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# Multi-Component Reactive Transport Modelling in the Rhizosphere

The special case of arsenate

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# 1. Introduction

## *1.1 Relevance of arsenic contamination*

Arsenic (As) became infamous in history as the poison of kings and the king of poisons (Newman, 2005). Its toxic effect on plants, animals and humans makes it also important considering geoscienctific aspects (Frost and Griffin, 1977). Soil arsenic can be derived from natural (dissolution from rocks) or anthropogenic (mining, agricultural and industrial activity) sources (Bhumbla and Keefer, 1994; Smith et al., 1999; Fitz and Wenzel, 2002; Smith et al., 2002; Schmidt et al., 2003). A recent example for an environmental hazard related to As is found in Bangladesh, where As concentration in drinking and irrigation water is much higher than the limit determined by the WHO (0.01mg/L in water) due to mobilisation of As in shallow aquifers (Bachmann et al., 1999; WHO, 2001). Arsenic contamination represents a serious environmental problem at several agricultural sites around the world, for example in France, Australia, Romania and the USA (Smedley and Kinniburgh, 2002; Heikens et al., 2007).

Arsenic from geogenic origin, exposed to the environment by mining of a range of minerals in the Erzgebirge (Ore mountains, Germany), is present in elevated concentrations in alluvial soils along the rivers Elbe and Mulde in Saxony and Saxony-Anhalt (Germany). A screening conducted after the flood event in 2002 provided detailed information on the extent of As contamination in these soils, which are still used for agriculture, predominantly as meadows for fodder production (Serfling and Klose, 2008).

A fundamental problem for assessing the risk of As transfer into the food chain associated with these contaminated sites is that no simple relationship can be found between As concentration in the soil and As concentration in the plants grown at these sites. This is illustrated for a site north of Wurzen (Fig. 1.1) for which total soil As concentration (XRF) is plotted against As concentration in the standing biomass in May for a meadow with *Lolium perenne* as the dominant species. Soil As concentration were in a range of 90 to 560 mg/kg, plant concentrations varied between 0.2 to 11 mg/kg (Ackermann et al. EJSS submitted; Vetterlein, pers. comm.).

In 2004 a research group (Helmholtz-University Young Investigators Group BASS[1]) was established to reveal the dominant processes for soil-plant transfer of As and develop a procedure for the characterization of As bioavailability in contaminated soils. The current work was conducted within this research group and focuses on implementing the processes which are relevant for the transport and uptake of arsenic in the rhizosphere in a computer model, which can be used for identifying the relative importance of individual processes and may be used for the calculation of different scenarios.

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[1]Bioavailability of Arsenic in Soil Sediments, Project leader: PD Dr Doris Vetterlein, Cooperating institutes: Martin Luther University Halle-Wittenberg and the Helmholtz Centre for Environmental Research – UFZ.
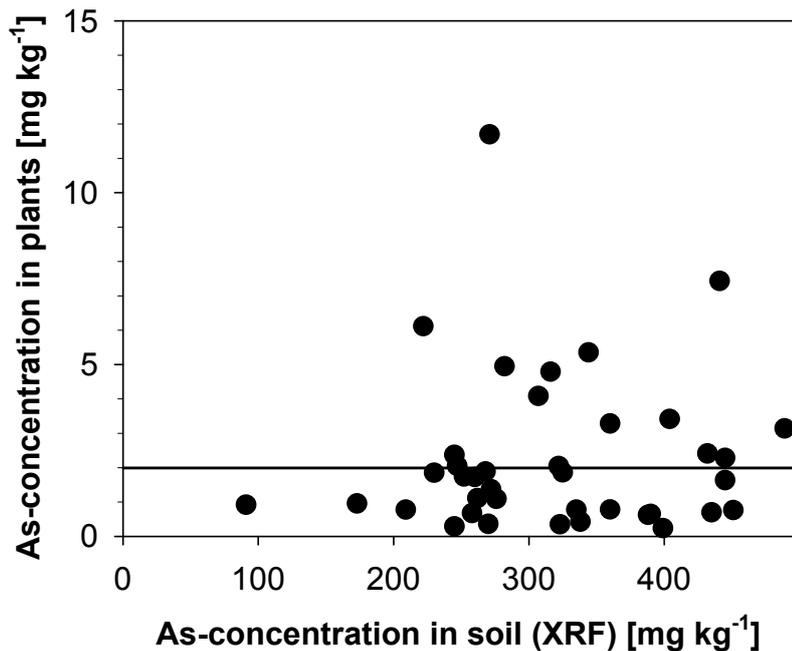
*Figure 1.1: Arsenic (As) concentration in plants collected at 40 different points of a field site in the flood area of the river Mulde (Germany) vs. As concentration in upper soil at the same sampling points (Ackermann et al. EJSS submitted; Vetterlein, pers. comm.). The horizontal line indicates the German threshold value for the use as fodder.*

## 1.2 The complexity of arsenic bioavailability

In a soil As can be found in 25 different chemical forms (species). The most important of these 25 As-species are: arsenite — $As^{III}$, arsenate — $As^{V}$, monomethylarsenic acid — MMAA and dimethylarsenic acid — DMAA. Different As species differ in their mobility, uptake by plant roots and toxicity (Fitz and Wenzel, 2002). For the toxicity of As it is more important which species is present than its absolute concentration. The toxicity of the different species was tested for plants and mammals. Arsenic toxicity was found to decrease in the following order: $As^{V}$> $As^{III}$> MMAA, DMAA (for plants) and $As^{III}$> $As^{V}$ > MMAA, DMAA (for rats) (Schmidt et al., 2003).

Toxicity and mobility of the inorganic species is much higher than that of the organic ones. In soils these inorganic species are the dominant ones. Thus, most soil related studies are focused on arsenate and arsenite (Roussel et al., 2000). Changes in soil aerobic conditions, root respiration and the increase of microbial activity in the vicinity of roots may alter redox potential at the root surface and thus affect the speciation of arsenic.

The reduced As species, $As^{III}$, can be formed when soil redox potential decreases to 200-300 mV or lower (Marin et al., 1993; Jones et al., 2000). It can be sorbed to metal oxides (Sun and Doner, 1996). Only recently it has been discovered that $As^{III}$ is taken up through channels which primarily serve as pathways for Si (Ma et al., 2008).

Under aerobic conditions $As^{III}$ is rapidly oxidised to $As^{V}$, which is a chemical analogue of the nutrient phosphate ($P^{V}$). $As^{V}$ competes with $P^{V}$ for binding sites in the

soil, as they are provided by goethite or ferrihydrite (Jain and Loeppert, 2000; Smith et al., 2002), and also for root membrane transporters (Meharg and Macnair, 1992; Poynton et al., 2004). $P^V$ in soil can be mobilized by plants through different mechanisms like ligand exchange through organic acids or by acidification through proton release (Hinsinger et al., 2003). The same mechanisms may act in mobilizing $As^V$ or will at least alter the competition between $As^V$ and $P^V$ (Vetterlein et al., 2007). Speciation and mobility of As in the rhizosphere and its uptake by plants are strongly influenced by other chemical compounds that are present. Considerations about soil-plant transfer of As should include all compounds that affect the reactive transport of As in the rhizosphere.

## *1.3 The role and necessity of rhizosphere modelling*

The rhizosphere is defined as the soil micro-site which is affected by root activity (Hinsinger, 1998). According to Darrah and Roose (2001), the most striking feature of the rhizosphere are gradients of solute concentration extending from the root surface into the surrounding soil. The gradients include depletion and accumulation of minerals as well as gradients in soil pH and exudate concentration (Hinsinger et al., 2009). Thus, the chemical composition of the rhizosphere can be totally different from that of the bulk soil. That's why the understanding of rhizosphere processes can be the key for many actual environmental issues and technologies, for example low input farming, phytoremediation and use of contaminated landscapes.

Transfer of nutrients or contaminants from bulk soil to roots and into plants depends on the integration of many individual plant and soil processes, each of them having its own temporal dynamics (Fig. 1.2). Models can be used to identify, separate and test the relevance of these co-occurring processes. Larger scale transport models represent root uptake only with a sink term that is related to a macroscopic root distribution function. This limits the applicability of these models for modelling processes in the rhizosphere to some special problems (Nowack et al., 2006; Szegedi et al., 2008). Microscopic rhizosphere models describe concentration gradients formed with increasing distance from the surface of a single root: root uptake is described as a boundary condition at the root-soil interface. So far most microscopic rhizosphere models (Tinker and Nye, 2000), in contrast to geochemical models, abstain from calculating full speciation of the soil solution for sake of simplicity. This is justified if the dominant form of the ion in question is known and if no strong interactions with other ions are expected or if these can be reproduced by empirical factors. For the description of the soil-plant-transfer of contaminants like arsenic such simplified approaches may not satisfy the needs due to the complex chemical and biochemical behaviour summarised in the previous chapter.

Although there are computer models that are able to describe individual processes that are relevant for the soil-plant transfer of As, there is no existing code in which all of these processes are implemented (see next section for details and references). Thus, for modelling As-dynamics in the rhizosphere a multispecies model has to be developed which simultaneously calculates the transport of various As-species taking into

account their interactions with other compounds and phases and the dynamic impact of the plant.
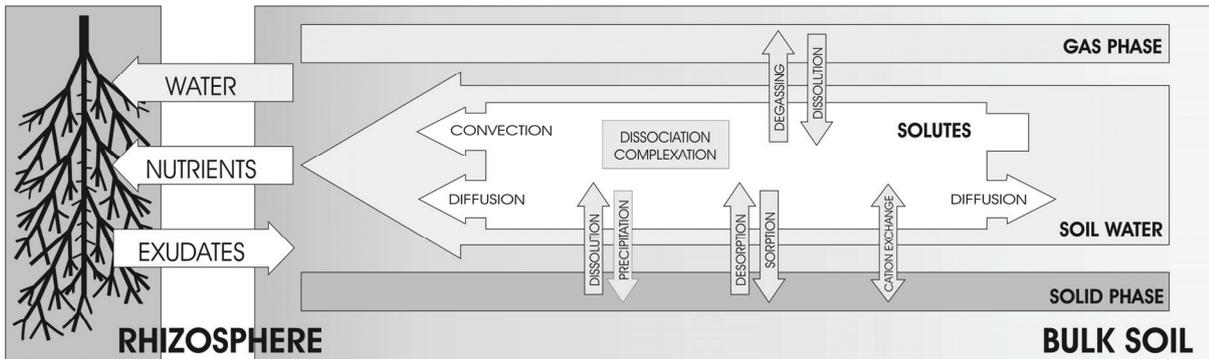


*Figure 1.2: The conceptual model of the simultaneously occurring physicochemical and chemical processes in the rhizosphere. Besides the transport and uptake of water and nutrients, the numerous interactions between solutes, solvent, solid (minerals) and gaseous phases (air, soil gas phase) are represented*

## 1.4 Considerations on the development of a new rhizosphere transport model

According to the state of the art in rhizosphere modelling, there is no code available that would fulfil the specific requirements for modelling the reactive transport of As in the rhizosphere. Thus, a new rhizosphere model had to be developed for this purpose. The performed work focused on implementing the relevant processes in a model and not on the applied numerical procedure. Thus, it was reasonable to develop the new model on the basis of existing codes.

Hoffland (1990), Geelhoed et al. (1999) and Nietfeld (2001) presented different coupled speciation-transport rhizosphere models. The first two considered only a small number of ions. The Nietfeld's model, addressing aluminium transport and uptake, is probably the most applicable reported rhizosphere model for small-scale, high-resolution scenarios. It is also the only model that includes a correction term (equation 3.8) in the transport equations, ensuring the electroneutrality of the system. Electroneutrality should be considered when systems in which mass flow and diffusion of the same order of magnitude are modeled. However, it should be noted that Nietfeld's model is purely mathematical and not directly based on experimental data. It also does not include surface complexation and reaction kinetics.

It has been recently shown by Nowack et al (2006) that commonly available geochemical codes [PHREEQC, MIN3P, ORCHESTRA, (Parkhurst and Appelo, 1999; Mayer et al., 2002; Meeussen, 2003), respectively] are theoretically applicable for rhizosphere modeling. These codes have been applied as 'numerical engines' to solve the problem of diffusion toward a single cylindrical root. However, as these geochemical programs were not developed to model processes in the rhizosphere; their application requires a very good understanding of their functionality and input syntaxes.

The complex behaviour of As in the rhizosphere can be divided into the following issues: (i) complex geochemical behaviour (ii) competitive uptake with $P^V$.

Modelling geochemistry of As requires a code that can calculate chemical speciation in the soil solution (e.g. dissociation of $As^V$), competitive sorption (e.g. with $P^V$ and organic acids), equilibrium with minerals (e.g. with calcium phosphates) and equilibrium with gases (e.g. $CO_2$). All of these processes are already implemented in existing geochemical codes (ORCHESTRA, PHREEQC and MIN3P) and are only partly implemented in existing coupled speciation-transport rhizosphere models [Hoffland (1990), Geelhoed et al. (1999) and Nietfeld (2001)].

The amount of work which would be required to implement geochemical processes in an existing rhizosphere transport model would shift the focus of the current work too much towards modelling geochemical processes in the rhizosphere. However, existing geochemical codes are able to describe geochemical behaviour of As. These codes have been thoroughly tested by their authors and other researchers as well. Thus, it is reasonable to use an existing geochemical code as basis for the development of a new rhizosphere model with coupled speciation.

The applicability of geochemical codes ORCHESTRA, PHREEQC MIN3P and HP1 as a basis of a new rhizosphere model were considered. All of these codes have advantages in particular applications; these advantages can be disadvantageous in other applications. In the following the major advantages and disadvantages are highlighted in respect to there use in rhizosphere modelling using a microscopic approach:

ORCHESTRA:
+ Very flexible, almost a separate programming language.
+ Sorption can be modelled using any approach [Geelhoed et al.(1999) used the CD-MUSIC approach in ORCHESTRA]
± User should implement new approaches himself
− Due to its flexibility implementing an own model needs a lot of practice and time (van Beinum, 2006), e.g. chemical database has to be defined by the user, many processes are not included.

PHREEQC:
+ A very complex chemistry is implemented.
+ The most extended chemical database among these codes
+ Easily extendable database
− Modelling non-Darcian flow needs coupling to external code (e.g. HP1).
− Modelling diffusion towards a single root (radial case) requires the use of stagnant zones; transport between stagnant zones is defined using the MIX keyword (Nowack et al., 2006; PHREEQC input file provided by Diederik, J., 2005). Parameters of the MIX keyword are calculated separately from PHREEQC in a spreadsheet. This makes a re-definition of the applied geometry time consuming.
− Sorption is primarily described with the diffuse double layer model, which describes surface sorption in simpler way than the CD-MUSIC model.

± The CD-MUSIC approach has been already implemented in PHREEQC. However, corresponding chemical database has to be compiled by the user.

MIN3P:

+ Unsaturated water flow can be modelled in 2D/3D.

+ A complex chemistry is included, although it's not as complex as in PHREEQC.

− The implemented surface sorption model does not include the effect of surface charge

− Modelling diffusion towards a single root requires the use of 2D Cartesian geometry that approximates radial geometry where the radial root is represented by a square (Nowack et al., 2006; MIN3P input file provided by Oswald, S., 2005). This approach can cause errors close to the root surface. Moreover, many unnecessary grid points are defined.

HP1:

The HP-1 code unites the advantages of HYDRUS-1D and PHREEQC. Radial geometry could be implemented in HP1 either by a modification of the source code or, eventually, by a 'tricky' definition of the soil profile. Root uptake can by defined here also only by using sink terms.

Considering the above presented advantages and disadvantages of the codes, PHREEQC seems to be the most appropriate to describe chemistry of As in the rhizosphere. However PHREEQC alone is not able to calculate the multicomponent transport (diffusion and mass flow) in the rhizosphere. Implementing the required transport equations (see forthcoming chapters) in PHREEQC would require the modification of the PHREEQC code. A more efficient alternative to this would be the coupling of PHREEQC with an external code that solves the transport equations (partial differential equations – PDE's) separately from PHREEQC. A possible and time-effective way is to use the mathematical package MATLAB to solve the transport equations. The transport equations could be also solved with a C or FORTRAN code. However, solving the transport equations in C or FORTRAN would shift the focus of this work towards technical aspects, i.e. towards discussing and testing the applied numerical methods. The biggest advantage of MATLAB in comparison to C or FORTRAN is, that MATLAB (with installed PDE Toolbox) has several already implemented PDE solvers. Additionally, the formulation of the MATLAB language is closer to the mathematical formulation than C or FORTRAN codes.

Development of a coupled speciation-transport rhizosphere model should be supported by the use of a physical model of the rhizosphere as reference. The physical model should have a well defined geometry and well defined chemical composition of the applied substrate and fertilization. These features are both available using the compartment system setup (Vetterlein and Jahn, 2004b).

# 2. Experimental Setup, Hypotheses and Objectives

## *2.1 Compartment system experiments*

Experimental investigations on nutrient transport in the rhizosphere require the collection of soil solution samples at well defined distances from the root surface. This is almost impossible in a cylindrical system such as the rhizosphere of a single root. Compartment systems (Fig. 2.1) are used as physical models of the rhizosphere (Wenzel et al., 2001; Vetterlein and Jahn, 2004b; Vetterlein et al., 2007). This setup provides the possibility of the experimental investigation of rhizosphere processes using planar geometry.

A main feature of the compartment system is that roots can explore only the so called root compartment which is separated from the two bulk soil compartments by two nylon nets. This leads to the formation of a root mat along the nylon nets. The compartment system can be described as a linear system based on the assumption that the root mat is homogenous and represents the root surface (Vetterlein and Jahn, 2004b).

With this assumption the fact that the root mat consists of roots of different age and activity is neglected. The impact of individual roots or root architecture on the soil cannot be studied in compartment system experiments. Due to the close packing of roots in the root mat, the impact of roots on the rhizosphere may be amplified in comparison to the field situation. This is not necessarily a disadvantage, as this amplification enables the identification of processes that occur in the field but their direct impact on soils is below detection limit under field conditions. Inter-root competition for nutrients (and also for water) occurs only within the root compartment. This can be a disadvantage, as inter-root competition can not be studied with this
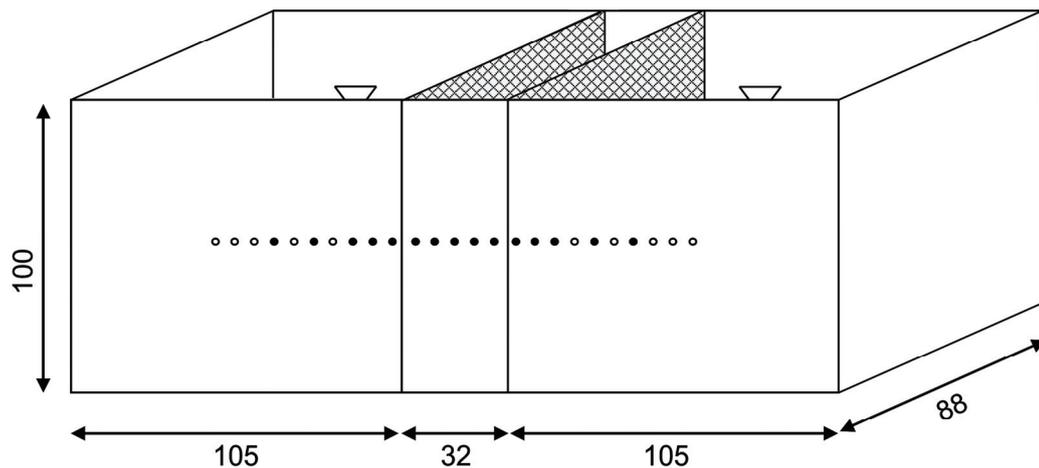


*Figure 2.1: The compartment system presented by Vetterlein and Jahn (2004b) offers a simplified geometry in which the root mat is separated from bulk soil by a nylon mesh. This enables the description of the rhizosphere as a linear system with well defined distances from the root surface. The compartment system is equipped with regularly placed micro suction cups (represented by black circles) for sampling the soil solution in low volumes. The dimensions of the system are given in mm. Figure modified after Vetterlein and Jahn (2004b).*

setup. On the other hand, this is an advantage, as the impact of roots on soil extends to a larger distance from the root surface in comparison to the zone tapped by a single root.

The main advantage of the linear compartment system is that sensors like micro suction cups for soil solution sampling can be installed at a known distance from the root mat representing the root surface.

The volume of soil from which soil solution samples are collected by the micro suction cups depends on a range of parameters like soil moisture and sampling time. Substantial concentration differences between neighbouring suction cups were detected in soil solution samples collected under unsaturated conditions in several experiments (Vetterlein and Jahn, 2004a; Vetterlein et al., 2007). However, as micro suction cups collect soil solution samples from a finite soil volume and not from one point, it is possible that gradients in the compartment system are steeper as measured gradients.

The temporal resolution of the sampling system is limited by the need of minimizing the impact of sampling on the measured parameter: i.e. sufficient time is required for re-equilibration after removing part of the soil solution and sampling should not introduce a sink competing with the roots.

Modeling the processes in compartment systems can provide data with a much higher spatial and temporal resolution compared to what can be obtained with measurements.

## *2.2 Experimental setup of the reference system*

The experiments used as reference for the modelling were performed in the framework of the BASS project but not as a part of this thesis. That's why the experimental part is presented only in an extent that is required for understanding the current work.

*Zea mays* was grown in nine compartment systems under controlled conditions on an artificial quartz substrate spiked with known amounts of nutrients, $As^V$ and with increasing amounts of goethite ($0g\ kg^{-1}$, $1g\ kg^{-1}$, $4g\ kg^{-1}$ – G-0, G-1, G-4, respectively) (Vetterlein et al., 2007).

The choice of quartz as substrate material provided a system in which the number and kind of surface sorption sites can be manipulated by the addition of pure minerals like goethite. The applied quartz was of high purity. This allowed us to set soil chemical composition by mixing different fertilizers to the substrate. Additionally, quartz did not contain any organic matter. Thus, all organic compounds that were detected in soil solution samples collected during the experiments were released by the plants.

A mixture of quartz of different grain size (sand, silt, clay) was applied to provide the water retention characteristic of a 'real' soil. It was the aim to simulate water and ion transport comparable to soil systems, including the formation of gradients, in contrast to flow through cultures based on coarse quartz sand, which are based on the idea of determining the chemistry of the system by flushing it with a nutrient solution of a certain composition.

Fertilization was chosen to maintain the nutrient requirements of the plant. Due to the spatial restrictions of the compartment system and the low sorption capacity of the applied quartz substrate, nutrient concentrations were higher as it would be expected

under field conditions. However, initial $P^V$ and $As^V$ concentrations in the G-4 treatment were still in the same order of magnitude as nutrient concentrations measured in soil solution samples from an As-contaminated field site at the river Mulde (0.05 to 0.14 mM $P^V$ and 0.005 to 0.063 mM $As^V$).

The parameters of the experiment are summarised in Tables A1.1 and A1.2 in Appendix 1. Each compartment system was placed on a sand bed that was regularly irrigated by capillary rise with de-ionized water after planting to maintain the initial water content. Micro suction cups were assembled according to Göttlein et al. (1996) and installed horizontally with a spatial resolution of 6 mm. Soil solution was sampled every week. A sample volume of 100 µl was collected each time through each cup. The weight of the compartment systems and the sand bed was continuously registered in order to determine the evapotranspiration rate. Concentration of major elements and species in the soil solution samples were analysed with different chromatographic and spectroscopic methods (Table A1.1) and soil solution pH was measured with an ISFET microelectrode. The specific surface of goethite was measured with the BET $N_2$ adsorption technique.

## 2.3 Results of physical experiments – hypotheses to be tested

The results and qualitative analysis of the compartment system experiments were presented in detail by Vetterlein et al. (2007). Particular results are going to be emphasised later in the current work. The most important observations are going to be presented here.

Goethite addition decreased both $As^V$ and $P^V$ concentration in treatments G-1 and G-4 in comparison to the G-0 treatment. The magnitude of both $As^V$ and $P^V$ concentrations were lower in the treatment with more added goethite (G-4). This initial difference between the treatments remained during the whole experiment. $P^V$ concentration in soil solution strongly increased in the rhizosphere and root compartment in treatment G-1 10 and 17 days after planting. A slight increase in $P^V$ concentrations was observed in treatment G-4 10 days after planting. $As^V$ showed neither depletion nor accumulation in this treatment (Vetterlein et al, 2007, Figs. 2, 3).

Organic acids released by the plant were analysed in a similar but separate experiment (Schulz and Vetterlein, 2007). The presence of citrate in low concentration was shown in the rhizosphere in a treatment without added goethite.

During the interpretation of the experiments (Vetterlein et al., 2007) it was hypothesised that the observed increase in $P^V$ concentration at the root surface in treatment G-1 was caused by the mobilisation of adsorbed $P^V$ by root citrate release. This hypothesis can not be fully proven based on the presented experimental results: it can not be distinguished whether the increased $P^V$ concentration was caused by $P^V$ accumulation (transport with mass flow exceeded plant uptake) or by $P^V$ mobilization (desorption of adsorbed $P^V$). However this hypothesis can be tested by performing model calculations.

That increased $P^V$ concentration was only observed in the G-1 treatment but not in the G-4 treatment was explained by the differences between the available sorption sites in the two treatments. This hypothesis can be also tested with model calculations.

The relevance of competitive uptake of $As^V$ and $P^V$ was also discussed by Vetterlein et al. (2007). However, the effect of competitive uptake of $As^V$ and $P^V$ on the bioavailability of $As^V$ in the rhizosphere could not be estimated based on the performed experiments, but can be shown with model calculations.

## *2.4 Objectives*

Due to the complexity of the involved processes, a full interpretation of the compartment system experiments performed to study the fate of arsenic in the rhizosphere is only possible with the aid of a rhizosphere model with chemical speciation. According to the state of the art in rhizosphere modelling, there is no code available that would fulfil the specific requirements of this issue.

The main objective of the current work was to develop a rhizosphere model that includes all relevant biological and physicochemical processes that are required for the interpretation of the performed compartment system experiments. The model should be able to describe the following processes:

- chemical speciation in soil solution
- competitive sorption
- interactions of the soil solution with minerals and gases
- multi-component reactive transport of solutes in the rhizosphere (including root uptake as boundary condition)
- competitive uptake of solutes

Based on considerations presented previously, the new model is based on coupling the mathematical package MATLAB and the geochemical code PHREEQC.

Reactive transport modelling can not be successful without a correct description and a sufficient understanding of the chemistry of applied solutes and media. The processes and parameters that are required to describe soil solution composition had to be included in the model without using unjustified assumptions or unreasonable parameters values. Thus, special attention was given to the description of soil solution composition in the compartments systems without the presence of the plants.

The performed compartment system experiments began with seeding. The development of the root mat took several days. There are different approaches on modelling nutrient uptake by a developing root system with microscopic rhizosphere models (Darrah et al., 2006). However, these approaches have been developed for systems in which the roots are not forced to grow in a limited soil volume, which is the case for compartment system experiments. Thus, it was necessary to find a mathematical description of the changing nutrient uptake by a developing root mat and to implement it in the computer model.

After the above described goals were fulfilled and the model was comprehensively tested we focused on modelling the experiments presented by Vetterlein et al. (2007).

The primary goal of the modelling was to test and extend the hypotheses made based on the experimental results. The following questions had to be answered:

- Do organic acid anions (citrate) released by roots influence the availability of $P^V$ and $As^V$ in the compartment system?
- Can organic acid anion exudation explain the observed increase of $P^V$ concentration at the root surface in treatment G-1?
- Can the different amounts of added goethite in the established treatments explain the observed differences in soil solution concentrations?
- What was the relevance of competitive uptake of $P^V$ and $As^V$ in respect to $P^V$ and $As^V$ concentrations?
- Can the model reproduce all measured $P^V$ and $As^V$ concentration profiles?
- Are there any additional processes that affect $P^V$ and $As^V$ availability in rhizosphere which should be implemented in the model in the future?

The current work has been carried out in the framework of the BASS project which aims to develop a procedure for the characterization of As bioavailability in contaminated soils. Thus, the relevance of the current work for understanding processes in the field system will be discussed.

# 3. The New Tool RhizoMath for Modeling Coupled Transport and Speciation in the Rhizosphere

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## 3.1 Abstract

The transfer of nutrients and contaminants from bulk soil to roots and into plants depends on many plant and soil processes. The RhizoMath approach for modeling co-occurring processes in the rhizosphere, including speciation in the soil solution, is based on coupling the mathematical package MATLAB with the geochemical code PHREEQC. In addition to the built-in initialization module that performs calibration against experimental data, the RhizoMath's greatest advantage is that different geochemical models (with and without charge balance) and geometries (planar and radial) are already included. Moreover, due to its graphical user interface the tool can be applied without changing the source code or a complex input file. The model was verified using a benchmark and experimental data: (i) The initialization module was successfully applied to describe concentrations measured in soil solution samples. (ii) The theoretical problem 'diffusion of K toward a single root' was used to demonstrate that the performance of applied numerical methods is comparable to other approaches. (iii) For compartment system experiments involving more complex speciation, RhizoMath was able to describe the observed effects of citrate exudates on the simultaneous transport of $As^V$ and $P^V$ that compete for surface binding sites with each other and with other oxyanions such as citrate.

## 3.2 Introduction

The rhizosphere is the part of the soil that is affected by root activity (Hinsinger, 1998). According to Darrah and Roose (2001), the most striking feature of the rhizosphere is the formation of solute gradients extending from the root surface into the surrounding soil. Depletion and accumulation of solutes at the root surface, as well as gradients in the soil pH-value, were reported in the literature (e.g. Marschner et al., 1987). The transfer of nutrients or contaminants from the bulk soil to the roots and into the plants depends on the combined effects of many plant and soil processes. Water flow and solute transport are driven by hydraulic potential gradients induced by atmospheric processes, such as precipitation and transpiration, as well as by concentration gradients. Transpiration induced water flow involves the convective transport of all ions present in the soil solution toward the root surface. On the other hand, diffusive fluxes may occur both toward and away from the root surface. The concentration and chemical speciation of a particular element in the soil solution at a defined distance from the root surface depends not only on net transport, but also on chemical reactions such as redox reactions, surface sorption, complex formation or dissolution, acid-base changes, changes in the composition of the cation exchanger and dissolution or formation of mineral phases.

In contrast to available geochemical models, a majority of approaches for modelling transport processes in the rhizosphere omit calculating full speciation in the soil solution for the sake of simplicity. This omission is justified if the dominant form of a particular nutrient is known, and if strong interactions with other nutrients do not exist or can be described using empirical factors, such as those reported for potassium (Claassen et al., 1986; Kelly et al., 1992). However, observed reactions of trace elements can be solved only using coupled speciation-transport models.

Arsenic (As) presents an urgent environmental problem at many agricultural sites around the world (Smedley and Kinniburgh, 2002; Heikens et al., 2007). Simplified approaches are not capable of describing As soil-plant transfer. Different arsenic species [e.g. $As^{III}$, $As^{V}$, DMA, etc.] present in the soil may differ in their mobility, uptake by plant roots, and toxicity (Fitz and Wenzel, 2002). Variations of root metabolism and microbial activity may alter redox potential in the rhizosphere and affect arsenic speciation. The oxidized form of arsenic, arsenate ($As^{V}$), is a chemical analogue of phosphate ($P^{V}$), which competes with $P^{V}$ for binding sites in the soil, like goethite or ferrihydrite (Jain and Loeppert, 2000; Smith et al., 2002). Plants may mobilize $As^{V}$ using mechanisms similar to those used in mobilizing $P^{V}$ (Vetterlein et al., 2007). $As^{V}$ and $P^{V}$ also compete for binding sites at root membranes (Meharg and Macnair, 1992; Poynton et al., 2004). None of the many reported approaches for modelling transport in the rhizosphere sufficiently describes and explains the complex behaviour of arsenic.

Hoffland (1990), Geelhoed et al. (1999) and Nietfeld (2001) presented different coupled speciation-transport rhizosphere models. The first two considered only a small number of ions. The Nietfeld's model, addressing aluminium transport and uptake, is probably the most applicable reported rhizosphere model for small-scale, high-resolution scenarios. It is also the only model that includes a correction term (equation 3.8) in the transport equations, ensuring the electroneutrality of the system. Electroneutrality should be considered when systems in which mass flow and diffusion of the same order of magnitude are modelled. However, it should be noted that the Nietfeld's model is purely mathematical and not directly based on experimental data. It also does not include surface complexation and reaction kinetics.

A group of European researchers (Nowack et al., 2006) has recently shown that commonly available geochemical codes [PHREEQC, MIN3P, ORCHESTRA, (Parkhurst and Appelo, 1999; Mayer et al., 2002; Meeussen, 2003), respectively] are theoretically applicable for rhizosphere modelling. These codes have been applied as 'numerical engines' to solve the problem of diffusion toward a single cylindrical root. Results generated using these computer codes were compared with the analytical solution presented by Roose et al. (2001) to test their numerical accuracy. However, as these geochemical programs were not developed to model processes in the rhizosphere, their application requires a very good understanding of their functionality and input syntaxes. This may explain the existing lack of published work comparing geochemical model results with experimental data. Nowack et al. (2006) pointed out that each of the three codes mentioned above has advantages in some applications, but may reveal themselves as having disadvantages in other applications.

The objective of the research reported in this manuscript has been to develop a rhizosphere model that would consider chemical speciation and all relevant biological and physicochemical processes so that it could be used to interpret compartment system experiments (Wenzel et al., 2001; Vetterlein and Jahn, 2004a; Vetterlein and Jahn, 2004b). The model should also be used by other experimenting scientists to guide interpretations of observed data and to help in designing new experiments. The performance of the newly developed model RhizoMath is compared with other existing approaches using published data sets. It is demonstrated in this paper that RhizoMath is capable of describing the concentration profiles of $P^V$ and $As^V$ observed in a compartment system experiment with *Zea Mays* following the application of goethite.

