# How soil organic matter composition controls hexachlorobenzene–soil-interactions: Adsorption isotherms and quantum chemical modeling

Ashour A. Ahmed [a,c,d,*], Oliver Kühn [a,d], Saadullah G. Aziz [e], Rifaat H. Hilal [c,e], Peter Leinweber [b,d]

[a] University of Rostock, Institute of Physics, D-18051 Rostock, Germany
[b] University of Rostock, Soil Science, D-18051 Rostock, Germany
[c] University of Cairo, Faculty of Science, Department of Chemistry, 12613 Giza, Egypt
[d] University of Rostock, Interdisciplinary Faculty, Department of Life, Light and Matter, D-18051 Rostock, Germany
[e] King Abdulaziz University, Faculty of Science, Chemistry Department, Jeddah 21589, Saudi Arabia

## HIGHLIGHTS

- Conduction of adsorption experiment of different soil samples on HCB.
- Development of a new SOM model for the study of the HCB-SOM interaction.
- Carrying out quantum mechanical calculations and QSAR study.
- The unsaturated and aromatic centers are relevant to the HCB-SOM interaction.
- The polarizability is the most relevant property monitoring the HCB-SOM interaction.

## GRAPHICAL ABSTRACT
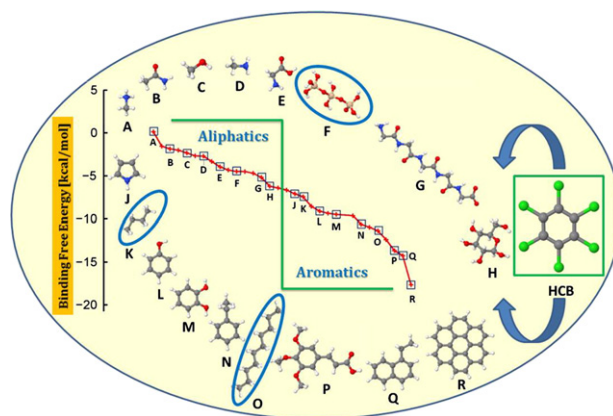
## ABSTRACT

Hazardous persistent organic pollutants (POPs) interact in soil with the soil organic matter (SOM) but this interaction is insufficiently understood at the molecular level. We investigated the adsorption of hexachlorobenzene (HCB) on soil samples with systematically modified SOM. These samples included the original soil, the soil modified by adding a hot water extract (HWE) fraction (soil + 3 HWE and soil + 6 HWE), and the pyrolyzed soil. The SOM contents increased in the order pyrolyzed soil < original soil < soil + 3 HWE < soil + 6 HWE. For the latter three samples this order was also valid for the HCB adsorption. The pyrolyzed soil adsorbed more HCB than the other samples at low initial concentrations, but at higher concentrations the HCB adsorption became weaker than in the samples with HWE addition. This adsorption combined with the differences in the chemical composition between the soil samples suggested that alkylated aromatic, phenol, and lignin monomer compounds contributed most to the HCB adsorption. To obtain a molecular level understanding, a test set has been developed on the basis of elemental analysis which comprises 32 representative soil constituents. The calculated binding energy for HCB with each representative system shows that HCB binds to SOM stronger than to soil minerals. For SOM, HCB binds to alkylated aromatic, phenols, lignin monomers, and hydrophobic aliphatic compounds stronger than to polar aliphatic compounds confirming the above adsorption isotherms. Moreover, quantitative structure–activity relationship (QSAR) of the binding energy with independent physical properties of the test set

* Corresponding author at: University of Rostock, Institute of Physics, D-18051 Rostock, Germany. Tel.: +493814986954; Fax: +493814986942.
E-mail addresses: ashour.ahmed@uni-rostock.de (A.A. Ahmed), oliver.kuehn@uni-rostock.de (O. Kühn), saziz@kau.edu.sa (S.G. Aziz), rhilal@kau.edu.sa (R.H. Hilal), peter.leinweber@uni-rostock.de (P. Leinweber).

systems for the first time indicated that the polarizability, the partial charge on the carbon atoms, and the molar volume are the most important properties controlling HCB–SOM interactions.

## 1. Introduction

Persistent organic pollutants (POPs) comprise an environmentally hazardous compound class that resists chemical, biological, and photolytic degradation in the environment (Ritter et al., 2007). They are ubiquitously distributed in the environment having long life times, which can be several days in the atmosphere and years or decades in soil/sediment (Jones and de Voogt, 1999). In aqueous systems and soil, POPs preferentially move into the solid fraction because of their hydrophobicity. In soil, POPs can be taken up by plant roots and/or adsorbed on soil constituents, especially on soil organic matter (SOM). Binding of POPs to SOM is influenced by several factors, including physical and chemical properties of the pollutant, moisture and chemical composition of soil, and the type and strength of the interactions between the pollutant and the reactive soil surfaces (Senesi and Loffredo, 2008). Interactions of hydrophobic pollutants with soil have been studied by adsorption experiments, which usually show an initial rapid and a following slower stage (Chen et al., 2004; Weber et al., 1991). The most common mechanism for the slow stage is diffusion into the SOM (Chiou et al., 1983).

