sorption

Technical report

Concepts and User Manual

Developed by
Birgitte Gjettermann
At
DHI Water and Environment
Hydrology, Solid and Waste Department

In corporation with
The Royal Veterinary and Agricultural University
Department of Natural Science
&
Department of Agricultural Science

28 December 2004

Agern Allé 11
DK-2970 Hørsholm, Denmark

Tel: +45 4516 9200
Fax: +45 4516 9292
Dept. fax:
e-mail: dhi@dhi.dk
Web: www.dhi.dk

Modelling P Dynamics in soil - Decomposition and Sorption

Technical report

Concepts and User Manual

Author	Date
Industrial Ph.D. student Birgitte Gjettermann	28 December 2004

Preface

This report presents a technical description of a code/model concept simulating mobilization and immobilization of phosphorous (P). The mobilization and immobilisation processes of P are represented by sorption and desorption of P and by decomposition of organic matter with mineralization or immobilisation of P. The code/model, referred to as the P-Model, works with another model, called Daisy. Daisy[1] is a public shareware developed at the Royal Veterinary and Agricultural University (KVL), which simulates N and C dynamics in the soil-plant-atmosphere system and consists of several sub-models for soil water and solute movement, soil temperature, soil organic matter, soil mineral N, crop growth, and system management {Hansen, 1990 90 /id}.

The report and model were developed as part of the industrial Ph.D.-project *Modelling Phosphorus Dynamics in Soil – Decomposition and Sorption,* at DHI Water & Environment in corporation with The Royal Veterinary and Agricultural University (KVL). The Danish Academy of Technical Science and DHI Water & Environment financed the industrial Ph.D.-project. Furthermore, the industrial Ph.D.-project has worked together with a research program *Regional Groundwater Protection by Optimized Organic Farming Systems* financed by Danish Research Centre for Organic Farming.

I would like to thanks Finn Pilgaard Vinther at Danish Institute of Agricultural Science, Department of Agroecology, for helpful corporation, information and making data available for calibration and validation of the P-Model. Anders Pedersen from KVL, Department of Agricultural Science, has been very helpful, providing participation for the simulations with grazing cattle and grass-clover. Per Abrahamsen from KVL, Department of Agricultural Science, has also been very helpful with programming in C++ and running the Daisy model. Also, I would like to thanks the supervisors of the Ph.D.-project Søren Hansen and Hans Christian Bruun Hansen at KVL, Department of Agricultural Science and Department of Natural Sciences, respectively; and the supervisor Merete Styczen at DHI Water & Environment, Department of Hydrology, Solid and Waste.

Birgitte Gjettermann

(EF 879, Lc 2052)

---

[1] For further information of the public model Daisy, see http://www.dina.kvl.dk/~daisy/.

Summary

Weather-driven simulation modelling has become an important component of studies of soil nutrients, both for crop growth and for losses by leaching to the environment. In order to model phosphorus (P) dynamics in soil, the mobilisation and immobilisation processes of inorganic and organic P species is important for quantifying P leaching from the unsaturated zone. The mobilization and immobilisation processes of P are represented in this project by sorption and desorption of P and by decomposition of organic matter with mineralization and immobilisation of P.

The code/model presented here, referred to as the P-Model, works with another model, called Daisy. The Daisy code delivers input data of water content, water flux, temperature, inorganic nitrogen (N), crop uptake of N, and crop root exudates, to the P-Model. The P-Model must be considered as a prototype of a P module in Daisy, as the user-friendliness is limited and not all aspects are described in details. For instance crops are described as very simple sink terms, in spite of the fact that they are very important in the P dynamic of soils. Soil ploughing and harrowing are not included in the P-Model and therefore some limitations of the Daisy set up must be considered.

The concept of the turnover of soil organic matter is based on the organic matter module in Daisy. The simulation of the organic matter balance and the nitrogen dynamics is strongly interconnected in Daisy as the organic matter model is considered an integral part of the overall nitrogen balance model. It is assumed that the activity of soil microbial biomass is related to the substrate availability; and that it is reasonable to relate the N mineralization and immobilization with decomposition of soil organic matter (SOM). Daisy does not include P in the organic matter module. However, like N it seems reasonable to relate P mineralization and immobilization to the decomposition of SOM.

In the P-Model organic matter is defined with respect to C, N, and P and is represented by different pools in the model, representing easily degradable and recalcitrant pools, microbial pools, and a dissolved pool. The dissolved organic matter (DOM) pool is produced by microbial degradation of organic matter and by physical/chemical desorption from the most bio available pool of soil organic matter. Hence, DOM may also be immobilized by sorption to the soil organic matter pool. The P-model also includes addition of organic and inorganic fertilizers, crops, and solute transport by convection.

One of the main issues during parameterisation of the DOM dynamics has been to identify and particularly to quantify the sources of DOM in soil. It is assumed that DOM is produced by the soil microbial biomass (SMB) pool and the SOM pool. DOM production is not directly linked to the input of organic material as fresh litter, dead roots, and organic fertilizer, because the contribution of DOM from all these different sources probably is very different and not known at this stage. However, theses sources is very bioavailable to the microbial biomass promoting fast turnover and growing microbial biomass, which contribute to the production of DOM. Hence, the DOM dynamic is closely linked to the dynamic of the AOM pools. The biological decomposition of DOM and associated P in the P-Model has been parameterised from literature (e.g. C/P ratios, decay rates and diffusion coefficients of DOM).

The P-Model considers sorption and desorption of DOM in soil, by assuming that dissolved organic P (DOP) and dissolved organic N (DON) follows dissolved organic C (DOC) sorption/desorption in soil. When DOM is sorbed it is assumed to be associated to a part of the SOM pool. Sorption/desorption of DOC takes advantages of estimated relationships linking soil properties to sorption properties across a range of soil types. The Initial Mass approach is used to estimate a DOC concentration specific for the soil, where no net sorption/desorption of DOM occurs. The sorption/desorption dynamics of DOM and associated P in the P-Model have been parameterised from sorption data and field experiments. An empirical, kinetic term couples the

'equilibrium' concentration to the actual DOM concentration in the soil, incorporating considerations as diffusion and sorption time into the description of the sorption/desorption process. Depending on whether the DOM concentration is above or below the 'equilibrium' concentration then the DOC concentration in the soil is reduced or increased, respectively. Reducing the sorption/desorption rate coefficients the exchange between part of the SOM pool and the DOM pool is reduced. The best fit of simulations to measured DOC and DOP concentrations in batch experiments was found by using desorption and sorption rate coefficients of 0.001 hour^{-1}.

Additionally, the P-Model considers sorption of inorganic P, which is described by a three-step mechanism: 1) A fast sorption mechanism, and, 2) a relative slow absorption mechanism, plus 3) a very slow fixation process. Thus, its is hypothesised that inorganic phosphate first binds to easily available sorption sites with high affinity, and then the less available sites which is limited by diffusion and further migration into the soil particle to sorption sites less available. Langmuir describes all three processes at 'equilibrium'. As for DOM, kinetic terms couples the 'equilibrium' concentrations of the different inorganic P pools to the actual P concentration in the soil, incorporating considerations as diffusion and sorption time into the description of the sorption/desorption processes. The sorption of inorganic P has been parameterised from sorption data and literature (e.g. sorption affinity constant and sorption capacities). Due to the concept of instantaneous process of adsorption, which implies an adsorption rate coefficient of 1 h^{-1} in this model, the other rates have been fitted based on this assumption. The process of absorption has been fitted to obtain equilibrium within 3-4 days. The fixation process has been adjusted not obtain equilibrium during 14 days. The slow desorption rate has not been included during these test. So, whether the slow process is considered reversible or irreversible is still up to discussion in the concept. The distribution of the sorption capacities between the three P pools was shown to have limited effect of the sorption dynamic The distribution of the total sorption capacity between the three sorbed phases has been parameterised based on the assumption that the quickly sorbed fraction has 1/3 of total sorption capacity. By fitting the P-Model to data of sorption experiments on two different soils, it was found that 1/4 of the total sorption capacity is allocated to the absorbed phase for both top and subsoils. The rest of the sorption capacity is allocated to the slow, fixed pool. The sorption affinities are very dominating for the sorption dynamic. The sorption affinities were initially assumed to be in the range of 10-120 mM^{-1} as often found by fitting Langmuir constants during sorption experiments. However, the best fit to measured sorption data to two subsoils were made by using rather high values for the sorption affinity constants (400-200 mM^{-1}) for the adsorbed, absorbed and fixed processes. The P sorption of the two topsoils behaves very different which could be due to a pH effect. It was not possible to parameterise the affinity constants for the three sorption processes similar for the two top soils, maybe because effects of initial soil pH are not taking into account in the parameterisation.

Only part of the P-Model has been validated on field data. The calculation of DOC and DON mobilisation / immobilisation is validated at three fields with different soil treatments located at the Burrehøjvej field at Research Center Foulum in the central part of Jutland. The simulations are compared with measured DOC, DON, NO3 and NH4 concentrations sampled from suctions cups installed in the three fields. The simulations show that in the topsoil the DOM is mainly produced by biological SOM turnover during summertime and chemical/physical release from SOM at all time. The yearly fluctuation of DOM concentration is related to the microbial activity. High fluctuations of DOM which are related to microbial activity are diminished by the chemical/physical sorption/desorption processes which attempts to keep the DOC concentration steady at a certain level. For the soil treated with 9 year of grass clover, the higher DOCand DON fluctuations in the topsoil are slightly diminished in the simulations in relation to the measured DOC and DON concentration. For the two other soil treatments the DOC and DON concentration show less fluctuations and are simulated better.

CONTENTS

1 INTRODUCTION

Phosphorus in the form of ortho-phosphate reacts readily with soil components, however, the soil capacity to bind phosphate may be limited if phosphorus systematically is applied in excess of plant need. Intensively cultivated soils accumulate phosphorus when the amount of phosphorus added in fertilizers, manure or sludge exceeds the amount exported in biomass, plant uptake, and P lost by leaching (Heckrath et al., 1995; Del Campillo et al., 1999). This enrichment has led to increased availability of phosphate beneficial to plant production. But at the same time the risk of phosphate transport out of the soil has increased (Heckrath et al., 1995). Phosphorus is an important nutrient for plants and animals; however, high levels of phosphorus especially in fjords and lakes may cause increased algae bloom affecting the environment negatively (Kronvang et al., 2001).

It is not clear to what extend roots and microorganisms compete for phosphorus sources (Frossard et al., 1995). However, mineralization of organic P is an essential process in maintaining the concentration of labile inorganic P in many soils (Stewart and Tiessen, 1987), and numerous laboratory and field studies indicate the important role of organic P in soil P dynamics. McLaughlin and Alston (1986) and McLaughlin et al. (1988) used isotopic techniques to evaluate the incorporation of $^{32}PO_4$ and $^{33}PO_4$ derived from mineral fertilizer and from plant residues into the microbial biomass. They found a rapid incorporation of P from plant residues and mineral fertilizers into the microbial biomass. Soil microorganisms affect P dynamics by their activity and represent an organic P compartment, which can act as a sink and source of plant available P (Macklon et al., 1997; Stewart and Tiessen, 1987).

Dissolved organic matter (DOM) is supposed to represent the most active and mobile form of organic matter in soil (Zech et al., 1997; Zsolnay, 1996). DOM mobility is a major factor affecting the export of nutrients from soils to surface waters. E.g. nitrogen (N) and phosphorus (P) in DOM can make up a significant fraction of total dissolved concentrations of N and P in soil pore water. Thus, Qualls et al. (1991) estimated that > 90 % and > 66 %, respectively, of total dissolved N and P leaching from a deciduous forest soil were in the form of dissolved organic N (DON) and dissolved organic P (DOP), respectively. Additionally, Grant et al. (1996) estimated that DOP accounted for 16 - 23 % of the annual loss of total P from four arable catchments in Denmark. DOM is usually quantified in term of its carbon content, which is referred to as dissolved organic carbon (DOC) and generally, DOC compromises 50 % of DOM (Tipping et al., 1999). However, DON and DOP also play an important role in nutrient cycling as dissolved organic N and P represent labile, readily mineralizable pools that will be important to the availability of these nutrients particularly in unfertilized soils.

DOM contains numerous organic compounds, from simple sugars to complex fulvic and humic acids (McDowell and Wood, 1984). It is produced principally by microbial activity, root exudation, and leaching from litter and humus in the soil (Kalbitz et al., 2000). However, the quantitative contribution made by each of these sources is controversial (Hagedorn et al., 2004). Large concentrations of hydrophilic neutral compounds after litter fall have been interpreted as an indicator for temporarily contributions of recent litter to DOM in forest floor (Qualls et al., 1991). However, Yano et al. (2000) hypothesized that roots and root exudates were a significant source of DOC as no correlation was found between DOC and freshly fallen litter, but a correlation between DOC and fine root biomass was obtained. Structural analysis of DOM from a coniferous forest by Guggenberger et al. (1994) suggested that DOM release into forest mineral soil is related to microbial activity by oxidative degradation of plant derived organic matter and by production of microbial metabolites. However, similarities between the NMR spectra of DOC humic fractions and solid soil organic matter (SOM) and close relationship between dissolved and solid organic matter (McDowell and Wood, 1984) indicate that there is a reactive or soluble fraction of the total SOM pool that may be solubilized and lost to either microbial decomposition or leaching (David and Vance, 1991). Zsolnay (1996) stated that the greatest and most consistent source of DOM presumably is the immobile SOM, which is approximately 100 fold more abundant than the DOM itself. Additionally, it is often found that soil is able to release DOM when exposed to aqueous solution containing no or very low concentrations of DOM (Kaiser, 2001; Nodvin et al., 1986). Thus, the soil solid phase may not only sorb DOM but may also release it depending on solution DOM concentrations.

Weather-driven simulation modelling has become an important component of studies of soil nutrients, both for crop growth and for losses by leaching to the environment as pollutants. In order to model P dynamics in soil, mobilisation and immobilisation processes of inorganic and organic P species is important for quantifying P leaching from the unsaturated zone.

1.1 Purpose of this report

This report presents a technical description of a code/model concept simulating mobilization and immobilization of inorganic and organic P fractions in soils. The code/model presented here is referred to as the P-Model. Despite indication of, that particle associated P contributes significantly to the total loss of P in agricultural soil (Grant et al., 1996), this is out of scope in the P-Model at this stage. Hence, in this report DOM is defined as dissolved organic substances passing through a 0.45 μm filter. The dissolved substances are quantified with respect to C, N and P which is referred as DOC, DON, and DOP, respectively. Additionally, this report describes how to use the P-Model in practice.

The description of inorganic P sorption and sorption of DOM associated P together with the generation of DOM-associated P form the basis of the P-Model. In order to develop a model that can simulate P mobilisation processes in different soils, it has been attempted to relate sorption/desorption mechanisms of inorganic and organic P to soil properties. Therefore, when possible the description of the sorption/desorption mechanisms has been related to soil parameters (e.g. aluminium, iron, organic matter content) instead of arbitrary constants.

The Daisy-P-Model is composed of the Daisy code and the stand-alone code, the P-model. The stand-alone code is considered as a prototype for a future implemented code in Daisy. The objective of the Daisy-P model is to model mobilization and immobilization processes of inorganic and organic dissolved phosphorus at field scale. Hence, the future goal is to use Daisy as a tool to recognize potential risk areas for dissolved P loss and quantify the amount P leached with different management strategies. The use of the P-Model is then closely related to the use of Daisy; hence, the user guide builds on the assumptions that the user already has some knowledge of the Daisy model.

2 TURNOVER OF ORGANIC P

Soil organic matter usually comprises dead plant, animal and microbial material, both fresh and at all stage of decomposition as well as ‘humified’ material that cannot be assigned to any particular source. The pathways from fresh organic matter to humus are not well elucidated. However, this turnover can largely be attributed to microbial activity (Insam, 1996). Mineralization of organic P is thought to be an essential process in maintaining the concentration of labile inorganic P in many soils (Stewart and Tiessen, 1987). The production of phosphatase either by roots or associated microorganisms is an efficient strategy for the acquisition of phosphate by plants (Tarafdar and Claassen, 1988). However, the process of soil P mineralization is not the only process favouring the mobility of P. Hence, Kaiser (2001) found that DOM is very important for the export and loss of organically bound plant nutrients as P.

The microbial biomass is itself part of the soil organic matter, typically about 2 % of the total organic C. It is defined as the living microbial component of the soil and includes bacteria, actinomycetes, fungi, protozoa, algae and micro fauna (Sparling, 1985). In the rhizosphere bacterial numbers are much higher than in the bulk soil and the organism differ in their species physiological requirements (Sparling, 1985). In the rhizosphere, bacteria benefit from the diffusion of a wide variety of soluble materials, especially sugars and amino acids leached from the roots and also from the mucilage produced by the root cap and from sloughed-off plant cell materials (Lynch and Whipps, 1990). Roots can lose a considerable proportion of their photosynthate to their growth medium, and for soil-grown plants losses up to 23 % of the fixed photosynthate are recorded (Sparling, 1985).

Soil microorganisms are an important reservoir of labile C, N, S, and P compounds. Microbial P can range 7-100 kg P ha^{-1}, depending on the type of cultivation (Brookes et al., 1984) and consist of about 60 % of nucleic acids, 20 % of sugar and nucleotide esters and various phosphorylated co-enzymes and polyphosphates, and less than 10 % of phospholipids (Stewart and Tiessen, 1987). Soil organic P constitutes between 20 and 80 % of total P in the surface layer of soils. Organic P compounds in soils are derived from plants and microorganisms. Most forms of organic P are common to microbes and occur as relatively low molecular weight compounds such as inositol phosphates, nucleic acids, phospholipids and a small amount of sugar phosphates (Frossard et al., 1995). Phytate, *myo*-inositol 1,2,3,4,5,6-hexakisphosphate is ubiquitous in the plant kingdom particular in mature seeds such as in cereal grains and legumes, fruits and vegetables. In mammalians such as swine, horse, and fowl, phytase activity is too low to digest the phytate. As a result swine, horses, and fowls excrete large amounts of undigested phytate with manure into the soil (Pandey et al., 2001). Rhizosphere organisms are commonly high in phosphates and often contain inositol polyphosphates granules. Away from roots most bacterial activity is isolated in discrete micro sites around organic residues, and the bacteria are usually smaller and lack polyphosphates granules (Foster, 1986). Organic P released by secretion or cell lysis into the soil environment can be taken up by soil organisms, or after hydrolysis, by plants. Alternatively, it can be stabilized as part of the soil organic matter through its organic moiety, or by interactions of the phosphate group with mineral components (Stewart and Tiessen, 1987).

This paragraph describes the biologically driven turnover of organic matter which is considered with respect to organic C and N in the Daisy model. The concept in Daisy is the base of the organic P turnover in the P-Model. However, as dissolved organic P seems to be an important factor for P loss, a new pool of DOM is introduced in the organic matter model.

2.1 The organic matter fractions

Microbes selective degrade the less recalcitrant compounds and thus gradually increase the average recalcitrance of the non-respired organic matter (Sollins et al., 1996). In order to divide the dead native soil organic matter into recalcitrant and less recalcitrant fractions, it is fractionated into three pools with different turnover rates, SOM1, SOM2 and SOM3, respectively. In some organic soil as peat soils, a large humified pool may be almost inert. The SOM3 pool represents a deactivated pool of humified organic matter. SOM1 is considered as the chemically stabilized organic matter, which is decomposed at a relatively slow rate. SOM2 is physically stabilized organic matter decomposing relatively fast, approximately three times faster than SOM1. SOM2 is considered as the least recalcitrant and stabilized fraction of SOM and it is the most bioavailable fraction for microbes.

Added organic matter (AOM) is defined as input of new organic substances to the soil system. AOM could be organic fertilizer as farmyard manure or slurry. Additionally, green crops, roots or plant residues left on the field after harvest, are input of new organic material and subject for degradation in the organic matter cycle. As for SOM, input of new organic substances is fractionated into two fractions, AOM1 and AOM2, which consist of relatively slowly and easily degradable organic matter, respectively. However, some fraction of partly decomposed organic matter as farmyard manure or slurry can also be allocated to the SOM2 fraction as it is already partly degraded by microbes.

Microorganisms in soil may be classified into two groups with different strategies. The primary stage of decomposition of readily decomposable substrates is performed by rapidly responding life forms. The subsequent stage is dominated by slower growing, highly specialized life forms {Insam, 1996 180 /id}. In order to have a stable as well as a dynamic microbial biomass; the soil microbial organic matter fraction is subdivided into SMB1 and SMB2. The SMB1 fraction is considered to be the stable fraction while SMB2 is the dynamic fraction.

In summary, organic matter is allocated to three defined fractions in Daisy: Added organic matter (AOM), dead native soil organic matter (SOM), and soil microbial biomass (SMB) which is divided into more and less dynamic pools. A fourth more arbitrary fraction is defined in the following section, dissolved organic matter (DOM).

2.1.1 Dissolved organic matter

Soil solutions contain varying amounts of DOC, which originate from plant litter, soil humus, microbial biomass or from root exudates (Kalbitz et al., 2000). As DOC moves deeper into the soil, its biological availability decreases, reflecting either transport of residual, recalcitrant components of DOC, or a physical desorption / dissolution flux of C from SOM to DOM (Qualls and Haines, 1992). DOM is produced principally by microbial activity, root exudation, and leaching from litter and humus in the soil. However, the quantitative contribution made by each of these sources is controversial as mentioned in the introduction.

Data of change in ^{14}C indicate that most DOC in the soil is fairly old, at least 30 years at 5 cm depth (Tegen and Dorr, 1996) and at 10-25 cm (Trumbore et al.,1992) supporting that leaching of DOM from SOM rather than of recent litter is the major source of DOM. This is supported by findings of Hagedorn et al. (2004) who investigated the origin of DOC in a 4-year experiment exposing spruce and beech, growing on a sandy loam and on calcareous sand, to CO_2 depleted in ^{13}C. In the soil solution of the topsoil, DOC contained only 5-10 % new C from the trees. Apparently, throughfall, fresh litter and roots made only minor contributions to DOC. However, water-extractable organic C contained significantly larger fractions of new C (25-30 %) implying that the sampling method strongly influences the characteristics and sources of DOM. Hence, Hagedorn et al. (2004) suggested that DOM is produced during incomplete decomposition of recalcitrant native C in the soils, whereas easily degradable new components are rapidly consumed by microbes and thus make only a minor contribution to DOM.

In the P-Model it is considered, that DOM is rather old, assuming that easily degradable new components are rapidly consumed by microbes and cannot be distinguished from the AOM pools. Hence, DOM is mainly produced from SOM by some physical/chemical/biological processes resulting in that some part of SOM in soil is dissolved. The physical/chemical processes are described in the next paragraph. The biological processes, described in this paragraph, release a fraction of metabolites as DOM during microbial degradation of organic matter. When some transformation occurs in the organic matter fractions, for instance by external cellular enzymes or chemical hydrolyses, a water-soluble organic matter fraction is produced. In this way the DOM fraction is related to decomposition of the other organic fractions. Depending on the sources, DOM has variable C/N- and C/P-ratios in accordance with the sources.

2.2 Decomposition and mineralization of substrate

Mineralization of organic C follows microbial P with time in different farming systems, indicating that organic C mineralization occurs concomitantly with organic P (Oberson et al., 1996). In the P-Model organic matter and nutrients support high microbial activity, stimulating C turnover and mineralization of inorganic P. Additionally, the production and degradation of organic P in the organic pools is correlated to the C production and degradation.

Each organic pool is quantified according to C and N in Daisy. The P-Model quantifies also the pools with respect to P by simulating the same C transformations between the organic pools and correlate C to P by C:P ratios. This paragraph presents briefly the organic matter module defined in Daisy and couples it to turnover of P. An overview of the individual soil organic fractions and the internal dynamics between the fractions can be viewed in Figure 1. The C flow between the organic pools, X, is described by the following seven equations in which the subscripts (se Figure 1) refers to the various flow fractions of C in organic matter.

eq. 2-1

$$\frac{dC_{AOM1}}{dt} = f_{AOM1}I_D - \varsigma_{AOM1}$$

eq. 2-2

$$\frac{dC_{AOM2}}{dt} = f_{AOM2}I_D - \varsigma_{AOM2}$$

eq. 2-3

$$\frac{dC_{SMB1}}{dt} = E_{SMB1}\left[\varsigma_{SOM1} + (1 - f_{SOM1} - f_{DOM})\varsigma_{SOM2}\right] - \varsigma_{SMB1}$$

eq. 2-4

$$\frac{dC_{SMB2}}{dt} = E_{SMB2}\left[(1 - f_{SOM2} - f_{DOM})D_{SMB2} + f_{SMB2}D_{SMB1} + \varsigma_{AOM1} + \varsigma_{AOM2} + \varsigma_{DOM}\right] - \varsigma_{SMB2}$$

eq. 2-5

$$\frac{dC_{SOM1}}{dt} = (f_{SOM1})\varsigma_{SOM2} - \varsigma_{SOM1}$$

eq. 2-6

$$\frac{dC_{SOM2}}{dt} = (1 - f_{AOM1} - f_{AOM2})I_D + f_{SOM2}D_{SMB2} + (1 - f_{DOM} - f_{SMB2})D_{SMB1}) - \varsigma_{SOM2}$$

$$\frac{dC_{DOM}}{dt} = f_{DOM}(D_{SMB1} + D_{SMB2} + \varsigma_{SOM2}) - \varsigma_{DOM} \qquad \text{eq. 2-7}$$

C_X: Carbon concentration in soil of pool X [kg m^{-3}]
ς : Turnover rate of pool X [kg m^{-3} $hour^{-1}$].
E : Substrate utilization efficiency of pool X.
D : Death rate of pool X [kg C m^{-3} $hour^{-1}$].
f : Flow fraction of pool X.
I_D: Carbon input.

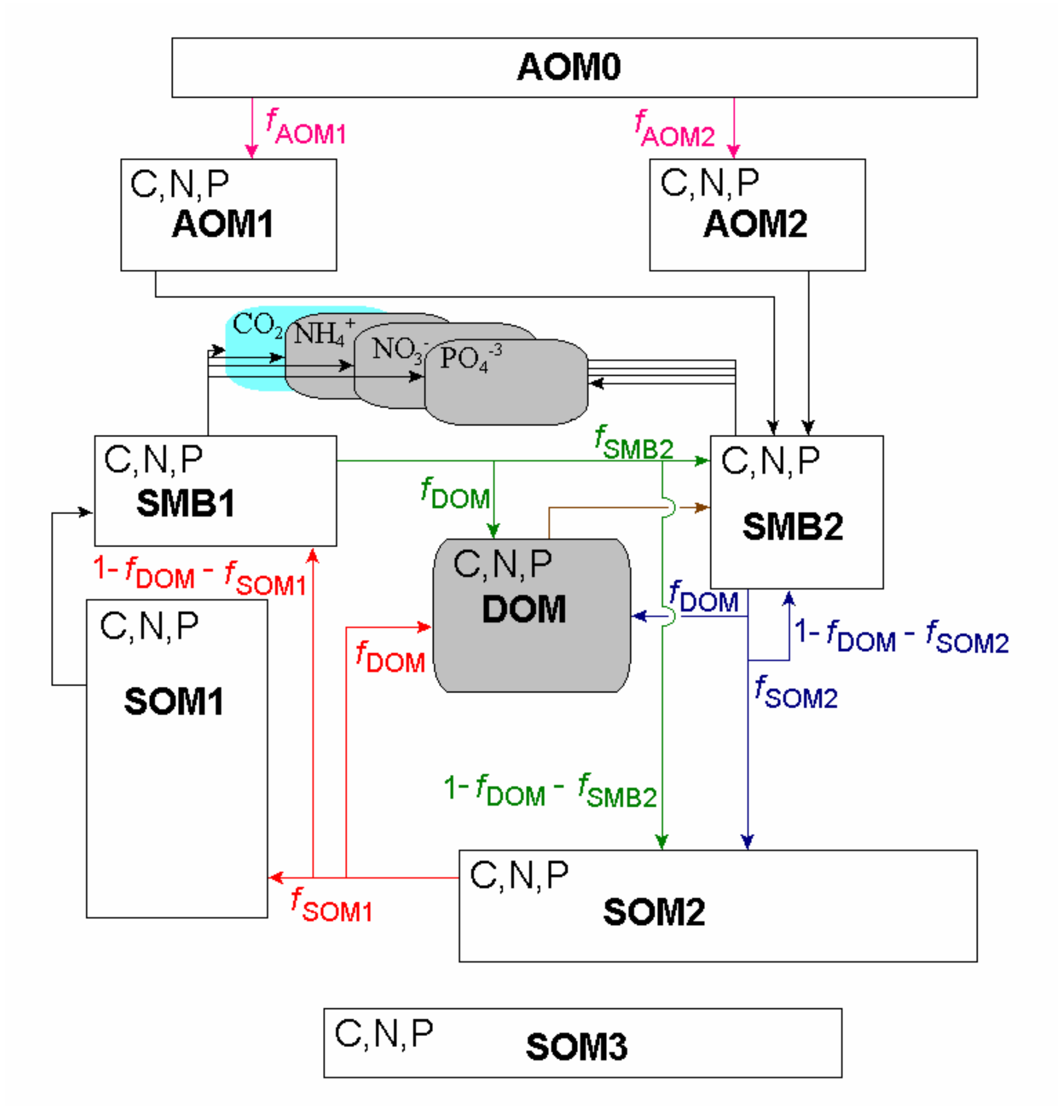


Figure 1. *Interrelationship between the soil organic fractions in the Daisy-P Model showing the flow fractions, f_X, to the different pools X. AOM1 and AOM2 corresponds to the slowly and easily degradable added organic matter, respectively. SOM1 and SOM2 corresponds to the slowly and easily degradable soil organic matter, respectively. SOM3 is inert soil organic matter. The soil microbial biomass is subdivided into SMB1 and SMB2 which is considered to be the stable and the dynamic fraction, respectively.*

If we consider equation eq. 2-6 the SOM2 pool receives every time step (1 hour) inputs from partly decomposed organic matter, such as manure, if there is any input. Additionally, SOM2 receive the death microbes from the SMB2 and SMB1 pools. The SOM2 pool is decomposed at a given rate described in eq. 2-9. Hence, the amount decomposed is lost from the pool. Thus, the change in C content of every organic pool during one time step is net fluxes of the amount received and lost.

New organic substrate, dead roots or leaves, root exudates, and organic fertilisers are applied to the systems as inputs to the fractions AOM1 and AOM2. Depending on the substrate it is fractionated to the two pools in specific fractions given by f_{AOM1} and f_{AOM2}, respectively (Figure. 1). In case of farmyard or manure, some of the added organic matter is already partly degraded into smaller molecules and contribute to the SOM2 fraction. Carbon input of new organic substrate is given by I_D, which is an input function given by eq. 2-8 (Hansen et al., 1990):

$$I_D = \begin{cases} \dfrac{I_C}{\Delta t} & t_0 \langle \; t \; \langle \; t_0 + \Delta t \\ 0 & \text{else} \end{cases} \tag{eq. 2-8}$$

t : Time [s].
I_C : Organic carbon input [kg C m^{-3}].

The Delta functions ensure that inorganic matter is added in short time intervals between time t_0 and the time $t_0+\Delta t$.

As microbes assimilate low molecular-weight compounds, some C is respired to produce energy, and the rest is synthesized into either new tissues (growth) or metabolites that are released to the extracellular environment (Sollins et al., 1996). The SMB1 and SMB2 are characterized by a substrate utility coefficient, *E*, which depend on the microbial community and the bioavailability of the substrate, *X*. The substrate utility coefficient, *E*, refers to the fraction of substrate which is incorporated into the microbial biomass. The rest is mineralised, releasing CO_2 and inorganic N and P.

The decomposition of the SOM1 and SOM2 pools is mainly driven by the turnover of SMB1. Microbes selectively degrade the less recalcitrant compounds. Thus, a gradually increase in average recalcitrance of the non-respired C results in, that some fraction of SOM2 enters SOM1. Furthermore, the SMB2 receive C input of death microbes from SMB1 and also from its own population for further decomposition, Figure 1.

2.2.1 Kinetics of C flow

The turnover rates are considered as 1-order kinetics. For substrate in pool X the turnover rate is given as (Hansen et al., 1990):

$$\zeta = k_x C_C \tag{eq. 2-9}$$

ζ_x : Turnover rate of pool X [kg C m^{-3} $hour^{-1}$].
k_x : Turnover rate coefficient for pool X [$hour^{-1}$].
C_c : Carbon concentration [kg C m^{-3}].

The soil microbial biomass is dependent on substrate availability. When substrate is limited the microbial biomass dies. The death rates, D_x, of SMB1 and SMB2 are calculated like the turnover rates by substituting the turnover rate coefficient in eq. 2-9 with the death rate coefficient, d_x.

$$D_x = d_x \; C_C$$ eq. 2-10

d_x : Death rate coefficient for pool X [hour^{-1}].

The turnover rate coefficients at standard conditions of the microbial biomass SMB1 and SMB2 are the sum of the manitenance rate coefficient and the death rate coefficient.

$$k_x^* = d_x^{\;*} + m_x^{\;*}$$ eq. 2-11

d_x^* : Death rate coefficient for microbial biomass pool, X, at standard conditions [hour^{-1}]
m_x^* : Maintains rate coefficient for the microbial biomass pool, X, at standard conditions [hour^{-1}].

Hence, turnover of organic matter is partly due to the maintenance of the microbes, which depend on the utilisation efficiency, and the death of the microbes.

Environmental factors as temperature and soil moisture are taken into account by linking the turnover rates to functions describing effect of temperature, water content, and clay content. Hence, the extent and rate of conversion of organic P into soluble or stable inorganic forms is highly dependent upon the nature of the original organic material, as well as environmental factors such as pH, temperature, and soil moisture (Pierzynski et al., 2000). Turnover rate coefficients for AOM1 and AOM2 and DOM are given as:

$$k_x = k_x^* F_m^T(T) F_m^\psi(\psi)$$ eq. 2-12

k_x^*: Turnover rate coefficient at standard conditions [hour^{-1}]
$F_m^T(T)$: Temperature function,
T : Soil temperature [˚C]
$F_m^\Psi(\psi)$: Pressure potential function,
ψ: Pressure potential of soil water [m water].

Additionally, the clay content is considered as a factor that protects soil organic matter from decomposition. The abiotic functions $F_m^C(X_C)$, $F_m^T(T)$, and $F_m^T(T)$ which affects the turnover rates are defined in the next paragraphs. Standard conditions for the abiotic factors (temperature, soil water moisture, and clay content) are defined as when the respective factors return the value of 1 (Hansen et al., 1990). The turnover rate coefficients for SOM1 and SOM2 are given as:

$$k_x = k_x^* F_m^C(X_C) F_m^T(T) F_m^\psi(\psi)$$ eq. 2-13

$F_m^c(X_c)$: Clay content function,
X_c : Clay content [%],

The death rate coefficient, d_x, is like the turnover rate coefficient dependent of the abiotic conditions. Hence, for the SMB1 pool the death rate coefficient is calculated from eq. 2-13 substituting the turnover rate coefficient with the death rate coefficient. For the SMB2 pool the death rate coefficient is calculated from eq. 2-12 substituting the turnover rate coefficient with the death rate coefficient. The abiotic functions of temperature, $F_m^T(T)$, pressure potential $F_m^\Psi(\psi)$, and clay content $F_m^c(X_c)$ defined in Daisy (Hansen et al., 1990) are briefly reviewed in the following sections.

2.2.2 *Effect of temperature*

It is assumed that the effect of soil temperature on decomposition rate of organic matter increases linearly in the temperature range 0-20˚C and exponentially at soil temperature greater than 20 °C.

$$F_m^T(T)=\begin{cases}0 & T\le 0\\ 0.1\,T & 0<T\le 20\\ \exp\left(0.47-0.027\,T+0.00193\,T^2\right) & T>20\end{cases}$$

eq. 2-14

$F_m^T(T)$: Function to account for effect of soil temperature
T: Soil temperature [˚C].

The variation of the temperature factor with temperature described in from eq. 2-14 is illustrated in Figure 2.

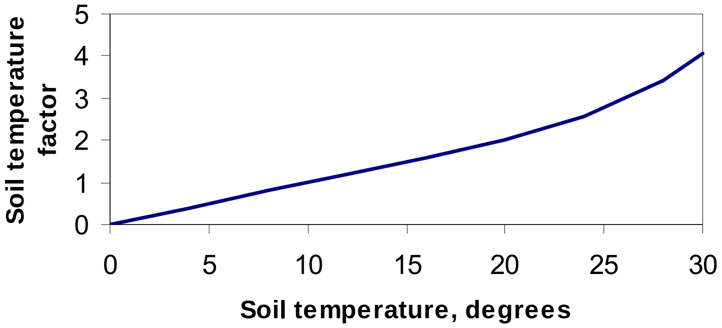


Figure 2. Soil temperature factor.

2.2.3 *Effect of soil moisture*

Only a small fraction of the organic matter in soils is likely to be in close proximity to the microbial biomass. Consequently, transport processes through the liquid phase of the soil are very important for the decomposition rate of organic matter in soils. Thus, the turnover rate of organic matter is strongly related to the corresponding pressure potential of soil water, since the soil water content considerably influences transport processes in soils. It is assumed that turnover of soil organic matter approaches zero at pF = 6.5, that optimal conditions exist in the range 1.5 < pF < 2.5. Furthermore, it is assumed that the turnover rate increases linearly from 0.6 at water saturation to 1 at pF 1.5, and that the function decreases linearly from 1.0 at pF 2.5 to zero at pF 6.5.

$$F_m^{\psi}(\psi)=\begin{cases}0.6 & \psi\ge -(10^{-2})\\ 0.6+0.4\log(-100\psi)/1.5 & -(10^{-2})>\psi\ge -(10^{-0.5})\\ 1.0 & -(10^{-0.5})>\psi\ge -(10^{0.5})\\ 1.0-\log(-100\psi)/4.0 & -(10^{0.5})>\psi\ge -(10^{-4.5})\\ 0 & -(10^{4.5})>\psi\end{cases}$$

eq. 2-15

$F_m^T(T)$: Function to account for the effect of soil water content.
ψ: Pressure potential of soil water [m water].

The variation of the pressure potential factor with pressure potential described in eq. 2-15 is illustrated in Figure 3.

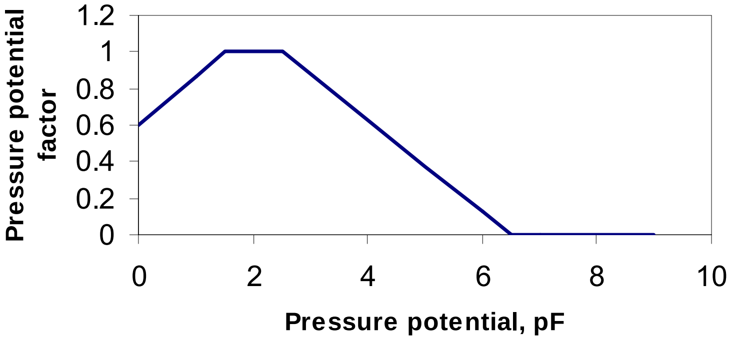


Figure 3. Pressure potential factor.

2.2.4 Effect of clay content

The protection of organic matter against decomposition or decay varies with the degree of aggregation or clay content of the soil. The function applied to account for the effect of clay content of the soil on the rate of decomposition or decay of organic matter is given as:

$$F_m^C(X_C) = \begin{cases} 1.0 - a\,X_C & 0 < X_C \le X_C' \\ 1.0 - a\,X_C' & X_C > X_C' \end{cases} \qquad \text{eq. 2-16}$$

$F_m^C(X_C)$: Function accounting for the effect of clay content.
a : Constant (a = 2).
X_C : Clay content [kg kg^{-1}].
x_C' : Limit for effect of clay contents (0.25 kg kg^{-1}).

The variation of the factor clay content with clay content described in eq. 2-16 is illustrated in Figure 4.

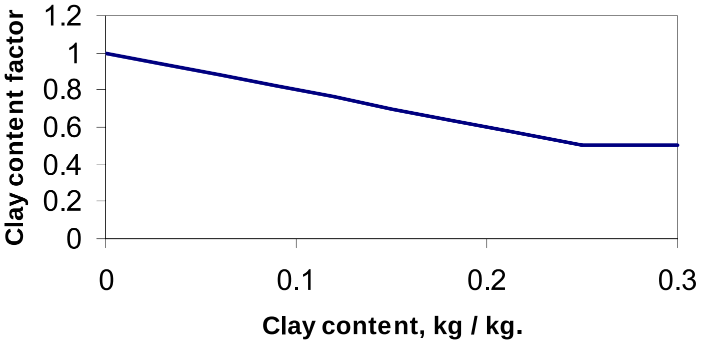


Figure 4. Clay content factor.

2.2.5 Immobilisation and mineralization of inorganic N and P

If the C/N- and C/P-ratios in the substrate are insufficient for decomposition it is tested whether or not there is available dissolved inorganic P and N in the bulk soil. If available N and P exist the microbial biomass is supplied with inorganic N and P by a first order reaction at a rate, which is related to diffusion and is proportional to the concentration of NH_4-N, NO_3-N and PO_4-P, respectively, in the bulk soil solution. By using first-order reactions it is assumed that the microbial biomass can be supplied with N and P from the inorganic pools, at a rate which is proportional to the concentration of NH_4^+-N, NO_3^-N (Hansen et al., 1990), and PO_4^{3-}-P in the soil solution, respectively:

$$\xi^{im}_{NH_4-N} = k^{im}_{NH_4-N}\, N_{NH_4-N} \qquad \text{eq. 2-17}$$

$$\xi^{im}_{NO_3-N} = k^{im}_{NO_3-N}\, N_{NO_3-N} \qquad \text{eq. 2-18}$$

$$\xi^{im}_{PO_4-P} = k^{im}_{PO_4-P}\, P_{PO_4-P} \qquad \text{eq. 2-19}$$

$k^{im}_{NH_4-N}$, $k^{im}_{NO_3-N}$, $k^{im}_{PO_4-P}$: Immobilization rate coefficient for NH_4-N, NO_3-N, and PO_4-P [$hour^{-1}$].

N_{NH_4-N}, $N_{NO_3^--N}$, P_{PO_4-P}: Amount of dissolved NH_4-N, NO_3-N, and PO_4-P in soil [$kg\ m^{-3}$].

$\xi^{im}_{NH_4-N}$, $\xi^{im}_{NO_3-N}$, $\xi^{im}_{PO_4-P}$: Rate by which dissolved NH_4-N, NO_3-N, PO4-P and can be utilized by the microbial biomass [$kg\ m^{-3}\ hour^{-1}$].

If sufficient mineral nitrogen is present in the soil, it is assumed that NH_4^+-N is utilized in preference to NO_3^--N. If the decomposition is limited due to lack of inorganic nutrients, the death rates and the decay rates of the organic fractions will be reduced until the nutrient demands are in correlation with the decay rates (Hansen et al., 1990).

Net mineralization of N and P, i.e. transformation of organic nitrogen to NH_4 and organic P to PO_4 is a result of two opposite processes, mineralization, and immobilization. Net mineralization is a function of:

- Substrate availability for the soil microbial biomass.
- The difference between growth rate and death rate of soil microbial biomass.
- The efficiency by which soil microbial biomass utilizes dissolved organic matter as substrate.
- The C/N- and C/P-ratio in the various fractions of organic matter being decomposed.
- The C/N- and C/P-ratio in the microbial biomass are being synthesized.