## 3.3 Theory

### The Nye & Tinker model

Microscopic rhizosphere models describe concentration gradients formed with increasing distance from the surface of a single root. Published microscopic approaches are based on the work of Nye, who applied the convection-diffusion equation to rhizosphere modelling (Nye and Marriott, 1969; Tinker and Nye, 2000):

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}\left( rD_e \frac{\partial C}{\partial r} + \frac{r_0 v_0 C}{b'} \right), \tag{3.1}$$

where $C$ (mol L$^{-3}$) is the concentration of the given species in the soil solution, $D_e$ (L² T$^{-1}$) is its effective diffusion coefficient, $v_0$ (L T$^{-1}$) is the water flux at the root surface, $r_0$ (L) is the root radius and $r$ (L) is the distance from the root surface. The buffer power $b'$ (dimensionless) is defined here as $b' = \theta + \rho K_d$, where $\theta$ (dimensionless) is the (constant) volumetric water content, $\rho$ (M L$^{-3}$) is the bulk soil density and $K_d$ (L$^3$ M$^{-1}$) is the distribution coefficient. Another possible definition of the buffer power is $b = \rho K_d$, and thus $b' = \theta + b$ (Van Rees et al., 1990; Darrah and Roose, 2001). The effective diffusion coefficient is defined as

$$D_e = \frac{Df\theta}{b'} = \frac{Df\theta}{\theta + b}, \tag{3.2}$$

where $f$ (dimensionless) is the soil impedance factor and $D$ (L² T$^{-1}$) is the diffusion coefficient in water.

In contrast to current hydrological models, in which root uptake is usually represented using a macroscopic sink term (Hopmans and Bristow, 2002; Simunek et al., 2005), microscopic rhizosphere models include root uptake as a boundary condition (Darrah and Roose, 2001):

$$J^{upt} = D_e b' \frac{\partial C}{\partial r} + r_0 v_0 C \bigg|_{r=r_0}, \tag{3.3}$$

where $J^{upt}$ (mol L$^{-2}$ T$^{-1}$) is the nutrient uptake flux that depends on the concentration at the root surface, the delivery rate to the root surface, and plant uptake characteristics.

The modified Michaelis-Menten kinetics is an experimentally justified and widely applied approach describing nutrient uptake flux in a wide range of concentrations (Barber and Cushman, 1981; Barber, 1995):

$$J^{upt} = J_{max} \left( \frac{C - C_{min}}{K + C - C_{min}} \right), \qquad (3.4)$$

where $J_{max}$ (mol $L^{-2}$ $T^{-1}$) is the maximal, concentration-independent influx of a particular ion, $K$ (mol $L^{-3}$) is the Michaelis-Menten constant, i.e., the concentration at which the uptake rate is half of the possible maximum uptake, and $C_{min}$ (mol $L^{-3}$) is the minimum concentration of the ion in the soil solution below which no uptake occurs. The Michaelis-Menten constant and the minimum concentration are assumed to be the same for all ions in some models (e.g.,Nietfeld, 2001). Approaches describing root uptake as a constant (De Willigen and van Noordwijk, 1994b) or linear sink (Baldwin et al., 1972) can be interpreted as special cases of Michaelis-Menten kinetics in the higher and lower range of concentrations, respectively. The root acts as a zero-sink at low nutrient concentrations, which means that the nutrient is taken up at the same rate as it is transported toward the root surface (De Willigen and van Noordwijk, 1994a). Concentration dependent Michaelis-Menten kinetics was reported by Nissen (1973). Fluxes from the root surface toward the bulk soil include protons, hydrogencarbonate and organic acids, which plants release to maintain the electroneutrality in the rhizosphere and to mobilize nutrients, such as adsorbed $P^V$ (Geelhoed et al., 1999; Kirk, 1999).

Including a sink (or source) term in equation (3.1) enables microscopic rhizosphere models to describe solute uptake by mycorrhizal hyphae and to include microbial activity or kinetic processes:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r D_e \frac{\partial C}{\partial r} + \frac{r_0 v_0 C}{b'} \right) - R, \qquad (3.5)$$

where $R$ (mol $L^{-3}$ $T^{-1}$) is a function of time and position (Darrah and Roose, 2001; Schnepf and Roose, 2006).

Some more complex models, often based on semi-empirical formulas, can describe the effects of water and nutrient uptake on root growth, and the feedback of root growth on the uptake of water and nutrients. The uptake is then controlled by the actual size of the plant and does not necessarily include time as an explicit parameter (e.g., Somma et al., 1998; Dunbabin et al., 2002; Hopmans and Bristow, 2002).

**Reactive transport in the rhizosphere**

Multispecies models describe the simultaneous transport of several ions in the rhizosphere, while taking into account their interactions. The simplest approach is presented in the model of Nye (1983), which describes the diffusion of interacting solutes using interaction coefficients in the transport equations that account for kinetic conversions between different species. Although these coefficients describe only some of many possible interactions and do not take into account speciation of elements, the

model predicted the root-induced solubilization process very well, such as $P^V$ solubilization due to organic anions excreted from plant roots (Kirk, 1999). Theoretically this approach is expandable for describing cases with several solutes. However, that would involve many interaction coefficients, which would have to be optimized against experimental data. The final outcome wouldn't necessarily provide a better understanding of the studied system.

Chemical equilibrium, e.g., the speciation of solutes in the soil solution, could be implemented by coupling the multispecies (with the index $i$ going over all species) form of the convective diffusive equation (3.1)

$$\frac{\partial C_i}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_i f\frac{\partial C_i}{\partial r} + \frac{r_0 v_0 C_i}{\theta}\right) - R_i \qquad (3.6)$$

with a set of corresponding mass action equations:

$$K_i = \gamma_i C_i \cdot \prod_j \gamma_j C_j^{n_{i,j}}, \qquad (3.7)$$

where $K_i$ is the equilibrium constant, $i$ indicates the species index, $C_i$ is the concentration in the soil solution, $\gamma_i$ is the activity coefficient, $j$ goes over all reaction partners of species $i$, $n_{i,j}$ is the stoichiometric coefficient of the components in the reaction equations, with the convention that the coefficients at the left side of the equation are negative (Parkhurst and Appelo, 1999). The set of mass action equations equation (3.7) represents various chemical and physicochemical reactions, such as (i) reactions between solutes, (ii) precipitation and dissolution of solid phases, (iii) dissolution and exsolution of gases, (iv) ion exchange, and (v) sorption on solid surfaces. Equations representing these processes and implemented numerical methods are described in detail in the Users' Manual of PHREEQC (Parkhurst and Appelo, 1999). When interactions between the solid phase and the soil solution are described using mass action equations, the buffer power $b$ in equation (3.1) is zero ($b'$ is equal to $\theta$) as it is in equation (3.6).

To ensure electroneutrality during the transport, the diffusion coefficient $D_i$ has to be corrected using a term that represents the effect of Coulomb forces between dissolved ions (Nietfeld, 2001):

$$D_i^{corr} = \frac{D_i z_i C_i}{\sum_j z_j^2 C_j D_j}\sum_k z_k D_k \frac{\partial C_k}{\partial r}, \qquad (3.8)$$

where $z_{i/j/k}$ (dimensionless) is the charge; $j$ and $k$ go over all species.

The common weakness of available computer codes calculating the equilibrium of soil solutions is the inconsistency of their databases. The constants included in these databases are often from separate sources and determined using different measurement methods (Parkhurst and Appelo, 1999). This shortcoming can cause major difficulties in calculations involving the surface sorption of microelements (Essington, 2006; Goldberg, 2006). Published values of thermodynamic parameters describing surface complexation on hydrous ferric oxides are highly variable due to differences in applied

experimental methods, the type of hydrous ferric oxide, and the model assumptions used to fit the experimental data (Dzombak and Morel, 1990; Venema et al., 1996). The parameter set includes not only the equilibrium constants of the corresponding stoichiometric reactions, but also the density of surface binding sites. Recent studies combining batch experiments and modelling using different codes and assumptions confirmed that satisfactory results can be achieved only after reconsidering processes and constants in the chemical database of geochemical codes (Tretner, 2002; Le Guern et al., 2003; Gustafsson, 2006)

## *3.4 The new code RhizoMath*

The computer model RhizoMath is being developed in MATLAB (The MathWorks, 1984-2008). It is comprised of two main modules: (i) the initialization module that determines using inverse modelling certain parameters (Table 3.1) describing the chemical speciation in the solution at the beginning of the experiment, and (ii) the coupled speciation and transport module that solves the problem of plant uptake, transport, and speciation in the rhizosphere by alternating between transport and speciation calculations. Chemical speciation is calculated in both modules using the geochemical code PHREEQC (Parkhurst and Appelo, 1999), which is coupled to MATLAB via an interface function. This function carries out data exchange between the two programs using ASCII files. PHREEQC input files are generated before each optimization step of the initialization module, and for each equilibrium calculation of the transport module. In the latter, each grid point is defined as a separate solution. The quantities of minerals, surface sorption sites and exchange capacity (related to one kg soil) are corrected by the volumetric water content and the density of the solid phase to establish a one litre soil solution, which is the default volume in PHREEQC (Parkhurst and Appelo, 1999). The output file (a tab-separated ASCII spread sheet) after each calculation contains concentrations of all relevant species, the saturation indices of all mineral phases contained in the database that could be formed from the present elements, and the detailed speciation of surface binding sites. This file is then automatically read by the interface function. This type of coupling is less efficient than direct coupling and compiling of two codes, as done for example in the HP1 code (Jacques et al., 2002; Jacques et al., 2008). While a large number of file I/O operations slows down the calculations carried out, this type of coupling allows for the use of, and simple upgrading to, the most recent version of PHREEQC. The slowing of calculations due to I/O operations was hardly noticeable, as the CPU speed turned out to be the limiting factor.

RhizoMath is controlled using a graphical user interface, and is available from the *www.bass.ufz.de* homepage in two versions: the stand-alone version that requires the installation of the MATLAB Runtime Environment (free of charge), and the pre-compiled (p-code) version that requires the installation of MATLAB and provides users with higher flexibility as they can freely replace any RhizoMath functions. The source code of RhizoMath is available directly from the corresponding author. PHREEQC has to be downloaded directly from its homepage.

*Table 3.1. Overview of different parameters used in calibration and transport modelling. The calibration module applies the Nelder-Mead simplex algorithm to minimize the root mean square error between measured (user input) and modelled (from PHREEQC output) concentrations by changing optimized parameters. The optimized values are going to be used as constants during the transport modelli*ng.

| Parameter | Calibration | Transport |
|---|---|---|
| Concentrations of elements and species | Variable | variable |
| Initial concentrations of primary components | can be optimized | constant |
| Amounts of weak and strong surface binding sites | Optimized | constant |
| Equilibrium constants of selected reactions | Optimized | constant |
| Environmental parameters (water content, partial pressure of $CO_2$, bulk density and moles of exchanger) | Constant | constant |

## Initialization - Numerical procedure

Reactive transport modelling requires a correct description and a sufficient understanding of the chemistry of applied solutes and porous media. The processes and parameters describing the soil solution composition have to be decided at the beginning of the experiment. To avoid using unjustified assumptions or unreasonable values for required parameters, their values should be determined by means of inverse modelling (Hopmans and Bristow, 2002).

Input parameters of the transport module of RhizoMath are either known (added nutrients and minerals), can be measured (volumetric water content, specific surface area of sorbents, such as goethite) or are uncertain (the number of surface binding sites or values of equilibrium constants of the stoichiometric equations describing surface complexation). Sorption of different ions on hydrous ferric oxides is described in PHREEQC using the generalized two-layer model [GTL, (Dzombak and Morel, 1990)] that is included in RhizoMath. The Charge-Distribution and Multisite Complexation [CD-MUSIC, (Hiemstra and van Riemsdijk, 1996)] model that is available in versions of PHREEQC higher than 2.13 is currently not available in RhizoMath.

Values of parameters marked by the user as uncertain are optimized by minimizing the weighted root mean square error *RMSE* (2.9) between concentrations measured using batch experiments and those calculated using the geochemical model (Kool et al., 1987):

$$RMSE = \sum_i \left( \frac{C_i^{meas} - C_i^{mod}}{C_i^{meas}} \right)^2 , \qquad (3.9)$$

where *i* goes over all elements and species, concentrations of which were measured, $C_i^{meas}$ represent measured and $C_i^{mod}$ modelled concentration values. Optimized

parameters can include both variables from the PHREEQC input file, as well as constants from the geochemical database.

Initial values of optimized parameters required to describe batch experiments have to be provided as user input. Speciation in the solution is calculated using PHREEQC, which communicates with MATLAB via the interface function described above. To avoid the need for calculating derivatives during the optimization process, which is a common disadvantage of methods based on the Gauss-Levenberg-Marquardt algorithm (Dubus, 2002), we used the Nelder-Mead simplex method (Lagarias et al., 1998), which is integrated in the fminsearch function of MATLAB, to determine the optimal values of unknown parameters.

**Coupled transport-speciation problem - Numerical procedure**

Transport in the rhizosphere is described in RhizoMath using equation (3.1) for scenarios that neglect chemical speciation, and using equation (3.6) for scenarios that consider chemical speciation. One-dimensional linear forms of equations (3.1) and (3.6), suitable for planar systems such as rhizoboxes or compartment systems (Wenzel et al., 2001; Vetterlein and Jahn, 2004b), are also included in RhizoMath. Diffusion coefficients can be corrected using equation (3.8) to maintain the charge balance during transport. If the charge balance is neglected, transport equations for total concentrations are solved, instead of transport equations representing each species. Root water uptake can either be constant or a function of time, using theoretical (modeled) values or deducing uptake from measured evapotranspiration.

Root uptake and excretion of ions are represented using the inner boundary condition and need to be defined for each solute. Zero-sink (De Willigen and van Noordwijk, 1994a), constant sink (De Willigen and van Noordwijk, 1994b), linear sink (Baldwin et al., 1973) and modified Michaelis-Menten kinetics (Barber and Cushman, 1981; Barber, 1995) are available options. It is suggested that plant and nutrient specific uptake parameters be looked up in the existing literature (e.g. Barber, 1995) or to be determined using pot experiments.

Equation (3.6) and coupled algebraic equations (3.7) are solved numerically using a non-iterative split-operator technique, i.e., transport and speciation are calculated in two separate steps (Miller and Rabideau, 1993; Parkhurst and Appelo, 1999; Nietfeld, 2001; Jacques et al., 2002)). We implemented the operator splitting approach, in which transport equations are solved first for one time step and then chemical speciation, assuming equilibrium is calculated with PHREEQC at the end of each time step. The length of time steps has to be set by the user with respect to the Courant criterion (e.g. Jacques et al., 2006).

The PDE (partial-differential equations) solver pdepe built-in MATLAB (Skeel and Berzins, 1990; Shampine and Reichelt, 1997) is used to solve the transport equations in dimensionless form (Darrah and Roose, 2001). The applied numerical method is based on a simple piecewise nonlinear Garlekin/Petrov-Garlekin method with second order accuracy. The method solves ODEs (ordinary-differential equations) resulting from the spatial discretization using a built-in MATLAB ODE solver. The derivation of the algorithm is presented by Skeel and Berzins (1990). The authors demonstrated

the applicability of the method for solving convection-diffusion and diffusion problems on different examples. Although the applied time step is selected dynamically by MATLAB to provide the stability of the integration, a minimum time step can be adjusted when needed. Spatial discretization is uniform for planar geometry, and logarithmic for radial geometry. The interface function uses concentrations, amounts of present mineral phases, and surface sorption data to generate a single input file and to run PHREEQC. Thereafter, corresponding MATLAB variables are automatically updated. To reduce the computational time for problems that neglect chemical speciation, equation (3.1) is solved using only the PDE-solver of MATLAB without operator splitting.

**Verification of the initialization module**

The initialization module was used to determine the number of surface binding sites and values of the equilibrium constants of corresponding stoichiometric equations describing the surface complexation of $As^V$ on goethite at the beginning of compartment system experiments reported by Vetterlein et al. (2007). Concentration values derived from soil solution samples of compartment systems without goethite were used as initial values for systems containing 1 or 4 g kg$^{-1}$ goethite. Based on saturation indices, quartz, gypsum, strengite and $CO_2$ were defined as equilibrium phases. The applied minteq.dat database was modified to exclude nitrification and
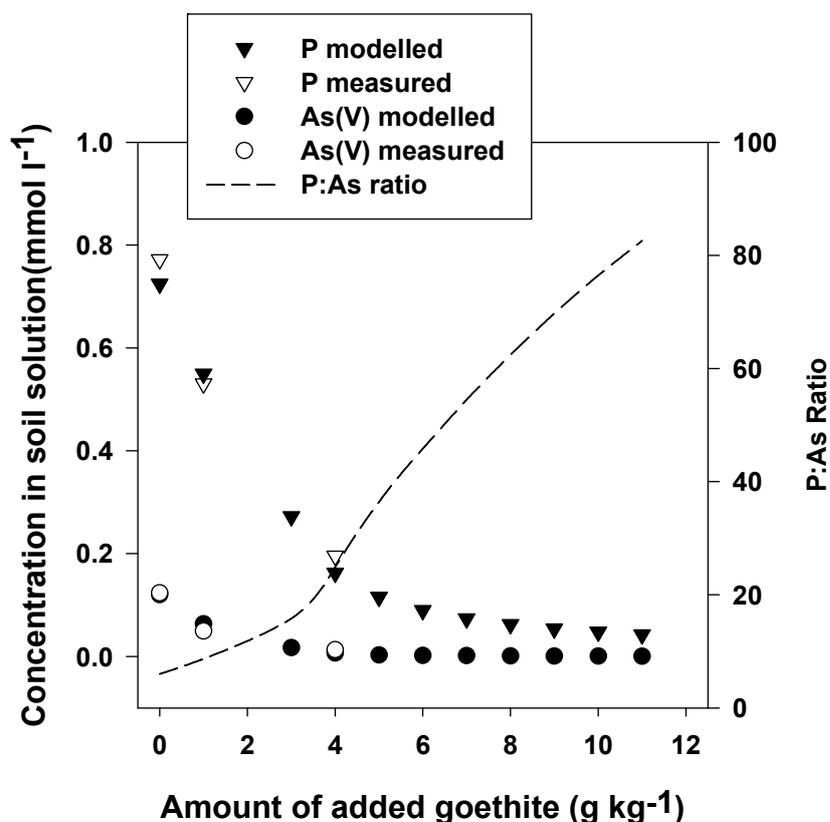


*Figure 3.1. Concentrations of $As^V$ and $P^V$ in the soil solution with increasing amounts of added goethite, calculated with PHREEQC using the sorption parameters optimized with RhizoMath for 0, 1 and 4 g kg$^{-1}$ goethite (G-0, G-1, G-4, respectively).*

extended with the sorption of carbonate according to Appelo et al. (2002). The specific surface of goethite was measured using the BET $N_2$ adsorption technique. Initial numbers (e.g., starting values for the optimization) of weak and strong surface binding sites of hydrous ferric oxide were estimated according to Tretner (2002). Initial values of the equilibrium constants of the surface binding reactions were taken from Dzombak and Morel (1990). The optimized parameter set enabled PHREEQC to describe the initial soil solution composition of the compartment system experiments with 1 and 4 g kg$^{-1}$ goethite. The same parameter set was applied to model hypothetical scenarios with different amounts of added goethite (Fig. 3.1). The increasing $P^V$:$As^V$ ratio with increasing amount of added goethite was found to agree well with observations of Violante and Pigna (2002).

**Verification - Description of the case studies**

Two simple published datasets were used first to test RhizoMath and to compare it to other models (Nowack et al., 2006). As suggested by Nowack et al. (2006), diffusion of potassium toward a single root was chosen as the first benchmark problem. We used the same parameters (Table 3.2) as the previously mentioned authors, and quantified the accuracy of calculated concentration profiles using the same norm:

$$\|C\|_2 = \frac{\sqrt{\sum_{n=1}^{N}(C_n - C_{n,an})^2}}{N \cdot C_0}, \tag{3.10}$$

where $C_0$ is the initial concentration, $C_n$ is the calculated concentration at the $n^{th}$ (of $N$) grid point at $t = 120$ days, and $C_{n,an}$ is the corresponding concentration calculated using the analytical solution of Roose et al. (2001):

$$C_{n,an}(t) = C_0 - \frac{C_0\lambda}{1 + C'_\infty + L(t) + \{4C'_\infty + [1 - C'_\infty + L(t)]\}} \times E_1\left(\frac{r_n^2}{4D_e t}\right), \tag{3.11}$$

where $C'_\infty = C_0/K$, $\lambda = J_{max}r_0/(\theta D_w f K)$, $r_n$ is the position of the $n^{th}$ grid point, $E_1$ is the exponential integral

$$E_1(x) = \int_x^\infty \frac{e^y}{y}dy, \tag{3.12}$$

and

$$L(t) = \frac{\lambda}{2}\ln[4\exp(-0.5772)D_e r_0^{-2}t + 1]. \tag{3.13}$$

To test if any artifacts were created by the coupling of MATLAB and PHREEQC, the concentration of potassium in the soil solution was calculated using RhizoMath (i) while neglecting the chemical speciation, and (ii) when coupling chemical speciation to the transport problem, but including only K$^+$ as K-species from the database. Numerical solutions of equation (3.1) in case (i) and equations (3.6) and (3.7) in case (ii) are expected to be the same. Since the transport equation (3.6) applied in case (ii)

does not include buffer capacity, but uses the diffusion coefficient in water, the corrected diffusion coefficient $D'$ was selected to result in the same effective diffusion coefficients in both cases: $D' = D_w / (\theta+b)$. The chemical database of PHREEQC contained only $K^+$ as K-species. pH was adjusted to reach the charge balance (Parkhurst and Appelo, 1999).

The second case study represented a qualitative benchmark for RhizoMath. Its goal was to test if the model is capable of simulating more complex rhizosphere processes. Whether or not RhizoMath is capable of reproducing patterns of concentrations in the soil solution was tested against the experimental data of Vetterlein et al. (2007). Vetterlein et al. (2007) used a compartment system with *Zea Mays* (corn), in which $P^V$ and $As^V$ concentrations were manipulated using applications of different quantities of goethite. The analysis of soil solutions sampled at increasing root distances ten days after planting showed an increase in $P^V$ concentrations close to the root surface and in the root zone. Such distribution of concentrations was not observed for $As^V$. As roots are known to exudate citrate to mobilize $P^V$, the transport module of RhizoMath was applied to simulate the effect of citrate exudation by a single root of corn (*Zea Mays*) on the competitive sorption of $As^V$ and $P^V$ on goethite. Stoichiometric equations describing the sorption of citrate on goethite are available only for the constant capacitance model (Lackovic et al., 2003) that converges to the GTL model in solutions with higher ionic strength (Goldberg, 1995). The only difference between these two models is the relation between the surface charge and the surface potential, which affects the Coulomb correction terms of the equilibrium constants, but not the intrinsic equilibrium constants themselves. Therefore we decided to include the intrinsic equilibrium constants for the sorption of citrate on goethite published for the constant capacitance model. Besides $P^V$, $As^V$ and citrate, $K^+$ and $H^+$ were also present as cations in the solution. The initial $K^+$ concentration was selected to provide electroneutrality, and the initial $H^+$ concentration was set to an initial pH of 5.5 (based on the experimental value). The input parameters of the RhizoMath simulation are summarized in Table 3.3. The minteq.dat database was extended with the stoichiometric equations for sorption and speciation of citrate, and the corresponding equilibrium constants using Table 1 of Lackovic et al. (2003). Sorption parameters were the same as in the first test. The citrate exudation rate was estimated based on Schulz and Vetterlein (2007). Uptake parameters for $P^V$ and K were adapted from Barber (1995). Parameters of $As^V$ uptake kinetics were calculated according to Meharg and Macnair (Meharg and Macnair, 1992) assuming that $As^V$ uptake by *Zea Mays* is similar to other grass species (Gulz et al., 2005). Calculations were repeated without citrate exudation.

*Table 3.2. Input parameters for modeling diffusion of potassium towards a single root with RhizoMath (i) while neglecting the chemical speciation and (ii) when coupling chemical speciation to the transport problem and not allowing interactions for K. Values adapted from Nowack et al (2006), Table 1.*

| Parameter | Value |
|---|---|
| Root radius $(r_0)$, cm | 0.02 |
| Water flux $(v_0)$, cm s$^{-1}$ | 0 |
| Water content $(\theta)$, m$^3$ m$^{-3}$ | 0.3 |
| Bulk soil density $(\rho)$, g cm$^{-1}$ | 1.15 |
| Buffer capacity $(b)$ | 39 †     0 ‡ |
| Soil impedance factor $(f)$ | 0.3 |
| Initial K concentration $(C_0)$, nmol cm$^{-3}$ | 46 |
| K concentration at the outer boundary $(C_\infty)$, nmol cm$^{-3}$ | 46 |
| Diffusion coefficient in water $(D_w)$, cm$^2$ s$^{-1}$ | $1.00\times10^{-5}$ † |
| Corrected diffusion coefficient§ $(D')$, cm$^2$ s$^{-1}$ | $7.63\times10^{-8}$ ‡ |
| Maximal influx of K $(J_{max})$, nmol cm$^{-2}$ s$^{-1}$ | 0.03 |
| Michaelis-Menten constant for K $(K)$, µmol cm$^{-3}$ | 0.014 |
| Minimal uptake limit for K $(C_{min})$, nmol cm$^{-3}$ | 0 |
| Elapsed time, days | 120 |
| Number of cells§ | 100 |
| Operator splitting§ | after each 0.1 day |
| Position of the outer boundary, cm | 4 |

†,‡ : Applied for cases (i) and (ii), respectively

§: specific for RhizoMath

*Table 3.3. Input parameters for modeling the effect of oxalate exudates from a single root on the availability of $P^V$ and $As^V$ adsorbed by goethite.*

| Parameter | Value |
|---|---|
| Root radius ($r_0$), cm | 0.02 † |
| Water flux ($v_0$), cm s$^{-1}$ | $2\times10^{-7}$ |
| Water content ($\theta$, m$^3$ m$^{-3}$ | 0.21 § |
| Bulk soil density ($\rho$), g cm$^{-1}$ | 1.35 § |
| Soil impedance factor ($f$) | 0.3 |
| Mass of added goethite, g kg$^{-1}$ dry soil | 1, 4 † |
| Specific surface of added goethite, m$^2$ g$^{-1}$ | 128 § |
| Initial P concentration ($C_{0,P}$), mmol cm$^{-3}$ | 5 |
| Initial As concentration ($C_{0,As}$), mmol cm$^{-3}$ | 2 |
| Initial citrate concentration ($C_{0,Cit}$), mmol cm$^{-3}$ | 0 |
| Diffusion coefficient of P$^V$ in water ($D_{w,P}$), cm$^2$ s$^{-1}$ | $8.46\times10^{-4}$ †† |
| Diffusion coefficient of As$^V$ in water ($D_{w,As}$), cm$^2$ s$^{-1}$ | $8.46\times10^{-4}$ †† |
| Diffusion coefficient of K$^+$ in water ($D_{w,K}$), cm$^2$ s$^{-1}$ | $1.96\times10^{-5}$ †† |
| Diffusion coefficient of citrate in water ($D_{w,Cit}$), cm$^2$ s$^{-1}$ | $8.10\times10^{-6}$ |
| Maximal influx of P$^V$ ($J_{max}$), µmol cm$^{-2}$ s$^{-1}$ | 4 ‡ |
| Maximal influx of As$^V$ ($J_{max}$), µmol cm$^{-2}$ s$^{-1}$ | $2.98\times10^{-7}$ §‡‡ |
| Maximal influx of K$^+$ ($J_{max}$), µmol cm$^{-2}$ s$^{-1}$ | $2.6\times10^{-5}$ ‡§ |
| Michaelis-Menten constant for P$^V$ ($K$), µmol cm$^{-3}$ | $2\times10^{-3}$ ‡ |
| Michaelis-Menten constant for As$^V$ ($K$), µmol cm$^{-3}$ | $2.4\times10^{-2}$‡‡ |
| Michaelis-Menten constant for K$^+$($K$), µmol cm$^{-3}$ | $1.7\times10^{-2}$‡ |
| Minimal uptake limit for P$^V$ ($C_{min}$), µmol cm$^{-3}$ | $4\times10^{-3}$‡ |
| Minimal uptake limit for As$^V$ ($C_{min}$), µmol cm$^{-3}$ | 0 |
| Minimal uptake limit for K$^+$ ($C_{min}$), µmol cm$^{-3}$ | $7\times10^{-5}$‡ |
| Citrate efflux ($J_{Cit}$), µmol cm$^{-2}$ s$^{-1}$ | $3\times10^{-12}$ † |
| Elapsed time, days | 10 § |
| Position of the outer boundary, cm | 4 |

†: Estimated after Schulz and Vetterlein. (2007); ‡: Barber (1995)

§: Vetterlein et al (2007) ††:Parkhurst and Appelo (1999) ‡‡: Meharg and Macnair (1992)

**Verification – Results and discussion**

Figure 3.2 compares concentration profiles of potassium calculated using either RhizoMath or the analytical solution at 120 days for the first case study. Results of numerical solutions carried out with RhizoMath with and without considering chemical speciation are almost identical and both approximate the analytical solution very well. The $\|C\|_2$ norm (equation 3.10) calculated for the entire coordinate range is $\underline{O}(10^{-4})$ in both cases. The relative error of both numerical solutions increases at the root surface, with a maximum relative error lower than 4% in both cases (Fig. 3.2b). These two measures of accuracy were comparable to or better than corresponding values calculated for other codes applied to the same problem (Nowack et al., 2006; Roose et al., 2007). The same accuracy in both cases (with and without speciation) indicates that no artifacts were caused by the coupling of PHREEQC and MATLAB.

The difference between the analytical solution and the numerical results increased close to the root surface for all three codes (ORCHESTRA, PHREEQC, MIN3P) due to the fact that the analytical solution is only an approximation (Roose et al., 2001). As the degree of difference between the numerical results and the analytical solution
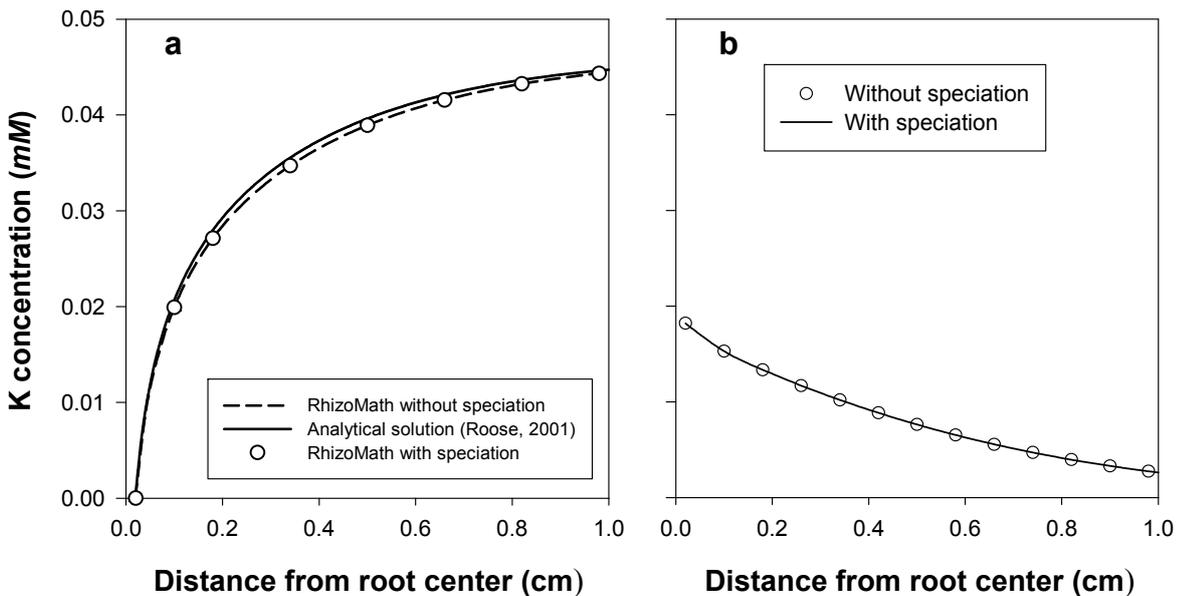


*Figure 3.2. Concentration profiles of potassium after 120 days calculated using two different modes of RhizoMath (with and without speciation) and using the analytical solution of Roose et al (2001). Results are presented using (a) absolute values and (b) relative errors*

varies depending on the code, the accuracy of applied numerical procedures likely differs as well. Probable reasons for these differences are: (i) root uptake is represented in ORCHESTRA as a sink and not as a boundary condition, which can be inaccurate for higher fluxes; (ii) the root in PHREEQC is defined as a zero sink to increase speed; and finally (iii) MIN3P uses the Cartesian coordinate system instead of radial coordinates.

Concentration profiles of $As^V$ and $P^V$ in the soil solution ten days after planting are shown in figure 3.3 for the second case study. The choice of different grid sizes and

time steps showed that the shape of the $As^V$ concentration profile is not a numerical artifact. In the case with citrate exudation, calculated concentration profiles agreed well with those presented by Vetterlein et al. (Vetterlein et al., 2007). However, in contrast to simulated results, no decrease of $As^V$ concentrations was observed in the experiments. Variations in experimental $As^V$ concentrations had the same order of magnitude as the calculated $As^V$ depletion. Concentration profiles calculated without considering citrate exudation represent a hypothetical case as this process can not be "turned off" in plants.

