



When desorption does not meet sorption: accumulated free energy as a basis for quantitative analysis of hysteretic behavior of organic compounds in soils

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Sorption-desorption hysteresis, widely observed phenomenon in soil environment, is well known to affect the environmental behavior and fate of multiple organic compounds, including pesticides, the products of their transformation as well as many other chemicals reaching the field (e.g. pharmaceuticals, toxins, hormones). The appearance of hysteresis might represent artifacts due to the loss of the system integrity or be related to slow kinetics of sorption and/or desorption and diffusion into soil and soil organic matter aggregates. “True” sorption-desorption hysteresis associated with apparently equilibrated distribution of solute molecules between sorbent and solution phases was related in the earlier literature to formation of metastable sorbed states that may finally control organic compound-soil interactions. The appearance of such metastable states resembles often intuitively claimed “changes of sorbent” along sorption. This work presents a new and original approach (Chemosphere, 2019, 215: 490-499) demonstrating how these changes in a sorbent, due to its interactions with sorbing molecules, may be easily expressed in terms of free energy differences thus proposing way for quantifying and modeling “true” sorption-desorption hysteresis. When sorption-desorption sequence (demonstrating a non-closed loop) is supposed to represent formation of metastable states, \ln (solution concentration) is to be integrated with respect to sorbed concentration along the sequence to provide a free energy quantity. This accumulated free energy is essentially assigned to changes in a sorbent structure/architecture responsible for formation of metastable sorbed states. This approach leads to particularly simple formulas when the isotherms follow the Freundlich model trends, but it is not limited by any specific isotherm model. Its applicability is illustrated by examining the experimental data on sorption/desorption of pesticides (triazines and ureas) and aromatic hydrocarbons on soils and sediments thus showing how better understanding of the role of compound molecular structure and sorbate-sorbent interactions may be reached by using this novel approach. In particular, computed free energy quantities demonstrate a parallelism in ability of pesticide molecules to induce perturbations in different sorbents. This work also explains when and why commonly used empirical indices for quantifying sorption-desorption hysteresis may lead to erroneous conclusions.