Thus the rate of N and P net mineralization are overall results of transformation processes given by eq. 2-1-eq. 2-7 and the C/N- and C/P-ratios of the organic matter fractions in the soil. The net mineralization of P, $\xi_{m.P}$, is given by:

$$\xi_{m.P} = -\frac{\frac{dC_{AOM1}}{dt}}{\left[\frac{C}{P}\right]_{AOM1}} - \frac{\frac{dC_{AOM2}}{dt}}{\left[\frac{C}{P}\right]_{AOM2}} - \frac{\frac{dC_{SOM1}}{dt}}{\left[\frac{C}{P}\right]_{SOM1}} - \frac{\frac{dC_{SOM2}}{dt}}{\left[\frac{C}{P}\right]_{SOM2}} - \frac{\frac{dC_{SMB1}}{dt}}{\left[\frac{C}{P}\right]_{SMB1}} - \frac{\frac{dC_{SMB2}}{dt}}{\left[\frac{C}{P}\right]_{SMB2}} - \frac{\frac{dC_{DOM}}{dt}}{\left[\frac{C}{P}\right]_{DOM}} \qquad \text{eq. 2-20}$$

If the net mineralization rates of N or P are negative, net immobilization occurs of N or P. When immobilization occurs, the upper limit for the immobilization rate is determined by the availability of inorganic N and P.

The C/N- and C/P-ratios of the SMB1, SMB2, and SOM1 pools are fixed. In the AOM1 and AOM2 pools the C/N- and C/P-ratios are substrate dependent. The C/N- and C/P-ratios of the DOM pools are variable as the sources have different ratios. The SOM2 pool also has variable C/N and C/P ratio, as this pool is able to desorb and sorb DOM (described in the next section).

3 SORPTION OF DISSOLVED ORGANIC MATTER

The bulk of the organic matter in most soils is bound to clay minerals, probably through linkages with Fe, Al, and other polyvalent cations (Stevenson, 1994). Evidence from studies in soil systems indicates that sorptive protection of DOM may be of particular importance; hence, according to several authors (e.g McDowell and Wood, 1984; Guggenberger and Zech, 1992; Kaiser et al., 1996; Qualls and Haines, 1992) the change in quantity of DOM during passage through the mineral soil is caused by sorption of DOM on to the soil mineral phase. A first indication of the importance of sorptive protection in soils is the frequently reported positive relationship between organic C content and the clay content (e.g. Burke et al., 1989; Hassink, 1997). Secondly, fluxes of DOC generally decrease from litter layer to deeper mineral horizons and in virtually every soil with substantial clay content, DOC concentrations drops by 50 % - 90 % from the surface organic layers to subsurface minerals soils (Neff and Asner, 2001).

Because sorption is defined as the transfer of a solute (the sorbate) from solution to an existing solid phase (the sorbent), a prerequisite for the sorptive stabilisation of soil organic matter is that, it must occur in a dissolved state prior to sorption or precipitation (Guggenberger and Kaiser, 2003). Bonding mechanisms differ depending on the nature of the sorbate and sorbent. Clay, including layer- and amorphous aluminiumsilicates, and the so called sesquioxides (oxides, hydroxides, and oxyhydroxides of Al and Fe), provide the vast majority of sorbent surface area in soil (Sollins et al., 1996). Clay surfaces can be divided into two fundamentally distinct types (Borggaard, 1998) namely variable charged surfaces and permanent charged surfaces. On hydroxylated surfaces, net surface charge varies, becoming increasingly negative as pH increases. Such variable-charge surfaces occur on kaolinite, sesquioxides, and amorphous aluminosilicates. Permanent charge arises from substitution of ions of lower valence for ones of higher valence within the crystal structure of clays. The resulting negative charge is a permanent feature of the clay and is largely unaffected by pH. Permanently charged surfaces occur on smectite, illite, and other layer silicate clays (Sollins et al., 1996).

Sorption of negatively charged organic groups (e.g., dissociated carboxylic acid groups) can occur through replacement of surface hydroxyl groups (ligand exchange) (Parfitt, 1978). Since surface hydroxyl groups are restricted to variable charge surfaces, sorption of negatively charged organics by ligand exchange should be most important in oxide-rich and allophanic soils. Sorption of organic anions by electrostatic interactions (anion exchange) would require positive surface charge (Sollins et al., 1988); however, cation bridging should also be possible in the presence of polyvalent metal ions such as Ca^{2+}, Al^{3+}, $Fe^{2+/3+}$ (Stevenson, 1994). Other bonding mechanisms involved in sorption of organic substances include water bridging, hydrogen bonding, and van der Walls forces. In addition, (Jardine et al., 1989) concluded that due to the diversity of soil sorbents and sorbates, several mechanisms involved in sorption of humic substances will likely be involved simultaneously.

3.1 Sorbed phase of DOM

Much evidence suggests that clay somehow stabilizes SOM. Hence, correlations between clay content and accumulation of microbial biomass derived from ^{14}C-glucose (Amato and Ladd, 1992) and SOM content have been obtained (Burke et al., 1989). The quantitative importance of sorption in SOM stabilization and accumulation is even less well understood than the mechanisms and controls of sorption (Sollins et al., 1996). How much of the OM in soil might be sorbed? Chemisorption of organic matter to clay-sized particles and physical protection of organic matter within organo-clay aggregates often cannot be clearly distinguished (Guggenberger and Kaiser, 2003). It has been hypothesized that a pool of potential DOM exists as a part of soil organic matter "that is not in solution but is part of the soil solids and able to pass into the solution under realistic conditions" (Tipping, 1998 cf. Kalbitz et al., 2000). Hence, according to this hypothesis some part of SOM has potential to release DOM and to 'remove' or sorb DOM from solution.

It is often found that soil is able to release DOM when exposed to aqueous solution containing no or very low concentrations of DOM (Kaiser, 2001). Thus, the soil solid phase may not only sorb DOM but may also release it depending on solution DOM concentrations. The quantitative importance of sorption of DOM in stabilization and accumulation of SOM could be related to the amount of organic matter associated to clay minerals and sesquioxides, as they provide the vast majority of sorbent surface area in soil. Extraction of DOM from soil bulk samples using a chelating reagent which had a high affinity for polyvalent cations, released approximately 50 % of the organic matter in the soil to the solution phase (Gjettermann et al., 2005). This fraction of extracted DOM is released by removing polyvalent cations as Fe^{3+}, Al^{3+} from SOM. This could indicate that approximately half of the SOM was associated to polyvalent cations and could be a potential pool of DOM able to pass into the solution if released. These findings are in accordance with Greenland (1971) who observed that 52-98 % of the C in soil examined was associated to clay minerals.

In the P-Model it is considered, that DOM is rather old, assuming that easily degradable new components are rapidly consumed by microbes and can not be distinguished fro the AOM pools. Hence, DOM is mainly produced from SOM by some physical/chemical/biological processes resulting in that some part of SOM in soil is dissolved. Based on the above mentioned observations of DOM extraction and amount of SOM associated to minerals, it is assumed that the relative bioavailable fraction of SOM, the SOM2 pool, has potential for releasing DOM to or removing DOM from solution. Only the SOM2 pool contributes to the sorptive preservation/destruction of organic substances, as SOM2 is the most bioavailable and less stabilised fraction of SOM. Additionally, the quantity of SOM2 approximates to be 1/3 of total SOM.

The biological processes of mobilizing DOM from SOM and *vice versa* was described in the previous paragraph. The physical/chemical process is described in this paragraph, release a fraction of solid SOM as DOM during desorption and removing DOM from solution to solid SOM by sorption.

3.2 DOM sorption at equilibrium

Desorption and sorption of DOC has been described by an approach called the Initial Mass isotherm. It is developed and described by Nodvin et al. (1986) for a number of anions and DOC. The Initial Mass (IM) isotherm is a simple partitioning model that additionally accounts for the substance initially present within the soil. In several studies IM isotherms have been able to describe the amount of DOC, removed or released to the solution by the soil, as a linear function of the initial amount of DOC added to the soil-water system (Moore et al., 1992; Vance and David, 1992; Guggenberger and Zech, 1992). It has also been able to describe the exchange of DOP (Kaiser, 2001) and DON (Kaiser and Zech, 2000) using the IM isotherm.

The following paragraphs describe the IM isotherm in relation to DOM sorption. It is noted that the IM isotherm is not a traditional isotherm with sorbed and soluble equilibrium concentrations (final values) but with initial values of added solute concentrations as the abscissa. The IM isotherm is linked to soil properties such as soil content of Al, Fe, and organic matter by pedotransfer functions. The IM isotherm represents the basis for description of DOM sorption in the P-Model. In the P-Model the IM isotherm is also used to estimate the DOC concentration optimum in the soil system where no net change of sorption/desorption occurs.

3.2.1 The Initial Mass isotherm

In the IM isotherm the amount of substance sorbed or released (normalized to soil mass) is termed *RE*. Negative values of *RE* indicate a net release to the solution and a positive value indicate a net removal of substance from the solution. It is not a measure of total sorbed substances, for additional substance may have been present within the soil at the outset of an equilibration experiment. A linear function is obtained when plotting the amount of solute (normalized to soil mass) removed from or released to the soil solution as a function of initial amount of solutes (normalized to soil mass) added to the soil:water system (Nodvin et al., 1986). When *RE* is plotted as a function of the initial amount of that substance X_i (normalized to soil mass) the release or removal, *RE*, of DOC or DOP is given by:

$$RE = mX_i - b \qquad \text{eq. 3-1}$$

RE: Amount released or removed from solution after 24 hours [g kg^{-1}]
X_i: Initial amount of solute added [g kg^{-1}]
m: Partitioning coefficient or slope of linear regression [g g^{-1}]
b: Intercept of linear regression [g kg^{-1}]

The slope of the linear function, *m*, is related to the partitioning coefficient and is a measure of the affinity of the substance to the sorbent. The numerical value of *m* represents the fraction of substances in the soil:water system that is associated with the soil (Nodvin et al., 1986). The intercept of the linear regression, *b*, represents the amount of substances released from or sorbed by the soil when a solution with no sorbate (DOM) is added. Thus, the intercept may be called a desorption term. The relationship is consistent with a simple partitioning of DOM between soil and solution with *m* as a partitioning coefficient.

In a sorption experiment the amount of solute remaining in solution is the difference between the amount added and the amount removed or released by the soil. The plot of *RE* as a function of the final amount of solute, X_f, is equivalent to an IM isotherm given by eq. 3-1, in which the abscissa has been rescaled by the variable *RE*. The axes *RE* and X_f are not independent, because both parameters are dependent upon X_i, ($X_f = X_i - RE$). Nodvin et al. (1986) showed that if the IM isotherm deviates from linearity at high values of X_i by a distance *d* then *RE* is reduced by a value *d*. As shown in the right figure in Figure 5, the endpoints of the curves, which correspond to the same point of sorption, are separated by a 45° vector of the length $(2d^2)^{1/2}$. Thus, regressions using initial values should provide a better linear fit of sorption data than regression with final values, as curvature will appear enhanced in plots using final values relative to plots using initial values (Nodvin et al., 1986).

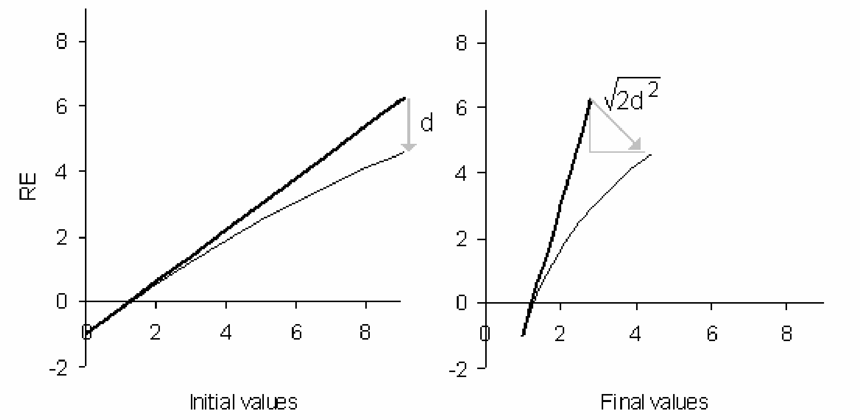


Figure 5. Analysis of rescaling of plots using initial and final values. Modified from Nodvin et al. (1986).

To utilize the IM isotherm, the concentrations used in sorption experiment must produce data that result in a statistically linear fit to the IM isotherm. Use of the IM isotherm will therefore be precluded above a certain solute concentration, which will vary depending on the soil, substance, and experimentally conditions (Nodvin et al., 1986). In a batch sorption experiment the pH-dependent sorption of DOM to an agricultural top- and subsoil was conducted with two pH levels (pH 5 and 7). For the range of DOC concentration of 0-56 mg L^{-1} the IM isotherm was able to describe the DOC sorption isotherms with correlation factors r^2 >0.9 (Gjettermann et al., 2005c). DOC concentration obtained by suction cups for the same soil as used in the sorption experiments varied between 17 and 45 mg L^{-1} for the topsoil and 5 and 16 mg L^{-1} for the subsoil (Gjettermann et al., 2005a). This is in the range of reported DOC concentrations in agricultural soils varying from 3 and 70 mg L^{-1} (Zsolnay, 1996). Other batch experiments with forest soil have used DOC concentrations up to 81 mg L^{-1} (Moore et al., 1992) and found good correlation factors in fitting the IM isotherm.

A number of sorption studies of DOC sorption have indicated that extractable Fe and Al, organic C content, and mineralogy are important controls on the ability of soils to sorb DOC, (McDowell and Wood, 1984; Moore, 1989). Moore et al. (1992), Kaiser et al. (1996), and Neff and Asner (2001) have attempted to estimate correlations between soil properties and parameters of the IM isotherm to describe DOC sorption in general terms for different soils. Table 1and Table 2 lists the pedotransfer functions estimated in a number of studies, correlating the desorption parameter, *b*, and the partitioning parameter, *m*, respectively to soil properties.

Table 1. Pedotransfer functions estimating the desorption parameter, b, across a range of soil types (modified from Neff and Asner (2001)).

	Relationship	*R^2*	*References and comments*
Without carbonates	Total DOC: Log b = 0.32 + 0.72 log OC	0.76	Kaiser et al. (1996):
	Hydrophilic DOC:		Batch experiments: pH 3.95, 24 hours of reaction, 0-6.0 mM DOC added).
	Log b = 0.20 + 0.71 log OC	0.75	
	Hydrophobic DOC:		Soils from Germany, the Netherlands, and Sweden. Most with Norway spruce.
	Log b = -0.46 + 0.84 log OC	0.65	
With carbonates	Total DOC: Log b = - 0.02 + 0.88 log OC		93 carbonate-free soils.
	Hydrophilic DOC:	0.82	31 carbonate-containing soils.
	Log b = - 0.16 + 0.71 log OC		Soil orders represented: Spodosols, inceptisols, alfisols, entisols, mollisols.
	Hydrophobic DOC:	0.80	
	Log b = -0.46 + 0.84 log OC		
		0.71	
	b = 0.145 + 0.103 log (% OC) - 0.055√(% Al_{ox}) - 0.045 log (%Fe_{dcb})	0.72	Moore et al. (1992): 48 soils. Soil orders represented: inceptisols, spodosols, mollisols.
	b = 0.05 (% OC) + 0.09	0.48	Neff and Asner (2001): Correlation gathering many soils and studies.

OC: Organic C, Al_{ox}: oxalate extractable Al, Fe_{dcb}: dithionite-citrate-bicarbonate extractable Fe. Units in g kg^{-1} if not specified otherwise. b: Desorption parameter in g kg^{-1}.

Generally, positive correlations were obtained between the intercept *b* and the organic C content, Table 1. Contrary to the partitioning coefficient, a negative correlation was obtained between *b* and dithionite extractable iron, Fe_{dcb}, and oxalate extractable aluminium, Al_{ox} by Moore et al. (1992).

Table 2. Pedotransfer functions estimating the partitioning coefficients, m, across a range of soil types (modified from Neff and Asner (2001)).

	Relationship	R^2	*References and comments*
Without carbonates	Total DOC:	0.75	Kaiser et al. (1996):
	$m = 0.64 + 0.15 \log Fe_{dcb} + 0.19 \log Al_{ox} - 0.26 \log OC$		Batch experiments: pH 3.95, 24 hours of reaction, 0-6.0 mM DOC added).
	Hydrophilic DOC:	0.58	
	$m = 0.53 + 0.17 \log Fe_{dcb} + 0.11 \log Al_{ox} - 0.34 \log OC$		Soils from Germany, Netherlands, and Sweden. Most with Norway spruce.
	Hydrophobic DOC:	0.77	
	$m = 0.71 + 0.13 \log Fe_{dcb} + 0.24 \log Al_{ox} - 0.20 \log OC$		93 carbonate-free soils.
With carbonates	Total DOC:	0.67	
	$m = 0.66 + 0.44 \log Fe_{dcb} - 0.45 \log OC$		31 carbonate-containing soils.
	Hydrophilic DOC:	0.58	
	$m = 0.84 + 0.46 \log Fe_{dcb} - 0.72 \log OC$		Soil orders represented: Spodosols, inceptisols, alfisols, entisols, mollisols
	Hydrophobic DOC:	0.59	
	$m = 0.53 + 0.43 \log Fe_{dcb} - 0.28 \log OC$		
	$m = 0.451 + 0.02 \log (\%Fe_{dcb}) + 0.032 \sqrt{(\% Al_{ox})} + 0.064 \log (\% OC)$	0.39	Moore et al. (1992): 48 soils: inceptisols, spodosols, Mollisols
	$m = 0.51 + 0.15 \ln (\% OC)$	0.41	Neff and Asner (2001): Correlations gathering many soils and studies.

OC: Organic C, Al_{ox}: oxalate extractable Al, Fe_{dcb}: dithionite-citrate-bicarbonate extractable Fe. Units in g kg^{-1} if not specified otherwise. *m*: partitioning coefficient with unit in fraction.

Additionally, positive correlations were obtained between *m* and dithionite extractable iron, Fe_{dcb}, and oxalate extractable aluminium, Al_{ox}, se Table 2. Neff and Asner (2001) and Kaiser et al. (1996) obtained positive correlations for organic C content; in contrast Moore et al. (1992) found negative correlation with the partitioning coefficient.

In the P-Model the pedotransfer functions developed by Moore et al. (1992) are incorporated to estimate the two parameters, *m* and *b*. These functions were found to describe measured DOC sorption experiments very well (Gjettermann et al., 2005c). The DOC sorption experiments and the soil used for the sorption experiments are described in details in paragraphs 10.2.1 and 10.2.2. In order to study the mobility of DOM in soil, the pH-dependent sorption of DOM to an agricultural top- and subsoil was conducted at two pH levels (pH 5 and 7) for each of the Ap, EB, and Bt horizons. The IM sorption parameters, *m* and *b*, were estimated for each horizon used in the sorption experiments by the pedotransfer functions listed in Tables 1 and 2, by inserting the soil content of organic matter, Al_{ox}, and Fe_{dcb} for each horizon. Figure 6 shows the IM isotherms from the estimated sorption parameters together with measured sorption data at two pH levels (pH 5 and pH 7) for the Ap, EB, and Bt horizons.

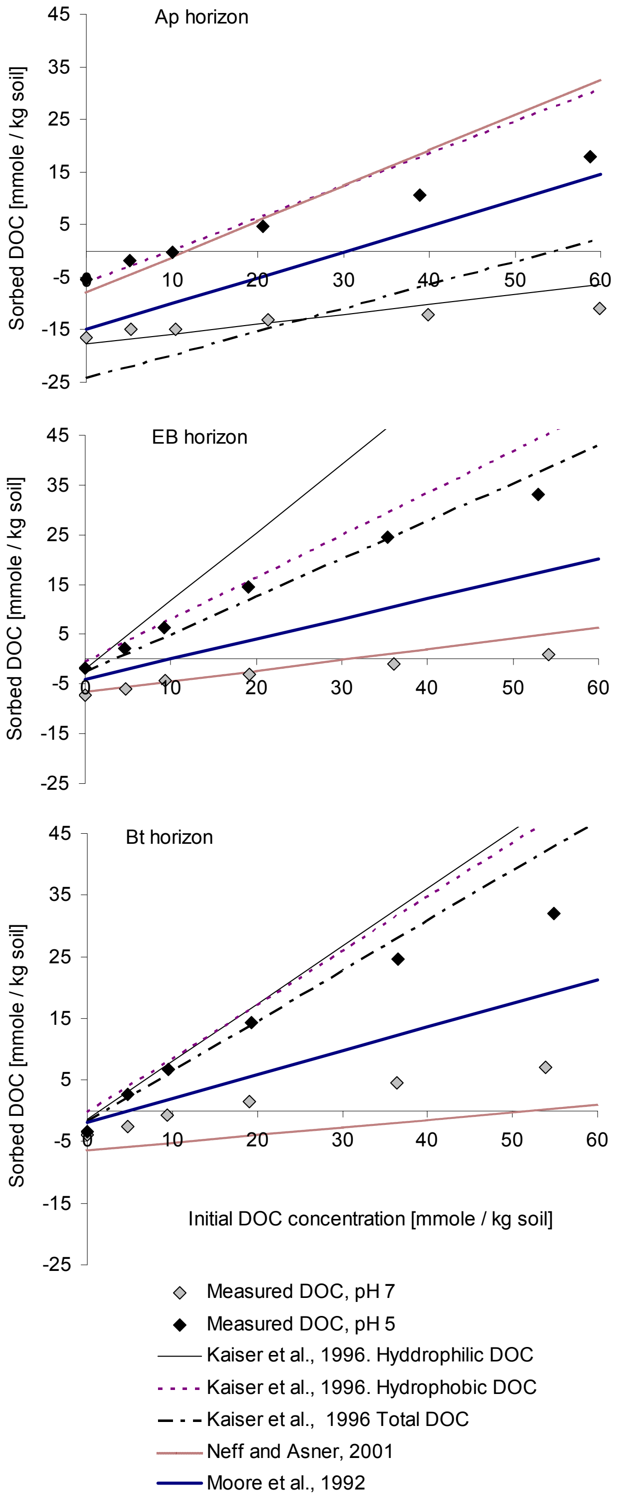


Figure 6. *DOC sorption isotherms from estimated sorption parameters, m and b, by the pedotransfer functions listed in Tables 1 and 2 (lines), respectively, together with measured data at pH 5 and pH 7 (dots) for the Ap, EB, and Bt horizons, respectively.*

As shown in Figure 6 the IM isotherms estimated by the parameters from the pedotransfer function by Moore et al. (1992) were in between the measured data at pH 5 and pH 7 for all horizons. At this stage the pH effect is not incorporated into the sorption parameters in the P-Model, as insufficient data are available linking pH effect to the sorption parameters of the IM. Hence, the best fit of the DOM sorption experiments to the soil is taken to be right in between the observed data at pH 5 and 7.

3.2.2 Null-point concentration of DOC

The DOC sorption isotherm described by the IM isotherm is the amount of DOC sorbed or released after 24 hours of reaction. When no DOC is removed from or release to the solution then RE = 0. Inserting RE = 0 into eq. 3-1, the amount of DOC in solution (normalized to soil mass) at this point, DOC_{np}, is given by eq. 3-2.

$$DOC_{np} = \frac{b}{m} \qquad \text{eq. 3-2}$$

DOC_{np}: The null-point concentration of DOC [mg g^{-1}].

The null-point concentration of DOC at which there is no net removal or release of DOC from the solution is then given by the intercept of the x-axis on the IM isotherm. This point correspond to the change in DOC after 24 hours of reaction in the soil:water system. Figure 7 schematise the IM isotherm and the null-point concentration of DOC where there is no net removal or release of DOC in the P-Model.

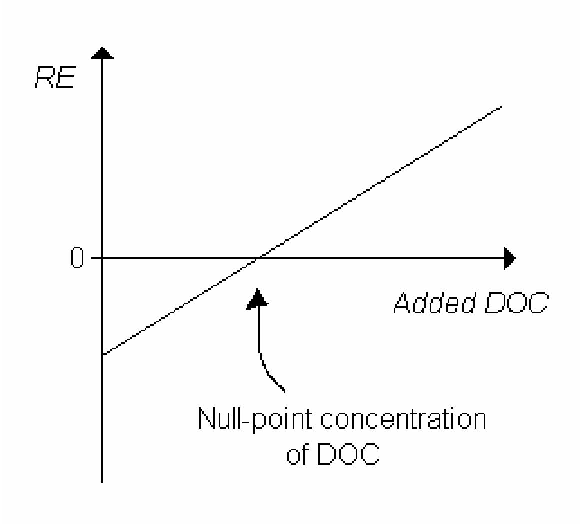


Figure 7. The Initial Mass isotherm.

In the P-Model the sorbed phase is considered to be a large proportion of SOM. The sorbed phase is then an infinitely large sink and source of DOM in the topsoil. In describing DOM sorption by the IM isotherm the sorbed phase is not a limiting factor for DOM sorption or desorption capacity. This implies that only the DOM concentration in the soil solution determines whether sorption or desorption occurs. To avoid that the DOM sorption/desorption process description continues to only desorb DOM from SOM, emptying the SOM pool, or the opposite, it is assumed that the soil seeks to equilibrate the solution concentration towards the DOC_{np}. The parameter DOC_{np} is considered to be constant with time, however, changing land use markedly might influence DOC_{np}. Hence, in the P-Model the DOC_{np} is considered to be the soil:water systems optimum DOC concentration at equilibrium, $DOC_{eq\_optimum}$, the soil system will approach with time.

However, this null-point concentration which is normalised to soil mass is established at soil:water ratios of 1:10 in sorption batch experiments (Moore et al., 1992). Transferring the DOC_{np} from per soil mass units to per soil solution unit is done by taking this soil:water ratio into account.

$$DOC_{eq\_optimum} \approx DOC_{np} \frac{m_{batch}}{V_{batch}} \qquad \text{eq. 3-3}$$

$DOC_{eq\_optimum}$: Optimum concentration of DOC in solution at equilibrium [g L^{-1}].
DOC_{np}: The null-point concentration of DOC [g kg^{-1}].
m_{batch}: Soil mass in batch system [kg].
V_{batch}: Volume of solution in batch system [L].

According to this, the IM isotherm is used to estimate a DOC concentration optimum in the soil solution, a concentration the soil system will approach with time.

3.3 The kinetic approach of DOM sorption

It is assumed that the least recalcitrant pool of soil organic matter, the SOM2 pool, has potential for release of DOM to or removal of DOM from solution. The system of dissolved phase and solid phase is then described as:

$$\text{SOM2-DOM} \equiv \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{SOM2} \equiv + \text{DOM} \qquad \text{eq. 3-4}$$

$SOM2$: Bioavailable fraction of soil organic matter [g kg^{-1}].
DOM: Dissolved organic matter [g L^{-1}].
K_1: First order sorption rate coefficient [$hour^{-1}$].
K_2: First order desorption rate coefficient [$hour^{-1}$].

The exchange between the dissolved and solid phase is described by a first order reaction as it is assumed only to depend on the solute concentration. However, it couples the defined optimum for DOC concentration to the actual DOC concentration. The kinetics must be considered as an empirical, kinetic expression (eq. 3-4) linking the difference in concentration between wanted and actual conditions in the soil. Hence, in a very simplified view it lumps together considerations as diffusion and sorption kinetics into the description of the sorption/desorption process, as it is not possible at present to incorporate considerations of variable such as pore geometry and particle surface availability in the model.

The 'reaction rate coefficients' k_1 and k_2 in eq. 3-4 are constants. The kinetics concept of the P-Model describes the sorption and desorption as functions of the difference between the solute and the optimum concentration and a rate coefficient. The change of amount of sorbed DOC is given by equation, eq. 3-5.

$$\frac{dDOC_{sol}}{dt} = \begin{cases} -k_1(DOC_{sol} - DOC_{eq\_optimum}), & DOC_{sol} - DOC_{eq\_optimum} > 0 \\ -k_2(DOC_{sol} - DOC_{eq\_optimum}), & DOC_{sol} - DOC_{eq\_optimum} \leq 0 \\ 0 & , \quad SOM2 < 10^{-9} \end{cases} \qquad \text{eq. 3-5}$$

DOC_{sol}: Actual concentration of DOC in solution [g L^{-1}].
k_1,k_2: Rate constants [$hour^{-1}$].
$\frac{dDOC_{sol}}{dt}$: Change of DOC with time t [g L^{-1} $hour^{-1}$].

Depending on whether the DOC concentration is above or below the optimal concentration, $DOC_{eq\_optimal}$, desorption or sorption is activated. However, the processes of sorption and desorption are activated if there is DOM or SOM in the soil. For instance, in the subsoil SOM may limit desorption of DOM, if the amount of SOM is below a critical value. During sorption and desorption of DOM the change in DOC is correlated by the change of C in the SOM2 pool. The change in DOP and DON depends on the C:N:P ratio of the SOM2 pool if desorption occurs. If sorption occurs the change of DOP and DON depends on the C:N:P ratio of the DOM pool. Hence, the C:N:P ratio of the source determines the change of N and P in the sink.

4 SORPTION OF DISSOLVED INORGANIC P

The soil capacity to bind inorganic P may reach an upper limit if phosphorus continuously is applied in excess of plant needs. Intensively cultivated soils accumulate phosphorus when the amount of phosphorus added in fertilizers, manure or sludge exceeds the amount exported in biomass and plant uptake plus any lost by leaching (Del Campillo et al., 1999). This enrichment has led to increased availability of P beneficial to plant production, but at the same time the risk of P transport out of the soil has increased (Heckrath et al., 1995). The degree of P saturation (DPS), defined as the ratio of oxalate-extracted P to total P sorption capacity, has been useful in estimating the risk of P leaching from field soil. Thus, the critical DPS value for producing an equilibrium soil solution P concentration of 0.1 mg L^{-1} was established at DPS of 25 % reported by Breeuwsma and Silva (1992, cf. Khiari et al., 2000). Lookman et al. (1995b) state that a soil is 'phosphate saturated' if it's DPS exceeds 24 %. Above this value P equilibrium concentrations in soil solution are believed to rise above 0.1 mg L^{-1}, the basic quality norm for P in surface water in the Netherlands (Lookman et al., 1995b) and also in Denmark (Rubæk et al., 2001).

Sorption of DIP in soil has often been fitted successfully by the Langmuir isotherm. However, one must keep in mind that Langmuir describes equilibrium conditions and it is well known that equilibrium conditions do not occur in relation to P sorption in soil. The interaction of P with soil components depends on the phosphate concentration in soil solution as well as the time and the amount already sorbed. Thus, the value of a measured pseudo-sorption-maximum, as often observed in soils, depends on the applied DIP concentration and on the equilibration time (Van Riemsdijk et al., 1984) which may extend for periods of weeks to months. Another disadvantage of using Langmuir to describe DIP sorption is that it assumes that the adsorbate-adsorbent affinity is unchanged with time. This is a rough approximation partly because increased saturation may affect the 'availability' of the free sorption sites (Goldberg and Sposito, 1984) and partly due to the assumption that all soil adsorbate components have the same energy of bonding (Holford et al., 1974; Ryden et al., 1977). Several modifications of the Langmuir equation have been used to solve some of these complications (e.g. Holford et al., 1974; Ryden, et al., 1977). However, the use of the Langmuir isotherm is of practical interest because the total sorption capacity can be estimated from soil properties by pedotransfer functions.

The sorption process of DIP to soil component is complicated for one main reason, namely that apparent DIP sorption is a combination of several processes, including fast (almost instantaneous) reversible sorption processes on soil particle surfaces, plus various slower time-dependent processes (Mansell et al., 1977; Van Riemsdijk et al., 1984; Hansen et al., 1999). These slower processes can be further subdivided into relatively faster and very slow components, and they are described in literature as 'slow adsorption', 'slow reaction', 'deposition', 'fixation', precipitation' or 'solid state diffusion'. Opinion differ about the extent to which such processes are reversible (McGechan and Lewis, 2002).

The concept of DIP sorption processes in the P-Model is based on the concept of a three-step mechanism: 1) A fast sorption reaction, and, 2) a relative slow absorption reaction, followed by 3) a very slow fixation process. Thus, it is hypothesized that DIP first binds to easily available sorption sites with high affinity, and secondly to the less available sites that are limited by diffusion; thirdly further migration into the soil DIP reaches the least available sorption sites.

4.1 DIP sorption at equilibrium

In the P-Model the overall sorption mechanism of inorganic phosphate is divided into three processes: a fast, a relative slow, and a slow process, which are mutually dependent on one another. Langmuir isotherms describe all three processes at equilibrium. Thus, considering the system composed of four phases that is dissolved phase, adsorbed phase, absorbed phase, and fixated phase:

$$M \equiv + P_{sol\_eq} \overset{\rightarrow}{\leftarrow} P_{ads} \qquad \text{eq. 4-1}$$

$$M \equiv + P_{sol\_eq} \overset{\rightarrow}{\leftarrow} P_{abs} \qquad \text{eq. 4-2}$$

$$M \equiv + P_{sol\_eq} \overset{\rightarrow}{\leftarrow} P_{fix} \qquad \text{eq. 4-3}$$

P_{sol_eq}: DIP concentration at equilibrium [mmole L^{-1}].
P_{ads}: Adsorbed inorganic P [mmole kg^{-1}].
P_{abs}: Absorbed inorganic P [mmole kg^{-1}].
P_{fix}: Fixed inorganic P [mmole kg^{-1}].

The Langmuir equation for the fast sorption process in eq. 4-1 is given by eq. 4-4, which determines the phase distribution between the dissolved and adsorbed phase at equilibrium.

$$P_{ads} = \frac{K_{L\_ads} P_{\max\_ads} P_{sol\_eq}}{1 + K_{L\_ads} P_{sol\_eq}} \qquad \text{eq. 4-4}$$

P_{ads} : Adsorbed DIP to soil components [mmole kg^{-1}].
P_{max_ads}: Sorption capacity of adsorbed DIP [mmole kg^{-1}].
K_{L_ads} : Equilibrium constant for the adsorption process [L $mmole^{-1}$].

The same equation can be adopted for the relatively slow process of absorption, eq. 4-2, using abbreviates *abs* instead of *ads* in eq. 4-4. The Langmuir equation for the relatively slow process thus determines the phase distribution between the absorbed and dissolved phases at equilibrium. Additionally, the same equation can be adopted for the very slow process of fixation, eq. 4-3, using abbreviates *fix* instead of *ads* in eq. 4-4.

4.1.1 Sorption capacities

In many soils the oxides, hydroxides and oxyhydroxides of aluminium and iron(III) are the components predominantly influencing phosphate sorption (Borggaard et al., 1990}; Freese et al., 1992) and close correlation is often observed between sorbed phosphate and the content of aluminium and iron oxides in bulk samples (Hansen et al., 1999}; Borggaard et al., 1990; Sakadevan and Bavor, 1998). For instance Van der Zee and Van Riemsdijk (1986,1988) found that P sorption in non-calcareous soils was linearly related to the sum of amorphous Fe and Al referred to as oxalate extractable Fe and Al. It has been shown that the maximum P sorption capacity of soils can be correlated to the oxalate extractable fractions of Fe and Al (Beek et al., 1980) and both the oxalate and the citrate-dithionite-bicarbonate (CDB) extractable fractions of Fe and Al (e.g. Borggaard et al., 1990). The oxalate extractable fraction of Fe and Al corresponds to the more or less amorphous fractions of Fe and Al oxides, while the CDB extractable fraction corresponds to the amorphous plus the crystalline fractions.

The total DIP sorption capacity, P_{max_total}, can be estimated from pedotransfer functions, which is related to soil components as iron and aluminium oxides in non-calcareous soil. The pedotransfer function developed by Borggaard et al. (1990) takes into account the crystalline fraction of iron oxide, measured as citrate-dithionite-bicarbonate (CDB) extractable iron, minus the amorphous fraction of iron oxide, measured as oxalate extractable iron:

$$P_{\max} = x_0 + x_1 Fe_{ox} + x_2 Al_{ox} + x_3 (Fe_{cbd} - Fe_{ox}) \qquad \text{eq. 4-5}$$

P_{max}: DIP sorption capacity [mmole kg^{-1}].
Fe_{ox}: Oxalate extractable iron [mmole kg^{-1}].
Al_{ox}: Oxalate extractable aluminium [mmole kg^{-1}].
Fe_{CDB}: Citrate-dithionite-bicarbonate extractable iron [mmole kg^{-1}].
X_0: Constant = 0.3.
X_1: Constant = 0.115.
X_2: Constant = 0.221.
X_3: Constant = 0.05.

However, this function does not consider the amount of inorganic P already sorbed to the soil components, only the additional amount sorbed. Oxalate extractable P has been used to estimate the reversibly sorbed P fraction in the soil (Freese et al., 1992; Lookman et al., 1995). Thus, in the P-Model eq. 4-5 is modified by adding oxalate extractable P to the right side, giving:

$$P_{\max\_total} = P_{ox} + x_0 + x_1 Fe_{ox} + x_2 Al_{ox} + x_3 (Fe_{cbd} - Fe_{ox}) \qquad \text{eq. 4-6}$$

P_{max_total}: Total DIP sorption capacity [mmole kg^{-1}].
P_{ox}: Oxalate extractable P [mmole kg^{-1}].

Using Langmuir for the slow, relative slow, and the fast sorption process the sorption capacity must be defined for all the processes. The fast adsorption is defined as the amount of P sorbed within an hour for laboratory experiments. The relatively slow process is related to the amount sorbed during days and/or weeks. Consequently, fractions of the total sorption capacity must be allocated to the three processes. Thus, P_{max_ads}, must be related to the max amount of P adsorbed during one hour. The relation between P_{max_total}, P_{max_ads}, P_{max_abs}, and P_{max_fix} can be expressed as:

$$P_{\max\_ads} = \gamma\, P_{\max\_total} \qquad \text{eq. 4-7}$$

$$P_{\max\_abs} = \varepsilon\, P_{\max\_total} \qquad \text{eq. 4-8}$$

$$P_{\max\_fix} = P_{\max\_total} - P_{\max\_ads} - P_{\max\_abs} \qquad \text{eq. 4-9}$$

P_{max_total}: Total DIP sorption capacity [mmole kg^{-1}].
P_{max_ads}: Adsorbed DIP sorption capacity [mmole kg^{-1}].
P_{max_abs} Absorbed DIP sorption capacity [mmole kg^{-1}].
P_{max_fix}: Fixed DIP sorption capacity [mmole kg^{-1}].
ε and γ : Fractions, constants.

The distribution between P_{max_total}, P_{max_ads}, P_{max_abs}, and P_{max_fix} is estimated by fitting to sorption data from two agricultural soils in Denmark, see paragraph 10.3.5. For the Unreacted Shrinking Core Model (Del Campillo et al., 1999) it is found that the soil is phosphate saturated, about two-thirds of the phosphate sorption capacity corresponds the soil capacity to precipitate phosphate and about one-third to accommodate reversible adsorbed phosphate. Hence, in the P-Model it has been assumed that $\gamma = 1/3$. The best fit for DIP concentration ranging from 3 μM to 600 μM was obtained by using $\varepsilon = 1/4$ in eq. 4-8.

4.1.2 Sorption affinities

To describe sorption of DIP with Langmuir the affinity constant has to be known. However, according to the above discussion it is an approximation that the affinity constant is constant for a given soil with time. Results obtained by Hansen et al. (1999) shows that the fitted Langmuir affinity constant increases with time, which may indicate that more favourable but less accessible sorption sites are activated with time. Hansen et al. (1999) found that the fitted affinity constant from sorption isotherms increased from 25 mM^{-1} to 50 mM^{-1} during 9 days. Assuming that DIP first adsorbs to the most available sites and then migrates into soil aggregates to more favourable sorption sites, it makes sense that the affinity increases with time. However, it was not possible to fit sorption experiments with increasing affinities for the slower processes (not shown). In the P-Model this is incorporated in the concept by assuming that the fast process of adsorption occurs to sites with very high affinities. Then the slower processes consider the diffusion limited sorption to less favourable and accessible sites.

The affinity constants are constant with time in the P-Model; the model uses different affinity constants for the three-sorption processes K_{L_ads}, K_{L_abs}, and K_{L_fix}, respectively, for the rapid adsorption and for the relatively slow absorption and slow fixation. Thus, the relations between K_{L_ads}, K_{L_abs} and K_{L_fix} are:

$$K_{L\_ads} = K_{L\_soil} \qquad \text{eq. 4-10}$$

$$K_{L\_abs} = K_{L\_fix} = \beta K_{L\_soil} \qquad \text{eq. 4-11}$$

K_{L_soil}:	Affinity constant specific for the soil.
K_{L_ads}:	Affinity constant for adsorption [L $mmole^{-1}$].
K_{L_abs}:	Affinity constant for absorption [L $mmole^{-1}$].
K_{L_fix}:	Affinity constant for fixation [L $mmole^{-1}$].
β:	Constant.

The distribution between K_{L_ads}, K_{L_abs} and K_{L_fix} are estimated by fitting to sorption data from two agricultural soils in Denmark, see paragraphs 10.3.6 and 10.3.7. For the two subsoils the best fit was obtained by using the constant, $\beta = 0.5$. Hence, for the subsoils K_{L_abs} and K_{L_fix} should be approximately half the size of K_{L_ads}. For the two topsoil β varied and could not be fitted consistently, but ranged between 0.33 -0.5.

In modelling the fast DIP adsorption process in the Unreacted Shrinking Core-Model Van Riemsdijk et al. (1984) used the Langmuir isotherm with a constant affinity constant of 35 mM^{-1}. However, for another soil an affinity constant of 90 mM^{-1} was used (Van der Zee et al. 1989). It was attempted to parameterise the affinity constants to values in the range of 20-50 mM^{-1}, see paragraph 10.3.6-10.3.7. For the topsoil this also fits very well, but for the subsoils affinity constants seems to be a factor 10 larger than in the topsoils.

4.2 The kinetic approaches of DIP sorption

The condition at 'equilibrium' is described by Langmuir, estimating the amount of phosphate in solution at equilibrium, P_{sol_eq}, and the amount of phosphate adsorbed at equilibrium, P_{ads_eq}. However, the actual amount of phosphate in solution and adsorbed, P_{sol} and P_{ads}, respectively, are not necessary at equilibrium.

Considering the system of dissolved phase, adsorbed phase, and absorbed phase the ‘reaction rate constants’ k_1, k_2, k_3, k_4, k_5, and k_6 in eq. 4-12 – eq. 4-14 are constants. The exchange between the dissolved and the solid phases is related to pseudo-first order reactions as they only depend on the solute concentration.

$$M \equiv + P_{sol} \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_{ads} \qquad \text{eq. 4-12}$$

$$M \equiv + P_{sol} \underset{k_4}{\overset{k_3}{\rightleftarrows}} P_{abs} \qquad \text{eq. 4-13}$$

$$M \equiv + P_{sol} \underset{k_6}{\overset{k_5}{\rightleftarrows}} P_{fix} \qquad \text{eq. 4-14}$$

P_{sol}: DIP concentration [mmole L^{-1}].
P_{ads}: Adsorbed inorganic P [mmole kg^{-1}].
P_{abs}: Absorbed inorganic P [mmole kg^{-1}].
P_{fix}: Fixed inorganic P [mmole kg^{-1}].
k_1: Fast adsorption first order rate coefficient [$hour^{-1}$].
k_2: Fast desorption first order rate coefficient [$hour^{-1}$].
k_3: Relative slow absorption first order rate coefficient [$hour^{-1}$].
k_4: Relative slow desorption first order rate coefficient [$hour^{-1}$].
k_5: Slow fixation first order rate coefficient [$hour^{-1}$].
k_6: Very slow desorption first order rate coefficient [$hour^{-1}$].

The kinetics must be considered as an empirical, kinetic term linking the difference in concentration between equilibrium and actual conditions in the soil. Hence, as for DOM sorption, this kinetics incorporates in a very simplified view considerations as diffusion and sorption time into the description of the sorption/desorption processes, as it is not possible at the moment to incorporate the effects of pore geometry and particle surface availability in the model.