A comparison of results calculated with and without citrate exudation shows that the increase in $P^V$ concentrations with a decreasing distance to the root surface is not caused by $P^V$ delivery, but is a result of citrate induced $P^V$ mobilization. While the experimental data based on soil solution sampling can only show net changes in concentrations occurring with distance and time, RhizoMath has the potential to separate underlying processes and thus to support interpretation of the experimental results. Quantitatively correct predictions of concentration changes during the entire experiment would require the additional extensions of RhizoMath that are outlined below in conclusions.
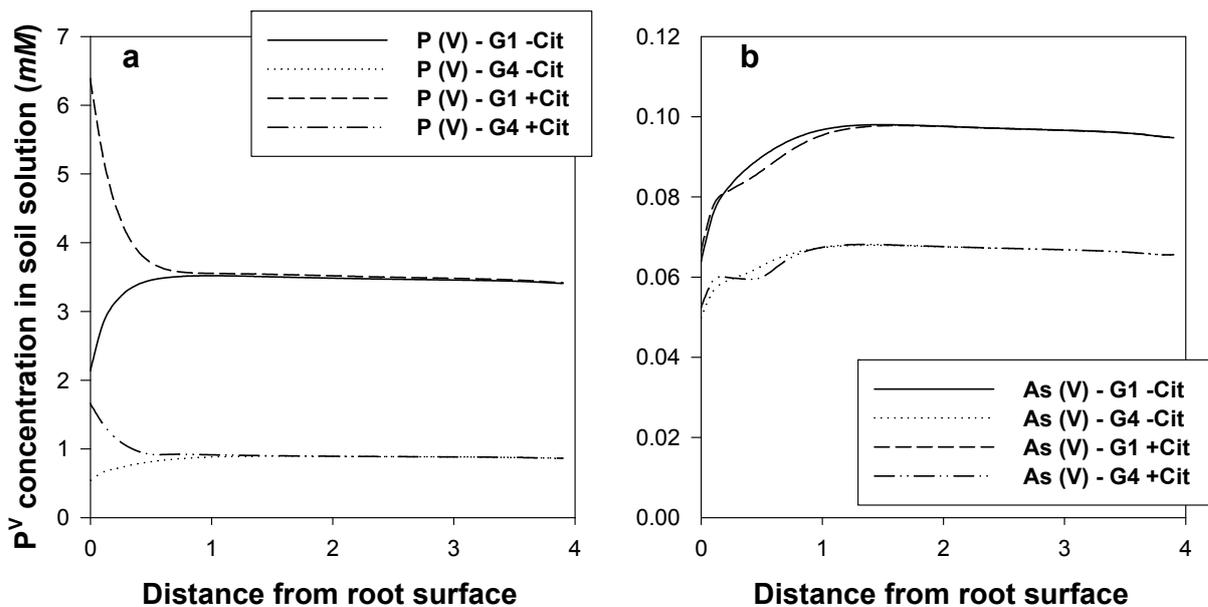


*Figure 3.3. Concentrations of a) $P^V$ and b) $As^V$ in the soil solution ten days after planting at constant citrate exudation (+Cit) and without citrate exudation (-Cit) in the presence of 1 and 4 g kg$^{-1}$ goethite (G-1, G-4, respectively), calculated with the transport module of RhizoMath.*

## *3.5 Conclusions*

The new computer tool RhizoMath for calculating transport and speciation in the rhizosphere uses a microscopic approach. The model allows for the calculation of scenarios involving steady-state water uptake and various interactions among nutrients and solid or gas phases, as well as surfaces and cation exchangers. The model performance was found to be satisfactory when compared against other codes (Nowack et al., 2006) and when used to model the laboratory experiments of Vetterlein et al. (Vetterlein et al., 2007). The model was capable of describing complex rhizosphere processes, such as the effect of organic root exudates on competitive sorption of $P^V$ and $As^V$.

Considering the advantages and disadvantages of the RhizoMath model, added values include the following:

Due to the RhizoMath graphical user interface, the program can be applied by researchers who are not familiar with syntaxes of transport codes.

An initialization module for the calibration of initial parameters is included in RhizoMath and thus there is no need to learn additional calibration software, such as UCODE or PEST.

The system geometry can be simply changed from planar (geometry of compartment system experiments) to radial (a single root) in the graphical user interface.

Root uptake is represented as a boundary condition of the transport equation and not as a sink term in the last cell. This results in a higher accuracy of calculated root uptake in the last cell.

Upcoming studies will apply RhizoMath to describe a series of compartment system experiments similar to the one presented in Vetterlein et al. (Vetterlein et al., 2007), but with minerals such as ferrihydrate and allophane instead of goethite. This will, however, require additional changes to RhizoMath. A nutrient-nutrient competition due to root uptake has to be included, in addition to chemical kinetics, in order to describe a competitive uptake of $As^V$ and $P^V$ (Esteban et al., 2003).

RhizoMath represents a basis on which a computer program can be developed to model coupled transport and chemical speciation in three dimensional root systems. This is a prerequisite for our future goal of using RhizoMath in combination with compartment system experiments to identify processes at the micro-scale of roots that are relevant for soil-profile and field scale models. This will allow us to describe and predict bioavailability and fate of arsenic and other contaminants in the field.

# 4. Extending the Multi-Component Rhizosphere Transport Model RhizoMath by Including Dynamic Parameters for Driving Force and Nutrient Requirement

Krisztian Szegedi, Doris Vetterlein, Reinhold Jahn

## *4.1 Abstract*

Combining compartment system experiments and computer modelling enable the study and separation of complex processes in the rhizosphere. The mathematical description of root uptake in a compartment system was extended by including the root compartment factor (*RCF*). This factor accounts for root growth behind the constant cross section of the nylon mesh that separates root and bulk soil compartments and it can also describe a higher active root surface as the area of the nylon mesh. The *RCF* was included in the rhizosphere model RhizoMath. The code was then applied to calculate different scenarios in the compartment system. It was shown that temporal development of root uptake could be represented by the development of leaf area and that temporal development of water flux should not be neglected. A review of available literature on root uptake parameters showed a high variability of Michaelis-Menten parameters ($K_m$, $C_{min}$, $I_{max}$). This allowed the successive approximation of maximum influx of the Michaelis-Menten kinetics. Using the so determined uptake parameters for modelling transport in the compartment system led to a very good representation of measured concentration profiles and their temporal dynamics.

## *4.2 Introduction*

Understanding the physicochemical and biological processes that control the transfer of contaminants from the soil to plants is important for the utilization and remediation of contaminated soils. Some contaminants, such as arsenic, can show a very complex chemical behaviour: arsenate ($As^V$), the dominant arsenic species in aerobic soils, competes with $P^V$ for binding sites in the soil, i.e. goethite or ferrihydrite (Jain and Loeppert, 2000; Smith et al., 2002) and for binding sites at the root membranes (Meharg and Macnair, 1992; Poynton et al., 2004). $P^V$ in soil can be mobilised by plants through different mechanisms like ligand exchange through organic acids or by acidification of the rhizosphere through proton release (Hinsinger et al., 2003). It was shown that the same mechanisms may alter the competition between $As^V$ and $P^V$ (Vetterlein et al., 2007) for soil binding sites. Rhizosphere processes have a strong influence on the chemical composition of soil micro-sites at the root surface (Hinsinger, 1998). Thus, any prediction on the uptake of contaminants that have such a complex chemistry as As can be made only after studying the relevant interactions using simplified physical and mathematical models of soil-plant system. These model systems enable the separation of individual processes that occur in an integrated form in nature (Darrah and Roose, 2001).

Compartment system experiments in which *Zea mays* was grown in nine compartment systems (Vetterlein and Jahn, 2004b) under controlled conditions on artificial quartz

substrate spiked with known amounts of nutrients, $As^V$ and with increasing amounts of goethite (Vetterlein et al., 2007) showed an influence of added goethite on the competition between $P^V$ and $As^V$ in the rhizosphere. The interpretation of the results was supported by computer modelling, but a full simulation of the experiments is still missing. There are only a few approaches for modeling coupled transport and speciation in the rhizosphere (Hoffland et al., 1990; Parkhurst and Appelo, 1999; Geelhoed et al., 1999; Nietfeld, 2001; Mayer et al., 2002; Meeussen, 2003; 2006) and none of them has been applied to model experiments that provided such temporally and spatially resolved data on the soil solution composition as it was provided by Vetterlein et al (2007). The newly developed code RhizoMath (Szegedi et al. 2008) includes multicomponent diffusion and a built in calibration module that determines the highly uncertain intrinsic equilibrium constants of surface sorption reactions and the amount of surface binding sites that are both required to describe the competitive sorption of $P^V$ and $As^V$ on goethite. This version of RhizoMath was already able to qualitatively reproduce experimentally observed effects of goethite addition on the concentrations of $P^V$ and $As^V$ in the soil solution using a simplified chemistry. However, in order to describe the temporal changes quantitatively the model must be extended to take growth into account which is reflected in increased water consumption (driving convection), nutrient requirement and also changes of the root surface for uptake.

Thus, we focus in this paper on extending RhizoMath for modelling multicomponent transport for a growing plant, i.e. including dynamic terms for nutrient requirement and uptake capacity besides dynamic water flux. The main objectives of this paper are (i) to include the description of temporal development of root mat in RhizoMath, (ii) and to find the best function that describes it, (iii) to separate its effect from the effect of temporally changing root water uptake on root nutrient uptake, (iv) to collect the relevant uptake parameters from existing literature and (v) to apply these achievements to quantitatively model the compartment system experiments presented by Vetterlein et al. (2007).

**Representation of root system in models**

Compartment systems are accepted to be treated as linear systems (Vetterlein and Jahn, 2004a), in which gradients are formed only with an increasing distance from the root compartment. Its prerequisite is the presence of a homogenous root mat. However, these experiments usually begin with seeding, which means that it can take several days till the development of a root mat, i.e. until the roots fill the root compartment. Schnepf represented a static root mat with a 60% coverage of the root compartment by multiplying the root influx described by the Michaelis-Menten kinetics with 0.6 (Schnepf, 2002; Puschenreiter et al., 2005). One dimensional microscopic models (single root approach) operate with fluxes concerning unit root surface. Uptake by a growing, intact plant is only possible by combining results gained with a microscopic approach with upscaling methods that describe a root system (Darrah et al., 2006). This happens either by integrating the uptake flux calculated for a single root over the growing root surface of homogeneously distributed roots

(Barber-Cushman method, Barber, 1995) or by considering root architecture using more complex mathematical instruments (Roose and Fowler, 2004). Cushman (1984) has included time dependency for root uptake parameters besides for root length density. The time-dependency of the uptake parameters represent the effect of aging processes of the plant. The single root approach included in RhizoMath does not directly allow the consideration of root growth or the dynamics of root mat formation. Thus, a critical point for the applicability of RhizoMath (and other microscopic approaches) for modelling compartment system experiments is that root uptake should be a function of time (or plant size) besides nutrient concentration in the soil solution.

**Accuracy of Michaelis Menten parameters**

The influx ($J_{MM}^{upt}$) is described for most nutrients and contaminants with the modified Michaelis-Menten (Barber, 1995) kinetics:

$$J_{MM}^{upt} = J_{max} \left( \frac{C - C_{min}}{K + C - C_{min}} \right), \qquad (4.1)$$

where $J_{max}$ (mol cm$^{-2}$ s$^{-1}$) is the maximal, concentration-independent influx of an ion, $K$ (mol cm$^{-3}$) is the Michaelis-Menten constant, i.e., the concentration at which the uptake rate is half of the possible maximum uptake, and $C_{min}$ (mol cm$^{-3}$) is the minimum concentration of the ion in the soil solution below which no uptake occurs. A collection of experimentally determined uptake parameters available in existing literature is presented in Tables 4.1 and A2.1 (in the Appendix). Substantial variability can be noticed for a range of elements although only values for the same plant species were compiled. This diversity has several reasons: (i) The uptake parameters are different almost for all genotypes of maize. (ii) The parameters are determined with different methods: either by the analysis of excised roots (Meharg and Macnair, 1992) or with the solution depletion technique (Claassen and Barber, 1974). The first method captures the short-term uptake of roots of a certain age and size whereas the latter method gives an average over a whole or trimmed root system on a longer time-scale. (iii) The $J_{max}$ has different units in different literature sources. Instead of using the uptake rate per unit root surface (mol·cm$^{-2}$·s$^{-1}$), which is required for the microscopic approach, the uptake rate is often related to root dry (mol·g$^{-1}$ dw·s$^{-1}$) of fresh weight (mol·g$^{-1}$ fw·s$^{-1}$) or to root length (mol·cm$^{-1}$·s$^{-1}$) (see the references of Tables 4.1 and A1.1). Although these dimensions are theoretically interconvertible, conversion factors from mol·g$^{-1}$·s$^{-1}$ to mol cm$^{-2}$·s$^{-1}$ are not given in most cases. A reasonable cause for it is that weight measurements are more rapid and contain no statistical simplifications such as the determination of specific root length and average root diameter do (Newman, 1966; Zobel, 2003). Additionally, calculating a most accurate root surface from the length and radii of individual root segments would require the consideration of each root segment or the use of a 3D imaging technique. Although imaging methods that would allow such methods are available, they are still not wide spread enough. In the case of missing data on root geometry, units with root fresh weight in the nominator have to be converted to surface-normed dimensions with average values: Lehto et al (2006) and Roose (2001) applied an average root diameter

and a root density of 1g·cm$^{-3}$. These values were also applied for compiling Table 4.1 and Table A2.1 (in Appendix 2). (iv) The relevance of the Michaelis-Menten kinetics in describing root influx was experimentally justified in many cases, although it is not always tested whether the root uptake is mediated by a transporter (Barber, 1995; pp 62-65) or occurs through a gated channel. The parameters of the Michaelis-Menten kinetics are not necessarily always constant: they can be influenced by cross-effects between different compounds such as in the case of Mg$^{2+}$ and Ca$^{2+}$ (Barber, 1995) and P$^{V}$ and As$^{V}$. Uptake by different transporters that contribute differently at different concentration ranges, such as it is in the case of potassium, is described in existing literature (Barber, 1995) by different values of root uptake parameters. Hence, in the case of same maize genotypes, the difference between the pre-treatment of the plants and the differences between the applied nutrient solutions could explain most of the heterogeneity of the $K_m$ and $C_{min}$ that both can be traced back to concentration measurements that can be assumed to be highly accurate.

Table 4.1. (Next page) Parameters of Michaelis-Menten kinetics (maximum influx $J_{max}$, Michaelis-Menten constant $K_m$, minimal concentration $C_{min}$). Min, Med and Max indicate the minimum, maximum and median of values collected from existing literature, respectively. Applied sources are indicated in brackets. A full list is provided as supporting material. An average root diameter of 0.02 cm and a root density of 1g•cm-3 (Lehto et al. 2006, Roose 2001) was applied where it was required. Mod indicates the parameters used for calculating scenarios i-vi (Table 4.3, Figs 4.2 to 4.5)). Opt indicates the modified parameters that allowed the best model performance (Fig. 4.6)

References:

[1]: Abbas and Meharg (2008), [2]: Horn et al. (2006), [3] Barber (1995), [4] Claassen and Barber (1974),

[5] Claassen et al.(1986), [6] Maas and Ogata (1971), [7] Claassen and Barber (1977),

[8] Jungk & Barber 1975, [9] Edwards and Barber (1976), [11] Warncke and Barber (Warncke and Barber, 1974), [12] Bhadoria et al (2004), [13] Berlier et al 1969, [14] Nissen (1973), [15] Ferrari and Renosto (1972), [16] Nocito et al (2002)

Table 4.1.

| Nutrient [References] | | $J_{max}$ $10^{-8}$ mmol cm$^{-2}$ s$^{-1}$ | $K_m$ μM | $C_{min}$ μM |
|---|---|---|---|---|
| **As$^{III}$** | Min | 0.37556 | 2050 | - |
| [1] | Med | 0.56958 | 3645 | - |
| | Max | 1.3453 | 9320 | - |
| | Mod | - | - | - |
| | Opt | - | - | - |
| **As$^V$** | Min | 0.015667 | 10 | - |
| [1] | Med | 0.1475 | 1250 | - |
| | Max | 0.27972 | 4690 | - |
| | Mod | 0.0198 | 0 | 0 |
| | Opt | 0.0198 | 0 | 0 |
| **Ca$^{2+}$** | Min | 14.781 | 40 | 5.34 |
| [3] | Med | 18.407 | 50.4 | 6.41 |
| | Max | 19.069 | 300 | 6.43 |
| | Mod | 0.59 | 39 | 5 |
| | Opt | 0.90 | 39 | 5 |
| **Cl-** | Min | 0.861 | 50 | - |
| [6] | Max | 1.083 | 100 | - |
| | Mod | 1 | 1 | 0 |
| | Opt | 1 | 1 | 0 |
| **K$^+$** | Min | 0.04 | 5 | 1 |
| [2,3,4,5,7,8] | Med | 3.515 | 17 | 5.2 |
| | Max | 318.31 | 39.1 | 15.3 |
| | Mod | 0.4 | 15 | 1 |
| | Opt | 6 | 15 | 1 |
| **Mg$^{2+}$** | Min | 0.417 | 24.5 | 0.56 |
| [2,3,6] | Med | 24.71 | 29.85 | 0.58 |
| | Max | 53.65 | 150 | 0.63 |
| | Mod | 0.071 | 15 | 0 |
| | Opt | 0.30 | 15 | 0 |
| **N** | Min | 0.0045 | 12 | 3 |
| [3,9,11] | Med | 0.087 | 16 | 6 |
| | Max | 1.2 | 20 | 9 |
| | Mod | 0.1 | 10 | 4 |
| | Opt | 0.1 | 10 | 4 |
| **N$^V$** | Min | 0.1 | 10 | 2 |
| [2,3,10] | Med | 255.1 | 37.1 | 5.09 |
| | Max | 375.5 | 70.6 | 17.6 |
| | Mod | 0.1 | 10 | 4 |
| | Opt | 0.1 | 10 | 4 |
| **P$^V$** | Min | 0.0127 | 3 | 0 |
| [2,3,8,12] | Med | 1.65 | 16.05 | 0.145 |
| | Max | 27.75 | 22 | 1.21 |
| | Mod | 0.04 | 3 | 0.2 |
| | Opt | 0.10 | 3 | 0.1 |
| **S$^V$** | Min | 0.028 | 20.5 | 0.11 |
| [3,12,13,14,15,16] | Med | 0.223 | 166 | 0.11 |
| | Max | 4.83 | 1100 | 2800 |
| | Mod | 0.16 | 28 | 0.021 |
| | Opt | 0.50 | 28 | 0.11 |

## 4.3 Modelling - Theory

Further developments were performed on the RhizoMath code: we implemented the $J^{upt}$ uptake flux in the code. This flux represents the flux through thy nylon mesh that separates the root compartment from the bulk soil compartment. It is expressed as the $J_{MM}^{upt}$ nutrient uptake flux (or influx) which is calculated from the nutrient concentration at the root surface and plant uptake characteristics (Szegedi et al., 2008) multiplied by the newly introduced *RCF* root compartment factor:

$$J^{upt} = RCF \cdot J_{MM}^{upt} . \tag{4.2}$$

*RCF* is expressed as the product of two time-dependent factors $g(t)$ and $d(t)$ regarding geometry and relative plant development, respectively:

$$RCF = g(t) \cdot d(t) . \tag{4.3}$$

Physically, the $g(t)$ function is the ratio of active root surface behind the nylon mesh and the area of the nylon mesh. To avoid an unnecessarily complicated $g(t)$ and to match the idea that only lateral fluxes exist in the compartment system the roots can be assumed to develop homogenously distributed in the root compartment. In this case $g(t)=g$ (constant).

The $d(t)$ function expresses the relative coverage of the nylon mesh: it is the proportion of the projected root area and the area of the nylon mesh. The temporal development of $d(t)$ can not be directly determined using the same compartment system setup. It can be either *a priori* defined, for example as a linear or exponential function following the analogy to the different models that describe plant growth (Barber, 1995), or related to measured transpiration or a measure of plant development such as leaf area. This resolves the controversy between calculating with homogenous flux across the constant cross section of the nylon net and the changing root surface of a growing plant.

According to the considerations in the introduction we suggest to select $K$ and $C_{min}$ from existing literature using the typical soil solution composition and the plant genotype as selection criteria. $J_{max}$ should be selected similarly from references and converted to mol cm$^{-2}$ s$^{-1}$ dimensions using data which mostly correspond to the studied plant. As the $J_{max}$ determined this way can be very uncertain it should only be taken as a starting value which would need to be modified: optimized or successively approximated.

## 4.4 Modelling - Practice

Concentrations of elements collected before planting were modelled with PHREEQC (Parkhurst and Appelo, 1999). The applied minteq.dat database was reduced, additionally modified to exclude nitrification and extended with the sorption of carbonate according to Appelo et al. (2002). Based on their saturation indices gypsum (SI=0.36) and CaHPO$_4$ (SI=-0.25) were defined as equilibrium phases (Kölling, 1988) besides quartz and CO$_2$. Both of the modelled Ca$^{2+}$ and S$^V$ concentrations in the soil solution appeared to be lower as the respective measured values (Table 4.2). This indicated an incorrect description of the dissolution of gypsum. The solubility product

of gypsum has divergent values in the different databases delivered with PHREEQC and in different literature sources (Bennett and Adams, 1972; Glas et al., 1979a; Glas et al., 1979b).

After trying each available value, based on the best agreement between our measured and modelled concentrations, we decided to use log_k=4.53 in the database (Bennett and Adams, 1972). A repeated calculation of soil solution composition showed the total dissolution of $CaHPO_4$. Thus, it was not included thereinafter as initial equilibrium phase. The modelled pH of the soil solution was only satisfying when the charge keyword of PHREEQC was placed by ammonium instead of pH. This means that charge balance was adjusted by adding or removing $NH_4^+$ ions instead of $H^+/OH^-$ ions. It is acceptable as a well described $H^+$ concentration is more important for modelling the interaction between the soil solution and goethite. The so introduced or removed $NH_4^+$ ions compensate the uncertainties of concentration measurements caused by microscopic heterogeneities and the (small) differences between different replications.

Transport in the compartment systems was modelled with the transport module of RhizoMath. The same phases and optimized parameters were applied during the transport modelling as for modelling the initial state of the system. The Nietfeld approach was used for transport modelling, i.e. diffusion was locally corrected to maintain charge balance in the soil solution. The approach of Tinker and Nye (2000) was also considered, but did not lead to significant changes in the results. Root water uptake was described as a quasi-steady flow derived from the transpiration rate. Soil water content was assumed to be constant. Root uptake of most species was described with the Michaelis-Menten kinetics. Applied parameters are presented in Table 4.1. Exceptions are the citrate exudation rate that was estimated based on Schulz and Vetterlein (2007) and $H^+/OH^-$ efflux that were calculated to maintain charge balance during the uptake. Table 4.3 gives an overview about the scenarios calculated to study the effect of different assumptions for mass flow (constant, linear increase, measured water consumption) and different *RCF* functions (linear, scaled with water flux, scaled with leaf area). Water fluxes were determined to have the same water passage through the nylon mesh after all scenarios. The first scenario (i) in which water flux is constant and *RCF* = 1 corresponds the Tinker-Nye-Barber model (Tinker and Nye, 2000). The other two scenarios (ii-iii) in which *RCF* = 1 correspond the approach previously included in RhizoMath (Szegedi et al., 2008). The last three scenarios (iv-vi) require the newly implemented feature (RCF) of RhizoMath that were described in the theory section. The water flux was taken as measured in these scenarios while different temporal developments of nylon mesh coverage (Fig. 4.1.) were applied in each. Scenarios in which the temporal development of mesh coverage was varied but constant or linearly changing water flux are assumed, were not considered as they are unrealistic. As it is described later, after selecting the most appropriate temporal development of $d(t)$ and $g$, $J_{max}$ were successively modified to achieve the best overall model performance. The shape and temporal development of the concentration profiles is as important as the absolute differences between modelled and measured concentrations. Thus, we decided to visually compare modelled and measured

concentration profiles and use successive approximation for achieving the best $J_{max}$ instead of minimizing the quadratic difference between measured and modelled values.

*Table 4.2. Total concentrations of ions ($C_{meas}$ )that were measured by analyzing the soil solution samples collected after one week of relaxation without the presence of the plants, compared to modelled concentrations calculated with PHREEQC using log_k= - 4.848 and log_k= - 4.53 for the solubility product of gypsum ($C_{mod1}$ and $C_{mod2}$, respectively). Concentrations of ions that were present in the soil solution but are not included in table 4.2. but were not affected by changing the solubility product of gypsum.*

| Analyzed in soil solution | $C_{meas}$ (mmol L$^{-1}$) | $C_{mod1}$ (mmol L$^{-1}$) | $C_{mod2}$ (mmol L$^{-1}$) |
|---|---|---|---|
| $NH_4^+$ | 10.52 | 22.94 | 14.02 |
| $S^V$ | 14.46 | 10.35 | 11.49 |
| $P^V$ | 0.72 | 0.81 | 0.72 |
| $Ca^{2+}$ | 13.89 | 7.24 | 12.24 |
| pH | 5.54 | 6.02 | 5.41 |

*Table 4.3. Summary of the scenarios calculated using different assumptions on water flux and the development of plant nutrient demand (expressed with d(t)).*

| Scenario | Water flux | d(t) |
|---|---|---|
| (i) | constant [1] | 1 |
| (ii) | linear [2] | 1 |
| (iii) | as measured | 1 |
| (iv) | as measured | linear (0..1) |
| (v) | as measured | scaled with water flux [3] |
| (vi) | as measured[4] | scaled with leaf area [3] |

[1] $v$=8.23·10$^{-7}$; [2] $v = 4·10^{-8}$ $t$ + 2.9·10$^{-}$7, 3 see Fig. 4.1, [4]determined with weighing cells measurements of the compartment system.

## *4.5 Results*

Compartment system experiments carried out by Vetterlein et al. (2007) were used as reference for the modelling. The experimental setup and a qualitative interpretation of the observations were presented by the authors, parameters of the experiment are briefly summarised in the Appendix in Tables A1.1 and A1.2. Figures 4.2 to 4.5 include measured concentrations averaged over right and left compartments. The first data point in front of the dashed vertical line in the figures 4.2 to 4.5 shows an average over all samples in the root compartment that can be interpreted as samples from the immediate vicinity of the roots. Results beyond 24 days after planting are not discussed to avoid the difficulty of describing water relations in the system during the last week when the plants required a frequent watering. Although concentration profiles can be calculated for any ion, we concentrated here on presenting results for $Ca^{2+}$, $P^V$, $Cl^-$ and pH. $Ca^{2+}$ is interesting as it is in interaction with the solid phase already in the treatment without added goethite and because it is a potential precipitation partner of P. P is an important nutrient and a chemical analogue of $As^V$ that is also present in the system. $Cl^-$ can be used as a nonreactive tracer and the pH is going to be an important parameter later when sorption on goethite would be also included in the calculations.

Scenarios i-iii were calculated using RCF = 1, which means that nutrient uptake was calculated according to equation (4.1). Figure 4.1 shows the measured temporal development of mass flow and leaf area which are non-linear with time and differ from each other: mass flow reaches 10 percent of its maximal value after ~3 days, while the
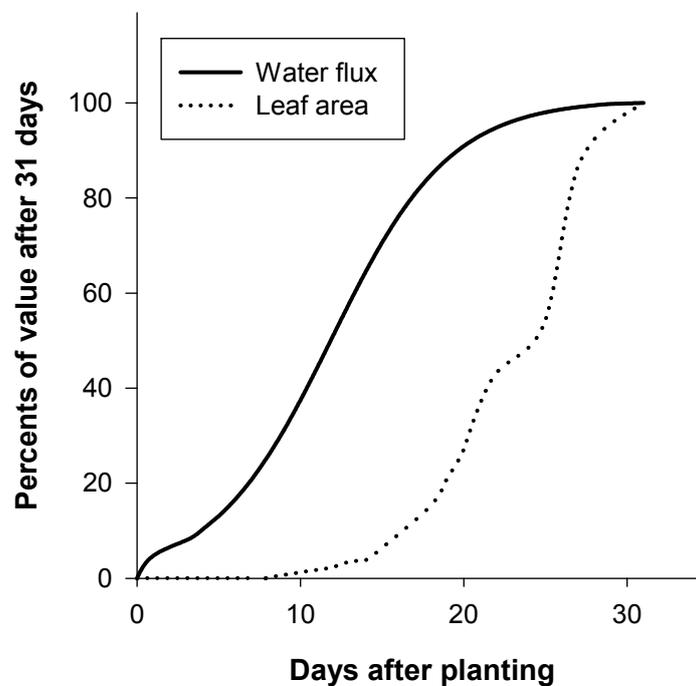


*Figure 4.1. Temporal development of water flux (estimated from weighing cell measurement of evapotranspiration) in the compartment system (solid) and temporal development of the leaf area of maize plants grown in the system (dotted). Both data are expressed as a percentage of the corresponding value on the 31st day after planting.*

leaf area needs ~16 days for this. Over 90% of the saturation value is reached after ~18 days by mass flow and only after ~27 days by leaf area. The true temporal development of water flux is taken into account in scenarios iii − vi. A non-linear change of RCF is taken into account in scenario v-vi.

The analysis of soil solution samples gained from the compartment system experiments showed a depletion of $Ca^{2+}$ at the root surface after ten days, depletion at the root surface and an accumulation close to the root surface after 17 days, which turned into a monotonous decrease of $Ca^{2+}$ concentration with an increasing distance from the root surface after 24 days. The concentration at the root surface exceeded the initial $Ca^{2+}$ concentration after 24 days (Fig. 4.2). $Ca^{2+}$ concentration in the bulk soil showed an overall decrease. Measured P concentrations showed a strong decrease at the root surface which is followed by accumulation close to the root surface (Fig. 4.3). Bulk soil concentration shows a decrease in time. Measured $Cl^-$ concentrations show a similar behaviour (Fig. 4.4). Measured pH values showed a low increase at the root surface and were homogeneous in bulk soil ten days after planting (Fig. 4.5). This was
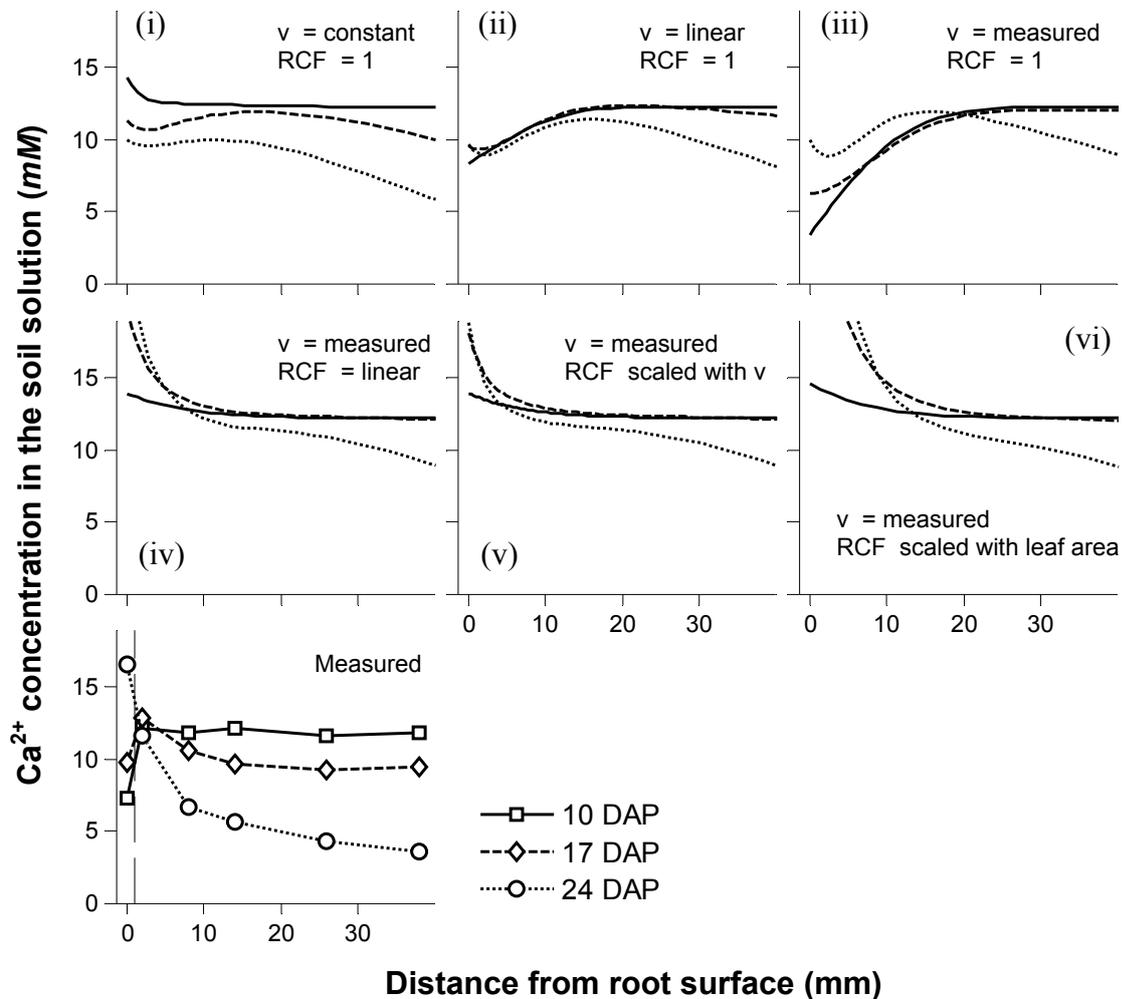


*Figure 4.2. Concentration profiles of $Ca^{2+}$ calculated for different scenarios (i-vi) with RhizoMath compared to the Ca concentration of soil solution samples collected from the compartment system 10, 17 and 24 days after planting (□,◇,○, respectively). Concentrations that belong to points in front of the dashed vertical line represent an average of concentrations in soil solution samples collected from the root compartment.*

followed by a decrease at and close to the root surface during the next two weeks. This was accompanied by a slight increase of pH in bulk soil.

