Interactions of organic pollutants with soil components investigated by means of molecular modelling

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Abstract
The major objective of our work is to develop new tools based on theoretical methods for a quick first assessment of the potential behaviour of new compounds in soil interfaces based on a hypothesis that the behaviour of organic compounds on micro scale is driven by interactions of these compounds on the nano scale. Methods of computational chemistry can contribute to elucidate basic processes involved. These methods cover a large range of techniques (especially quantum chemical methods (DFT, DFTB), force-field methods, molecular dynamics (MD), and Monte Carlo(MC)). In this work an intensive study was conducted concerning sorption of polycyclic aromatic hydrocarbons (PAHs) on soil mineral goethite. Here, relatively large sorption energies were calculated. We found a relation between the surface structure/shape of the PAHs molecules and sorption energies. Linear PAHs, especially anthracene, showed the strongest sorption. The origin of adsorption is mostly in dispersion/polarization interactions between surface OH groups and π-electrons of PAHs. Studies of interactions of humic moieties under different chemical environment showed a clear impact of the hydrophobicity of the environment on the observed Gibbs free energies. Owing to the structural complexity and flexibility of humic substances (HS) various "nano" pores and holes can be formed in their structure. These spaces can be filled by various small molecules, e.g. water. Water molecules can form in these spaces a stable network of hydrogen bonds, thus creating "wet spots" in HS.

Key Words
goethite, humic substances, MCPA, molecular modelling, PAHs

Introduction
The progress in a computational power and performance allows an increasing use of various methods developed in theoretical chemistry also for more complex systems like soil. During last ten years, a wide range of model systems was investigated. This includes e.g. the complexation of aluminium cation in the soil solution (Tunega *et al*., 2000), molecular models of functional groups in humic acids and their interactions (Aquino *et al*., 2008), interactions of organic chemicals with active sites on surfaces of aluminosilicates and iron oxide-hydroxides (Aquino *et al*., 2003, 2007), benzene and polycyclic aromatic hydrocarbons (PAHs) in the adsorbed state on iron oxide-hydroxides (Tunega *et al*., 2009), the interaction of herbicides (phenoxyacetic acid derivatives) with clay surfaces (Tunega *et al*., 2004) and organic moieties (Aquino *et al*., 2007). In the present paper we show examples of our most recent research work, elucidating specific mechanisms of interactions on the molecular level. Number of organic compounds on the market possibly released to the environment is increasing year by year and as is the necessity of an early screening of the environmental behaviour of such compounds. The general aim is to develop a toolbox of theoretical methods and models as a basis for an early evaluation of the possible mobility of organic compounds in the soil matrix.

Methods
Goethite
Goethite is a common soil mineral. Its sorption affinity is directly related to surface structure and shape of particles. The size of particles, can vary from 10 to 1000 nm. Goethite specific surface area is relatively high (50–200 m^2/g) (Schwertmann and Cornell 1991). One of the most populated goethite surfaces is parallel to the (110) crystallographic plane. This surface is formed from three types of hydroxyl groups: i) OH bound to one iron atom referred as hydroxo sites, ii) hydroxyl groups connected to two iron atoms refered as μ-OH sites, and iii) sites, where oxygen atom is bound to three iron atoms (μ3-O_IH, μ3-O_{II}H, and μ3-O_{III}), referred

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as μ3-hydroxo sites. In this work, density functional theory (DFT) calculations were preformed to study the interaction of the (110) goethite surface structure with a set of mono- and polyaromatic compounds, respectively. For this aim the periodic slab model of the (110) surface was constructed on the basis of the experimental bulk structure. The vacuum space of ~20 Å was added in a direction to separate individual slabs. The final computational super cell was orthorhombic with lattice vectors a = 30 Å, b = 10.97 Å, and c = 18.23 Å. The electronic structure calculations were performed with the Vienna ab initio simulation package (VASP) using a spin-polarized DFT (SP-DFT) formalism. The local density approximation (LDA) and the generalized gradient approximation (GGA) were used for the description of the electron exchange-correlation interaction.

