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New Tool RhizoMath for Modeling Coupled Transport and Speciation in the Rhizosphere

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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, 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; and (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 arsenate and phosphate that compete for surface binding sites with each other and with other oxyanions such as citrate.

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, 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 modeling 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 K (Claassen et al., 1986; Kelly et al., 1992). Observed reactions of trace elements, however, can be explained only by using coupled speciation–transport models.

Arsenic presents an urgent environmental problem at many agricultural sites around the world (Heikens et al., 2007; Smedley and Kinniburgh, 2002). Simplified approaches are not capable of describing As soil–plant transfer. Different As species [e.g., As(III), As(V), dimethylarsinic acid (DMAA), 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 As speciation. The oxidized form of As, As(V), is a chemical analog of P(V) and competes with P(V) for binding sites in

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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). Arsenic(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 modeling transport in the rhizosphere sufficiently describes and explains the complex behavior of As.

Hoffland (1992), 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 model, addressing Al 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 (see Eq. [8] below) 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. It should be noted, however, that the Nietfeld 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 (ORCHESTRA [Meeussen, 2003], PHREEQC [Parkhurst and Appelo, 1999], and MIN3P [Mayer et al., 2002]) 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. Results generated using these computer codes were compared with the analytical solution presented by Roose et al. (2001) to test their numerical accuracy. As these geochemical programs were not developed to model processes in the rhizosphere, however, 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 our research 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,b). The model should also be able to 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 was compared with other existing approaches using published data sets. RhizoMath was capable of describing the concentration profiles of P(V) and As(V) observed in a compartment system experiment with *Zea mays* L. following the application of goethite.

Theory

The Nye and 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 modeling (Nye and Marriott, 1969; Tinker and Nye, 2000):

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{\mathrm{e}}\frac{\partial C}{\partial r} + \frac{r_0 v_0 C}{b'} \right) \qquad [1]$$

where C [mol L^{-3}] is the concentration of the given species in the soil solution, t is the time, D_{e} [L^{2} 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 center. The buffer power b' (dimensionless) is defined here as $b' = \theta + \rho K_{\mathrm{d}}$, where θ (dimensionless) is the (constant) volumetric water content, ρ [M L^{-3}] is the soil bulk density, and K_{d} [L^{3} M^{-1}] is the distribution coefficient. Another possible definition of the buffer power is $b = \rho K_{\mathrm{d}}$, and thus $b' = \theta + b$ (Darrah and Roose, 2001; Van Rees et al., 1990).

The effective diffusion coefficient is defined as

$$D_{\mathrm{e}} = \frac{Df\theta}{b'} = \frac{Df\theta}{\theta + b} \qquad [2]$$

where f (dimensionless) is the soil impedance factor and D [L^{2} T^{-1}] is the diffusion coefficient in water.

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

$$J^{\mathrm{upt}} = D_{\mathrm{e}} b' \frac{\partial C}{\partial r} + r_0 v_0 C \Big|_{r=r_0} \qquad [3]$$

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 under a wide range of concentrations (Barber and Cushman, 1981; Barber, 1995):

$$J^{\mathrm{upt}} = J_{\max}\left(\frac{C - C_{\min}}{K + C - C_{\min}} \right) \qquad [4]$$

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, 1994a) or linear sink (Baldwin et al., 1973) 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, 1994b). Concentration-dependent Michaelis–Menten kinetics were reported by Nissen (1986). Fluxes from the root surface toward the bulk soil include protons, HCO_3^{-}, 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 Eq. [1] enables microscopic rhizosphere models to describe solute uptake by mycorrhizal hyphae and to include microbial activity or kinetic processes:

$$\frac{\partial C}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left(rD_{\mathrm{e}}\frac{\partial C}{\partial r}+\frac{r_0 v_0 C}{b'}\right)-R \qquad [5]$$

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

Some more complex models, often based on semiempirical formulae, 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., Dunbabin et al., 2002; Hopmans and Bristow, 2002; Somma et al., 1998).