In the case of constant water flow (scenario i) an accumulation of $Ca^{2+}$ at the root surface was predicted already after 10 days (Fig. 4.2). The magnitude of the accumulation was decreasing in time accompanied by an overall decrease of $Ca^{2+}$ concentration. The final $Ca^{2+}$ concentration at the root surface was lower than the initial $Ca^{2+}$ concentration. A repeated calculation with linearly growing water flux (ii) showed a monotonous increase of $Ca^{2+}$ concentration with an increasing distance from the root surface during the first 17 days. This was followed by a very low accumulation at the root surface, a depletion towards the root surface between ~0.3 and ~1.7 cm from the root surface and a depletion towards bulk soil from ~1.7 cm. Introducing a water flux that was estimated from measured evapotranspiration into the model (scenario iii) led to an exaggerated depletion of $Ca^{2+}$ towards the root surface in the first 17 days. This was followed by a moderate accumulation at the root surface, depletion towards the root surface between ~0.2 and ~1.7 cm from the root surface and
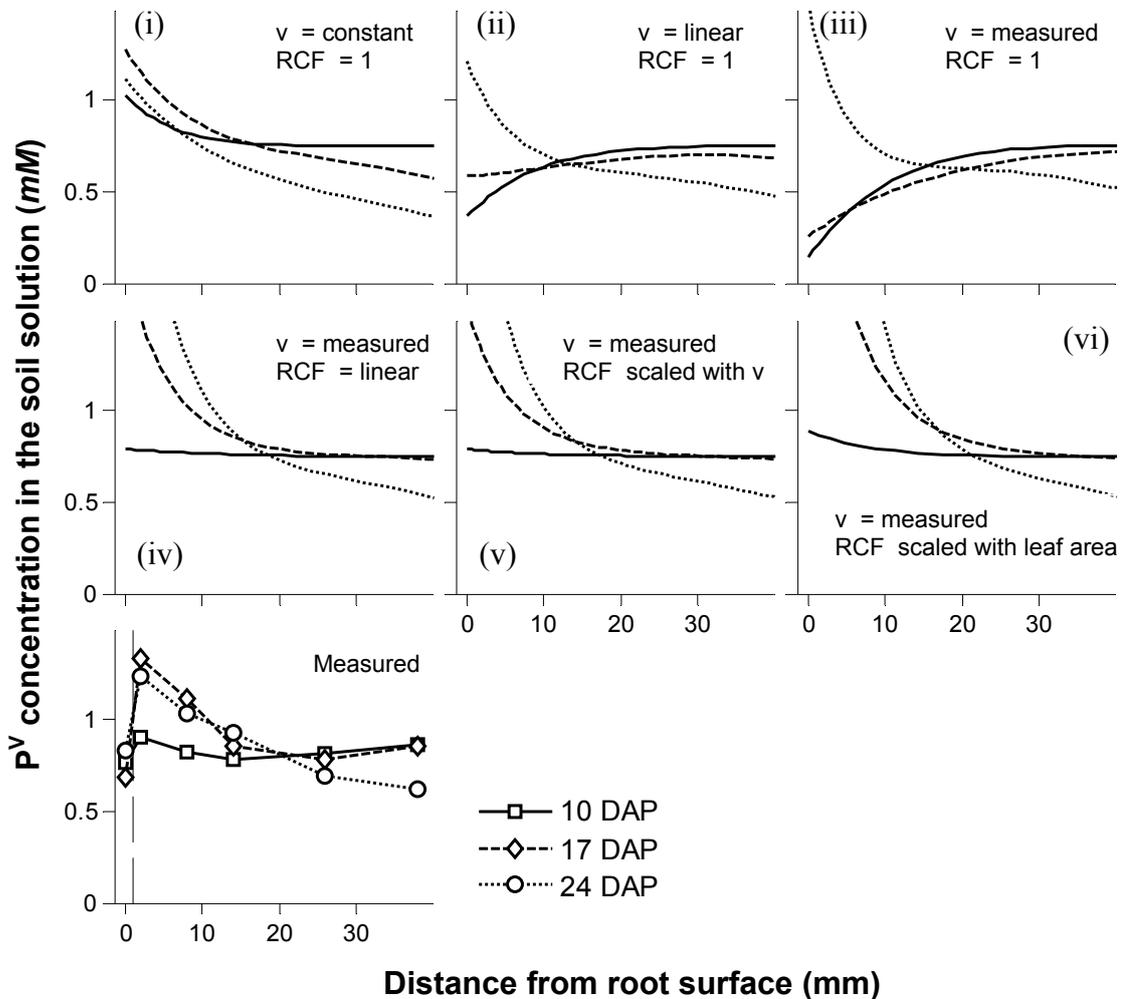


*Figure 4.3. Concentration profiles of $P^V$ calculated for different scenarios (i-vi) with RhizoMath compared to the P concentration of soil solution samples collected from the compartment system 10, 17 and 24 days after planting ($\square,\Diamond,\bigcirc$, respectively). Concentrations that belong to points in front of the dashed vertical line represent an average of concentrations in soil solution samples collected from the root compartment.*

depletion towards bulk soil from ~1.7 cm. The calculated $Ca^{2+}$ concentration at the root surface was lower compared to its initial value. Model calculations for the three other scenarios (iv-vi) that were calculated with the experimentally determined water flux and changing RCF resulted in concentration profiles that show a similar temporal behaviour for each of these scenarios but with different enlargements. A monotonous, in time increasing accumulation of $Ca^{2+}$ was observable with a decreasing distance to the root surface. This was accompanied by depletion towards bulk soil from ~1.4 cm at the root surface after 17 days. The magnitude of this depletion was almost the same in the scenarios iii-vi. The maximum concentration of $Ca^{2+}$ was always much higher as at the beginning, the highest values were calculated in scenario vi, where RCF followed the development of the leaf area. The lowest concentration of accumulated $Ca^{2+}$ among scenarios iv-vi appeared in scenario v, in which the temporal development of nutrient uptake followed the temporal development of water uptake. However, this concentration was still higher as the highest $Ca^{2+}$ concentration in scenarios i-iii. A depletion of $Ca^{2+}$ was accompanied in any case and any position by a total dissolution of Gypsum. Whereas, even for low accumulation of $Ca^{2+}$ at the root surface precipitation of gypsum was observed, except in scenario vi. In scenarios iv and vi a precipitation of $CaHPO_4$ at the root surface was predicted.

Concentration profiles of $P^V$ calculated for scenarios i and iv-vi (Fig. 4.3) show similar trends to each other, but in different magnitudes. An accumulation of $P^V$ at the root surface can be observed in all of these four cases with time. This is followed by a monotonous decrease in concentration with an increasing distance from root surface. This appeared as a depletion in bulk soil from ~1 cm and ~1.8-2.2 cm from the root surface (scenario i and iv-vi, respectively). The maximum concentration of $P^V$ is the highest in scenario vi and the lowest in scenario i. The magnitude of the depletion in bulk soil was the highest for scenario i, in which the depletion occurs most rapidly among these four scenarios. The measured accumulation of P close to the root surface was most accurately reproduced in scenario vi and the temporal development of the accumulation (a higher accumulation after 17 days as after 24 days) in scenario i. The final concentration of P in bulk soil is similar in scenarios iv-vi. Concentration profiles showed totally different development in scenarios ii and iii. An overemphasized depletion of $P^V$ occurred towards the root surface between 0 and ~2 cm in the first three weeks. The magnitude of the depletion became lower in time and turned into accumulation after three weeks. This temporal development was more rapid and had a higher magnitude in scenario iii as in scenario ii.

The overall temporal developments of patterns in $Cl^-$ concentrations (Fig. 4.4) predicted by modelling are similar to the temporal development of $P^V$ concentration patterns in corresponding scenarios.

Changes in modelled pH for scenarios i and ii were hardly observable. However, some trends can be recognized only in the magnified inlays. A monotonous decreasing pH with an increasing distance from the root surface was observable in scenario i. The development of patterns in pH was similar through the scenarios ii and iii. The temporal development of pH was similar in scenarios iv-vi: a stronger and in time proceeding decrease at the root surface and a very low decrease with an increasing

distance from ~2.5 cm in bulk soil were predicted. The lowest pH occurred in scenario vi, followed by scenario iv and v.
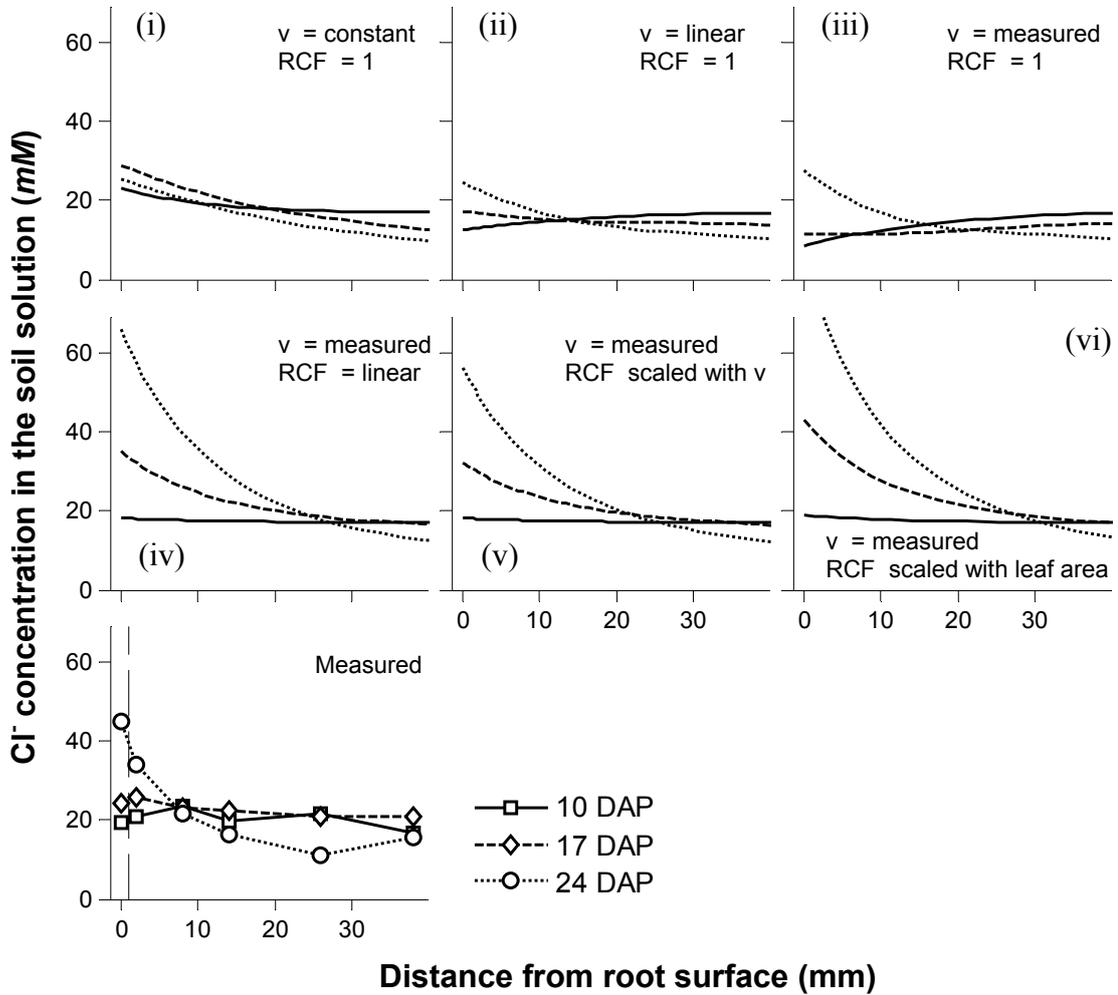


*Figure 4.4. Concentration profiles of Cl⁻ calculated for different scenarios (i-vi) with RhizoMath compared to the Cl- concentration of soil solution samples collected from the compartment system 10, 17 and 24 days after planting (□,◇,○, respectively). Concentrations that belong to points in front of the dashed vertical line represent an average of concentrations in soil solution samples collected from the root compartment.*
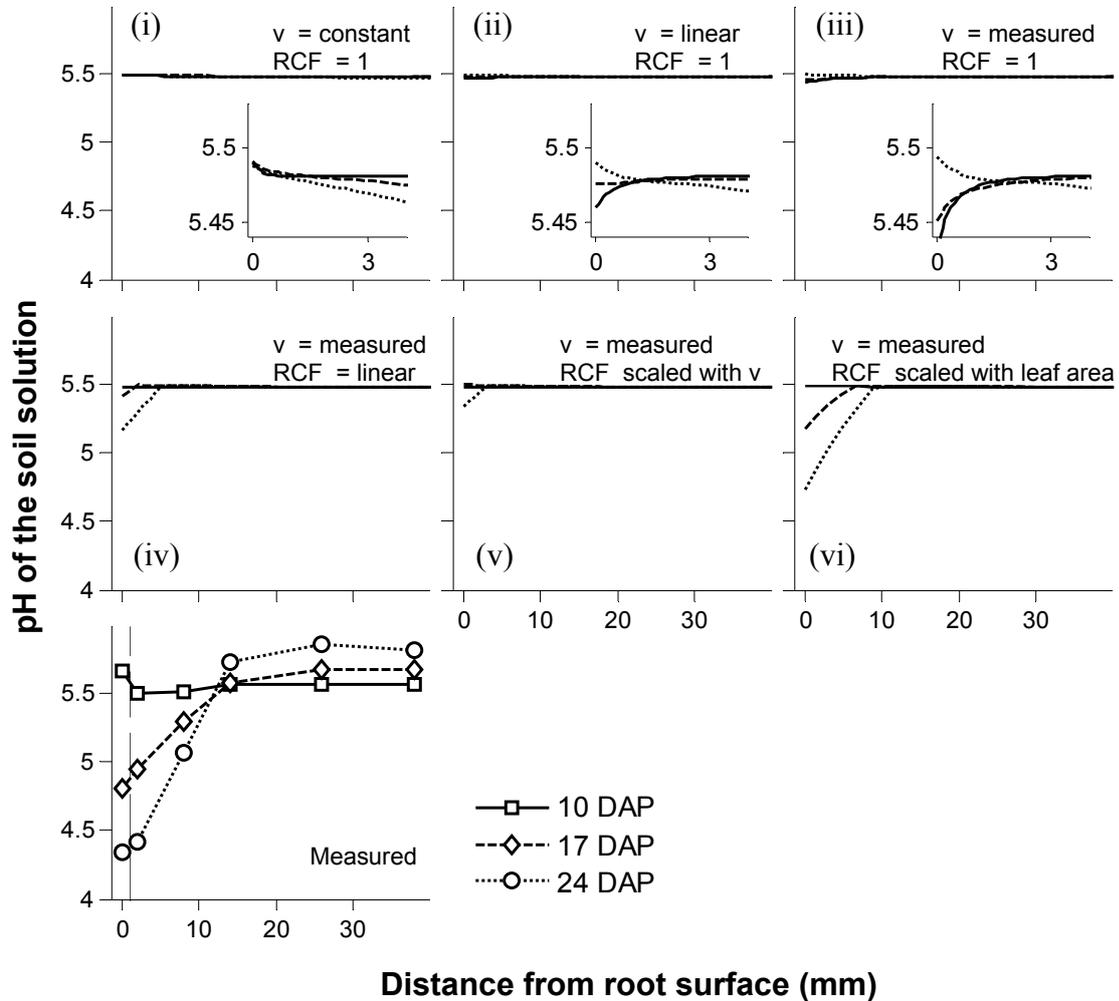
*Figure 4.5. pH calculated for different scenarios (i-vi) with RhizoMath compared to the pH of soil solution samples collected from the compartment system 10, 17 and 24 days after planting (□,◇,○, respectively). pH values that belong to points in front of the dashed vertical line represent an average of concentrations in soil solution samples collected from the root compartment.*

## *4.6 Discussion*

$Ca^{2+}$ is delivered to any point by mass flow, diffusion and by dissolution of gypsum. $Ca^{2+}$ can be removed in the case of the oversaturation of gypsum or $CaHPO_4$ by the precipitation of these minerals. For the interpretation of these processes it is important to consider that the stoichiometric equations include activities, not concentrations (Essington, 2004). Thus, due to its influence on the activity coefficient, ionic strength affects equilibrium concentrations: the high ionic strength at the root surface can result in $Ca^{2+}$ (and P) concentrations that would not be expected in a pure solution of $CaSO_4$ or $CaHPO_4$. $Ca^{2+}$ concentration at the root surface is thus not only determined by the balance of delivery and root $Ca^{2+}$ uptake. In scenario i the initial accumulation of $Ca^{2+}$ at the root surface was caused by the delivery of dissolved gypsum from bulk soil towards the root. The total dissolution of gypsum in the bulk soil led to an overall decrease of $Ca^{2+}$ concentration. A strong removal of other species led to the decrease of ionic strength at the root surface and that allowed the precipitation of gypsum at concentrations lower than the initial $Ca^{2+}$ concentration. In scenarios ii and iii the initial $Ca^{2+}$ uptake exceeded its delivery to the root surface that led to the development of a wide depletion zone. This occurred to a larger magnitude in scenario iii as water flux increased slower in this case. The resulting formation of higher gradients as in scenario ii induced a higher diffusive flux towards the root surface that was supported by the increase in water flux with time and resulted in a final $Ca^{2+}$ concentration at the root surface that was comparable to the final values in scenario ii. In scenarios iv..vi $Ca^{2+}$ delivery was always overestimated or $Ca^{2+}$ uptake underestimated. A precipitation of gypsum and $CaHPO_4$ occurred only in scenarios iv and vi among these three scenarios. None of the calculated scenarios reproduced the observed $Ca^{2+}$ depletion at the root surface in the first 17 days. This can have the following reasons: (i) the predicted precipitation of gypsum and $CaHPO_4$ is underestimated (a) due to the overestimation of ionic strength that originates from underestimation of uptake of all species, (b) due to the differences in dissolution and precipitation kinetics that is not expressed by chemical equilibrium, (c) due to the fact that reaction kinetics were disregarded; (ii) the underestimation of Ca uptake.

In scenarios i and iv-vi the delivery of $P^V$ to the root surface always exceeds uptake. The depletion of $P^V$ in bulk soil is caused by its delivery towards the root surface by mass flow. Diffusive fluxes counteract mass flow as they occur in the other direction according to the gradients in $P^V$ concentration. The initially higher uptake in scenario (i) leads to a lower accumulation at the root surface as in other cases. The initially higher water flux causes a stronger and more rapid $P^V$ depletion in bulk soil in case i as in the other scenarios. The different behaviour of scenarios ii and iii in comparison to the other scenarios was caused by the initial overestimation of root uptake which was not overcompensated by the delivery as it occurred in scenario i. The increasing water flux in scenario iii delivered later more P than could be taken up. This was supported by higher diffusive fluxes in scenario iii due to the high gradients. The similarities in the temporal and spatial patterns in $P^V$ and $Cl^-$ concentration supports the modeling

results that P concentration is not (or, as it was discussed above for $Ca^{2+}$, only after ~3 weeks and only close to the root surface) controlled by any mineral phase.

A decreasing pH in the rhizosphere is caused by the increase of $H^+$ concentration which occurred after the release of $H^+$ ions by the root. This indicated that more cations were taken up by the root as anions. This was reproduced in all scenarios except the first one. The lowest pH at the root surface and the closest pH to measured pH was predicted in scenario vi. As pH, a critical parameter in modelling sorption processes, came off best in scenario vi, the key assumption of scenario vi were used subsequently, namely that true water consumption is used to drive water flux and that root nutrient uptake has to be coupled to actual plant size (i.e. leaf area development). In this case the delivery of ions to the root surface by mass flow started to increase much earlier as the root uptake starts its rapid increase. This caused an initial accumulation of all ions in the first ~15 days at the root surface. This could not be compensated for by root uptake later on. The relatively high concentrations of almost all ions in the quartz based substrate without addition of minerals which provide sorption sites were in or close to the range where the Michaelis-Menten uptake flux is constant. This is the maximal uptake rate of these ions. The qualitatively well reproduced changes in pH suggest that the assumptions used in scenario vi represent the processes the best among the considered scenarios. However, the overestimation of pH and overestimation of the concentration of other elements suggests that root uptake of all elements has to be increased. As the uptake flux has already reached its maximum, this can be only made by increasing the uptake capacity behind one $cm^2$ nylon mesh. This is realistic as roots do not only grow at the nylon mesh but also inside the root compartment. This can be realized by multiplying the $g(t)$ in the *RCF* factor by a constant that is higher than one. It has to be noticed that the same result would be achieved when the $J_{max}$ parameter of root uptake would be increased. As $J_{max}$ has a high variety in existing literature increasing $J_{max}$ would also be realistic. An increase of both parameters simultaneously could be also an option as $J_{max}*g(t)$ is the intrinsic parameter that determines the uptake rate of a species. However it has to be kept in mind that changing $g(t)$ affects all species to the same extent and changing $J_{max}$ is specific for a species is question.

The optimization of $g$ and $J_{max}$ led to a definite improvement of the model performance. The new values of $J_{max}$ for different species are included in Table 4.1. The optimal value for $g$ appeared to be 8. The comparison of measured and modelled concentration profiles of $Ca^{2+}$, $P^V$, $Cl^-$ and K are shown in Fig. 4.6. The overall trends as well as orders of magnitudes were satisfyingly reproduced for all elements. However, modelled concentrations at higher distances from the root surface where depletion occurred (~1.5-2.5 cm, depending on the scenario) were always higher than the measured ones. A general observation was that modelled $Ca^{2+}$, $S^V$, $Mg^{2+}$ and $As^V$ concentrations (not all shown) showed the highest deviation from measured values. On the contrary, $P^V$, $K^+$ and $N^V$ concentrations could be satisfyingly reproduced (not all shown). The good model performance in the case of these nutrients is not surprising as they belong to the most studied compounds due to their agricultural relevance. A major reason for the deviation between modelled and measured values is that some

relevant interactions are not included in RhizoMath. First, the applied Michaelis-Menten kinetics is a very rough simplification of the various parallel pathways of $Ca^{2+}$-uptake: besides $Ca^{2+}$ uptake via channels it can not be disclosed that apoplastic transport to the xylem also occurs – at least where lateral roots are released (White, 1998). As S(V)-concentration is linked to $Ca^{2+}$-concentration in our system due to the presence of gypsum, an incorrect description of $Ca^{2+}$-uptake indirectly affects S(V) concentrations as well. Neglecting cross-effects between $Ca^{2+}$ and $Mg^{2+}$ contributes also to the low model performance in the case of these elements. This applies also for $As^V$ as its uptake is influenced by the uptake of $P^V$ due to their chemical similarity. As the $As^V{:}P^V$ ratio (~1:7 in the beginning) is relatively high it also affects P uptake (Esteban et al., 2003). Moreover, only one $P^V$ and one $As^V$ transporters were considered here, although the simultaneous presence of high and low affinity transporters was reported (Marschner, 1995). These could explain why the rapid decrease of $P^V$ concentration at the root surface that was experimentally observed after 17 days did not appear in the modelling. In spite of the better agreement between modelled and measured concentrations a worse reproduction of the pH was reached. This can be explained by the high sensitivity of pH to the cation/anion balance by root uptake and thus a high sensitivity to the concentration at the root surface. The temporal development of the net charge balance during uptake, and thus that of the H+/OH-efflux, depends on the concentration of all ions at the root surface. A better overall representation of the temporal development of concentration profiles does not self-evidently grant a better representation of concentration at the root surface or the best reproduction of the pH.
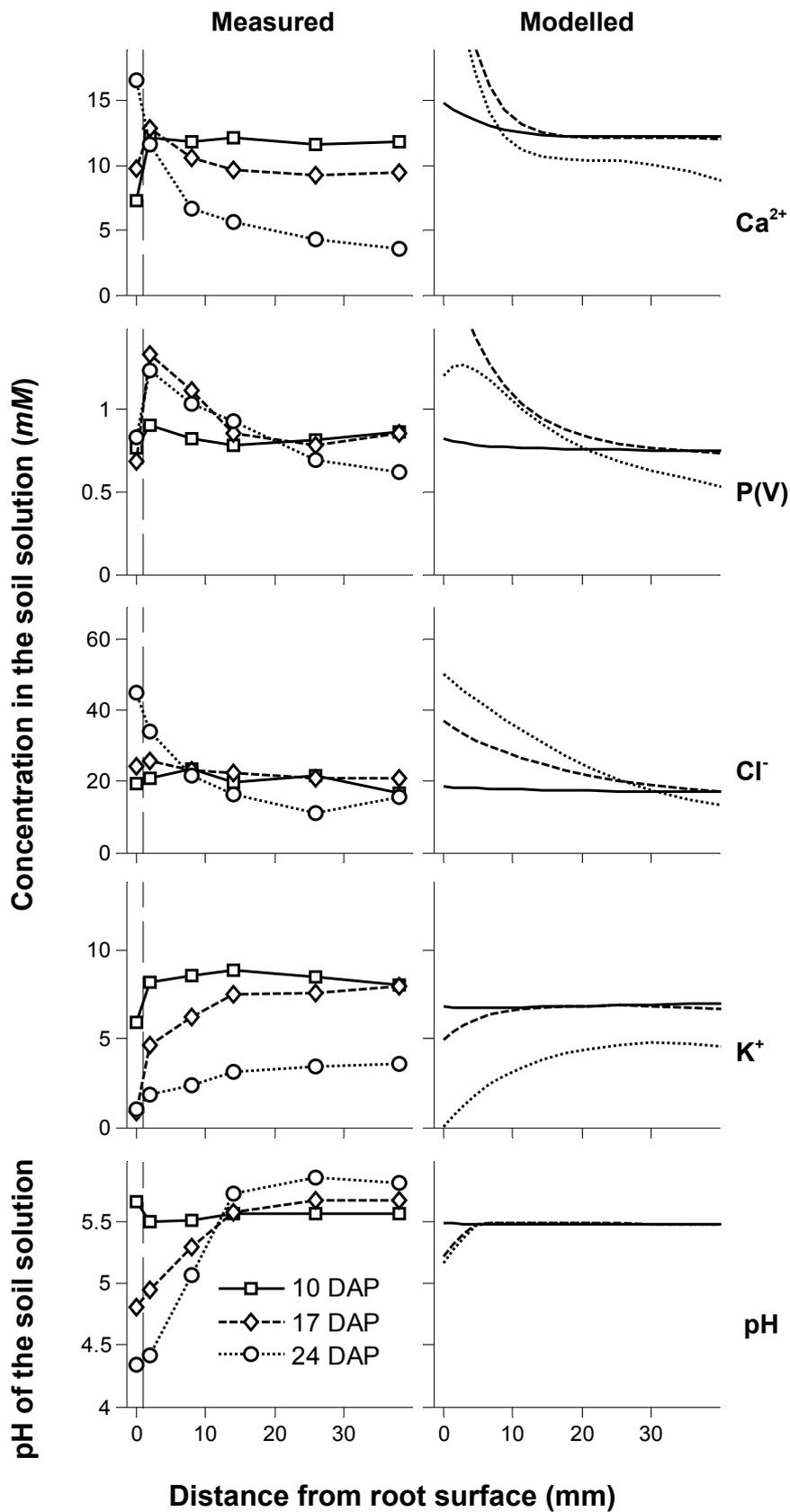
*Figure 4.6. Concentration profiles calculated using modified parameters of the Michaelis-Menten kinetics that allowed the best model performance (Table 4.1)*

## 4.7 Conclusions

Theoretical considerations and model calculations above showed that modelling multicomponent transport in the rhizosphere requires a step-by step implementation of relevant processes and a careful selection of model parameters. We extended the RhizoMath code by including dynamic parameters for root nutrient uptake. This allowed modelling a growing plant in the compartment system and to independently study the effects of temporal changes in water flux from the effects of temporal changes in nutrient demand. Water uptake, due to the low Péclet numbers, is often referred as a not determining factor in the rhizosphere (Roose et al., 2001). However, our results show, that the difference between the time course of root water uptake and plant development can have a determining effect in the system and on the results of the modelling: the best model performance was achieved by using the actually measured temporal development of water uptake in the model and by coupling nutrient uptake rate to the development of leaf area. The time lapse of these two quantities are very different from each other as water uptake is controlled by stomatal apparture which in term is controlled by light, temperature, humidity and wind - parameters that are independent from the plant and thus from plant size. Modelling has shown that in our experiments the initially higher water flux caused an accumulation of most nutrients at the root surface that induced uptake fluxes that reached their possible maximal values.

By applying a multicomponent transport model for describing compartment system experiments one had to notice that the biggest advantage of such models appears to be their biggest disadvantage: a very detailed chemistry is considered, which results in a complex system with a lot, often hidden interrelations. In particular, attention has to be given to the applied parameters. Besides a correct description of the soil solution chemistry a special attention has to be given to the parameters that describe nutrient uptake kinetics: the maximum influx of Michaelis-Menten kinetics should be adjusted to achieve the best possible model performance.

In contrary to experimental setups that provide information only for one point in time (Hedley et al., 1994; Kirk, 1999; Wenzel et al., 2001) the performed compartment system experiments provided temporal resolved information on soil solution composition within the same repetition. This allowed the comparison of measured and modelled data for intermediate time steps. By looking at the results of the different scenarios one can notice that some of the calculated concentration profiles showed a perfect agreement with measured ones, but only at a certain time. A comparison of modelled and measured results during the whole experiment showed that this was only a coincidence. This suggests that models that describe temporal dynamics in the rhizosphere should be tested using in-situ methods as reference that provide information on soil solution composition also for intermediate steps, such as compartment systems equipped with micro suction cups.

RhizoMath has still some limitations: only including the competition between $Ca^{2+}$ and $Mg^{2+}$, $P^V$ and $As^V$ are not yet included. In spite of this, the code is already a useful tool for studying the effect of changes in soil chemistry and water flux on transport and uptake of nutrients and contaminants.

# 5. Modelling Rhizosphere Transport in the Presence of Goethite, including Competitive Uptake of Phosphate and Arsenate

Krisztian Szegedi, Doris Vetterlein, Reinhold Jahn
*Plant and Soil*, in press (as a revised version)

## *5.1 Abstract*

Compartment system experiments in which *Zea mays* was grown showed that competition between arsenate ($As^V$) and phosphate ($P^V$) for soil binding sites (goethite) can be altered by root citrate exudation. Our objective was to simulate $P^V$ and $As^V$ dynamics in compartment systems by computer modelling, taking into account competition for sorption sites and simultaneously, for root membrane transporters. The RhizoMath code was applied to describe multicomponent reactive transport in the compartment systems. The chemical database was tested with hypothetical scenarios (amount of goethite, pH, and citrate concentrations). The code was extended with different approaches that describe the competitive uptake of $As^V$ and $P^V$. Transport modelling in compartment systems showed that experimentally observed increase in $P^V$ concentration at the root surface is a consequence of citrate exudation and not of convective transport exceeding uptake capacity. Both approaches that described the competitive uptake of $As^V$ and $P^V$ underestimated $As^V$ uptake, Apparent underestimation might be a result of disregarding recently discovered $As^{III}$ efflux and re-oxidation. Predicted $P^V$ concentrations agreed with measurements. The model should be extended by including all transporters involved in uptake of $As^V$ and $P^V$, taking into account changing nutrient requirement at different growth stages of the plant and efflux of $As^{III}$.

## *5.2 Introduction*

For the utilization and remediation of arsenic (As) contaminated landscapes it is necessary to understand the physicochemical and biological processes that control the transfer of toxic As from soil to plants.

The oxidised form of arsenic, arsenate ($As^V$) is the dominant As species in aerobic soils. It competes with phosphate ($P^V$) for binding sites in soils, like the ones provided by goethite (Smith et al., 2002). Goethite is a strong sorbent for $As^V$ (Manning and Goldberg, 1996; Gao and Mucci, 2001) as well for $P^V$ (Manning and Goldberg, 1996; Geelhoed et al., 1997). A higher affinity of goethite surface for $As^V$ than for $P^V$ was reported by Gao & Mucci (2001) and Violante & Pigna (2002), while similar affinities for $P^V$ and $As^V$ were found by Hiemstra & Van Riemsijk (1996) and Manning & Goldberg (1996; 1997). Plants can mobilize adsorbed $P^V$ via ligand exchange through organic anions like citrate (Hinsinger et al., 2003). Organic anions can desorb also $As^V$ from the goethite surface, but to a smaller extent compared to $P^V$ (Liu et al., 2001). Vetterlein et al. (2007) showed that root exudation of organic anions may alter the competition between arsenate and $P^V$ for soil binding sites.

Besides the effect of root exudation, the formation of solute gradients extending from the root surface into the surrounding soil, that occurs as a net result of the transport

and uptake processes in the rhizosphere (Darrah and Roose, 2001), has a strong influence on the chemical composition of soil micro-sites at the root surface (Hinsinger et al. 2009): e.g. precipitation of minerals as well as an increase of ionic strength of soil solution were also reported.

These simultaneously acting processes in the rhizosphere, which have their own temporal dynamic, lead to complex cross-effects between different ions and phases present in soil and soil solution. These processes can be identified, separated and tested with computer models. So far there are only a few approaches for modeling coupled transport and speciation in the rhizosphere each addressing a specific problem and taking into only a very limited number of species into account (Hoffland et al., 1990; Nietfeld, 2001; Nowack et al., 2006).

The recently presented code RhizoMath (Szegedi et al., 2008) is based on coupling the geochemical code PHREEQC with the mathematical package MATLAB. RhizoMath includes multicomponent diffusion and a built in calibration module that determines the highly uncertain intrinsic equilibrium constants of surface sorption reactions and the amount of surface binding sites that are both required to describe the competitive sorption of $P^V$ and $As^V$ on goethite.

The first version of RhizoMath using a simplified chemistry was able to qualitatively reproduce the experimentally observed effects of goethite addition and citrate exudation on the concentrations of $P^V$ and $As^V$ in the soil solution in the rhizosphere of *Zea mays*, which was grown in compartment systems under controlled conditions (Vetterlein et al., 2007). A quantitative agreement between modelled and measured data could not be achieved.

In a second step, the transport module of RhizoMath was extended with a root compartment factor (RCF) that expresses the relative coverage of the root compartment by the roots and the active root surface behind the unit area of the compartment cross section. This allowed modelling a growing plant in the compartment system. In addition, temporal changes in water flux, driving mass flow to the root surface, and nutrient demand, determining sink strength, could be represented independently from each other. A good agreement between modelled and experimental data was thus achieved for experiments without added goethite, i.e. without activating the surface sorption calculation in RhizoMath (chapter 4).

Uptake of a solute can be suppressed by the uptake of another solute if they share the same pathway(s) with a limited transport capacity. This process is not yet implemented in RhizoMath. $As^V$ competes with $P^V$ for binding sites at the root membranes (e.g. Zhao et al., 2009). Experimental studies on $As^V$ - $P^V$ competition during root uptake have shown that an increasing molar $P^V$: $As^V$ ratio in nutrient solution strongly reduced $As^V$ uptake (Meharg, 1994; Esteban et al., 2003; Meharg and Jardine, 2003; Zhao et al., 2009). Model fits to the experimental data showed an increase of the Michaelis-Menten constant of $As^V$ as $P^V$ was added; the maximum influx remained almost unchanged.

Thus, including competitive $P^V$ and $As^V$ uptake in the model calculations may be necessary for a good quantitative prediction of dynamic changes in $P^V$ and $As^V$ concentrations in the compartment system experiments.

Shaw and Bell (1991) mathematically described the competitive uptake of solutes via transporters. They considered root uptake as a two-step reaction. In the first step membrane transporters bind selected ions from the soil solution. In the second step the previously bound ions are released from the transporters inside the root cell. The binding and release of ions by the transporters were considered as kinetic reactions.

An alternative approach for describing competitive uptake can be derived based on the experimental observations of Lazaroff and Pitman (1966), who studied the competitive uptake of $Ca^{2+}$ and $Mg^{2+}$. They found that cumulative passive uptake of two competing ions over 24 hours was proportional to the respective concentrations of the ions in soil solution. This indicates that a limited influx via the uptake pathway is shared among the ions proportionally to their concentrations in soil solution. In this approach the affinity of the different solutes for the pathway which they share is similar, in contrast to the approach by Shaw and Bell (1991) based on Michaelis-Menten kinetics with different affinities ($K_m$ values) for each solute.