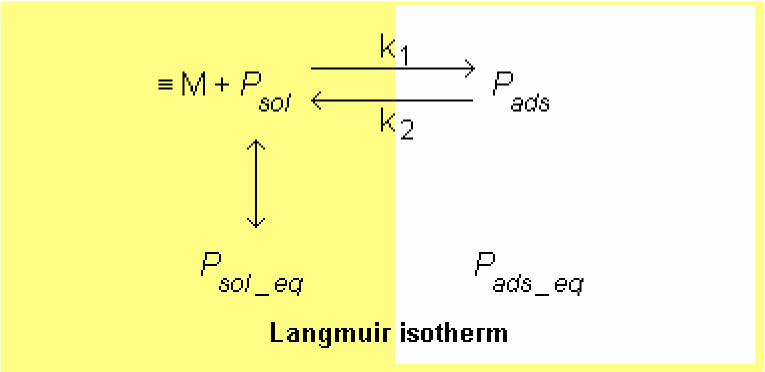


Figure 8. Schematic representation of the sorption kinetics coupled to the equilibrium given by the Langmuir isotherm.

The kinetics concept of the P-Model considers the sorption rates as proportional to the difference between the actual and the equilibrium concentration and sorption rate coefficients, Figure 8. The change of amount of sorbed P, dP_{ads}, dP_{abs}, *and* dP_{fix} are given by eq. 4-15 - eq. 4-17. First the change in adsorbed phase is calculated, then the change in absorbed phase and fixated phase, and at last the dissolved phase is given as the sum of change in the above mentioned phases.

$$\frac{dP_{ads}}{dt} = \begin{cases} -k_1(P_{sol} - P_{sol\_eq})\dfrac{V}{m}, & P_{sol} - P_{sol\_eq} > 0 \\ -k_2(P_{sol} - P_{sol\_eq})\dfrac{V}{m}, & P_{sol} - P_{sol\_eq} > 0 \end{cases} \qquad \text{eq. 4-15}$$

$$\frac{dP_{abs}}{dt} = \begin{cases} -k_3(P_{sol} - P_{sol\_eq})\frac{V}{m}, & P_{sol} - P_{sol\_eq} > 0 \\ -k_4(P_{sol} - P_{sol\_eq})\frac{V}{m}, & P_{sol} - P_{sol\_eq} > 0 \end{cases} \qquad \text{eq. 4-16}$$

$$\frac{dP_{fix}}{dt} = \begin{cases} -k_5(P_{sol} - P_{sol\_eq})\frac{V}{m}, & P_{sol} - P_{sol\_eq} > 0 \\ -k_6(P_{sol} - P_{sol\_eq})\frac{V}{m}, & P_{sol} - P_{sol\_eq} > 0 \end{cases} \qquad \text{eq. 4-17}$$

P_{sol_eq}: DIP concentration at equilibrium [mmole L^{-1}].
P_{sol}: Actual DIP concentration [mmole L^{-1}].
m: Soil mass [kg].
V: Volume of solute [L].
k_1,k_2, k_3, k_4, k_5, k_6: Rate constants [$hour^{-1}$].
$\frac{dP_{ads}}{dt}$, $\frac{dP_{abs}}{dt}$, and $\frac{dP_{fix}}{dt}$: Change of adsorbed, absorbed and fixated P with time [mmole kg^{-1} $hour^{-1}$].

The total change of DIP is thus the sum of the sorption processes:

$$\frac{dP_{sol}}{dt} = -\left(\frac{dP_{ads}}{dt} + \frac{dP_{abs}}{dt} + \frac{dP_{fix}}{dt}\right)\frac{m}{V} \qquad \text{eq. 4-18}$$

$\frac{dP_{sol}}{dt}$: Change of dissolved P with time [mmole L^{-1} $hour^{-1}$].

Depending on whether DIP concentration in soil solution is above or below the equilibrium concentration, the specific desorption or sorption rates are activated in the P-Model. For the relatively slow process of absorption the change in absorbed P with time can be expressed by including the term for the DIP concentration at equilibrium. When adsorption occurs, i.e. P_{sol} – P_{sol_eq} > 0, eq. 4-16 can be rearranged:

$$\frac{dP_{abs}}{dt} = -k_3(P_{sol} - P_{sol\_eq}) = -k_3\left(P_{sol} - \frac{P_{abs}}{K_{L\_abs}P_{\max\_abs} - P_{abs}K_{L\_abs}}\right) \qquad \text{eq. 4-19}$$

K_{L_abs}: Affinity constant for absorption [L $mmole^{-1}$].
P_{abs}: Absorbed phosphate [mmole kg^{-1}].
P_{max_abs}: Absorbed phosphate sorption capacity [mmole kg^{-1}].

The same considerations can be adopted for the adsorption and fixation processes. Hence, the P_{sol_eq} is not similar for the three sorption processes but depending on the affinity and capacity of the specific process.

The fast adsorption is considered to be instantaneously, thus achieving equilibrium immediately in the P-Model. As the time step in the P-Model is one hour, the process is characterised by the amount of P sorbed within an hour. The reaction rates of the relatively slow process are based on equilibrium within days. The reaction rate of the slow process is the best fit to the slope of the sorption data with time at high concentration levels. The relatively slow absorption process may achieve equilibrium within a couple of days. However, the slow fixation process may take years to reach equilibrium.

5 WATER AND SOLUTE TRANSPORT

In Daisy the soil water content is a function of numerous processes as soil water retention and water flow in the unsaturated zone, water flow in macropores, evaporation and extraction of soil water by roots. Hence, the settings in Daisy define how these are calculated. The standard settings describing water flow is by numeric solution of Richard's equation. For solute transport numeric solutions of the convection-dispersion equation is used; however for strong sorbing chemicals solute transport described by only convection may be acceptable as diffusion and dispersion contribute negligible to the transfer.

The P-Model imports the water content and water flux from Daisy to calculate the convective flux of soluble inorganic and organic P. The P-Model does not support macropore flow, which may under certain circumstances underestimate the leaching of P from the root zone.

5.1 Water transport

Water may be flowing in and out of the soil volume at different rates, causing the water content of the soil volume to change. Additionally, if plant roots are present inside the soil volume, some of the water will be removed from the volume by the plant. Calculating the mass balance for the system during an arbitrary small time period for one-dimensional vertical flux, derives the equation for water conservation (Jury et al., 1991):

$$\frac{\partial q}{\partial z} + \frac{\partial \theta}{\partial t} + S = 0 \qquad \textit{eq. 5-1}$$

θ: Volumetric soil water content [m^3 m^{-3}].
S: Volumetric sink term e.g. plant uptake [m^3 m^{-3} $hour^{-1}$].
t: Time [hour].

In unsaturated soil, the water phase is bounded partially by solid surfaces and partially by an interface with the air phase. In Daisy the matrix flow of water in the unsaturated zone is assumed to be Darcy flow and takes place in one dimension only. The positive direction of flow is assumed to be in the direction of decreasing gravitational potential.

For unsaturated soils the Buckingham-Darcy flux law may be expressed for vertical flow as (Jury et al., 1991):

$$q = -K(\psi)\frac{\partial H}{\partial z} = -K(\psi)\left(\frac{\partial}{\partial z}(\psi - z)\right) = -K(\psi)\left(\frac{\partial \psi}{\partial z} - 1\right) \qquad \textit{eq. 5-2}$$

q: Water flux [m^3 m^{-2} $hour^{-1}$].
$K(\psi)$: Hydraulic conductivity as a function of ψ [m^2 (m water)$^{-1}$ $hour^{-1}$].
H: Hydraulic potential ψ - z [m water].
ψ: Pressure potential [m water].
z: Distance in flow direction [m].

The hydraulic potential, H, is assumed to consist of the gravitational potential, z, and a pressure potential, ψ. For uniform wetting or drying processes the water capacity function, C_w, expresses the increase in pressure potential per unit increase in water content, eq. 5-3. Hence, the largest values of C_w are associated with the capillary region of the retention curve, where the largest pores are emptying with modest changes in suction.

$$C_w = \frac{\partial \theta}{\partial \psi} \qquad \text{eq. 5-3}$$

C_w: Water capacity [m water].

By combination of eq. 5-2, eq. 5-1, and eq. 5-3, Richard's equation is obtained in eq. 5-4 (Jury et al., 1991):

$$C_w(\psi)\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z}\left(K(\psi)\frac{\partial \psi}{\partial z} + 1\right) - S \qquad \text{eq. 5-4}$$

This is the pressure potential form of the Richard's equation which may be solved numerically if two boundary conditions and an initial condition are specified, and that $C_w(\theta)$ and $K(\psi)$ are known. Hence, $C_w(\psi)$ and $K(\psi)$ must be estimated for each numerical soil layer.

The upper limit of the amount of soil water by the soil, which can be transported to the soil surface during evaporation, is estimated by eq. 5-5:

$$q_0 = -\frac{K(\psi)}{C_w(\psi)}\frac{\partial \theta}{\partial z} \qquad \text{eq. 5-5}$$

q_0: Water flux at the soil surface [$m^3\ m^{-2}\ hour^{-1}$].

The gradient $\partial\theta / \partial z$ is estimated by assuming that $\theta = 0$ when $z = 0$.

5.1.1 Boundary conditions

The upper boundary condition depends on the state of the soil surface. Daisy operates with the following conditions:

1. A specified flux in or out of the soil surface is used when infiltration of water occurs at a rate that does not exceeds the infiltrability of the soil, or when evaporation from the soil surface takes place.
2. A specified potential at the soil surface is used when infiltration of water occurs at a rate that exceeds the infiltrability of the soil causing ponding on the surface.
3. A specified flux at a specified depth is used when Richard's equation is not solved for the whole profile, for instance when freezing and thawing takes place.

The lower boundary condition can be:

1. A specified potential at a specific depth for instance if the groundwater table is known or the position of tile drains.
2. A specified flux at a specific depth is used if free drainage is assumed.

5.2 Solute transport

At the scale of the soil pore, there are two transport mechanisms that can move solutes through the medium: convection and diffusion. Convection refers to the transport of a dissolved chemical by virtues of bulk movement of the water phase, and unless a compound is very volatile, this is the dominant mechanism by which it is transported through soil (Jury and Fluhler, 1992). The convection or mass flow of soil water carries with it a convective flux of solutes proportional to their concentration. Vertical solute transport by convection in one dimension is given by eq. 5-6:

$$J_X = q_w C_X \qquad \text{eq. 5-6}$$

J_X: Flux density of substance X [kg m^{-2} $hour^{-1}$].
q_w: Water flux [m^3 m^{-2} $hour^{-1}$].
C_X: Concentration of inorganic P or DOM in soil [kg m^{-3}].

However, solutes do not merely move with the water as inactive passengers but move with the flowing water in response to concentration gradients in the twin processes of diffusion and hydrodynamic dispersion. Diffusion processes are very important in the soil. Diffusion in the air phases of gasses as oxygen, carbon dioxide, and nitrogen (in the elemental, oxide, and ammonia form) as well as in water vapour, can have a decisive influence on the soil's chemical and biological processes. Equally important are diffusion processes involving solutes in the soil liquid phase, including nutrients along with potential harmful salts and toxic compounds that affect plant growth. If solutes are not distributed uniformly throughout a solution, concentration gradients inevitably exist. Consequently, solutes tend to diffuse from zones where their concentration is higher to where it is lower. In bulk water at rest, the rate of diffusion is related to the concentration gradient and the diffusion coefficient by Fick's first law, eq. 5-7:

$$J_{ld,X} = -D_X^l \frac{\partial C_X}{\partial z} \qquad \text{eq. 5-7}$$

$J_{ld,X}$: Liquid diffusion flux of substance X [kg m^{-2} $hour^{-1}$].
D^l_X: Liquid diffusion coefficient of substance X [m^{-2} $hour^{-1}$].
z: Distance in flow direction [m].

However, in soil water the liquid phase occupies only a fraction of the soil volume and the passages between soil pores are tortuous so that the actual path length of diffusion is significant greater than the apparent straight-line distance. Hydrodynamic dispersion is another motion of any inhomogeneous solution in a porous body; it results from the microscopic non-uniformity of flow velocity in the soil conduction pores. Because water moves faster through wide than through narrow pores and faster in the centre of each pores than along its walls, some portions of the flowing solution move ahead while other portions lag behind. Thus, the degree of dispersion is largely affected by the pore size distribution in the soil and the degree of saturation. The solute hydrodynamic dispersion flux has a form that is mathematically identical to the diffusion flux. Hence, the total solute convection is describes by (Jury et al., 1991):

$$J_X = q_w C_X + J_{lh,X} = q_w C_X - D_X^{lh} \frac{\partial C_X}{\partial z} \qquad \text{eq. 5-8}$$

$J_{lh,X}$: hydrodynamic dispersion flux of substance X [kg m^{-2} $hour^{-1}$].
D^{lh}_X: Liquid hydrodynamic dispersion coefficient of substance X [m^{-2} $hour^{-1}$].

The total flux of dissolved solute X is then;

$$J_X = q_w C_X - D_X^{lh} \frac{\partial C_X}{\partial z} - D_X^l \frac{\partial C_X}{\partial z} \qquad \text{eq. 5-9}$$

which is commonly written as:

$$J_X = q_w C_X - D^*_X \frac{\partial C_X}{\partial z}$$ eq. 5-10

D^*_X: Effective liquid diffusion-dispersion coefficient of substance X [m^{-2} $hour^{-1}$].

Unless water is flowing very slowly through homogeneous soil, D^*_X, is normally dominated by the hydrodynamic dispersion term (Jury et al., 1991).

The solute conservation equation in one dimension is given by eq. 5-11:

$$\frac{\partial J_X}{\partial z} + \frac{\partial C_X}{\partial t} + S_X = 0$$ eq. 5-11

S_X: Sink-source of substance X. Reaction rate per volume [kg m^{-2} $hour^{-1}$].
J_X : Flux density of substance X [kg m^{-2} $hour^{-1}$].
C_X : Concentration of inorganic P or DOM in soil [kg m^{-3}].
t : Time [hour].

Combining eq. 5-10 and eq. 5-11 the convection-dispersion equation may be written as:

$$\frac{\partial (A_X + \theta C_X)}{\partial t} = -\frac{\partial}{\partial z}\left(q_w C_X - D^*_X \frac{\partial C_X}{\partial z} \right) - S_X$$ eq. 5-12

A_X: adsorbed amount of substance X [kg m^{-3}].
q_w: Water flux [m^3 m^{-2} $hour^{-1}$].
θ : Volumetric soil water content [m^3 m^{-3}].

The source sink term, S_X, describe the net rate of solute X from for instance mineralization, immobilisation, denitrification and crop uptake. The convection-dispersion equation must be solved numerically.

In Daisy one-dimensional transport of NH_4^+ and NO_3^- and DOM may take place as a result of diffusion, dispersion, and convection. Hence, during transfer of DOC and DON, the adsorption term in eq. 5-12 is calculated as previously described in section 3 when DOM is transported by the convection-dispersion equation. In the P-Model, inorganic P and DOM are transported by convection only. Hence it is out of scope in this model to solve the convection-dispersion equation, which is necessary if diffusion and dispersion is considered.

However, the retardation of inorganic P in soil is high due to sorption. Hence, according to eq. 5-12 relatively small changes in solution concentration are expected for strong sorbing substances, limiting the effect of diffusion and dispersion. Additionally, large molecules as DOM will diffuse more slowly than small molecules as NH_4^+ and NO_3^-. Thus, in the P-Model the vertical solute transport of soluble inorganic and organic P is calculated by convection, which is described by eq. 5-6. The water flux, q_W, is calculated by Daisy and given as input parameter for every numerical layer in the P-Model.

5.2.1 Boundary conditions

The upper boundary in Daisy is always a flux condition, which may be a zero flux or a positive flux. If any input of solute X is dissolved in the precipitate the boundary will be a positive flux.

At the lower boundary in Daisy, it is assumed that the concentration gradient is equal to zero at the bottom of the soil column.

6 CROPS

The P requirement for optimal growth is in the range of 0.3-0.5 % of the plant dry matter during the vegetative stage of growth (Marschner, 1995). P is present in all cells as parts of their nucleic acid and lipid material, and in some carbohydrate and related components. In addition to genetic nucleic acid, P is important in the processes of energy storage and transfer. Photosynthetic phosphorylation produce energy-rich compounds, a major one being adenosine triphosphate (ATP) from which many other energy-rich compounds may be derived (Halstead and McKercher, 1975).

Rhizosphere studies of association between roots, soil, and soil solution generally consider that crops are able to absorb HPO_4^{2-} and $H_2PO_4^-$. Also, there is good evidence that soil organic phosphorus compounds may support some plants. Enzymes in soils and on roots and excreted by many soil organisms are able to facilitate the hydrolysis of organic phosphates to inorganic phosphates. If these reactions occur in intimate association with the plant roots, the plant feeding may occur before immobilization by sorption (Halstead and McKercher, 1975). However, it has never been fully resolved whether organic P must be mineralized before plant uptake.

Generally, mass flow contributes only a small proportion of the P uptake. Depletion of P in solution due to root uptake is mainly controlled by the amount and rate of diffusion in the soil solution. This depletion generates a concentration gradient toward the root (Wang et al., 2004). The P depleted solution is immediately replenished from sorbed pools of inorganic P, which are relatively labile or moderate labile pools (Stewart and Sharpley, 1987).

In the P-Model crops are defined as very simple sink terms where the removal of soluble inorganic P from the soil solution by root uptake is coupled to the N uptake.

6.1 Crop N uptake

In Daisy the crop will continue to take up N from the soil solution until an upper limit of the N content in the crop dry matter is reached. If N supply is extremely low the N content in the dry matter is assumed to reach a lower limit below which the crop ceases functioning. Each part of the crop defined in Daisy (top, roots, and storage organs) is characterised by these limits for N content in the dry matter content. Furthermore, these limits vary with the development stage of the crop.

6.2 Crop P uptake

The P-model correlates the P uptake with the N uptake, which is calculated by Daisy. The P uptake is correlated with N uptake by a defined N:P ratio which may be crop specific. However, the crop N:P ratio is, at this stage, parameterised to $N{:}P_{crop} = 8$. Norms for crop N:P ratios of fresh crops as animal foodstuff are listed in Table 3.

The inorganic P supply for root uptake mainly occurs from the solution phase. If the solution phase can’t provide enough P the adsorbed phase deliver the rest. However, according to stability in the calculations only 2/3 of the actual P content in the solution phase may be removed by root uptake in a time step.

Table 3. Animal foodstuff of fresh total crops. (Landbrugets Rådgivningscenter, 2001).

	Dry matter (DM) %	protein %	N g N /kg DM	P g P / kg DM	N/P mass ratio
Italian rye-grass	19	21	33.6	4.3	8
Grass	19	21	33.6	3.4	10
Pasture grass	18	20	32	4	8
White clover, flowering	13	25	40	4	10
Red clover, flowering	15	17	27.2	3	9
Barley	35	11	16.8	2.5	7
Oat	25	13	20.8	3	7
Rye, green	16	14	22.4	3.3	7
Maize	23	10	16	3	5

6.3 Dead plant residues and root exudes

In Daisy root exudes and dead plant residues (leaf) enters the soil systems by the AOM pools, which is characterised by C:N ratios, see paragraph. In the P-Model the content of P in these AOM pools is determined by the crop N:P ratio.

6.4 Harvest

The P-model correlates the harvest of crop P with the harvest of crop N, which is calculated by Daisy. The harvest of crop P is also correlated with harvest of crop N by the crop N:P ratio.

7 SYSTEM AND MODEL STRUCTURE OF DAISY-P

The Daisy-P model is composed of the Daisy code and a stand-alone code, the P-model. Hence, the stand-alone code is considered as a prototype for a future implemented code in Daisy. The objective of the Daisy-P model is to model mobilization and immobilization processes of inorganic and organic dissolved phosphorus at field scale. Hence, the future goal is to use Daisy as a tool to recognize potential risk areas for dissolved P loss and quantify the amount P leached with different management strategies. To construct the model, the soil system is schematized in order to recognize relevant system variables.

7.1 Daisy a Soil-Plant-Atmosphere system model

Before executing the P-model the Daisy model has to be set-up and calibrated. Daisy is a Soil-Plant-Atmosphere system model designed to simulate water balance, heat balance, solute balance and crop production in agro-ecosystems subjected to various management strategies. The water balance model comprises a surface water balance and a soil water balance. The surface water includes a model for snow accumulation and melting, a model for interception, throughfall, evaporation of water in the crop canopy, and a model for infiltration and surface run-off. The soil water balance includes water flow in the soil matrix as well as in macropores. Furthermore, it includes water uptake by plants and drainage to pipe drain. The heat balance model describes soil temperature and freezing and melting in the soil. The solute balance model describes transport, sorption and transformation processes. Special emphasis is put on nitrogen dynamics in agro-ecosystems where mineralization-immobilization, nitrification and denitrification, sorption of ammonium, uptake of nitrate and ammonium, and leaching of nitrate and ammonium are simulated. The crop production model simulates plant growth and development, including accumulation of dry matter and nitrogen in different plant parts. Furthermore, the development of leaf area index and distribution of root density are included. Competition for light, water and nitrogen between plant species are also simulated (Hansen, 2002).

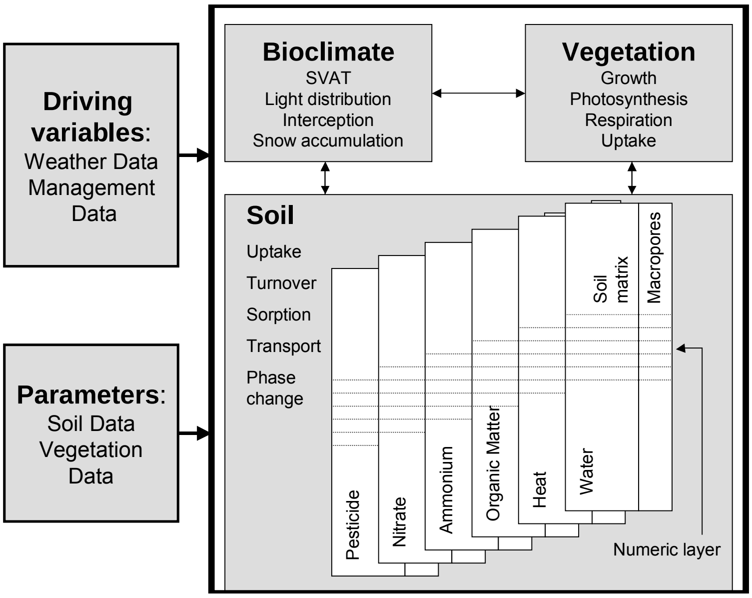


Figure 9. Schematic representation of the agro-ecosystem model Daisy. The model comprises three main modules, a bio climate, vegetation, and a soil component (Hansen, 2002).

A basic assumption in Daisy is that a one-dimensional model can represent the modelled system, which in Daisy constitutes the soil plant system with the atmosphere and groundwater level constituting the system environment. The vegetation system is characterized by a number of processes as crop growth, photosynthesis, respiration and uptake, and of main system variables as dry matter contents and nitrogen contents of shoots, storage organs, roots, and leafs. The soil system refers to the unsaturated zone, and is characterized by a number of processes i.e. organic matter decomposition, water and solute transport, and sorption. It also contains main system variables as soil water content, soil temperature, soil nitrate and ammonium content, pesticides, and soil organic matter content with respect to C and N, Figure 9. The state of the system variables in Daisy changes due to the influences of a number of processes, which take place within the system. These processes include transformation and transport processes involving heat, water, carbon, and nitrogen, which are influenced by the weather variables as precipitation, air temperature, deposition and global radiation.

7.2 The P-Model

The P-Model system is part of the soil plant system of Daisy, where Daisy output data define the changing soil plant environment, affecting the processes. The model comprises two main modules, a simple crop component and a soil component, Figure 10. The crop (or vegetation) system is characterized as a source and sinks term. It removes inorganic P and N from the soil system and supplies the soil system with exudes from the roots and dead organic residues. The main system variables of the crop system are the total crop content of C, P, and N. The soil system defined refers to the unsaturated zone, and is characterized by a number of processes i.e. organic matter decomposition, solute transport by convection, and sorption and desorption. It also contains main system variables as soil and dissolved organic matter content with respect to C, N, and P, and dissolved inorganic P content.

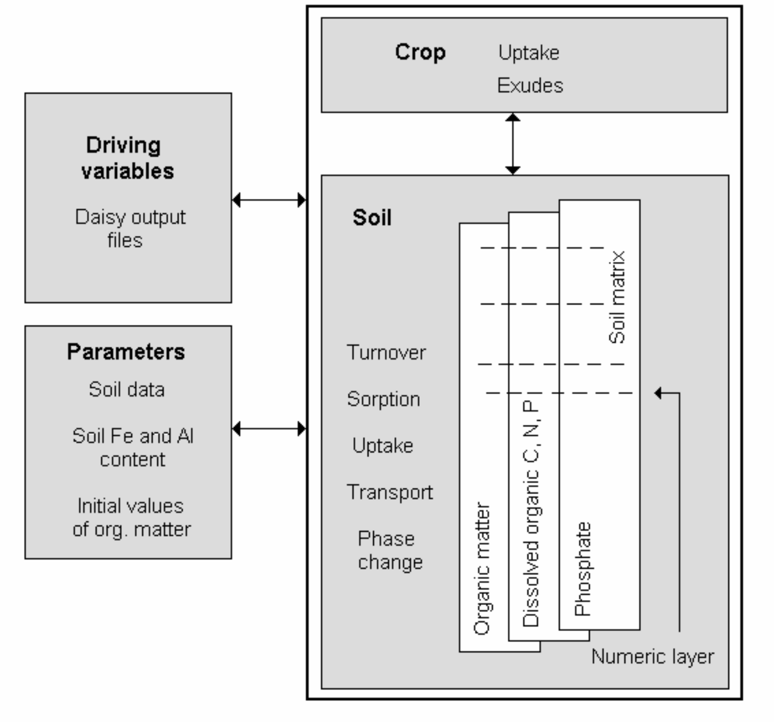


Figure 10. Schematic representation of the ecosystem in the P-Model.

Figure 11, shows the P-Model system in more details, illustrating the relationship between the processes and the state variables. The main processes are the immobilization, mineralization, sorption, and desorption of DIP and DOM.

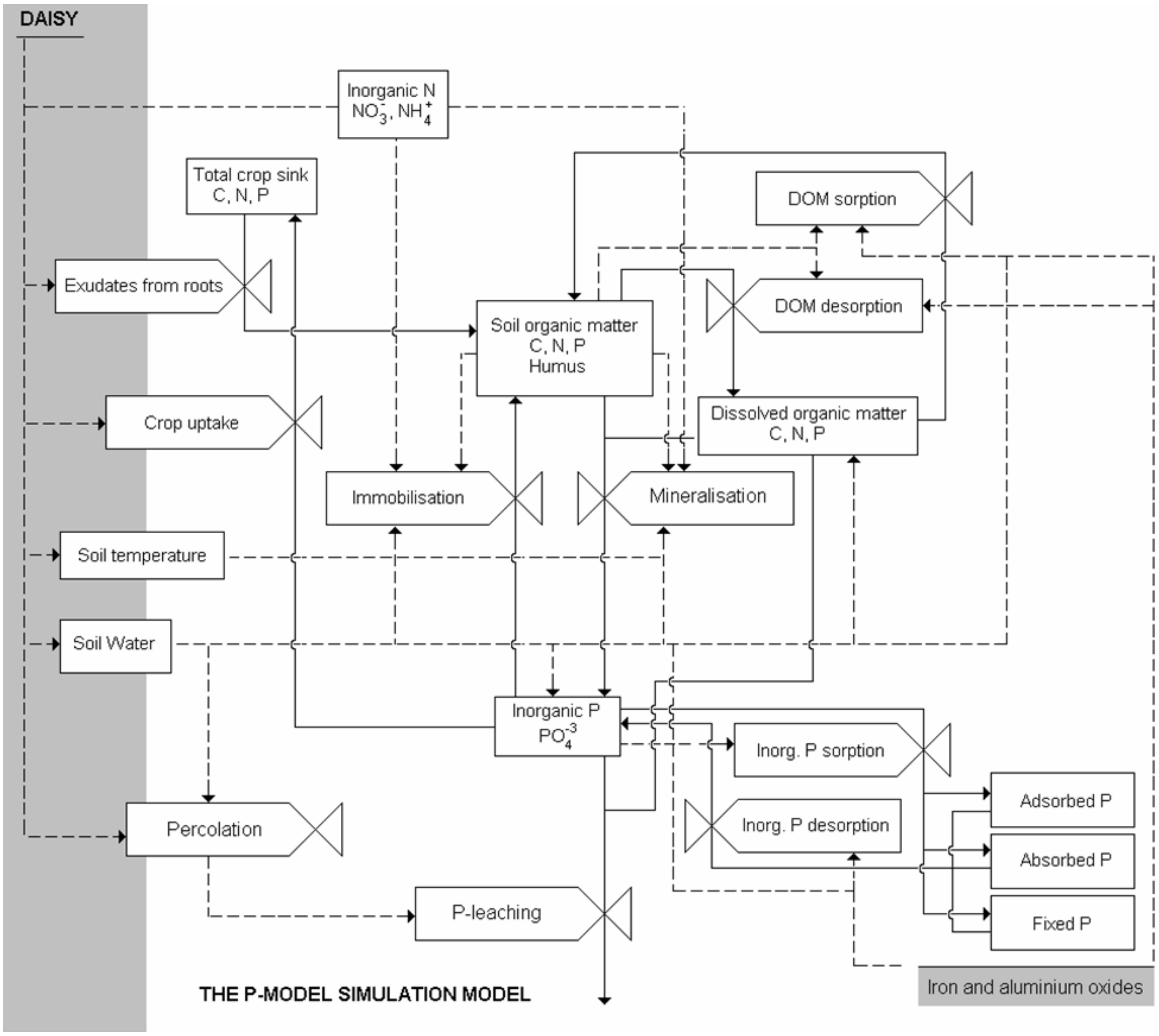


Figure 11. *Relational diagram of the P-model receiving its driving variables from Daisy. Rectangles represent system state variables, while valve symbols represents processes. Solid lines represent flows of matter while broken lines represent flows of information.*

The concept of the turnover of organic matter is based on the concept of the organic matter module in Daisy, where it is assumed that the activity of soil microbial biomass is affected by the substrate availability; and that it is reasonable to relate the N mineralization and immobilization with decomposition of C. The P-Model includes P in the organic matter module and, like N, it seems reasonable to relate P mineralization and immobilization with decomposition of C.

In the P-Model crops are defined as very simple sink terms where the removal of DIP from the soil solution by root P uptake is coupled to the N uptake by a specific N:P-ratio which may be plant specific. The crops only take up phosphate from the soil solution if present. The root exudes, plant residues and the crop P content removed by harvest is defined by the actual N:P-ratio of the crop. The crops in the system act as sink of dissolved inorganic P, which affects the three sorbed pools of inorganic P fractions. The inorganic P may be immobilized by sorption, incorporated to the soil organic matter fraction by the soil microbial biomass or taken up by crops. It may be mobilized by desorption, mineralization and transported further down the profile by convection. The inorganic P sorption module is based on the concept of a three step mechanism: 1) A fast sorption mechanism, and, 2) a relative slow absorption mechanism, plus 3) a very slow fixation process. Thus, its is assumed that DIP first binds to easily available sorption sites with high affinity and then the less available sites which is limited by diffusion and further migration into the soil particle to sorption sites less available.

The P-Model uses the organic matter decomposition process as a source of dissolved organic phosphorus, which may be immobilized by sorption, further degraded, mineralized to phosphate, or mobilized further down the profile by convection. It is recognized that not all-significant aspects are fully described at this stage, for instance the effect of pH, electrolyte concentration and species, and temperature on the sorption processes. However, the basic processes considering dissolved P fractions in agricultural fields are integrated, which hopefully is further developed by future studies.

7.3 General data flow

The Daisy model requires a number of input data and a weather file, and after simulation of a simulation it generates a set of output data files, Figure 12. Weather data are used as driving variables. The minimum data requirement is daily values of global radiation, air temperature and precipitation. The Daisy model deliver the driving variables of water and solute transport and to the organic matter decomposition process to the P-Model, such as water flux data, temperature data, water pressure potentials, and water content data in each numeric layer defined in the profile. Daisy also delivers the initial values of the organic matter pools with respect to C and N content.

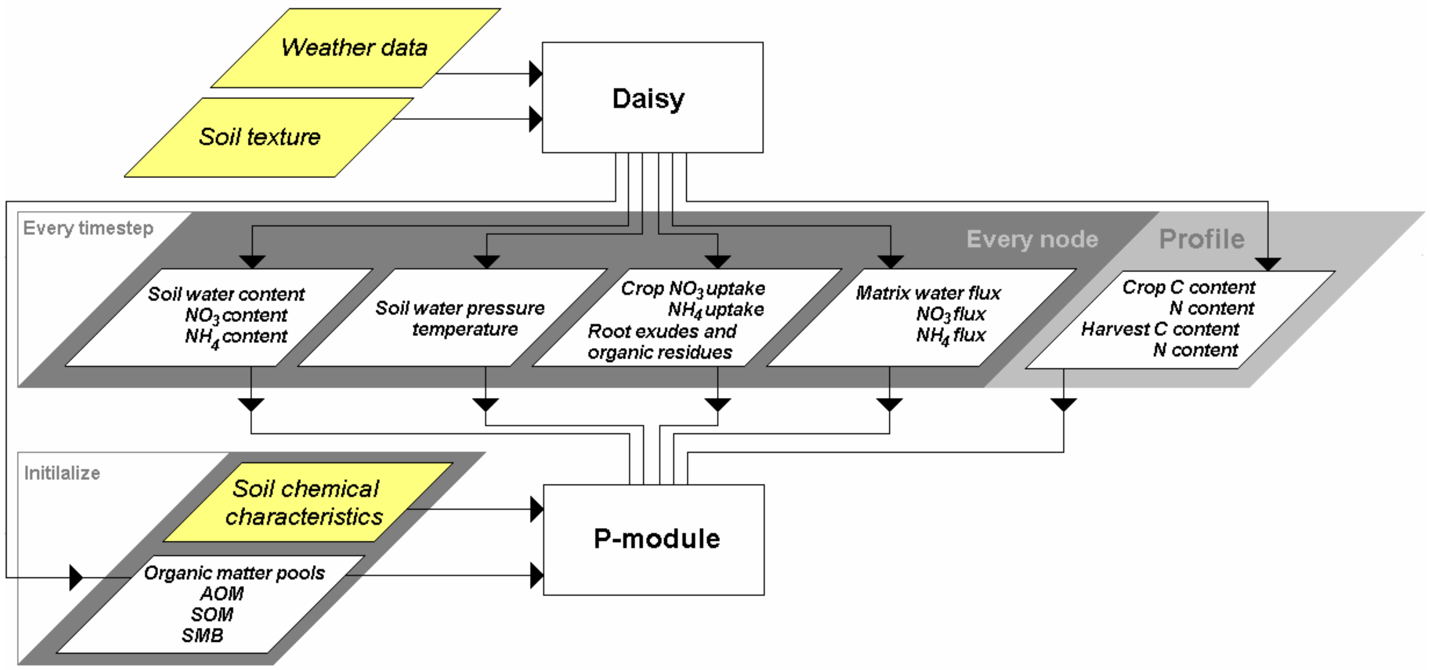


Figure 12. Flow chart of the input and output data of Daisy and the P-module.

Besides output data from the Daisy simulation, the P-Model requires a number of soil chemical characteristics as input data for the sorption modules. A spreadsheet works as the interface for all the information the P-Model needs before executing a simulation. This is further explained in the section, *User Manual*.

7.3.1 The main program

The computer program is written in C++ using Microsoft Visual C++, version 6.0. The main program calls every node defined in the set up and steps it trough for every time step (1 hour), until the time is equivalent to the end of simulation time, Figure 13. For every 24 hours output is logged.

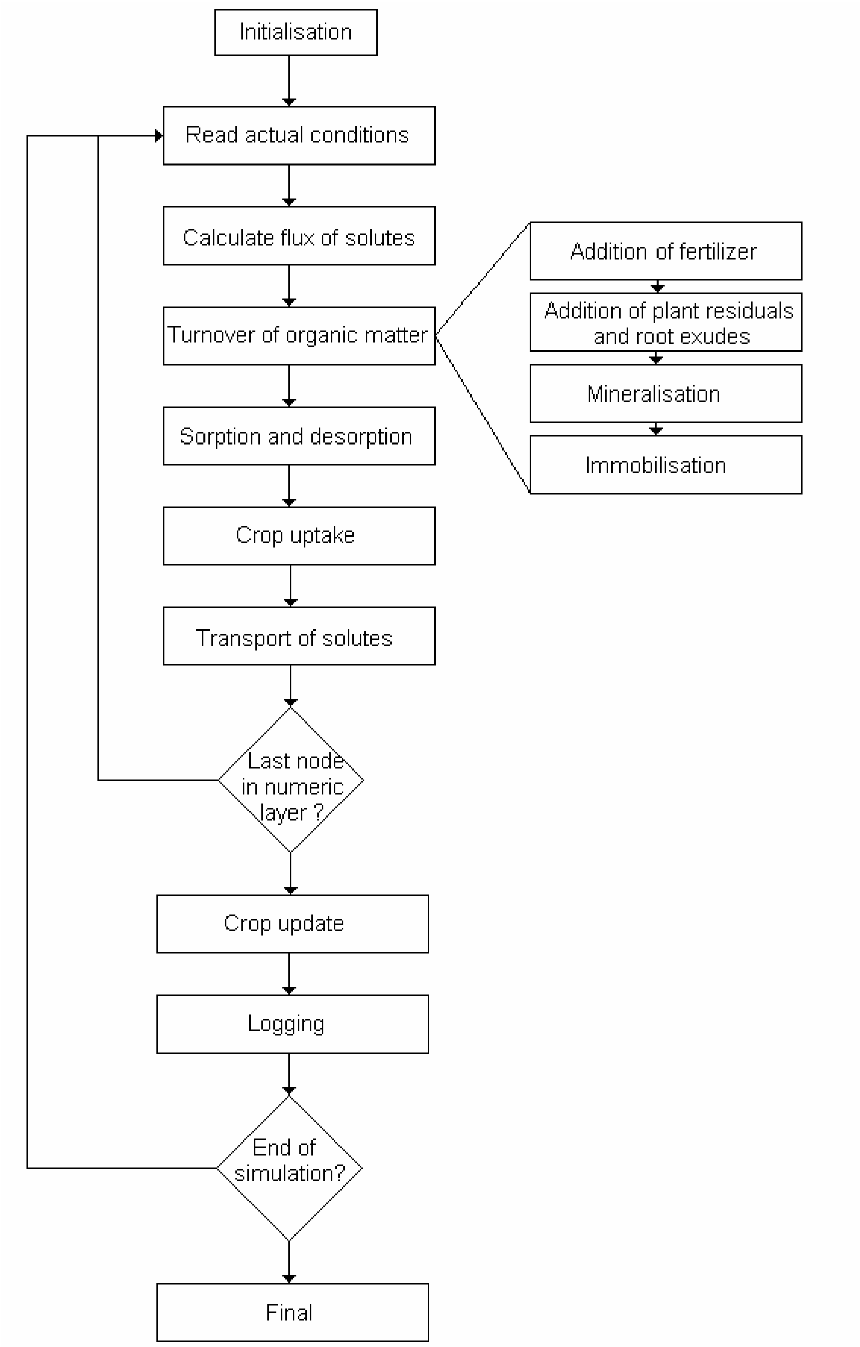


Figure 13. Conceptual illustrating the items called by the main program.

8 USER MANUAL

The Daisy-P-Model is composed of the Daisy model and a stand-alone model, the P-model. Before executing the P-model the Daisy model has to be set-up and calibrated with respect to boundary conditions of water level, nitrate loss by leaching, crop production and input of organic manure or inorganic N fertilizer. To run the P-Model some limitations occur in the Daisy set-up which include: 1) macropore transport and bio-incorporation by earthworms must be turned off, 2) no ploughing, rotovation, or harrowing must occur in the simulation, 3) a DOM pool must be defined in the organic matter module. 4) Except for the flow fractions between the organic pools (SOM and SMB) and the definition of DOM pool, default values must be used in the organic matter module, and 5) DOM transport must be described with convection only. 6) Parameterisation of dead plant material must be standardized in relation to the C:N-ratios and turnover rates of $AOM_{residual}$ and AOM_{root} defined in the P-model.

The limitations in the Daisy set up will be further explained in the following paragraphs, where the basic framework of a Daisy *.dai file as input to the P-Model is illustrated. Further information of the setup of Daisy can be found in the *Daisy tutorial* and the *Daisy Reference Manual* which can be downloaded from the Daisy homepage http://www.dina.kvl.dk/~daisy/. At the homepage also installation of the Daisy model is described. The following user manual is aimed at users already familiar with Daisy.

8.1 Installation and running the P-Model

A number of *.exe files are included in the CD as different versions of the P-Model. To be executed successfully the exe-file must be located in a directory named Daisy-P placed in the root of C. Thus, it is suggested that the content of the CD is copied to this folder “C:\Daisy-P\”. Then the exe-files are executed correctly.

8.1.1 Daisy-P.exe

The version called Daisy-P includes the total version of the P-model described. Thus, it includes inorganic and organic P transport and sorption processes, organic matter turnover including DOM decomposition and mineralization as well as crop P uptake.

8.1.2 Check-setup.exe

The version called Check-setup is a minor and faster version that turns off sorption processes and may be used for checking that the set-up is correct. The sorption processes also affect the organic matter dynamics so the output from the Check-setup.exe cannot be compared to any measurements or other simulations. However, the 'reading' of the input files by the P-Model takes time also in this version. To save time it may be feasible to run a short (one year) Daisy simulation during the set-up test, which will reduce the time of 'reading'.

8.2 Input data

Besides output data from the Daisy simulation, the P-Model requires a number of soil chemical characteristics as input data for the sorption modules. A spreadsheet works as the interface for all the information the P-Model needs, which include:

1) The file names and paths for the location of in- and output files.

2) Conversion of input files to the P-Model from Daisy log files. For every time step and every node, input data are transferred from Daisy log files to the P-Model. This is done for driving

variables as soil water pressure, water content, water flux, NO_3 and NH_4 flux, crop root uptake of NO_3 and NH_4, soil temperature, root exudes or dead plant material as organic C and N. Additionally, parameters necessary to estimate mass balances (crop C and N content, harvested C and N) are transferred from Daisy log files to the P-Model every time step.

3) The simulation time and number of nodes in each horizon, which must match the Daisy setup.

4) Soil chemical properties for the P-Model which include oxalate and citrate-dithionite-bicarbonate extractable Fe and Al content as well as the oxalate extractable P and humus content in the horizons.

5) Definition of inorganic fertilizer must include the fraction of NO_3-N, NH_4-N, and PO_4-P. Organic fertilizer must be defined with respect to C:N:P-ratios, fraction of inorganic P and N of total P and N, decay rates and flow fraction to the AOM1 and AOM2 pools. The setting must match the settings of the added fertiliser in Daisy. Standard fertiliser is defined in the Daisy library file *fertiliser.dai*.

