

Modelling rhizosphere transport in the presence of goethite, including competitive uptake of phosphate and arsenate

Krisztian Szegedi · Doris Vetterlein ·
Reinhold Jahn

Received: 19 March 2009 / Accepted: 30 October 2009 / Published online: 12 December 2009
© Springer Science+Business Media B.V. 2009

Abstract A modelling approach was used to extend the knowledge about the processes that affect the availability of the nutrient P and the toxic agent As^V in the rhizosphere in the presence of a strong sorbent. Based on compartment system experiments in which *Zea mays* was grown the following hypothesis were assumed: a) measured P concentration gradients can be explained by the mobilisation of P by the root exudate citrate, and b) measured As^V concentration gradients can be explained by the simultaneous effect of the competitive sorption of As^V and P and the competitive uptake of As^V and P. First, the feasibility of the applied description of soil chemical processes was justified. Then competitive uptake was implemented in the computer code using two different

mathematical approaches. Our model calculation provided support for hypothesis a) and suggested that hypothesis b) has to be extended. The results show that the competitive uptake of As^V and P has an influence on As^V concentrations in the rhizosphere, but including competitive uptake was not sufficient to predict observed As^V concentration profiles. Recent results on plant As-metabolism like As^{III} efflux and Si As^{III} interaction probably have to be included in addition for simulation of measured As^V concentration profiles.

Keywords Rhizosphere · Modelling · Speciation · Phosphate · Arsenate · Goethite

Responsible Editor: Robert Reid.

Electronic supplementary material The online version of this article (doi:10.1007/s11104-009-0221-9) contains supplementary material, which is available to authorized users.

K. Szegedi (✉) · D. Vetterlein
Department of Soil Physics,
Helmholtz Centre for Environmental Research-UFZ,
Theodor-Lieser-Str. 4,
06120 Halle (Saale), Germany
e-mail: krisztian.szegedi@ufz.de

K. Szegedi · D. Vetterlein · R. Jahn
Soil Science and Soil Protection Group,
Institute of Agricultural and Nutritional Sciences,
Martin Luther University Halle-Wittenberg,
Weidenplan 14,
06108 Halle (Saale), Germany

Introduction

The rhizosphere is the soil micro-site which is affected by the roots (Hinsinger et al. 2009). The chemical composition of this micro-site is affected by various mechanisms including equilibration of solution with solid and gaseous phase, transport of solutes towards and away from the root surface, solute uptake at the root surface and root exudation (Darrah and Roose 2001; Hinsinger et al. 2009). Several experimental results showed that competitive behaviour of solutes in the rhizosphere can strongly influence their bioavailability and their uptake by plants (Barber 1995; Kirk et al. 1999; Zhao et al. 2009). Competition among solutes can occur in the soil (competition for

soil binding sites) and at the root surface (competition for membrane transporters).

There are several publications with experimental and modelling studies on competitive sorption (Dzombak and Morel 1990). A classical example is the competitive sorption of phosphate (P) and citrate by hydrous ferric oxides. This process has been modelled by several authors using models with different complexity: using sorption isotherms, using surface complexation with a simplified (Kirk 1999) and a more detailed speciation (Geelhoed et al. 1999).

The relevance of competitive uptake has been reported by several authors. The uptake of Ca^{2+} can suppress the uptake of Mg^{2+} and vice versa (Lazaroff and Pitman 1966), similar interaction has been described for K^+/Cs^+ (Shaw and Bell 1991), $\text{As}^{\text{III}}/\text{Si}^{\text{III}}$ (Zhao et al. 2009) and $\text{As}^{\text{V}}/\text{P}$ (Esteban et al. 2003; Zhao et al. 2009). The molecular mechanisms behind this competitive behaviour still have not been fully understood for all ion pairs (Zhao et al. 2009). This may be a reason why the modelling of these processes in the rhizosphere is underrepresented in existing literature. Additionally, up to our best knowledge, there is no publication available that simultaneously studies competitive sorption and competitive uptake.

An example for the simultaneous occurrence of these processes is the transport of arsenate (As^{V}) and P in the rhizosphere. This example has a high practical relevance as arsenic (As) contamination is a serious environmental problem at many agricultural sites around the world, including Europe, South and North America and in particular South–East Asia (Smedley and Kinniburgh 2002; Heikens et al. 2007). Arsenic is listed as the number one toxic agent by the US authorities.¹ For the utilization and remediation of arsenic contaminated landscapes it is necessary to understand the physicochemical and biological processes that control the transfer of toxic As from soil to plants.

P-transport in soil and its uptake by plants has been recently reviewed by Lambers et al. (2006), As-transport and uptake by Zhao et al (2009), rhizosphere modelling by Luster et al. (2009). In the following we

will briefly outline the behaviour of phosphorous and arsenic in soil plant systems and the related rhizosphere processes and how they have been reflected in existing modelling approaches.

The oxidised form of arsenic, arsenate (As^{V}) is the dominant As species in aerobic soils. It competes with phosphate (P) for binding sites in soils, like the ones provided by goethite (Smith et al. 2002). Goethite is the prevalent Fe-oxide in temperate soils (Schwertmann and Taylor 1989) and a strong sorbent for As^{V} (Gao and Mucci 2001; Manning and Goldberg 1996) as well as for P (Geelhoed et al. 1997; Manning and Goldberg 1996). A higher affinity of goethite surface for As^{V} than for P was reported by Gao and Mucci (2001) and Violante and Pigna (2002), while similar affinities for P and As^{V} were found by Hiemstra and van Riemsdijk (1996) and Manning and Goldberg (1996, 1997). Plants can mobilize adsorbed P via ligand exchange through organic anions like citrate (Hinsinger et al. 2003b). Organic anions can desorb also As^{V} from the goethite surface, but to a smaller extent compared to P (Liu et al. 2001). Vetterlein et al. (2007) showed that root exudation of organic anions may alter the competition between arsenate and P for soil binding sites.

The simultaneously acting processes in the rhizosphere (transport, uptake and release of solutes; reactions in the soil solution; precipitation and dissolution of minerals, surface sorption, cation exchange, microbial activity), 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 only a very limited number of species into account (Hoffland et al. 1990; Nietfeld 2001; Nowack et al. 2006).

The recently presented code RhizoMath (Szegeedi 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 and As^{V} on goethite.

¹ 2007 CERCLA Priority List of Hazardous Substances, Released biannually by the US Agency for Toxic Substances and Disease Registry. Online available at <http://www.atsdr.cdc.gov/cercla/07list.html>.

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 for binding sites at the root membranes (e.g. Zhao et al. 2009). Experimental studies on As^{V} –P competition during root uptake have shown that an increasing molar P: As^{V} ratio in nutrient solution strongly reduced As^{V} uptake (Esteban et al. 2003; Meharg 1994; 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 was added; the maximum influx remained almost unchanged.

Thus, including competitive P and As^{V} uptake in the model calculations may be necessary for a good quantitative prediction of dynamic changes in P 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 h 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 goal of our work was to study whether use a modelling approach based on the above presented processes can explain the dynamics of P and As^{V} in the rhizosphere in the presence of goethite. Based on the experiments presented by Vetterlein et al. (2007), as a first hypothesis we assumed that a) measured gradients in P^{V} concentrations can be explained by the mobilisation of P^{V} by the root exudate citrate; b) measured gradients in As^{V} concentrations can be

explained by the simultaneous effect of the competitive sorption of As^{V} and P^{V} and the competitive uptake of As^{V} and P^{V} . However, these hypotheses could be tested only after a sufficient and justified description of soil chemical processes that govern the competitive sorption of P^{V} , As^{V} , and citrate.

Up to our best knowledge, there is no computer code available up to now that contains all of the above mentioned processes. Thus, the implementation of these processes in the code of our choice (RhizoMath; implemented processes are summarised in the “Appendix”) had to be performed before we could test our hypotheses.

Although the current work is based on the RhizoMath code, the achieved results can be applied by users and developers of other rhizosphere models with chemical speciation. According to the state of the art, potentially applicable codes for repeating the performed calculations could be MIN3P (Mayer et al. 2002) and ORCHESTRA (Meeussen 2003). However, not all of the studied processes have been yet implemented in these codes.

Material and methods

Compartment system experiments were performed 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 g kg^{-1} , 1 g kg^{-1} , 4 g kg^{-1} ; G-0, G-1, G-4, respectively). The treatment G-1 is a system in which the number of sorption sites is limited. In the G-4 treatment there are still empty sorption sites available.

