

# From atom to pedon: Linking processes to phenomena and function

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## Abstract

The fundamental fact that the processes in soil cannot be observed directly demands inverse methods which explain the phenomena on the continuum scale with processes at the local scale in a mechanistic way. In this paper, an approach will be presented which links retardation, a continuum scale phenomena related to reactive transport, to the governing sorption processes. This approach builds upon effective models considering both the role of soil structure and the physicochemical properties of the interface. A multi-domain sorption model has been developed accordingly and will be used to predict sorption and retardation of polycyclic aromatic hydrocarbons at the local and the pedon scale, respectively. The parameters and coefficient functions can be directly parameterized from local scale spectroscopic and spectromicroscopic information. An important additional back-up on the “atom scale” is provided by molecular modelling techniques which can be used to confirm the validity of the measured properties and interaction mechanisms.

## Key Words

Biogeochemical interfaces, sorption, effective model, spectro-microscopy, molecular modelling.

## Introduction

Soils are basis to key ecosystem functions including plant productivity, biodiversity and water quality. The processes in soils control fate and transport of contaminants and nutrients in the critical zone. The three-dimensional structure of soil, its “architecture”, is a dynamic, frequently hierarchically organized system of aggregates formed out of the biogenic and lithogenic parent materials by diverse biotic and abiotic structuring processes. This architecture defines a three-dimensional system of interconnected voids and pores ranging from the (nano)pores of the primary particles to the macropores and fractures of aggregated soils. As such, it provides a large, complex structured and physicochemically heterogeneous biogeochemical interface (BGI). The properties and processes at BGI control interactions, bioavailability, the stability of the pore structure as well as the spatial distribution and movement of liquid and gaseous phases (Totsche *et al.* 2010). Organic compounds of different origin may enter soil as dissolved species or may be attached to colloidal or suspended particles (Totsche *et al.* 2007). Once in soil, they might be transported to deeper soil horizons, to the vadose zone or even to the aquifer. The major fraction, however, is dispersed and retained by interactions with BGI. Due to the opaque nature of soil, direct observation of the processes and properties which control the fate of organic compounds is impossible. We are thus constrained to obtain the information on the governing mechanisms by the rigorous analysis of the related phenomena employing inverse techniques. Organic compound sorption to BGI, e.g., results in retardation, a phenomenon that can be observed on the continuum scale. Retardation can be quantified by the comparison of the mean transport velocity of a solute to the mean pore water velocity using an adequate continuum pedon scale mathematical formulation of reactive transport. Exemplified by the process of sorption and the phenomena of retardation, this paper presents an approach which links phenomena at the continuum or pedon scale to information on the local or atomic scale obtained by spectromicroscopic techniques.

## Methods

### *Sorbates*

As model solutes, we selected polycyclic aromatic hydrocarbons (PAHs) of different polarity: Phenanthrene, anthracene, pyrene and benzo(a)pyrene. For standard solutions, crystalline PAHs (Promochem, Germany) were weighed and dissolved in methanol (Suprapur; Merck, Germany). Stock solutions for the batch sorption experiments were diluted from the standard solutions.

### *Sorbents*

For the sorption studies, different soil minerals and subsurface soil materials were used. Pure Ca-exchanged montmorillonite (Ca-MM) from Wyoming (Source Clay Minerals Repository, University of Missouri) with particle sizes  $< 2 \mu\text{m}$  and specific surface area of  $33.6 \text{ m}^2 \text{ g}^{-1}$  was used. The total concentration of iron including that which is in the lattice and on particle surfaces was determined by means of Mössbauer

spectroscopy and comprised  $29 \text{ mg g}^{-1}$ . Approximately  $1 \text{ mg g}^{-1}$  of iron was found to be on the particle surfaces. Goethite-coated quartz samples with Fe concentrations of 0.6 and  $1.3 \text{ mg g}^{-1}$  were prepared via mixing of goethite dissolved in a  $\text{NaNO}_3$  solution with the quartz sand.

#### *Batch sorption and column transport experiments*

The sorption of PAH to the individual sorbents was studied at different time steps of increasing contact time 4, 8, 16, 24, 48, 72, 96, and 120 hours, respectively, using batch sorption experiments. The batch experiments were conducted with a sorbent:solution ratio of 1:5, under dark conditions at a temperature of  $20^\circ\text{C}$  and by horizontally shaking of the samples 15 min per hour to reduce abrasion. After equilibration, the liquid and solid phases were immediately separated by centrifugation and decantation of the supernatant. Residues of the liquid phase in the solid phase were determined by weighing. Both the PAH concentrations in the separated liquid and in the separated solid phase were analyzed by GC-MS. Transport experiments were run with a soil column system using the same soil materials as for the batch sorption experiments