8.2.1 Setup a *.dai file for the Daisy model

Initialisation and parameterisation of Daisy is done in a special set up file. The input system allows for storing full or partial parameterisations of selected process models in separate library files. The information stored in the library file is included in the set-up by a simple reference to the library file (Abrahamsen and Hansen, 2000). E.g., this facility is used for storing crop parameterisations in a crop library, and by including the crop library or crop libraries the various crop parameterisations are available just by referring to the name under which the parameterisation is stored. Similarly, soil information required to parameterise a soil horizon can be stored in a soil horizon library and referred to by name. Furthermore, the input system allows for the allocation of default values to model parameters. This facility is applied to allocate default values to model parameters whenever it is feasible. Parameters, which are not given a specific value, need not appear in the input files (Hansen, 2002).

Setting up a Daisy *.dai file is demonstrated in Textbox 1, where the style of defining file locations and working directories are shown together with parameterisation of the different modules. Text behind a semicolon, “;”, until end of line is ignored by the input system; hence, explaining comments are allowed behind semicolon. In this set up, the included input files are located in the specified directories. At least the path referring to the standard libraries must be specified, e.g. “C:/Program Files/Daisy/daisy-lib“. However, modified libraries may be located in a personal folder, located in e.g. “C:/My Documents/Daisy/“. Only the file “P-Model_log.dai” refereed here is not a standard directory in Daisy, but contains the style of output files so the spreadsheet, “Daisy-P.xls”, can convert Daisy output files to input files of the P-Model. The file, “P-Model_log.dai”, is located in the CD and must be added to the directory "C:/Daisy-P /settings for Daisy-P" which is specified in the *.dai file.

The weather file is an input file for Daisy. The file must contain daily data of precipitation, air temperature, and global radiation for the investigated area. How this file must be set up is described in the *Daisy Tutorial*.

In order to translate the data from the Daisy log files to input files of the P-Model through the spreadsheet, it is important that the description in Daisy log files fills exactly three. The description is written in the top of the Daisy log files so it is feasible to make a note of the location, model settings and source of data.

All the horizons in the profile must be defined according to texture and hydraulic properties. In Textbox 1 a horizon called Ap_Buhr is defined where the hydraulic settings are defined according to "hypres". The hypres function calculates the parameters for the van Genuchten retention curve model with Mualem theory. However, other hydraulic settings are allowed together with the P-Model. Daisy also allows parameterisations of the SOM pools in each horizon, with respect to C/N-ratio and flow fractions. However, as mentioned in the beginning of this section, these conditions must not be specified together with the present P-Model.

*Textbox 1. Setup a Daisy *.dai file for further simulation in the Daisy-P-model*

```
;;;;;;;;;;;;; Daisy *.dai file ;;;;;;;;;;;;;;;;;;;

;;  Setting the working directory.  If the working directory is set correctly the log-file will be found here:
(directory " C:/Daisy-P/Sim/")                    ; Location of Daisy log files after simulation
;;  Setting search path for library-files:
(path "." "C:/Program Files/Daisy/daisy-lib"      ; Location of standard Daisy input files
          " C:/Daisy-P /settings for Daisy-P")    ; location for P-Model input files

;; Standard parameterization:
(input file "log.dai")
(input file "fertilizer.dai")
(input file "tillage.dai")
(input file "crop.dai")                           ; Standard *.dai files defined in Daisy

(input file "DOM_sorp.dai")                       ; Definition of the DOM sorption.
(input file "P-Model_fertilizer.dai")             ; Definition of  fertiliser for the P-Model
(input file "P-Model_log.dai")                    ; Log form defined for further simulation of the P-Model

;;Weather data.                                   ; Path and filename of the weather file.
(weather default "C:/Daisy-P /settings for Daisy-P/weather.dwf")

;; Description
(description                                      ; Description must fill 3 lines, otherwise data is not transfer-
"*.dai file.                                      ; red correctly.
Test of ….
…soil.")

;; Horizons in profile                            ; Do not define any C/N ratios in defhorizon!
(defhorizon Ap_Burh default
 (clay 12.6)
 (silt 11.4)
 (coarse_sand 23.57)
 (fine_sand 52.43)                                ; Sum of clay, silt, coarse_sand and fine_sand must be 100
 (humus 4.243)                                    ; Used for initialising the SOM and SMB pools.
 (dry_bulk_density 1.72)                          ; The dry bulk density must be specified
 (hydraulic hypres))                              ; Hydraulic parameters. Hypres is optional!
```

The soil component must be loaded with all the defined horizons in the profile, however max 5 horizons may be defined. The number of nodes is optional, as long as nodes are equally distributed in each horizon having the same distance between each numeric layer. But that does not mean that the same distance must proceed in the whole profile. The top horizon may have 5 cm between the nodes and a sub horizon may have 10 cm between the nodes.

The P-Model does not consider processes as nitrification and denitrification in soil, thus the content of the inorganic fractions of N, NO_3 and NH_4, in the soil are overwritten in each time-step. Hence, the P-Model just use the values calculated by Daisy. Therefore the settings of nitrification, denitrification, NO_3, and NH_4 are up to the user. Also the heat transport is not considered in the P-Model, so the setting of soil heat is also up to the user. The matrix water flow is defined in Daisy and may be described by Richard’s equation. The matrix water flux is used in the P-Model to calculate the matrix flux of PO_4 and DOP. No macropore flow is considered in the P-Model; therefore the macropore flow must be turned off in the soil water component. The lover boundary of the groundwater must be specified as deep in Daisy, as the P-Model can not consider other boundaries.

The organic matter component in Daisy must be set up specifically for the P-Model. Incorporation of organic matter by earthworms must be turned off. The initial incorporated amount of AOM present in the soil must be defined according to default settings of the added matter ‘am’ component. The default settings of ‘am’ state that the AOM1 pool contains 80 % of total C allocated to the AOM pools, and have a C/N ration of 90. Only the SMB2 degrade AOM1, with a turnover rate of 0.000204 hour^{-1} and an efficiency of 50 % meaning that half is mineralised to CO_2, the rest is immobilized into SMB2. The AOM2 pool contains the rest, 20 % of total C allocated to the AOM pools. The AOM2 pool has a variable C/N ratio. Only SMB2 degrades AOM2 with a turnover rate of 0.00204 hour^{-1}and an efficiency of 50 %.

In Daisy numerous pools of AOM may be defined according to different additions of organic matter. When the AOM pools become small due to degradation Daisy puts them together. However, by specifying (min_AM_C 0.0) and (min_AM_N 0.0) this is prevented. The SOM pools use default settings except for the flow fractions to the DOM pool. The DOM pool does not have default settings and must therefore be defined by the flow fractions from the SOM2 and the SMB pools. The flow fractions state that the SOM1 pool is decomposed only by the SMB1. The SOM2 pool is decomposed by the SMB2 (0.65), and a fraction is allocated to the SOM1 pool (0.30). The rest (0.05) is allocated to the DOM pool. The SOM3 pool is inert. The parameter for the DOM pool is also specified in the Textbox. The initial amount of C and N in DOM are optional values for the P-Model. DOM is decomposed by the SMB2 pool with a turnover rate of 0.0015 hour^{-1} and an efficiency of 50 %. Transport of DOM must be by convection for the P-Model; hence the diffusion coefficient is not used, but must be assigned a value. The DOM sorption is calculated by the "DOM_sorp" module, which is defined in the input file "DOM_sorp.dai".

*Textbox 1 continue. Setup a Daisy *.dai file for further simulation in the Daisy-P-model*

```
;; Use this column:
 (defcolumn Burh default
  (Bioclimate default)
  (Groundwater deep)                              ; Only deep groundwater settings
  (Soil          (horizons  (-30 Ap_Buhr))        ; Number of horizons here = 1. Max 5 horizons!
                 (zplus -5 -10 -15 -20 -25 -30)   ; Number of  nodes defined here  =  6. For every horizon
                                                  ; defined, the nodes must be spread with equal distance.
                 (MaxRootingDepth 30))            ; Max depth of root must not exceed the lowest node.
  (Nitrification soil)                            ; Nitrification settings are up to the user
  (Denitrification)                               ; Denitrification settings are up to the user
  (SoilNH4 )
  (SoilNO3 )
  (SoilWater     (macro none)                     ; No macropore transport!
                 (UZtop richards))                ; Richards is optional!
  (SoilHeat)
  (OrganicMatter  (active_underground true)              ; Decomposition and mineralization and below the
                 (active_groundwater true)               ; root zone and the ground water level turned on.
                 (Bioincorporation
                    (R_max 0))                           ; No incorporation of org. matter by earthworms
                 (min_AM_C 0.0)                          ; AOM pools not mixed before empty
                 (min_AM_N 0.0)
                 (am)                                    ; Default settings of AOM already present.
                 (smb                                    ; Definition of SMB. Default setting except for the
                    ((fractions 0 0.6 0 0.35 0 0.05))    ; flow fractions to SMB1, SMB2, SOM1, SOM2,
                    ((fractions 0 0.35 0 0.6 0 0.05)))   ; SOM3 and DOM, respectively.
                 (som                                    ; Definition of SOM.
                    ((fractions 1 0 0 0 0 0))            ; Flow fractions to SOM1, SOM2, SOM3, SMB1,
                    ((fractions 0.65 0 0.3 0 0 0.05))    ; SMB2, and DOM, respectively
                    ((fractions 0 0 0 0 1 0)))
                 (dom                                    ; Definition of DOM. No default setting defined!
                    ((C (M 0.0 [g/cm^3]))                ; Initial amount of DOM-C and DOM-N. Optional
                     (N (M 0.0 [g/cm^3]))
                     (fractions 0 1)                     ; DOM is only decomposed by SMB2
                     (efficiency 0.0 0.5)                ; Efficiency of SMB2 pool. 50 % goes to CO2.
                     (turnover_rate 1.5e-3)              ; The turnover rate equals  1.5 10^-3 per hour
                     (adsorption none)                   ; This parameter is not used in this set up.
                     (diffusion_coefficient 6.75e-6 [cm^2/s])  ; Not used by convective transport
                     (transport convection))))           ; Transport by convection
                 (domsorp DOM_sorp)                      ; Dom sorption defined by the DOM_sorp module

;;Use this column:
(column Burh)
```

The crop component contains many sub models in Daisy e.g. the canopy, N uptake, photosynthesis, and harvest, which are specific for each crop type. In order to make the organic matter that is incorporated into the soil similar for all crops, the harvest modules must be overwritten according to the definitions of My_Crop in Textbox 1. The defaction component defines the management activity, when sowing, fertilizing, or harvesting occurs. It is important that no ploughing occur, otherwise the background mineralization does not match.

*Textbox 1 continue. Setup a Daisy *.dai file for further simulation in the Daisy-P-model.*

```
;; Definition of crops
(defcrop "My_Crop" Crop_module                          ; Any crop defined in the crop.dai file
 (Harvest                                               ; The 'Harvest' module must be overwritten
    (Dead        ((initial_fraction 0.80) (C_per_N 90.0)
                  (efficiency 0 0.5) (turnover_rate 2.0e-4) (fractions 0 1 0))
                 ((efficiency 0 0.5) (turnover_rate 2.0e-3) (fractions 0 1 0)))
   (Stem         ((initial_fraction 0.80) (C_per_N 90.0)
                  (efficiency 0 0.5) (turnover_rate 2.0e-4) (fractions 0 1 0))
                 ((efficiency 0 0.5) (turnover_rate 2.0e-3) (fractions 0 1 0)))
   (Leaf         ((initial_fraction 0.80) (C_per_N 90.0)
                   (efficiency 0 0.5) (turnover_rate 2.0e-4) (fractions 0 1 0))
                  ((efficiency 0 0.5) (turnover_rate 2.0e-3) (fractions 0 1 0)))
   (SOrg          ((initial_fraction 0.80) (C_per_N 90.0)
                   (efficiency 0 0.5) (turnover_rate 2.0e-4) (fractions 0 1 0))
                  ((efficiency 0 0.5) (turnover_rate 2.0e-3) (fractions 0 1 0)))
   (Root          ((initial_fraction 0.80) (C_per_N 90.0)
                   (efficiency 0 0.5) (turnover_rate 2.0e-4) (fractions 0 1 0))
                  ((efficiency 0 0.5) (turnover_rate 2.0e-3) (fractions 0 1 0)))))

;; Definition of management activity
(defaction My_activity activity            ; Tillage activity. Se Daisy Reference Manager. No ploughing!
  (fertilize (PO4 (weight 1E-20))))        ; Additions of mineral fertiliser called PO4. PO4 is defined in the input
                                           ; file P-Model_fertiliser.dai
;; Simulation start date:
(time 1994 1 01 01)                        ; Start of simulation is here 1994, January  the 1, at 1 a.m.

;; Calling the activity defined above
(manager activity My_activity
 (wait (at 1997 01 01 01))                 ; This simulation stops at 1997, January the 1, at 1 a.m.
 (stop))
```

Repeated application of fertilizer or addition of several kinds of fertilizers must not take place at the same time. At least one hour must separate applications otherwise the P-Model skip the second application. If organic fertiliser is incorporation into the soil to a certain depth, the depth must match a lower depth of a numeric layer in the top horizon, otherwise the P-model does not incorporate it right.

Application of mineral P fertilizer is not possible in Daisy. However, 'reading' the "daisy.log" file activates application of any fertiliser in the P-Model. To apply mineral P fertiliser in the P-Model a fictive application of a mineral N fertiliser must occur in Daisy where the amount is almost zero (1E-20). The name of the P fertilizer must match the fictive application name displayed in the "Command Results" window in Textpad or the logged name in "daisy.log".

The output system is very flexible in Daisy and allows the user to define specific output. For the P-Model the following output components listed in Textbox 1 are required. The components that are not standard in Daisy are defined in the file P-Model_log.dai. However, more output components may be added if necessary. It is important that the 'Organic Matter' and 'DOM pools' are listed for every node defined and correct heights are inserted, as these log files initiates the organic pools in the P-Model.

*Textbox 1 continue. Setup a Daisy *.dai file for further simulation in the Daisy-P-model.*

```
;; Logging the following output:
 (output
                          ; Initial input of organic matter (AOM, SOM, SMB) of C and N in each node
                          ("Organic Matter 1"  (when yearly) (from -0 [cm])(to -5 [cm]))
                          ("Organic Matter 2"  (when yearly) (from -5 [cm])(to -10 [cm]))
                          ("Organic Matter 3"  (when yearly) (from -10 [cm])(to -15 [cm]))
                          ("Organic Matter 4"  (when yearly) (from -15 [cm])(to -20 [cm]))
                          ("Organic Matter 5"  (when yearly) (from -20 [cm])(to -25 [cm]))
                          ("Organic Matter 6"  (when yearly)  (from -25 [cm])(to -30 [cm]))
                          …. For every node!!

                           ; Initial input of DOM of C and N in each node
                          ("DOM Pools 1" (when yearly) (from -0 [cm])(to -5 [cm]))
                          ("DOM Pools 2" (when yearly) (from -5 [cm])(to -10 [cm]))
                          ("DOM Pools 3" (when yearly) (from -10 [cm])(to -15 [cm]))
                          ("DOM Pools 4" (when yearly) (from -15 [cm])(to -20 [cm]))
                          ("DOM Pools 5" (when yearly) (from -20 [cm])(to -25 [cm]))
                          ("DOM Pools 6" (when yearly) (from -25 [cm])(to -30 [cm]))
                          …. For every node!!

                          ;Input to every numeric nodes  every  time step:
                          ("Soil Water Content")              ; Water content
                          ("Soil NO3")                        ; Soil NO3-N content
                          ("Soil NH4")                        ; Soil NH4-N content
                          ("Soil temperature")                ; Temperature in every node
                          ("Soil N Residuals")                ; Root C exudes
                          ("Soil C Residuals")                ; Root N exudes
                          ("Soil water potential")            ; Water potential
                          ("Matrix Water Flux")               ; Water flux (matrix)
                          ("NO3 Root Uptake")                 ; Root NO3-N uptake by crops
                          ("NH4 Root Uptake")                 ; Root NH4-N uptake by crops
                          ;Input every  time step:
                          ("Harvest_N_C")
                          ("Crop C N" (when hourly) (from 0 [cm])(to -200[cm]))

                          ; For output analysis. Displaying the results
                          ("Harvest_N_C daily")
                          ("Organic Matter"  (when daily))
                          ("DOM Pools"  (when daily))
                          ("Surface Water Balance" (when daily))
                          ("Crop C N daily" (when daily))
                          ("Daily Soil Content" (when daily))
                           ("N Balance" (when daily))
                           ("Carbon Balance" (when daily)))
;;;;;;;;;;;;;;;;; *.dai ends here ;;;; ;;;;;;;;
```

8.2.2 *The spreadsheet Daisy-P.xls*

The spreadsheet, "Daisy-P.xls", works as the interface between Daisy and the P-Model, Figure 14 and Figure 15. It transforms Daisy output files to input files of the P-Model and provide the other information the P-Model needs. When opening the spreadsheet, macros have to be enabled.

The spreadsheet contains 11 points before the results are displayed:

1. Insert the filename of this worksheet. If renamed the new name must be in the textbox.

2. Insert the soil specific data in the table. Max 5 horizons can be defined. For each horizon parameters of oxalate (ox) and citrate-dithionite-bicarbonate (cdb) extractable Fe and Al content must be specified, as well as the oxalate extractable P and humus content in the horizons, soil dry bulk density, and height of the horizons.

3. Insert the type of added matter in the table. The name of the fertilizer added must match the name displayed in the "Command Results" window in Textpad or the logged name in "daisy.log". However, it must not contain the letter 'h', as the spreadsheet reads until it gets a space or a letter 'h'. Hence, the name in the spreadsheets must match the name until a 'h' appears in the name. For instance the mineral fertilizer called 'N25S' in Daisy becomes 'N25S-N/ha' in "daisy.log" after simulation. Hence, this name of 'N25S' must be added '-N/' to the name in the scheme.

   For inorganic fertilizers, all the parameters shown in the table should not be defined. Undefined parameters must contain '-1' in the table. If mineral P is added it must be added alone, not together with mineral N. Then the PO4 fraction must be set to '–1' and the weight of mineral P added must be listed.

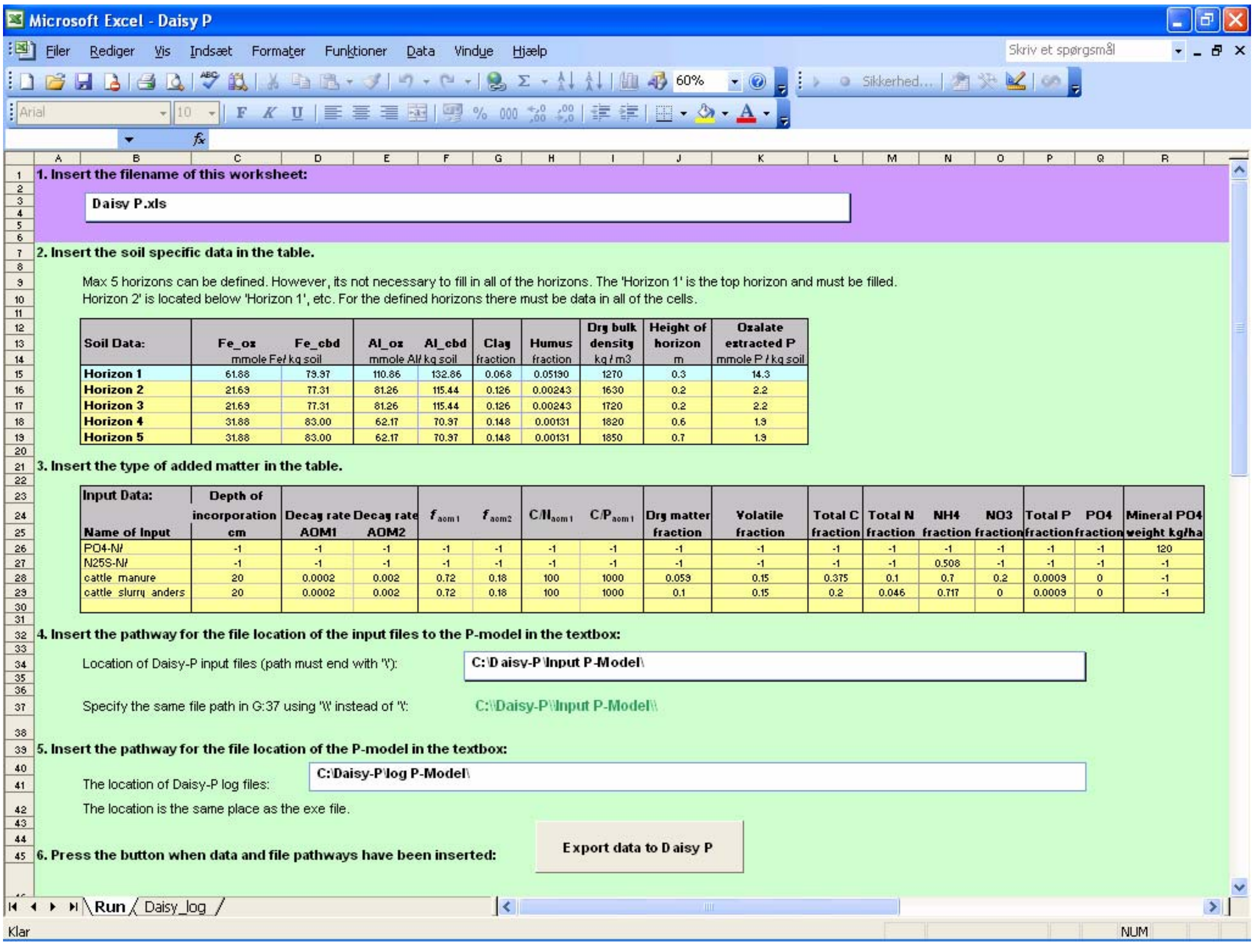
   For organic fertilizers, the parameters of decay rates, flow fractions, C/N-ratio, dry matter fraction, volatile fraction, total C and N fractions, NH_4^+ and NO_3^- fractions must match the parameters for the same fertilizer defined in Daisy. If NO_3^- fraction is undefined the scheme must contain a '-1'. The parameters of C/P-ratio, total P fraction, and PO_4^{3-} fraction is specific for the P-Model. The C/P-ratio correspond to the mass ratio of dry fertiliser, the total P fraction relates to the dry matter content of total P, and the PO_4^{3-} fraction corresponds to the fraction of total P that is inorganic. Remember that the incorporation depth of added organic matter must match a lower depth of a numeric layer.

   Two types of fertilizer must not be added at the same time. At least one hour must separate the actions.

4. Insert the pathway for the file location of the input files to the P-model in the textbox. The P-Model reads file paths as '\\' instead of '\', thus the same path must be specified in cell G37 with '\\' instead of '\'.

5. Insert the file location of the P-model in the textbox. This directory also contains the input files to the P-model.

6. Press the button when data in the above mentioned points have been inserted. If asked to overwrite existing files then accept.



1. Insert the filename of this worksheet:

Daisy P.xls

2. Insert the soil specific data in the table.

Max 5 horizons can be defined. However, its not necessary to fill in all of the horizons. The 'Horizon 1' is the top horizon and must be filled. Horizon 2' is located below 'Horizon 1', etc. For the defined horizons there must be data in all of the cells.

Soil Data:	**Fe_ox** mmole Fe/ kg soil	**Fe_cbd** mmole Fe/ kg soil	**Al_ox** mmole Al/ kg soil	**Al_cbd** mmole Al/ kg soil	**Clay** fraction	**Humus** fraction	**Dry bulk density** kg / m3	**Height of horizon** m	**Oxalate extracted P** mmole P / kg soil
Horizon 1	61.88	79.97	110.86	132.86	0.068	0.05190	1270	0.3	14.3
Horizon 2	21.69	77.31	81.26	115.44	0.126	0.00243	1630	0.2	2.2
Horizon 3	21.69	77.31	81.26	115.44	0.126	0.00243	1720	0.2	2.2
Horizon 4	31.88	83.00	62.17	70.97	0.148	0.00131	1820	0.6	1.9
Horizon 5	31.88	83.00	62.17	70.97	0.148	0.00131	1850	0.7	1.9

3. Insert the type of added matter in the table.

Input Data: Name of Input	**Depth of incorporation** cm	**Decay rate** AOM1	**Decay rate** AOM2	f_{aom1}	f_{aom2}	C/N_{aom1}	C/P_{aom1}	**Dry matter** fraction	**Volatile** fraction	**Total C** fraction	**Total N** fraction	**NH4** fraction	**NO3** fraction	**Total P** fraction	**PO4** fraction	**Mineral PO4** weight kg/ha
PO4-N/	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	120
N25S-N/	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	0.508	-1	-1	-1	-1
cattle manure	20	0.0002	0.002	0.72	0.18	100	1000	0.059	0.15	0.375	0.1	0.7	0.2	0.0009	0	-1
cattle slurry anders	20	0.0002	0.002	0.72	0.18	100	1000	0.1	0.15	0.2	0.046	0.717	0	0.0009	0	-1

4. Insert the pathway for the file location of the input files to the P-model in the textbox:

Location of Daisy-P input files (path must end with '\'): C:\Daisy-P\Input P-Model\

Specify the same file path in G:37 using '\\' instead of '\': C:\\Daisy-P\\Input P-Model\\

5. Insert the pathway for the file location of the P-model in the textbox:

The location of Daisy-P log files: C:\Daisy-P\log P-Model\

The location is the same place as the exe file.

6. Press the button when data and file pathways have been inserted:

Export data to Daisy P

Figure 14. View of the spreadsheet Daisy-P.xls point 1-6.

7. Run Daisy after setting up a *.dai file as explained in the previous paragraph.

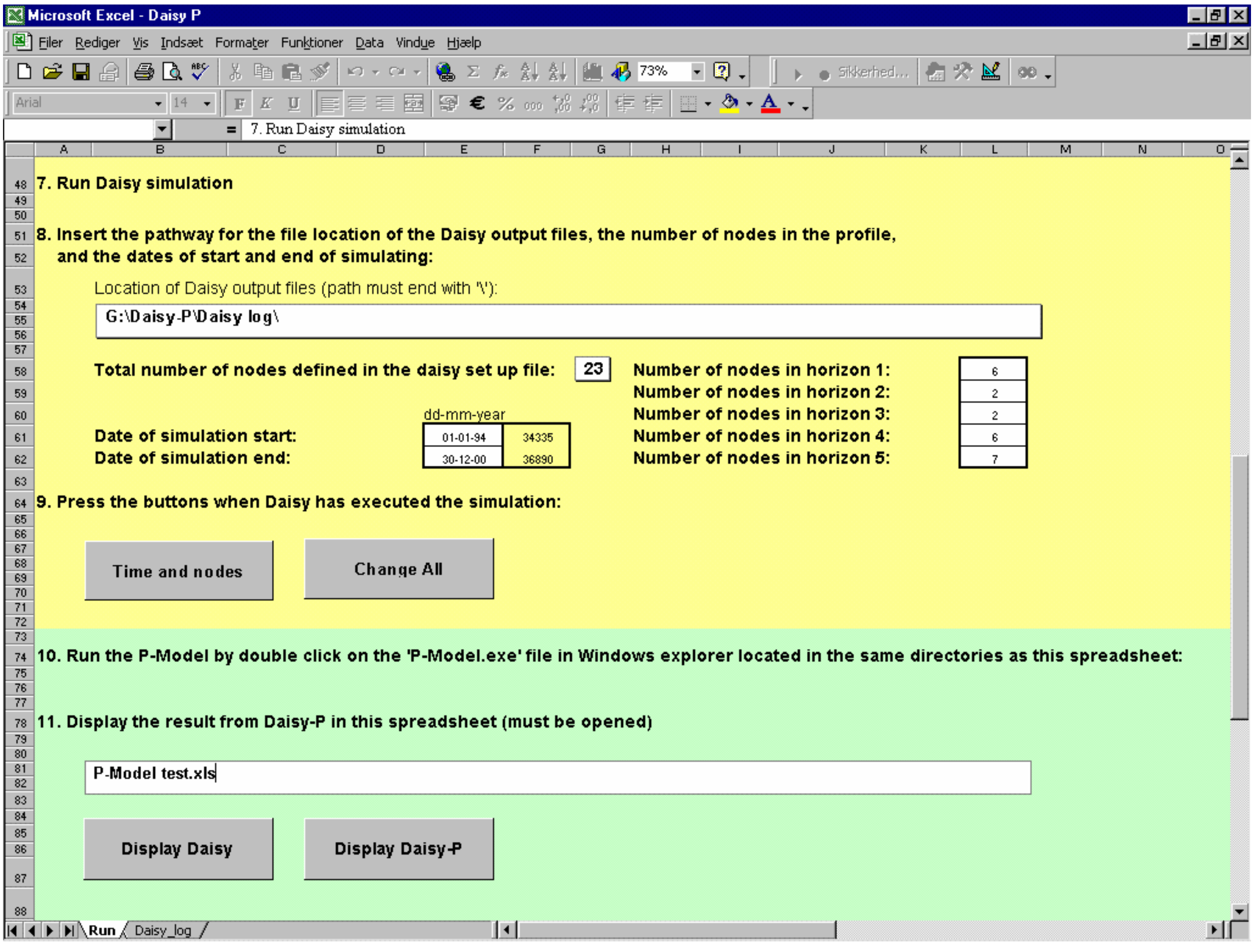
8. Insert the pathway for the file location of the Daisy output files, the total number of nodes in the profile, and the dates of start and end of simulation. The number of nodes in each horizon must match the number of nodes defined in the *.dai file in Daisy. However, the height of the horizon must be dividable by the number of nodes in that horizon. If not all five horizons are defined, the number is equal to zero in the undefined horizons. Insert the start and end time period (dd-mm-year) of the simulated time interval in Daisy in the white cells.

9. Press the "time and nodes" button to create an input file to the P-Model, which provide information of the start and end times, the nodes and where to find the other input files. If asked to overwrite existing files then accept. When Daisy has finished the simulation all the output files is transformed to input files of the P-Model, by activating the button 'Change all data'. This action takes some time especially if the simulation time is long. If asked to overwrite existing files then accept.

10. Run the P-Model by double click on the "P-Model.exe" file.

11. Display the result from Daisy-P in the spreadsheet that is listed in the textbox by pressing the button 'Display Daisy-P'. The spreadsheet that is listed in the textbox must be based on an output template spreadsheet "Daisy-P output template.xls", which are located in the CD. Hence, by renaming "Daisy-P output template.xls" to for instance "Burrehøjvej_P-Model.xls" and list the new filename in the last textbox, the results are displayed in this sheet. To check

if the P dynamic of the P-Model match the C and N dynamic of Daisy then press the button 'Display Daisy'.



= 7. Run Daisy simulation

7. Run Daisy simulation

8. Insert the pathway for the file location of the Daisy output files, the number of nodes in the profile, and the dates of start and end of simulating:

Location of Daisy output files (path must end with '\'):

G:\Daisy-P\Daisy log\

Total number of nodes defined in the daisy set up file: 23

	dd-mm-year	
Date of simulation start:	01-01-94	34335
Date of simulation end:	30-12-00	36890

Number of nodes in horizon 1:	6
Number of nodes in horizon 2:	2
Number of nodes in horizon 3:	2
Number of nodes in horizon 4:	6
Number of nodes in horizon 5:	7

9. Press the buttons when Daisy has executed the simulation:

10. Run the P-Model by double click on the 'P-Model.exe' file in Windows explorer located in the same directories as this spreadsheet:

11. Display the result from Daisy-P in this spreadsheet (must be opened)

P-Model test.xls

Figure 15. View of the spreadsheet Daisy-P.xls point 7-11.

8.3 Output data

The P-Model creates eight output files: Settings.log, P.log, N.log, C.log, Sorb_out.log, Flux_leach.log, Plant.log, and Climate.log. All the log files are copied to the output template spreadsheet listed in the last textbox in Daisy-P.xls.

8.3.1 Settings.log

The settings.log file displays the settings of the organic matter modules and the contents of the inorganic nutrients, and the settings of the sorption modules for every node.

8.3.2 P.log, N.log, and C.log

The three files P.log, N.log, and C.log contain daily values of the content of P, N, and C of the organic matter pools and the dissolved inorganic fractions, in the whole profile, given in units of kg ha^{-1}.

8.3.3 Sorb_out.log

The Sorb_out.log file contains the different inorganic and organic phases of dissolved and sorbed inorganic P and DOC, DON, and DOP. The phases of inorganic P include dissolved, adsorbed phase, slower absorbed phase, and very slowly fixed phase. Only the solute concentration of DOM is logged in this file, hence, the sorbed phase corresponds to SOM2. The units of dissolved phases are given in mg P L^{-1} as average values of the whole profile, together with kg P ha^{-1}. The units of sorbed phases are given in kg P ha^{-1}.

8.3.4 Flux_leach.log

The Flux_leac.log file contains daily values of water flux in mm per day, and the flux of NH4, NO3, PO4, DOC, DON and DOP given in kg ha^{-1} day^{-1}. Additionally it contains concentration of PO4, DOC, DON, DOP in all depths defined by the horizons. Hence, the concentrations are logged in the bottom of each horizon.

8.3.5 Plant.log

The Plant.log file contains daily values of plant C, N and P content and amounts of C, N, and P removed by harvest, given in values of kg ha^{-1}. It also contains information of N and P crop uptake and amount of N fixated from the atmosphere, which are given in kg ha^{-1} day^{-1}.

8.3.6 Climate.log

The Climate.log file contains daily values of soil temperature in degree Celsius, water pressure potential in m heads, both given as average values of the whole profile, along with total water content of the whole profile given in mm water.

9 TEST OF CODE

The test of code is performed to make sure that the code calculates the respective processes in a correct way. Setting parameters to simple values and comparing simulations with spreadsheet calculations, tests the processes of inorganic P sorption and crop P-uptake. When possible, the test is performed by comparing the output of the P-Model with the output of Daisy. Comparing the Daisy model with the P-Model tests the turnover of organic N and C and if the dynamics of organic P turnover is similar to organic N and C, it is assumed that the code of organic matter and P turnover is correct. A similar assumption is assumed with the transport in the profile. If the flux of NO_3, NH_4, DOC, and DON is similar to the Daisy output, then it is assumed that the flux of PO_4 and DOP is correct if it follows the same pattern.

The calculation of inorganic N by the P-model is comparable with the Daisy model when the deposition of N, the denitrification and the nitrification is turned off in Daisy and the flux of NO_3 and NH_4 is calculated by convection. In the following tests these processes are turned off in the Daisy model and overwriting of NO_3 and NH_4 from the Daisy log files are cancelled in the P-Model. All the following tests are based on the same basic set-up in Daisy, which is enlarged continuously with each test. The levels of concentrations and parameter values used in these tests are not necessarily comparable with actual conditions or parameters.

9.1 Test of basic turnover of organic matter

To test the basic decomposition, mineralization and immobilization processes of organic C, N, and P a simulation, with no crop, tillage, adsorption, transport of solutes or water, nitrification or denitrification was run by the Daisy model for further simulation in the P-Model. The test results are displayed in Figure 16 and Figure 17.

The mineralization of organic N to NH_4 and the microbial evolution of CO_2 are calculated similarly by the two models (the curves of the P-Mod simulations equals the curves of Daisy simulations). It is noted that no microbial immobilisation of NO_3 occurs. The mineralization of organic P to PO_4 follows the same dynamic as mineralization of NH_4. The test shows that the mineralization of organic matter in the P-Model is calculated in accordance with the Daisy model.

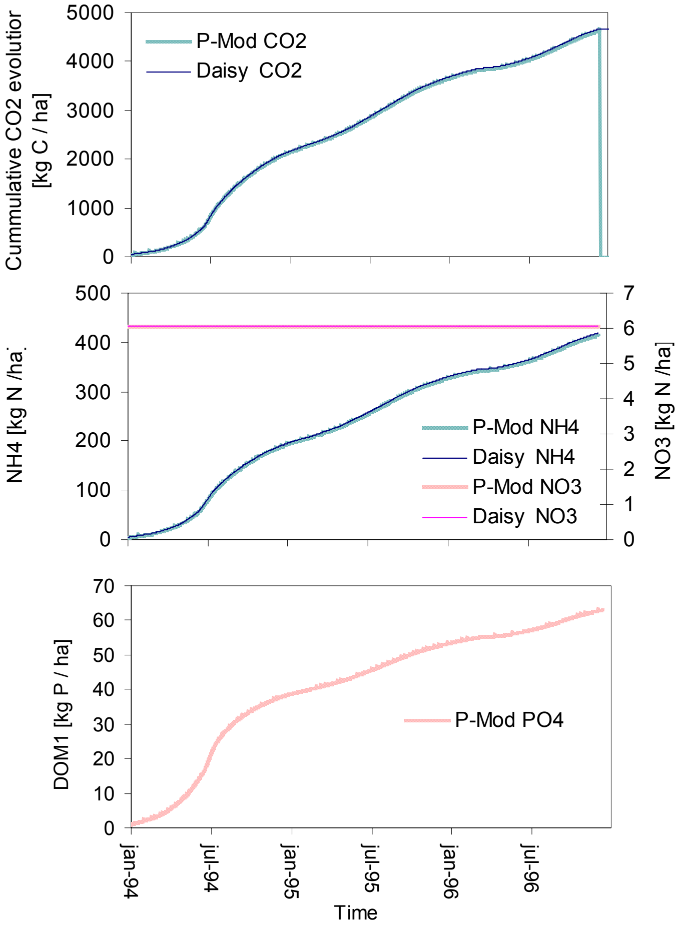


Figure 16. Comparing basic mineralization calculated by the P-Model and the Daisy model.

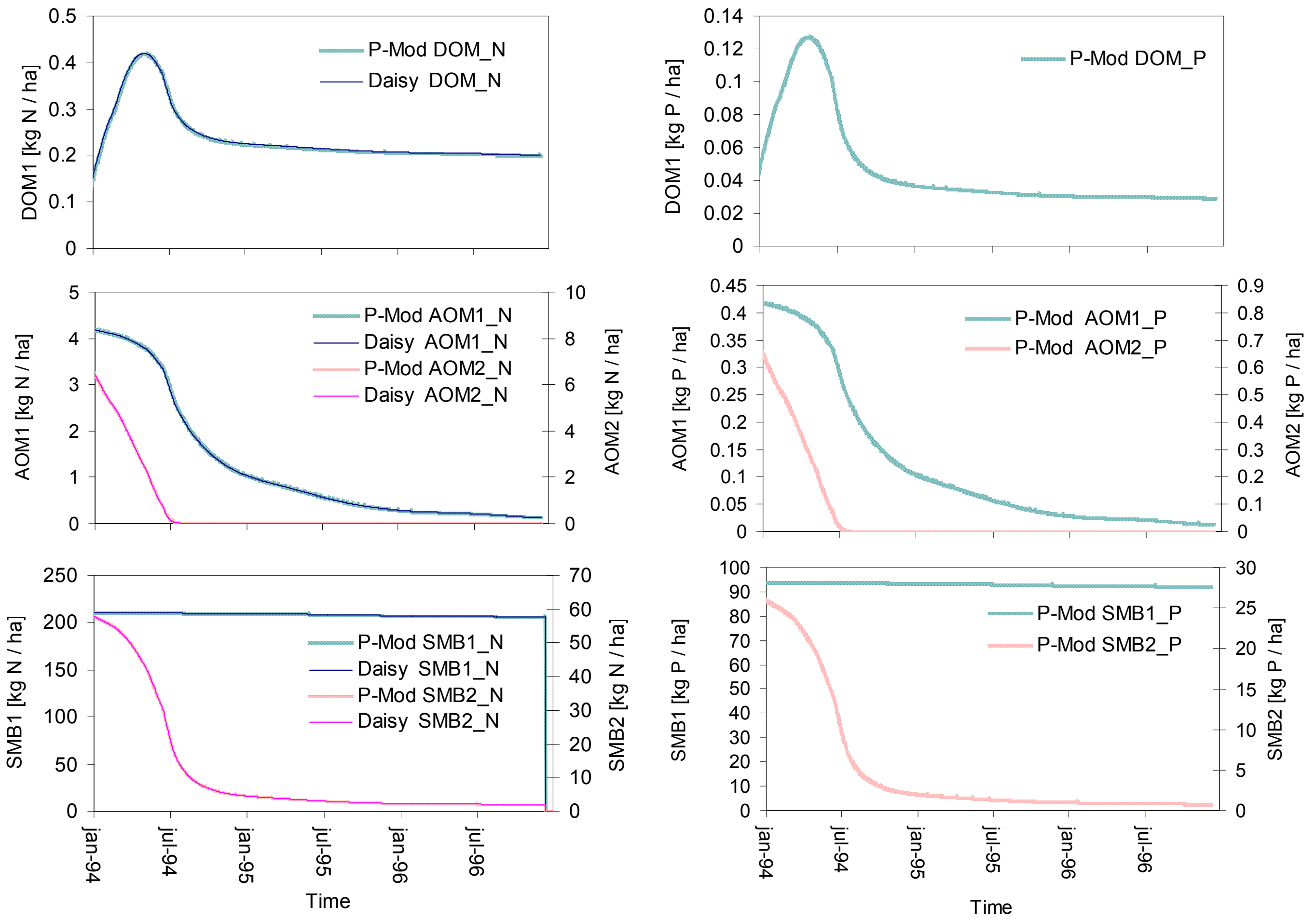


Figure 17. Comparing basic turnover of organic matter calculated by the P-Model and the Daisy model.

The production and degradation of the dissolved organic matter (DOM) are similar in the two models, and DOP follows the same dynamic as DON and DOC. That also accounts for the degradation of the added organic matter pools (AOM) initially present in the soil, the soil organic matter (SOM) pools (not shown) and the population dynamic of the soil microbial biomass pools (SMB), Figure 17. Hence, the calculation of production and degradation of organic matter in the P-Model seems to be similar to the calculation by the Daisy model.

9.2 Test of transport

To test the transport processes of DOP and DIP a simulation with no crop, tillage, adsorption, transport of solutes or water, nitrification or denitrification was run by the Daisy model for further simulation in the P-Model. The test results are displayed in Figure 18 and Figure 19 together with the precipitation data in the weather file. The Daisy model calculates water transport by a numeric solution to Richards's equation. The water content and flux data for every node and time step are input parameters to the P-Model. The transport of inorganic N species and DOC, DON, DOP, and DIP are calculated by convection in both models.

The test of the transport calculations shows that the soil water content are similar in the two models, Figure 18. Hence, the transferring of water content data from Daisy to the P-Model is correct. Also the DOC (not shown), DON, NO3, and NH4 content are similar in the two models, which imply that the turnover of organic matter together with the transport processes are similar in the P-Model and the Daisy model, Figure 19.

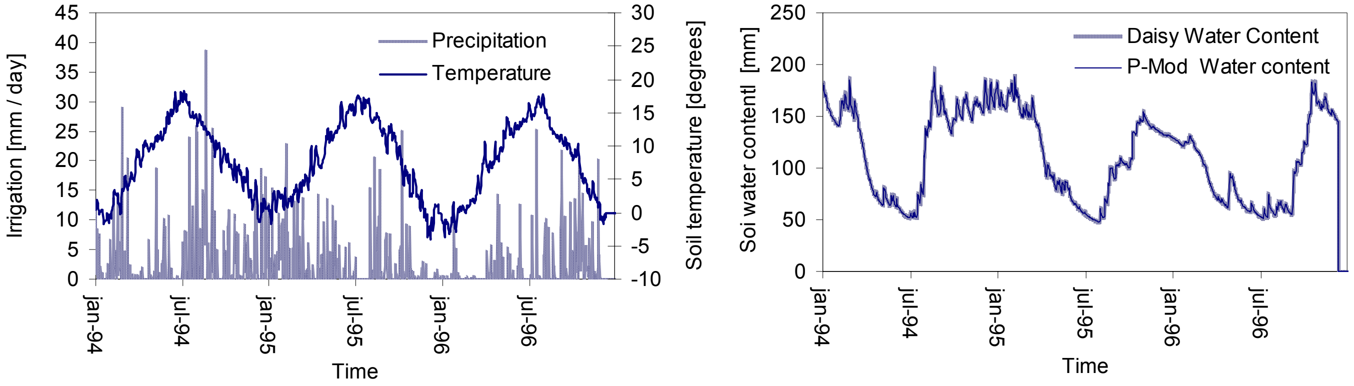


Figure 18. The precipitation specified in the weather file, the soil temperature calculated by the heat module in the Daisy model, and the total soil water content in the profile (0-50 cm) calculated by Daisy (Richards's equation) and transferred to the P-Model.