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 Szegedi (2009). Initial soil solution composition (collected at the beginning of the experiment, before planting) was used to calibrate surface sorption parameters in the model. Soil solution compositions (concentration profiles of solutes) collected weekly during the experiment were used to test if the model can reproduce observed trends and concentration ranges.

Soil solution samples collected from the compartment systems had a sample volume of ~100 μL for

each micro suction cup for each sampling. To provide a sufficiently large volume for chemical analysis of all ions of interest, bulk samples were created for each of the 15 suction cup positions from the three replications of each treatment (compare Vetterlein et al. 2007, experiment was set up as a randomized block design with three replications for each treatment). This reduced the number of data points for the same position (distance from the root surface) and sampling to 2 (right and left compartments). Thus a standard error cannot be calculated. The average error (average deviation from the mean) of these two points had a maximum of 12%. Error bars were not included as their sizes would have been about the same or smaller as the diameter of symbols used in the Figs. 4 to 6. The first data point in front of the dashed vertical line in Figs. 4 to 6 shows an average over all five suction cup positions within 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.

Trends in modelled and measured concentration profiles were visually compared with each other. The reason for visual comparison instead of using widespread qualitative measures of model performance (quadratic difference between measured and modelled values, correlations coefficient) was, that these can be applied only in specific cases like monotonous changes of measured concentration profiles (Smith et al. 1997; Anscombe 1973).

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 Szegedi (2009), here we only summarize the major points.

Compilation of the chemical database and the PHREEQC input file

A database compiled by Allison et al. (1990) (delivered with PHREEQC in the minteq.dat file) was used as a basis for compiling the chemical

database that includes the stoichiometric reactions that are considered by the model. We reduced it by removing reactions of elements and phases that do not occur or cannot occur in the system. Additionally, nitrification was excluded. In all calculations gypsum, quartz and CO_2 were defined as equilibrium phases. CaHPO_4 was considered as an initial equilibrium phase for the optimization of the database and for hypothetical scenarios with changing pH. However, based on the results of the latter calculations (will be presented and discussed later), CaHPO_4 was not considered as an initial mineral phase for hypothetical scenarios with different amounts of added goethite and increasing addition of citrate, and for transport modelling. However, its precipitation was allowed. To achieve correct Ca^{2+} and SO_4^- concentrations the solubility product of gypsum was replaced with 2.95×10^{-5} (PHREEQC: $\log K = -4.53$) in the database (Bennett and Adams 1972).

Initial soil solution composition in treatments with 1 g kg^{-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. Weak and strong surface binding site of goethite were additionally included 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).

Optimization of surface sorption parameters in the chemical database and in the PHREEQC input file

The initialization module of RhizoMath was used to determine the number of surface binding sites and values of the equilibrium constants of corresponding stoichiometric equations that describe the surface complexation of As^{V} . The initialisation (Szegedi et al. 2008) is based on minimizing the weighted root mean square difference (RMSE) between measured and modelled concentrations using the simplex method. Soil solution concentrations were calculated

considering the full soil solution composition and considering minerals, gases, and surfaces that are present in the system. Starting numbers (e.g., starting values for the optimization) of weak and strong surface binding sites of hydrous ferric oxide (Hfo_w and Hfo_s, respectively) 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. These changes reduced the number of optimized parameters from 6 to 2.

From treatments G-1 and G-4, concentrations of the following species were compared simultaneously to predicted concentrations during the optimization (i.e. contributed to the RMSE): P, As^V, Ca²⁺, SO₄²⁻, H⁺. The initial homogeneity of the system allowed that each of these concentration values were determined as the average of concentrations in 15 soil solution samples for each treatment (samplings from the 15 different micro suction cup positions, analysed as bulk samples from three replications).

Further reduction of the chemical database was considered in respect to the dominant surface species in the pH range observed during the experiments. We followed the standard procedure for geochemical codes: minor species of an element whose concentration was in the whole studied pH-range several orders of magnitude lower than the concentration of its major species were removed from the database. After removing this species it was controlled if it had a major effect on predicted soil solution composition.

Testing the chemical database

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 with and without citrate exudation

Transport in the compartment systems was modelled with the transport module of RhizoMath. The same phases and optimized parameters which were obtained to describe the initial state of the system were applied to describe soil chemistry during the transport modelling. 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. Applied model parameters are presented in Table S1.

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 (Szegedi 2009). 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:

$$J_{citr} = -J_{citr,u} \cdot RCF(t), \quad (1)$$

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 $J_{\text{cit},u}$ was $3 \cdot 10^{-11} \text{ mM cm}^2 \text{ s}^{-1}$. Citrate degradation was neglected in the calculations. The reasons for this are presented in the “Discussion”.

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 ($J_{\text{MM},1}^{\text{upt}}$) can be described with the following modification of the Michaelis–Menten kinetics:

$$J_{\text{MM},1}^{\text{upt}} = J_{\text{max}} \frac{C_1}{C_1 + K_1 \left(1 + \frac{C_2}{K_2} \right)}, \tag{2}$$

where 1 and 2 indicate the two ions, $J_{\text{MM},1}^{\text{upt}}$ 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 Eq. 2 is the same for the influx of ion 2, except the subscripts that are mirrored.

The general form of Eq. 2 in the case when n ions are competing for the same transporter is

$$J_{\text{MM},i}^{\text{upt}} = J_{\text{max}} \frac{C_i}{C_i + K_i \left(1 + \sum_{n \neq i} \frac{C_n}{K_n} \right)}, \tag{3}$$

where $J_{\text{MM},i}^{\text{upt}}$ 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 concentra-

tion of another 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 Eq. 3 in analogy to Barber (1995, p65) to account for the minimum solute concentration required for root uptake:

$$J_{\text{MM},i}^{\text{upt}} = J_{\text{max}} \frac{C_i - C_{i,\text{min}}}{C_i - C_{i,\text{min}} + K_i \left(1 + \sum_{n \neq i} \frac{C_n - C_{n,\text{min}}}{K_n} \right)}, \tag{4}$$

where $C_{i,\text{min}}$ is the minimum concentration of the i^{th} solute below which no uptake occurs.

To describe influx in the compartment system $J_{\text{MM},i}^{\text{upt}}$ are multiplied by RCF to account for the uptake by a root system behind the nylon mesh of the root compartment (Szegedi 2009).

The second implemented approach for describing competitive uptake of nutrients is based on the experimental findings of Lazaroff and Pitman (1966). Equations 5a and 5b express that the influx J' is shared among the competing solutes proportionally to their concentrations in the soil solution:

$$J_i^{\text{upt}} = J' \frac{C_i}{\sum_n C_n}, \tag{5a}$$

$$\sum_i J_i^{\text{upt}} = J' \text{ (consequence of equation 5a)}, \tag{5b}$$

where J_i^{upt} is the influx of a solute. The sum goes over the C_n concentrations of all solutes that compete with each other.

J' is the influx of the pathway where the competing solutes are taken up. The value of J' depends on the concentration of the solutes that are taken up via this pathway. A possibility to define J' is to take it as the highest of the (actual) influxes via this pathway, according to Eq. 6:

$$J' = \max(J_1, J_2, \dots, J_n), \tag{6}$$

where $J_1 \dots J_n$ are the influxes of each of 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:

$$J_i^{upt} = \max(J_1, J_2, \dots, J_n) \frac{C_i}{\sum_n C_n}, \quad (7)$$

To describe influx in the compartment system J_i^{upt} 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 (Eq. 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 Eq. 4 only as a modifying factor of the Michaelis-Menten constant. If $K_1 = K_2 = \dots = K_n \ll \sum_i (C_i - C_{i,\min})$ Eq. 4 approximates

$$J_{MM,i}^{upt} = J_{\max} \frac{C_i - C_{i,\min}}{\sum_n C_n - C_{n,\min}}, \quad (8)$$

i.e. in this concentration range the maximal influx is reached and the overall influx J_{\max} is constant. This differs from Eq. 5a, in which $J' = \max(J_1, J_2, \dots, J_n) \neq J_{\max} = \sum_i J_{\max,i}$.

The second approach (Eq. 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 and As^{V} , transport in the compartment system was modelled with RhizoMath using both approaches separately (Eqs. 4 and 7, respectively).