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 very well the root-induced solubilization process, 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 across all species) form of the convective–diffusive equation (Eq. [1]):

$$\frac{\partial C_i}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left(rD_i f\frac{\partial C_i}{\partial r}+\frac{r_0 v_0 C_i}{\theta}\right)-R_i \qquad [6]$$

with a set of corresponding mass action equations:

$$K_i=\gamma_i C_i\prod_j \gamma_j C_j^{\,n_{i,j}} \qquad [7]$$

where K_i is the equilibrium constant, i indicates the species index, C_i is the concentration in the soil solution, γ_i is the activity coefficient, j goes across all reaction partners of species i, and $n_{i,j}$ 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 (Eq. [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 for PHREEQC in 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 Eq. [1] is zero (b' = θ) (Eq. [6]).

To ensure electroneutrality during transport, the diffusive flux has to be corrected by adding a term that represents the effect of Coulomb forces between dissolved ions (Nietfeld, 2001):

$$D_i^{\mathrm{corr}}=\frac{D_i z_i C_i}{\sum_j z_j^2 C_j D_j}\sum_k z_k D_k\frac{\partial C_k}{\partial r} \qquad [8]$$

where z_i–z_j–z_k (dimensionless) is the charge, and j and k go across 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 reactios, but also the density of surface binding sites. Recent studies combining batch experiments and modeling 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 (Le Guern et al., 2003; Tretner, 2002; Gustafsson, 2006).

The New Code RhizoMath

The computer model RhizoMath is being developed in MATLAB (MathWorks, Natick, MA). It is comprised of two main modules: (i) the initialization module that determines, using inverse modeling, certain parameters (Table 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

TABLE 1. Overview of different parameters used in calibration and transport modeling. The calibration module applies the Nelder–Mead simplex algorithm to minimize the root mean square error between measured (user input) and modeled (from PHREEQC output) concentrations by changing optimized parameters. The optimized values are used as constants during the transport modeling.

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

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. The 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 1 kg of soil) are corrected by the volumetric water content and the density of the solid phase to establish a 1-L soil solution, which is the default volume in PHREEQC (Parkhurst and Appelo, 1999). The output file (a tab-separated ASCII spreadsheet) 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, 2008). While a large number of file I/O operations slows down the calculations performed, this type of coupling allows 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 precompiled (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. The PHREEQC code has to be downloaded directly from its homepage.

Initialization: Numerical Procedure

Reactive transport modeling 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 modeling (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 and 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 (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) between concentrations measured using batch experiments and those calculated using the geochemical model (Kool et al., 1987):

$$\mathrm{RMSE} = \sum_i \left(\frac{C_i^{\mathrm{meas}} - C_i^{\mathrm{mod}}}{C_i^{\mathrm{meas}}} \right)^2 \qquad [9]$$

where i goes across all elements and species, concentrations of which were measured, and C_i^{meas} represent measured and C_i^{mod} modeled 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 Eq. [1] for scenarios that neglect chemical speciation and using Eq. [6] for scenarios that consider chemical speciation. One-dimensional linear forms of Eq. [1] and [6], suitable for planar systems such as rhizoboxes or compartment systems (Wenzel et al., 2001; Vetterlein and Jahn, 2004b), are also included in RhizoMath. Diffusive fluxes can be corrected using Eq. [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, 1994b), constant-sink (De Willigen and van Noordwijk, 1994a), linear-sink (Baldwin et al., 1973), and modified Michaelis–Menten kinetics (Barber and Cushman, 1981; Barber, 1995) are available options. We suggest that plant- and nutrient-specific uptake parameters be looked up in the existing literature (e.g., Barber, 1995) or be determined using pot experiments.

