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Reactive transport modelling of As- and P-species in the rhizosphere

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The toxic arsenate competes with the nutrient phosphate for binding sites in soil, i.e. at goethite or ferrihydrite surfaces and for binding sites at root membranes. P in soil can be mobilised by plants through exudation of organic anions like citrate or by release of protons. These mechanisms may alter the competition between As(V) and P for binding sites and thus enhance arsenate transfer into the food chain.

In a compartment system experiment with corn plants the temporal and spatial dynamics of different parameters (soil solution P, As(V), citrate and proton concentration) were measured with different initial application rates of goethite (Vetterlein et al, 2007). For the integration of the different parameters the experiment was modelled using the RhizoMath code (Szegedi et al, 2008), that is based on coupling the mathematical package MATLAB with the geochemical code PHREEQC. The initialization module of RhizoMath was used to determine the number of surface binding sites of goethite and values of the equilibrium constants of corresponding stoichiometric equations describing the surface complexation of As(V) on goethite as given in Szegedi et al. (2008). The transport module of RhizoMath was used to model transport and speciation in the compartment system.

Although the model was able to qualitatively represent experimental observations, a quantitative agreement between modelled and measured data could not be achieved. Thus, in a second step, the transport module was extended with a 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. This allowed modelling a growing plant in the compartment system.

As temporal changes in water flux and nutrient demand are not necessarily identical, temporal changes in water flux and nutrient demand were scaled independently from each other, using constant, linear or measured water consumption and leaf area development, respectively. It was shown after calculating different model scenarios that good agreement between modelled and experimental data was only achieved as the actually measured temporal development of water uptake was included in the model and nutrient demand was coupled to the development of leaf area.

Water flux and nutrient demand had different time lapse during the experiment: relative water flux increased faster in the first ten days of the experiment than relative nutrient demand; the reverse relationship was observed at later stages. Model calculations showed that this led to an accumulation of most nutrients, including P, at the root surface in the first week of the experiment. Thus during this time I_{max}, the maximum influx parameter of the Michaelis-Menten kinetics for P transporters was limiting nutrient uptake. Later during the experiment, plant nutrient demand increased. This was represented by an increasing relative coverage of the compartment cross section expressed by the root compartment factor. This increased the total influx so that plant P uptake in the third week was higher than P delivery to the root surface. As a result soil solution P concentration at the root surface decreased but not yet below the concentration in the bulk soil, which would have induced contribution of diffusive transport towards the root surface. A critical review of available literature on uptake kinetics of nutrients showed a high variance of I_{max} in different sources. The adjustment of this parameter increased the agreement between modelled and measured concentrations.

Szegedi et al. 2008. The New Tool RhizoMath for Modeling Coupled Transport and Speciation in the Rhizosphere, Vadose Zone Journal, Special Issue “Vadose Zone Modeling”, 7, 712-720.

Vetterlein et al. 2007. Competitive mobilisation of phosphate and arsenate associated with goethite by root activity. Journal of Environmental Quality 36, 1811-1820.