Results

Modelling initial soil solution composition and hypothetical scenarios using PHREEQC

Optimization of surface sorption parameters

The optimization was repeated optimizing all combinations of equilibrium constants that belong to dominant P

and As^{V} surface complexes. The best agreement between modelled and measured data was achieved as the equilibrium constant of Hfo_wH2AsO4 (Hfo_w indicates weak surface binding site of goethite) was optimized. Its initial value for the optimization was $4.68 \cdot 10^8$ (PHREEQC: $\log K=8.67$) and its optimized value was $1.58 \cdot 10^{10}$ (PHREEQC: $\log K=10.2$). A similar difference between initial and optimal equilibrium constant was found by Tretner (2002). Optimized numbers of weak and strong surface binding sites were $5.83 \cdot 10^{-5}$ and $1.45 \cdot 10^{-5} \text{ g}^{-1}$ goethite, respectively. Uniqueness of optimized parameters was tested by repeating the optimization using 13 different combinations of starting values.

Testing the chemical database using hypothetical scenarios

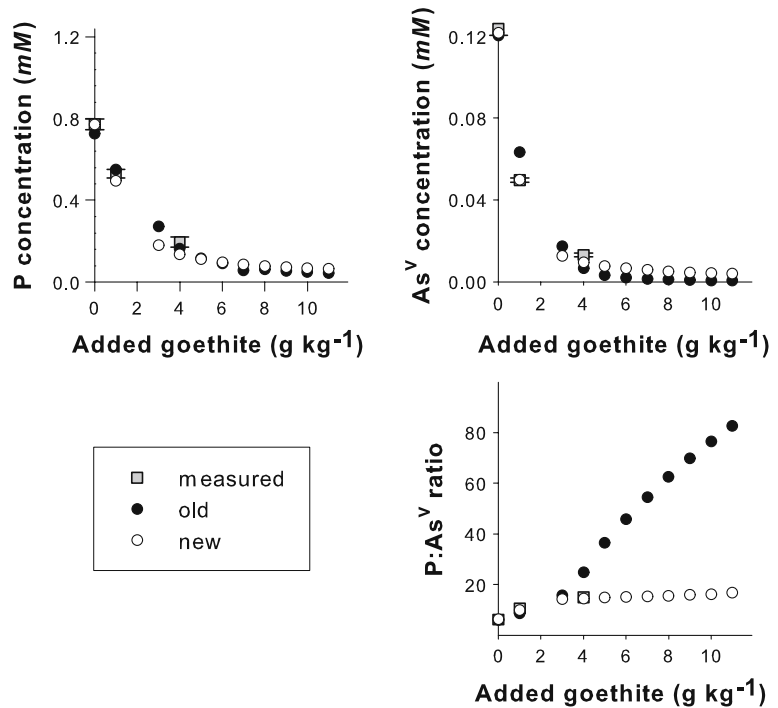
Model calculations for hypothetical scenarios with different amounts of added goethite showed slightly different results in P and As^{V} concentrations (Fig. 1) with the reconsidered chemical database (this paper) compared to the old database (Szegedi et al. 2008). A better agreement between predicted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

There are apparently only minor differences between P, 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: As^{V} ratio (Fig. 1). Calculations with the old database predicted a continuously increasing P: As^{V} ratio with increasing goethite addition. Above $\sim 4 \text{ g kg}^{-1}$ added goethite, calculations with the reconsidered database predicted the “saturation” of the P: As^{V} ratio. These calculations led to a better agreement between predicted and measured P: 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 adsorbed on goethite with decreasing pH (Fig. 2). In the case of 4 g kg^{-1} added goethite predicted amount of adsorbed P is about four times higher as in the case of 1 g kg^{-1} added goethite. This is similar to the experimental observations.

In contrast to the experimental results, predicted P concentration in the soil solution was strongly

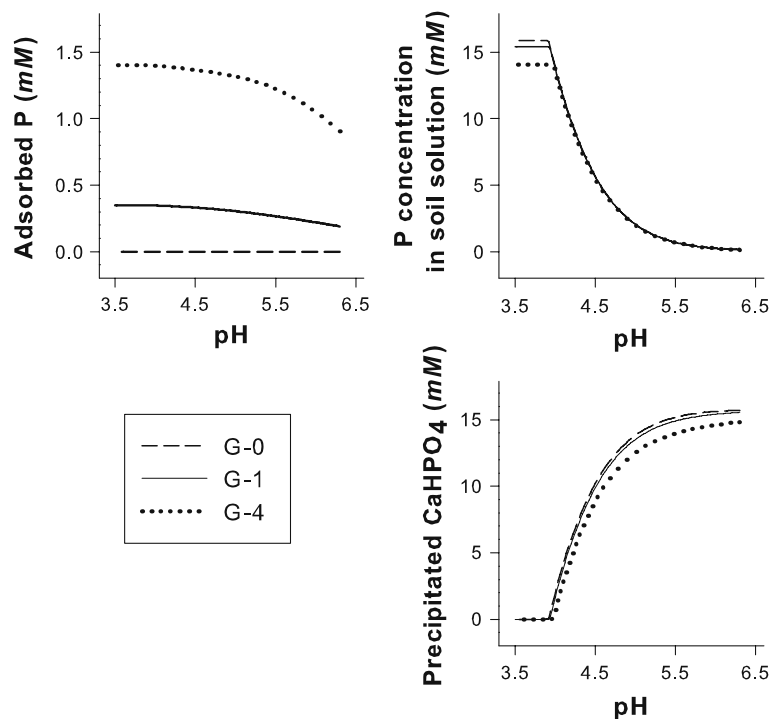
Fig. 1 Concentrations of As^{V} and P in the soil solution with increasing amounts of added goethite, calculated with PHREEQC using the sorption parameters optimized with RhizoMath for 0 g kg^{-1} , 1 g kg^{-1} , and 4 g kg^{-1} goethite. ● indicates results of current calculations with re-optimized sorption parameters (see text for details) and ○ results with the parameter set used in Szegedi et al. (2008). Measured values (average of 15 soil solution samples collected at the beginning of the experiment) are indicated by □. Error bars show standard deviation



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 but its precipitation was allowed.

Fig. 2 pH dependence of the amount of P adsorbed by goethite, P concentration in the soil solution and the amount of precipitated CaHPO_4 calculated with PHREEQC for 0 g kg^{-1} , 1 g kg^{-1} , and 4 g kg^{-1} goethite. Adsorbed amounts are presented per litre soil solution to facilitate comparison between soil solution and goethite. Strong dissolution of CaHPO_4 was predicted with decreasing pH, which was not observed in the experiments. Thus, in further calculations CaHPO_4 was not considered as an initial mineral phase. However, its precipitation has been allowed. Please refer to the “Discussion” for further explanation



Model calculations predicted increasing P concentration with increasing citrate addition in both treatments (Fig. 3). After adding the same amount of citrate (for each mol of added citrate), predicted increase in P concentration was higher in the G-1 treatment than in the G-4 treatment. In the treatment G-1, predicted As^{V} concentration was slightly increasing with increasing citrate addition. However predicted increase in As^{V} concentration was by far lower than predicted increase in P concentration.

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

Reduction of the chemical database

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

Fig. 3 Effect of citrate addition on the soil solution concentration of As^{V} , P, and citrate as well as on the amount of empty binding sites, calculated with PHREEQC for 0 g kg^{-1} , 1 g kg^{-1} , and 4 g kg^{-1} goethite using the reduced database. Amount of adsorbed As^{V} , P, and citrate mirrored soil solution concentrations (not shown). *: Lines for G-1 and G-4 overlay each other

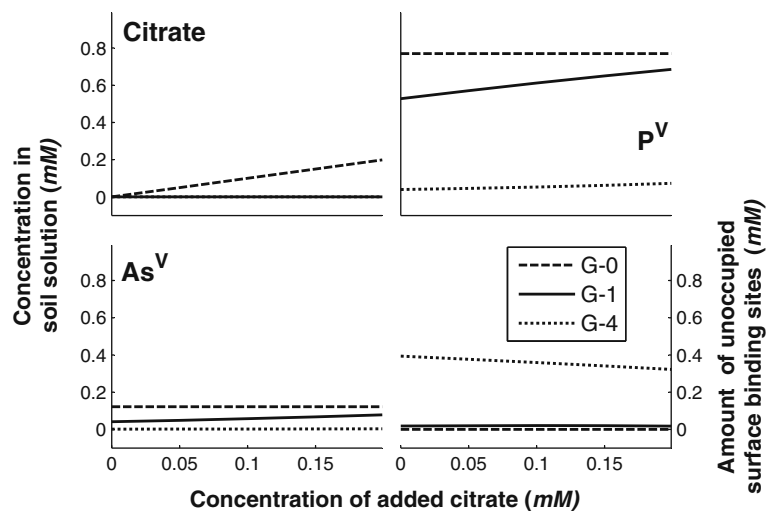


Table 1. Surface sorption reactions were re-organised according to the tableau-method (Morel and Hering 1993) so that Hfo_sOH_2^+ and Hfo_wOH_2^+ , the dominant surface species of unloaded goethite at low pH (Dzombak and Morel 1990), became the SURFACE_MASTER_SPECIES (PHREEQC nomenclature). This allowed the removal of non-dominant dissociations of goethite, which led to a further reduction of the database.