Since adsorption experiments yield only information, which can be correlated statistically to soil properties, computational chemistry is a promising approach to develop an atomistic understanding of the binding of POPs to soil (Gerzabek et al., 2001; Schaumann and Thiele-Bruhn, 2011). For instance, Kubicki, Sparks and coworkers modeled processes at mineral surfaces such as surface complexation with a variety of compounds (Kubicki et al., 2007; Kwon and Kubicki, 2004; Paul et al., 2006; Tribe et al., 2006; Zhu et al., 2009). Other atomistic simulation studies covered, e.g., the binding of polycyclic aromatic hydrocarbons to soot (Kubicki, 2006) and the dynamics of phenol-water (Lock and Skipper, 2007) or salt (Jardat et al., 2009) solutions at clay surfaces. Lischka and coworkers studied the effect of protonation, deprotonation, and dehydroxylation of different reactive sites on a goethite model surface (Aquino et al., 2008a, 2008b) as well as adsorption of polycyclic aromatic hydrocarbons on such a surface (Tunega et al., 2008, 2009). Furthermore, they investigated interactions between a 2,4-dichlorophenoxy acetic acid herbicide and various functional groups (Aquino et al., 2007) and the role of hydrogen bonds in stabilizing poly(acrylic acid) oligomer structures mimicking humic acid (Aquino et al., 2008a, 2008b, 2009). There are different opinions about the principal structural organization of humic substances and SOM, i.e. macromolecular vs. supramolecular structure (Piccolo, 2002; Schaumann, 2006; Sutton and Sposito, 2005). The perhaps most complex polymeric-type, effective atomistic model of SOM has been developed by Schulten and coworkers on the basis of bio- and geochemical, NMR-spectroscopic and mass spectrometric analyses (Schulten, 2002; Schulten and Leinweber, 2000; Schulten and Schnitzer, 1995, 1997). Polymer-like modeling of SOM could be criticized because of the huge number of possibilities for combining all of SOM compounds and functional groups together into a single macromolecule. Therefore, modeling SOM by separate representative systems covering most relevant functional groups as well as analytically determined compound classes is an alternative, which is followed here for the first time using a large test set.

The objective of the present work is to study the interaction of HCB, one of the most dangerous POPs (Jones and de Voogt, 1999), with SOM experimentally and theoretically. For linking the experimentally observed HCB adsorption by samples with systematically changed SOM composition (Ahmed et al., 2012) a test set of representative species of the SOM building blocks as well as different functional groups is developed. Then this test set is used to study the interaction of HCB with

each representative system computationally by calculating the binding energy between HCB and each representative system employing density functional theory (DFT). We hypothesize that an improved atomistic understanding of the HCB–SOM-interaction can be derived from correlating the binding energy with the molecular properties of the representative systems using quantitative structure–activity relationships (QSAR) (Nantasenamat et al., 2010).

## 2. Materials and methods

### 2.1. Soil samples

The original soil sample was collected from the unfertilized rye plot of the long-term Eternal Rye Cultivation experiment at Halle (Saale), Germany. Controlled experimental modification of SOM in this soil sample was established by changing the polarity character of SOM in two different ways (Ahmed et al., 2012). Firstly, a hot water extract (HWE) fraction, containing mostly polar functional groups such as carbohydrates, N-containing compounds, and peptides, was removed from the original soil sample. Then, this HWE was added into different samples of the same original soil in two different amounts. These amounts were three and six times the HWE content in the original soil sample, and produced the samples soil + 3 HWE and soil + 6 HWE. This procedure enriched the SOM in mostly polar oxygen-containing functional groups (Ahmed et al., 2012). Secondly, thermal heating by off-line pyrolysis at 600 °C of the original soil sample was performed in order to decrease its polar character. These soil samples were characterized using a multi-methodological approach combining elemental analysis, pyrolysis-field ionization mass spectrometry (Py-FIMS), and C and N K-edge X-ray absorption near-edge structure spectroscopy (XANES). These analyses provided evidence for systematically altered SOM compositions (Ahmed et al., 2012) which probably affect the binding of HCB to SOM.

### 2.2. Adsorption of hexachlorobenzene

For the adsorption experiments, a stock solution of 100 μg/ml HCB (CAS number 118-74-1, Sigma-Aldrich) was prepared in n-hexane. Different initial HCB concentrations were prepared by dilution of this HCB stock in $CaCl_2$ solution.

One gram of each air-dry soil sample (original soil, soil + 3 HWE, soil + 6 HWE, and pyrolyzed soil) was mixed with 30 ml of different initial concentrations of HCB in Teflon tubes. These HCB concentrations are 0.25, 0.50, 0.75, 1.00, 2.00, 3.00, 4.00, and 5.00 μg/ml. They were prepared in 0.01 M $CaCl_2$ solution using the HCB stock solution in n-hexane. To suppress microbial activity, 100 μl of 100 mg/l $NaN_3$ was added to each suspension. These soil solutions have acidic character with pH values around 5.3. In addition, two blank measurements were also processed at the same time. One of them with 5.00 μg/ml HCB without soil sample and the other with soil sample at 0.00 μg/ml HCB. All the adsorption and blank measurements were done in duplicates. The suspensions were shaken at 22 rpm using a special overhead rotator (GFL overhead rotator 3040) for 24 h. Then they were centrifuged for 20 min at 3500 × g. For HCB analysis, 50 μl of n-hexane layer, containing HCB, was sampled from each tube. HCB concentration was determined by using a G1530A (Agilent Technologies, Santa Clara, USA) gas chromatograph with two parallel capillary columns with different polarities, each equipped with an electron capture detector (ECD). The separation was performed by a 60 m Varian FactorFour capillary column VF-5 ms (5% phenylmethyl- and 95% dimethylpolysiloxane) with