# Towards a molecular level understanding of the sulfanilamide-soil organic matter-interaction

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## HIGHLIGHTS

- Experiment and theory showed that SAA obeys a site-specific sorption on soil surfaces.
- SAA-SOM-interaction increases by increasing polarity of SOM sorption site.
- H-bonds, dispersion, and π-π-interactions were observed for SAA-SOM-interaction.
- Dipole moment and atomic charges of SOM sorption sites control SAA-SOM-interaction.
- The Freundlich unit capacities were estimated from the calculated binding energies.
- The current SOM model is flexible to describe interactions of SOM with other pollutants.

## GRAPHICAL ABSTRACT
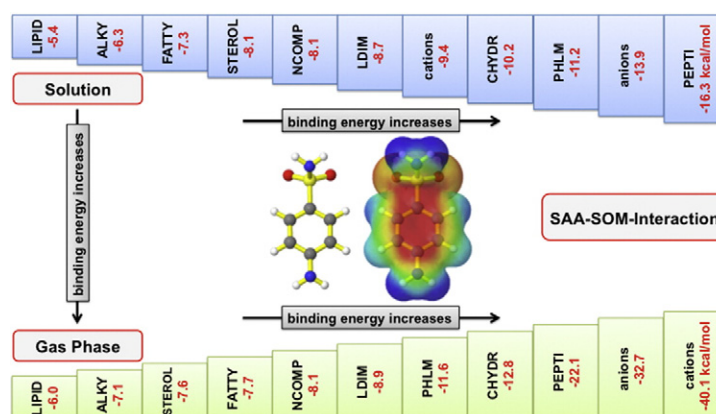
## ABSTRACT

Sorption experiments of sulfanilamide (SAA) on well-characterized samples of soil size-fractions were combined with the modeling of SAA-soil-interaction via quantum chemical calculations. Freundlich unit capacities were determined in batch experiments and it was found that they increase with the soil organic matter (SOM) content according to the order fine silt > medium silt > clay > whole soil > coarse silt > sand. The calculated binding energies for mass-spectrometrically quantified sorption sites followed the order ionic species > peptides > carbohydrates > phenols and lignin monomers > lignin dimers > heterocyclic compounds > fatty acids > sterols > aromatic compounds > lipids, alkanes, and alkenes. SAA forms H-bonds through its polar centers with the polar SOM sorption sites. In contrast dispersion and π-π-interactions predominate the interaction of the SAA aromatic ring with the non-polar moieties of SOM. Moreover, the dipole moment, partial atomic charges, and molecular volume of the SOM sorption sites are the main physical properties controlling the SAA-SOM-interaction. Further, reasonable estimates of the Freundlich unit capacities from the calculated binding energies have been established. Consequently, we suggest using this approach in forthcoming studies to disclose the interactions of a wide range of organic pollutants with SOM.

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## 1. Introduction

Pharmaceutical antibiotics, that are mostly polar and ionizable compounds, have been identified as emerging pollutants. Typically, they reach the soil through contaminated manure from medicated livestock used as fertilizer (Boxall et al., 2004; Thiele-Bruhn, 2003). Sulfonamides, a class of antibiotic substances, are applied in large quantities and were often detected in agricultural soils (Kim et al., 2011). Although knowledge about the extent and kinetics of sulfonamides' sorption in soil accumulated in the past years, uncertainties about sites and mechanisms of sorption still exist (Figueroa-Diva et al., 2010). Consistently, low soil sorption coefficients are determined for sulfonamides (Białk-Bielińska et al., 2012; Figueroa-Diva et al., 2010; Thiele-Bruhn et al., 2004). Sorption substantially increases within hours leading to a decline in extractability (Müller et al., 2012; Wang et al., 2006). The spontaneous and not fully reversible immobilization is partly explained by surface complexation (Figueroa-Diva et al., 2010; Lertpaitoonpan et al., 2009; Schwarz et al., 2012). Furthermore, it is assumed that diffusion and entrapment in micropores of soil sorbents contribute to the strong immobilization (Schwarz et al., 2012; Wang et al., 1993). Sorption of sulfonamides is largely governed by soil organic matter (SOM) while it is subordinate to clay minerals and pedogenic oxides (Figueroa-Diva et al., 2010; Thiele-Bruhn et al., 2004). From experimental findings it was concluded that sorption to SOM is preferred at functional groups of high polarity such as keto, enol, alcoholic and phenolic OH as well as carboxyl groups (Gao and Pedersen, 2005; Thiele-Bruhn et al., 2004). Sorption is assumed to occur via ion exchange and ion bridging of charged species as well as van der Waals forces and hydrogen bridges, but possibly also through π-π-interactions of less polar molecular moieties of the neutral species with aromatic ring systems of the sorbent (Gao and Pedersen, 2005; Schwarz et al., 2012; Thiele-Bruhn et al., 2004; Tolls, 2001). It is controversially discussed, though, if hydrophobic partitioning is also relevant (Figueroa-Diva et al., 2010; Lertpaitoonpan et al., 2009). The specific sorption of the sulfonamides is mirrored in non-linear sorption isotherms that are often best described by the Freundlich model (Białk-Bielińska et al., 2012; Lertpaitoonpan et al., 2009; Sanders et al., 2008; Thiele-Bruhn et al., 2004).