Modelling transport and reaction in the compartment system using RhizoMath

Reactive transport in the compartment systems with the plant was modelled with three models of different complexity: neglecting citrate exudation and competitive uptake (a, b), taking citrate exudation into account (c, d) and finally considering citrate exudation and competitive uptake (e, f). For comparison measured soil solution concentrations and pH are provided (g, h). Results are presented for 10 days, 17 days and 24 days after planting in Figs. 4, 5 and 7. Model parameters are provided in Table S1 in the supporting material.

Results of model calculations without citrate exudation and competitive uptake (a,b)

Predicted pH followed similar trends in all of the performed calculations (Fig. 4). For both G-1 and G-4 treatments, predicted pH was constant 10 days after planting and was linearly increasing with increasing

Table 1 Surface and solution species in the final compilation of the chemical database

SURFACE_SPECIES
Hfo_wOH ₂ ⁺
Hfo_sOH ₂ ⁺
Hfo_sH ₂ PO ₄
Hfo_wH ₂ PO ₄
Hfo_wCitrateH ⁻
Hfo_wHCO ₃
SOLUTION_MASTER_SPECIES and SOLUTION_SPECIES
H ⁺
OH ⁻
H ₂ O
NH ₄ ⁺ (included in PHREEQC as AmmH ⁺)
H ₂ AsO ₄
Ca ²⁺
Cl ⁻
EDTA
Fe ⁺³
FeEDTA ⁻
K
NO ₃ ⁻
H ₂ PO ₄ ⁻
SO ₄ ²⁻
CO ₃ ²⁻
HCO ₃ ⁻
H ₂ CO ₃

Hfo_s, *Hfo_w* strong and weak binding sites of Hydrous ferric oxide (represents goethite in the calculations), respectively. *Amm* stands for NH₃ and N for NO₃⁻ in the calculations. Including ammonium as NH₃ in the calculations would require the consideration of nitrification

distance from the root surface later on. For treatment G-1 predicted pH was lower than predicted pH for the G-4 treatment, which is in good agreement with the measured data.

For treatment G-1 increase in P concentration at the root surface was predicted for 10 days and 17 days after planting (Fig. 5a). The predicted increase in P concentration was lower than the experimentally observed increase in P concentration at the root surface in the same treatment at respective times (Fig. 5g). For the treatment G-4 predicted P concentration reproduced the experimentally observed decrease in P concentration at the root surface well (Fig. 5b, d, f).

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

For both G-1 and G-4 treatments model calculations predicted As^V depletion at the root surface (Fig. 7a, b).

Results of model calculations with citrate exudation but without competitive uptake (c,d)

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 lower in G-1 treatment compared to G-4 (Fig. 4b, d compared to Fig. 4a, c).

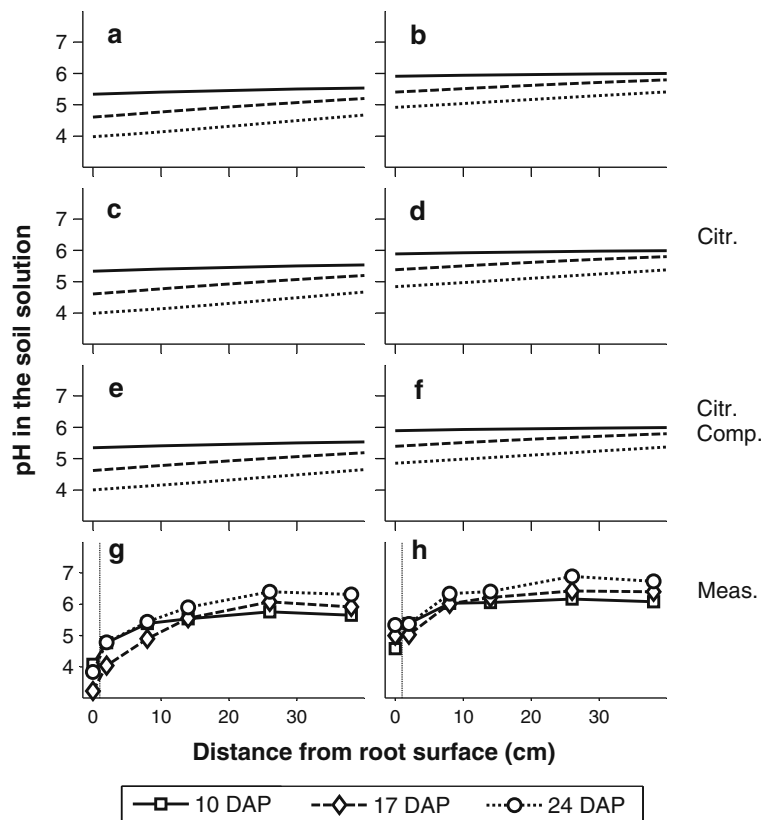
Including citrate exudation in the model calculation substantially enhanced the predicted increase in P concentration at the root surface for both 10 days and 17 days after planting for treatment G-1 (Fig. 5c). P concentration profiles predicted for 10 days and 17 days after planting with citrate exudation (Fig. 5c) agreed better with measured P concentration profiles at respective times than P concentration profiles predicted without citrate exudation (Fig. 5a). Predicted P concentration was lower at any distance from the root surface for 24 days after planting in model calculations both with and without citrate exudation.

For treatment G-4, including citrate exudation in the model calculation decreased the predicted width of the P depletion zone for 10 days and 17 days after planting (Fig. 5b, d). However, it did not affect the general trends.

With including citrate exudation in the calculations the model predicted for the G-1 treatment the total desorption of P from goethite in the first 2 mm from the root surface for 10 days after planting (Fig. 6c). The width of the zone where total P desorption was predicted was increasing with time. For the G-4 treatment the model predicted also P desorption close to the root surface, but it started later than in the G-1 treatment (Fig. 6d). Additionally, in the G-4 treatment the width of the zone where P was totally desorbed was smaller and predicted to increase slower than in the G-1 treatment.

Predicted saturation index of CaHPO₄ was monitored during the calculations. A slight oversaturation (maximum saturation index ~0.17) of CaHPO₄ was predicted in the calculations with citrate exudation for 10 days and 17 days after planting in the treatment G-

Fig. 4 Predicted soil solution pH with increasing distance from the root surface calculated for different treatments with RhizoMath for 10 days, 17 days and 24 days after planting without (**a, b**) and with citrate exudation (**c, d**) (Citr.) and with citrate exudation and competitive uptake (**e, f**) (Comp.) of As^{V} and P. Measured pH at 10 days, 17 days and 24 days after planting (\square, \diamond, \circ , respectively) (**g, h**) is reproduced after Vetterlein et al. (2007)



1 as P 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).

For both G-1 and G-4 treatments model calculations predicted As^{V} depletion at the root surface (Fig. 7c, d).

Similar trends were predicted in calculations with citrate exudation for adsorbed amounts of As^{V} (Fig. 8) as the trends predicted for adsorbed amounts of P (Fig. 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.