Solvent effects
The thermodynamic cycle was used to compute formation Gibbs free energies of three hydrogen-bonded complexes (acetic acid dimer, acetic acid-acetamide, acetic acid-methanol) in three solvents with a different polar strength: water, chloroform, and n-heptane. Only the most stable complexes in gas phase with two cyclic hydrogen bonds were considered. Gibbs free energies of solvation were calculated by means of the explicit and implicit solvation models. Within the explicit solvation model, force-field based MD and MC statistical mechanical simulations in a canonical (NVT) ensemble with a free energy perturbation technique (FEP) were performed on models where studied species were placed in a certain number of solvent molecules in a periodic box. In gas phase, full geometry optimisations of the investigated hydrogen-bonded complexes and their individual constituents were performed quantum-chemically at the DFT level of theory using the hybrid B3LYP functional and the TZVPP basis set. Implicit solvation model (solvent is represented by dielectric continuum with a specific dielectric constant) was studied by means of the COSMO (COnductor like Screening Model) and PCM (Polarizable Continuum Model) approaches as implemented in quantum chemical programs Turbomole and Gaussian using the B3LYP/TZVPP level of theory. For all examined complexes and their respective monomers in solution, full geometry optimisations were performed.

Humic acid nano pores
The modeled configuration involves a stable hydrogen-bonded complex of two polyacrylic acid trimers (TC), formed as each carboxyl group of one trimer is bound via two hydrogen bonds to the opposite carboxyl group of the second trimer. An increasing number of water molecules are added to this aggregate, which is used to study their above-mentioned capacity of holding the two chains together even though their distance is too far for direct hydrogen bonding between the carboxyl groups. Consecutive hydration of TC was studied at different distances between the trimer chains by adding 1-10 water molecules to the TC structure. The geometry optimisations were carried out using two quantum chemical approaches, DFT and DFTB. DFT calculations were performed with the PBE functional and the SVP basis set in order to obtain benchmark results. In addition to the geometry optimisations, molecular dynamics (MD) simulations were performed using the DFTB method.

Results
Goethite – PAHs interactions
A systematic DFT study of interactions between a set of mono- and polyaromatic hydrocarbons (PAHs) and the (110) goethite surface was performed in this work (Figure 1). It was found that PAHs form relatively weak surface complexes having their molecular plane practically parallel to the surface plane. The origin of the interactions is in the polarization of the π-system by polar OH groups and in the formation of weak hydrogen bonds where the π-system acts as a proton acceptor. The computed averaged perpendicular distances of the molecular plane of PAHs to the hydrogen atoms of the surface OH groups range from 2.3 to 2.7 Å. Computed interaction energies regularly increase for the linearly shaped molecules from benzene to anthracene. Two other PAHs with a non-linear shape, phenanthrene and pyrene, are less strongly bound to the surface although they have a similar (phenanthrene) or even larger size (pyrene) than anthracene. These differences were explained by the specific configuration of the surface hydroxyl groups of goethite. The three types of OH groups, μ-OH, μ3-O_{II}H, and –OH, form a valley, the width of it fits very well the molecular shape of the linear PAHs. It was found that with anthracene as example the linear PAHs can easily slide along the valley of OH groups with practically no barrier. In summary it is concluded from our results that the (110) goethite surface will withhold linear PAHs significantly better than non-linear ones.

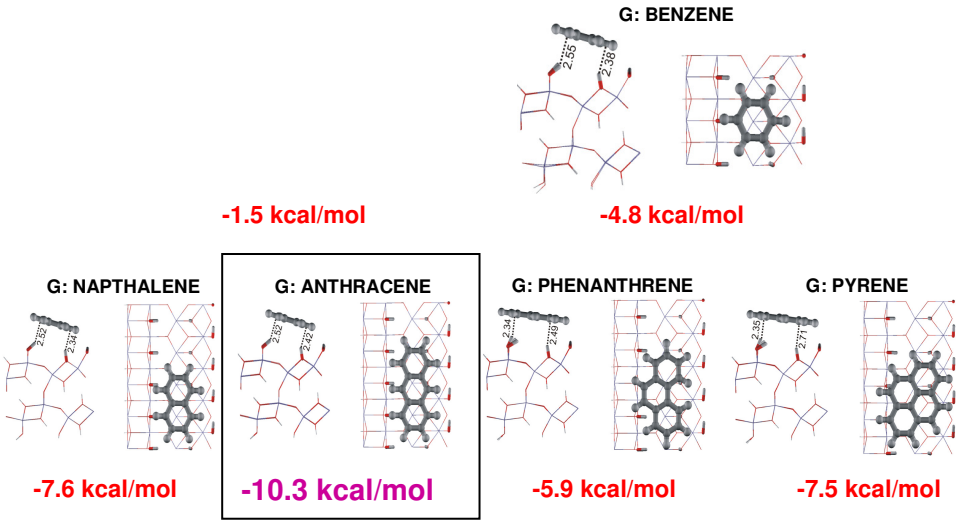

Figure 1. Two views on the optimized surface complexes of the (110) goethite surface with benzene, naphthalene, anthracene, phenanthrene, and pyrene. Dotted lines and numbers represent the averaged perpendicular distances between the molecular plane of the PAHs and the hydrogen atoms of the surface OH groups μ-OH (left) and μ_3-OH (right), respectively. Black circles represent the surface OH groups with the shortest distance to PAHs (Tunega *et al.,* 2009)