Equation [6] and coupled algebraic Eq. [7] are solved numerically using a noniterative split-operator technique, i.e., transport and speciation are calculated in two separate steps (Jacques et al., 2002; Miller and Rabideau, 1993; Nietfeld, 2001; Parkhurst and Appelo, 1999). 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 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 was presented by Skeel and Berzins (1990), who 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, Eq. [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 extended with the sorption of $CO_3{}^{-2}$ 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. 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 data sets were used first to test RhizoMath and then to compare it with other models (Nowack et al., 2006). As suggested by Nowack et al. (2006), diffusion of K toward a single root was chosen as the first benchmark problem. We used the same parameters (Table 2) as the researchers mentioned above, and quantified the accuracy of calculated concentration profiles using the same norm:

$$\|C\|_2 = \frac{\sqrt{\sum_{n=1}^{N}\left(C_n - C_{n,\mathrm{an}}\right)^2}}{NC_0} \qquad [10]$$

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

$$C_{n,\mathrm{an}}(t) = C_0 - \frac{C_0\lambda}{1 + C_\infty{}' + L(t) + \left\{4C_\infty' + \left[1 - C_\infty{}' + L(t)\right]\right\}} E_1\left(\frac{r_n^2}{4D_\mathrm{e}t}\right) \qquad [11]$$

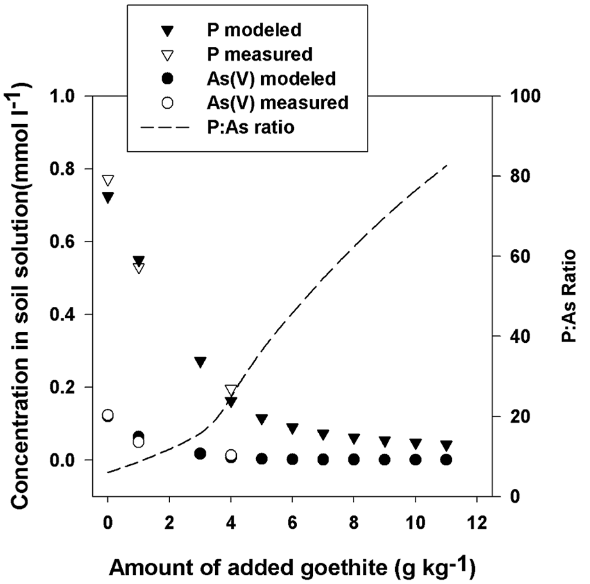

FIG. 1. Concentrations of As(V) and P(V) in the soil solution with increasing amounts of added goethite, calculated with PHREEQC using the sorption parameters optimized with RhizoMath for 0, 1, and 4 g kg^{-1} goethite.

TABLE 2. Input parameters for modeling diffusion of K toward 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 (θ), m^3 m^{-3}	0.3	
Soil bulk density (ρ), g cm^{-3}	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_∞), nmol cm^{-3}	46	
Diffusion coefficient in water (D_w), cm^2 s^{-1}	1.00 × 10^{-5}†	
Corrected diffusion coefficient (D'), cm^2 s^{-1}§	7.63 × 10^{-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, d	120	
Number of cells§	100	
Operator splitting§	after each 0.1 d	
Position of the outer boundary, cm	4	

† Applied for Case (i).
‡ Applied for Case (ii).
§ Specific for RhizoMath.

where $C_\infty' = C_0/K$, $\lambda = J_{\max} r_0/(\theta D_w f K)$, r_n is the position of the nth grid point, D_w is the diffusion coefficient in water, E_1 is the exponential integral

$$E_1(x)=\int_x^\infty \frac{e^y}{y}\mathrm{d}y \qquad [12]$$

and

$$L(t)=\frac{\lambda}{2}\ln\left[4\exp(-0.5772)D_e r_0^{-2}t+1\right] \qquad [13]$$

To test if any artifacts were created by the coupling of MATLAB and PHREEQC, the concentration of K 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 Eq. [1] in Case (i) and Eq. [6] and [7] in Case (ii) are expected to be the same. Since the transport Eq. [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. The 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 corn (*Zea mays* L.), 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 10 d 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 exude citrate to mobilize phosphate, the transport module of RhizoMath was applied to simulate the effect of citrate exudation by a single root of corn 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 generalized two-layer 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 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. 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 (1992) assuming that As uptake by *Zea mays* is similar to other grass species (Gulz et al., 2005). Calculations were repeated without citrate exudation.