Predicted changes in the amount of adsorbed citrate (Fig. 9) mirrored the predicted changes in amounts of adsorbed P and As^{V} . The model predicted for the G-1 treatment that citrate occupied all the available sorption sites in the first 2 mm from the root surface 10 days after planting. The predicted width of this zone was increasing with time. Similar trends were predicted for the G-4 treatment. However, for the G-1 treatment predicted width of the zone where

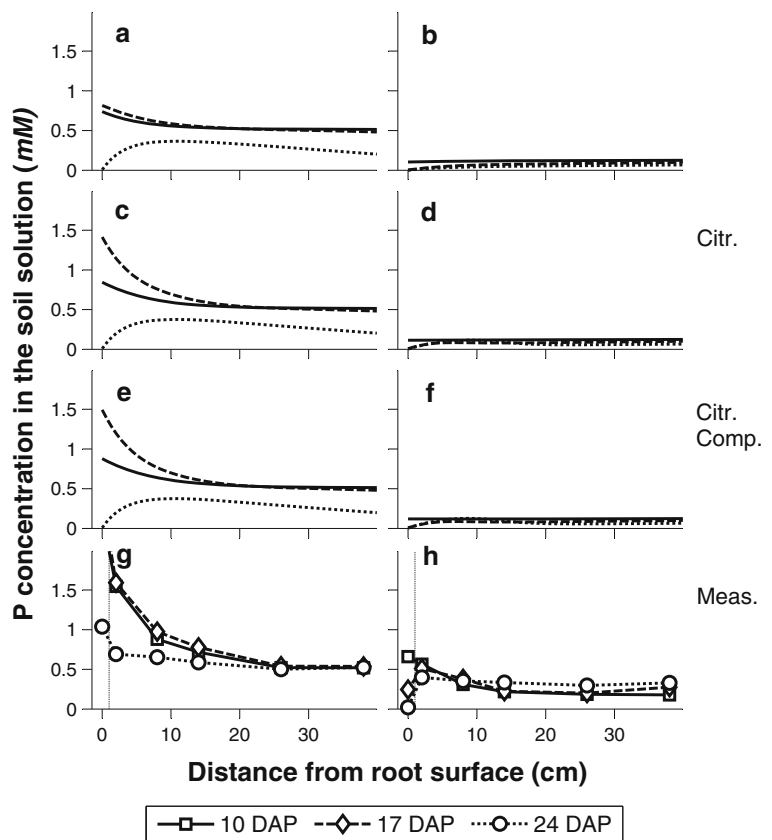
citrate occupied all the available sorption sites was increasing faster compared to the G-4 treatment (Fig. 9c, d).

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

Results of model calculations with both citrate exudation and competitive uptake (e,f)

Including competitive uptake in the calculations changed predicted concentration profiles in the same direction using both assumptions (Eqs. 4 and 7). However, the induced changes had much higher amplitudes in the calculations with Eq. 7. Thus, only the results of model calculations with Eq. 4 are presented in Figs. 4–9,ef.

Fig. 5 Predicted P concentration in the soil solution with increasing distance from the root surface calculated for different treatments with RhizoMath for 10 days, 17 days and 24 days after planting without (**a**, **b**) and with citrate exudation (**c**, **d**) (Citr.) and with citrate exudation and competitive uptake (**e**, **f**) (Comp.) of As^V and P. Measured P concentration in the soil solution at 10 days, 17 days and 24 days after planting (\square, \diamond, \circ , respectively in **g** and **h**) (**g**, **h**) is reproduced after Vetterlein et al. (2007)



Predicted pH was not noticeably influenced by including P- As^V competition in the calculations (Fig. 4e, f). The experimentally observed strong decrease of pH close to the root surface (Fig. 4g, h) could not be reproduced.

Predicted P concentrations in calculations with competition between As^V and P for root uptake

(Fig. 5f) did not substantially differ from P concentrations which were predicted without P- As^V competition (Fig. 5d).

Including P- As^V competition in the calculations for the G-1 treatment did not affect adsorbed P amounts (Fig. 6c, e). Calculations for the G-4 treatment including competitive As^V and P uptake besides

Fig. 6 Predicted amount of adsorbed P with increasing distance from the root surface calculated for different treatments with RhizoMath for 10 days, 17 days 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. Adsorbed amounts are presented per litre soil solution to facilitate comparison between soil solution and goethite

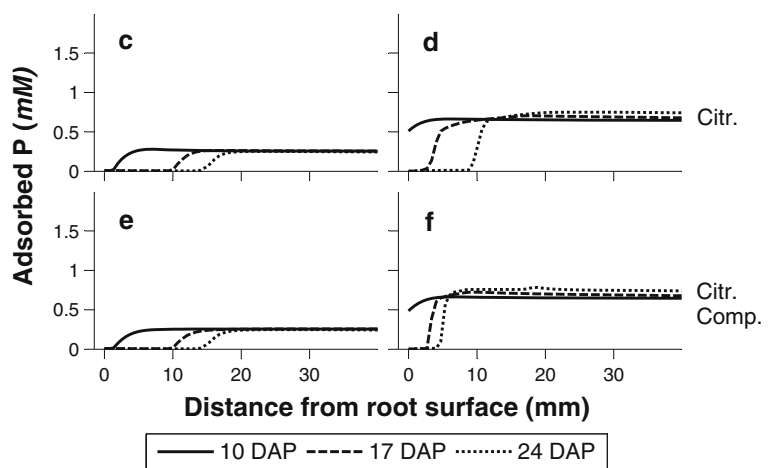
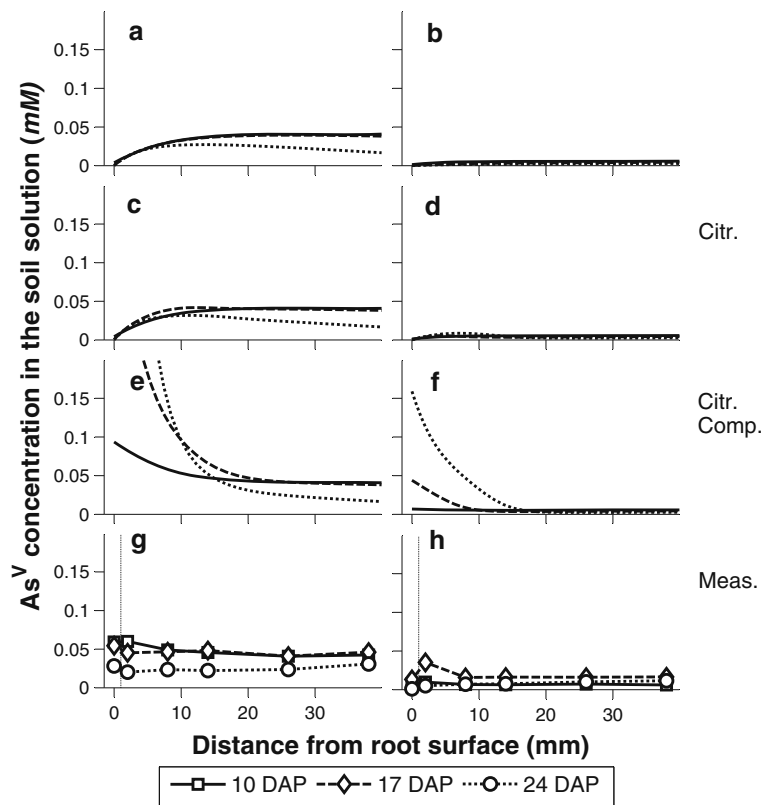


Fig. 7 Predicted As^V concentration in the soil solution with increasing distance from the root surface calculated for different treatments with RhizoMath for 10 days, 17 days and 24 days after planting without (a, b) and with citrate exudation (c, d) (Cit.) and with citrate exudation and competitive uptake (e, f) (Comp.) of As^V and P. Measured As^V concentration in the soil solution at 10 days, 17 days and 24 days after planting (\square, \diamond, \circ , respectively) (g, h) is reproduced after Vetterlein et al. (2007)



citrate exudation (Fig. 6f) predicted a narrower zone where P was totally desorbed than without P- As^V competition (Fig. 6d).

For both G-1 and G-4 treatments, including Eq. 4 to describe competitive As^V and P uptake besides citrate exudation in the calculations led to a predicted As^V accumulation at the root surface (Fig. 7e, f). Calculations with Eq. 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.

Including P- As^V competition in the calculations did not substantially affect predicted amounts of adsorbed citrate for any of the treatments (Fig. 9c-f).