#### *Numerical analysis and identification of the parameters*

To inversely identify the parameter values of the effective sorption model, a constrained nonlinear minimization algorithm, implemented within Mathcad 14.0 (Mathsoft inc., USA), was applied to the batch sorption data. The objective function subject to minimization is based on the sum of the squared Euclidian distances of the observed and the predicted values (SSQ). Beside maximum error and root mean square error (RMSE) the precision of the particular fits was estimated by the coefficient of determination (CD) and the modeling efficiency (MEF). In addition, the performance of the model was evaluated by comparison to the linear partitioning model, the nonlinear Freundlich-model and the Pore-filling-partitioning model (Allen-King *et al.* 2002.) within a model discrimination exercise. Model performance was based on a newly developed general reference criteria which is based on the weighted differences of the sum of the squared Euclidian distances of the paired modeled and observed data points. Forward simulations of the breakthrough behavior using such parameterized effective model were done with the GNU C++ computer code CARRY (Totsche *et al.* 1997; Totsche & Kögel-Knabner 2004).

## **Results**

### *The effective sorption model*

For the derivation, it is presumed that the soil is composed of three domains, i.e. the Langmuir domain (I), the Polanyi domain (II) and the partitioning domain (III). In the Langmuir domain, the solutes interact with surface sorption sites. Within the Polanyi-domain, sorption is controlled by interactions of the solutes with the micropores of the sorbent. In the partitioning domain, the interactions are controlled by equilibration in between two bulk phases. The sorption sites of domain I are located on the surface of the aggregates and on the walls of the pores distinctly larger than  $20 \text{ \AA}$ . Solute interactions with the surface in terms of a sorption process holds for pore surfaces with apertures larger than  $20 \text{ \AA}$ . At the surface, the adsorbates may form two-dimensional layers or a two-dimensional interfacial solution phase. Such a sorption process can be formulated in terms of a mass-action law and results therefore in Langmuir-type/Lattice Gas sorption processes. The interactions of solutes with surfaces within pores and voids smaller than  $20 \text{ \AA}$  (domain II) is assumed to be controlled by a different mechanism. At this small dimensions (only a few adsorbate diameters), the adsorbate molecule is affected by the overlapping potential fields of the walls of the voids and micropores. Thus, the attractive or repulsive interactions between the adsorbate and the sorbent wall will be much larger than the interactions between the adsorbent and plane or weakly curved sorbent surfaces. The sorption is thus like filling process powered by the overlapping potential fields of the sorbent walls. For microporous solids, e.g. zeolites, solid gels and coals, Polanyi's potential is used and adapted for liquid-solid systems. The overall mass adsorbed is then calculated by integrating the three domains.

### *Batch sorption isotherms*

Figure 1 shows the sorption of pyrene to the different sorbents (data of the sorption to the minerals from Müller *et al.* 2007). The sorption kinetics of PAHs to the mineral sorbents was fast and obviously completed within 4 hours of contact time. This fairly rapid sorption was found for the soil material (Spodosol B-horizon), also.

In the absence of organic matter the mineral surfaces sorbed considerable amounts of PAHs, except for phenanthrene and anthracene sorption to quartz at low liquid phase concentrations (data not shown). Under these conditions sorption to quartz is limited to HOCs with a  $\log K_{OW}$  value larger than 4.6.

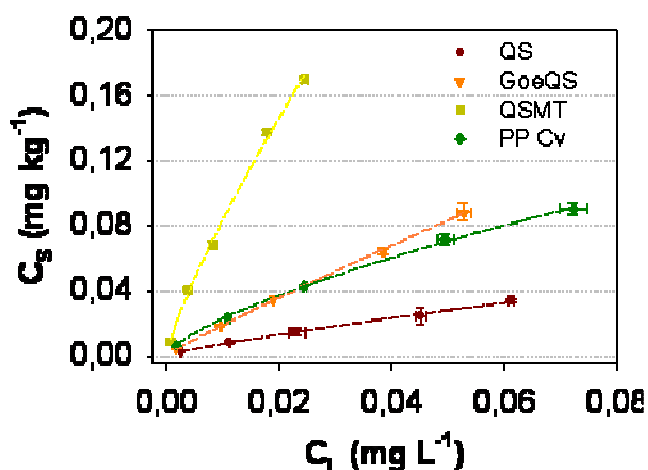


Figure 1. Sorption of pyrene to quartz (QS), goethite-coated quartz-(GoeMS), a mixture of quartz with montmorillonite (QS/MT) and a Spodosol B horizon. Symbols: measured data. Broken lines: results of the parameterization using the effective model.

The sorption isotherms of pyrene to all three minerals are convex-shaped, indicating a saturation of the solid phase at increasing aqueous phase concentrations. Nonlinear convex-shaped isotherms are well known in literature for the sorption of HOCs to soil or sediment material (Weber *et al.* 1983; Huang *et al.* 1998). The curvatures increase in the order goethite-coated quartz < quartz < quartz–montmorillonite. The pyrene isotherms contrast with the sorption results of phenanthrene (data not shown), indicating a sorbent saturation already attained at lower liquid phase concentrations for the more hydrophobic PAH.