The major objective of the present work was to activate the surface sorption calculation in RhizoMath in order to quantitatively describe systems with added goethite in which citrate exudation by plants could play a major role for $P^V$ and $As^V$ uptake.

The transport module of RhizoMath was extended with equations for description of competitive uptake of solutes. It was studied how predicted $P^V$ and $As^V$ concentrations changed after their competitive uptake was included in the model calculations.

As a basis for these objectives the chemical database of PHREEQC was critically reviewed, possible simplifications were performed. Additionally, the database was comprehensively tested to show that it enables PHREEQC to describe basic geochemical processes in the compartment systems with added goethite without the presence of the plant.

## 5.3 Material and Methods

Compartment system experiments in which *Zea mays* was grown under controlled conditions on artificial quartz substrate spiked with known amounts of nutrients, $As^V$ and with increasing amounts of added goethite (0, 1, 4 g kg$^{-1}$; G-0, G-1, G-4, respectively) were available as a reference for the current modelling. The experimental setup and a qualitative interpretation of the observations were presented in Vetterlein et al (2007). Measured and modelled concentrations of the compartment systems without added goethite (G-0) were presented in chapter 4.

Figures 5.4 to 5.6 include measured concentrations averaged over right and left compartments. The first data point in front of the dashed vertical line in the figures 5.4 to 5.6 show an average over all samples in the root compartment that can be interpreted as samples from the immediate vicinity of the roots. Results beyond 24 days after planting are not discussed to avoid the difficulty of describing water relations in the system during the last week when the plants required a frequent watering.

**Modelling initial soil solution composition with surface sorption using PHREEQC**

Chemical composition of soil solution samples collected before planting from treatments (initial soil solution composition) without goethite addition (G-0) were modelled with PHREEQC (Parkhurst and Appelo, 1999). Details were presented in chapter 4, here we only summarize the major points.

The applied minteq.dat database was reduced to include relevant dissolved species only, modified to exclude nitrification. Gypsum, $CaHPO_4$, quartz and $CO_2$ were defined as equilibrium phases. To achieve correct $Ca^{2+}$ and $SO_4^-$ concentrations the solubility product of gypsum was replaced with log_k=4.53 in the database (Bennett and Adams, 1972).

Initial soil solution composition in treatments with 1 and 4 g kg$^{-1}$ goethite (G-1 and G-4, respectively) were modelled using the modified version of the PHREEQC input file as described above for the G-0 treatment. The input file was extended with the SURFACE data block to describe surface sorption using the diffuse double layer model (Dzombak and Morel, 1990; Parkhurst and Appelo, 1999).

Including surface sorption in the calculations required further changes in the chemical database, which are described below. The database was extended with the sorption of carbonate (Appelo et al., 2002). Stoichiometric equations describing the sorption of citrate on goethite were adapted for the database after Lackovic et al. (2003).

The initialization module of RhizoMath was used to determine the number of surface binding sites (part of the SURFACE data block in the PHREEQC input file) and values of the equilibrium constants of corresponding stoichiometric equations that describe the surface complexation of $As^V$ (parts of the chemical database). Starting numbers (e.g., starting values for the optimization) of weak surface binding sites of hydrous ferric oxide were estimated according to Tretner (2002). Initial values of the equilibrium constants of surface binding reactions were taken from Dzombak and Morel (1990).

The optimization published in Szegedi et al. (2008) was reconsidered: (i) proportion of weak and strong surface binding sites was kept unchanged during the optimization (Dzombak and Morel, 1990); (ii) only the equilibrium constants were optimized that belong to the dominant surface species and, thus, were expected to have a strong influence on the model performance.

Further reduction of the chemical database was considered in respect to the dominant surface species in the pH range observed during the experiments.

The same parameter set (PHREEQC input files with the optimized database) was applied to model hypothetical scenarios with different amounts of added goethite, changing pH, increasing addition of citrate, respectively. To avoid superimposing the effects of changing pH and citrate addition the latter was studied at the same pH for each treatment.

**Modelling transport in the compartment system with RhizoMath**

Transport in the compartment systems was modelled with the transport module of RhizoMath. The same phases and optimized parameters were applied to describe soil chemistry during the transport modelling as described above for modelling the initial

state of the system. The Nietfeld (2001) approach was used for transport modelling: diffusion was locally corrected to maintain charge balance in the soil solution. Root water uptake was described as a quasi-steady flow derived from the measured transpiration rate. Soil water content was assumed to be constant.

Root influx per unit root surface of most species was described with Michaelis-Menten kinetics. To express the influx through the nylon mesh of the root compartment the influx per unit root surface was multiplied by the root compartment factor (Chapter 4). The term that expresses the relative coverage of the nylon mesh was scaled with the leaf area development of the plant to take into account plant growth. The other term that expresses the active root surface behind the unit nylon mesh was kept constant. Its value was selected to achieve the best agreement between modeled and measured concentrations of most solutes. Maximum influx parameter of Michaelis-Menten kinetics of each element was chosen to have the best model performance for the G-0 system.

Citrate exudation rate was estimated based on the work of Schulz and Vetterlein (2007). The authors reported a citrate concentration of ~120 µM 21 days after planting in soil solution samples collected in compartment system experiments that had the same setup and fertilization as our G-0 system. It was assumed that the citrate exudation rate was constant per unit root surface in the experiment. Thus, citrate efflux was proportional to the RCF in the model calculations:

$$J_{citr} = -J_{citr,u} \cdot RCF(t), \tag{5.1}$$

where $J_{citr}$ is the citrate efflux through the nylon mesh that separates the root compartment from bulk soil, $J_{citr,u}$ is the citrate efflux per unit root surface. $J_{citr,u}$ was successively approximated so, that predicted citrate concentration in the soil solution was 120 µM 21 days after planting in the G-0 treatment. The thus estimated value of $J_{citr,u}$ was $3 \cdot 10^{-11}$ mM cm$^2$ s$^{-1}$

$H^+/OH^-$ efflux were calculated to maintain charge balance during the uptake.

**Implementing competitive uptake in RhizoMath**

Competitive uptake of nutrients was implemented in the RhizoMath code. Two different approaches were included for the mathematical description of the competition. User can define groups of solutes that compete with each other during uptake. Several disjunctive groups of competing solutes can be defined; the mathematical description of competitive uptake uses the same approach for each solute within the same group.

The first approach is based on the work of Shaw and Bell (1991). When a transporter can bind and subsequently release two types of ions from the soil solution at different reaction rates, influx of ion 1 ($J^{upt}_{MM,1}$) can be described with the following modification of the Michaelis–Menten kinetics:

$$J^{upt}_{MM,1} = J_{max} \frac{C_1}{C_1 + K_1 \left(1 + \dfrac{C_2}{K_2}\right)}, \tag{5.2}$$

where 1 and 2 indicate the two ions, $J^{upt}_{MM,1}$ is the influx of ion 1, $C_1$ is its concentration in the soil solution of ion 1, $K_1$ is the respective Michaelis-Menten coefficient (without the presence of ion 2), $C_2$ is the concentration of solute 2 and $K_2$ is Michaelis-Menten coefficient of ion 2 (without the presence of ion 1). $C_2=0$ gives the unsuppressed Michaelis-Menten kinetics of ion 1. $J_{max}$ is the maximum influx of the two ions together. The form of equation (5.2) is the same for the influx of ion 2, except the subscripts that are mirrored.

The general form of equation (5.2) in the case when n ions are competing for the same transporter is

$$J^{upt}_{MM,i} = J_{max} \frac{C_i}{C_i + K_i \left(1 + \sum_{n \neq i} \frac{C_n}{K_n}\right)}, \qquad (5.3)$$

where $J^{upt}_{MM,i}$ is the influx of a given solute, *i* is its index, $C_i$ is its concentration in the soil solution, $K_i$ is its Michaelis-Menten coefficient, $C_n$ is the concentration of an other ion and $K_n$ is its Michaelis-Menten coefficient. The sum goes over all n solutes except the $i^{th}$. This mathematical model may probably not be applicable for solutes that are taken up via diffusion.

We modified equation (5.3). in analogy to (Barber, 1995, p65) to account for the minimum solute concentration required for root uptake:

$$J^{upt}_{MM,i} = J_{max} \frac{C_i - C_{i,min}}{C_i - C_{i,min} + K_i \left(1 + \sum_{n \neq i} \frac{C_n - C_{n,min}}{K_n}\right)}, \qquad (5.4)$$

where $J^{upt}_{MM,i}$ is the uptake flux of a given solute, i is its index, $C_i$ is its concentration in the soil solution, $K_i$ is its Michaelis-Menten coefficient, $C_n$ is the concentration of any other solute that competes with the $i^{th}$ solute and $K_n$ is its Michaelis-Menten coefficient. The sum goes over all n solutes that compete with $i^{th}$ solute. $C_{i,min}$ is the minimum concentration of the $i^{th}$ solute below which no uptake occurs.

To describe influx in the compartment system $J^{upt}_{MM}{}^i$ are multiplied by RCF to account for the uptake by a root system behind the nylon mesh of the root compartment.

The second implemented approach for describing competitive uptake of nutrients is based on the experimental findings of Lazaroff and Pitman (1966). Equations (5.5a) and (5.5b) express that the total influx J' is shared among the competing solutes proportionally to their concentrations in the soil solution:

$$J^{upt}_i = J' \frac{C_i}{\sum_n C_n}, \qquad (5.5a)$$

$$\sum_i J^{upt}_i = J' \text{ (consequence of equation 5.5a)}, \qquad (5.5b)$$

where $J^{upt}_i$ is the influx of a solute, i is its index, $C_i$ is its concentration in the soil solution. The sum goes over the $C_n$ concentrations of all solutes that compete with each other.

J' is the potentially highest influx of the pathway where the competing solutes are taken up. Thus it is reasonable to define J' as given in equation (5.6):

$$J' = \max(J_1, J_2..J_n),$$ (5.6)

where $J_1... J_n$ are the influxes the competing solutes, calculated according to the Michaelis-Menten kinetics in the absence of the other solutes that can influence its uptake. max indicates the highest value in the bracket.

Thus, the influx of any of the competing solutes is:

$$J^{upt}_i = \max(J_1, J_2..J_n) \frac{C_i}{\sum_n C_n},$$ (5.7)

To describe influx in the compartment system $J^{upt}_i$ are multiplied by RCF to account for the uptake by a root system behind the nylon mesh of the root compartment.

Each of the two approaches has its advantages and disadvantages. An advantage of the first approach (equation 5.4) is that it was derived considering the fundamental processes that occur during the uptake of solutes via transporters. A disadvantage of this approach is that it does not account for different transporters or different transport pathways that can be involved in the uptake of the competing solutes. Competitive uptake appears in equation (5.4) only as a modifying factor of the Michaelis-Menten constant. If $K_1 = K_2 = ... = K_n << \Sigma_i (C_i - C_{i,min})$ Equation 5.4 approximates

$$J^{upt}_{MM,i} = J_{max} \frac{C_i - C_{i,min}}{\sum_n C_n - C_{n,min}},$$ (5.8)

i.e. in this concentration range the maximal influx is reached and the overall influx $J_{max}$ is constant. This differs from equation 5.5a, in which $J' = \max(J_1, J_2..J_n) \neq J_{max} = \Sigma_i J_{max,i}$.

The second approach (equation 5.7) neglects the type of the transport pathways. Individual processes during the uptake are also neglected. This is not necessarily a disadvantage: it can be advantageous in the case of lack of information on the transport pathways. Another advantage of the second approach is that it requires less parameter compared to the first approach.

To decide which of the above presented approaches is more suitable to describe the competitive uptake of $P^V$ and $As^V$, transport in the compartment system was modelled with RhizoMath using both approaches separately (equations 5.4 and 5.7, respectively).

## 5.4 Results

**Modelling initial soil solution composition and hypothetical scenarios using PHREEQC**

Several runs of the optimization showed that the best agreement between modelled and measured data was achieved as the equilibrium constant of Hfo_wH2AsO4 was optimized. Its initial value for the optimization was log_k = 8.67 and its optimized

value was log_k = 10.2. Similar difference between initial and optimal equilibrium constant was found by Tretner (2002). Uniqueness of optimized parameters was proven by repeating the optimization using several different combinations of starting
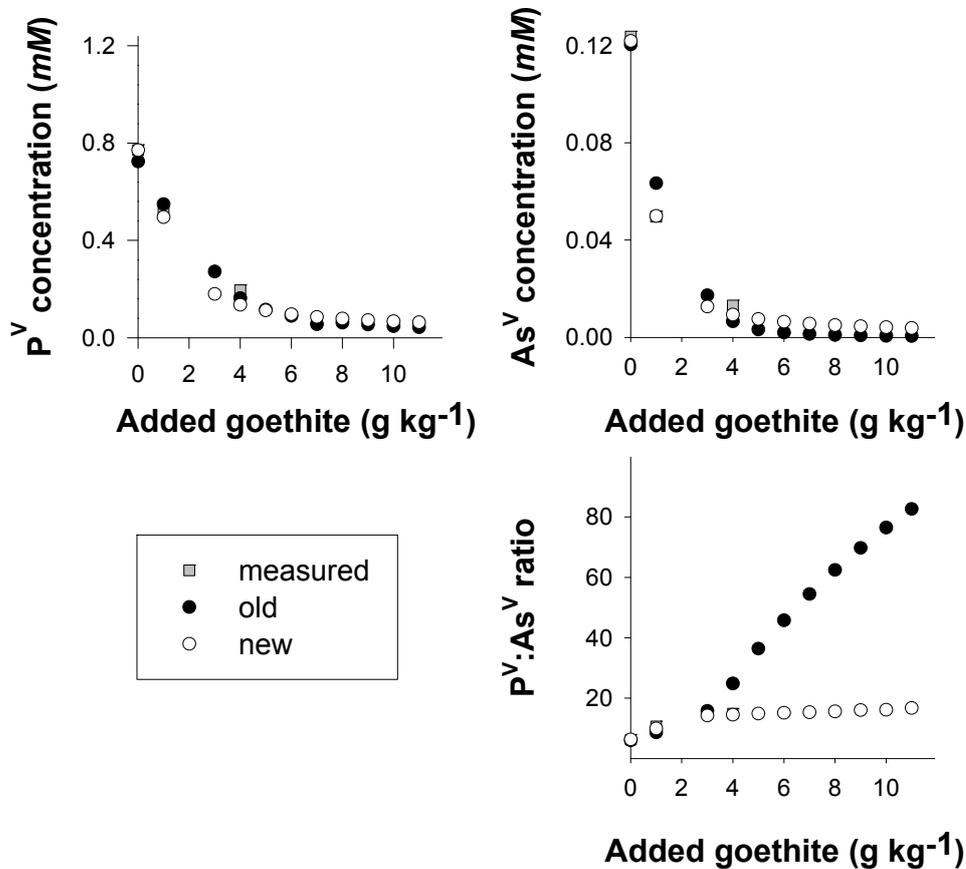


*Figure 5.1. Concentrations of $As^V$ and $P^V$ in the soil solution with increasing amounts of added goethite, calculated with PHREEQC using the sorption parameters optimized with RhizoMath for 0, 1, and 4 g kg$^{-1}$ goethite. ● indicates results of current calculations with re-optimized sorption parameters (see text for details) and ○ results with the parameter set used in Szegedi et al. (2008). Measured values are indicated by □.*

parameters. Optimized number of weak and strong surface binding sites was $5.83 \cdot 10^{-5}$ and $1.45 \cdot 10^{-5}$ g$^{-1}$ goethite, respectively.

Model calculations for hypothetical scenarios with different amounts of added goethite showed slightly different results in $P^V$ and $As^V$ concentrations (Fig. 5.1) with the reconsidered chemical database (this paper) compared to the old database (Szegedi et al., 2008). A better agreement between predicted and measured $P^V$ and $As^V$ concentrations for 0, 1 and 4 g kg$^{-1}$ added goethite was achieved with the reconsidered chemical database.

There are apparently only minor differences between $P^V$, and also $As^V$, concentrations that were calculated with the two databases. In spite of this, there is a clearly notable difference in the resulting $P^V$:$As^V$ ratio (Fig. 5.1). Calculations with the old database predicted a continuously increasing $P^V$:$As^V$ ratio with increasing goethite addition. Calculations with the reconsidered database predicted the "saturation" of the $P^V$:$As^V$
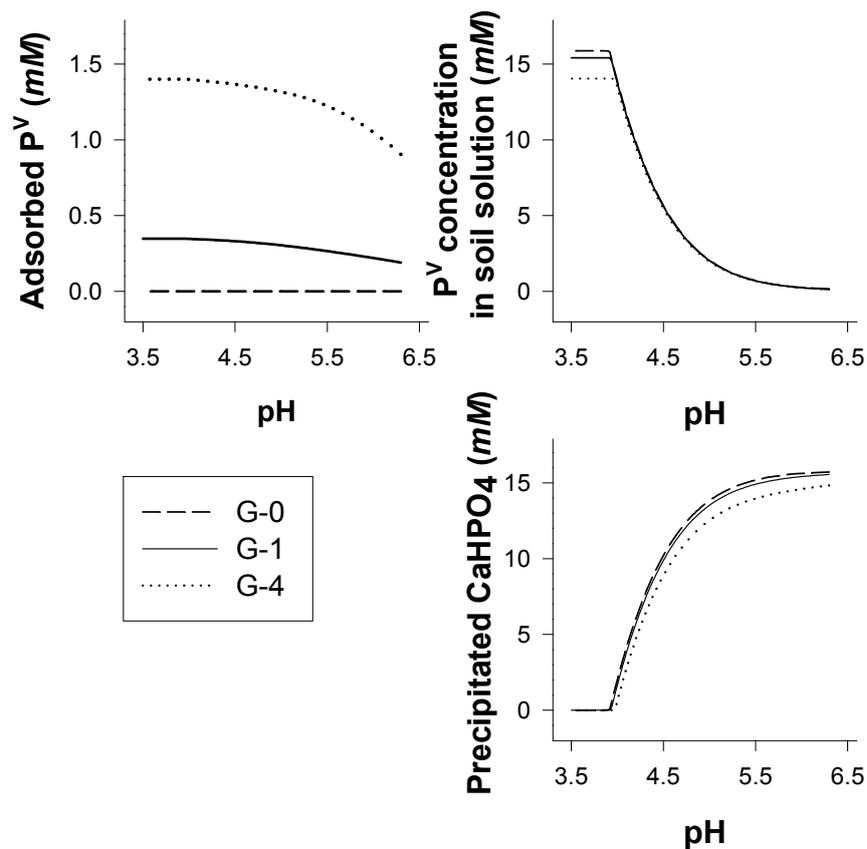
*Figure 5.2. pH dependence of the amount of $P^V$ adsorbed by goethite, $P^V$ concentration in the soil solution and the amount of precipitated $CaHPO_4$ calculated with PHREEQC for 0, 1, and 4 g $kg^{-1}$ goethite. Adsorbed amounts are presented per litre soil solution to facilitate comparison between soil solution and goethite.*

ratio above ~4g $kg^{-1}$ added goethite. These calculations led to a better agreement between predicted and measured $P^V$:$As^V$ ratio compared to Szegedi et al (2008).

Model calculations for hypothetical scenarios with different pH values in the range relevant for the experiment (3.5-6.5) predicted increasing amount of $P^V$ adsorbed on goethite with a decreasing pH (Fig. 5.2). Predicted amount of adsorbed $P^V$ is about 4 times higher in the case of 4 g kg-1 added goethite as in the case of 1 g kg-1 added goethite. This is similar to the experimental observations.

Predicted PV concentration in the soil solution was strongly increasing with decreasing pH as strong dissolution of $CaHPO_4$ was predicted with decreasing pH. Total dissolution of $CaHPO_4$ was predicted at pH ~4. This suggests that the $CaHPO_4$ in PHREEQC has a different chemical behaviour as the applied $CaHPO_4$. Thus, in further calculations $CaHPO_4$ was not considered as an initial mineral phase. However, its precipitation will be allowed.

Model calculations predicted increasing $P^V$ concentration with increasing citrate addition in both treatments (Fig. 5.3). Predicted increase in $P^V$ concentration was higher in the G-1 treatment than in the G-4 treatment after adding the same amount of citrate (for each mol of added citrate). Predicted $As^V$ concentration was slightly increasing with increasing citrate addition in the treatment G-1. Predicted increase in
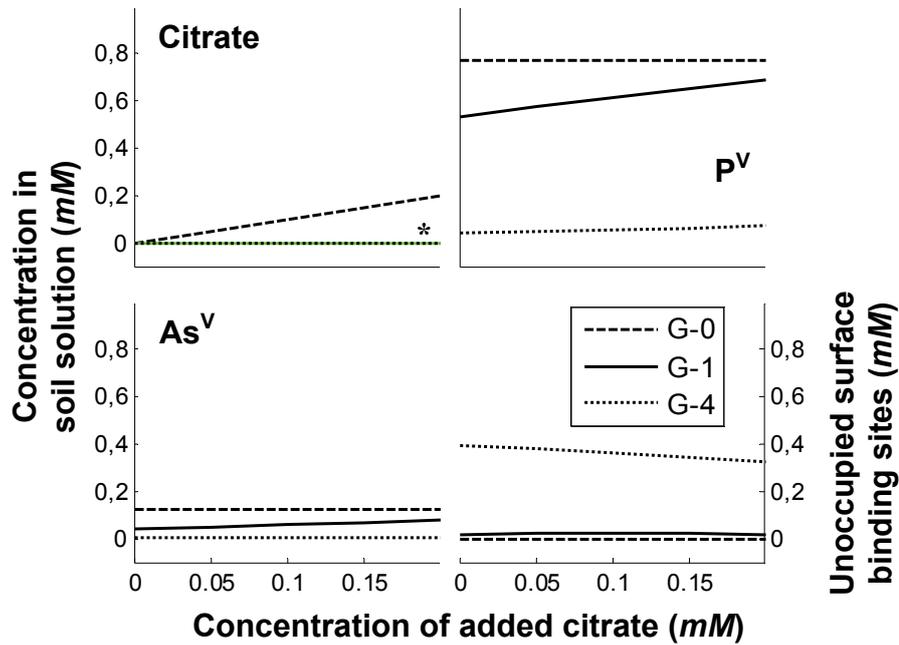
*Figure 5.3. Effect of citrate addition on the soil solution concentration of $As^V$, $P^V$, and citrate as well as on the amount of empty binding sites, calculated with PHREEQC for 0, 1, and 4 g $kg^{-1}$ goethite using the reduced database. Amount of adsorbed $As^V$, $P^V$, and citrate mirrored soil solution concentrations (not shown). *: Lines for G-1 and G-4 overlay each other.*

$As^V$ concentration was lower in the G-1 treatment as predicted increase in $P^V$ concentration.

Predicted $As^V$ concentration was not affected by citrate addition in the G-4 treatment. Predicted changes of adsorbed $P^V$ and $As^V$ mirrored predicted changes of dissolved $P^V$ and $As^V$ concentrations in both treatments (data not shown). Predicted amount of unoccupied surface binding sites of goethite was close to zero and was not affected by citrate addition in the G-1 treatment. Number of unoccupied surface binding sites of goethite was decreasing with increasing citrate addition in the G-4 treatment. Model calculations predicted the adsorption of all the added citrate by goethite in both treatments: dissolved citrate concentration remained zero in both treatments at any rate of citrate addition.

*Table 5.1. Species included in the chemical database of PHREEQC*

| SURFACE_SPECIES | SOLUTION_MASTER_SPECIES and SOLUTION_SPECIES |
|---|---|
| Hfo_wOH2+, Hfo_sOH2+, | H+, OH-, H2O, |
| Hfo_wH2PO4, Hfo_sH2PO4, | AmmH+, Ca+2, K+, Fe+3, |
| Hfo_wH2AsO4, | Cl-, SO4-2, NO3-, Edta-4, FeEdta-, |
| Hfo_ wCitrateH-, | CO3-2, HCO3-, |
| Hfo_wHCO3 | H2AsO4-, H2PO4-, |

The chemical database was reduced in small steps leaving dominant surface species only. It was controlled after each of these steps that the chemical behaviour of the system (which was presented above) did not change. The remaining species are given in Table 5.1. Surface sorption reactions were re-organised according the tableau-method (Morel and Hering, 1993) so that Hfo_sOH2+ and Hfo_wOH2+, the dominant surface species of unloaded goethite at low pH (Dzombak and Morel, 1990), became the SURFACE_MASTER_SPECIES (PHREEQC nomenclature). This allowed a further reduction of the database.

**Modelling transport in the compartment system using RhizoMath**

Measured and modelled pH and concentration profiles of $P^V$ and $As^V$ are presented in figures 5.4, 5.5 and 5.7 for the compartment system with the plant for 10, 17 and 24 days after planting. Concentration profiles are presented neglecting citrate exudation and competitive uptake (a, b), taking citrate exudation into account (c, d) and finally
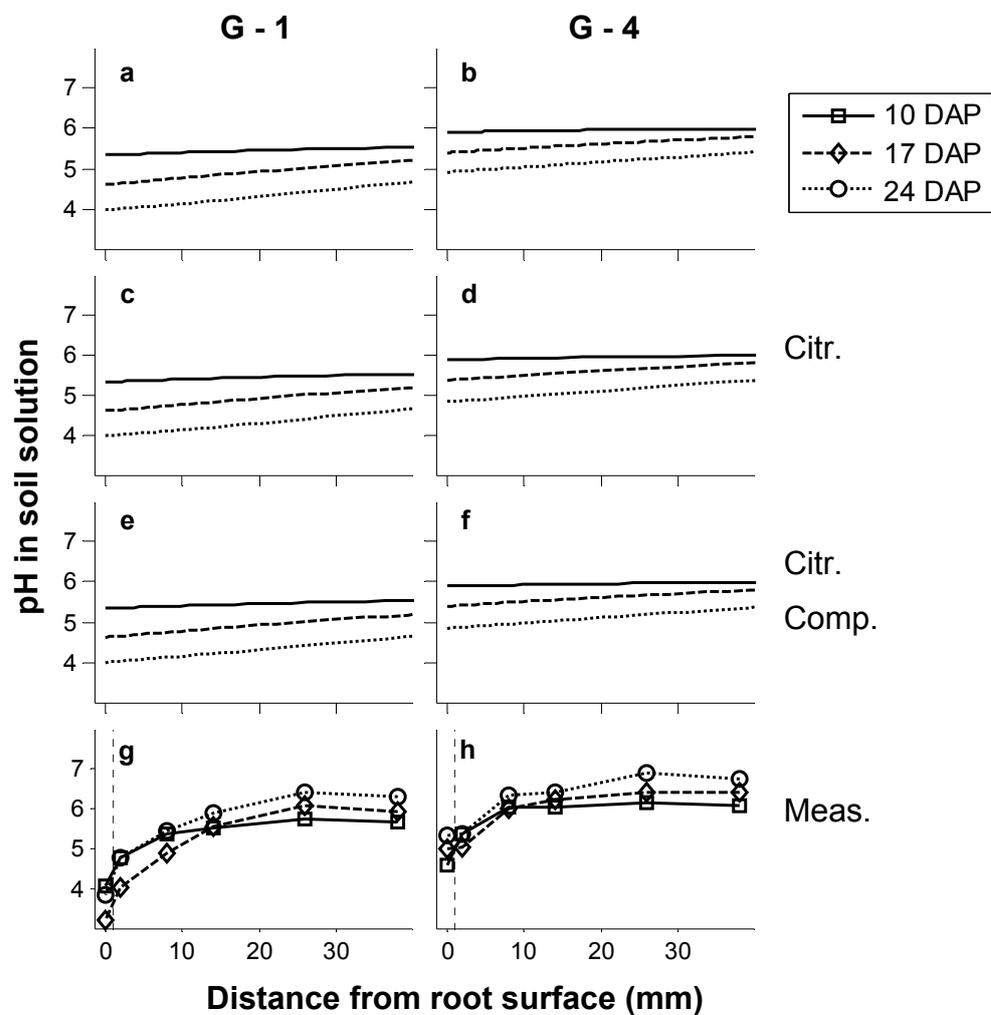


*Figure 5.4. Predicted soil solution pH with increasing distance from the root surface calculated for different treatments with RhizoMath for 10, 17 and 24 days after planting without (a, b) and with (c, d) citrate exudation (Citr.) and with citrate exudation and competitive uptake (e, f) (Comp.) of $As^V$ and $P^V$. Measured pH at 10, 17 and 24 days after planting (□,◇,○, respectively)(g, h) is reproduced after Vetterlein et al. (2007).*

considering citrate exudation and competitive uptake (e, f). For comparison measured soil solution concentrations are provided (g, h).

Predicted pH followed similar trends in all of the performed calculations (Fig. 5.4). Predicted pH was constant 10 days after planting and was linearly increasing with an increasing distance from the root surface later on in both G-1 and G-4 treatments. Predicted pH was affected only by the amount of added goethite but not by citrate exudation: it was at all distances from the root surface and at all times higher in G-4 treatment compared to G-1 (Fig. 5.4b, d compared to Fig. 5.4a, c). Predicted pH was not noticeably influenced by including $P^V$-$As^V$ competition in the calculations (Fig. 5.4e, f). The experimentally observed strong decrease of pH close to the root surface (Figs. 5.4g, h) could not be reproduced by either modelling approach.

Increase in $P^V$ concentration at the root surface was predicted for 10 and 17 days after planting in treatment G-1 (Fig. 5.5a). The predicted increase in $P^V$ concentration was lower than the experimentally observed increase in $P^V$ concentration at the root surface
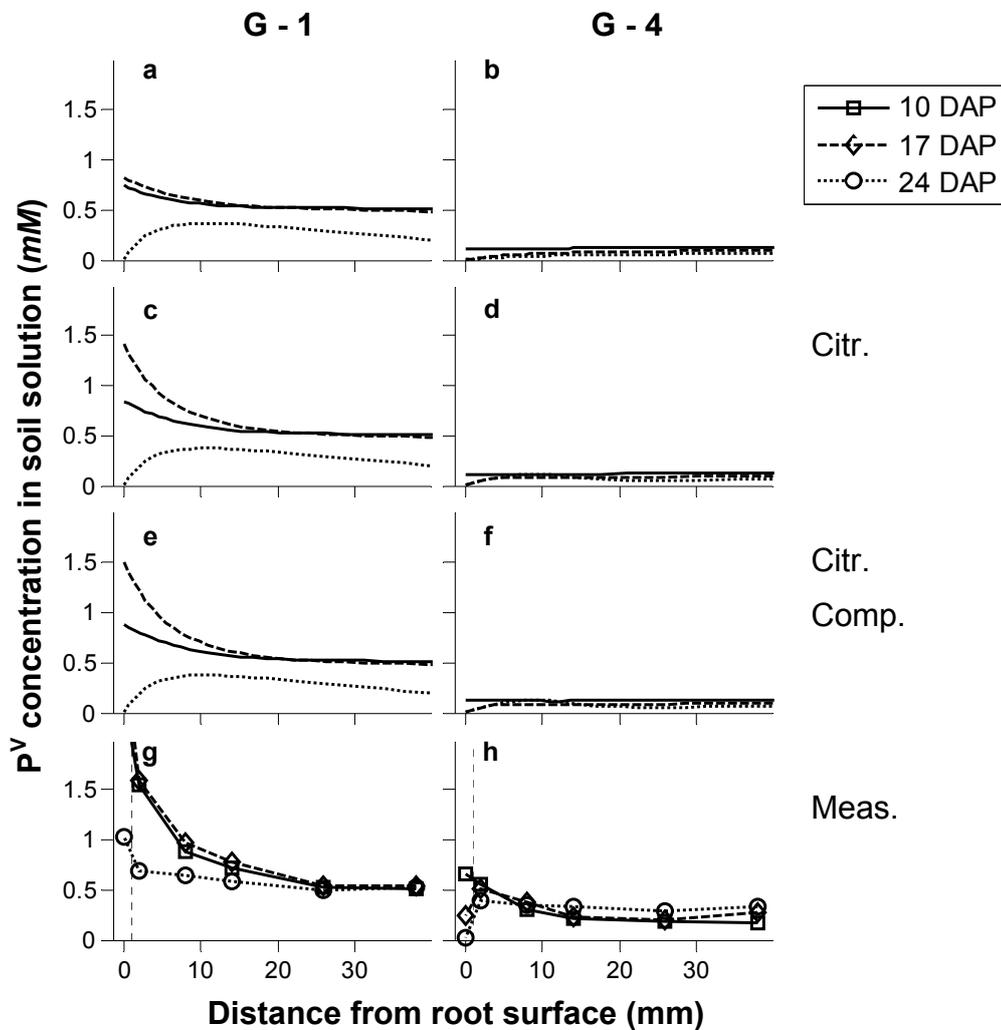


*Figure 5.5. Predicted $P^V$ concentration in the soil solution with increasing distance from the root surface calculated for different treatments with RhizoMath for 10, 17 and 24 days after planting without (a, b) and with (c, d) citrate exudation (Citr.) and with citrate exudation and competitive uptake (e, f) (Comp.) of $As^V$ and $P^V$. Measured $P^V$ concentration in the soil solution at 10, 17 and 24 days after planting (□,◇,○, respectively)(g, h) is reproduced after Vetterlein et al. (2007).*

in the same treatment at respective times (Fig. 5.5g). Including citrate exudation in the model calculation substantially enhanced the predicted increase in P$^V$ concentration at the root surface for both 10 and 17 days after planting in the same treatment (Fig. 5.5c). P$^V$ concentration profiles predicted for 10 and 17 days after planting with citrate exudation (Fig. 5.5c) agreed better with measured P$^V$ concentration profiles at respective times than P$^V$ concentration profiles predicted without citrate exudation (Fig. 5.5a). Predicted P$^V$ concentration was lower at any distance from the root surface for 24 days after planting in model calculations both with and without citrate exudation.

P$^V$ concentration profiles predicted for the treatment G-4 reproduced the experimentally observed decrease in P$^V$ concentration at the root surface well (Figs. 5.5b, d, f). Including citrate exudation in the model calculation decreased the predicted width of the P$^V$ depletion zone for 10 and 17 days after planting in the same treatment (Fig. 5.5d, Fig. 5.5b). However, it did not affect the general trends.

Predicted P$^V$ concentrations in calculations with competition between As$^V$ and P$^V$ for root uptake (Fig. 5.5f) did not substantially differ from P$^V$ concentrations which were predicted without P$^V$-As$^V$ competition (Fig. 5.5d).

