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Sorption/desorption characteristics of hydrophobic organic compounds on black carbon containing soil and carbonaceous materials

Guohui Wang, Peter Grathwohl, Sybille Kleineidam

Center for Applied Geoscience, University of Tübingen, Germany

(grathwohl@uni-tuebingen.de Phone: +49-7071-2975429 Fax: +49-7071-5059)

Black carbon (BC) and carbonaceous materials are nowadays found in many soil and sediment matrix and they are important carriers of organic pollutants in natural environment. The sorption/desorption characteristics of hydrophobic organic compounds on theses geosorbents play an important role in contaminant fate and transport. In this study batch sorption/desorption experiments were conducted on three BC related samples: German chernozem, lignite and high volatile bituminous coal (HC), where the first two samples were recommended (in a symposium, University Washington) as the BC reference materials and the materials potentially creating BC in black carbon analysis, respectively. In addition to elemental composition analysis (organic carbon, nitrogen and hydrogen contents) for all the samples, a detailed organic phase petrography analysis on German chernozem was carried out by using optical microscopes method, and found that the charred organic carbon (e.g., recent and fossil charcoal, coke carbon forms and char) accounts for about 30% of the total organic carbon in this soil matrix. For the two carbonaceous samples, the specific surface area, pore as well as micro-pore volumes were also determined by BET method.

Batch equilibrium sorption/desorption isotherms were measured for phenanthrene at four different temperatures (4˚C, 20˚C, 46˚C and 77˚C) using a new designed experimental protocol. Differently from conventional decant-and-refill batch method, the sorption/desorption process within a closed reaction vials can be conducted driven by temperature changes. Based on the isotherm parameters measured at different temperatures, the sorption/desorption isosteric heats (enthalpy) of phenanthrene on above sorbents were calculated with Clausius-Clapeyron equation, which gives insights into

the sorption/desorption processes in an energetic view. The sorption and desorption isotherms agree with each other very well at all temperature steps. The sorption capacity decreases with increasing temperature at rates of 12 – 36% per every 10˚C for different sorbents. All isotherms are nonlinear and a trend of greater linearity with increasing temperature was observed. The subcooled liquid solubility - normalized sorption/desorption isotherms at different temperatures collapsed well for each sample, and the normalized Freundlich coefficients ($\log K^*_{Fr}$) of 2.69, 4.87 and 4.99 were determined for German chernozem, lignite and HC samples, respectively. The determined enthalpy absolute values located in a range of 19 - 37 kJ/mol, which is comparable with the subcooled heat of solution. Although with a certain deviations, the enthalpy absolute values from sorption and desorption processes are very close. In addition to phenanthrene, the sorption coefficients of trichloroethene (TCE) and 1,4-dichlorobenzene (1,4-DCB) were also determined for these three samples at 20˚C.