Fig. 8 Predicted amount of adsorbed As^V with increasing distance from the root surface calculated for different treatments with RhizoMath for 10 days, 17 days and 24 days after planting with citrate exudation (c, d) (Cit.) and with citrate exudation and competitive uptake (e, f) (Comp.) of As^V and P. Adsorbed amounts are presented per litre soil to facilitate comparison between soil solution and goethite

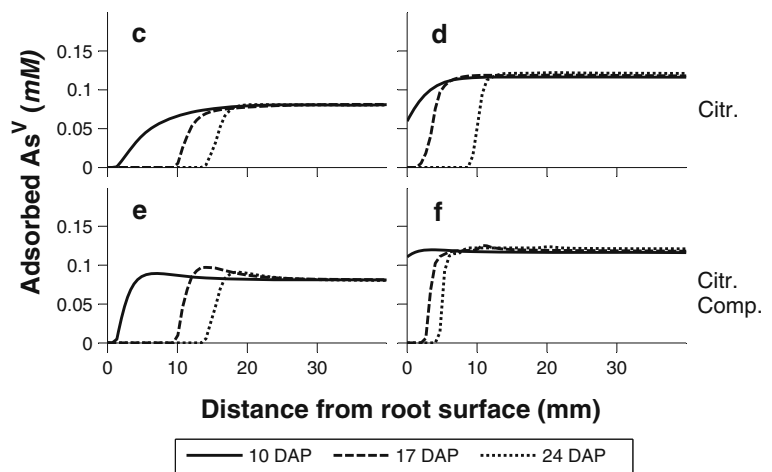
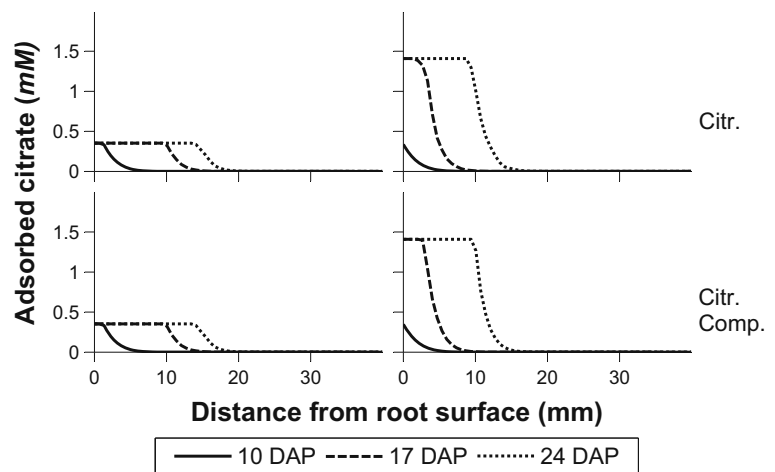


Fig. 9 Predicted amount of adsorbed citrate with increasing distance from the root surface calculated for different treatments with RhizoMath for 10 days, 17 days and 24 days after planting without (c, d) and with competitive uptake (e, f) (Comp.) of As^{V} and P. Adsorbed amounts are presented per litre soil solution to facilitate comparison between soil solution and goethite



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 and As^{V} in the soil solution. Additionally, the predicted P: 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 unexpected behaviour of CaHPO_4 in the hypothetical scenarios with changing pH 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 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 (Szegedi 2009) as well as by the finding that sorption on goethite controlled P 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 from the goethite via ligand exchange. This was predicted to a higher extent in the G-1 treatment where the competition between P, 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 or As^{V} . This agreed with experimental observations and theoretical expectations (Hinsinger et al. 2003; Liu et al. 2001; 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 treat-

ments. This means a good representation of initial soil solution chemistry.

Predicted gradients of soil solution pH for both treatments were smaller than measured pH gradients. The major source of H^+ in the system is efflux by the root in order to maintain charge balance. Predicted H^+ efflux was sufficiently high to assure that the net transport of H^+ occurred away from the root surface. Transport away from the root surface occurs only by diffusion. Mass flow, driven by transpiration takes place in the opposite direction. For ions with high mobility no steep gradients can be expected as concentration gradients equilibrate rapidly. Thus lowering the mobility (more specifically the effective diffusion coefficient of H^+) would result in steeper gradients (Tinker and Nye 2001). Hence a possible explanation for the predicted low pH gradients in our modelling approach could be an overestimated mobility of H^+ ions 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. 2 in Szegedi et al. 2008). The least accurate among these parameters is the soil impedance factor, as its value is only an estimate (Millington and Quirk 1960).

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 than 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.

Kim and Silk (1999) extended the simple model of Nye (1981) to study the effect of root growth on soil solution pH. They found that a growing root system can result in a time-independent pH pattern. This is similar to our experimental observations. However, their model has a major disadvantage: their calculations used a varying H^+ efflux with a varying distance from the root tip, which was experimentally measured and was not calculated from charge balance during root uptake as it is done in the current work.

Predicted soil solution pH was neither affected by including citrate exudation nor by including P- 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.

In general, the overestimation of soil solution pH can lead to the underestimation of the sorption of anions like P and As^V and thus to the overestimation of the concentration of these solutes (Dzombak and Morel 1990). However, both predicted and measured pH were below the range for which large changes for sorption of P and As^V have been predicted. Liu et al. (2001) studied the effect of pH on the mobilisation of P and As^V by an organic acid. They found that the amount of mobilised P, but not the amount of mobilised As^V increased with decreasing pH. This pH effect was substantial (1% increase in desorption/1 pH unit) in the pH range of 5.8. pH values in this range were underestimated at distances >20 mm from the root surface, where citrate was not present in substantial amounts. Thus, the sorption of P, As^V and citrate was not substantially influenced by the poor modelling of pH gradient. This is also supported by the experimental results presented in Vetterlein et al. (2007, Fig. 10. and corresponding text) illustrating that P and As^V concentration were controlled by another parameter apart from soil solution pH.

G-1 treatment (limited number of sorption sites)

Model calculations without citrate exudation predicted P uptake by the root that matched or exceeded delivery to the root surface. This led to the predicted slightly increased P concentration before 17 days after planting and later P 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 concentration at the root surface is not due to transport exceeding uptake.

Model calculations with citrate exudation predicted increase in P concentration at the root surface, accompanied by a decrease of the amount of adsorbed P 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 (Geelhoed et al. 1999; Kirk 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 can be microbially degraded in soils (Jones and Edwards 1998; Jones et al. 2003). However, citrate degradation can be almost completely reduced by the rapid sorption of citrate to iron oxides (Jones and Edwards 1998), like goethite which is present in the G-1 and G-4 treatments. Thus, as no substantial citrate degradation is expected in these treatments, it was not implemented in the model.

Citrate degradation can take place in the G-0 treatment in which no strong adsorbent is present. If citrate degradation is not considered, citrate exudation rate estimated based on citrate concentration in this treatment appears to be lower than the real citrate exudation rate. However, due to the complex behaviour of citrate in soil (Jones et al. 2003), using a simple citrate degradation model would lead to the overestimation of citrate exudation rate (Kirk 2002). Thus, instead of using an unjustified model, we decided to adjust citrate exudation rate manually to achieve predicted P concentrations in the G-1 treatment that are comparable to measured P concentrations. The so adjusted citrate exudation rate appeared to be realistic compared to data available in existing literature: Geelhoed et al. (1999) used in their work a constant citrate efflux of $6.1 \cdot 10^{-10} \text{ mM cm}^{-2} \text{ s}^{-1}$, which was determined as a mean value of different experimental values published by other authors. This is closer to the efflux of $1 \cdot 10^{-9} \text{ mM cm}^{-2} \text{ s}^{-1}$ (applied in our calculations) than to the efflux of $3 \cdot 10^{-11} \text{ mM cm}^{-2} \text{ s}^{-1}$ (estimated based on data from Schulz and Vetterlein 2007). However, for modelling systems in which citrate degradation is a dominant process (i.e. systems in which citrate is not rapidly adsorbed), citrate degradation shall be included in the code. This will be done at a later stage of model development (Table 2).

Hoffland (1992) has shown using the combination of modelling and experiments that only the youngest roots of a root system release organic acids that mobilize P. They included this as a constant scaling factor of the organic acid exudation rates into their model. Our calculations include a scaling factor of citrate exudation rate as well, which implicitly accounts for this phenomenon. The authors described P mobilization by including experimental isotherms in their model and emphasised the necessity of imple-

menting detailed soil chemistry in the model, as it is done in the current work.

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

The disagreement between predicted and measured P 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 concentrations were lower than measured P concentration at any distance from the root surface. A possible explanation for the underestimation of P concentration in the calculations could be that the plant P demand might decrease beyond 17 days after planting. So far the model is based on the assumption that P uptake increases proportionally to leave area development as no time resolved data on P 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. Hoffland (2006) have experimentally shown for lowland rice, that citrate exudation depends on the P-nutritional status of the plant. Coupling the citrate exudation rate to cumulative P-uptake can also improve the model performance for last week of the experiment.