Predicted amount of adsorbed P$^V$ in the calculations without citrate exudation followed similar trends as dissolved P$^V$ (data not shown).

With including citrate exudation in the calculations the model predicted the total desorption of P$^V$ from goethite in the first 2 mm from the root surface for 10 days after planting for the G-1 treatment (Fig. 5.6c). The width of the zone where total P$^V$ desorption was predicted was increasing time. The model predicted the same trends for the G-4 treatment (Fig. 5.6d). However, the width of the zone where P$^V$ was totally desorbed was smaller and predicted to increase slower in the G-4 treatment as in the
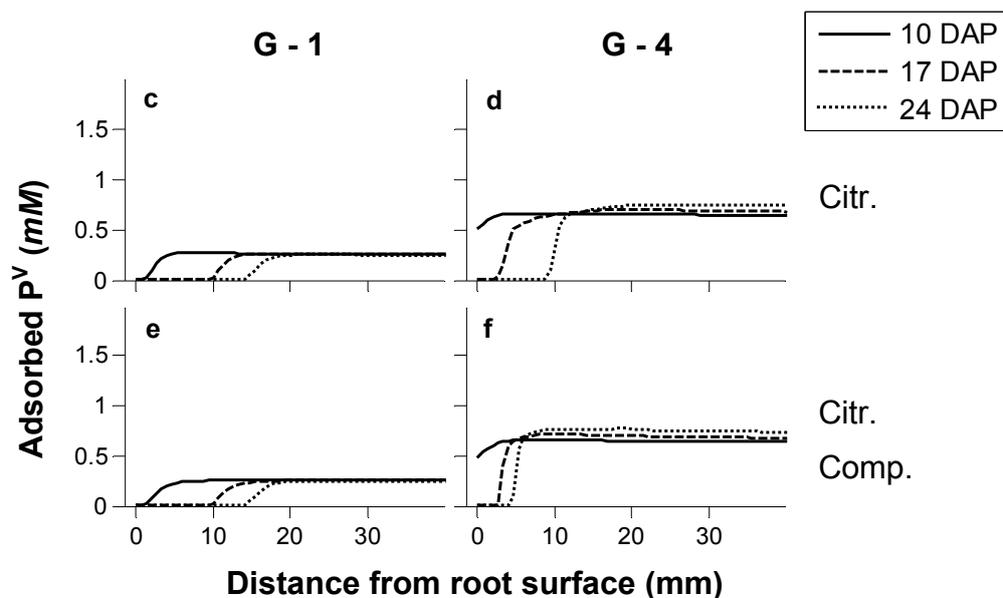


*Figure 5.6. Predicted amount of adsorbed P$^V$ with increasing distance from the root surface calculated for different treatments with RhizoMath for 10, 17 and 24 days after planting with citrate exudation (**c, d**)(Citr.) and with citrate exudation and competitive uptake (**e, f**)(Comp.) of As$^V$ and P$^V$. Adsorbed amounts are presented per litre soil solution to facilitate comparison between soil solution and goethite.*

G-1 treatment.

Including $P^V$-$As^V$ competition in the calculations did not affect adsorbed $P^V$ amounts for the G-1 treatment (Fig. 5.6c, e). Calculations including competitive $As^V$ and $P^V$ uptake besides citrate exudation (Fig. 5.6f) predicted a narrower zone where $P^V$ was totally desorbed in the G-4 treatment than without $P^V$-$As^V$ competition (Fig. 5.6d).

Predicted saturation index of $CaHPO_4$ was monitored during the calculations. A slight oversaturation (maximum saturation index ~0.17) of $CaHPO_4$ was predicted in the calculations with citrate exudation for 10 and 17 days after planting in the treatment G-1 as $P^V$ concentration increased at the root surface. This indicated the possibility of $CaHPO_4$ precipitation. However, a saturation index of 0.17 does not mean that $CaHPO_4$ would precipitate in a real system (Kölling, 1988).

Model calculations predicted $As^V$ depletion at the root surface for both G-1 and G-4 treatments both with and without citrate exudation (Figs. 5.7a, b, c, d). Including equation (5.4) to describe competitive $As^V$ and $P^V$ uptake besides citrate exudation in the calculations led to a predicted $As^V$ accumulation at the root surface for both G-1
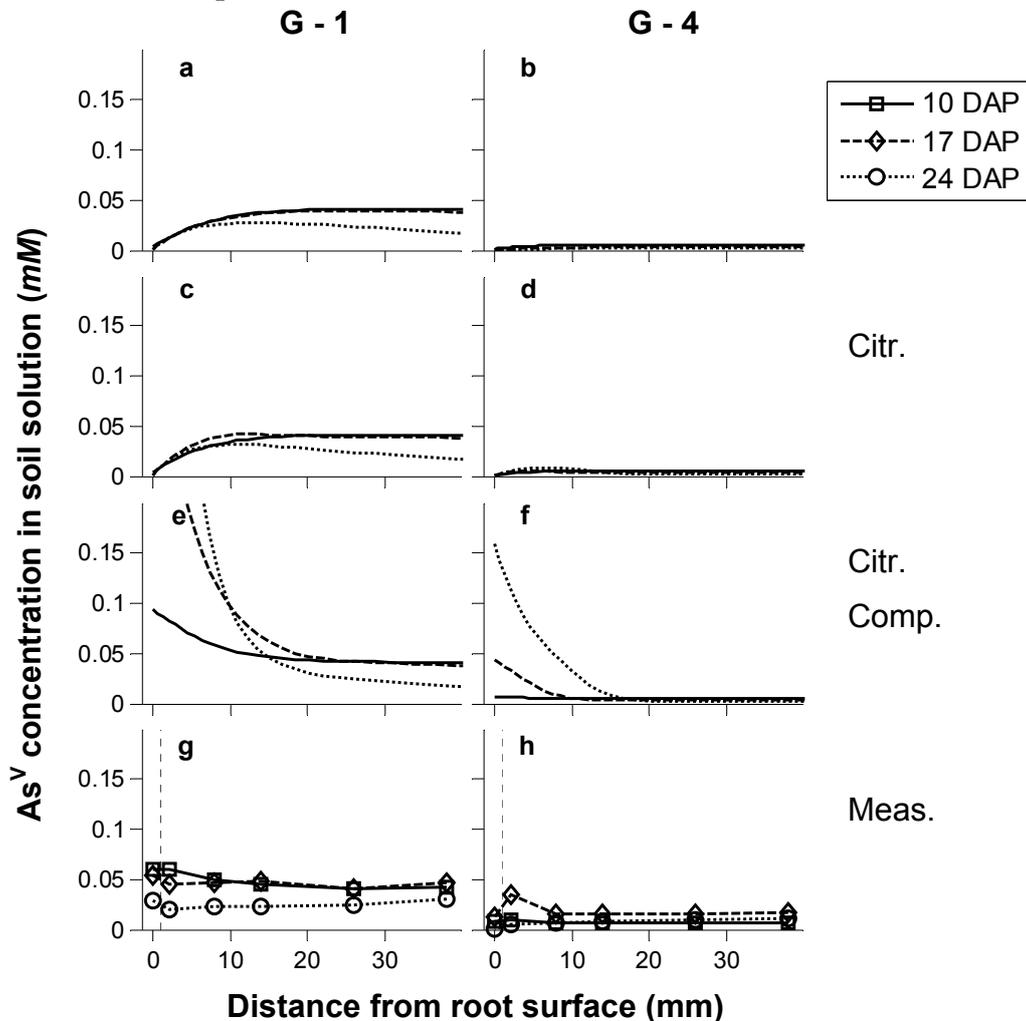


*Figure 5.7. Predicted $As^V$ concentration in the soil solution with increasing distance from the root surface calculated for different treatments with RhizoMath for 10, 17 and 24 days after planting without (**a, b**) and with (**c, d**) citrate exudation (Citr.) and with citrate exudation and competitive uptake (**e, f**) (Comp.) of $As^V$ and $P^V$. Measured $As^V$ concentration in the soil solution at 10, 17 and 24 days after planting ($\square$,$\diamond$,$\bigcirc$, respectively)(**g, h**) is reproduced after Vetterlein et al. (2007).*

*Figure 5.8. Predicted amount of adsorbed $As^V$ with increasing distance from the root surface calculated for different treatments with RhizoMath for 10, 17 and 24 days after planting with citrate exudation (c, d)(Citr.) and with citrate exudation and competitive uptake (e, f)(Comp.) of $As^V$ and $P^V$. Adsorbed amounts are presented per litre soil to facilitate comparison between soil solution and goethite.*

and G-4 treatments (Figs. 5.7e, f). Calculations with equation (5.7) predicted an even higher accumulation of $As^V$ at the root surface (data not shown). None of the calculations performed with different model assumptions could correctly predict experimentally observed trends of $As^V$ concentration profiles.
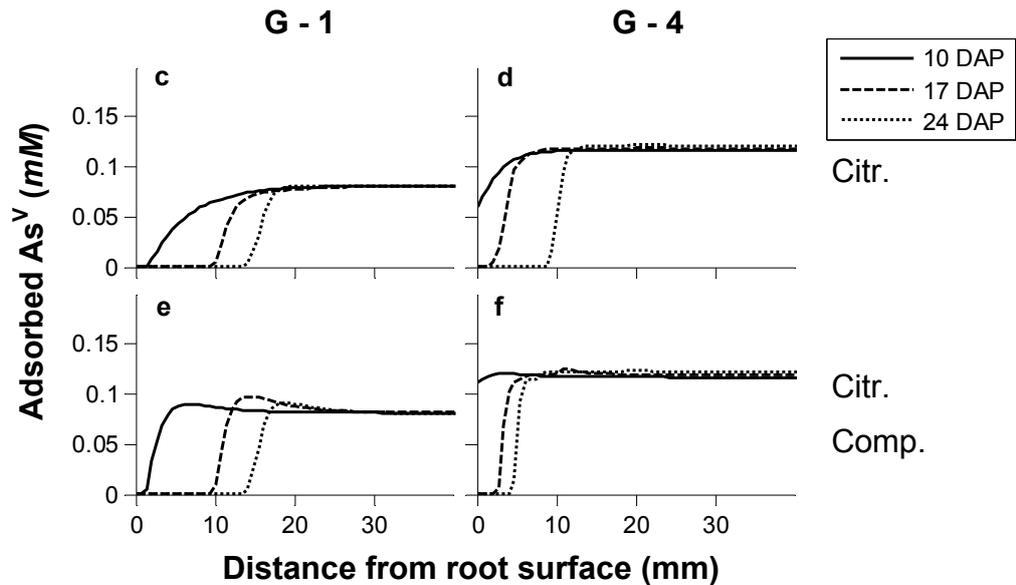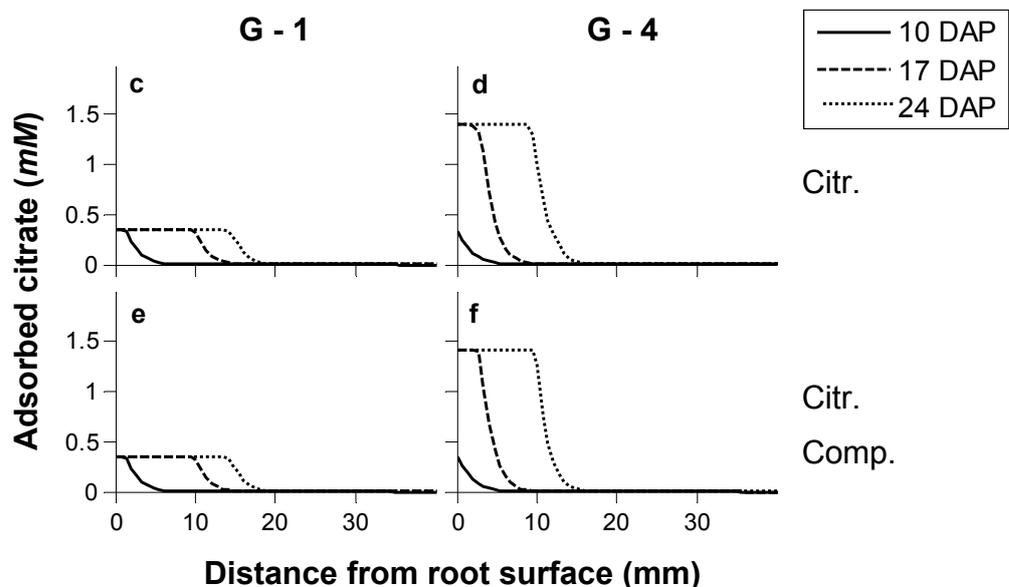


*Figure 5.9. Predicted amount of adsorbed citrate with increasing distance from the root surface calculated for different treatments with RhizoMath for 10, 17 and 24 days after planting without (c, d) and with (e, f) competitive uptake (Comp.) of $As^V$ and $P^V$. Adsorbed amounts are presented per litre soil solution to facilitate comparison between soil solution and goethite.*

Similar trends were predicted in calculations with citrate exudation for adsorbed amounts of $As^V$ (Fig. 5.8) as the trends predicted for adsorbed amounts of $P^V$ (Fig. 5.6) in the same calculations (described above). However, predicted gradients in the amount of adsorbed $As^V$ were lower as predicted gradients in amount of adsorbed $P^V$.

Predicted changes in the amount of adsorbed citrate (Fig. 5.9) mirrored the predicted changes in amounts of adsorbed $P^V$ and $As^V$. The model predicted that citrate occupied all the available sorption sites in the first 2 mm from the root surface 10 days after planting in the G-1 treatment. The predicted width of this zone was increasing with time. The same was predicted for the G-4 treatment. However, the predicted width of the zone where citrate occupied all the available sorption sites was increasing at a lower rate in the G-4 treatment compared to the G-1 treatment (Fig. 5.9 c, d).

Including $P^V$-$As^V$ competition in the calculations did not substantially affect predicted amounts of adsorbed citrate for any of the treatments (Fig. 5.9c, d, e, f).

The above presented calculations (where citrate exudation was included) were performed with a citrate exudation rate which was about 50 times higher ($J_{citr,0} = 1 \cdot 10^{-9}$ mM cm$^2$ s$^{-1}$) as it was initially estimated after Schulz and Vetterlein (2007). Calculations with a lower citrate exudation rate predicted a negligible mobilisation of $P^V$ in the treatment G-1 (data not shown), that disagreed with the experimental observations.

## 5.5 Discussion

### Modelling initial soil solution composition and hypothetical scenarios using PHREEQC

The reconsideration of the optimization procedure reduced the number of optimized parameters from 6 to 2. This increased the possibility that the parameter values which resulted from the optimization are globally optimal and not only locally in comparison to the results presented in Szegedi et al (2008). This was justified by the achieved better agreement between measured and modelled concentrations of $P^V$ and $As^V$ in the soil solution. Additionally, the predicted $P^V$:$As^V$ ratio is not increasing infinitely with the reconsidered database, but approaches saturation, which is more realistic. This shows that the reconsideration of the optimization improved the model performance.

The different behaviour of $CaHPO_4$ in the experimental system and in the model calculations can have different reasons. It is possible that the applied $CaHPO_4$ powder has undergone aging between its production (by Merck) and its application in the experiments. Another possibility is the transformation of $CaHPO_4$ to another phosphate form during the experiment.

It is known, that $CaHPO_4$ slowly transforms in soils to octacalcium phosphate (Sposito, 2008) that has a lower solubility than $CaHPO_4$. Thus, it can be assumed that a certain proportion of the applied $P^V$ is present in a less available form in the system. An extensive study of the kinetic processes that control the transformation of phosphate minerals would be required before they could be included in more detail in RhizoMath. Such work is currently carried out by Devau et al. (personal communication).

Removing $CaHPO_4$ as an initial equilibrium phase from the speciation calculations was supported by a successful modelling of dynamic changes in soil solution composition of the treatment without added goethite without the need of defining $CaHPO_4$ as an initial equilibrium phase (Chapter 4) as well as by the finding that sorption on goethite controlled $P^V$ concentration in soil solution in the treatments with added goethite (Vetterlein et al., 2007).

Hypothetic calculations with citrate addition predicted the mobilisation of adsorbed $P^V$ from the goethite via ligand exchange. This was predicted to a higher extent in the G-1 treatment where the competition between $P^V$, $As^V$ and citrate was stronger for surface binding sites as in the G-4 treatment. In the latter treatment adsorbed citrate preferred the unoccupied surface binding sites of goethite to the surface binding sites occupied by $P^V$ or $As^V$. This agreed with experimental observations and theoretical expectations (Liu et al., 2001; Hinsinger et al., 2003; Vetterlein et al., 2007).

The removal of "unnecessary" species from the database improved its consistency and reduced calculation time. However, it restricted the applicability of the model to the pH range between 3.5 and 6.7. This pH-range overlaps with the experimentally observed pH range.

**Modelling transport in the compartment system with RhizoMath without competition**

Predicted pH reproduced differences in soil solution pH which were observed between different treatments. This means a good representation of soil solution chemistry during transport modelling.

Predicted gradients of soil solution pH for both treatments were smaller than measured pH gradients. A possible explanation for this could be an overestimated mobility of $H^+$ ions in the calculations. Predicted pH was decreasing (increasing $H^+$ concentration) in time even at ~40 mm from the root surface due to the rapid diffusion of $H^+$ ions from the root surface towards bulk soil. This supports the hypothesis that the mobility of $H^+$ ions was overestimated in the calculations.

The effective diffusion coefficient of a solute in soil is determined by its diffusion coefficient in water, by the soil impedance factor and the soil water content (Eq. 3.2). The least accurate among these parameters is the soil impedance factor, as its value is only an estimate (Millington and Quirk 1960). Predictions on the transport of $H^+$ are influenced more by the soil impedance factor as predictions on transport of other solutes. Transport of $H^+$ is diffusion controlled ($H^+$ is transported against mass flow) while transport of other solutes is controlled by mass flow and diffusion.

$H^+$ efflux was determined in the calculations by the charge balance of root influx of other solutes than $H^+$. The incorrect prediction of the influx of these ions can lead to an incorrect prediction of $H^+$ efflux and thus false soil solution pH. Soil solution pH was sensitive (calculations not shown) to the variation of charge balance of root influx (the influxes of $NH4+$ and $NO_3^-$ were varied). However, changing the charge balance of root uptake did not change basic trends: predicted pH was linearly increasing with an increasing distance from the root surface ($H^+$ concentration was exponentially decreasing).

Soil solution pH is also affected by the partial pressure of $CO_2$ in the soil. For the present calculations it was assumed that the system was well aerated and no gradients of $CO_2$ concentration with increasing distance from the root surface were considered; i.e. the partial pressure of $CO_2$ in air was applied at each distance from the root surface. However, there are reports that $CO_2$ concentration close to the root surface can be several orders of magnitude higher as in bulk soil (Bidel et al. 2000; Gollany et al. 1993). Such gradients could result in high pH gradients and might explain why the model could not reproduce the measured pH values.

Predicted soil solution pH was neither affected by including citrate exudation nor by including $P^V$-$As^V$ competition by root uptake. This can be explained by the low efflux of citrate and the low influx of $As^V$ that did not dominate charge balance by root uptake.

The differences between predicted and measured pH were not in a range that they would substantially affect the predicted sorption of $P^V$ and $As^V$. Thus, the sorption of $P^V$ and $As^V$ in the studied system was mainly determined by the competitive sorption of $As^V$, $P^V$, and citrate.

### G-1 treatment (limited number of sorption sites)

Model calculations without citrate exudation predicted $P^V$ uptake by the root that exceeded delivery to the root surface. This led to the predicted $P^V$ depletion at the root surface. This prediction disagreed with experimental observations and confirms the hypothesis of Vetterlein et al. (2007) that the experimentally observed increase in $P^V$ concentration at the root surface is not due to transport exceeding uptake.

Model calculations with citrate exudation predicted increase in $P^V$ concentration at the root surface, accompanied by a decrease of the amount of adsorbed $P^V$ and an increase of the amount of adsorbed citrate. Thus ligand exchange of citrate with phosphate at the surface of goethite as it has been postulated by many authors (e.g. Geelhoed et al., 1999; Hinsinger, 2001) built into RhizoMath enabled the model to reproduce the experimental data. However, the rate of citrate exudation required to obtain this result was about 50 times higher as it was estimated after Schulz and Vetterlein (2007). Citrate is microbially degraded in soils. This process was not included in the calculations. According to Jones et al (2003), all the citrate which is not adsorbed will be rapidly degraded. This can lead to substantial gradients of citrate concentration within the first millimetre from the root surface. Model calculations of Geelhoed et al. (1999) predicted a citrate concentration of 0.15 mM in the soil solution at the root surface for 1 day after planting in the absence of citrate degradation. As they included citrate degradation in the calculations predicted citrate concentration in the soil solution was 0.05 mM at the root surface for 1 day after planting. Geelhoed et al. (1999) used in their purely theoretical work a constant citrate efflux of $6.1 \cdot 10^{-10}$ $mM\,cm^{-2}\,s^{-1}$. This is closer to the efflux of $1 \cdot 10^{-9}$ $mM\,cm^{-2}\,s^{-1}$ (applied in the calculations) as to the efflux of $3 \cdot 10^{-11}$ $mM\,cm^{-2}\,s^{-1}$ (estimated based on data from Schulz and Vetterlein, 2007). Both the findings of Jones et al. (Jones et al. 2003) and Geelhoed et al. (1999) support that the citrate exudation rate in the current calculations was realistic.

The good agreement in both trends and values of predicted $P^V$ concentration with experimental observations at 10 and 17 days after planting suggests that the processes that determine $P^V$ dynamics in the real system in the first 17 days were well implemented in the model.

The disagreement between predicted and measured $P^V$ concentrations at 24 days after planting show that there are some processes that are not included in the model but are relevant in the experimental system in the later stage. At that time predicted $P^V$ concentrations were lower than measured $P^V$ concentration at any distance from the root surface. A possible explanation for this could be that in the real system $P^V$ is delivered from a mineral phase with slow desorption kinetics, which is not included in the calculations. Another possible explanation for the underestimation of $P^V$ concentration in the calculations could be that the plant $P^V$ demand might decrease beyond 17 days after planting. So far the model is based on the assumption that $P^V$ uptake increases proportionally to leave area development as no time resolved data on $P^V$ uptake during plant development are available from the experiment. However, it is well documented that nutrient requirement is different for the different growth stages (Marschner, 1995) and this aspect should be taken into account for future refinement of the model.

Model calculations predicted $As^V$ depletion at the root surface both with and without citrate exudation. This prediction disagrees with experimental observations. A possible explanation for this is that in the experimental system $As^V$ uptake was suppressed by $P^V$ uptake (Zhao et al., 2009) and the suppressed uptake of $As^V$ did not exceed $As^V$ delivery to the root surface. This hypothesis is going to be discussed in the next caption.

Another possibility is, that $As^{III}$ uptake and efflux, which was recently demonstrated to be mediated by aquaglyceroporins known as Si transporters (Xu et al., 2007; Ma et al., 2008; Bienert et al., 2008), would need to be included in the model for a correct As balance. An increase in $As^{III}$ concentration in the immediate vicinity of the roots was observed in the experiment (Vetterlein et al. 2007). As $As^{III}$ is not thermodynamically stable under aerobic conditions, the $As^{III}$ released by the roots will most likely at least in parts be re-oxidized to $As^V$ and would thus show up as increased $As^V$ concentration in the rhizosphere.

Another possible explanation would be that the description of sorption processes in the model does not include all the processes that occur in the experimental system. Liu et al. (2001) found in batch experiments, that the competitive sorption of $P^V$ and $As^V$ on goethite was asymmetric. They also found that the mobilisation of $As^V$ and $P^V$ by organic anions was kinetically controlled. None of these processes can be represented by the currently applied equilibrium approach.

However, including hysteresis in the calculations would not lead to a better prediction of $As^V$ concentrations. Allowing different equilibrium for sorption and desorption would decrease the predicted mobilisation of adsorbed $As^V$. This would further decrease the predicted concentration of $As^V$ in the soil solution. This would lead to an even stronger predicted depletion of $As^V$ at the root surface. This supports the assumption that $As^V$ uptake was overestimated in the calculations.

Predicted gradients of adsorbed amounts of $As^V$ were lower compared to predicted gradients of adsorbed $P^V$ and the zone where no $P^V$ was adsorbed was slightly wider as the zone where no $As^V$ was adsorbed. This means, that in the zone where citrate concentration was not high enough to mobilise all $P^V$ and $As^V$, amount of mobilized $As^V$ was much lower compared to the amount of mobilized $P^V$. This agrees well with the results of batch experiments of Liu et al (2001). It also suggests that the transport fluxes in the system are low enough to allow the use of a local equilibrium approach for describing sorption processes.

G-4 treatment (still empty sorption sites available)

Changes predicted by the model for both $P^V$ and $As^V$ concentrations in G-4 treatment were an order of magnitude lower compared to G-1 treatment and were thus in a measurement range which can not be verified experimentally due to the limited sensitivity of the applied instrumentation (Ackermann et al., 2009).

The correctness of the model calculations for the G-4 treatment can be accepted considering that observed trends of $P^V$ and $As^V$ concentrations were reproduced by the model. Major differences that were observed between treatments G-1 and G-4 in the experiments were also reproduced by the model. This confirms the assumption that the experimentally observed differences between the two treatments can be explained by the effect of surface coverage on the competition between ions for sorption sites.

**Modelling transport in the compartment system with RhizoMath including competition during uptake**

$As^V$ influx was overestimated in the calculations without competitive uptake of $As^V$ and $P^V$. $As^V$ influx was underestimated in the calculations with competitive uptake of $As^V$ and $P^V$ with both assumptions for the mathematical description of the competition (equations 5.4 and 5.7, respectively). The underestimation of the influx in these calculations was caused by the simplicity of the applied assumptions during the derivation of equations (5.4) and (5.7). In a real plant several types of transporters can be involved in the uptake of $P^V$ and $As^V$ that can differ in their uptake kinetics and in the concentration range in which they operate. However, according to Zhao et al (2009), selectivity of different transporters for $P^V$ and $As^V$ is still not fully understood and described adequately. The mathematical description of the competitive uptake could be substantially improved once more molecular details for describing all involved mechanisms and processes at the transporter level are available.

Until this information becomes available, an empirical modification of the equations (5.4) and (5.7) could help to derive a formula that expresses competitive uptake of $As^V$ and $P^V$.

RhizoMath using the reconsidered chemical database was able to quantitatively reproduce the experimentally observed effects of goethite addition and citrate exudation on $P^V$ concentration in the soil solution in the rhizosphere of *Zea mays*. However, for a good agreement of predicted and measured $P^V$ concentrations also at later stages of the experiment it is necessary to consider changing nutrient requirement at the different growth stages of the plant (Marschner, 1995) in the calculations.

$As^{III}$ release may be an additional process that affects $As^V$ concentration in soil. Its order of magnitude in a soil based system could probably be derived from split root approaches utilizing bioreporters to visualize As concentration gradients around single roots with high spatial resolution (Kuppardt et al. prior to submission).

The strong effect of including competitive uptake of $P^V$ and $As^V$ on the predicted concentrations of the respective elements suggests that a more detailed description of the suppression of $As^V$ influx by $P^V$, considering different P transporters, and of the release of $As^{III}$, derived from arsenate reduction during detoxification in cells, could improve the model performance. However, this would require additional information from experiments on the rate of $As^{III}$ efflux and its re-oxidation in the rhizosphere. As $As^{III}$ is transported through channels which primarily serve as pathways for Si (Ma et al., 2008) and strong negative correlation between Si and As uptake has been reported (Bogdan and Schenk, 2008) it might be necessary to include Si chemistry into the model.

# 6. Discussion

## *6.1 General*

In the current work a new code (RhizoMath) for modelling reactive transport in the rhizosphere has been developed. The model development was carried out in small steps, new processes were introduced in the model one after the other. Model predictions were compared with experimental data after each development step. This procedure allowed us to study and understand the relevance of individual processes for the transport of As in the rhizosphere. Each process that was implemented in the model was individually discussed. This allowed to identify limits and weaknesses of existing approaches for modelling individual processes (chapters 3..5).

It was shown that modelling multicomponent transport in the rhizosphere requires many parameters to describe soil chemical, physical and plant physiological processes. Several parameters that are available in existing literature may be suitable for modelling theoretical problems and to qualitatively reproduce observed effects. However, these parameters have to be adjusted (optimised or approximated) using experimental data as reference to reach quantitatively good model performance. It was tested in each case whether the adjustment of certain parameters was allowed.

At a first glance, one could conclude that the number of optimized/adjusted parameters is large. However, compared to other approaches, it isn't. For example, Puschenreiter et al. (2005) applied a simple transport model (chemical speciation is not considered, sorption is described with an isotherm, competitive uptake is missing) to describe the transport of nickel in the rhizosphere. Despite these simplifications, the model they applied also required the calibration of sorption parameters and adjustment of uptake parameters. The number of calibrated/adjusted parameters was similar to the number of parameters that were optimised/adjusted in the current work.

## *6.2 Alternatives and extensions for applied model assumptions*

### Surface complexation

Sorption of different ions by hydrous ferric oxides is described in RhizoMath using the generalized two-layer model (GTL, Dzombak and Morel, 1990) that is included in PHREEQC. This implementation of the GTL model has been successfully applied to describe the sorption of $As^V$ and $As^{III}$ on goethite and manganese oxide surfaces (Tretner, 2002, This work, chapters 2 and 4). However, the GTL model in PHREEQC applies a simplified description of the electrochemical double layer which is formed between the charged surface (e.g. goethite) and the electroneutral water. This simplification may be disadvantageous for describing the sorption of large, polar, organic anions. The numbers of weak and strong surface binding sites, that are input parameters of the model, are related to the sort and amount of the sorbent. Their values which were published by Dzombak and Morel (1990) are averages of several experimental results. As it was shown in Tretner (2002) and in this work (chapter 3), using these numbers for modelling the sorption of As on goethite leads to the overestimation of surface sorption. However, this can be corrected either with the

successive approximation (Tretner, 2002) or with the optimization (this work, chapter 3) of the number of surface binding sites.

An alternative sorption model is the CD-MUSIC model that describes the spatial charge distribution in the interfacial region instead of treating surface complexes as point charges (Hiemstra and Van Riemsdijk, 1999). This allows a better prediction of the pH dependency of multicomponent sorption and a better prediction of the point of zero charge. The CD-MUSIC approach enables a direct and consistent incorporation of spectroscopic data in the sorption model. This model has been successfully applied in modelling sorption of phosphate and organic matter on goethite (Geelhoed et al., 1997; Filius et al., 2000). This sorption model was first implemented in the geochemical code ORCHESTRA (Meeussen 2003) but now it became a part of other geochemical codes, including PHREEQC, as well. Disadvantage of the CD-MUSIC model is that there is not such an extensive reaction database available as it is available for the GTL model in PHREEQC. Additionally the model performance strongly depends on the accuracy of surface site density (has the same role as the number of surface binding sites in the GTL model), whose experimental determination is still challenging (Filius et al., 2000; Lützenkirchen, 2006). Applying the CD-MUSIC model to describe surface sorption in RhizoMath would require the optimization of surface site densities using experimental data as reference.

For some future applications, for example modelling sorption in the presence of dissolved organic matter the CD-MUSIC model can be more advantageous than the GTL model. Thus, the CD-MUSIC model should be implemented in RhizoMath as well. Moreover, a direct comparison of the two surface complexation models for modelling surface sorption in the rhizosphere can be possible only if both models are implemented in RhizoMath.

**Missing chemical processes – reaction kinetics, redox chemistry**

As it was shown by Liu et al (2001), the sorption and desorption of $As^V$ and $P^V$ on goethite is asymmetric, partly kinetically controlled. Although these processes could be neglected in the current work (chapter 5), they can be relevant in the case of higher transpiration rate or in the case of rapidly changing aerobic conditions (simulating flood event, rain). The implementation of reaction kinetics in RhizoMath would require the extension of its source code.

Redox processes were not discussed in this work. However, these processes play an important role in systems with changing aerobic conditions, like in the case of alluvial soils. Additionally, including redox processes in the model is a prerequisite for modelling the recently discovered $As^{III}$ efflux and potential re-oxidation (Kuppardt et al. submitted; Vetterlein et al., 2007; Xu et al. 2007,). Experimental investigations that provide relevant information on this issue were performed by Ackermann et al. (2009) within the framework of the BASS project. Including redox speciation in RhizoMath requires the extension and re-optimization of the applied chemical database.

However, including $As^{III}$ in the model is a more complex issue than only extending the database. As it was recently published, $As^{III}$ uptake is mediated by aquaglyceroporins previously described as Si transporters (Bienert et al. 2008; Ma et al. 2008; Zhao et al.

2009). Si concentration in rice tissue was shown to show a strong negative correlation with tissue As concentration (Bogdan and Schenk 2008). Thus, Si and the uptake of Si and As$^{III}$ via the same pathway should be in the future included in the model for a correct prediction of As balance (chapter 5).

**Mass flow**

Based on typical (low, ~$10^{-2}$) Péclet numbers in the rhizosphere diffusion can be indicated to be more important than mass flow (Roose et al., 2001). However, the Péclet number is purely based on soil physical parameters. It neglects root uptake parameters and soil solution concentrations. However, whether a solute accumulates or depletes at the root surface is determined by the balance of its root uptake rate and its delivery rate to the root surface. In spite of a low Péclet number, in the case of low root influx and/or high soil solution concentration of a solute, the convective flux of this solute towards the root surface can be higher as the sum of its root influx and its diffusive flux away from the root surface. Thus the accumulation of this solutes at the root surface can occur. The relevance of this effect at the beginning of the compartment system experiment was shown in chapter 3 with comparing model calculations to experimental data. This result is supported by recent theoretical calculations of Roose and Kirk (2009).

When evaporation is neglectable (the compartment system is covered), water transport in the compartment system is driven by the transpiration of the plants. However, transpiration depends not only on the plant but also on air temperature and humidity. Thus, lower humidity and higher temperature can increase transpiration and, thus, mass flow in the system. Such scenarios can represent the effect of climate change on the bioavailability of nutrients and contaminants. The increased mass flow would most probably lead to the accumulation of mobile species at the root surface. However, due to complexity of the involved processes, such estimations can not be made for less mobile species, like As$^V$ or P$^V$ without the help of a model.

Air humidity and temperature can be accurately controlled in a modern climate chamber. Compartment system experiments performed in such a chamber would deliver more accurate data on water relations within the compartment system. Besides the above described scenarios, these experiments would provide a good reference for implementing a more detailed water uptake and transport model (Richards equation) in RhizoMath.