The sorption of pyrene to the spodosol B-horizons compares quite well with the sorption to the goethite-coated quartz material. This indeed indicates that the dominant sorbents in this soil material are the pedogenic iron-oxides. This points to the important role of iron-oxides as sorbents for hydrophobic organic substances in natural soil, also

#### Inverse modeling of the sorption data

Figure 2 shows the results of the inverse modelling of the batch sorption data exemplified for the sorption of pyrene to the spodosol B-material.

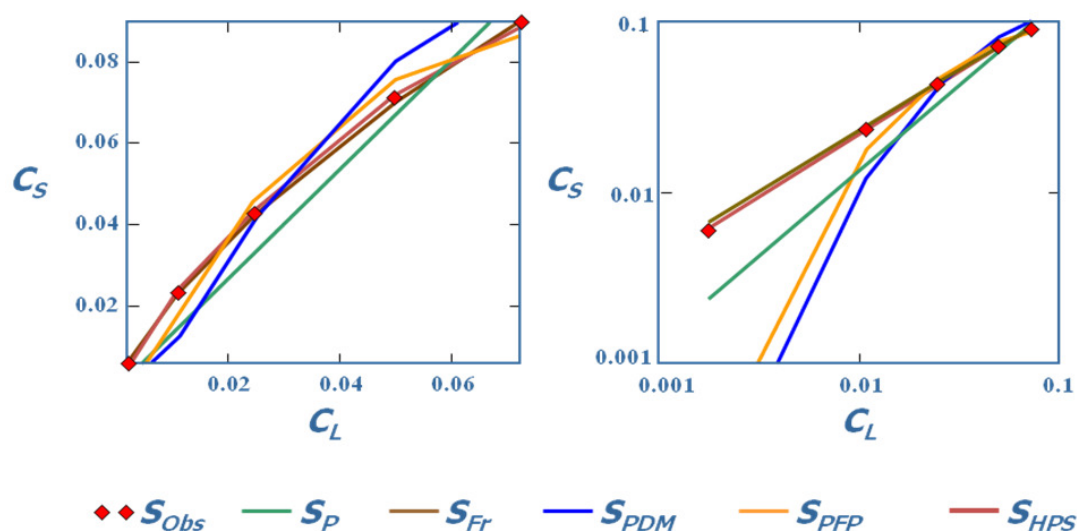


Figure 2. Results of the discrimination of the different sorption models. Symbols: Measured data of pyrene sorption to the spodosol B material.  $S_p$ : Partitioning-Model;  $S_{Fr}$ : Freundlich-Model;  $S_{PDM}$ : Pore-filling model;  $S_{PFP}$ : Pore-filling partitioning;  $S_{HPS}$ : effective sorption model.

Among the different isotherm models the sorption isotherms of pyrene were best described by the effective continuum or pedon scale model and, equally good, by the Freundlich isotherm model except for phenanthrene sorption to quartz sand (linear sorption isotherm, data not shown). High fit qualities were also

obtained for the multi-site dual-mode isotherm. The discrimination within the isotherm models highlighted the advantages of the model efficacy approach. Unfortunately, the sorption experiments including microporous sorbents were not finished at time of preparation of this paper. Thus, the superiority of the developed effective sorption model still awaits proof.

Back-up information on the local scale can be obtained from spectroscopic and spectromicroscopic observations and/or from theoretical considerations. Results employing computational chemistry (Tunega *et al.* 2009) corroborate our experimental findings that iron-oxides indeed can serve as specific sorbents for HOC. At present, we apply atomic force microscopy (AFM) to characterize sorbent properties and interactions. AFM is an emerging yet powerful tool to study surfaces and their properties such as morphology, roughness, and specific basal and edge areas (see also presentation of Macht *et al.*). Using more advanced modes of operation of the AFM, surface properties such as surface potential, elasticity and mass as well as interaction forces and energies can be measured. Such information is used to back up theoretical studies (e.g. molecular modeling), but also to link such information to continuum or pedon scale phenomena in a mechanistic way.

## Conclusion

It is meanwhile accepted that the phenomena at the pedon scale are controlled by processes and structural properties operative at much smaller spatial scales (atomic, molecular). Yet, we still lack a conceptual framework which allows linking processes at the local scale to the phenomena at the pedon scale in a mechanistic way, thereby considering the interplay and interdependencies of physical, chemical and biological processes at biogeochemical interfaces (Totsche *et al.* 2010). A successful approach can build on the development of process models on the continuum scale to replace the widely used empirical approaches. These “physically” based models must acknowledge the governing role of soil structure, the properties of which are parameterized in effective ways: The parameters and coefficient functions used with the model must be either physically based or derived by a rigorous scaling approach from “first principles”. Additional back-up information on the “atom scale” is provided by molecular modelling techniques which can be used to confirm the validity of the measured properties and interaction mechanisms.

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