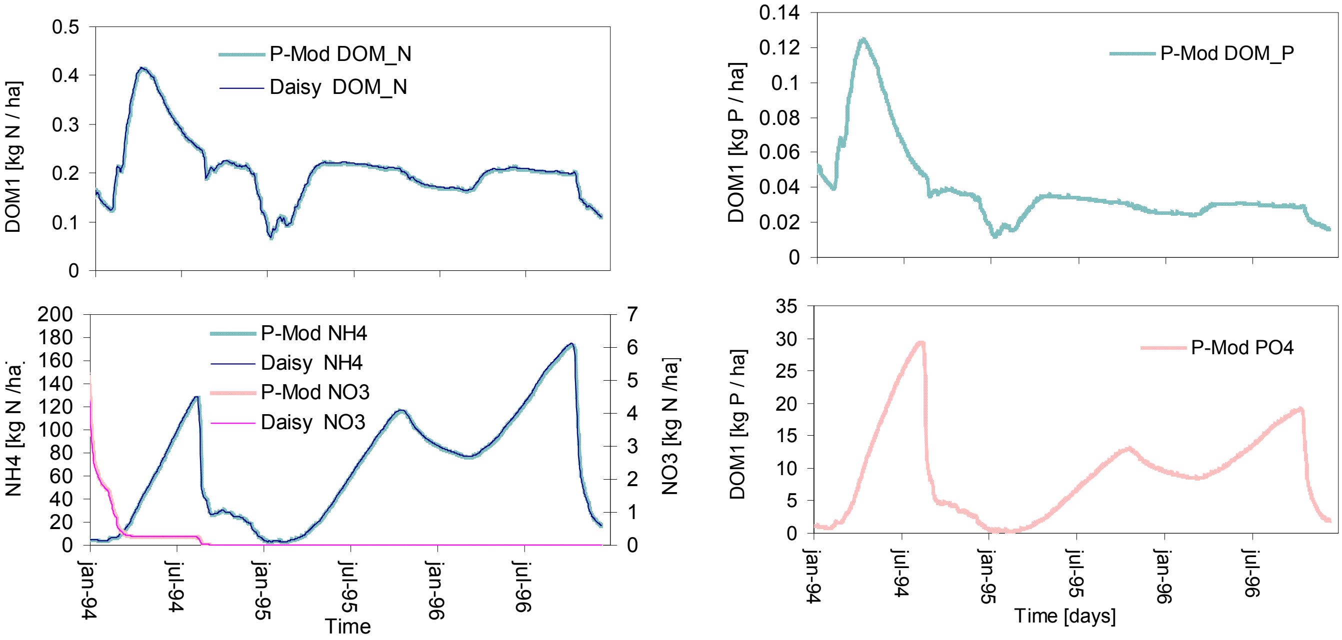


Figure 19. Amount of DON, NH_4, and NO_3 (left) in the profile (0-50 cm) calculated by the two models, and amount DOP and DIP (right) in the profile (0-50 cm) calculated by the P-Model, when solutes are transported by convection.

It is noted that the level of PO_4 does not follow the level of NH_4 which reflect that the mineralization of organic P does not necessarily follow the mineralization of organic N. The mineralization rate is dependent by the C/P and C/N ratio of the organic matter, respectively. Also the level of DOP does not follow the level of DON exactly, reflecting that the C/N/P ratio of DOM is variable and source depending.

9.3 Test of fertilizer addition

Supplying the soil with organic fertilizer from grassing cattle, tests the turnover of added organic matter (AOM). In the Daisy set up the organic fertiliser supplied by grassing cattle occurs every day from May to October in two years. The cattle manure is parameterized in the test as organic slurry with a total N/P mass ratio that equals 10, where 70 % of the nutrients are allocated to the inorganic pools.

Addition of inorganic fertilizer is also tested by addition of 120 kg N (59.1 kg NO3-N and 60.9 kg NH4-N) and 20 kg P (PO4-P) to the surface. A simulation similar to the test for transport calculations, and with the above-mentioned fertilizer additions to the soil was run in Daisy for further simulation in the P-Model.

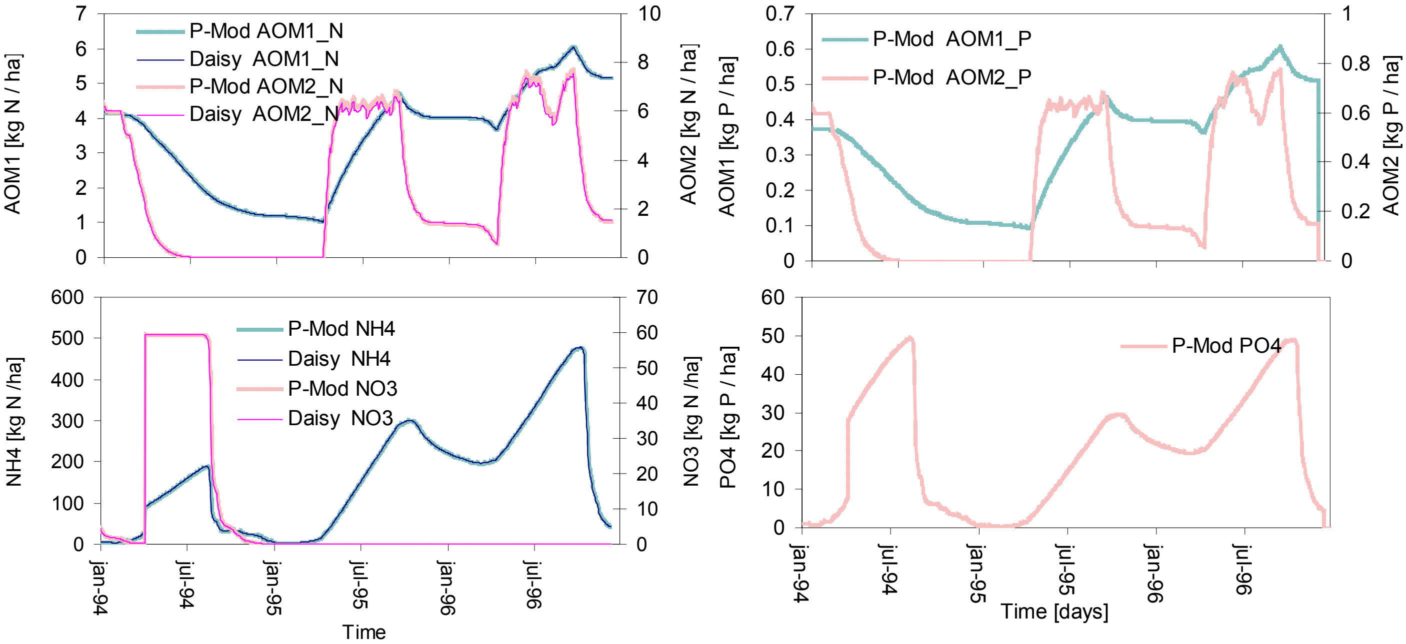


Figure 20. The turnover of the AOM pools of N and P in the top figures, left and right, respectively. The dynamic of the inorganic N pools and P pool in the bottom figures, left and right, respectively.

The additions of manure from grassing cattle in the period of May to October in the years1995 and 1996 are reflected in the AOM pools. The AOM2 pool is decomposed relatively fast. The AOM1 pool degrades more slowly and a gradual increase of the AOM1 pool occurs through the periods with grassing cattle. The additions of cattle manure with N/P=10 for both the AOM pools are reflected in the P content of the AOM pools shown in the top figures, Figure 20.

When the organic N is mineralised to inorganic N, an increase in NH4 is observed. Only when the NO3 is less than needed by the soil microbial biomass (SMB), NH4 is immobilized to the organic matter pool by the SMB pools. When the organic P is mineralised to inorganic P, an increase in DIP is observed. Hence, the pattern of DIP is comparable to the pattern of the NH4 when the concentration of NO3 is low.

9.4 Test of crops

A simulation with ryegrass tests the calculations of crop uptake, crop contents, and additions of organic substances from dead plant residues and root exudes. The set up for the Daisy model was expanded with sowing and harvesting of ryegrass. In the P-Model the crop is parameterised with a N/P mass ratio that equals 10 in this test to simplify the results. Hence, the N and P ratio of crop uptake, crop content, release of root exudes to the soil, and addition of dead plant parts to the soil surface, must show the same pattern with a N/P ratio of 10 if the calculations are true. Figure 21 shows some details of the test results. The crop uptake of N and P, the crop N and P content, and the dead plant residues content of N and P, follows the same pattern with a constant N/P ratio of 10.

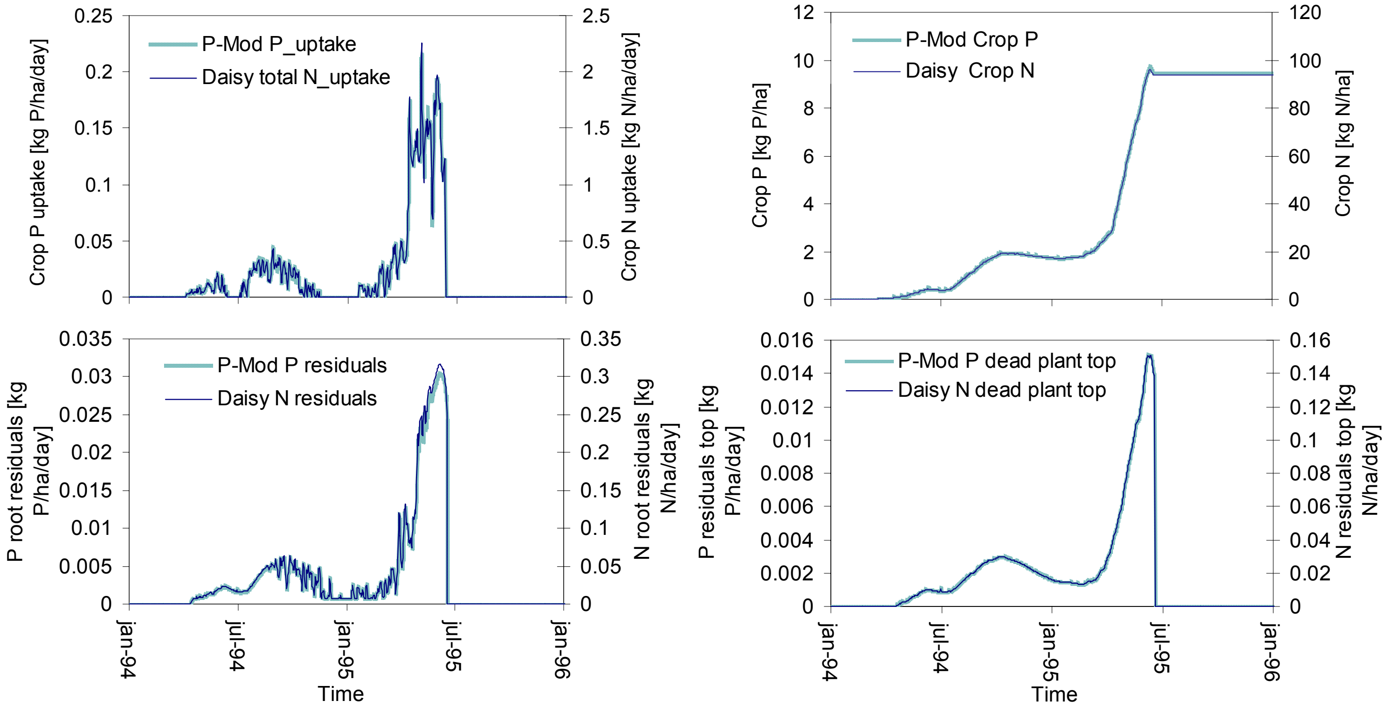


Figure 21. Ryegrass crop uptake of N and P and crop contents of N and P in the top figures, left and right, respectively. Root exudes and dead roots of N and P to the soil, called plant residuals, and dead plant parts on the surface are shown in the bottom figures, left and right, respectively.

9.5 Test of DOM sorption module

The sorption module of DOM is tested by comparing three simulations of three soil layers, each defined with a specific optimum equilibrium concentration, $DOC_{eq\_optimum}$ Three levels of DOC concentration is defined corresponding to the soil specific $DOC_{eq\_optimum}$ of the three layers. If the concentration of DOC is above $DOC_{eq\_optimum}$ sorption will occur and the DOC concentration will decrease with time. If DOC = $DOC_{eq\_optimum}$, the system is at equilibrium and will cause the DOC concentration to be steady state. If DOC is below $DOC_{eq\_optimum}$, desorption occurs and the DOC concentration will decrease with time.

Figure 22 show the test result applying 0.3, 0.1, and 0.05 mmole DOC / L to each soil layer, Layer 1, 2, and 3 with $DOC_{eq\_optimum}$ = 0.3, 0.1, and 0.05 mmole DOC / L, respectively. The results show that when DOC = $DOC_{eq\_optimum}$ steady state occurs for all layers. Applying DOC concentrations below the levels of $DOC_{eq\_optimum}$, desorption will occur releasing DOC from the SOM2 pool, Figure 22 top. Applying DOC concentrations above the level of $DOC_{eq\_optimum}$, sorption occurs, removing DOC to the SOM2 pool, Figure 22 bottom.

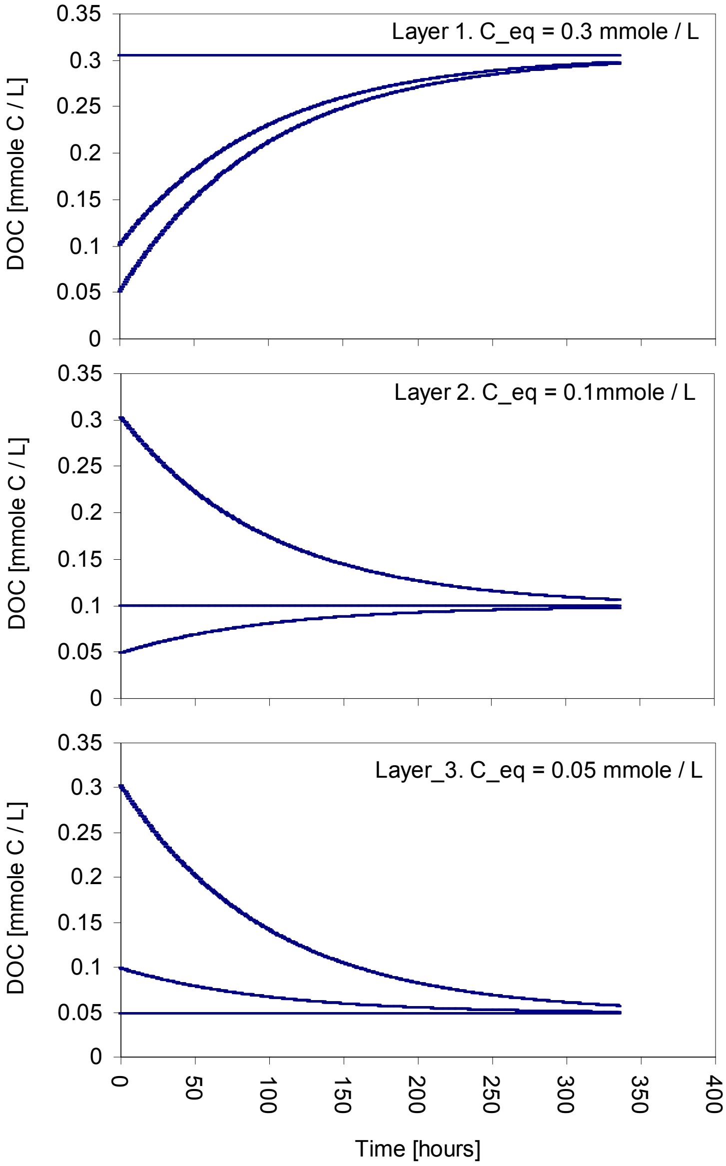


Figure 22. Test of the DOM sorption module. Applying three different concentration levels of DOC corresponding to the optimum equilibrium concentrations of the three layers.

9.6 Test of the inorganic P sorption module

The sorption module of dissolved inorganic P is tested by comparing simulated data of a sorption process, assuming instantaneous equilibrium (rate constant = 1 hour^{-1}), with spreadsheet calculation of Langmuir estimated sorbed P. The three sorption processes, adsorption, absorption, and fixation, are tested separately. Assuming that the processes are at equilibrium instantaneously, then the calculation of the sorbed fractions is calculated by the Langmuir equation. Langmuir constants as the sorption capacity and affinity (Langmuir constants) are set manually in the test to 728 mmole P / kg soil and 40 L / mmole, respectively. Figure 23 show the test results comparing simulated with manually calculated equilibrium concentrations of P in the sorbed and dissolved phases.

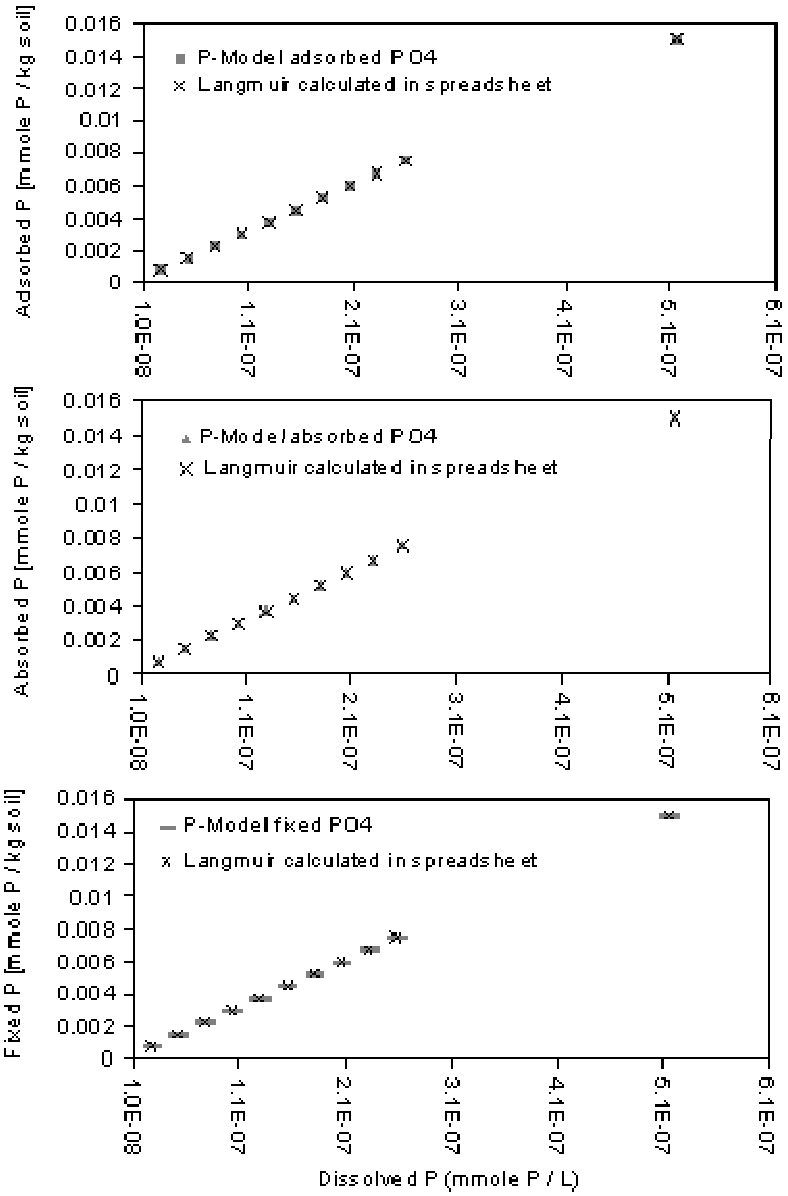


Figure 23. Test of the calculation of equilibrium equations for the three sorption processes, adsorption, absorption and fixation. Calculations by the P-Model are compared with spreadsheet calculations of Langmuir estimated immobilized fractions.

10 PARAMETERISATION

This chapter presents a description of the parameterization of the organic matter module with respect to the dissolved organic matter (DOM) fraction and the C:N:P ratios in the organic matter pools. Furthermore, the parameterization of the sorption modules of DOM and inorganic P is described by showing the sensitiveness of parameter sizes. The parameterization of the organic matter module is based on literature values. The parameterization of the inorganic P and organic P sorption module is based on batch experiments.

10.1 Turnover of organic P

Several experimental studies have been considered in relation to parameterization of Daisy's organic matter module, both long-term field experiments and short-term incubation experiment with different applied organic fertilizer. The parameter values in Table 4 have been used for the SOM and SMB pools.

The new parameters defined in the P-Model in the organic matter module, are the C/P ratios of the SOM and SMB pools and the parameterization of the DOM pool. The parameterization of this module will be discussed in the following paragraphs.

Table 4. Standard parameterization values in Daisy (Hansen et al., 1990; Mueller et al., 1997) and parameterization of the P-Model.

	SMB1	SMB2	SOM1	SOM2	DOM§
C/N-ratio	6.7	6.7	11	11	Variable
C/P-ratio	15	15	110	110	Variable
Flow fraction, f_x	0	1.0	0.1	0.4	0.05
Microbial efficiency, E	0.6	0.6	0.4	0.5	0.5
Death rate coefficient, d^* [day^{-1}]	$1.85\ 10^{-4}$	$1.0\ 10^{-2}$			
Maintenance, m^* [day^{-1}]	$1.80\ 10^{-3}$	$1.0\ 10^{-2}$			
Standard decay rate coefficient, k_x^* [day^{-1}]	$1.98\ 10^{-3}$	$2.0\ 10^{-2}$	$2.7\ 10^{-6}$	$1.4\ 10^{-4}$	$3.6\ 10^{-3}$

10.1.1 C:P ratios

A definite relationship has been observed between organic C, total N, organic P, and total S in soils (e.g. Walker and Adams, 1958). While considerable variation is found in the C/N/P/S ratio for individual soils, the mean values for soils from different regions of the world is remarkably similar (Stevenson, 1994). As an average of soils from Iowa, Brazil, Scotland, New Zealand and India, the proportion of C:N:P:S in soils is approximately 140:10:1.3:1.3. In well aerated, temperate region soils the average mass ratio for the C:N:S:P concentrations is approximately 100:10:1:1 (Borggaard, 1998).

According to these general terms and the standard parameterization of SOM in Daisy, Table 4, the SOM1 and SOM2 pool are parameterized to have N:P mass ratios of 10:1, giving C:P mass ratios of 110:1.

Up to now, only a few data are available that characterizes the size of microbial P and the microbial P turnover. Approximately 2-5% of organic P in cultivated soils occurs as part of the microbial biomass, although higher and lower values are not uncommon (Stevenson, 1994).

Hence, Brookes et al. (1984) accounted for 5-24% of organic P as biomass P in some grassland soils, and 2.5-3.4% for some arable soils. The C:P ratios for the biomass ranged between 11.7:1 - 35.9:1. According to Chauhan et al. (1981,1979) incubation of P-deficient and P-sufficient soils with energy sources (cellulose) has been shown to result in a soil biomass of widely differing C:P ratios of 15:1 to 45:1. Oehl et al. (2001) found, in long term field experiments (Switzerland) of biological and conventional farming systems, microbial C:P ratios of 10.8:1 to14.8:1. Microbial P in organically cultivated soils was twofold higher than in soils receiving none or only mineral fertilizer.

According to these findings in literature the soil microbial biomass (SMB1 and SMB2) are parameterized to have C:P ratios of 15:1 in the P-model, Table 4.

10.1.2 Flow fraction

Although the release of DOM has been researched extensively (mainly from forest soil studies) it is still not clear weather DOM originates from recent litter or from relatively stable organic matter fractions (Kalbitz et al., 2000). It has been hypothesized that microbial decay of humus rather than that of recent litter are largely responsible for DOM production in forest floor (McDowell and Likens, 1988). Zsolnay (1996) also suggested that humified organic matter is the major source of DOM because of the relative high proportion of humus in relation to litter in soils. In contrast Qualls et al. (1991) reported that within a deciduous forest the greatest net increase in DOM fluxes occurred in the upper part of the forest litter. The rhizosphere is often associated with a large carbon flux attributed to root turnover and exudation, associated with high microbial activity. Substantial amounts of DOM may well derive from this important below-ground C source. However, there has been no attempt to measure directly the contribution of root derived DOM (Kalbitz et al., 2000). The soil microbial biomass is also considered to be a potentially important source of DOM. Recent studies of fractionation and structural analysis of DOM in soil solutions have shown that microbial metabolites constitute a significant fraction of DOM (Guggenberger et al., 1994).

In the P-model it is hypothesized that DOM is produced by the SMB2, SOM1, and SOM2. The contribution of these pools to DOM production is not fully understood and therefore the flow fractions to the DOM pool are assumed to be equal, Table 4; however, as the size of the SOM pools is significant higher than the SMB2 pool the SOM pools have the largest contribution to DOM production. DOM production is not directly linked to the AOM pools, which represent fresh litter, dead roots, and organic fertilizer, because the contribution of DOM from all these different AOM pools is probably very different. Additionally, theses sources is very bioavailable to the microbial biomass promoting fast turnover and growing microbial biomass, which contribute to the production of DOM. Hence, the DOM dynamic is closely linked to the dynamic of the AOM pools.

10.1.3 Microbial efficiency

Microbial efficiency of DOM is parameterized as SOM2 and the AOM pools as these pools are important contributors to the DOM production.

10.1.4 Turnover rate

Initial rates of DOC decomposition in incubation experiments are generally rapid but then decline quickly to a lower, constant rate (e.g. Zsolnay and Steindl, 1991). A number of references have been found to correlate the rate at which DOM is decomposed with a first order rate constant, *k*, Table 5. Often several different pools of dissolved organic material are assumed, requiring two or more rate constants (e.g. Qualls and Haines, 1992). According to Kalbitz et al. (2000) up to 40 % of released DOM is potentially biodegradable in solutions within a period of days to a few months. However, it is out of scope in this version of the P-Model to consider more than one DOM pool.

Table 5. Reported values of first order rate constant of DOM decomposition.

	Turnover rate day^{-1}	References
Forest: Rapid fraction:	$30*10^{-3}$ - $80*10^{-3}$	Qualls and Haines, 1992§
Forest: Slow fraction:	$0.3*10^{-3}$ - $0.7*10^{-3}$	Qualls and Haines, 1992
Agricultural field: 0-100 cm	$6*10^{-3}$ – $10*10^{-3}$	Zsolnay and Steindl, 1991§

§ DOM-C is refereed as water extractable organic C, WEOC.

The values in Table 5 do not show considerable variation. Hence, the parameterization of turnover rates was attempted to be in the range $6*10^{-3}$ – $10*10^{-3}$ day^{-1}. Figure 24 shows the effect of varying the turnover rates within this limits and no notable effects were observed in DOM-C concentration in the profile. The turnover rate was calibrated to a value of $3.6*10^{-3}$ day^{-1} by fitting simulations of DOM concentrations to measured field data, see paragraph 11.3.

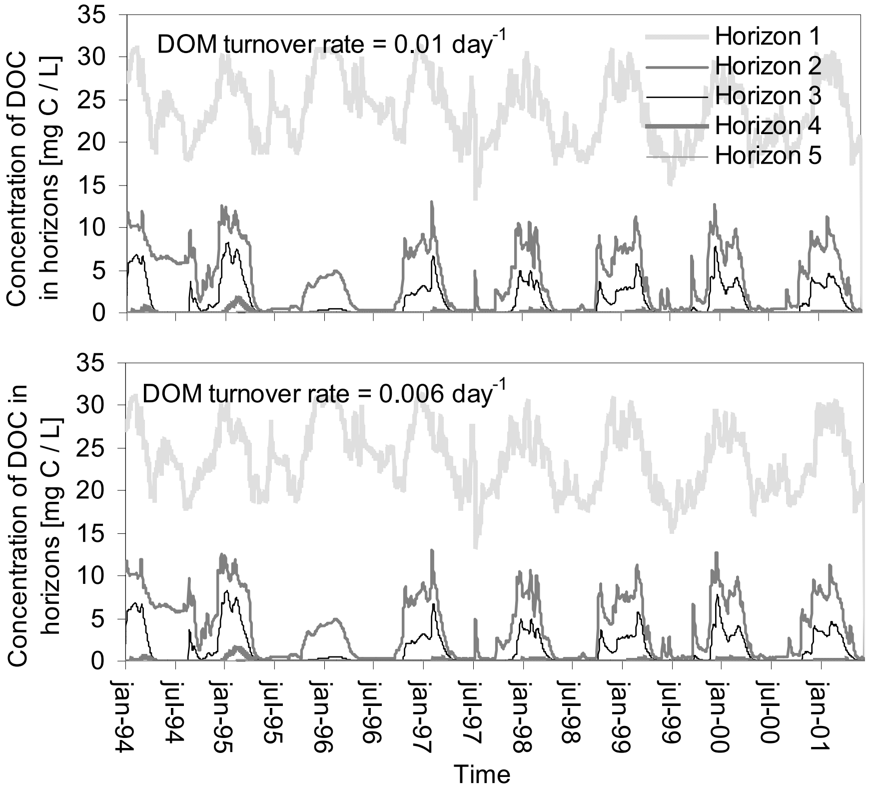


Figure 24. Effect of turnover rate on DOM-C concentrations in the profile. Simulation using two turnover rates for DOM. Horizon 1 = 0-30 cm. Horizon 2 = 30-50 cm. Horizon 3 = 50-70 cm. Horizon 4 = 70-130 cm. Horizon 5 = 130-200 cm.

10.1.5 Plant residuals and root exudates

Fresh plant residues may quickly release P into the soil solution where more stable forms or organic matter, such as soil humus and animal manures, generally act as long-term, slow release sources of P. Mineralization usually occurs rapidly if the C:P ratio of the organic material is <200:1, while immobilization occurs if C:P ratios are >300:1 (Pierzynski et al., 2000).

In Table 6 the parameterization of AOM1 and AOM2 pools in Daisy and the P-Model are listed. The C:P ratio of the AOM1 residuals and AOM1 root pool is based on the C:N ratio of this pool ($[C{:}N]_{AOM1\_residual} = [C{:}N]_{AOM1\_root} = 90$) and the [C:P] ratio of AOM2 is calculated from the C and P balances of the crop. The relatively slow AOM1 pool, with a C:P ratio of 900 is decomposed by SMB2 which immobilize P to account for the huge C:P ratio. The easily decomposable pool AOM2 obtain different C:P ratios depending on the source. The C:P ratio of AOM3 material ranges from 40:1-150:1.

Table 6. AOM pools defined in the P-Model. The AOM residuals pools correspond to dead plant residues and root exudes from the crop model in Daisy. The AOM root pools correspond to the default settings of the initial defined AOM pools in Daisy.

	AOM1 residuals and roots	AOM2 residuals and roots
C:N-ratio	90	Variable
C:P-ratio	900	Variable
Flow fraction, f_x	0.8	0.2
Microbial efficiency, E	0.5	0.5
Standard decay rate coefficient, k_x^* [day^{-1}]	$2.0\ 10^{-4}$	$2.0\ 10^{-3}$

10.1.6 Addition of organic fertilizer

From short-term incubation experiments, some parameters have been estimated for organic additions of plant residues, straw and pig slurry in the Daisy model {Hansen, 1990 90 /id}. Standardized norms of organic fertilizers in Denmark (Poulsen et al., 2001) as dry matter content , ammonium and total N content is given as input parameters for each type of fertilizers. For the P-Model some examples of standardised norms for P content in organic fertilisers is listed in Table 7.

In the Daisy model C/N ratio of the AOM1 pool is 100:1 for most organic fertiliser. The C/N ratio of the AOM2 pool is then estimated from the C and N mass balance of the substrate. In the P-model the C/P ratio of the AOM1 pool is assumed to be 1000:1 and the C/P ratio of AOM2 is calculated from the C and P balances of the substrate.

Table 7. Values of parameters for added organic matter to soil in the soil organic matter model assessed from standardized norms of organic fertilizer inputs in Denmark (Poulsen et al., 2001). The C/P ratio of the AOM1 pool is equal to 1000:1. The [C/P] ratio of AOM2 is calculated from the C and P balances of the substrate.

Organic fertiliser		Standardized norms		Parameters for the P-Model	
		Dry matter (DM in %)	P content (% of DM)	Total P fraction§	C/P_{AOM1}
Dairy cattle	Heavy race	15.3	0.72	0.007	1000
	Jersey	15.2	0.74	0.007	1000
bull calf	Heavy race	18.1	0.12	0.001	1000
	Jersey	17.9	1.03	0.010	1000
Swine	sow	16.1	1.32	0.013	1000
	porker	14.3	1.14	0.011	1000

§ Total P fraction of dry matter content.

10.1.7 Immobilization rate coefficient for PO_4-P

If available N and P exist in the soil solution the microbial biomass is supplied with inorganic N and P by a first order reaction at a rate, which is related to diffusion and is proportional to the concentration of NH_4-N, NO_3-N and PO_4-P, respectively. The immobilization rate coefficient for PO_4-P, eq. 2-19, is parameterized as the coefficients for NH4 and NO3 in Daisy:

$$k^{im}_{NH_4-N} = k^{im}_{NO_3-N} = k^{im}_{PO_4-P} = 0.0208333 \text{ s}^{-1}.$$

Hence, it is assumed that the diffusion of PO_4-P is comparable to NH_4-N, NO_3-N.

10.1.8 Summary of DOM turnover parameterisation

It is assumed that DOM is produced by the SMB2, SOM1, and SOM2 by equal flow fractions. However, as the size of the SOM pools is significant higher than the SMB2 pool the SOM pools have the largest contribution to DOM production. DOM production is not directly linked to the AOM pools, which represent fresh litter, dead roots, and organic fertilizer, because the contribution of DOM from all these different AOM pools is probably very different and not known at this stage. Additionally, theses sources is very bioavailable to the microbial biomass promoting fast turnover and growing microbial biomass, which contribute to the production of DOM. Hence, the DOM dynamic is closely linked to the dynamic of the AOM pools. According to literature the SOM1 and SOM2 pool are parameterized to have C:P mass ratios of 110:1 and the soil microbial biomass (SMB1 and SMB2) are parameterized to have C:P ratios of 15:1.

10.2 Sorption of DOM

Sorption experiments to the bulk samples from top- and sub soils have been used to calibrate the organic P sorption module of the P-Model. The P-Model is calibrated on data obtained on Burrehøjvej field soil by Gjettermann et al. (2005c).

10.2.1 Soil characteristics

The soil used is located at the Burrehøjvej field at Research Center Foulum in the central part of Jutland, Denmark (9°34′E, 56°29′N). In the previous 9 years (1994-2002) the soil has been covered by grass-clover and grassed by dairy cattle approximately 150 days per year. The soil is classified as a Humic Hapludult. Bulk soil material was sampled every 20 cm from the surface to 130 cm depth; samples from the genetic Ap, EB, and Bt horizons were collected from appropriate depths. For pedogenetic analyses air-dried soil passed through a 2 mm sieve was used. Selected data are listed in Table 8.

For the sorption experiments moist soil stored in the refrigerator were used. The water content of the soil material was measured by drying at 105 ^{o}C every time a sorption experiment was performed. A stock solution of DOM to be used in the sorption experiments was prepared by extraction of the A-horizon material using a chelating, sodium saturated resin, Chelex® 100 Resin, see Gjettermann et al. (2005b) for further details on the extraction procedure.

Table 8. Soil characteristics of Burrehøjvej field soil.

	Ap horizon	EB horizon	Bt horizon
pH	5.68	5.75	4.27
	------------------	*cm*	------------------
Depth	0-30	30-70	70-130
Particle sizes:	------------------	%	----------------
< 2 μm	6.8	12.6	14.8
2-20 μm	12.7	11.4	9.7
20-200 μm	80.5	76.0	75.5
Nutrients:	------------------	%	----------------
Total C	3.0	0.14	0.08
Total N	0.2	0.01	0.005
Total P	0.08	0.04	0.023
Aluminium and iron fractions	----------------	*mmole kg^{-1}*	---------------
$\mathrm{Al_{cbd}}^{\dagger}$	133	115	71
$\mathrm{Al_{ox}}^{\ddagger}$	111	81	62
$\mathrm{Fe_{dcb}}$	80	77	83
$\mathrm{Fe_{ox}}$	62	22	32

†: cbd acronym for citrate-bicarbonate-dithionite. ‡: ox acronym for oxalate.

10.2.2 Sorption experiments with DOM

Six series of sorption experiments were conducted with two pH levels (pH 5 and 7) for each of the Ap, EB, and Bt horizons. A sorption series comprised six bottles (250 ml Blue Cap) with a soil:solution ratio of 1:10, and with initial concentrations of DOM of 0, 0.4, 0.8, 1.7, 3.4 and 4.7 mmole C L^{-1}, respectively. A 10-mM NaCl solution was used as background electrolyte throughout, and all sorption experiments were carried out in duplicate. For each bottle 20 g of moist soil and 150 ml of triple-deionized (TI) water plus 1.8 - 2.0 ml of 1 M NaCl was pre-equilibrated at pH 5 or 7. The pH was adjusted twice using 0.01 M HCl / NaOH in the following hours and once again the following day, right before addition of TI water to reach a total of 200 ml solution, including the addition of 0 - 15 ml DOM stock solution. The bottles were shaken horizontally on a shaking table (60-rev min^{-1}). The amount of DOC, dissolved inorganic phosphorus (DIP), and total dissolved phosphorus (TDP) in solution was measured after 1, 120, 1440, and 4320 minutes of reaction by withdrawing 10 ml of suspension, centrifugation (4000 g) and filtering through 0.45 μm Millipore filters of regenerated cellulose. Quantification of DOC, TDP, and DIP in the supernatant was carried out as described in Gjettermann et al. (2005c).

Sorption isotherms for each soil and pH level were plotted as sorbed amounts of DOC and DOP versus the respective equilibrium solute concentrations of DOC and DOP, respectively. Sorbed DOC is calculated as the difference between added and measured DOC in solution at time of sampling. The DOP solute concentration is calculated as the difference between measured TDP and measured DIP in solution. Sorbed DOP is calculated as the difference between initial DOP concentration and DOP concentration in solution at time of sampling.

Figure 25 and Figure 26 show DOC and DOP sorption isotherms, respectively, for the Ap and Bt horizons, at pH 5 and 7, at different times of reaction. Similar results were obtained for the EB and Bt horizons. At both pH values, the Bt horizon has higher affinity for DOC than the Ap horizon, reflected by the steepness of the curves. After three days of reaction no sorption maximum is observed at pH 5 within the applied DOC concentrations. At pH 7 the very flat curves observed for the Bt horizon material reached a sorption maximum of approximately 15 mmole C kg^{-1} by extrapolating the curves to high solute concentrations (Figure 25).

DOC sorption is much lower at pH 7 than at pH 5. In fact, at pH 7 DOC is desorbed from the Ap horizon DOC no matter how much DOC is applied to the solution. Also the Bt horizon desorbs DOC at pH 7 up to solution DOC concentrations of 2-3 mM. At pH 5 desorption of DOC occurred only when zero or very small amounts of DOC is applied. The results indicate that pH exerts a strong control on the mobility of DOC.

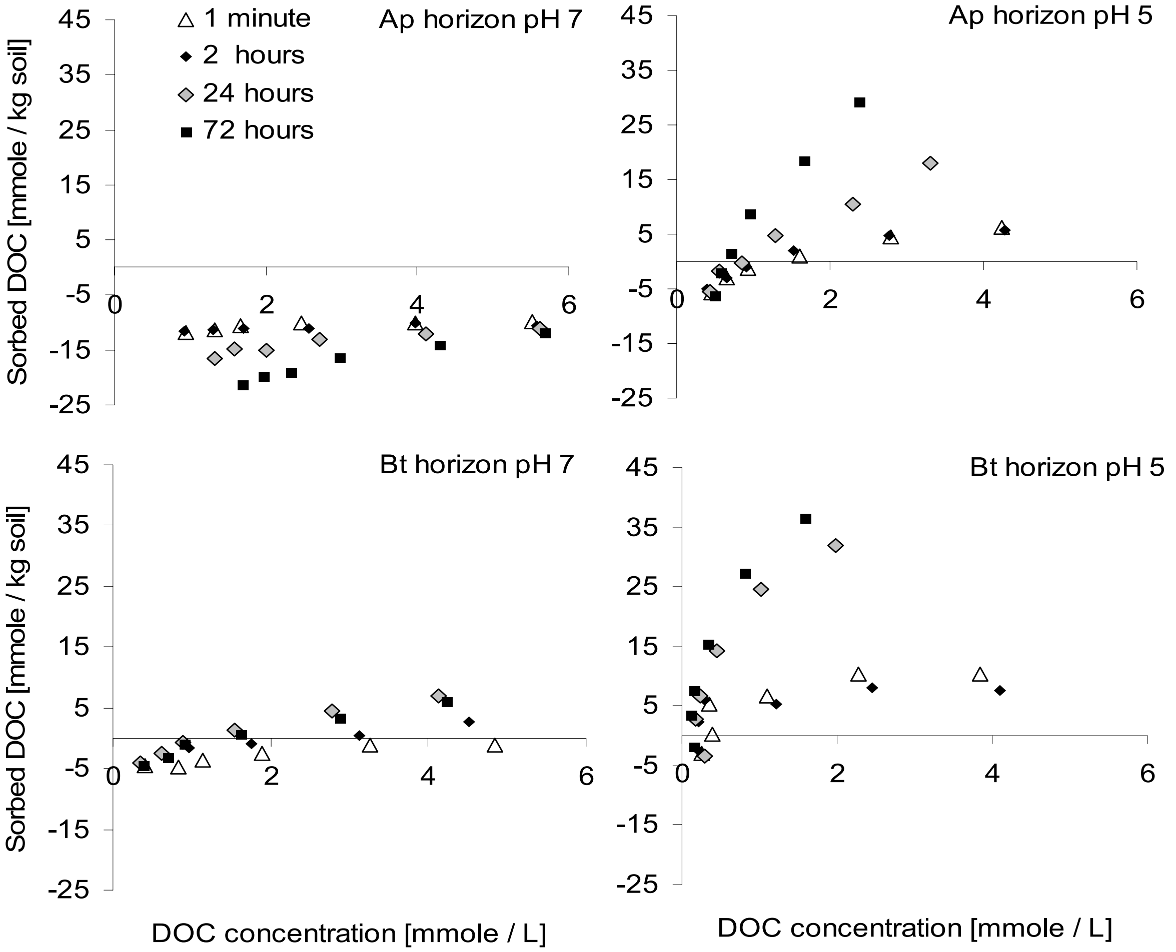


Figure 25. Effect of pH and time of reaction on DOC isotherms for the Ap and Bt horizons. Left: pH 7, right: pH 5. Each data point represents the average of two replicates.

Similar sorption patterns were observed for DOP sorption, but not as pronounced as for DOC sorption (Figure 26). Again, the results obtained with the EB and Bt horizons were similar. A notable pH effect was observed with increasing DOP sorption at decreasing pH, particularly for the Bt horizon. For the Ap horizon the pH effect was limited. The Bt horizon did not sorb DOP at pH 7, but rather desorbed DOP within the tested DOP concentration range (0–0.03 mM DOP). Also the Ap horizon desorbed DOP at pH 7 up to solution DOP concentrations of 0.01 mM. At pH 5, the affinity for sorption of DOP is somewhat higher for the B-horizon than for the A-horizon as for DOC. No sorption maxima are observed within the applied DOP concentrations (Figure 26).