**Compartment system experiments as reference for the modelling**

The compartment system setup was applied in the current work as a physical model of the rhizosphere. This setup was a well applicable reference system for developing the new rhizosphere model, as it provided data on soil solution composition collected at a certain distance from the root mat considered as a root surface. This data could be compared directly with modelled data without the need of any data conversion or transformation.

Still, there are some drawbacks of the system that should be always considered when experimental and modelled data sets are compared. General limitations of the system were presented in chapter 2. It was not discussed there, but was emphasised later, that

the performed experiments could not provide direct information on soil solution composition directly at the root surface (chapters 4 and 5). The average over all samples in the root compartment was interpreted as a sample from the immediate vicinity of the roots. This was based on the assumption, that the root compartment was homogeneously filled with roots and roots were present in the sampling volume of each micro suction cup in the root compartment. However, this assumption was not verified experimentally. Additionally, the assumption has to be treated as rough approximation in the first week of the experiment, when the root mat was not fully developed.

The other weakness of the experimental setup is that the volume of the collected soil solution samples is very low. The concentration of trace elements can thus be in a range which can not be accurately measured due to the limited sensitivity of the applied instrumentation (chapter 5). Additionally, the small sampling volume restricts the number of solutes and species that can be analysed in the soil solution.

We presented an empirical mathematical description for representing root mat development in a one dimensional model. This description was derived assuming a homogeneous root mat. However, the root mat does not develop homogeneously. The roots grow in the first days of the experiment similarly as they would grow in the field - until they reach the walls of the root compartment or the nylon mesh. Then the roots are forced to change their growth direction and explore the whole root compartment. Thus, in the beginning of the experiment convective and diffusive fluxes are inhomogeneous. However, due to small fluxes in the beginning this effect may be probably neglected. The time course of the root mat development could be studied using X-Ray or neutron radiography (Menon et al., 2006; Carminati, personal communication). Such results can be used as basis for the refinement of the description of root mat development in RhizoMath.

**Planar *vs.* radial geometry**

In the current work model calculations were performed with planar geometry that represents the geometry of the compartment system experiment. Nevertheless, RhizoMath is able to calculate transport in radial systems as well, that represent the geometry of a single root. Such calculations were not performed in the current work as no experimental data exist for a direct comparison. However, modelling transport in the rhizosphere of a cylindrical root is an important step from modelling transport in a compartment system to modelling transport at the root system scale. In contrary to the single root scale, in a root system inter-root competition occurs. Thus, predictions for a root system require the consideration of root architecture additionally to the cylindrical geometry of individual roots.

**Further code development**

Some technical improvements in the RhizoMath code can be advantageous for its application. The applied method for coupling PHREEQC and MATLAB using input and output files leads to a longer calculation time in comparison to the direct coupling of two codes like it is in the case for the HP1 code (Jacques et al. 2002). This is mainly

caused by the time-consuming pre-processing routine of PHREEQC (Jacques, personal communication). Thus, the speed of RhizoMath could be increased by a direct coupling of MATLAB and PHREEQC. However, the current speed of RhizoMath is satisfying for most problems.

During the development of RhizoMath the use of PHREEQC for calculating chemical speciation in the soil solution was the best among the possible alternatives. The most recent version of ORCHESTRA offers the possibility of defining the chemical system via a graphical user interface (Meeussen, personal communication). Additionally, the chemical database of PHREEQC has been already converted to the format of ORCHESTRA. Thus, it can be a future option to use ORCHESTRA besides PHREEQC in RhizoMath for calculating chemical speciation. An advantage of ORCHESTRA in comparison to PHREEQC is that it is completely written in Java that enables an easier migration of RhizoMath to UNIX/Linux systems. A further advantage of using ORCHESTRA within RhizoMath would be an easier implementation of new processes in RhizoMath by the users.

## 6.3 Compartment system scale applications

The RhizoMath code and modelling procedures applied in the current work can be used as basis for modelling any problem related to ion transport and uptake in the vicinity of roots. Although RhizoMath was developed considering the processes that are relevant for the specific behaviour of arsenic, the implemented processes are valid for other solutes as well.

An example was presented by Puschenreiter et al (2005). The authors applied a single species model to describe the transport of nickel in the rhizosphere. The applied model parameters were calibrated to experimental data and a detailed sensitivity analysis was also performed. However, a quantitatively good model prediction on the transport of nickel in the rhizosphere could not be achieved. The authors pointed out that most probably chemical speciation and competitive uptake were relevant in the experiment but were not included in the model – they would be available in RhizoMath.

### Conclusions for the field scale, theoretical scenarios

The use of RhizoMath to reproduce data measured in compartment system experiments helps to identify geochemical and plant physiological processes that are relevant for the bioavailability of arsenic under the conditions used in the experiment. This can be used as a basis for modelling theoretical scenarios: the effect of changing parameters of individual processes can be studied. For example P-fertilization, addition of goethite or other strong sorbents can be varied by changing parameters of soil chemistry. Changing soil chemical and physical parameters can represent differences between different soil horizons. The effect of using different plant genotypes can be represented by using other parameters for root uptake/exudation. Effects of climate changes can be represented in the model by changing water flux, soil water content or growth rates. The knowledge gained with such calculations can provide a good basis for planning the remediation or use of arsenic contaminated sites.

**Real soil samples instead of artificial substrate**

Not only the complexity of the model, but also the complexity of the reference system can be increased. This can be made either by increasing the number of different phases in the system (for example by adding different sorbents besides goethite, like ferrihydrate or allophanes) or by filling the compartment system with soil samples collected in the field. However, in both cases the individual contribution of different sorbents to the total sorption can not be separated from each other by the means of inverse modelling. Determining these parameters with optimization would lead to non-unique and thus uncertain sorption parameters (number or density of surface binding sites). Thus, modelling soil solution chemistry in a system in which different sorbents are present would require a series of batch measurements beside the compartment system experiments. Moreover, using soil samples can increase the number of processes that are relevant in the experiment but are not considered in the model (e.g. microbial activity, preferential flow, soil heterogeneity, etc.). Neglecting any of these relevant processes can cause that parameters of other processes are being adjusted to achieve a good agreement between modelled and measured data sets. This can lead to wrong assumptions, for example minor processes can be assumed to be dominant.

## *6.4 Upscaling*

The motivation of the current work is an existing environmental problem: arsenic contamination of alluvial soils. Some of these soils are used for agriculture. Thus, an important aspect of the current work is its relevance for field scale problems. RhizoMath applies a microscopic approach: gradients toward the root surface are calculated; root influx of a solute is a function of its concentration at the root surface. Thus, RhizoMath is able to predict solute dynamics in the vicinity of individual roots. However, to predict As uptake in the field upscaling from the single root scale to the root system and to larger scales is necessary. Upscaling may have different outcomes for mobile and less mobile solutes. Inter-root competition is more important in the case of mobile solutes, while the effect of root and soil heterogeneity may be more important for less mobile solutes (Darrah et al., 2006). This aspect should be considered for the choice of the appropriate upscaling method.

There are different numerical analytical methods for upscaling - without (e.g. Barber, 1995) and with (e.g. Dunbabin et al., 2002) considering root architecture. Advantages and disadvantages of different upscaling methods were discussed in detail by Darrah et al. (2006). To reduce computation time these methods are based on simplified descriptions of transport in the vicinity of the roots (Dunbabin et al., 2002; Roose and Kirk, 2009). However, such simplified methods may not reflect changes in local chemistry close to the root surface (Darrah et al., 2006). This can lead to wrong model predictions on the dynamics of compounds with a complex chemical behaviour such as As and P. RhizoMath can be already applied to test the limitations of simplified rhizosphere transport models.

Coupling RhizoMath to existing root system scale models like ROOTMAP (Dunbabin et al., 2002) may increase the quality of model predictions on the large-scale transport and uptake of these solutes by root systems.

Darrah et al. (2006) emphasised, that upscaling a microscale rhizosphere transport model without any simplification may not be "computationally feasible ". However, the long computing time required by a detailed model could be reduced by the use of parallel computing. Recent developments for using graphical processors for parallel computing offer an achievable alternative to supercomputing clusters (Garland et al., 2008). Thus, upscaling RhizoMath should be considered as an option.

# 7. Summary

Recent recognition of the extent of arsenic contamination at agricultural sites in Germany and several other countries led to the need for assessing the risk of arsenic transfer from the soil into the food chain. This motivated the investigation into rhizosphere processes (Vetterlein et al., 2007) and the development of a rhizosphere model (this work) which enables the integration of different rhizosphere processes in space and time.

The compartment system setup used as a reference system is a recently developed experimental technique for studying rhizosphere processes (Vetterlein and Jahn 2004b). In contrary to experimental setups that provide information only for one point in time (Hedley et al. 1994; Kirk 1999; Wenzel et al. 2001) this setup, supported by a high-end analytical apparatus (Mattusch et al., 2000; Vetterlein et al., 2007), provides temporal resolved information on soil solution composition.

$As^V$ has a complex behaviour in soil due to its analogy to $P^V$. Both anions compete with each other for binding sites in the soil (Jain and Loeppert, 2000; Smith et al., 2002) and for root membrane transporters (Meharg and Macnair, 1992; Poynton et al., 2004). $P^V$ in soil can be mobilized by plants through different mechanisms (Hinsinger et al., 2003). These processes can also affect the availability of arsenic in soils (Vetterlein et al., 2007).

Modelling the transport of As in the rhizosphere is only possible when the chemical speciation of As and the speciation of other solutes and phases that affect As speciation and availability are considered in the transport model. However, only a few of existing rhizosphere models are dealing with chemical speciation and they either consider only a small number of ions (Geelhoed et al. 1999; Hoffland et al. 1990) or they are developed based on theoretical considerations without verification with experimental data (Nietfeld 2001). The application of commonly available geochemical codes [MIN3P, PHREEQC, ORCHESTRA, (Mayer et al. 2002; Meeussen 2003; Parkhurst and Appelo 1999), respectively)] is theoretically possible but practically limited to certain problems (Nowack et al., 2006).

The major objective of the work reported in this thesis was to develop a rhizosphere model that includes the relevant biogeochemical processes for the interpretation of compartment system experiments performed to investigate the temporal and spatial changes of As availability in the rhizosphere.

The model development was performed stepwise with a continuous comparison of modelling results and experimental data. The following results have been achieved:

    (i)    A rhizosphere transport model, called RhizoMath, has been developed by coupling the mathematical package MATLAB and the geochemical code PHREEQC. RhizoMath has a graphical user interface, so the program can be applied by researchers who are not familiar with syntaxes of transport codes. The geometry of the modelled system can be simply changed from planar (geometry of compartment system experiments) to radial (a single root) in the graphical user interface. A flexible choice of species in soil

solution, mineral phases and surface sorbents is possible due to the flexibility of the chemical database of PHREEQC. (chapter 3)

(ii) The most important parameters for modelling the competitive sorption of $As^V$ and $P^V$ by goethite are the equilibrium constants of the stoichiometric reactions that describe the sorption by the surface binding sites of goethite and the numbers of the surface binding sites. Existing literature presents a high uncertainty of equilibrium constants of surface sorption reactions. Additionally, the use of literature data on the amount of surface binding sites leads to the overestimation of surface sorption. Thus, numbers of surface binding sites and uncertain equilibrium constants have to be optimized using experiments as reference. For this, an initialization module for the calibration of these parameters was included in RhizoMath. (chapter 3)

(iii) The chemical database for calculating chemical speciation in the soil solution was compiled to make it suitable to describe chemical speciation in the compartment system. Numbers of surface binding sites and uncertain equilibrium constants were determined with the initialization module of RhizoMath using soil solution samples, collected at the beginning of the experiments without the presence of the plants, as reference. Theoretical scenarios were calculated with PHREEQC with increasing amount of added goethite and citrate, respectively. These calculations showed that the compiled and optimized chemical database is able to describe equilibrium chemistry of the applied solutes and media. (chapter 5)

(iv) The RhizoMath code was extended with the root compartment factor that describes dynamic parameters for root nutrient uptake. This allowed modelling a growing plant in the compartment system and to independently study the effects of temporal changes in nutrient demand from the effects of temporal changes in water flux. (chapter 4)

(v) RhizoMath was applied to model transport in the compartment systems with added goethite. Results of the calculations confirmed the hypothesis (Vetterlein et al. 2007) that the experimentally observed increase in $P^V$ concentration at the root surface is a consequence of $P^V$ mobilization via citrate exudation by the roots. Predicted $P^V$ concentrations agreed well with measured data set. Predicted $As^V$ concentrations were lower at the root surface compared to measured ones. It was discussed that it could have been either caused by neglecting $As^{III}$ release by the plants or by overestimating $As^V$-uptake in the calculations. (chapter 5)

(vi) The transport module of RhizoMath was extended with equations for the description of competitive uptake of solutes. This allowed representing the suppression of $As^V$-uptake by $P^V$-uptake in the calculations. However, both applied approaches that described the competitive uptake of $As^V$ and $P^V$ underestimated $As^V$ uptake. Thus, predicted $As^V$ concentrations were higher at the root surface than measured ones. (chapter 5)

(vii)   It was shown that a more detailed description of the suppression of $As^V$ influx by $P^V$ influx is necessary in the model calculations for a good prediction of $As^V$ concentration profiles. The fact, that model predictions could not reproduce $As^V$ uptake in the experiments using one sort of transporter supports that further transporters should be implemented in the model. (chapter 5)

(viii)  It was discussed that $As^{III}$ release may be an additional process that affects $As^V$ concentration in soil. However for the characterisation of these processes further experimental investigations are necessary. (chapter 5)

Although there are still a range of processes that could be included in RhizoMath in more detail (see above) to further improve its performance, RhizoMath is now a readily available tool which allows calculating scenarios for spatial and temporal dynamics of interacting processes in the rhizosphere. It can be used to predict changes associated with changes in management (e.g. fertilizer application) or climate (e.g. higher transpiration rate). In addition, it might help to identify knowledge gaps. If experimental data can not be described by the model it is very likely that important processes were not yet included as it is the case for $As^{III}$ efflux. Most of the presented results have general relevance: they can be applied with a focus on other elements apart from the particular case of arsenic transport in the rhizosphere. Additionally, the obtained results provide a good basis for estimating and modelling bioavailability of nutrients and contaminants in the field.

# 8. Zusammenfassung

Neue Erkenntnisse über das Ausmaß der Arsenbelastung auf landwirtschaftlich genutzten Flächen in Deutschland und der Welt begründen die Notwendigkeit die Risiken des Arsentransfers vom Boden in die Nahrungskette abzuschätzen. Dies ist der Grund für die Untersuchung von Rhizosphärenprozessen im Zusammenhang mit der Arsenaufnahme von Pflanzen (Vetterlein et al., 2007) und für die Entwicklung eines Rhizosphärenmodells (diese Arbeit), das die zeitliche und räumliche Integration von unterschiedlichen Rhizosphärenprozessen ermöglicht.

Der Kompartimentsystemaufbau, der als Referenzsystem für die Modellentwicklung verwendet wurde, ist eine neu entwickelte Experimentaltechnik zur Untersuchung von Rhizosphärenprozessen (Vetterlein and Jahn 2004b). Im Gegensatz zu Untersuchungsmethoden, mit denen nur Information zu einem bestimmten Zeitpunkt erfasst werden können (Hedley et al. 1994; Kirk 1999; Wenzel et al. 2001), zeigt dieser Aufbau, unterstützt durch hoch entwickelte analytische Geräte, eine zeitliche Dynamik der Zusammensetzung der Bodenlösung (Mattusch et al., 2000; Vetterlein et al., 2007).

Aufgrund der Homologie von Arsenat ($As^V$) und Phosphat ($P^V$) ist die Verhaltensweise von $As^V$ in Böden sehr komplex. Diese zwei Anionen konkurrieren miteinander um Bindungsstellen in Böden (Jain and Loeppert, 2000; Smith et al., 2002) sowie um die Bindung an $P^V$-Transportern in den Zellmembranen der Pflanzen (Meharg and Macnair, 1992; Poynton et al., 2004). $P^V$ im Boden kann von Pflanzen durch mehrere Mechanismen mobilisiert werden (Hinsinger et al., 2003). Diese Mechanismen können auch die Verfügbarkeit von $As^V$ im Boden beeinflussen (Vetterlein et al., 2007).

Die Modellierung des Arsentransportes in der Rhizosphäre ist nur möglich, wenn die chemische Spezierung von As sowie die Spezierung von anderen gelösten Substanzen und Phasen, die die Spezierung und die Verfügbarkeit von As beeinflussen, in den Berechnungen ebenfalls berücksichtigt werden.

Jedoch, nur einige von den existierenden Rhizospärenmodellen rechnen mit chemischer Spezierung, und diese berücksichtigen nur eine geringe Anzahl von Ionen (Geelhoed et al. 1999; Hoffland et al. 1990), oder basieren nur auf theoretischen Überlegungen ohne Abgleich mit experimentellen Datensätzen (Nietfeld 2001). Die Verwendung von verfügbaren geochemischen Codes [MIN3P, PHREEQC, ORCHESTRA, (Mayer et al. 2002; Meeussen 2003; Parkhurst and Appelo 1999)] für die Rhizosphärenmodellierung ist theoretisch möglich, aber in der Praxis auf bestimmte Anwendungen beschränkt (Nowack et al., 2006).

Das Hauptziel dieser Arbeit war die Entwicklung eines Rhizosphärenmodells, das jene relevanten biogeochemischen Prozesse beinhaltet, die für die Interpretation der Kompartimentsystemversuche nötig sind, welche für die Untersuchung von zeitlichen und räumlichen Änderungen in der Arsenverfügbarkeit in der Rhizosphäre durchgeführt wurden.

Die Modellentwicklung wurde schrittweise durchgeführt. Die Ergebnisse der Modellberechnungen wurden nach jeder Änderung des Modells mit Messergebnissen abgeglichen. Daraus lassen sich die folgenden Ergebnisse zusammenfassen:

(i)    Das Rhizosphärenmodell RhizoMath wurde durch die Kopplung des mathematischen Paketes MATLAB mit dem geochemischen Code PHREEQC entwickelt. RhizoMath verfügt über eine graphische Benutzeroberfläche, die die Anwendung des Programms auch für Wissenschaftler ermöglicht, die mit den Syntaxen von Transportcodes nicht vertraut sind. Die Geometrie des modellierten Systems kann einfach über die graphische Oberfläche von planar (Geometrie der Kompartimentsystemversuche) zu radial (Einzelwurzel) geändert werden. Die Flexibilität der chemischen Datenbank von PHREEQC ermöglicht die flexible Auswahl von gelösten Spezies, Mineralphasen und adsorbierenden Oberflächen (Kapitel 3).

(ii)   Die wichtigsten Parameter für die Modellierung der kompetitiven Sorption von $As^V$ und $P^V$ an Goethit sind die Gleichgewichtskonstanten der stöchiometrischen Gleichungen, welche die Sorption an den Bindungsstellen von Goethit sowie die Anzahl der Bindungsstellen beschreiben. Existierende Literatur weist auf eine hohe Unsicherheit der Gleichgewichtskonstanten dieser Sorptionsgleichungen hin. Zusätzlich führt die Verwendung von in der Literatur gefundenen Anzahlen an Sorptionsstellen zu der Überschätzung des Ausmaßes der Oberflächensorption. Deshalb muss die Menge an Bindungsstellen sowie die Unsicherheit der Gleichgewichtskonstanten, mit Messwerten als Referenz, optimiert werden. Für diesen Zweck wurde ein Initialisierungsmodul in RhizoMath implementiert, das die Kalibrierung der oben benannten Parameter durchführt (Kapitel 3).

(iii)  Die chemische Datenbank für die Berechnung der Speziierung in der Bodenlösung ist so zusammengestellt worden, dass sie die Beschreibung der Speziierung in dem Kompartimentsystem ermöglicht. Die Anzahlen an Oberflächenbindungsstellen und die Gleichgewichtskonstanten wurden mit dem Initialisierungsmodul von RhizoMath bestimmt. Als Referenz hierfür wurden Bodenlösungsproben verwendet die am Anfang des Versuches, noch vor der Pflanzung, entnommen worden waren. Darüber hinaus wurden theoretische Szenarien mit PHREEQC berechnet. Dabei wurden jeweils die Mengen von zugegebenem Goethit und Zitrat systematisch erhöht. Diese Berechnungen haben gezeigt, dass die Zusammengestellte und optimierte chemische Datenbank in der Lage ist, das chemische Gleichgewicht der verwendeten Substanzen und Medien zu beschreiben. (Kapitel 5).

(iv)   Das Programm RhizoMath wurde mit dem „Root Compartment Factor" erweitert, welcher dynamische Parameter der Nährstoffaufnahme der Pflanze beschreibt. Dies ermöglicht die Modellierung einer wachsenden Pflanze im Kompartimentsystem und die unabhängige Untersuchung der

zeitlichen Änderungen des Nährstoffbedarfs und des Wasserflusses (Kapitel 4).

(v) RhizoMath wurde für die Transportmodellierung in den Kompartimentsystemen mit zugegebenem Goethit angewendet. Die Ergebnisse der Berechnungen bestätigten die Hypothese (Vetterlein et al., 2007), dass die experimentell beobachtete Erhöhung der $P^V$-Konzentration an der Wurzeloberfläche aus der $P^V$-Mobilisierung durch Zitratexsudation der Wurzeln resultiert. Die modellierte $P^V$-Konzentrationen zeigten eine gute Übereinstimmung mit den gemessenen Konzentrationen. Die modellierten $As^V$-Konzentrationen lagen an der Wurzeloberfläche niedriger als die gemessenen Konzentrationen. In der Diskussion wurden zwei Hypothesen für die Ursache dieser Unterschätzung aufgestellt: a) es wurde keine $As^{III}$-Abgabe der Pflanze berücksichtigt, b) die $As^V$-Aufnahme wurde in den Berechnungen überschätzt (Kapitel 5).

(vi) Das Transportmodul von RhizoMath wurde mit der mathematischen Beschreibung der kompetitiven Nährstoffaufnahme erweitert. Dies ermöglicht die Berücksichtigung der Unterdrückung der $As^V$-Aufnahme durch die $P^V$-Aufnahme. Jedoch führten beide verwendeten Ansätze für die Beschreibung einer kompetitiven $P^V$- und $As^V$-Aufnahme zu einer Unterschätzung der Letzteren. Als Folge waren die modellierten $As^V$-Konzentrationen an der Wurzeloberfläche höher als real gemessen (Kapitel 5).

(vii) Es wurde gezeigt, dass eine ausführlichere Beschreibung der Unterdrückung der $As^V$-Aufnahme durch die $P^V$-Aufnahme in den Berechnungen nötig ist, um eine gute Vorhersage von $As^V$-Konzentrationsprofilen zu gewährleisten. Der Tatsache, dass die Modellberechnungen, welche nur eine Art von Transportern berücksichtigten, die experimentelle $As^V$-Aufnahme nicht reproduzieren konnten, deutet darauf hin, dass weitere Transporter in das Modell implementiert werden müssen (Kapitel 5).

(viii) Es wurde postuliert, dass die $As^{III}$-Abgabe ein zusätzlicher Prozess sein könnte, welcher die $As^V$-Konzentration in der Bodenlösung beeinflusst. Für die Charakterisierung dieses Prozesses sind jedoch weitere experimentelle Untersuchungen nötig.

Obwohl es immer noch eine Reihe von Prozessen gibt, welche im entwickelten Modell noch ausführlicher implementiert werden müssten, ist RhizoMath schon jetzt ein nutzbares Werkzeug, das die Berechnung von Szenarien der räumlichen und zeitlichen Dynamik von interagierenden Rhizosphärenprozessen ermöglicht. Es kann für Vorhersagen herangezogen werden, die mit den Änderungen in der Landnutzung (z.B. Düngungsniveau) oder dem Klima (z.B. höhere Transpirationsraten) zusammenhängen. Darüber hinaus kann RhizoMath helfen Wissenslücken zu identifizieren. Wenn das Modell vorhandene Messdaten nicht beschreiben kann, sind

höchstwahrscheinlich noch weitere Prozesse in dem Modell zu implementieren, wie zum Beispiel im Fall der $As^{III}$-Abgabe. Die entwickelten Module von RhizoMath sind prozessbasiert und können daher auch im Bezug auf andere Elemente verwendet werden, unabhängig von dem speziellen Fall des Arsentransportes in der Rhizosphäre.

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# 10. List of abbreviations

| | |
|---|---|
| $As^{III}$ | arsenite (reduced arsenic species) |
| $As^{V}$ | arsenate (oxidised arsenic species) |
| BASS | Bioavailability of Arsenic in Soil Sediments – Project of the Martin Luther University Halle-Wittenberg and the Helmholtz Centre for Environmental Research – UFZ. Project leader: PD Dr Doris Vetterlein |
| CD-MUSIC | Charge-Distribution and Multisite Complexation (surface sorption model) |
| G-0 | treatment without goethite addition |
| G-1 | treatment with $1g\ kg^{-1}$ added goethite |
| G-4 | treatment with $1g\ kg^{-1}$ added goethite |
| GTL | generalized two-layer model (surface sorption model) |
| $I_{max}$ | maximum influx parameter of the Michaelis-Menten kinetics |
| $K_m$ | Michaelis-Menten constant |
| L (dimension) | length |
| DMAA | dimethylarsinic acid |
| M (dimension) | mass |
| $mM$ | mmol $l^{-1}$ – Concentration per litre soil solution |
| MMAA | monomethylarsonic acid |
| PDE | partial differential equation |
| $P^{V}$ | phosphate |
| RCF | root compartment factor |
| T (dimension) | time |
| XRF | X-ray fluorescence spoectrometry |

Variables and constants in equations are explained below the equations.

# Acknowledgements

# Appendix 1 – Parameters of Performed Compartment System Experiments

*Table A1.1: The initial fertilization of the compartments. The quartz substrate was fertilized with solutions of the salts below, except $CaSO_4$ and $CaHPO_4$ which were are added as powders. For $As^V$ treatment a solution of $Na_2HAsO_4 x 7H_2O$ was added. Solutions were let to dry on the substrate surface and thoroughly mixed into the substrate. In a next step the powdered chemicals were added and the substrate was thoroughly mixed. In a last step different amounts of (0, 1, 4 g $kg^{-1}$ soil) goethite was added and mixed into the substrate. The total concentration of the major elements and species were measured by analyzing the weekly collected soil solution samples by ICP-OES, flow solution technique, IC-ICP-MS and EOS. Each treatment was established in three replications.*

| Solute | Added as | Added amount (mg $kg^{-1}$ soil) | Analyzed in soil solution | Analyzed with |
|---|---|---|---|---|
| N | $NH_4NO_3$ | 100 | $NH_4^+$, $NO_3^-$ | flow solution |
| S | $K_2SO_4$, $CaSO_4$ x $2H_2O$ | 121 | S | ICP-OES |
| P | $CaHPO_4$ | 80 | P | ICP-OES |
| K | $K_2SO_4$ | 100 | K | ICP-OES |
| Ca | $CaSO_4$ x $2H_2O$, $CaHPO_4$ | 203.5 | Ca | ICP-OES |
| Mg | $MgCl_2$ | 50 | Mg | ICP-OES |
| Cl | $MgCl_2$ | 145.88 | Cl | IC |
| Mn | $MnSO_4 x H_2O$ | 3.25 | Mn | ICP-OES |
| Zn | $Zn(NO_3)_2 x 4H_2O$ | 0.79 | - | - |
| Cu | $CuSO_4 x 5H_2O$ | 0.50 | - | - |
| B | $H_3BO_3$ | 0.17 | - | - |
| Fe | Fe-EDTA | 3.25 | $Fe^{II}$, $Fe^{III}$ | EPOS |
| As | $Na_2HAsO_4 x 7H_2O$ | 5.00 | total As | ICP-OES |
| | | | $As^{III}$, $As^V$ | IC-ICP-MS |

*Table A1.2: Overview of the different treatments and the physical soil parameters*

| Treatment name | G-0 | G-1 | G-4 |
|---|---|---|---|
| Substrate | all as quartz: 85% sand, 10% slit, 5 % clay, all as Quartz | | |
| Bulk density | 1.45 g $cm^{-3}$ | | |
| Initial water content | 25 Vol.% | | |
| Amount of added goethite | 0 g $kg^{-1}$ | 1 g $kg^{-1}$ | 4 g $kg^{-1}$ |

# Appendix 2 – Review of Parameters of Michaelis-Menten Kinetics

Table A2.1 Parameters of Michaelis-Menten kinetics, collected from different publications.
Explanation of abbreviations follows below the table.

| Nutrient | Genotype | Plant part | Plant Age (d) | Special Treatment (If given) | Interval | $J_{max}$ $mM$ cm$^{-2}$ s$^{-1}$ | Km | $C_{min}$ or Efflux | Reference |
|---|---|---|---|---|---|---|---|---|---|
| **As$^{III}$** | Z1 | E | 7 | P+ (5mM) | st | 5.91E-09 | 4.48 mM L$^{-1}$ | - | [1] |
| | Z1 | E | 7 | P- | st | 1.35E-08 | 9.32 mM L$^{-1}$ | - | [1] |
| | Z2 | E | 7 | P+ (5mM) | st | 3.76E-09 | 2.55 mM L$^{-1}$ | - | [1] |
| | Z2 | E | 7 | P- | st | 5.12E-09 | 2.69 mM L$^{-1}$ | - | [1] |
| | Z3 | E | 7 | P+ (5mM) | st | 5.48E-09 | 2.05 mM L$^{-1}$ | - | [1] |
| | Z3 | E | 7 | P- | st | 6.25E-09 | 2.09 mM L$^{-1}$ | - | [1] |
| | Z4 | E | 7 | P+ (5mM) | st | 3.88E-09 | 3.00 mM L$^{-1}$ | - | [1] |
| | Z4 | E | 7 | P- | st | 7.31E-09 | 4.20 mM L$^{-1}$ | - | [1] |
| | Z5 | E | 7 | P+ (5mM) | st | 4.59E-09 | 3.36 mM L$^{-1}$ | - | [1] |
| | Z5 | E | 7 | P- | st | 1.01E-08 | 4.91 mM L$^{-1}$ | - | [1] |
| | Z6 | E | 7 | P+ (5mM) | st | 4.81E-09 | 3.93 mM L$^{-1}$ | - | [1] |
| | Z6 | E | 7 | P- | st | 9.16E-09 | 6.95 mM L$^{-1}$ | - | [1] |
| **As$^{V}$** | Z1 | E | 7 | P+ (5mM) | st | 1.66E-09 | 1.75 mM L$^{-1}$ | - | [1] |
| | Z1 | E | 7 | P- | st | 5.92E-10 | 0.055 mM L$^{-1}$ | - | [1] |
| | Z1 | E | 7 | P- | st | 1.90E-09 | 2.29 mM L$^{-1}$ | - | [1] |
| | Z2 | E | 7 | P+ (5mM) | st | 2.80E-09 | 4.69 mM L$^{-1}$ | - | [1] |
| | Z2 | E | 7 | P- | st | 8.22E-10 | 0.076 mM L$^{-1}$ | - | [1] |
| | Z2 | E | 7 | P- | st | 1.32E-09 | 1.45 mM L$^{-1}$ | - | [1] |
| | Z3 | E | 7 | P+ (5mM) | st | 2.10E-09 | 1.52 mM L$^{-1}$ | - | [1] |
| | Z3 | E | 7 | P- | st | 5.67E-10 | 0.0147 mM L$^{-1}$ | - | [1] |
| | Z3 | E | 7 | P- | st | 1.20E-09 | 0.71 mM L$^{-1}$ | - | [1] |
| | Z4 | E | 7 | P+ (5mM) | st | 1.23E-09 | 1.27 mM L$^{-1}$ | - | [1] |
| | Z4 | E | 7 | P- | st | 3.38E-10 | 0.015 mM L$^{-1}$ | - | [1] |
| | Z4 | E | 7 | P- | st | 1.99E-09 | 1.72 mM L$^{-1}$ | - | [1] |
| | Z5 | E | 7 | P+ (5mM) | st | 1.94E-09 | 3.00 mM L$^{-1}$ | - | [1] |
| | Z5 | E | 7 | P- | st | 2.81E-10 | 0.019 mM L$^{-1}$ | - | [1] |
| | Z5 | E | 7 | P- | st | 1.63E-09 | 0.71 mM L$^{-1}$ | - | [1] |
| | Z6 | E | 7 | P+ (5mM) | st | 2.25E-09 | 3.30 mM L$^{-1}$ | - | [1] |
| | Z6 | E | 7 | P- | st | 1.57E-10 | 0.01 mM L$^{-1}$ | - | [1] |
| | Z6 | E | 7 | P- | st | 1.66E-09 | 1.23 mM L$^{-1}$ | - | [1] |
| **Ca** | Z7 | I | 20 | | lt | 1.84E-07 | 50.4 μM L$^{-1}$ | 6.43 μM L$^{-1}$ | [2] |
| | Z8 | I | 20 | | lt | 1.91E-07 | 48.7 μM L$^{-1}$ | 5.34 μM L$^{-1}$ | [2] |
| | Z9 | I | 20 | | lt | 1.48E-07 | 58.4 μM L$^{-1}$ | 6.41 μM L$^{-1}$ | [2] |
| | Few values available | | | | | | 40..300 μM L$^{-1}$ | * | [3] |