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 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 (Bienert et al. 2008; Ma et al. 2008; Xu et al. 2007), 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. New techniques like the use of bioreporters to visualize As concentration gradients around single roots in soil systems with high spatial resolution (Kuppardt et al. 2009) might provide more information on this aspect.

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 and As^{V} on goethite was asymmetric. Already adsorbed species showed higher affinity for goethite bindings sites than the same species in the soil solution. They also found that the mobilisation of As^{V} and P by organic anions was kinetically controlled. None of these processes can be represented by the currently applied equilibrium approach.

Kinetic processes could be mimicked by including hysteresis, i.e. using different equilibrium constants for sorption and desorption. However, such an approach would result in even lower soil solution As^{V} concentrations and thus 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 and the zone where no P 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 and As^{V} , amount of mobilized As^{V} was much lower compared to the amount of mobilized P. This agrees well with the results of batch experiments of Liu et al (2001). This 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 and As^{V} concentrations in G-4 treatment were an order of magnitude lower compared to the G-1 treatment and were thus in a measurement range which cannot be verified experimentally due to the limited sensitivity of the applied instrumentation (Ackermann et al. 2008).

The correctness of the model calculations for the G-4 treatment can be accepted considering that observed trends of P 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. This agrees well with the results of Geelhoed et al (1999) who described surface complexation with the CD-MUSIC model, which is a more complex surface complexation model than the diffuse double layer model used in this work (Dzombak and Morel 1990; Parkhurst and Appelo 1999).

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. As^{V} influx was underestimated in the calculations with competitive uptake of As^{V} and P with both assumptions for the mathematical description of the competition (Eqs. 4 and 7, respectively). The underestimation of the influx in these calculations was caused by the simplicity of the applied assumptions during the derivation of Eqs. 4 and 7. In a real plant several types of transporters can be involved in the uptake of P 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 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 Eqs. 4 and 7 could help to derive a formula that expresses competitive uptake of As^{V} and P.

As it was already discussed above, As^{III} release may be an additional process that affects As^{V} concentration in soil. However, 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 the competitive uptake of As^{III} and Si, and Si chemistry into the model.

General remarks

The results of the current work have shown that measured gradients in P concentrations can be explained with the mobilisation of adsorbed P by citrate. However, a good agreement of predicted and measured P concentrations was not achieved at later stages of the experiment. To improve the model performance for the last week of the experiment it would be necessary to consider changing nutrient requirement at the different growth stages of the plant (Marschner 1995) in the calculations.

While pH differences between treatments and the magnitude of pH values could be well described by the model, the measured gradients in soil solution pH with increasing distance from the root surface could not be reproduced by the model. Further investigations are required to decide if this was caused by the simplified description of root growth in the model or by a wrong representation of H^+ mobility. However, within the pH range studied, this did not affect the model's ability in reproducing experimental patterns in P concentration.

Arsenate concentration at the root surface was either underestimated (calculations without competitive uptake) or overestimated (calculations without competitive uptake). This strong effect of including competitive uptake of P 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 is required. For example considering different P transporters, and the release of As^{III} , derived from arsenate reduction during detoxification in cells, could improve the model performance. However, the latter would require additional information from experiments on the rate of As^{III} efflux and its re-oxidation in the rhizosphere.

Recent results of Ma et al. (2008) and Bogdan and Schenk (2008) showing uptake and release of As^{III} and Si through the same transporters and an inverse relationship of As and Si uptake suggest, that soil solution Si concentrations should additionally be included in the modelling approach.

It can be concluded that P and As^{V} dynamics in the rhizosphere can be only explained if the chemical and biological processes that influence the behaviour of these solutes are studied simultaneously. Focusing on either soil chemical or plant physiological aspects would result in an incomplete understanding of the system.

Acknowledgements The authors thank for the valuable comments of the anonymous reviewers of this manuscript.

This work was conducted in the framework of the BASS Helmholtz-University Young Investigators Group, supported by the Helmholtz Association Germany.

Appendix

A short overview of the RhizoMath code

The first version of RhizoMath (Table 2 contains an overview about the development stages of RhizoMath) using a simplified chemistry was able to qualitatively reproduce experimentally observed effects of goethite addition and citrate exudation on the concentrations of P and As^{V} in the soil solution in the rhizosphere of *Zea mays*, which was grown in compartment systems under controlled conditions (Szegedi et al. 2008; Vetterlein et al. 2007). The calculations confirmed the hypotheses that the competitive sorption of As^{V} and P is a major process for As^{V} availability in the system, and citrate exudation has a stronger effect on P than on As^{V} concentrations. However, a quantitative agreement for different points in time between modelled and measured data could not be achieved.

In the second version, 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 (Szegedi 2009).

Table 2 Rhizosphere processes included in different versions of RhizoMath

Process	Implemented in RhizoMath
Transport and uptake in the rhizosphere according to the Tinker and Nye model.	
Charge balanced flux term in the transport equation according to Nietfeld (2003)	
Equilibrium description soil chemistry with PHREEQC, including speciation in the soil solution, equilibrium with minerals, gases and surface sorption (diffuse double layer model).	RhizoMath v0.9 (Szegedi et al. 2008)
H ⁺ /OH ⁻ exudation to maintain charge balance by root uptake.	
Citrate exudation.	
Quasi-steady state (not constant) water flux	
Root compartment factor 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.	RhizoMath v0.99 (Szegedi 2009)
Competitive uptake of solutes	RhizoMath v0.999 (This work)
Reaction kinetics (including biodegradation)	
Describing water transport according to the Rhichards eq.	Future work

References

- Allison JD, Brown DS, Novo-Gradac KJ (1990) MINTEQA2/PRODEFA2—A geochemical assessment model for environmental systems—version 3.0 user's manual: Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia, p 106
- Ackermann J, Vetterlein D, Tanneberg H, Neue H-U, Mattusch J, Jahn R (2008) Speciation of arsenic under dynamic conditions. *Eng Life Sci* 8:589–597
- Anscombe FJ (1973) Graphs in statistical analysis. *Am Stat* 27:17–21
- Appelo CAJ, van der Weiden MJJ, Tournassat C, Charlet T (2002) Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ Sci and Technol* 36:3096–3103
- Barber SA (1995) Soil nutrient bioavailability: a mechanistic approach. Wiley and Sons, New York
- Bennett AC, Adams F (1972) Solubility and solubility product of gypsum in soil solutions and other aqueous solutions. *Proc Soil Sci Soc Am* 36:288–291
- Bidel LPR, Renault P, Pages L, Riviere LM (2000) Mapping meristem respiration of *Prunus persica* (L.) Batsch seedlings: potential respiration of the meristems, O₂ diffusion-al constraints and combined effects on root growth. *J Exp Bot* 51:755–768
- Bienert GP, Thorsen M, Schussler MD, Nilsson HR, Wagner A, Tamas MJ, Jahn TP (2008) A subgroup of plant aquaporins facilitate the bi-directional diffusion of As (OH)(3) and Sb(OH)(3) across membranes. *BMC Biology* 6:26
- Bogdan K, Schenk MK (2008) Arsenic in Rice (*Oryza sativa* L.) Related to dynamics of arsenic and silicic acid in paddy soils. *Environ Sci Technol* 42:7885–7890
- Darrach PR, Roose T (2001) Modelling the rhizosphere. In: Pintor R, Varanini Z, Nannipieri P (eds) *The Rhizosphere*. Dekker, New York, pp 327–372
- Dzombak DA, Morel FMM (1990) Surface complexation modeling—hydrous ferric oxide. Wiley, New York
- Esteban E, Carpena RO, Meharg AA (2003) High-affinity phosphate/arsenate transport in white lupin (*Lupinus albus*) is relatively insensitive to phosphate status. *New Phytol* 158:165–173
- Gao Y, Mucci A (2001) Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7M NaCl solution. *Geochim Cosmochim Acta* 65:2361–2378
- Geelhoed JS, Mous SLJ, Findenegg GR (1997) Modeling zero sink nutrient uptake by roots with root hairs from soil: comparison of two models. *Soil Sci* 162:545–553
- Geelhoed JS, van Riemsdijk WH, Findenegg GR (1999) Simulation of the effect of citrate extrudation from roots on the plant availability of phosphate adsorbed on goethite. *Eur J Soil Sci* 50:379–390
- Gollany HT, Schumacher TE, Rue RR, Liu S-Y (1993) A carbon dioxide microelectrode for in situ pCO₂ measurement. *Microchem J* 48:42–49
- Hiemstra T, van Riemsdijk WH (1996) A surface structural approach to ion adsorption: the charge distribution (CD) model. *J Colloid Interf Sci* 179:488–508
- Hinsinger P (2001) Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant Soil* 237:173–195
- Hinsinger P, Plassard C, Tang CX, Jaillard B (2003) Origins of root-mediated pH changes in the rhizosphere and their responses to environmental constraints: a review. *Plant Soil* 248:43–59
- Hinsinger P, Bengough AG, Vetterlein D, Young IM (2009) Rhizosphere: biophysics, biogeochemistry and ecological relevance. *Plant Soil* 321:117–152
- Hoffland E (1992) Quantitative evaluation of the role of organic acid exudation in the mobilization of rock phosphate by rape. *Plant Soil* 140:279–289
- Hoffland E (2006) Organic anion exudation by lowland rice (*Oryza sativa* L.) at zinc and phosphorus deficiency. *Plant Soil* 283:155–162
- Hoffland E, Bloemhof HS, Leffelaar PA, Findenegg GR, Nelemans JA (1990) Simulation of nutrient uptake by a