Sorption strongly increases with time in particular at pH 5 and at higher DOC and DOP concentrations. Hence, in our study about 60 % of the sorption observed at 72 hours took place within the first 1 minute of reaction. After 24 hours an average of 90 % of the sorption had occurred. A preliminary study by {Moore, 1992 94 /id} using soil samples initially containing 40 mg DOC L^{-1}, showed that > 90 % occurred during the first 24 hours of reaction (total sorption time was 48 h), and most occurred in the first 2 hours. {McDowell, 1984 134 /id} also noted that equilibrium was essentially completed after 2 hours of reaction. DOP sorption also increases with time in particular at higher DOP concentrations. Thus, the sorption process is relative fast, achieving equilibrium within a couple of days.

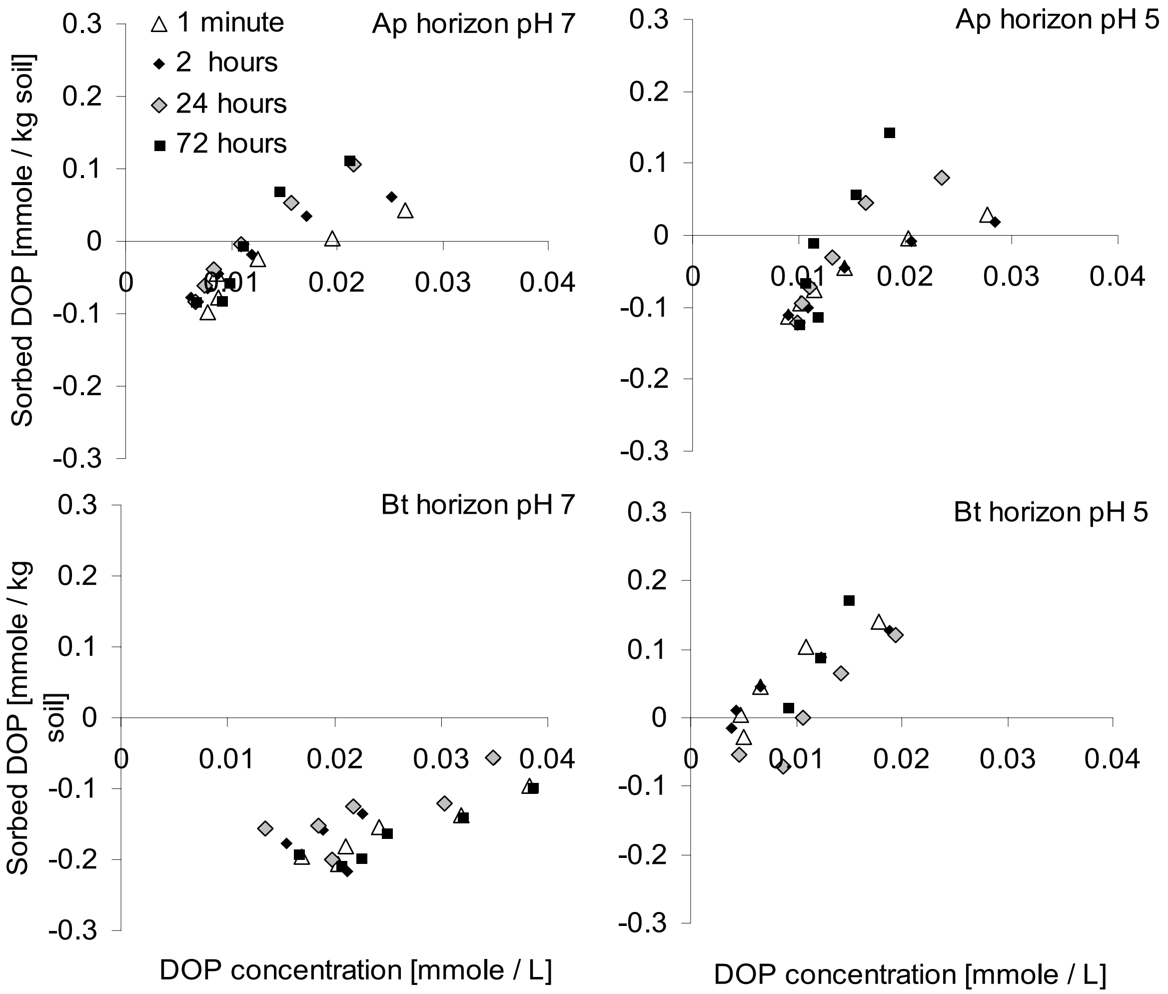


Figure 26. Effect of pH and time of reaction on DOP isotherms for the Ap and Bt horizons. Left: pH 7, right: pH 5. Each data point represents the average of two replicates.

The effects of parameterization of sorption parameters are shown in the following paragraphs. Only two parameters, sorption and desorption rate constants are fitted.

10.2.3 Effect of sorption/desorption rate constants at batch scale

The effect of different sorption/desorption rate constants (1.0, 0.1, 0.01, and 0.001 hour^{-1}) on the solute concentration of dissolved organic P is shown in Figure 27 in a batch experiments applying 0-0.03 mM DOP to a soil:solution system of 1:20. The top curves in the simulations corresponds to the highest concentration levels applied, the next curves corresponds to the next concentration applied, and so on. If rate coefficients equal 1 hour^{-1} the equilibrium is obtained instantaneously as one time step is one hour. Decreasing rate constants decrease change in DOP concentration with time.

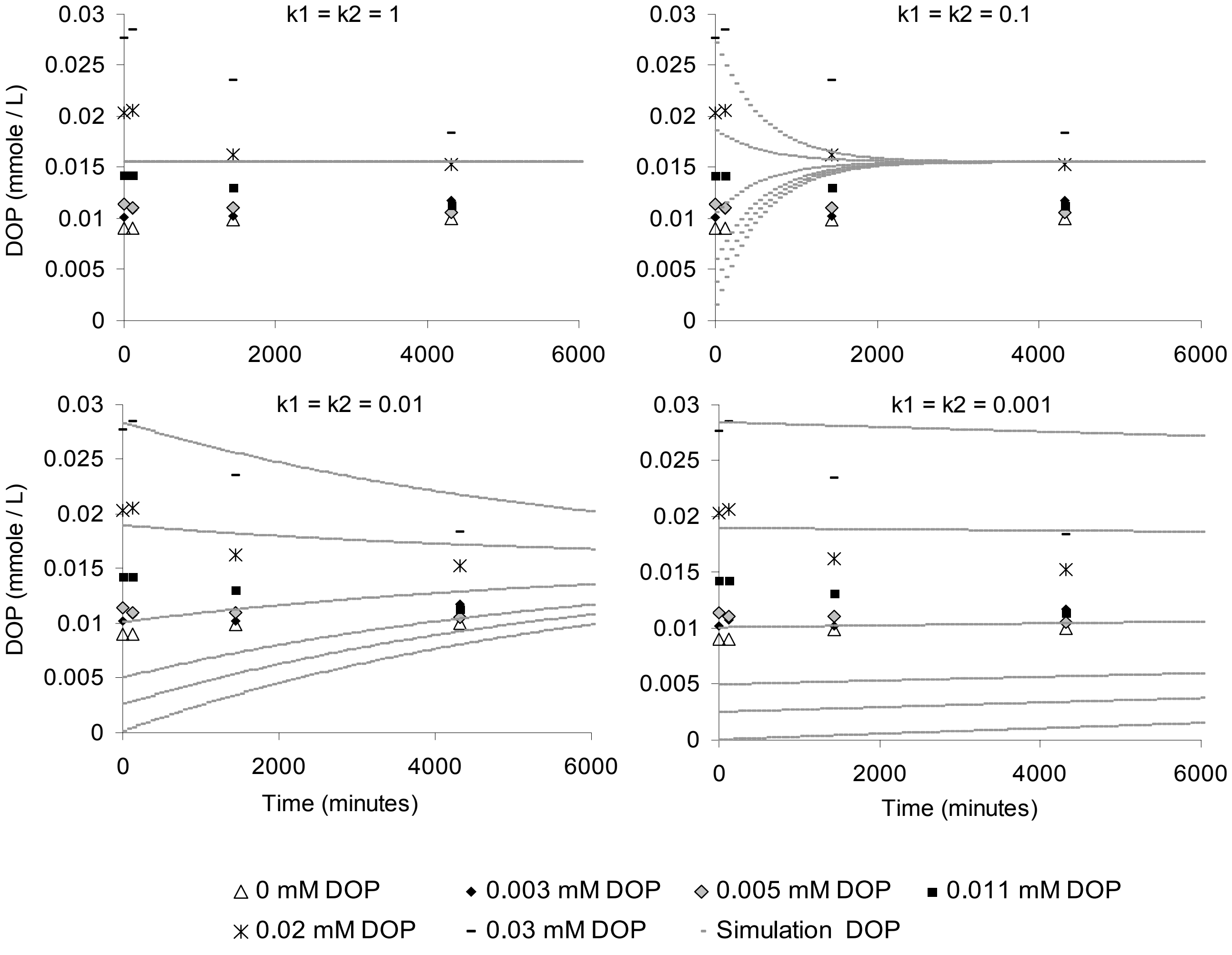


Figure 27. Kinetics of DOP sorption/desorption batch experiments using different values for rate constants when applying 0-0.03 mM DOP to a batch system. Simulations are compared to measured data of sorption experiments, Ap horizon pH 7.

10.2.4 Effect of sorption/desorption rate constants at field scale

The effect of different sorption/desorption rate constants on solute DOC concentration in the soil profile during one year is shown in Figure 28. The results shown are the results of simulations with organic matter turnover, DOM sorption, and solute and water transport. No crops are defined. Depending on whether the DOM concentration is above or below the $DOC_{eq\_optimum}$ then the DOC concentration in the soil is reduced or increased, respectively. If the sorption/desorption rate constant is reduced then the exchange between the SOM2 and DOM pool is reduced. In this test the simulated DOC concentration at different depths (bottom of horizons) is reduced by reducing the sorption/desorption rate constant, especially when reducing the rate constants from 0.01 hour^{-1} to 0.001 hour^{-1}. Additionally, the fluctuations in DOM concentrations are limited using large rate coefficients limiting the effect of DOM turnover by the microbial biomass.

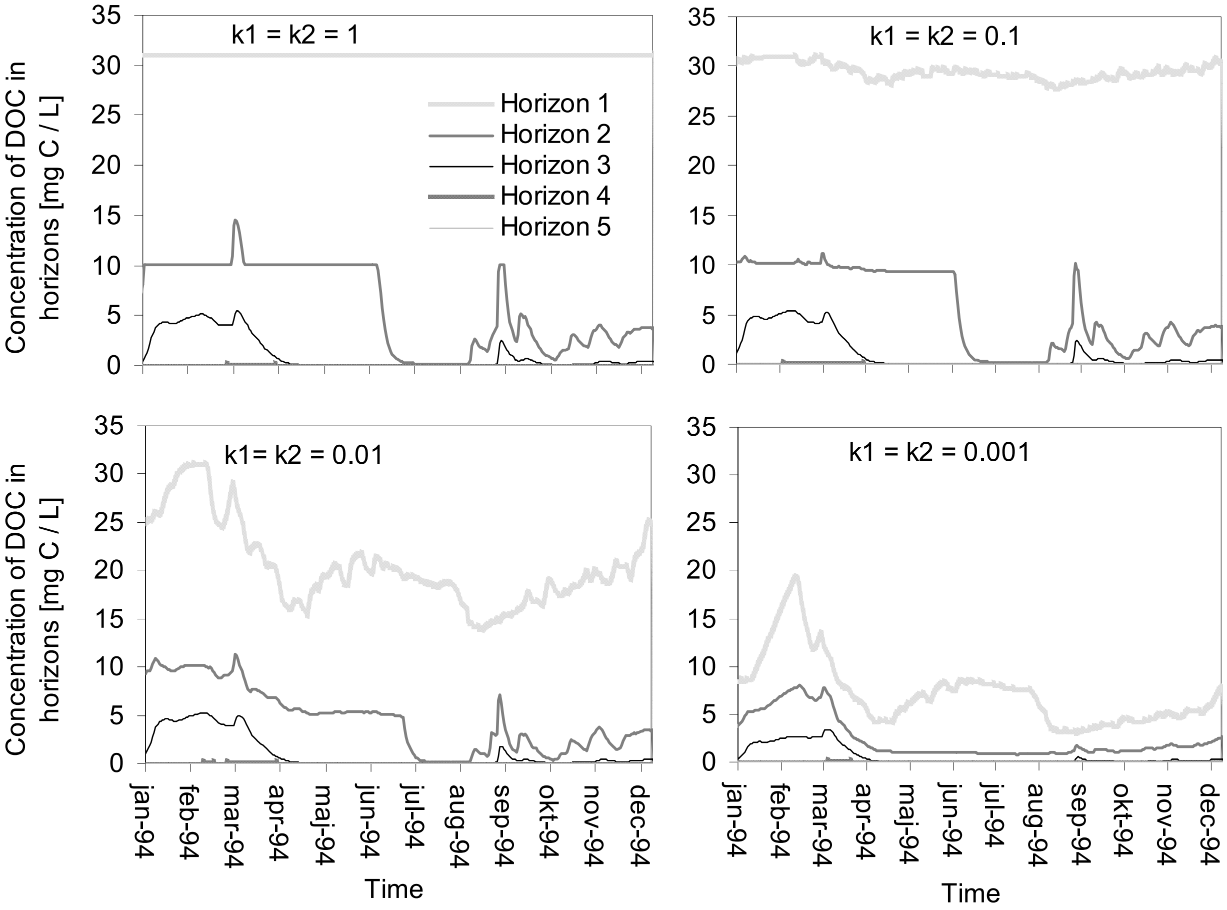


Figure 28. The effect of DOC sorption kinetics using different values for the rate constants on the DOC concentrations in the bottom of the horizons. The results shown are the results of simulations by the P-Model with organic matter turnover, DOM sorption, and solute and water transport. No crops are defined. Horizon 1 = 0-30 cm. Horizon 2 = 30-50 cm. Horizon 3 = 50-70 cm. Horizon 4 = 70-130 cm. Horizon 5 = 130-200 cm.

10.2.5 Calibration results fitting simulation to data of Burrehøjvej field soil

The calibration of DOM sorption has been focused on the DOC and DOP concentrations. DOC and DOP sorption patterns are comparable. A notable effect of pH was observed during the batch experiments, which is not included in the P-Model. Hence, the best fit to sorption data was assumed to be between pH 5 and pH 7.

The best fit of simulations to measured DOC and DOP concentrations in batch experiments was found by using desorption and sorption rate coefficients of 0.001 hour^{-1}. The calibration results of the batch experiments applying 0-4.7 mM DOC to a soil:solution system of 1:20 are shown in Figure 29-Figure 30. The top curves in the simulations corresponds to the highest concentration levels applied, the next curves corresponds to the next concentration applied, and so on. The simulated DOC concentrations simulate DOC sorption experiments very well at pH 7. However, the concentration levels are slightly underestimated. In contrast, at pH 5 the concentration levels are overestimated, especially for the subsoil horizons.

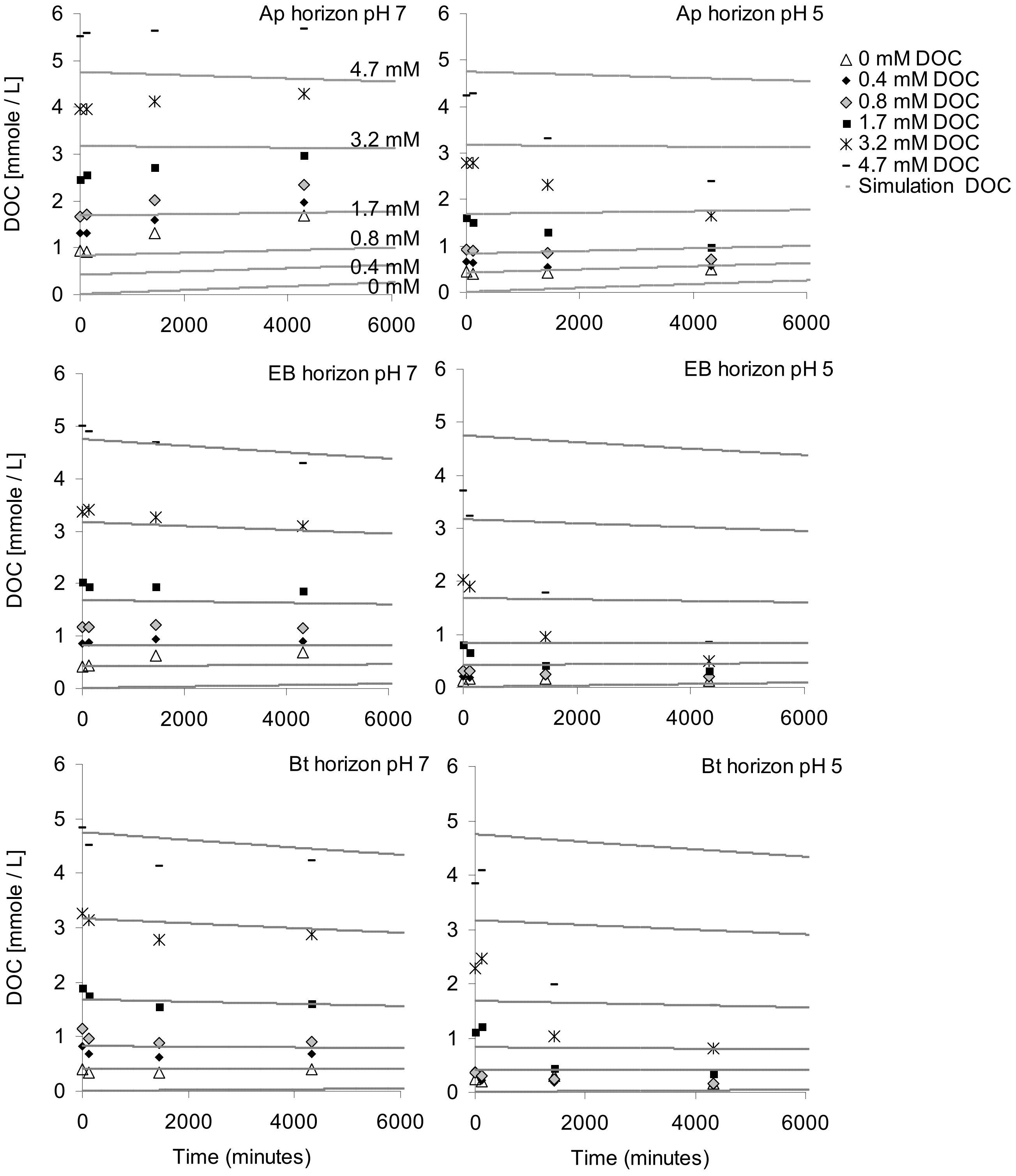


Figure 29. Calibration of DOC sorption with measured data of batch experiments using reaction rate constants k1 = k2 = 0.001 per hour.

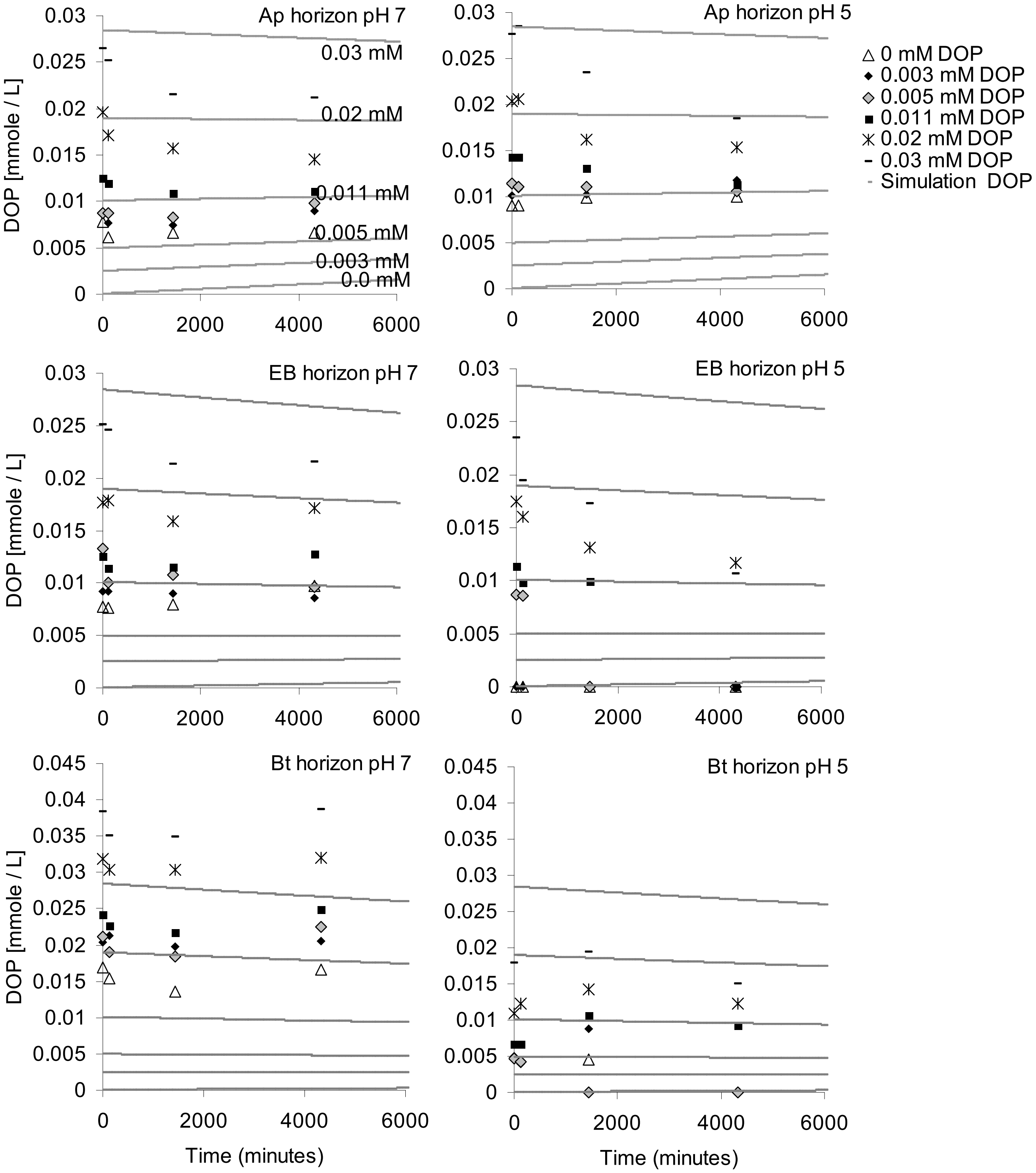


Figure 30. Calibration of DOP sorption with measured data of batch experiments using reaction rate constants k1 = k2 = 0.001 per hour.

The same pattern is obtained for DOP concentrations. The concentration levels are slightly underestimated at pH 7[2]. In contrast, at pH 5 the concentration levels are overestimated, especially for the subsoil horizons.

---

[2] The measured data of DOP in the Bt horizon at pH 7 in the sorption experiments is somehow different from the other horizons. Hence, the data is not considered in the calibration.

10.2.6 Effect of DOM sorption/desorption on the organic matter dynamics

The effects of DOM sorption/desorption on the organic matter dynamics in P-Model are illustrated in Figure 31, with a simulation of continuously applied manure by grassing cows and grass clover in the field. During 7.5 years of simulation the C content of the SOM2 pool is reduced approximately 13.5% when sorption is turned on and only 4.7 % if sorption is turned off. The DOM pool shows strong fluctuations when expressed as amount pr ha, which is due to change in microbial activity. Expressed in concentrations the fluctuations are small (not shown) which is due to change in water content. The SMB2 pool is stimulated by the addition of organic manure, which promotes the biologically production and degradation of DOM. Additionally, the chemically/physically production of DOM occurs by desorption of DOM from the SOM2 pool, Figure 31.

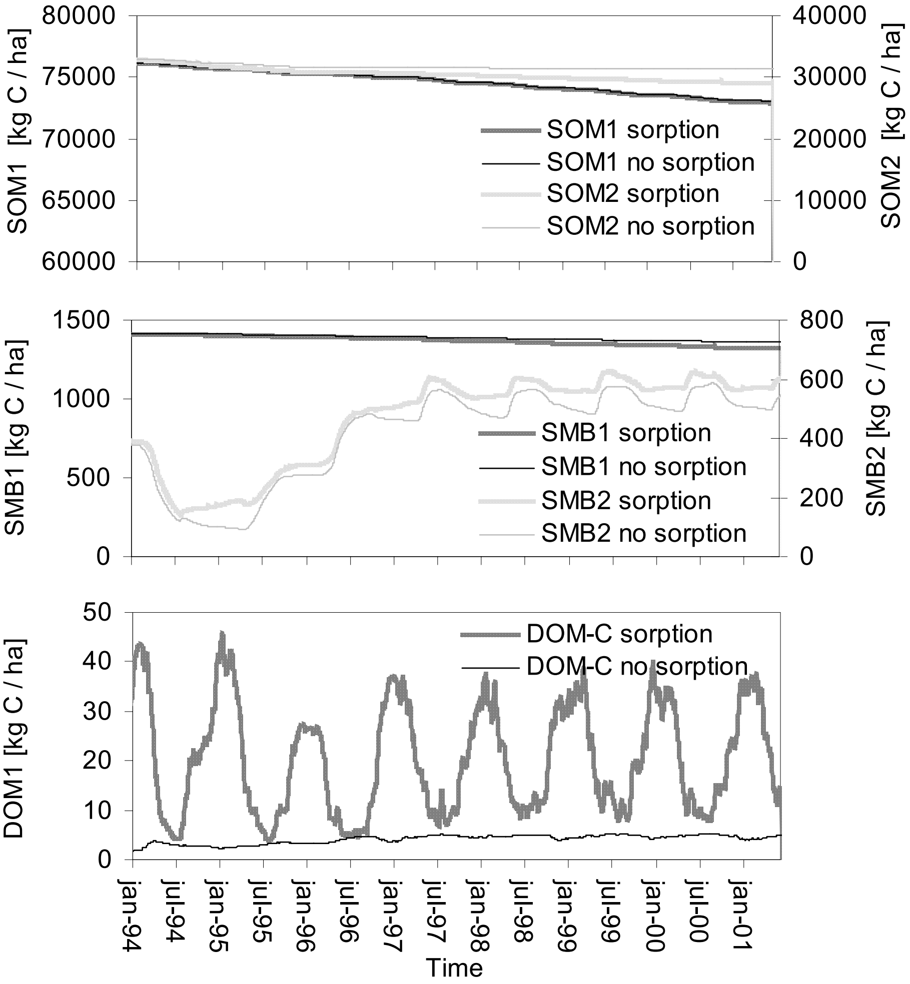


Figure 31. The effect of DOM sorption/desorption on the organic matter turnover in the profile (0-200 cm) with a simulation of continuously applied manure by grassing cows and clover grass in the field.

10.2.7 Summary of DOM sorption/desorption parameterisation

When the rate coefficients equals unity the sorption/desorption process are instantaneous, achieving equilibrium immediately, which is given by the $DOC_{eq\_optimum}$. Depending on the DOM concentration is above or below the $DOC_{eq\_optimum}$ then the DOC concentration in the soil is reduced or increased, respectively. Reducing the sorption/desorption rate coefficients the exchange between the SOM2 and DOM pool is reduced. The best fit of simulations to measured DOC and DOP concentrations in batch experiments was found by using desorption and sorption rate coefficients of 0.001 hour^{-1}. The simulated DOC concentrations are slightly underestimated at pH 7 and overestimated at pH 5, especially at high concentration levels. The effect of pH is not expressed in the simulations, which should be improved in order to simulate DOM sorption/desorption in soil.

10.3 Sorption of inorganic P

Sorption experiments to the bulk samples from top- and sub horizons have been used to calibrate inorganic P sorption module of the P-Model. The P-Model is calibrated on data obtained on Burrehøjvej field soil and on data obtained on Farre soil by (Hansen et al., 1999).

10.3.1 Soil characteristics

Both soils are located in Denmark. The Farre soil is an agricultural soil in the catchments of Gelbæk stream in eastern Jutland and has intense mottling due to redox-mobilization of iron and manganese. Fractures in B$_{tg}$ horizon have a bleached surface layer towards the fracture and a reddish layer towards the matrix soil. The field is artificially drained and has a history of rotational crop production. The Burrehøjvej field soil is located at the Burrehøjvej field at Research Centre Foulum in the central part of Jutland. In the previous 9 years (1994-2002) the soil was covered by grass-clover and grassed by dairy cattle approximately 150 days per year.

Table 9. Soil Chemical data for the Farre and Burrehøjvej field soil profiles.

	Farre Soil		Burrehøjvej field soil	
	Ap-horizon	Btg-horizon	Ap-horizon	Bt-horizon
Depth (cm)	0-26	65-110	0-30	70-130
pH	7.16	6.48	5.68	5.75
Total C in soil (%)	1.4	0.1	3.0	0.1
CEC$_7$ (cmole(+)kg^{-1})	10.2	10.5	10.4	5.8
Particle sizes:				
< 2 mm (%)	15.1	19.9	6.8	14.8
2-20 mm (%)	12.7	11.6	12.7	9.7
20-200 mm (%)	72.2	68.5	80.5	75.5
Al_{cbd}[§] (mmole P kg^{-1})	51.5	36.3	133	71
Al_{ox}[#] (mmole P kg^{-1})	75.6	37.1	111	62
$\mathrm{Fe}_{\mathrm{dcb}}$ (mmole P kg^{-1})	103.7	82.4	80	83
Fe_{ox} (mmole P kg^{-1})	82.4	63.2	62	32
P_{ox} (mmole P kg^{-1})	11.3[¤]	4.4[¤]	14.3	1.9
P_{total} (mmole P mg^{-1})	21.5	7.6	25.9	7.5
$P_{sorp\ max}$[$] (mmole P kg^{-1})	39.9	20.9	47.5	22.1

[§]: *cbd* acronym for citrate-bicarbonate-dithionite.
[#]: *ox* acronym for oxalate.
[¤]: Values predicted from another profile that is located 5 m apart.
[$]: Sorption capacity calculated according to eq. 4-6.

Table 9 shows the chemical data for the two soils. The soil materials are non-calcareous and they contain 7-20 % clay. The clay content increases markedly with increasing depth in the

Farre soil. The CEC_7 values for the soil are around 10 cmole (+) kg^{-1} except for the B-horizon of the Burrehøjvej field, where it is about half this value. The organic matter content in the Ap-horizon of the Burrehøjvej field soil is twice the size as in the same horizon in the Farre soil. The total P content in the Farre Ap horizon is only 80 % of the total P content in the Burrehøjvej field Ap horizon; however, similar amounts of total P exist in both B-horizons. The oxalate extractable P fraction, which can be regarded as a mobilizable P pool (Lookman et al., 1995), amounts to 25-55 % of total P, lowest in the B-horizon of the Burrehøjvej field soil.

10.3.2 Sorption experiments with DIP

Sorption of DIP to the four soil materials was studied at 10 different initial concentrations of added DIP and with sampling of the supernatants at nine different times. In 1000 ml polyethylene bottles 10 g of soil was mixed with 1000 ml of 0.01 M $CaCl_2$ and pre-equilibrated during 24 hours at pH 5.0 and 7.0 for Farre and Burrehøjvej soil, respectively. The pH was kept at 5.0 or 7.0 by repeatedly addition of acid or base. At time zero a NaH_2PO_4 or KH_2PO_4 for Farre and Burrehøjvej soil, respectively, was added to the soil suspension to give initial P concentrations in the range of 0-600 μM P. During pre-equilibration and sorption experiments the soil suspensions were shaken on a shaking table, except for the first five minutes of reaction, during which the samples were shaken manually. After 1, 5, 10, 30, 120, 300, 1440, 4320, and 10080 minutes of reaction for the Farre soil, and after 1, 60, 210, 1440, 4320, 10080, 216000 minutes of reaction for the Burrehøjvej field soil, and for each initial P concentration, 4 ml of the soil suspension was sampled, centrifuged and filtered. Two replicates of each initial concentration were made for both soils.

Figure 32 shows the P sorption isotherms for the Farre and Burrehøjvej field soils for different time of reactions. The P isotherms in Figure 32 are constructed by choosing a fixed time of sampling and plotting total sorbed P as function of dissolved P. Dissolved P is measured as molybdate reactive P. Total sorbed P is estimated here as reversible sorbed P already present in the soil (Hansen et al., 1999; Freese et al., 1992). Oxalate extractable P is used to estimate the reversible sorbed P fraction in the soil (Freese et al., 1992; Lookman et al., 1995). Thus, total sorbed P is calculated as the difference between added P and measured P in samples plus oxalate extractable P, P_{ox}. Langmuir fitted isotherms are also shown in Figure 32.

Table 10. Estimated Langmuir parameters from adsorption isotherms after 1 minute and 7 days of reaction.

	Time of reaction 1 minute	 7 days
Affinity constants:	------ L $mmole^{-1}$ ------	
Farre Ap-horizon	99	34
Farre B-horizon	78	79
Burrehøjvej Ap-horizon	-	129
Burrehøjvej B-horizon	$-^{\#}$	44
Sorption capacities:	------ mmole kg^{-1} ------	
Farre Ap-horizon	9	21
Farre B-horizon	8	18
Burrehøjvej Ap-horizon	12	51
Burrehøjvej B-horizon	2	23

$^{\#}$: Negative values were obtained for the Burrehøjvej field soil after 1 minute.

The isotherms differ with respect to the steepness (affinity) and to the asymptotic level of total P sorption. It was not possible to fit Langmuir to the measured data for the Burrehøjvej field soil after 1 minute of reaction as negative values of the affinity constant was obtained. Table 3 shows estimated Langmuir parameters for the two soils after 1 minute and 7 days of reaction. The affinity 'constant' are in the range of 34-129 L $mmole^{-1}$ after 7 days of reaction. However, no systematic trend can be obtained for the affinity 'constant' due to time of reaction or horizons. The sorption capacities are in the range of 21-51 mmole P kg^{-1} after 7 days of reaction. The increasing sorption capacities estimated from Langmuir fit follows the order: Burrehøjvej Ap >> Burrehøjvej B > Farre Ap > Farre B, Table 10. However, estimated sorption capacity from equation, eq. 4-6, follows the order: Burrehøjvej Ap > Farre Ap >> Farre B > Burrehøjvej B.

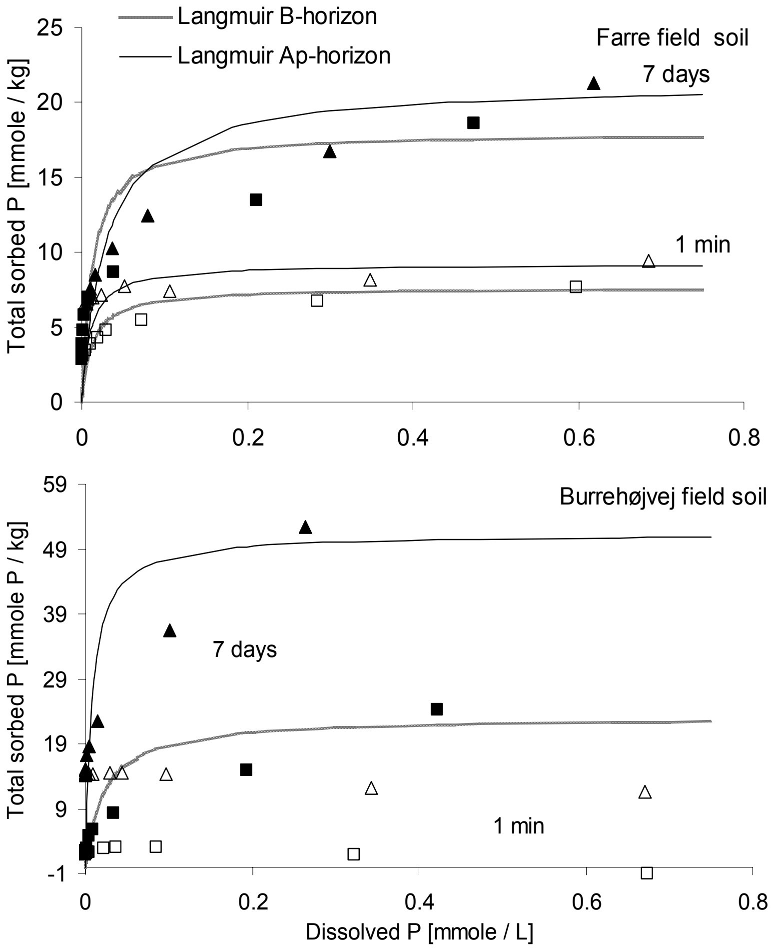


Figure 32. P sorption isotherms for the Farre (pH 5) and Burrehøjvej (pH 7) field soils for different time of reactions, 1 minute and 7 days. Points are measured data and lines are Langmuir fitted isotherms. Triangles = Ap-horizons. Squares = B-horizons. Open points = samples after 1 minute, and filled points = samples after 7 days. Total sorbed P is calculated as the difference between added P and measured P in samples plus oxalate extractable P, P_{ox}.

The amount of P sorbed during 7 days is very different between the two soils. Despite only ¼ of the capacity is occupied initially in the Farre Ap soil, desorption occurs to a large extend. To the Ap horizon of Burrehøjvej field soil, 37 μmole P kg^{-1} have sorbed during 7 day. Only 16 μmole P kg^{-1} has sorbed during the same time in the Ap-horizon of Farre soil, Figure 32. Of the two soils the Ap-horizon of Burrehøjvej field soil contains most initial P also in the reversible, sorbed fraction. After 7 days of P sorption this horizon still contains most P. The B-horizon of Burrehøjvej field soil contains less initial P also in the reversible, sorbed fraction. However, after 7 days of sorption the B-horizon of Farre soil contains less P. Thus, compared to the Farre B-horizon, the B-horizon of Burrehøjvej field soil had sorbed relatively more P after 7 days of sorption.

Important P sorbents in soils are those soil constituents that bear positive charge. Because of the rather high point of zero charge (usually pH 7-10) of metal oxides they are positively charged over the whole pH range usually encountered in soil (Hinsinger, 2001). Being variable charge anions means that their capacity to adsorb anions will increase with decreasing pH, because of the increase in positive charge as a consequence of their larger protonation at low pH (Parfitt, 1978). Therefore, when considering the sole process of sorption of P onto Fe- and Al-oxides, decreasing pH should result in a stronger retention of P.

The huge differences in amount of sorbed P, after 7 days of sorption between the two Ap-horizons, could not be due to the change in pH, since more P is sorbed in the sorption experiments at the highest pH (Burrehøjvej at pH 7). However, Murrmann and Peech (1969) showed that decreasing or increasing the pH of two soils resulted in both cases in an increased release of inorganic P to the solution. However, the soil with the lowest initial soil pH (ca. 4.5) sorbed more at pH below 7 than the other soil with initial pH around 6.5. This is in accordance with our results. The initial soil pH at Burrehøjvej field is lower than the initial soil pH of Farre soil, Table 9. Thus, the initial soil pH may have an effect on inorganic P sorption. Additionally, the difference in sorbed amount of P after 7 days of sorption may be an effect of the relative larger sorption capacity of the Burrehøjvej field soil. Another factor could be the relatively high amount of organic matter in the Burrehøjvej field soil. Organic matter does not sorb P directly in all circumstances, but it can have a strong influence on the sorption or desorption of P by other soil components (Addiscott and Thomas, 2000). However, often the observed effect of organic matter on P sorption have been that organic matter reduces P retention in soil either due to competition of sorption sites (Staunton and Leprince, 1996) or due to complex formation by polyvalent metal ions as Al and Fe (Haynes and Mokolobate, 2001).

The sorption pattern for the two soils differs with respect to amount of sorbed P. The difference is not clearly allocated to specific causes. But initial soil pH, content of soil organic matter, and sorption capacity may affect the sorption pattern.

10.3.3 Parameterization of sorption kinetics

Due to the concept of instantaneous process of adsorption, which implies an adsorption rate coefficient of unity in this model, the other rates have been fitted based on this assumption. The process of absorption has been fitted to obtain equilibrium within 3-4 days. The fixation process is fitted so it does not obtain equilibrium during 14 days. Thus, the relatively slow absorption and desorption rate has been fitted to a value of 0.02 per hour, and the slow fixation/desorption a factor 200 smaller. The slow desorption rate has not been included during these tests. So, whether the slow process is considered reversible or irreversible is still up to discussion of the concept.

k_1: Adsorption rate = 1 hour^{-1}.
k_2: Fast desorption rate = 1 hour^{-1}.
k_3: Relative slow absorption rate = 0.02 hour^{-1}.
k_4: Relatively slow desorption rate = 0.02 hour^{-1}.
k_5: Slow fixation rate = 0.0004 hour^{-1}.
k_6: Slow desorption rate = 0.0004 hour^{-1}.

The effects of different values (1.0, 0.1, and 0.01 hour-1) for the rate coefficients on the sorption dynamic are shown in Figure 33. Instant sorption process occur when the rate constant are equals unity; however, all three process are not in equilibrium when applying 0-0.6 mM P. Decreasing the sorption rate constants the processes occur to a larger extent at non-equilibrium.

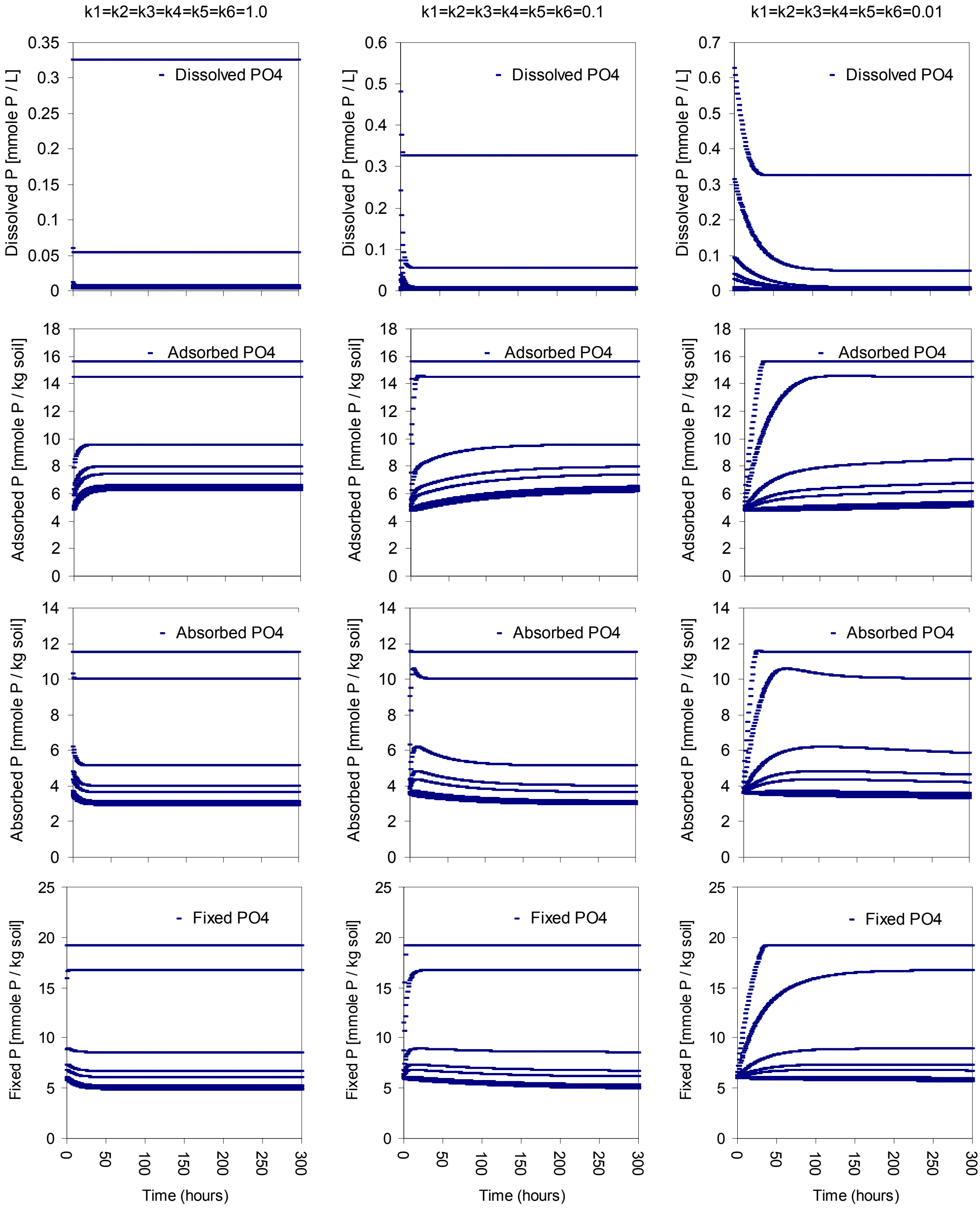


Figure 33. Dynamics of inorganic P sorption model using different rate constants. The simulations show a batch experiments applying 0-0.6 mM P to a 1:100 soil:water system.