Solvent effects

Solvent effects are of crucial importance to approach more realistic model systems. The thermodynamic stability of selected set of benchmark hydrogen-bonded systems was studied with the goal of obtaining detailed information on solvent effects using water, chloroform and n-heptane as representatives for a wide range in the dielectric constant. It was found that owing to the large perturbing effect of water, the cyclic acetic acid dimer is not stable in aqueous solution. In less polar solvents the double hydrogen bond structure of the acetic acid dimer remains stable. This finding is in agreement with previous theoretical and experimental results. A similar trend as for the acetic acid dimer is also observed for the acetamide complex. For the methanol complex it was found that it is thermodynamically neither stable in gas phase nor in any of the three solvents. Table 1 collects calculated complex formation Gibbs free energies for three complex models in three solvents.

Table 1. Gibbs free energies (ΔG^{sol}) at T = 298K for the complexation reactions in water (H_2O), chloroform ($CHCl_3$) and n-heptane (C_7H_{16}) determined from different free energy estimates. All values are given in kcal/mol. (Pasalic *et al.,* 2009)

	solvent	MD-FEP	MC-FEP	PCM	COSMO
AcOH+AcOH → AcOH···AcOH	H_2O	7.5	7.1	6.5	4.5
	$CHCl_3$	-3.5	-3.8	-1.5	0.7
	C_7H_{16}	-5.6	-8.0	-3.1	-2.9
AcOH+$AcNH_2$ → AcOH···$AcNH_2$	H_2O	8.0	7.5	7.5	7.3
	$CHCl_3$	-1.8	-2.1	0.9	3.2
	C_7H_{16}	-3.3	-5.6	-0.6	-0.6
AcOH+MeOH → AcOH···MeOH	H_2O	9.6	9.8	9.4	7.7
	$CHCl_3$	1.1	2.3	3.7	4.9
	C_7H_{16}	0.5	1.0	2.5	2.3

Humic substances – pore filling mechanism

Displaced polyacrylic acid trimer structures were constructed by horizontal motion of the chains relative to each other in order to study the capacity of the water cluster to hold the two chains together even though their distance is too far for direct hydrogen bonding between the carboxyl groups. DFT/DFTB geometry

optimisations and DFTB molecular dynamics simulations were used to investigate the hydrogen-bonded structures formed and to compute their relative energetic stabilities. At shorter distances between the two oligomer chains an outer solvation is only possible. However, with increasing distance between trimers the water molecules are able to penetrate into the inside of the created free space, keeping the two chains together by means of a formed hydrogen-bonded network. Significant stabilization effect in comparison with outer hydration of 10-20 kcal/mol was observed by this intrusion of water molecules at the distance of ~13 Å (Figure 2). The present model, therefore, strongly supports the hypothesized bridging and stabilization function of water molecules in humic substances provided a local distribution of appropriate functional groups available in the HS matrix (Aquino *et al.,* 2009).

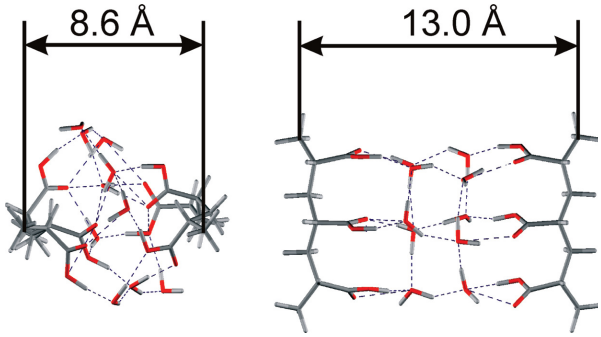

Figure 2. RI-PBE/SVP-optimised poly acrylic acid trimer complex hydrated with 10 water molecules with 4C fixation at two selected distances (according to Aquino *et al.,* 2009).

Conclusion

It was shown that tools of computational chemistry have a high potential to contribute to the elucidation of basic processes of interactions of soil constituents and organic compounds on soil interfaces on the molecular level.

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