- growing root system considering increasing root density and inter-root competition. In: Van Beusichem ML (ed) *Plant nutrition—physiology and applications* (pp. 9–15). Kluwer
- Jones DL, Edwards AC (1998) Influence of sorption on the biological utilization of two simple carbon substrates. *Soil Biol Biochem* 30:1895–1902
- Jones DL, Dennis PG, Owen AG, van Hees PAW (2003) Organic acid behavior in soils—misconceptions and knowledge gaps. *Plant Soil* 248:31–41
- Kim TK, Silk WK (1999) A mathematical model for pH patterns in the rhizospheres of growth zones. *Plant Cell Environ* 22:1527–1538
- Kirk GJD (2002) Modelling root-induced solubilization of nutrients. *Plant Soil* 255:49–57
- Kirk GJD (1999) A model of phosphate solubilization by organic anion excretion from plant roots. *Eur J Soil Sci* 50:369–378
- Kirk GJD, Santos EE, Findenegg GR (1999) Phosphate solubilization by organic anion excretion from rice (*Oryza sativa* L.) growing in aerobic soil. *Plant Soil* 211:11–18
- Kölling M (1988) Vom berechneten Sättigungsindex zur Reaktion im Grundwasser. *Zeitschrift d d geol Gesellsch* 139:393–405
- Kuppardt A, Vetterlein D, Harms H, Chatzinotas A (2009) Visualization of gradients in arsenic concentrations around individual roots of *Zea Mays* L. using agar-immobilized bioreporter bacteria. *Plant Soil*. doi:10.1007/S111104-009-0154-3
- Lackovic JC, Reeds JA, Wright MH, Wright PE (2003) Modeling the adsorption of Cd(II) onto goethite in the presence of citric acid. *J Colloid Interf Sci* 269:37–45
- Lambers H, Shane MW, Cramer MD, Pearse SJ, Veneklaas EJ (2006) Root structure and functioning for efficient acquisition of phosphorus: matching morphological and physiological traits. *Ann Bot* 98:693–713
- Lazaroff N, Pitman MG (1966) Calcium and magnesium uptake by barley seedlings. *Aust J Biol Sci* 19:991–1005
- Liu F, De Cristofaro A, Violante A (2001) Effect of pH, phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. *Soil Sci* 166:197–208
- Luster J, Göttlein A, Nowack B, Sarret G (2009) Sampling, defining, characterising and modeling the rhizosphere—the soil science tool box. *Plant Soil* 321:457–482
- Ma JF, Yamaji N, Mitani N, Xu XY, Su YH, McGrath SP, Zhao FJ (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. *PNAS* 105:9931–9935
- Manning BA, Goldberg S (1996) Modelling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Sci Soc Am J* 33:121–131
- Manning BA, Goldberg S (1997) Arsenic (III) and arsenic (V) adsorption on three California soils. *Soil Sci* 162:886–895
- Marschner H (1995) *Mineral nutrition of higher plants*, 2nd edn. Academic, London
- Mayer KU, Frind EO, Blowes DW (2002) Multicomponent reactive transport modeling in variably saturated porous media using a generalized formulation for kinetically controlled reactions. *Water Resour Res* 38:1174–1194
- Meeussen JCL (2003) ORCHESTRA: an object-oriented framework for implementing chemical equilibrium models. *Environ Sci Technol* 37:1175–1182
- Meharg AA (1994) Integrated tolerance mechanisms: constitutive and adaptive plant responses to elevated metal concentrations in the environment. *Plant Cell Environ* 17:989–993
- Meharg AA, Jardine L (2003) Suppression of the high affinity phosphate uptake system: a mechanism of arsenate tolerance in *Holcus lanatus* L. *J Exp Bot* 43:519–524
- Millington RJ, Quirk JP (1960) Transport in porous media. 7th International Congress of Soil Science, Madison
- Morel FMM, Hering JG (1993) *Principles and applications of aquatic chemistry*. Wiley and Sons, New York
- Nietfeld HWF (2001) Modeling the dynamics of the rhizosphere aluminium chemistry in acid forest soils. In: Gobran GR, Wenzel WW, Lombi E (eds) *Trace elements in the rhizosphere*. CRC, pp 253–308
- Nye PH (1981) Changes of pH across the rhizosphere induced by roots. *Plant Soil* 61:7–26
- Nowack B, Mayer KU, Oswald SE, van Beinum W, Appelo CAJ, Jacques D, Seuntjens P, Gérard F, Jaillard B, Schnepf A, Roose T (2006) Verification and intercomparison of reactive transport codes to describe root-uptake. *Plant Soil* 285:305–321
- Parkhurst DL, Appelo CAJ (1999) *User's guide to phreeqc (version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. Denver, Colorado, USGS Water-Resources Investigations Report 99-4259
- Schulz H, Vetterlein D (2007) Ion chromatographic determination of organic acids in small soil solution volumes sampled along a gradient from the bulk soil to the root surface. *J Plant Nutr Soil Sc* 170:640–644
- Shaw G, Bell JNB (1991) Competitive effects of potassium and ammonium on caesium uptake kinetics in wheat. *J Environ Radioactiv* 13:283–296
- Smith P, Smith JU, Powlson DU, McGill WB, Arah JRM, Chertov OG, Coleman K, Franko U, Frohling S, Gunnewiek HK, Jenkinson DS, Jensen LS, Kelly RH, Komarov AS, Li C, Molina JAE, Mueller T, Parton WJ, Thomley JHM, Whitmore AP (1997) A comparison of nine soil organic matter models using datasets from seven long-term experiments. *Geoderma* 81:153–225
- Smith E, Naidu R, Alston AM (2002) Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption. *J Environ Qual* 31:557–563
- Schwertmann U, Taylor RM (1989) Iron oxides. In: Dixon JB et al (eds) *Minerals in soil environment*. SSSA, Madison, pp 379–438
- Sposito G (2008) *The chemistry of soils*. Oxford University Press, Oxford
- Szegedi K (2009) *Multi-component Reactive Transport Modelling in the Rhizosphere—the special case of arsenate*. Dissertation, Faculty of Natural Sciences III (in press)
- Szegedi K, Vetterlein D, Nietfeld H, Jahn R, Neue HU (2008) The new tool RhizoMath for modeling coupled transport and speciation in the rhizosphere. *Vadose Zone J* 7:712–720

- Tretner A (2002) Sorptions- und Redoxprozesse von Arsen an oxidischen Oberflächen—Experimentelle Untersuchungen. Dissertation, Institut für Umwelt-Geochemie, Ruprecht-Karls-Universität Heidelberg
- Vetterlein D, Szegedi K, Ackermann J, Mattusch J, Tanneberg H, Jahn R (2007) Competitive mobilization of phosphate and arsenate associated with goethite by root activity. *J Environ Qual* 36:1811–1820
- Violante A, Pigna M (2002) Competitive sorption of arsenate and phosphate on different clay minerals and soils. *Soil Sci Soc Am J* 66:1788–1796
- Xu XY, McGrath SP, Zhao FJ (2007) Rapid reduction of arsenate in the medium mediated by plant roots. *New Phytol* 176:590–599
- Zhao FJ, Ma JF, Meharg AA, McGrath SP (2009) Arsenic uptake and metabolism in plants. *New Phytol* Early view