TABLE 3. Input parameters for modeling the effect of oxalate exudates from a single root on the availability of phosphate adsorbed by goethite.

Parameter	Value
Root radius (r_0), cm	0.02†
Water flux (v_0), cm s^{-1}	2×10^{-7}
Water content (θ), m^3 m^{-3}	0.21‡
Soil bulk density (ρ), g cm^{-3}	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 ($C_{0,\mathrm{P}}$), mmol cm^{-3}	5
Initial As concentration ($C_{0,\mathrm{As}}$), mmol cm^{-3}	2
Initial citrate concentration ($C_{0,\mathrm{Cit}}$), mmol cm^{-3}	0
Diffusion coefficient of P(V) in water ($D_{\mathrm{w,P}}$), cm^2 s^{-1}	8.46×10^{-4}§
Diffusion coefficient of As(V) in water ($D_{\mathrm{w,As}}$), cm^2 s^{-1}	8.46×10^{-4}§
Diffusion coefficient of K^+ in water ($D_{\mathrm{w,K}}$), cm^2 s^{-1}	1.96×10^{-5}§
Diffusion coefficient of citrate in water ($D_{\mathrm{w,Cit}}$), cm^2 s^{-1}	8.10×10^{-6}
Maximal influx of P(V) ($J_{\max}$), μmol cm^{-2} s^{-1}	4×10^{-5}¶
Maximal influx of As(V) ($J_{\max}$), μmol cm^{-2} s^{-1}	2.98×10^{-7}‡#
Maximal influx of K^+ ($J_{\max}$), μmol cm^{-2} s^{-1}	2.6×10^{-5}¶‡
Michaelis–Menten constant for P(V) (K), μmol cm^{-3}	2×10^{-3}¶
Michaelis–Menten constant for As(V) (K), μmol cm^{-3}	2.4×10^{-2}#
Michaelis–Menten constant for K^+(K), μmol cm^{-3}	1.7×10^{-2}¶
Minimal uptake limit for P(V) ($C_{\min}$), μmol cm^{-3}	4×10^{-3}¶
Minimal uptake limit for As(V) ($C_{\min}$), μmol cm^{-3}	0
Minimal uptake limit for K^+ ($C_{\min}$), μmol cm^{-3}	7×10^{-5}¶
Citrate efflux (J_{Cit}), μmol cm^{-2} s^{-1}	3×10^{-12}†
Elapsed time, d	10‡
Position of the outer boundary, cm	4

† Estimated after Schulz and Vetterlein (2007).
‡ Vetterlein et al. (2007).
§ Parkhurst and Appelo (1999).
¶ Barber (1995).
# Meharg and Macnair (1992).

Results and Discussion

Verification

Figure 2 compares concentration profiles of K calculated using either RhizoMath or the analytical solution at 120 d for the first case study. Results of numerical solutions performed with RhizoMath with and without considering chemical speciation are almost identical and both approximate the analytical solution very well. The $\|C\|_2$ norm (Eq. [10]) calculated for the entire coordinate range is in the order of magnitude of 10^{-4} in both cases. The relative error of both numerical solutions increases at the root surface, with a maximum of 4% in both cases (Fig. 2, lower). These two measures of accuracy were comparable to