10.3.4 Effects of sorption affinity constants

The effects of different values (1.0, 10, and 100 L mmole^{-1}) of the affinity constants on the sorption dynamic are shown in Figure 34. Increasing sorption affinity for all three processes, decrease solute concentration and increasing sorption. At high values of sorption affinities (100 L mmole^{-1}) no desorption occurs for the soil at this state.

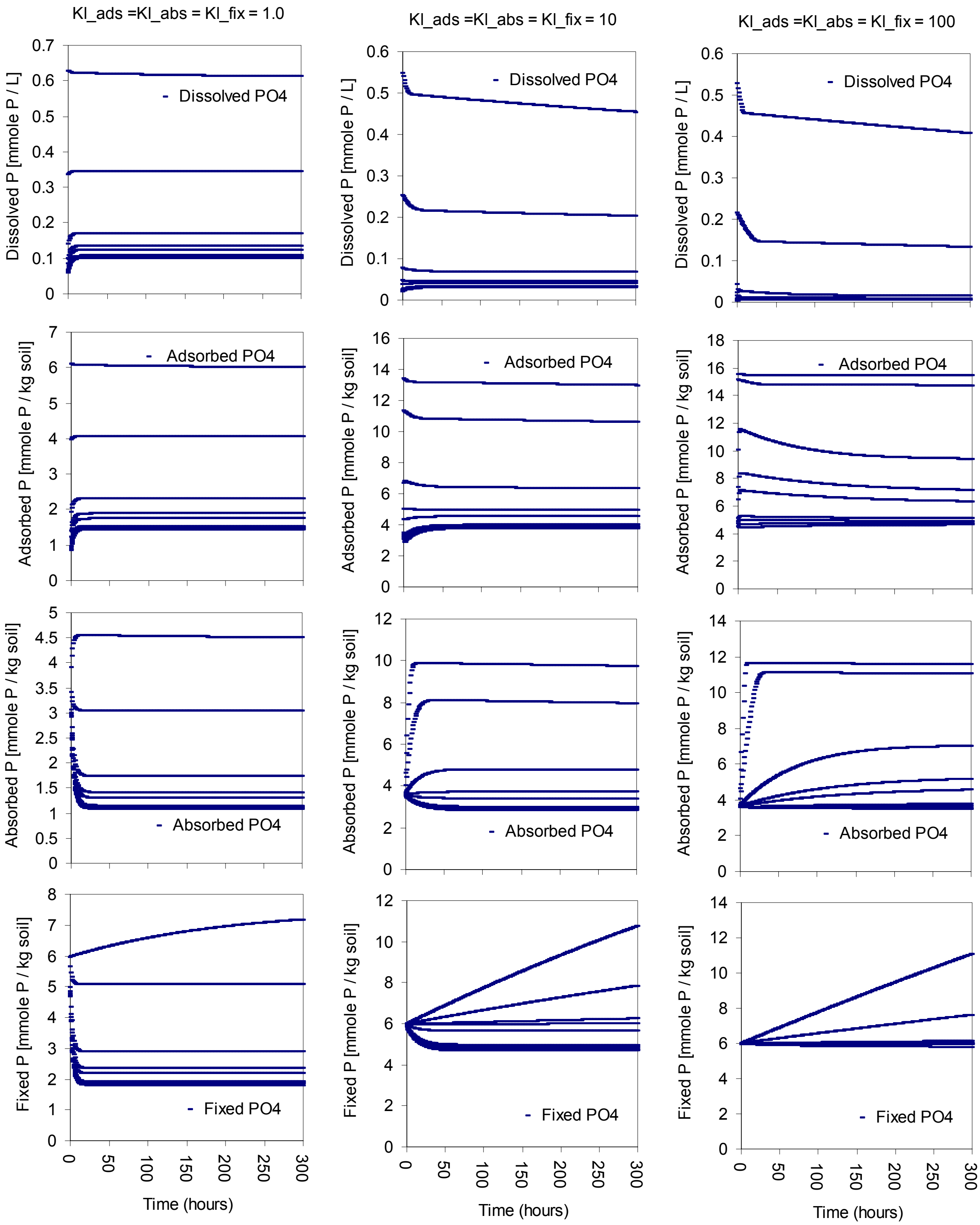


Figure 34. *Dynamic of inorganic P sorption model using different size of affinity constants. The simulations show a batch experiments applying 0-0.6 mM P to a 1:100 soil:water system.*

10.3.5 Effects of sorption capacity distribution

The effects of different distribution between sorbed fractions (adsorbed, absorbed, fixed) on the sorption dynamic are shown in Figure 35. The adsorbed fraction is initialised to be 1/3 of total initially sorbed P and the capacity is adjusted to be1/3 of total capacity.

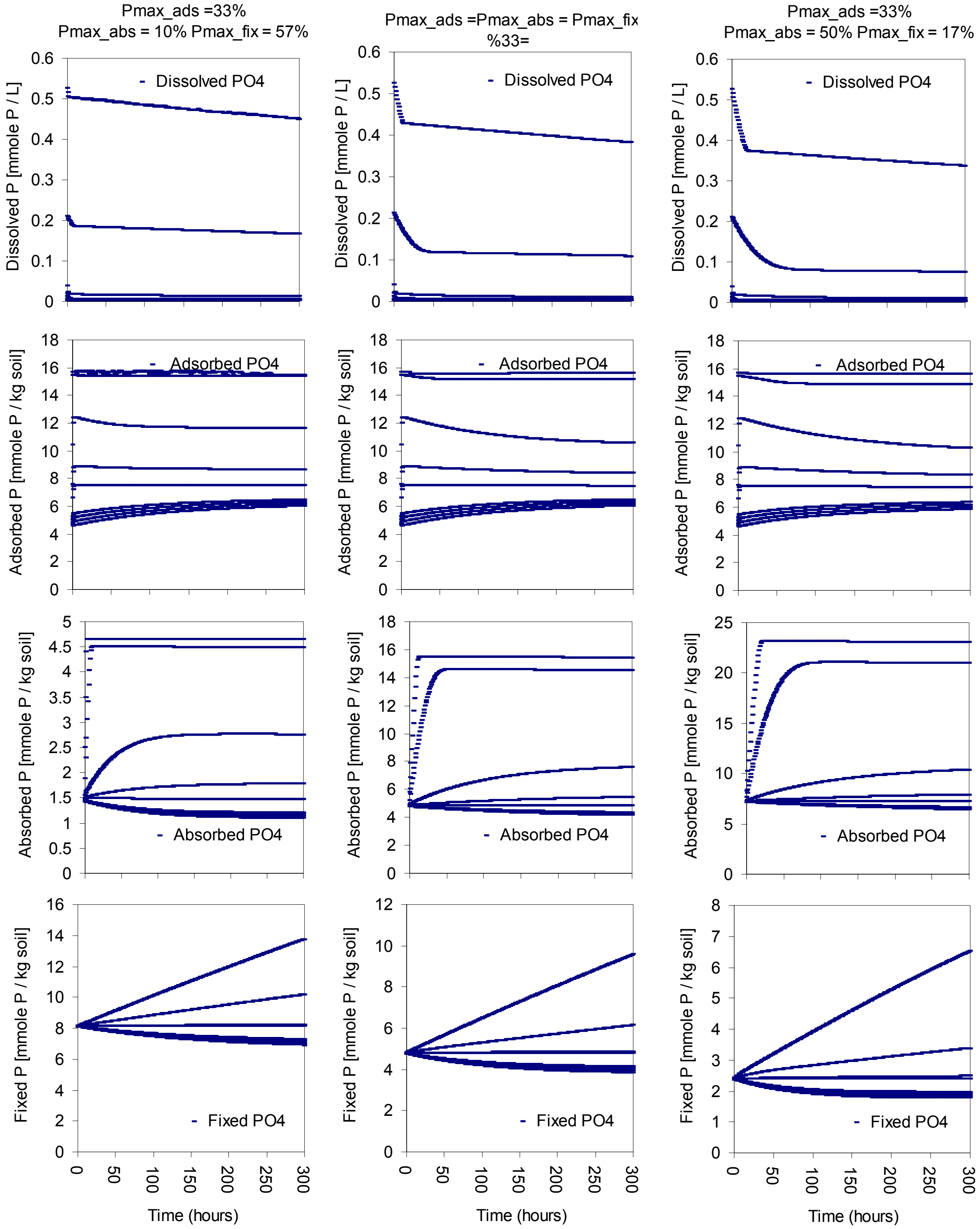


Figure 35. Dynamic of inorganic P sorption model using different distribution of absorbed and fixed fractions. The simulations show a batch experiments applying 0-0.6 mM P to a 1:100 soil:water system.

The absorbed fraction is increased in size in Figure 35 from 10% of total sorbed P (left), to 50 % of sorbed P (right). The fixed fraction is correspondently decreased.

The distribution of the sorption capacities between the three sorption processes was shown to have limited effect of the sorption dynamic, Figure 35. Only when applying high concentration levels (above 0.96 mM P) to the system a notable effect of the distribution was reflected in the solute P concentrations (simulated lines in Figure 35, top). Therefore it was assumed that the distribution of the quickly sorbed fractions was 1/3 of total sorption capacity, as used in another model approach {Van Riemsdijk, 1984 22 /id}; {Van der Zee, 1989 36 /id}.

10.3.6 Fitting sorption affinity constants to data of Burrehøjvej field soil

The relationship between P_{max_ads}, P_{max_abs}, P_{max_fix} and P_{max_total} were analysed based on the assumptions that the fast reaction should be responsible for the amount of sorbed P during the first hour in a laboratory experiment and that the fraction of fast adsorption should be approximately1/3 of the total sorption capacity. In addition, the initial amount of sorbed P in the soil, estimated as oxalate extractable phosphate, is distributed between the three sorbed phases by the same ratios as the capacities. The fraction of the absorbed phase was parameterised by assuming that top and subsoil should be parameterized similarly regarding the sorption capacity weight factors. Additionally, the absorbed phase must have enough capacity to fit the measured data at high concentration levels. The best fit of P sorption/desorption patterns to Burrehøjvej field soil by using $\gamma = 1/3$ for both top and sub soil, resulted in $\varepsilon = 1/4$.

The sorption affinities are very dominating for the sorption dynamics in this concept, Figure 34. The sorption affinities were initially assumed to be in the rage of 10-120 mM^{-1} as often found by fitting Langmuir constants during sorption experiments (e.g. {Hansen, 1999 41 /id}. However, initially sorbed P in the soil is seldom considered when fitting a Langmuir isotherm to the sorption data. This is a problem in this relation as we take into account initially sorbed P in the sorption capacity. The best fit to data of Burrehøjvej field soil was made by using rather high values for the sorption affinity constants (200-400 mM^{-1}), Table 11.

The best fit for concentrations ranging from 3 μM to 600 μM on Burrehøjvej field soil Ap and Btg horizon using parameters values of γ = 1/3 and ε = 1/4 in eq. 4-7 and eq. 4-8, respectively, for the Btg and Ap horizon are shown in Figure 36 and Figure 37. The parameter values used are listed in Table 11.

Table 11. Fitted values of sorption capacity and affinity constants to data of Burrehøjvej field soil.

		Ap-horizon	Btg-horizon
Affinity constants			
	K_{L_ads}	400	400
	$K_{L\_abs} = K_{L\_fix}$	200	200
Sorption capacity weight factor:			
	γ :	1/3	1/3
	ε :	1/4	1/4

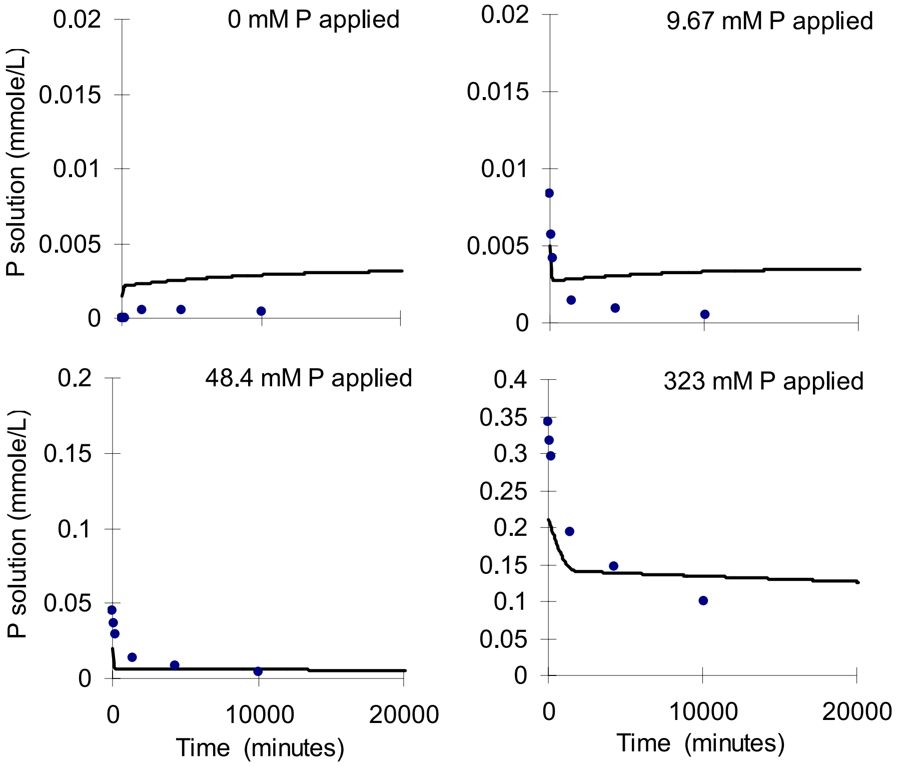


Figure 36. *Phosphate sorption with time for Burrehøjvej Ap horizon. P-Model (line) fitted to experimental results (dots) by parameters listed in Table 11. Note that the y-axis varies.*

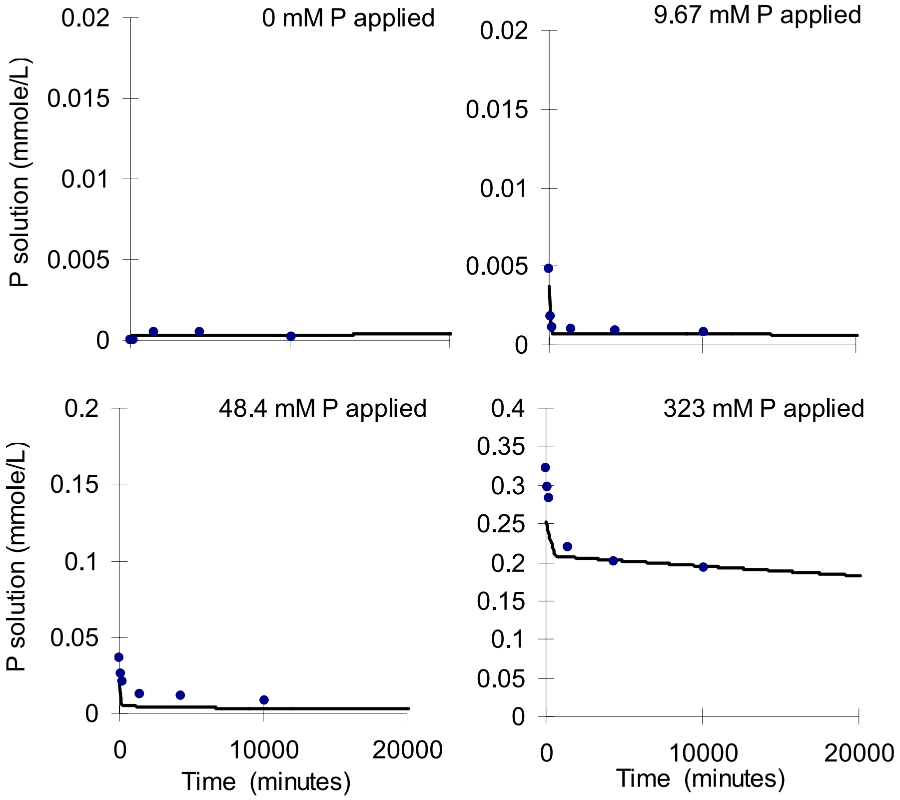


Figure 37. *Phosphate sorption with time for Burrehøjvej Bt horizon. P-Model (line) fitted to experimental results (dots) by parameters listed in Table 11. Note that the y-axis varies.*

10.3.7 Fitting sorption capacity and affinity constants to data of Farre soil

The same parameterization as given for the Ap horizon of Burrehøjvej field soil (Table 11) did not present a satisfactory simulation of P sorption/desorption for the Farre Ap horizon. The simulation underestimated the solute concentration of P immobilising too much. Some examples of simulating P sorption/desorption using the parameterization in Table 11, with different levels of solute P concentration applied to the soil system, are shown in Figure 38.

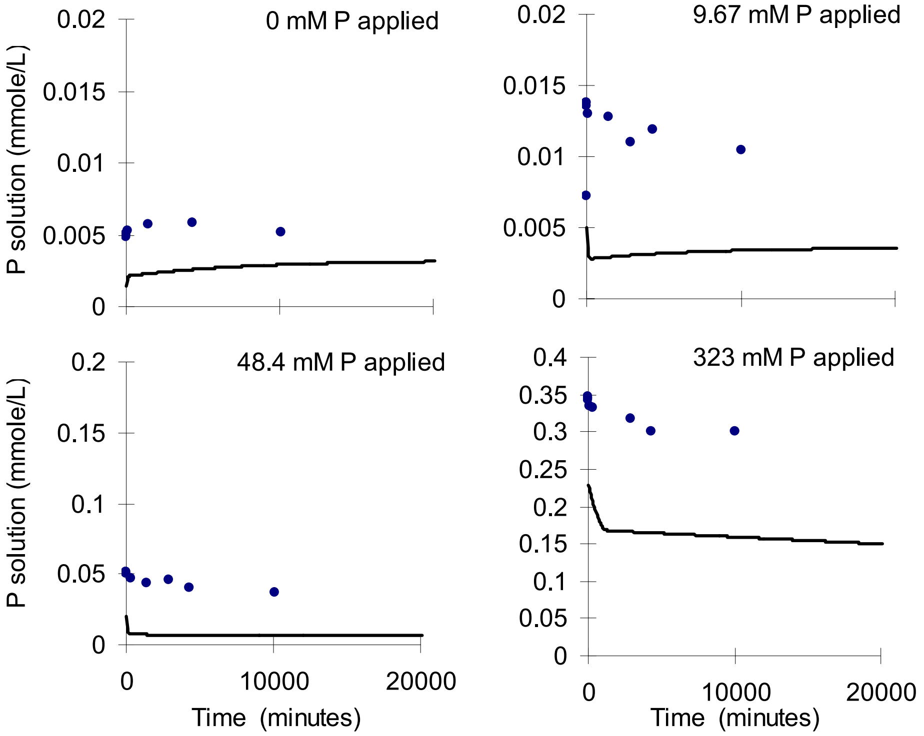


Figure 38. Phosphate sorption with time for the Farre Ap horizon. Simulation by the P-Model (line) by parameters listed in Table 11, and experimental results (dots) obtained by (Hansen et al.,1999). Note that the y-axis varies.

The best fit to the measured data on Farre Ap horizon was calibrated using the same distribution between the sorbed phases (γ and ε) as for Burrehøjvej field soil. The best fit to data of Farre Ap horizon was made by using rather low values for the sorption affinity constants (30-20 mM^{-1}),Table 12.

Table 12. Fitted values of sorption capacity and affinity constants to data of Farre soil.

	Ap-horizon	Btg-horizon
Affinity constant		
K_{L_ads}	30 mM^{-1}	400 mM^{-1}
$K_{L\_abs} = K_{L\_fix}$	20 mM^{-1}	200 mM^{-1}
Sorption capacity weight factors:		
γ :	1/3	1/3
ε :	1/4	1/4

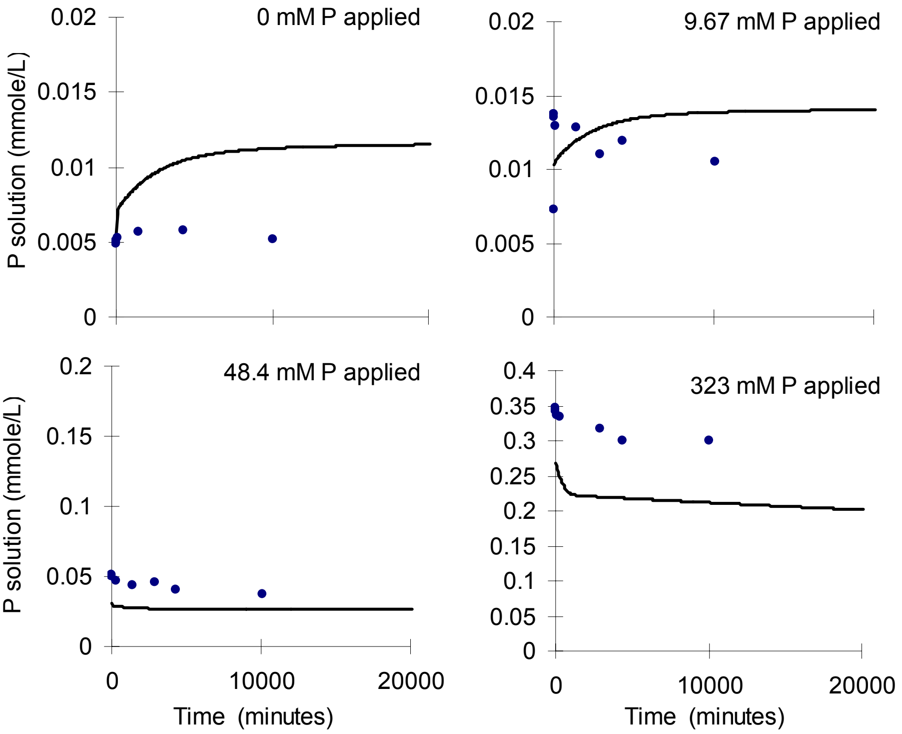


Figure 39. Phosphate sorption with time for Farre Ap horizon. Simulation by the P-Model (line) by parameters listed in Table 12, and experimental results (dots) obtained by (Hansen et al.,1999). Note that the y-axis varies.

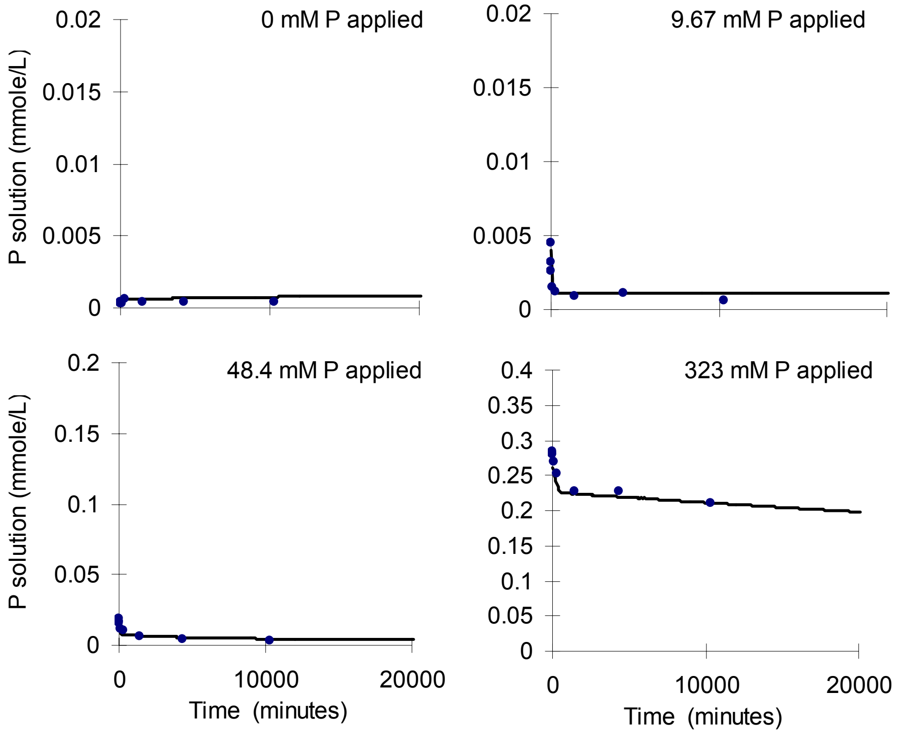


Figure 40. Phosphate sorption with time for Farre Btg horizon. Simulation by the P-Model (line) by parameters listed in Table 12, and experimental results (dots) obtained by (Hansen et al.,1999). Note that the y-axis varies.

Figure 39 and Figure 40 show some of the results of the best fit for Farre soil, Ap and Btg horizon, respectively. At low concentration levels the fitting of the P sorption of the Ap horizon is limited, simulating too much in solution. At high concentration levels the simulation overestimate the concentration of solute P. Thus, it was not possible to make a similar parameterisation for the two Ap horizons.

For the B horizons the simulated concentration of dissolved P using the same parameterization as Burrehøjvej field soil matched experimental data well also for the Farre subsoil. Thus, the same parameterizations are used for both B horizons, Table 11 and Table 12. Only at very low concentrations (< 6 mM P) the fitting for the Btg horizon is limited, simulating slightly more in solution than measured, Figure 40.

10.3.8 Summary of phosphate sorption/desorption parameterisation

Due to the concept of instantaneous process of adsorption the rate constants for absorption and fixation have been fitted based on this assumption. The process of absorption has been fitted to obtain equilibrium within 3-4 days. The fixation process has been assumed not to obtain equilibrium during 14 days. The slow desorption rate has not been included during these tests. So, whether the slow process is considered reversible or irreversible is still up to discussion in the model.

The distribution of the sorption capacities between the three pools was shown to have limited effect of the sorption dynamic The distribution of the total sorption capacity between the three sorbed phases has been parameterised based on the assumption that the quickly sorbed fraction make up 1/3 of total sorption capacity. By fitting the P-Model to data of sorption experiments on two different soils, it was found that 1/4 of the total sorption capacity is allocated to the absorbed phase for both top and subsoils. The rest of the sorption capacity is allocated to the slow, fixed pool.

The sorption affinities are very dominating for the sorption dynamics in this concept .The sorption affinities were initially assumed to be in the rage of 10-120 mM^{-1} as often found by fitting Langmuir constants during sorption experiments (e.g. {Hansen, 1999 41 /id}. However, the best fit to measured sorption data to two sub horizon soils was made by using rather high values for the sorption affinity constants (400-200 mM^{-1}) for the adsorbed, absorbed and fixed processes. The P sorption of the two topsoils behaves very differently which could be due to a pH effect. It was not possible to parameterise the affinity constants for the adsorbed, absorbed and fixed processes similar for the two top horizons. Effects of initial soil pH are not taken into account in the parameterisation.

11 VALIDATION OF DOM MOBILISATION AND IMMOBILISATION

As part of the research program *Regional Groundwater Protection by Optimized Organic Farming Systems* financed by Danish Research Centre for Organic Farming, the described concept of DOM sorption/desorption and microbial production/degradation by the organic mater module was incorporated in the Daisy model. However, DOM is only characterised with respect to C and N in Daisy. The validation of the DOM mobilisation and immobilisation processes were tested by the Daisy model at field scale to data obtained by Vinther et al. (2004) also part of the research program *Regional Groundwater Protection by Optimized Organic Farming Systems*.

This paragraph presents simulations of the Daisy model, comparing simulated DOC, DON, NO3, and NH4 concentrations at three depths in the soil profiles with measured data from suction cups installed at the fields. The only parameter that has been calibrated in these simulations is the turnover rate of DOM.

11.1 Burrehøjvej field experiments

Three fields located at the Burrehøjvej field at Research Center Foulum in the central part of Jutland, Denmark (9°34′E, 56°29′N) have been used for studying DOM leaching at field scale with different soil treatments. Suction cups were installed in the three fields at 30 cm, 60 cm and 90 cm depth. For further information of the field experiments, see Eriksen (2001); Eriksen et al. (2004) and Vinther et al. (2004).

11.1.1 Hydraulic and textural properties

Textural data and soil content of organic matter (humus) plus aluminium and iron fractions are listed in Table 8. Measured hydraulic properties at the Burrehøjvej field soils are listed in Table 13 and estimated hydraulic properties by the hypres function are listed in Table 14. For the soil horizons below 70 cm the hypres function calculates the parameters for the van Genuchten retention curve model with Mualem theory.

Table 13. Soil hydraulic parameters measured at Burrehøjvej field soils (Iversen, 2004). Data are averages of four replicates.

Depth (cm)	Theta residual	Theta saturation	Alpha	n	l	m	Ks (cm / time)
0-20	0.05	0.573	0.032	1.307	0.500	0.235	15.069
20-40	0.05	0.425	0.043	1.307	0.500	0.235	4.952
40-60	0.05	0.351	0.022	1.533	0.500	0.348	4.666

Table 14. Soil hydraulic parameters estimated by the hypres function for the Burrehøjvej field soils.

Depth (cm)	Theta residual	Theta saturation	Alpha	n	l	m	Ks (cm / time)
70-130	0.05	0.297	0.055	1.202	-1.485	0.168	0.452
130-200	0.05	0.288	0.397	1.191	-1.514	0.160	0.288

No data are available for the groundwater table at Burrehøjvej field. However, during soil sampling for textural analysis in February 2003 it was observed that the groundwater table was located at 130 cm depth. Thus it is assumed that the groundwater table rise to 130 cm during the winter and decline to 180 cm during the summer. The depth of 180 cm is the depth of the second last node in the profile and is thereby the lowest depth allowed for the groundwater table in Daisy.

The transport of DOM in the profile is calculated by solving the convection dispersion equation (eq. 5-12) in Daisy. The diffusion coefficient of DOM, D^*_{DOM}, is assumed to be 6,75 * 10^{-6} cm^2 s^{-1}. This is found for DOM in association commercial humic acid as average between two atomic mass unit fractions of humic acid (Hinedi et al., 1997).

11.1.2 Soil treatments

Three cropping sequence with different grassland frequency and management (Table 15) were established in the experimental area for unfertilised grass-clover (perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.).

Table 15. Soil treatments at the three fields at Burrehøjvej.

Year	1. Year ploughed	8. Year ploughed	9. Year grass clover
1993	Undersown grass-clover	Undersown grass-clover	Undersown grass-clover
1994	1. Year grass-clover (grazed)	1. Year grass-clover (grazed)	1. Year grass-clover (grazed)
1995	2. Year grass-clover (grazed)	2. Year grass-clover (grazed)	2. Year grass-clover (grazed)
1996	3. Year grass-clover (grazed)	3. Year grass-clover (grazed)	3. Year grass-clover (grazed)
1997	Barley with undersown ryegrass	4. Year grass-clover (grazed)	4. Year grass-clover (grazed)
1998	Wheat with undersown ryegrass	5. Year grass-clover (grazed)	5. Year grass-clover (grazed)
1999	Barley with undersown ryegrass	6. Year grass-clover (grazed)	6. Year grass-clover (grazed)
2000	Barley with undersown grass-clover	7. Year grass-clover (grazed)	7. Year grass-clover (grazed)
2001	1. Year grass-clover (grazed)	8. Year grass-clover (grazed)	8. Year grass-clover (grazed)
2002	Ploughing, wheat with undersown ryegrass	Ploughing, wheat with undersown ryegrass	9. Year grass-clover (grazed)
Sampling	Wheat stub	Wheat stub	Clover grass

In 2002 the soil was ploughed 2nd of March and the wheat was sown the 5th of April and harvested 20th of August (Vinther et al., 2004 198 /id).

11.2 Setup a *.dai file for grass clover and grazing cattle

The fields covered by grass-clover were grassed by approximately 4.8 dairy cattle approximately 150 days per year. The amount of dung and urine deposited in each field by grazing cows is unknown. However, from grazing experiments by Søegaard et al. (2001) it is assumed that 70 % of dung and urine per cow is deposited at the field. In 1994, 1995 and 1996 it was found that 233, 307, and 308 kg N ha^{-1} $year^{-1}$, respectively, was deposited at the field by grazing cows (Søegaard et al., 2001). It is assumed that the average of N deposited during 1994 -1996 (283 kg N ha^{-1} year^{-1}) is deposited by grazing cows in the following years.

The setup of fertilizer deposited by grazing cows is inspired by Daisy simulations performed earlier at Burrehøjvej (Pedersen, 2003). In Textbox 2 the definition of the fertiliser deposited on the field by grazing cows are shown. The fertilizer is called ‘slurry_fresh’ and is parameterised from data of Sorensen (1998) by Pedersen (2003). It is incorporated to 19 cm depth in the profile due to rooting up in the field by the cows.

*Textbox 2. Defining activity for deposition of fertilizer by grazing cows in a Daisy *.dai file.*

```
(defaction Fer_Clover_average activity
  (fertilize
    (slurry_fresh  (weight 0.4016))          ; corresponds to 283 kg N ha-1 year-1.
    (from 0.0) (to -19.0))
  (wait_days 1))
```

Growing both clover and ryegrass at the same time simulates the grass clover fields. The N_2 fixation has been measured in the same field trial as the field for studying DOM leaching at field scale with different soil treatments. In 1994 and 1995 the N_2 fixation was estimated to 232 and 408 kg N ha^{-1} year^{-1}, respectively (Søegaard et al., 2001). In 1997 and 1998 the N_2 fixation was estimated to 263 and 124 kg N ha^{-1} year^{-1}, respectively (Hansen et al., 2001). In 2001 the N_2 fixation was estimated to 101 kg N ha^{-1} year^{-1} (Eriksen et al., 2004). By sowing only one clover together with ryegrass in the setup the N_2 fixation was underestimated. It was found that growing three clovers at the same time together with only one ryegrass the N_2 fixation was increased to approximate 200 kg N ha^{-1} year^{-1}, Figure 41.

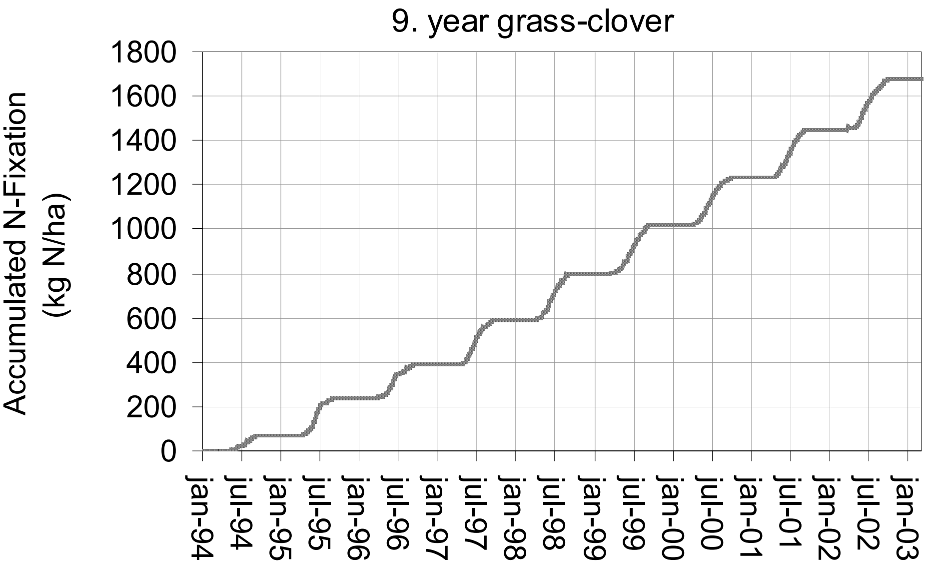


Figure 41. Simulated N_2 fixation by clover in the 9. year grass clover field.

The grazing cows ‘cuts’ the grass clover when the crops has reached a certain level of development stage (DS=0.7) or dry matter content (1000 kg DM ha^{-1}). At least 10 days separate the cuts of the grass clover, Textbox 3. When cutting the grass clover 80 % of leafs, stem, and storage organs are removed from the field and 5 cm stub is left.

*Textbox 3. Defining activity for harvesting white clover by grazing cows in a Daisy *.dai file.*

```
(defaction Clover_Grazing_1 activity
  (wait (or (crop_ds_after "WClover _1"   0.7)
              (crop_dm_over "WClover _1"  1000 [kg DM/ha]) )   )
  (harvest "WClover_1" (leaf 0.80)  (sorg 0.80) (stem 0.80) (stub  5))
 (wait_days 10))
```

11.3 Simulations of different soil treatments at Burrehøjvej fields

Besides textural and hydraulic data, weather data on daily basis at Research Center Foulum are given as input in the *.dai file. For the simulated period, January1993 to April 2003, the total precipitation (snow and rain) and the simulated actual evapotranspiration are shown in Figure 42.

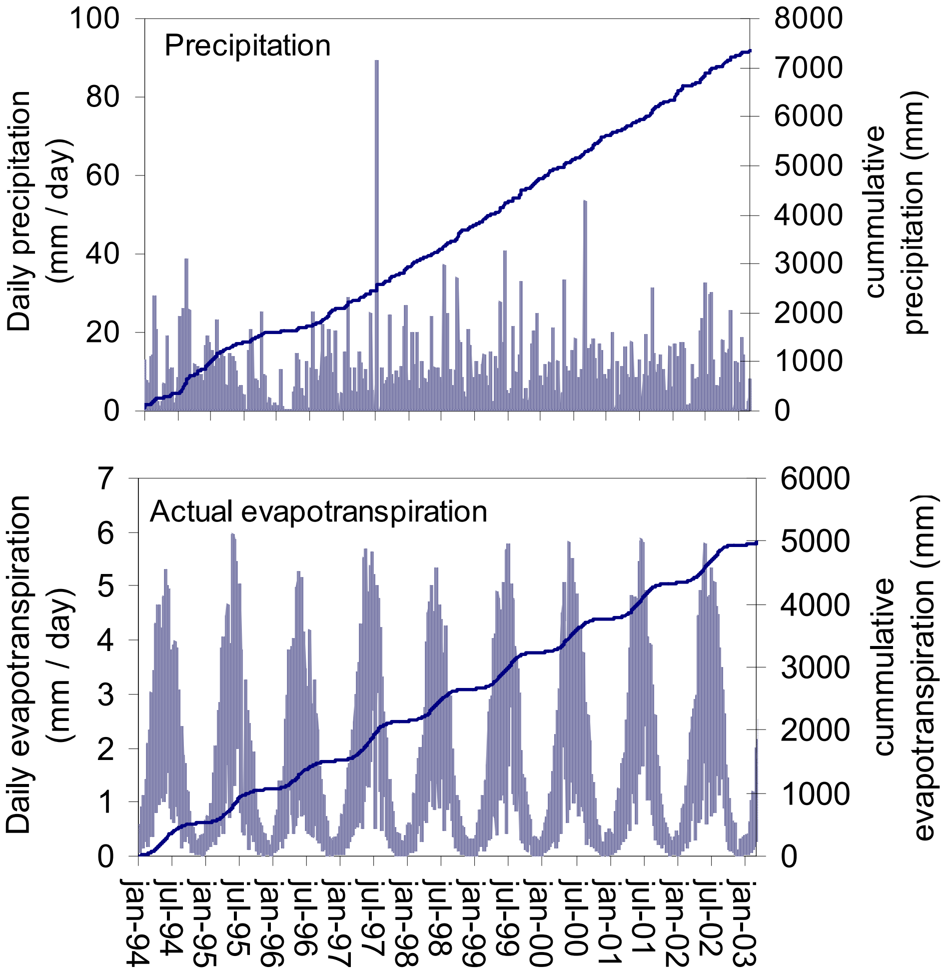


Figure 42. Daily and cumulative precipitation (top) and actual evapotranspiration (bottom) at Burrehøjvej field at Research Center Foulum given by the weather file and calculated by Daisy, respectively.

The crop productions of the three different soil treatments (Table 15) are shown in Figure 43. In 2002 the dry matter production of harvested wheat was 9267 kg/ha (Vinther et al., 2004) which corresponds well with the simulations, Figure 43.

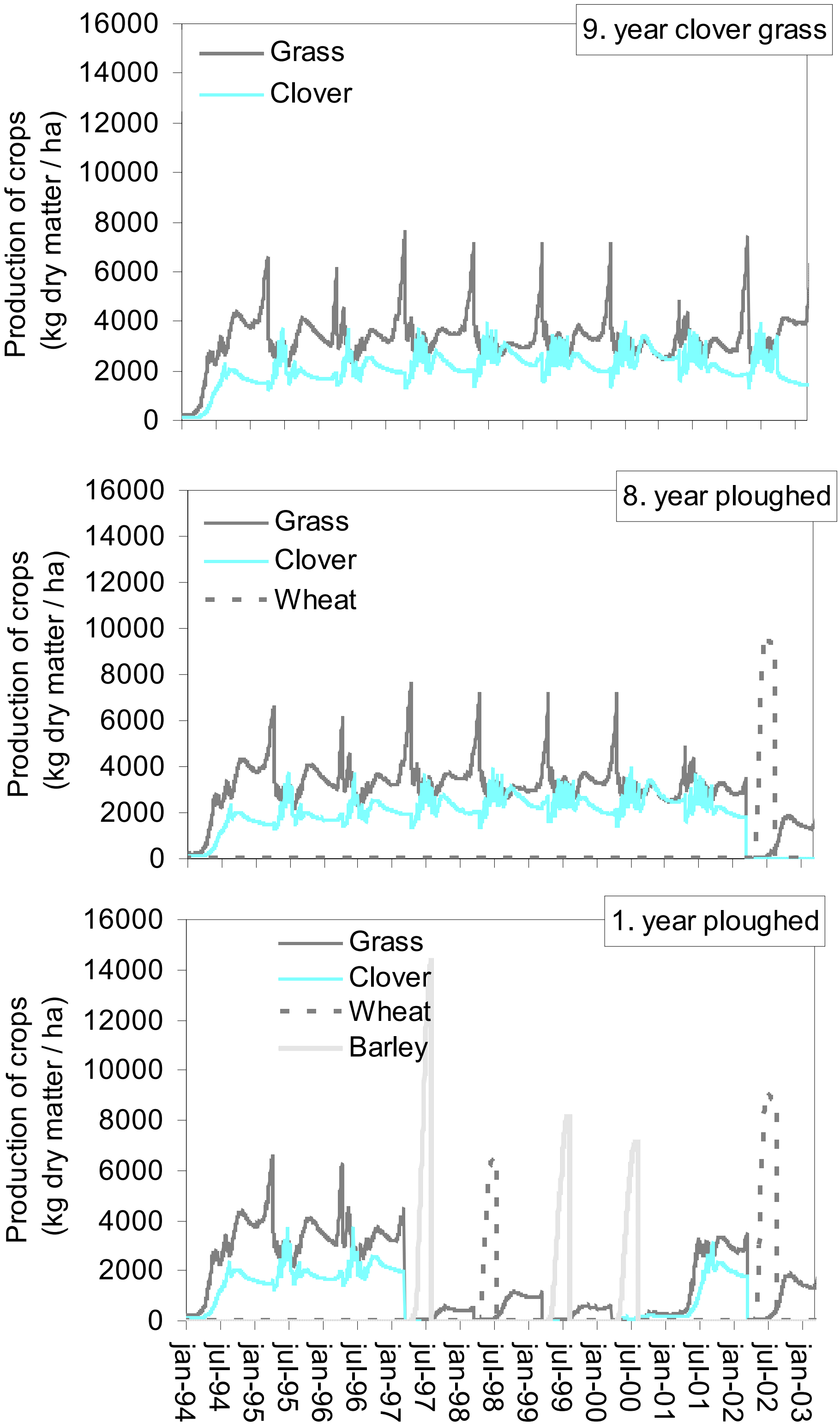


Figure 43. Simulated dry matter production of crops from 1994-2003 in the three fields at Burrehøjvej by the Daisy model. Top figure: 9 years of clover grass with grazing cows. Middle figure: 8 year of clover grass then soil ploughing. Bottom figure: 1 year of clover grass then soil ploughing.