* has no significance due to the high Ca concentration in soil

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Cl** | Z10 | A | 5 | Ca- | | 1.08E-08 | 0.1 mM | Mich.-Ment. | [6] |
| | Z10 | A | 5 | Ca+ | | 8.61E-09 | 0.05 mM | + linear term | [6] |
| | | | | | | | | | |
| **K** | Z | I | 18 | | lt | 3.18E-06 | 27.9 $\mu$M L$^{-1}$ | 55 $\mu$M L$^{-1}$ s$^{-1}$ | [3,4] |
| | Z | I | 17 | | | | 16.7 $\mu$M L$^{-1}$ | 0.07 Jmax | [3,5] |
| | Z11 | I | 10 | K-6mM | lt | 3.66E-08 | 5 $\mu$M L$^{-1}$ | 690 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 10 | K-9mM | lt | 3.37E-08 | 10.7 $\mu$M L$^{-1}$ | 350 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 10 | K-18mM | lt | 3.12E-08 | 14.2 $\mu$M L$^{-1}$ | 210 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 10 | K-52mM | lt | 3.98E-08 | 23.2 $\mu$M L$^{-1}$ | 150 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 10 | K-190mM | lt | 2.86E-08 | 11.7 $\mu$M L$^{-1}$ | 370 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 10 | K-1000mM | lt | 1.49E-08 | 17.5 $\mu$M L$^{-1}$ | 170 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 17 | Split root 100-0 | lt | 1.60E-08 | 17 $\mu$M L$^{-1}$ | 200 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 17 | Split root 75(K+)-25 | lt | 2.60E-08 | 17 $\mu$M L$^{-1}$ | 200 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 17 | Split root 50(K+)-50 | lt | 2.70E-08 | 18 $\mu$M L$^{-1}$ | 200 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 17 | Split root 25(K+)-75 | lt | 3.90E-08 | 17 $\mu$M L$^{-1}$ | 300 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11 | I | 17 | Split root 2..15(K+)-98..85 | lt | 3.80E-08 | 10 $\mu$M L$^{-1}$ | 400 $\mu$M L$^{-1}$ s$^{-1}$ | [7] |
| | Z11. | | 18 | | | 4.00E-09 | 16 $\mu$M L$^{-1}$ | 1 $\mu$M L$^{-1}$ | [3,8] |
| | Z7 | I | 20 | | lt | 1.73E-06 | 39.1 $\mu$M L$^{-1}$ | 4.52 $\mu$M L$^{-1}$ | [2] |
| | Z8 | I | 20 | | lt | 1.34E-06 | 37.4 $\mu$M L$^{-1}$ | 6.72 $\mu$M L$^{-1}$ | [2] |
| | Z9 | I | 20 | | lt | 2.15E-06 | 38.3 $\mu$M L$^{-1}$ | 3.77 $\mu$M L$^{-1}$ | [2] |
| | | | | | | | | | |
| **Mg** | Z10 | A | 5 | | | 4.17E-09 | 150 $\mu$M L$^{-1}$ | | [3,6] |
| | Z10 | A | 5 | Ca- | | 7.50E-09 | 0.1 mM L$^{-1}$ | Mich.-Ment. | [6] |
| | Z10 | A | 5 | Ca+ | | 4.31E-09 | 0.05 mM L$^{-1}$ | + linear term | [6] |
| | Z7 | I | 20 | | lt | 4.95E-07 | 35.2 $\mu$M L$^{-1}$ | 0.56 $\mu$M L$^{-1}$ | [2] |
| | Z8 | I | 20 | | lt | 4.87E-07 | 24.5 $\mu$M L$^{-1}$ | 0.69 $\mu$M L$^{-1}$ | [2] |
| | Z9 | I | 20 | | lt | 5.37E-07 | 48.7 $\mu$M L$^{-1}$ | 0.58 $\mu$M L$^{-1}$ | [2] |
| | | | | | | | | | |
| **N** | Z | | 7..13 | | | 1.20E-08 | 12..20 $\mu$M L$^{-1}$ | 3..9 $\mu$M L$^{-1}$ | [3,11] |
| | Z | I | 15 | trimmed roots | lt | 8.66E-10 | 12..20 $\mu$M L$^{-1}$ | 3..9 $\mu$M L$^{-1}$ | [3,9] |
| | Z | I | 18 | trimmed roots | lt | 1.01E-09 | 12..20 $\mu$M L$^{-1}$ | 3..9 $\mu$M L$^{-1}$ | [3,9] |
| | Z | I | 21 | trimmed roots | lt | 9.18E-10 | 12..20 $\mu$M L$^{-1}$ | 3..9 $\mu$M L$^{-1}$ | [3,9] |
| | Z | I | 24 | trimmed roots | lt | 8.74E-10 | 12..20 $\mu$M L$^{-1}$ | 3..9 $\mu$M L$^{-1}$ | [3,9] |
| | Z | I | 33 | trimmed roots | lt | 3.25E-10 | 12..20 $\mu$M L$^{-1}$ | 3..9 $\mu$M L$^{-1}$ | [3,9] |
| | Z | I | 46 | trimmed roots | lt | 6.80E-11 | 12..20 $\mu$M L$^{-1}$ | 3..9 $\mu$M L$^{-1}$ | [3,9] |
| | Z | I | 58 | trimmed roots | lt | 4.50E-11 | 12..20 $\mu$M L$^{-1}$ | 3..9 $\mu$M L$^{-1}$ | [3,9] |
| | | | | | | | | | |
| **NO3** | Z | I | | | est. | 1.00E-08 | 25 $\mu$M L$^{-1}$ | 2 $\mu$M L$^{-1}$ | [3] |
| | Z11. | | 18..22 | | | 1.00E-09 | 10 $\mu$M L$^{-1}$ | 4 $\mu$M L$^{-1}$ | [3,10] |
| | Z7 | I | 20 | | lt | 2.55E-06 | 37.1 $\mu$M L$^{-1}$ | 5.09 $\mu$M L$^{-1}$ | [2] |
| | Z8 | I | 20 | | lt | 3.76E-06 | 66 $\mu$M L$^{-1}$ | 17.6 $\mu$M L$^{-1}$ | [2] |
| | Z9 | I | 20 | | lt | 2.82E-06 | 70.6 $\mu$M L$^{-1}$ | 17.6 $\mu$M L$^{-1}$ | [2] |
| | | | | | | | | | |
| **P** | Z | I | 14 | | lt | 3.26E-08 | 5.8 $\mu$M L$^{-1}$ | 0.09 $\mu$M L$^{-1}$ | [3] |
| | Z11. | I | 7..42 | P++ (100 mM) | vlt | 1.27E-10 | 18 $\mu$M L$^{-1}$ | 0 $\mu$M L$^{-1}$ | [12] |
| | Z11. | I | 7..42 | P+ (1 mM) | vlt | 3.34E-10 | 22 $\mu$M L$^{-1}$ | 0.01 $\mu$M L$^{-1}$ | [12] |

| | | | | | | $I_{max}$ | $K_m$ | $C_{min}$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | Z11. | I | 7..42 | P+ (0.2 mM) | vlt | 3.58E-10 | 14 μM L⁻¹ | 0.08 μM L⁻¹ | [12] |
| | Z11. | | 14..28 | | | 4.00E-10 | 3 μM L⁻¹ | 0.2 μM L⁻¹ | [3,8] |
| | Z7 | I | 20 | | lt | 2.51E-07 | 21.1 μM L⁻¹ | 0.87 μM L⁻¹ | [2] |
| | Z8 | I | 20 | | lt | 1.58E-07 | 14.1 μM L⁻¹ | 1.26 μM L⁻¹ | [2] |
| | Z9 | I | 20 | | lt | 2.77E-07 | 19.7 μM L⁻¹ | 1.21 μM L⁻¹ | [2] |
| **S** | Z | E | | | | 1.69E-09 | 0.039 mM L⁻¹ | | [3,13,14] |
| | Z | E | | | | 1.75E-08 | 2.8 mM L⁻¹ | | [3,13,14] |
| | Z | E | | | | 4.83E-08 | 11 mM L⁻¹ | | [3,13,14] |
| | Z13 | E | 6 | | lt | 2.32E-09 | 0.166 mM L⁻¹ | | [3,15] |
| | Z14 | E | 6 | | lt | 2.14E-09 | 0.179 mM L⁻¹ | | [3,15] |
| | Z15 | E | 6 | | lt | 3.97E-09 | 0.055 mM L⁻¹ | | [3,15] |
| | Z12 | I | 6 | Cd+ | st | 5.78E-10 | 20.5 μM L⁻¹ | - | [16] |
| | Z12 | I | 6 | | st | 2.84E-10 | 20.3 μM L⁻¹ | - | [16] |

### *Zea Mays* genotypes:

Z – genotype not given, Z1 – single cross 10, Z2 – single cross 2030, Z3 – single cross 3084,
Z4 – single cross 30k8, Z5 – three-way cross 310, Z6 – three-way cross 323, Z7 – P32R21, Z8 – Plantalto,
Z9 – Traktor, Z10 – cv. DeKalb 441, Z11 – L, Z 12 – L. cv  Dekalb DK300, Z 13 – hybrid 75,
Z 14 – hybrid 79A,  Z15 – hybrid 75 + 79A

### Analysed plant parts:

E= Excised roots, C= Root cells, A = Apical segments, I=intact plant after Claassen and barber 1974

### Interval:

st = hort term (~mins), lt=long term (hours, up to one day), vlt = very long term = several days

### Transporter:

ha = high affinity, la = low affinity

### References:

[1]: Abbas and Meharg (2008), [2]: Horn et al. (2006), [3] Barber (1995), [4] Claassen and Barber (1974),
[5] Claassen et al.(1986), [6] Maas and Ogata (1971), [7] Claassen and Barber (Claassen and Barber, 1977),
[8] Jungk & Barber 1975, [9] Edwards and Barber (1976), [11] Warncke and Barber 1973,
[12] Bhadoria et al (2004), [13] Berlier et al 1969, [14] Nissen 1973, [15] Ferrari and Renosto (1972),
[16] Nocito et al (2002)

## Appendix 3 - RhizoMath Users' Manual

# RhizoMath v0.999

## A TOOL FOR MODELING COUPLED
## TRANSPORT AND SPECIATION IN THE RHIZOSPHERE

### QUICK STARTING GUIDE

Krisztian Szegedi & Doris Vetterlein

**Introduction**

The transfer of nutrients or contaminants from the bulk soil to the roots and into the plants depends on the integration of many individual plant and soil processes (Darrah and Roose, 2001). Transport is driven by hydraulic potential gradients induced by transpiration (convective transport) or by chemical gradients (diffusive transport). The concentration and chemical speciation of a certain element in the soil solution at a defined distance from the root surface depends not only on net transport but is coupled to chemical reactions such as redox-reactions, surface sorption, complex formation or dissolution, acid-base changes, changes of the composition of the cation exchanger and dissolution or formation of mineral phases. Most of these processes can be simplified in the case of macronutrients, but have a distinguished role in the case of trace elements, such as arsenic and heavy metals. As the mobility, toxicity and root uptake of these elements highly depend on their speciation, the application of coupled speciation-transport rhizosphere models is essential to make strategic decisions about the remediation or use of contaminated landscapes.

According to the state of the art in rhizosphere modelling, there is no code available that would fulfil the specific requirements for modelling the reactive transport of As in the rhizosphere. Thus, a new rhizosphere model had to be developed for this purpose. The performed work focused on implementing the relevant processes in a model and not on the applied numerical procedure. Thus, it was reasonable to develop the new model on the basis of existing codes.

Hoffland (1990), Geelhoed et al. (1999) and Nietfeld (2001) presented different coupled speciation-transport rhizosphere models. The first two considered only a small number of ions. The Nietfeld's model, addressing aluminium transport and uptake, is probably the most applicable reported rhizosphere model for small-scale, high-resolution scenarios. It is also the only model that includes a correction term (equation 3.8) in the transport equations, ensuring the electroneutrality of the system. Electroneutrality should be considered when systems in which mass flow and diffusion of the same order of magnitude are modeled. However, it should be noted that Nietfeld's model is purely mathematical and not directly based on experimental data. It also does not include surface complexation and reaction kinetics.

It has been recently shown by Nowack et al (2006) that commonly available geochemical codes [PHREEQC, MIN3P, ORCHESTRA, (Parkhurst and Appelo, 1999; Mayer et al., 2002; Meeussen, 2003), respectively] are theoretically applicable for rhizosphere modeling. These codes have been applied as 'numerical engines' to solve the problem of diffusion toward a single cylindrical root. However, as these geochemical programs were not developed to model processes in the rhizosphere; their application requires a very good understanding of their functionality and input syntaxes.

The RhizoMath code being developed in MATLAB consists of two main modules: (i) the initialization module determines the parameters which describe the chemical speciation in the initial solution, (ii) the transport module solves the problem of plant uptake, transport and speciation in the rhizosphere. The chemical speciation is calculated in both modules by the geochemical code PHREEQC (Parkhurst and Appelo, 1999), which is coupled to MATLAB via an interface function. The present minerals and gases are defined in PHREEQC as equilibrium phases. Surface sorption is described in PHREEQC with the diffuse double layer model. Goethite is represented as surface sorption sites of hydrous ferric oxide (Tretner, 2002).

(i) The initialization module determines the amount of weak and strong surface binding sites of hydrous ferric oxide and the equilibrium constants of the surface sorption reactions by minimizing the quadratic weighted difference between modelled and measured values was with the simplex method in MATLAB.

(ii) The transport module applies the split-operator technique to solve the speciation equations in PHREEQC separately from the transport equations, which are solved in MATLAB. The transport is described by the linear/radial form of the convective diffusion equation in the form applied for unsaturated soils (Darrah and Roose, 2001). The root uptake and excretion of ions appear as the inner boundary conditions of the transport equations. The uptake kinetics can be defined to be different for each nutrient. The plant water uptake is derived from the transpiration rate calculated from the weight changes of the compartment system.

Please mind, that RhizoMath and this guide are still under development and contact the authors for the most actual version.
Please cite Parkhurst and Appelo for using PHREEQC.

**References**

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**Installation requirements**

- a PC with Windows XP and MS Excel

- 260 MB space on the hard disk (installed files), > 1 GB space on the hard disk (model output)

**Installation**

1. Download RhizoMath from the www.bass.ufz.de homepage or contact the authors for a CD

2. Run  install.bat this will

    - install the MATLAB[2] Compiler Runtime v7.8   (read the legal stuff, please)

    - create the directory  c:\RhizoMath

    - copy the RhizoMath to c:\RhizoMath

    - copy phreeqc.exe   to c:\RhizoMath

    - copy some examples to c:\RhizoMath

3. Reboot your computer

4. Run RhizoMath by running c:\RhizoMath\rhizomath.exe

**Customized installation**

1. open install.bat in a text editor

2. change c:\RhizoMath to your preferred destination directory in the following lines:

```
mkdir c:\RhizoMath
xcopy RhizoMath c:\RhizoMath /e
copy PHREEQC\phreeqc.exe c:\RhizoMath
copy PHREEQC\*.dat c:\RhizoMath
```

3. if you are installing RhizoMath to a PC with german Windows, please change the following line:

    set PATH="C:\Program Files\MATLAB\MATLAB Component Runtime\v76";%PATH%

    to

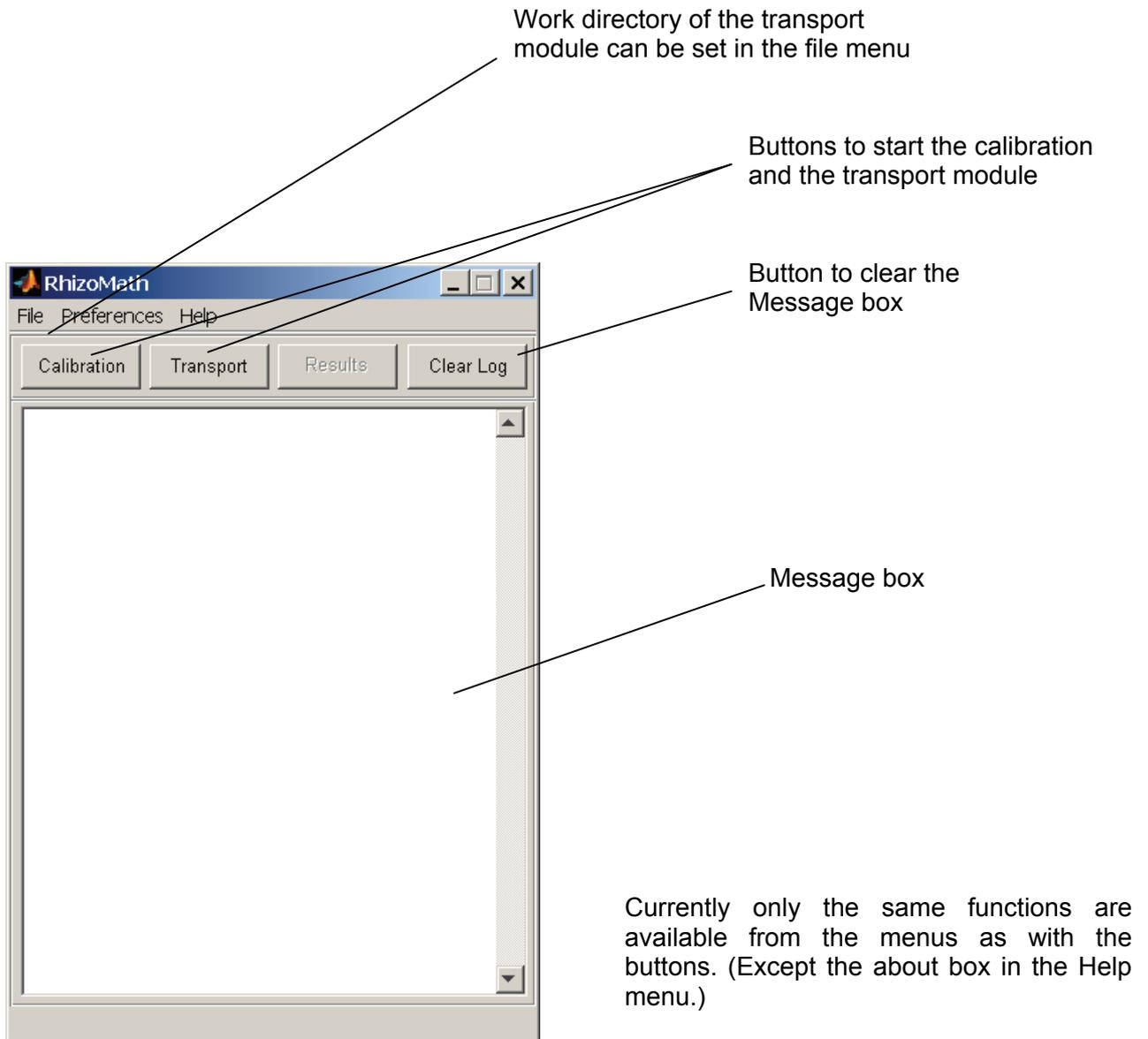    set PATH="C:\Programme\MATLAB\MATLAB Component Runtime\v76";%PATH%

**Uninstallation**

1. delete the c:\RhizoMath directory

2. remove the MATLAB[1] Component Runtime in Control Panel\Software

---

[2] The MathWorks, Inc. MATLAB. Copyright 1984 - 2007 The MathWorks, Inc. MATLAB is a registered trademark of The MathWorks, Inc.

**The main window**

0. The first launch of RhizoMath could take longer.

1. None of the RhizoMath Window or the black command window of rhizomath.exe shall be closed before finishing the work with RhizoMath.

Work directory of the transport module can be set in the file menu

Buttons to start the calibration and the transport module

Button to clear the Message box

Message box

Currently only the same functions are available from the menus as with the buttons. (Except the about box in the Help menu.)

**The user interface of the calibration module**

0. Use decimal point instead of comma throughout RhizoMath.

1. The name of the excel file which contains the measured concentrations used as a reference for the optimization. The file should have contain three worksheets with the following format:

- The first line hast to be the header (Number of solution | pH | pe | Master species … | Hfo)

- The following lines contain the corresponding numbers (1… | pH | pe | mmol/l | grams/kg soil)

- The file must contain more lines than columns

- The file must be in the main directory of RhizoMath

- Example:



The first worksheet contains measured valued that are used as reference for the calibration.

The second worksheet contains initial soil solution concentrations (~ SOLUTION in PHREEQC)

The third worksheets contains the weighing factors for the RMSE calculated for the optimization.

2. The master species of the Excel-file (e.g. the headers of the D..last-1 columns) appear here after pressing the read button.

3. Optimized concentrations can be selected/deselected with the arrows, initial values can be set with the Init. Conc. button.

4. Various parameters:

    - Logarithm of the partial pressure of $CO_2$

    - Soil density in $g/cm^3$

    - Volumetric water content in percents

    - If 'Force pH' is checked, the pH will be the same as it is given in the Excel file, otherwise will be calculated from the soil solution composition

    - If 'charge' is checked, solutions will be electroneutral.

    - The database selected here will be used for the calculations, but without any data that refers surface sorption

5. Stoichiometric data on the surface sorftion reactions is imported from the database selected here. Optimized equilibrium constants can be selected/deselected with the arrows, initial values can be set with the 'Init. logK.' button.

7. Initial number of weak and strong sorption sites pro grams of hydrous ferric oxide can be set here. The specific surface can be entered in $m^2/g$
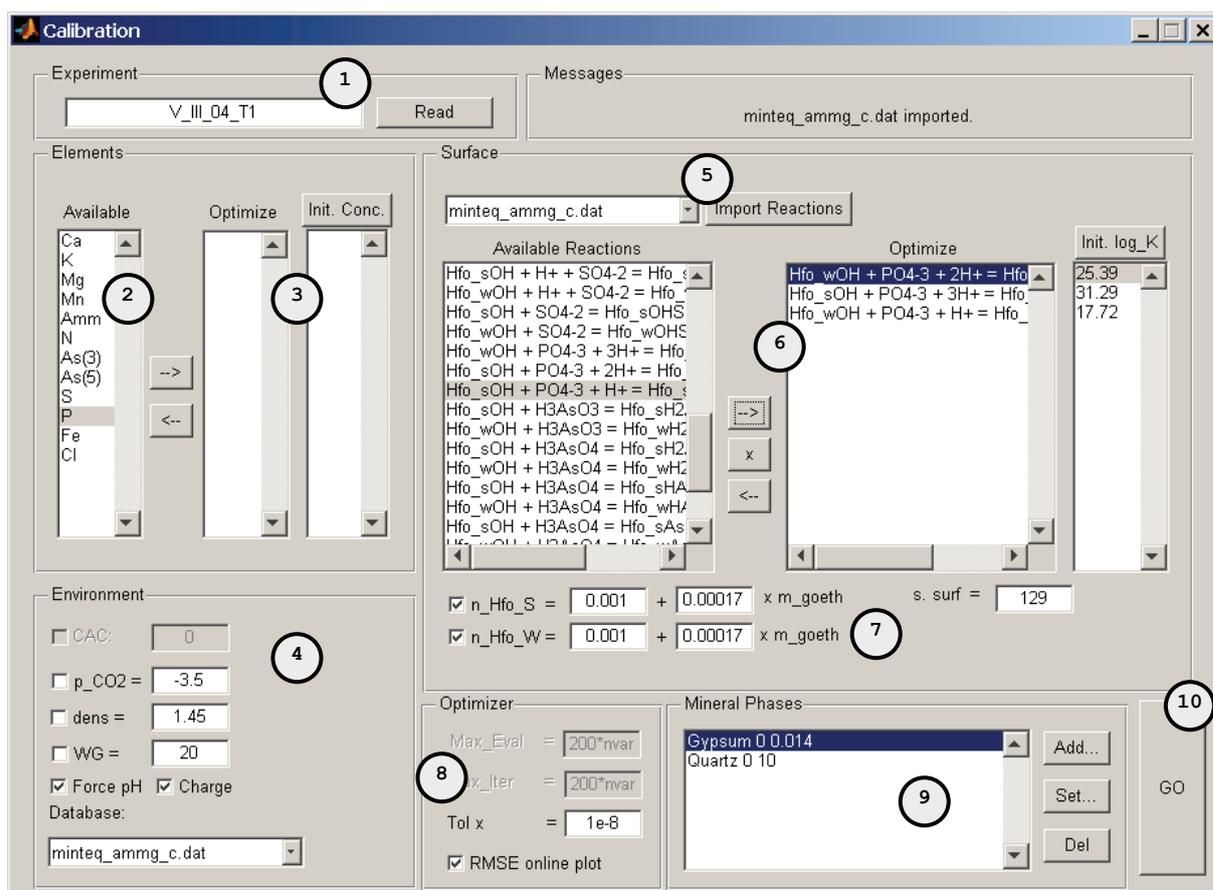
8.. Parameters of the optimization:

> - Max_Eval: Maximal number of function evaluations (default: 200*nvar, new value must be a number)
>
> - Max_Iter: Maximal number of iterations (default: 200*nvar, new value must be a number)
>
> - Tolerance: Tolerance on RMSE
>
> - RMSE online plot: The optimization process can be online followed on a diagram.

9. Selecting equilibrium phases from the database on the left. At least one phase has to be selected.

The watch option in the appearing dialog has an effect only in the transport module.

10. The optization starts with the GO button.

Output:

> - a summary of the optimization in html format
>
> - the used database (without the optimized reactions)
>
> - the calculated concentrations in a tab-separated text file that corresponds the Excel which includes the measured concentrations.

**The user interface of the transport module**

0. The dimensions of the physical quantities always appear if the pointer is moved over the corresponding input field

1. Transport equation:

      Nye ->     CDE Equation as given in Darrah and Roose, 2001

      Nietfeld -> includes a correction term representing the effect of Coulomb forces between the

            solved ions and assures the electro-neutrality in the species system
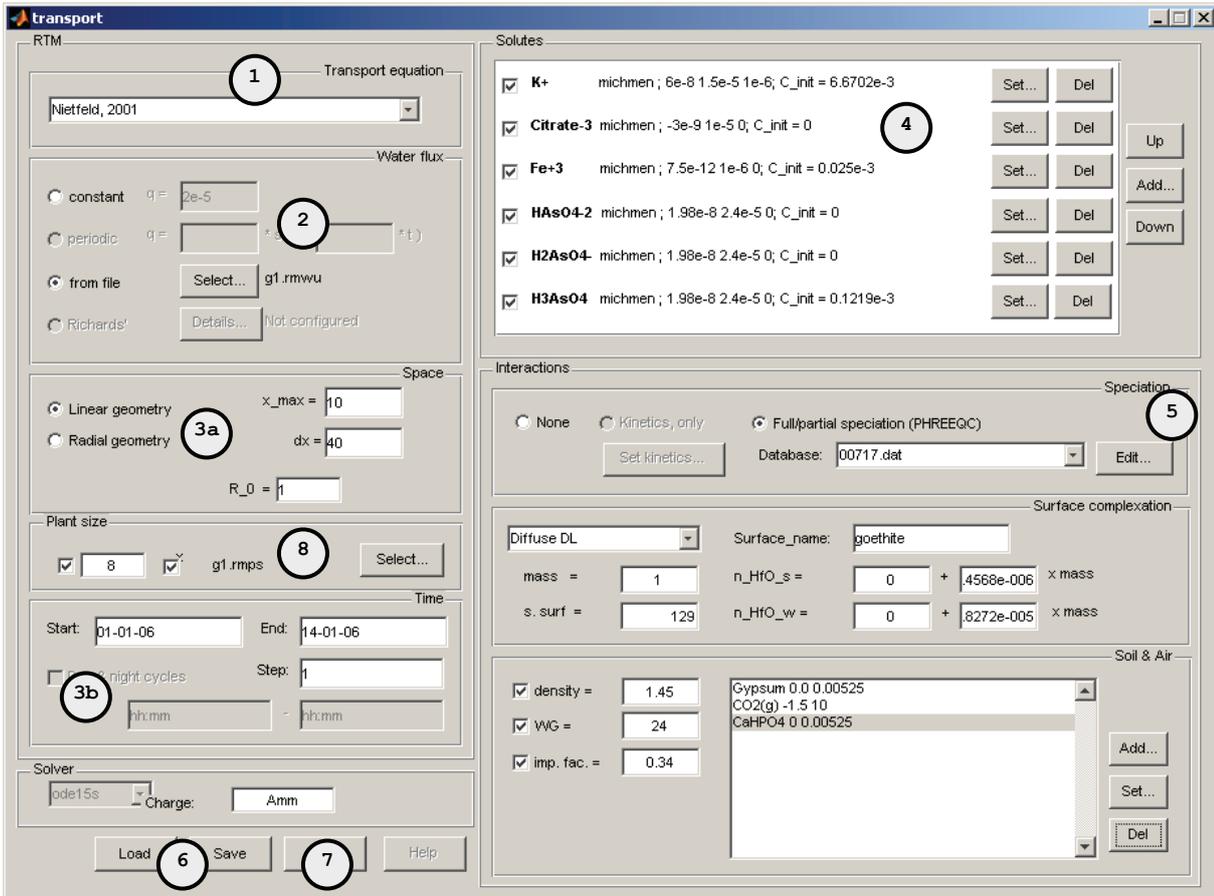


2. Water flux:

    - given in cm/s

    - 'from file' option: water flux as a function of time defined in a text file with the following format:

```
V-III-04-w2 (g-4) cm/s            header
1     2E-07                       day <tab> flux
3     2E-07
4     2E-07
5     2E-07
...       ...
```

    - the extension of the file is .rmwu

- the file has to be saved in c:\RhizoMath\water

3a, 3b.Time & Space

- Time is defined as dates

- *step* is the time after chemical equilibrium is calculated (take care of the courant number)

- dr (or dx) is the number of grid points in the r0..r_max (x_max) interval

- grid spacing is logarithmic with a higher grid density close to the root surface

4. Solutes:

- click add to add a new solute (-> solute_add dialog)

- when using the transport equation of Nietfeld , H+ has to be the last in the list

- the list is scrollable with up/down when having more than 6 solutes

- major species without charge have to be defined for the Tinker & Nye Equation

5. Chemical speciation:

- before selecting none, please select none in the surface complexation box as well

- surface sorption parameters are given as in PHREEQC, mass is given pro kg substrate

- calculations with chemical speciation require more time and HDD space as other calculations

- the input and output of each equilibrium calculation is saved with the extensions .in and .out

6. Load/Save:

- the model input has to be saved in the RhizoMath/Transport directory before the GO button is enabled

7. The simulation starts with the GO button. A progress bar appears, which is only active when chemical speciation is calculated.

8. Plant size (changing nutrient demand) is described with the newly implemented root compartment factor. The number corresponds the constant g(t) term, and the selected file contains the temporal development of d(t) in the following following format:

```
DAP   text                      header
0     0                         day <tab> rel. nutrient demand
1     0.02
5     0.4
15    0.9
...   ...
```

- the extension of the file is .rmps

Output:

- concentrations, surface and phase compositions are saved at each grid point as a tabulator separated file (.tx)

- graphical output is created from the final concentration profile of the elements and the cumulative uptakes

- concentrations at all grid points are saved for all time steps in a .mat file including the variables: uu (time, space, compound), uu_names, t, x, geometry, r0, c0_0, uptake_t, J_max, K,umin.

- concentrations at all grid points are saved for all time steps in an excel file with one worksheets for each solute

**Solute add dialog**

0. The dialog appears when clicking the Add.. button on the Transport window

1. Solutes can be selected by clicking their names at the list. The corresponding data files are stored at c:\RhizoMath\Solutes

2. The solute names have to be the same as in the PHREEQC .dat file

3. By setting a negative value for I_max, the selected solute will be exudated by the root at a constant flux given by I_max. K_m and c_min are ineffective in this case.

4. b = b'+θ (s. Schnepf, 2002)

5. The inatial concentration is the same at all grid points

6. New or changed solutes have to be saved, existing and unchanged can be added
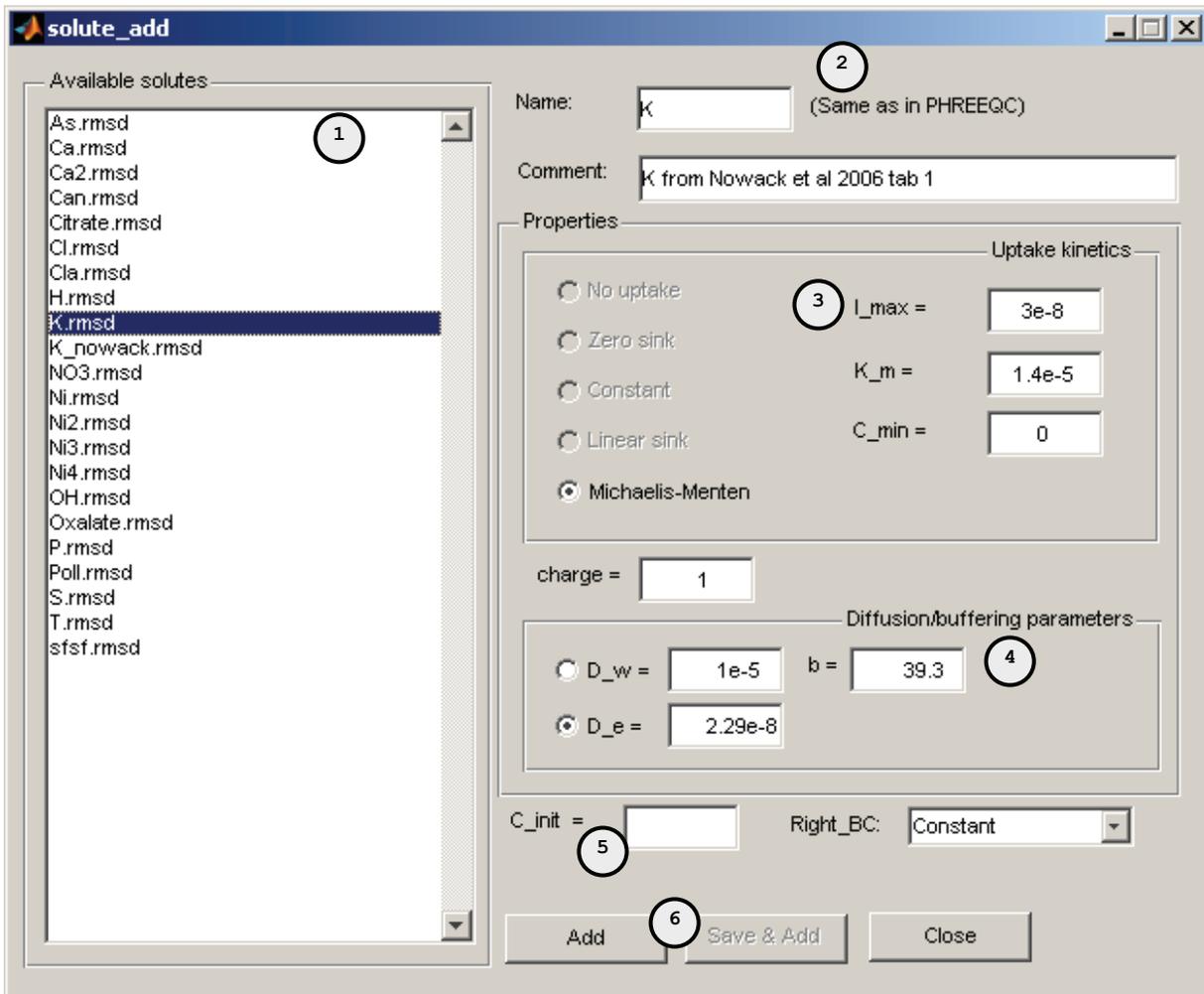
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