Combination of molecular modeling and computational chemistry is a complementary approach, in addition to sorption experiments, to develop a molecular understanding of the binding of pollutants to soil (Gerzabek et al., 2001; Schaumann and Thiele-Bruhn, 2011). Modeling of SOM is not straightforward due to its high variability in the chemical composition, spatial architecture, and multi-phase behavior (Senesi et al., 2009). Most notably, there are different hypotheses concerning the SOM principal structural organization (Schaumann and Thiele-Bruhn, 2011), i.e. macromolecular vs. supramolecular structure (Schaumann, 2006). Several concepts for molecular-scale SOM modeling have been introduced, ranging from (i) complex polymeric models (Schulten and Leinweber, 2000; Schulten, 2002) to (ii) the modeling of single functional groups (Aquino et al., 2007, 2009). These models could be criticized because of the huge number of possible combinations for all molecular building blocks into a single macromolecule (i) or due to the narrow selection of functionalities (ii). Therefore, to overcome these problems, recently Ahmed et al. (2014a,b) have developed a new approach for SOM modeling based on SOM characterization by different analytical techniques (Ahmed et al., 2012), which is combined with quantum chemical and molecular dynamics calculations. The model includes a large test set of separate representative systems covering the most relevant functional groups that exist in analytically quantified compound classes (Ahmed et al., 2012). The validity of this model has been proven by experimental adsorption of the non-polar hexachlorobenzene (HCB) on well-characterized soil samples (Ahmed et al., 2014a). The influence of SOM on soil sorption can be ideally determined using (i) soils from one area with similar mineral composition but with different SOM content (Ahangar et al., 2008) and (ii)

particle-size fractions of soil, exhibiting different SOM content and composition (Nkedi-Kizza et al., 1983; Schulten et al., 1993).

Complementary to the study on non-polar HCB, the main objective of the present study is exploring the sorption of a polar chemical, i.e. the pharmaceutical antibiotic sulfanilamide (SAA), with SOM at the molecular level. To this end, batch sorption experiments for SAA were performed using particle-size fractions of two soils differing in SOM content and composition due to long-term different fertilization. Furthermore, molecular modeling for the SAA—SOM binding based on the recent SOM model by Ahmed et al. (2014a,b) and quantum mechanical calculations was conducted. Finally, quantitative structure-activity relationship (QSAR) (Nantasenamat et al., 2010) was used to link the SAA—SOM binding to the physicochemical properties of the SOM functional groups.

## 2. Material and methods

### 2.1. Soil samples and particle-size fractionation

In order to test soil samples that differ specifically in SOM, topsoil samples were taken from the Ap horizon (0 to 20 cm depth) of a haplic Phaeozem from the long-term 'Eternal Rye Cultivation experiment' at Halle (Saale), Germany (Kühn, 1901; Schmidt et al., 2000). Representative samples from two differently fertilized plots, i.e. the unfertilized treatment (U), and a plot that received farmyard manure from 1878 until sampling date in 2000 (FYM) were used (Schmidt et al., 2000). Both soil samples had a similar mineral composition with illite, smectite and mixed layer minerals predominating in the clay fraction (<2 μm) but differed substantially in SOM content (Leinweber and Reuter, 1989). The samples were air dried and sieved (<2 mm) prior to experiments. Additionally, both samples U and FYM were separated each into five particle-size fractions (for details, see the supplementary information (SI)), i.e. sand (2000–63 μm), coarse silt (63–20 μm), medium silt (20–6.3 μm), fine silt (6.3–2 μm), and clay (<2 μm) (Leinweber et al., 2009; Amelung et al., 1998; Schmidt et al., 1999). Selected general characteristics of the whole topsoil samples and their respective particle-size fractions such as organic carbon (OC), nitrogen (N), sulfur (S), cation exchange capacity (CEC), pH, and content of the pedogenic oxides (iron, aluminum, and manganese) extracted by a dithionite-citrate-bicarbonate solution ($Fe_{dith}$, $Al_{dith}$, and $Mn_{dith}$) are listed in Table S1 in SI.

### 2.2. Pyrolysis field ionization mass spectrometry (Py-FIMS)

For each topsoil and particle-size fraction sample, the Py-FI mass spectrum, containing the marker signals of important SOM chemical compounds in the mass range of 55 to 500 au, was obtained (more details are given in SI). According to well established modes of spectra interpretation (Ahmed et al., 2012; Schulten and Leinweber, 1999) the particular ion intensity (I) of each (1) carbohydrates with pentose and hexose subunits (CHYDR), (2) phenols and lignin monomers (PHLM), (3) lignin dimers (LDIM), (4) lipids, alkanes, alkenes, bound fatty acids, and alkyl monoesters (LIPID), (5) alkyl aromatics (ALKY), (6) non-peptidic (e.g., nitriles, N-heterocyclic compounds) N-containing compounds (referred to as N-containing compounds) (NCOMP), (7) sterols (STEROL), (8) peptides (PEPTI), and (9) free fatty acids (FATTY) was calculated. Furthermore, total ion intensity ($I^{tot}$) that is the sum of ion intensities of all recorded marker signals was calculated for each sample.

### 2.3. Adsorption experiment

Adsorption of SAA (purity ≥99.0%, Sigma, Taufkirchen, Germany; for details see the 2D structure of SAA in Figure S1 in SI) was determined in batch trials according to OECD guideline 106 (OECD, 2000) and based on previous studies (Ahmed et al., 2015; Thiele-Bruhn et al., 2004). All samples were done in triplicate. For each replicate, 5.0 g of air-dried soil