As stated earlier, the turnover rate is calibrated by fitting the simulations at Burrehøjvej field to the measured data of DOC and DON (not shown) sampled from suction cups at 30, 60, and 90 cm depth of the profiles. The results of the calibration are shown in Figure 44 for DOC, in Figure 46 for NO3, and in Figure 47 for NH4.

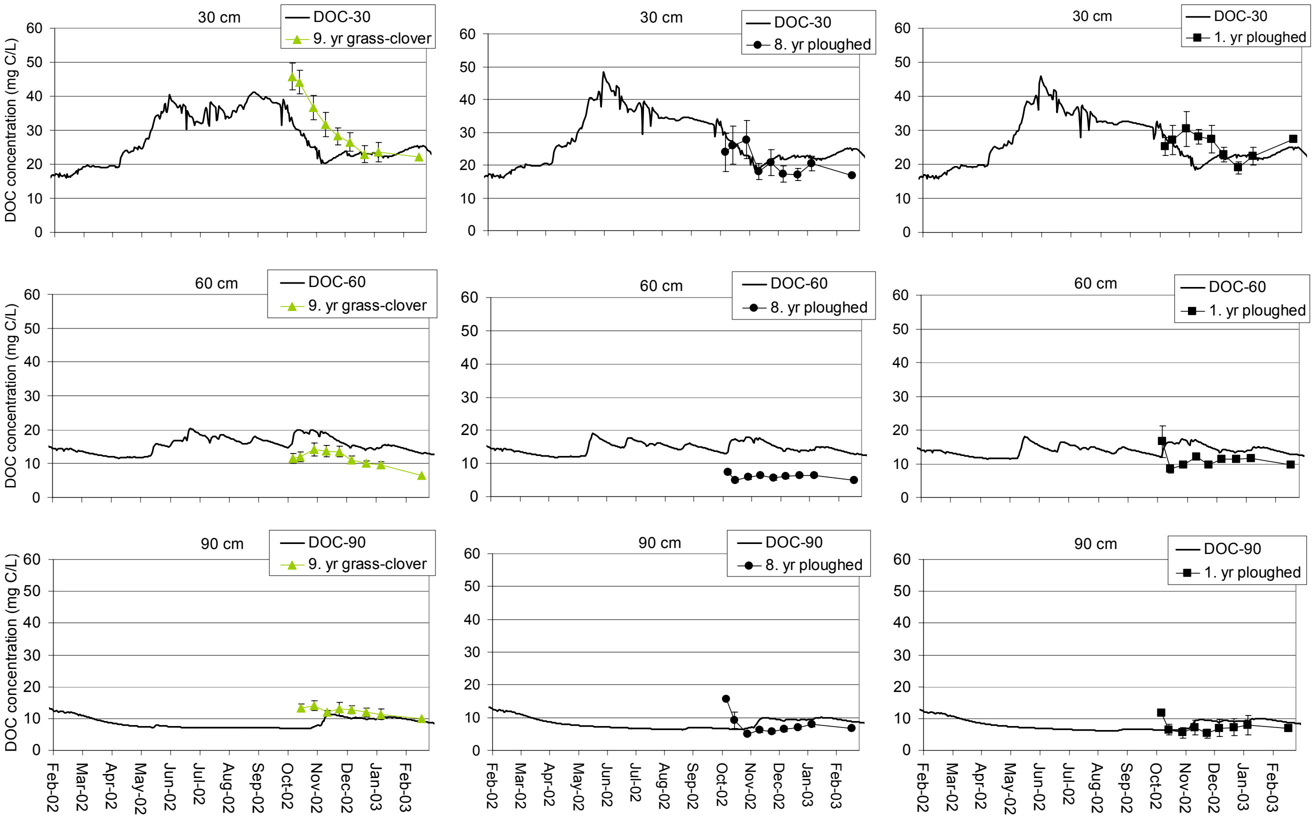


Figure 44. DOC concentration in suction cups (dots) (Vinther et al., 2004) and simulated by the Daisy code (lines) in the Burrehøjvej field soil profiles at 30, 60, and 90 cm depth in three soil treatments: left figures: 9 year grass clover with grazing cows. Middle figures: 8 year grass clover with grazing cows then soil ploughing. Right figures: 1 year grass clover with grazing cows then soil ploughing.

The simulations of DOC and DON concentrations at different depth and with different soil treatments at Burrehøjvej field soils for the last year during sampling are shown in Figure 44 and Figure 45, respectively. In the topsoil the DOM is mainly produced by biological SOM turnover during summertime and chemical/physical release from SOM at all time. Thus, the yearly fluctuation of DOM is related to the microbial activity. High fluctuations of DOM which are produced by microbial activity are diminished by the chemical/physical sorption/desorption process which attempts to keep the DOC concentration steady at a certain level. For the 9 year grass clover field the DOC fluctuations in the topsoil are diminished in the simulations in relation to the measured DOC concentration. For the two other soil treatments the DOC concentration show less fluctuations and is better simulated.

At the depth of 60 cm in the fields, DOC and DON concentrations are overestimated for all treatments in the simulations. This could be due to that the estimated equilibrium concentration of DOC was estimated too high for horizon EB (30-70 cm). However, according to the batch experiments, Figure 29, this should also account for the Bt horizon (70-130 cm) as the simulated DOC concentrations in the batch experiments are overestimated at pH 5. But this is not the case at field scale. At 90 cm depth the DOC and DON concentrations are simulated very well for all soil treatments, Figure 44 and Figure 45. Thus, the overestimation of DOC and DON concentration in the simulations at 60 cm is unclear but factors as DOM transport and macropores also affects the DOC and DON concentrations.

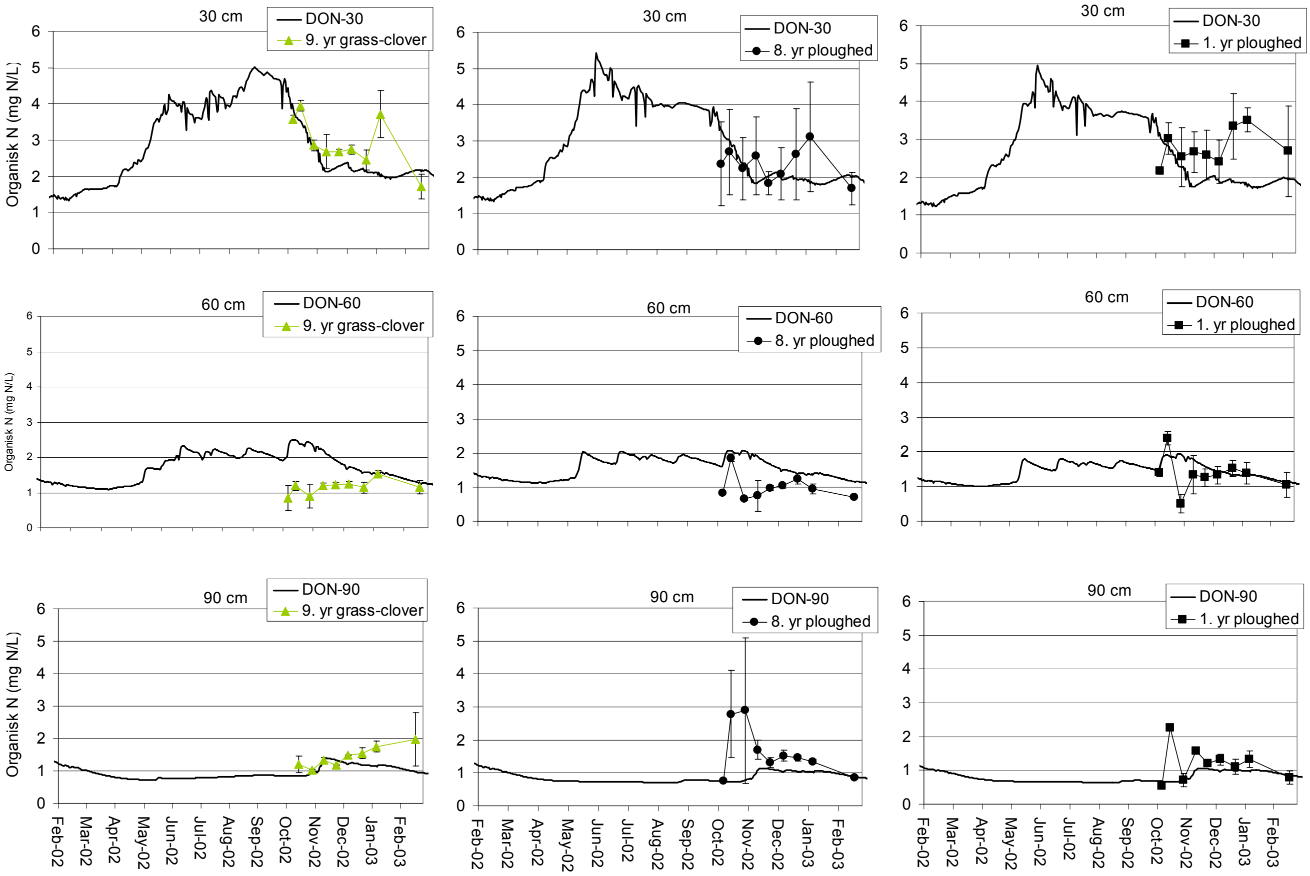


Figure 45. DON concentration in suction cups (dots) (Vinther et al., 2004) and simulated by the Daisy code (lines) in the Burrehøjvej field soil profiles at 30, 60, and 90 cm depth in three soil treatments: left figures: 9 year grass clover with grazing cows. Middle figures: 8 year grass clover with grazing cows then soil ploughing. Right figures: 1 year grass clover with grazing cows then soil ploughing.

Incorporation of grass clover into the soil by ploughing in March 2002 in the 8 year ploughed and 1 year ploughed fields did not show any effects on the DOM concentration during the sampling period the following autumn and winter. However, during the following spring and summer the simulated DOC and DON concentration topped in May and June due to increased microbial activity of the incorporated grass clover. High microbial activity of N rich material leads to increase mineralization. Hence, incorporation of grass clover had great effect on NO3 concentration and dynamic during the following spring and summer, Figure 46.

The simulated concentration of NO3 for the unploughed field, the 9 year grass clover, is simulated very well regarding concentration levels and dynamic. However, for the ploughed fields the model is very sensitive to the dates of ploughing, sowing, and harvesting. Changing the dates of these activities provided better fits (not shown). The mineralization of the incorporated plant residues and the wheat N uptake is not simulated in agreement with the observed pattern for the field with 8 year grass clover and ploughed soil. For the 1 year grass clover and ploughed soil the simulations is better, but still the dynamic for the subsoil is not quite well, Figure 46. It is not clear from the measured data of DOC, DON, and NO3 to whether the incorrect NO3 dynamic is due to DOM mineralization or due to incorporation of high N rich grass clover into the soil.

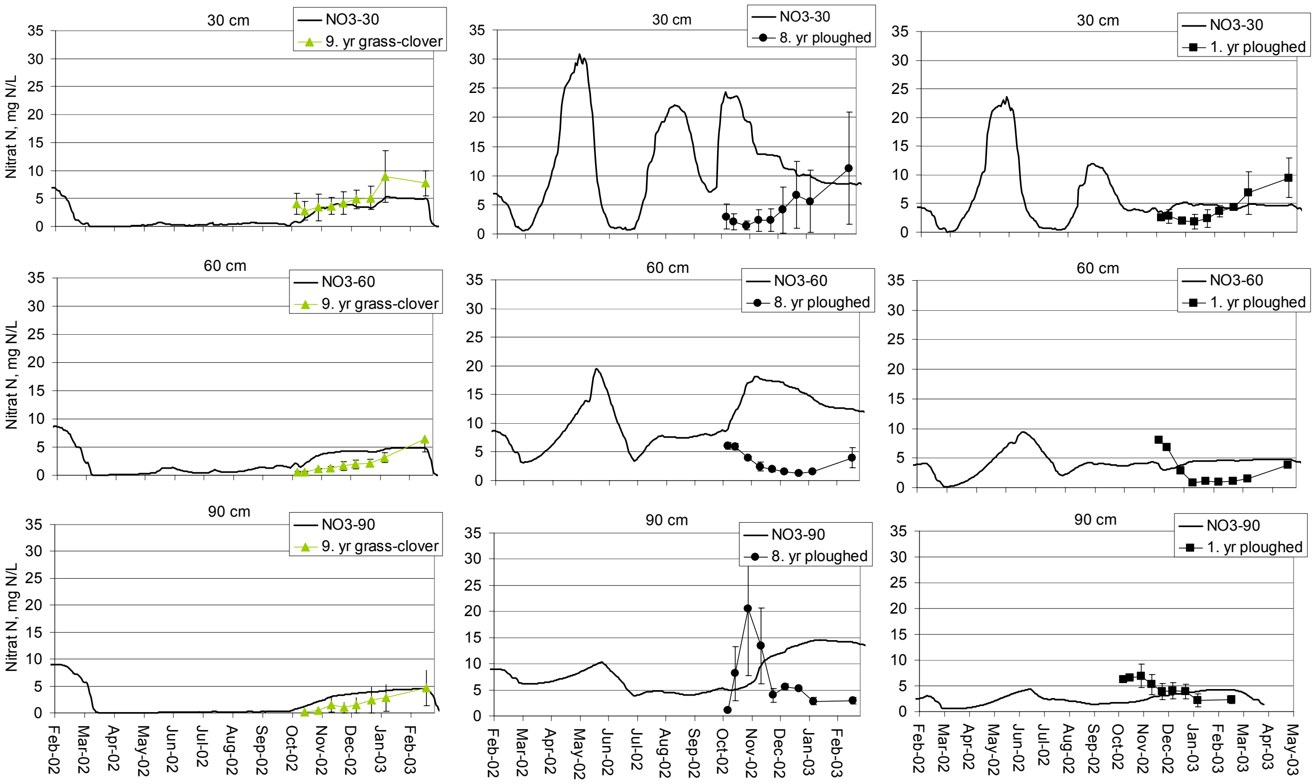


Figure 46. NO3 concentration in suction cups (dots) (Vinther et al., 2004) and simulated by the Daisy code (lines) in the Burrehøjvej field soil profiles at 30, 60, and 90 cm depth in three soil treatments: left figures: 9 year grass clover with grazing cows. Middle figures: 8 year grass clover with grazing cows then soil ploughing. Right figures: 1 year grass clover with grazing cows then soil ploughing.

The concentration of measured and simulated NH4 in all three soil treatments are very small (< 1 mg L^{-1}), Figure 47. From such small values it is not correct to determine whether the NH4 dynamic is simulated correct or not. Only that the concentration levels of NH4 seems to be simulated very well.

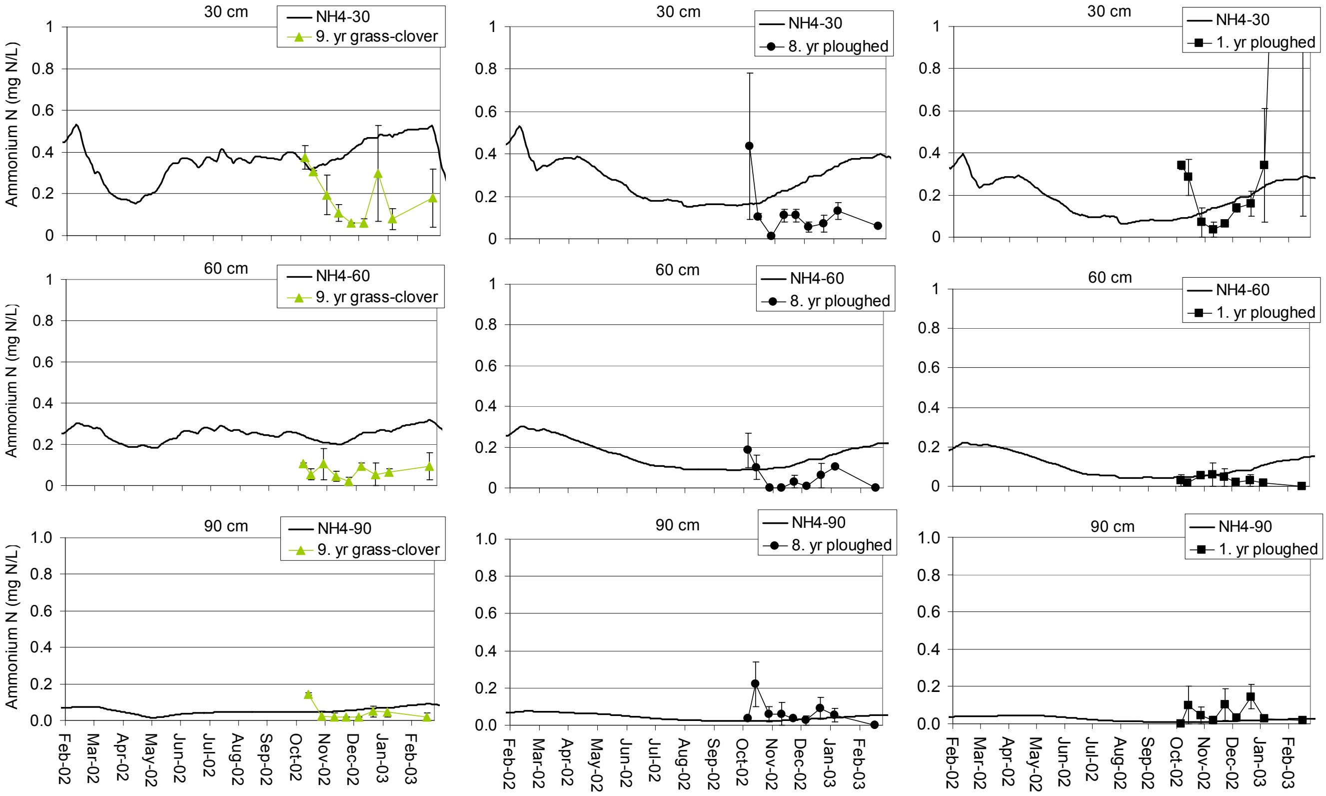


Figure 47. NH4 concentration in suction cups (dots) (Vinther et al., 2004) and simulated by the Daisy code (lines) in the Burrehøjvej field soil profiles at 30, 60, and 90 cm depth in three soil treatments: left figures: 9 year grass clover with grazing cows. Middle figures: 8 year grass clover with grazing cows then soil ploughing. Right figures: 1 year grass clover with grazing cows then soil ploughing.

11.4 Summary of DOM validation

In the topsoil the DOM is mainly produced by biological SOM turnover during summertime and chemical/physical release from SOM at all time. The yearly fluctuation of DOM concentration is related to the microbial activity. High fluctuations of DOM which are related to microbial activity are diminished by the chemical/physical sorption/desorption process which attempts to keep the DOC concentration steady at a certain level. For the 9 year grass clover field the DOC and DON fluctuations in the topsoil are diminished in the simulations in relation to the measured DOC and DON concentration. For the two other soil treatments the DOC and DON concentration show less fluctuations and is better simulated.

At the depth of 60 cm in the fields, DOC and DON concentrations are overestimated for all treatments in the simulations. The cause for this overestimation is unclear but factors as DOM transport and macropores also affects the DOC and DON concentrations. At 90 cm depth the DOC concentrations are simulated very well for all soil treatments.

12 FIGURE CAPTIONS

13 TABLE CAPTIONS

14 REFERENCE LIST

1. Abrahamsen,P. and Hansen,S., 2000. Daisy: an open soil-crop-atmosphere system model. Environmental Modelling & Software, 15(3): 313-330.

2. Addiscott,T.M. and Thomas,D., 2000. Tillage, mineralization and leaching: phosphate. Soil & Tillage Research, 53(3-4): 255-273.

3. Amato,M. and Ladd,J.N., 1992. Decomposition of C-14-Labeled Glucose and Legume Material in Soils - Properties Influencing the Accumulation of Organic Residue-C and Microbial Biomass-C. Soil Biology & Biochemistry, 24(5): 455-464.

4. Beek,J., Van Riemsdijk,W.H. and Koenders,K., 1980. Aluminium and iron fractions affection phosphate binding in a sandy soil treated with sewage water. In: A. Banin and U.Kafkafi (Editors), Agrochemicals in soils. Pergamon Press, Oxford, pp. 369-379.

5. Borggaard,O.K., 1990. Dissolution and adsorption properties of soil iron oxides. Royal Veterinary and Agricultural University. Frederiksberg, Denmark.

6. Borggaard,O.K., 1998. Soil Chemistry in a pedological context. DSR Forlag, p. -258.

7. Borggaard,O.K., Jørgensen,S.S., Møberg,J.P. and Raben-Lange,B., 1990. Influence of organic-matter on phosphate adsorption by aluminium and iron-oxides in sandy soils. Journal of Soil Science, 41(3): 443-449.

8. Breeuwsma,A. and Silva,S., 1992. Phosphorus fertilization and environmental effects in the Netherlands and the Po region (Italy). Agric. Res. Dep. Rep. 57, Winand Staring Centre for Integrated Land, Soil, and Water Res, Wageningen, the Netherlands.

9. Brookes,P.C., Powlson,D.S. and Jenkinson,D.S., 1984a. Phosphorus in the soil microbial biomass. Soil Biology & Biochemistry, 16(2): 169-175.

10. Brookes,P.C., Powlson,D.S. and Jenkinson,D.S., 1984b. Phosphorus in the Soil Microbial Biomass. Soil Biology & Biochemistry, 16(2): 169-175.

11. Burke,I.C., Yonker,C.M., Parton,W.J., Cole,C.V., Flach,K. and Schimel,D.S., 1989. Texture, climate, and cultivation effects on soil organic-matter content in us grassland soils. Soil Science Society of America Journal, 53(3): 800-805.

12. Chauhan,B.S., Stewart,J.W.B. and Paul,E.A., 1979. Effect of Carbon Additions on Soil Labile Inorganic, Organic and Microbially Held Phosphate. Canadian Journal of Soil Science, 59(4): 387-396.

13. Chauhan,B.S., Stewart,J.W.B. and Paul,E.A., 1981. Effect of Labile Inorganic-Phosphate Status and Organic-Carbon Additions on the Microbial Uptake of Phosphorus in Soils. Canadian Journal of Soil Science, 61(2): 373-385.

14. David,M.B. and Vance,G.F., 1991. Chemical character and origin of organic-acids in streams and seepage lakes of central Maine. Biogeochemistry, 12(1): 17-41.

15. Del Campillo,M.C., Van der Zee,S.E.A.T. and Torrent,J., 1999. Modelling long-term phosphorus leaching and changes in phosphorus fertility in excessively fertilized acid sandy soils. European Journal of Soil Science, 50(3): 391-399.

16. Eriksen,J., 2001. Nitrate leaching and growth of cereal crops following cultivation of contrasting temporary grasslands. Journal of Agricultural Science, 136: 271-281.

17. Eriksen,J., Vinther,F.P. and Søegaard,K., 2004. Nitrate leaching and N2 fixation in grasslands of different composition, age and management. Journal of Agricultural Science, 142: 141-151.

18. Foster,R.C., 1986. The Ultrastructure of the Rhizoplane and Rhizosphere. Annual Review of Phytopathology, 24: 211-234.

19. Freese,D., Van der Zee,S.E.A.T. and Van Riemsdijk,W.H., 1992. Comparison of different models for phosphate sorption as a function of the iron and aluminium-oxides of soils. Journal of Soil Science, 43(4): 729-738.

20. Frossard,E., Brossard,M., Hedley,M.J. and Metherell,A., 1995. Reactions controlling the cycling of P in soils. In: H.Tiessen (Editor), Phosphorus in the global environment: transfers, cycles and management. John Wiley and Sons, Chichester, pp. 107-137.

21. Gjettermann,B., Styczen,M., Hansen,H.C.B., Vinther,F.P. and Hansen,S., 2005a. Modelling dissolved organic matter dynamic in soil. European Journal of Soil Science, In preparation.

22. Gjettermann,B., Styczen,M., Hansen,S., Borggaard,O.K. and Hansen,H.C.B., 2005b. Extraction of dissolved organic matter from agricultural soil using a chelating resin. European Journal of Soil Science, In preparation.

23. Gjettermann,B., Styczen,M., Hansen,S., Borggaard,O.K. and Hansen,H.C.B., 2005c. Fractionation of dissolved organic C, N, and P during sorption to agricultural soil. European Journal of Soil Science., In preparation.

24. Grant,R., Laubel,A., Kronvang,B., Andersen,H.E., Svendsen,L.M. and Fuglsang,A., 1996. Loss of dissolved and particulate phosphorus from arable catchments by subsurface drainage. Water Research, 30(11): 2633-2642.

25. Greenland,D.J., 1971. Interactions between humic and fulvic acids and clays. Soil Science, 111(1): 34-&.

26. Guggenberger,G. and Kaiser,K., 2003. Dissolved organic matter in soil: challenging the paradigm of sorptive preservation. Geoderma, 113(3-4): 293-310.

27. Guggenberger,G. and Zech,W., 1992. Retention of dissolved organic-carbon and sulphate in aggregated acid forest soils. Journal of Environmental Quality, 21(4): 643-653.

28. Guggenberger,G., Zech,W. and Schulten,H.R., 1994. Formation and mobilization pathways of dissolved organic-matter - evidence from chemical structural studies of organic-matter fractions in acid forest floor solutions. Organic Geochemistry, 21(1): 51-66.

29. Hagedorn,F., Saurer,M. and Blaser,P., 2004. A C-13 tracer study to identify the origin of dissolved organic carbon in forested mineral soils. European Journal of Soil Science, 55(1): 91-100.

30. Halstead,R.L. and McKercher,R.B., 1975. Biochemistry and cycling of phosphorus. In: E.A.Paul and A.D.McLaren (Editors), Soil Biochemistry. Marchel Dekker, Inc., New York, pp. 31-63.

31. Hansen,H.C.B., Hansen,P.E. and Magid,J., 1999a. Empirical modelling of the kinetics of phosphate sorption to macropore materials in aggregated subsoils. European Journal of Soil Science, 50(2): 317-327.

32. Hansen,H.C.B., Jensen,M.B. and Magid,J., 1999b. Phosphate sorption to matrix and fracture wall materials in a Glossaqualf. Geoderma, 90(3-4): 243-261.

33. Hansen,J.P. and Vinther,F.P., 2001. Spatial variability of symbiotic N-2 fixation in grass-white clover pastures estimated by the N-15 isotope dilution method and the natural N-15 abundance method. Plant and Soil, 230(2): 257-266.

34. Hansen,S., Jensen,H.E., Nielsen,N.E. and Svendsen,H., 1990. DAISY - Soil Plant Atmosphere System Model. Miljøministeriet Miljøstyrelsen, The Royal Veterinary and Agricultural University.

35. Hansen,S., 2002. Daisy, a flexible Soil-Plant-Atmosphere system Model. http://www.dina.kvl.dk/~daisy/: pp. 1-47.

36. Hassink,J., 1997. The capacity of soils to preserve organic C and N by their association with clay and silt particles. Plant and Soil, 191(1): 77-87.

37. Haynes,R.J. and Mokolobate,M.S., 2001. Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: A critical review of the phenomenon and the mechanisms involved. Nutrient Cycling in Agroecosystems, 59(1): 47-63.

38. Heckrath,G., Brookes,P.C., Poulton,P.R. and Goulding,K.W.T., 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. Journal of Environmental Quality, 24(5): 904-910.

39. Hinedi,Z.R., Chang,A.C. and Borchardt,D.B., 1997. Probing the association of fluorobenzene with dissolved organic matter using NMR spectroscopy. Water Research, 31(4): 877-883.

40. Holford,I.C.R., Wedderbu,R.W. and Mattingl,G.E., 1974. Langmuir 2-Surface Equation As A Model for Phosphate Adsorption by Soils. Journal of Soil Science, 25(2): 242-255.

41. Insam,H., 1996. Microorganisms and Humus in Soils. In: A.Piccilo (Editor), Humic Substances in Terrestrial Ecosystems. Elsevier Science B.V., pp. 265-292.

42. Iversen,B.V., 2004. Soil Hydraulic Properties of Burrehøjvej field soil. Danish Institute of Agricultural Sciences. Department of Agroecology. Research Centre Foulum. Personal communication.

43. Jardine,P.M., Weber,N.L. and McCarthy,J.F., 1989. Mechanisms of dissolved organic-carbon adsorption on soil. Soil Science Society of America Journal, 53(5): 1378-1385.

44. Jenkinson,D.S., Hart,P.B.S., Rayner,J.H. and Parry,L.C., 1987. Modelling the turnover of organic matter in long-term experiments at Rothamsted. Intecol Bulletin, 15: 1-15.

45. Jury,W.A. and Fluhler,H., 1992. Transport of Chemicals Through Soil - Mechanisms, Models, and Field Applications. Advances in agronomy, 47: 141-201.

46. Jury,W.A., Gardner,W.R. and Gardner,W.H., 1991. Soil Physics. New York : J. Wiley, cop.

47. Kaiser,K., 2001. Dissolved organic phosphorus and sulphur as influenced by sorptive interactions with mineral subsoil horizons. European Journal of Soil Science, 52(3): 489-493.

48. Kaiser,K., Guggenberger,G. and Zech,W., 1996. Sorption of DOM and DOM fractions to forest soils. Geoderma, 74(3-4): 281-303.

49. Kaiser,K. and Zech,W., 2000. Sorption of dissolved organic nitrogen by acid subsoil horizons and individual mineral phases. European Journal of Soil Science, 51(3): 403-411.

50. Kalbitz,K., Solinger,S., Park,J.H., Michalzik,B. and Matzner,E., 2000. Controls on the dynamics of dissolved organic matter in soils: A review. Soil Science, 165(4): 277-304.

51. Khiari,L., Parent,L.E., Pellerin,A., Alimi,A.R.A., Tremblay,C., Simard,R.R. and Fortin,J., 2000. An agri-environmental phosphorus saturation index for acid coarse-textured soils. Journal of Environmental Quality, 29(5): 1561-1567.

52. Kronvang,B., Iversen,H.L., Jørgensen,J.O., Paulsen,I., Jensen,J.P., Conley,D., Ellermann,T., Lauersen,K.D., Wiggers,L., Jørgensen,L.F. and Stockmarr,J., 2001. Fosfor i jord og vand udvikling, status og perspektiver. Faglig rapport fra DMU. p. -308.

53. Landbrugets Rådgivningscenter, 2001. Håndbog i plantedyrkning. Landbrugets Rådgivningscenter, Landskontoret for uddannelse, Landbrugsforlaget.

54. Lookman,R., Freese,D., Merckx,R., Vlassak,K. and Van Riemsdijk,W.H., 1995a. Long-term kinetics of phosphate release from soil. Environmental Science & Technology, 29(6): 1569-1575.

55. Lookman,R., Van Deweert,N., Merckx,R. and Vlassak,K., 1995b. Geostatistical assessment of the regional distribution of phosphate sorption capacity parameters (fe-ox and al-ox) in northern Belgium. Geoderma, 66(3-4): 285-296.

56. Lynch,J.M. and Whipps,J.M., 1990. Substrate flow in the rhizosphere. Plant and Soil, 129(1): 1-10.

57. Macklon,A.E.S., Grayston,S.J., Shand,C.A., Sim,A., Sellars,S. and Ord,B.G., 1997. Uptake and transport of phosphorus by Agrostis capillaries seedlings from rapidly hydrolysed organic sources extracted from P-32-labelled bacterial cultures. Plant and Soil, 190(1): 163-167.

58. Mansell,R.S., Selim,H.M. and Fiskell,J.G.A., 1977. Simulated transformations and transport of phosphorus in soil. Soil Science, 124(2): 102-109.

59. Marschner,H., 1995. Mineral Nutrition of higher plants. Academic Press.

60. McDowell,W.H. and Likens,G.E., 1988. Origin, Composition, and Flux of Dissolved Organic-Carbon in the Hubbard Brook Valley. Ecological Monographs, 58(3): 177-195.

61. McDowell,W.H. and Wood,T., 1984. Podsolization: Soil Processes control dissolved organic Carbon concentrations in stream water. Soil Science, 137(1): 23-32.

62. McGechan,M.B. and Lewis,D.R., 2002. Sorption of phosphorus by soil, part 1: Principles, equations and models. Biosystems Engineering, 82(1): 1-24.

63. McLaughlin,M.J. and Alston,A.M., 1986. The relative contribution of plant residues and fertilizer to the phosphorus-nutrition of wheat in a pasture cereal system. Australian Journal of Soil Research, 24(4): 517-526.

64. McLaughlin,M.J., Alston,A.M. and Martin,J.K., 1988. Phosphorus cycling in wheat-pasture rotations .2. The role of the microbial biomass in phosphorus cycling. Australian Journal of Soil Research, 26(2): 333-342.

65. Moore,T.R., Desouza,W. and Koprivnjak,J.F., 1992. Controls on the sorption of dissolved organic-carbon by soils. Soil Science, 154(2): 120-129.

66. Moore,T.R., 1989. Dynamics of Dissolved Organic-Carbon in Forested and Disturbed Catchments, Westland, New-Zealand .1. Maimai. Water Resources Research, 25(6): 1321-1330.

67. Mueller,T., Jensen,L.S., Magid,J. and Nielsen,N.E., 1997. Temporal variation of C and N turnover in soil after oilseed rape straw incorporation in the field: Simulations with the soil-plant-atmosphere model DAISY. Ecological Modelling, 99(2-3): 247-262.

68. Murrmann,R.P. and Peech,M., 1969. Effect of pH on Labile and Soluble Phosphate in Soils. Soil Science Society of America Proceedings, 33(2): 205-&.

69. Neff,J.C. and Asner,G.P., 2001. Dissolved organic carbon in terrestrial ecosystems: Synthesis and a model. Ecosystems, 4(1): 29-48.

70. Nodvin,S.C., Driscoll,C.T. and Likens,G.E., 1986. Simple partitioning of anions and dissolved organic-carbon in a forest soil. Soil Science, 142(1): 27-35.

71. Oberson,A., Besson,J.M., Maire,N. and Sticher,H., 1996. Microbiological processes in soil organic phosphorus transformations in conventional and biological cropping systems. Biology and Fertility of Soils, 21(3): 138-148.

72. Oehl,F., Oberson,A., Probst,M., Fliessbach,A., Roth,H.R. and Frossard,E., 2001. Kinetics of microbial phosphorus uptake in cultivated soils. Biology and Fertility of Soils, 34(1): 31-41.

73. Pandey,A., Szakacs,G., Soccol,C.R., Rodriguez-Leon,J.A. and Soccol,V.T., 2001. Production, purification and properties of microbial phytases. Bioresource Technology, 77(3): 203-214.

74. Parfitt,R.L., 1978. Anion adsorption by soil and soil materials. Advances in agronomy, 30: 1-50.

75. Pedersen,A., 2003. Setup of grass clover and grazing cows in Daisy. The Royal Veterinary and Agricultural University. Department of Soil Science. Personal communication.

76. Pierzynski,G.M., Sims,J.T. and Vance,G.F., 2000. Soils and environmental quality. In: CRC Press, Boca Raton, Florida.

77. Poulsen,H.D., Børsting,C.F., Rom,H.B. and Sommer,S.G., 2001. Kvælstof, fosfor og kalium i husdyrgødning - normtal 2000. DJF Rapport. Husdyrbrug Nr. 36.

78. Qualls,R.G. and Haines,B.L., 1992. Biodegradability of dissolved organic-matter in forest throughfall, soil solution, and stream water. Soil Science Society of America Journal, 56(2): 578-586.

79. Qualls,R.G., Haines,B.L. and Swank,W.T., 1991. Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. Ecology, 72(1): 254-266.

80. Rubæk,G.H., Djurhuis,J., Heckrath,G., Olesen,S.E. and Østergaard,H.S., 2001. Fosfor i dansk landbrugsjord. In: Ministeriet for Fødevarer, Landbrug og Fiskeri. Danmarks Jordbrugsforskning, pp. 2-6.

81. Ryden,J.C., Mclaughlin,J.R. and Syers,J.K., 1977. Mechanisms of Phosphate Sorption by Soils and Hydrous Ferric-Oxide Gel. Journal of Soil Science, 28(1): 72-92.

82. Sakadevan,K. and Bavor,H.J., 1998. Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. Water Research, 32(2): 393-399.

83. Søegaard,K., Lund,P., Vinther,F.P., Petersen,S.O. and Aaes,O., 2001. Afgræsning med malkekøer. Betydningen af kløveriblanding, BPV- AAT-niveau i kraftfoder, slæt/afgræsning, ammoniakfordampning og N2 fiksering for udbytter og N-balancer. In.

84. Sollins,P., Homann,P. and Caldwell,B.A., 1996. Stabilization and destabilization of soil organic matter: Mechanisms and controls. Geoderma, 74(1-2): 65-105.

85. Sollins,P., Robertson,G.P. and Uehara,G., 1988. Nutrient Mobility in Variable-Charge and Permanent-Charge Soils. Biogeochemistry, 6(3): 181-199.

86. Sorensen,P., 1998. Effects of storage time and straw content of cattle slurry on the mineralization of nitrogen and carbon in soil. Biology and Fertility of Soils, 27(1): 85-91.

87. Sparling,G.P., 1985. The soil biomass. In: D.Vaughan and R.E.Malcom (Editors), Soil organic matter and biological activity. Martinus Nijhoff / Cr W. Junk Publishers, Dordrecht, pp. 223-263.

88. Staunton,S. and Leprince,F., 1996. Effect of pH and some organic anions on the solubility of soil phosphate: Implications for P bioavailability. European Journal of Soil Science, 47(2): 231-239.

89. Stevenson,F.J., 1994. Humus chemistry : genesis, composition, reactions. John Wiley, cop, New York, N.Y. : .

90. Stewart,J.W.B. and Sharpley,A.N., 1987. Controls on dynamics of soil and fertilizer phosphorus and sulfur. In: R.F.Follett, J.W.B.Stewart, C.V.Cole, and J.F.Power (Editors), Soil fertility and organic matter as critical components of production systems. Soil Science Society of America, Inc., America Society of Agronomy, Inc., Publishers, Madison, USA, pp. 101-121.

91. Stewart,J.W.B. and Tiessen,H., 1987. Dynamics of soil organic phosphorus. biogeochemistry, 4(1): 41-60.

92. Tarafdar,J.C. and Claassen,N., 1988. Organic Phosphorus-Compounds as a Phosphorus Source for Higher-Plants through the Activity of Phosphatases Produced by Plant-Roots and Microorganisms. Biology and Fertility of Soils, 5(4): 308-312.

93. Tegen,I. and Dorr,H., 1996. C-14 measurements of soil organic matter, soil CO2 and dissolved organic carbon (1987-1992). Radiocarbon, 38(2): 247-251.

94. Tipping,E., 1998. Modelling the properties and behaviour of dissolved organic matter in soils. Mitteilgn. Dtsch. Bondenk. Gesellsch, 87: 237-252.

95. Tipping,E., Woof,C., Rigg,E., Harrison,A.F., Ineson,P., Taylor,K., Benham,D., Poskitt,J., Rowland,A.P., Bol,R. and Harkness,D.D., 1999. Climatic influences on the leaching of dissolved organic matter from upland UK moorland soils, investigated by a field manipulation experiment. Environment International, 25(1): 83-95.

96. Trumbore,S.E., Schiff,S.L., Aravena,R. and Elgood,R., 1992. Sources and Transformation of Dissolved Organic-Carbon in the Harp Lake Forested Catchment - the Role of Soils. Radiocarbon, 34(3): 626-635.

97. Van der Zee,S.E.A.T., Leus,F. and Louer,M., 1989. Prediction of phosphate-transport in small columns with an approximate sorption kinetics model. Water Resources Research, 25(6): 1353-1365.

98. Van der Zee,S.E.A.T. and Van Riemsdijk,W.H., 1986. Sorption kinetics and transport of phosphate in sandy soil. Geoderma, 38(1-4): 293-309.

99. Van der Zee,S.E.A.T. and Van Riemsdijk,W.H., 1988. Model for long-term phosphate reaction-kinetics in soil. Journal of Environmental Quality, 17(1): 35-41.

100. Van Riemsdijk,W.H., Boumans,L.J.M. and Dehaan,F.A.M., 1984. Phosphate sorption by soils .1. a model for phosphate reaction with metal-oxides in soil. Soil Science Society of America Journal, 48(3): 537-541.

101. Vance,G.F. and David,M.B., 1992. Dissolved organic-carbon and sulfate sorption by spodosol mineral horizons. Soil Science, 154(2): 136-144.

102. Vinther,F.P., Hansen,E.M. and Eriksen,J., 2004. Udvaskning af organisk kulstof efter kløvergræs. In: J.E.Olesen (Editor), Kulstoflagring og drivhusgasser fra jordbruget - potentiale og reduktionsmuligheder.

103. Walker,T.W. and Adams,A.F.R., 1958. Studies on oilorganic matter: 1. Influencee of phossphorus content of parent material on accumulations of carbon, nitrogen, sulfur, and organic phosphorus in grassland soils. Soil Science, 85: 307-318.

104. Wang,Z.Y., Kelly,J.M. and Kovar,J.L., 2004. In situ dynamics of phosphorus in the rhizosphere solution of five species. Journal of Environmental Quality, 33(4): 1387-1392.

105. Yano,Y., McDowell,W.H. and Aber,J.D., 2000. Biodegradable dissolved organic carbon in forest soil solution and effects of chronic nitrogen deposition. Soil Biology & Biochemistry, 32(11-12): 1743-1751.

106. Zech,W., Senesi,N., Guggenberger,G., Kaiser,K., Lehmann,J., Miano,T.M., Miltner,A. and Schroth,G., 1997. Factors controlling humification and mineralization of soil organic matter in the tropics. Geoderma, 79(1-4): 117-161.

107. Zsolnay,A., 1996. Dissolved humus in soil waters. In: A.Piccilo (Editor), Humic substances in terrestrial ecosystems. Elsevier Science B.V., pp. 171-223.

108. Zsolnay,A. and Steindl,H., 1991. Geovariability and biodegradability of the water-extractable organic material in an agricultural soil. Soil Biology & Biochemistry, 23(11): 1077-1082.