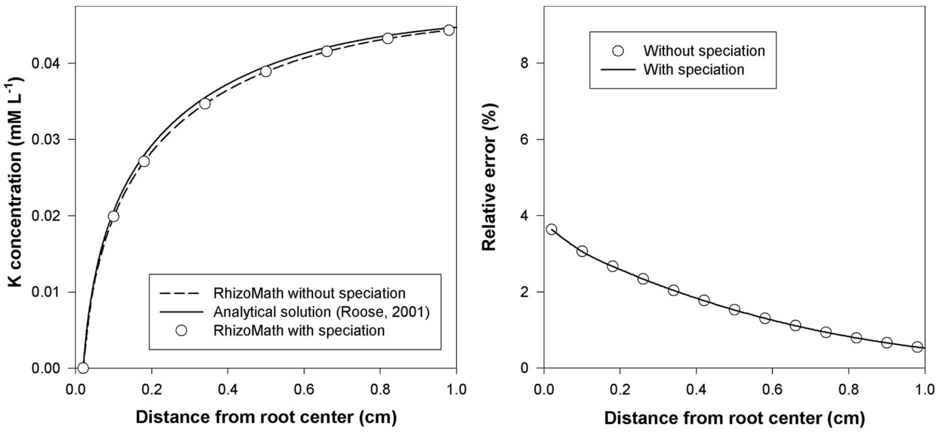

Fig. 2. Concentration profiles of K after 120 d calculated using two different modes of RhizoMath (with and without speciation) and using the analytical solution of Roose et al. (2001). Results are presented using absolute values (left) and relative errors (right).

or better than corresponding values calculated for other codes applied to the same problem (Nowack et al., 2006). 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, and 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 varies depending on the code, the accuracy of applied numerical procedures probably 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 10 d after planting are shown in Fig. 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. (2007). In contrast to simulated results, however, 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 cannot be "turned off" in plants.

A comparison of results calculated with and without citrate exudation shows that the increase in P(V) concentrations with 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.

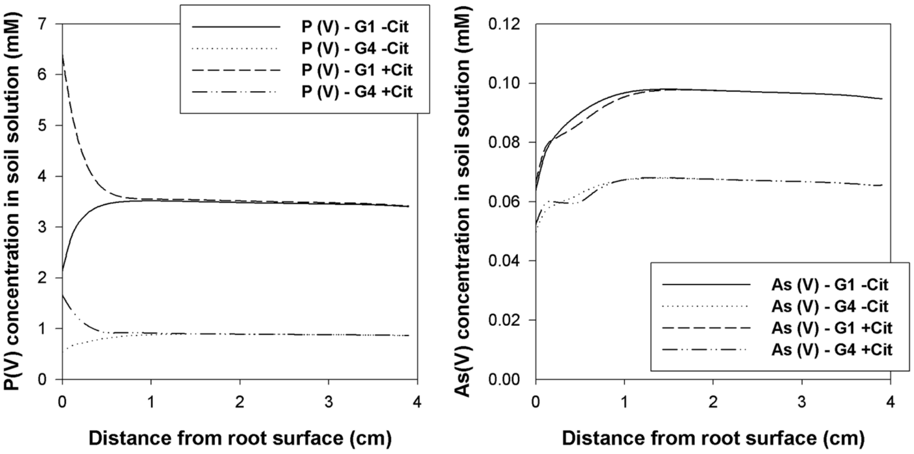

Fig. 3. Concentrations of P(V) and As(V) in the soil solution 10 d after planting at constant citrate exudation (+Cit) and without citrate exudation (−Cit) in the presence of 1 and 4 g kg^{-1} goethite (G1 and G4, respectively), calculated with the transport module of RhizoMath.

Conclusions

The new computer tool RhizoMath for calculating transport and speciation in the rhizosphere uses a microscopic approach. The model allows 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 and Jahn (2004a). 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. (i) Due to the RhizoMath graphical user interface, the program can be applied by researchers who are not familiar with the syntaxes of transport codes. (ii) 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. (iii) The system geometry can be simply changed from planar (geometry of compartment system experiments) to radial (a single root) in the graphical user interface. (iv) 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. (2007), but with minerals such as ferrihydrate and allophane instead of goethite. This will, however, require additional changes to RhizoMath. Nutrient–nutrient competition due to root uptake has to be included, in addition to chemical kinetics, to describe 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 microscale of roots that are relevant for soil-profile and field-scale models. This will allow us to describe and predict the bioavailability and fate of As and other contaminants in the field.

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