Adsorption/Desorption Hysteresis in Organic Pollutant and Soil/Sediment Interaction

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Adsorption and desorption of pollutants to soil and sediment materials are major fate mechanisms. The hypothesis that adsorption and desorption are reversible processes has been tested. The organic pollutants naphthalene, phenanthrene, and p-dichlorobenzene have been studied in the laboratory using batch reactors at room temperature from a few hours to over 2 months. The adsorption experiments were at equilibrium within 1–4 days and could be modeled using simple linear isotherms with \( K_p \) values consistent with published \( K_{oc} \) and \( K_{swr} \) relationships. Desorption experiments were conducted with the contaminated sediments by successive dilutions. Desorption experiments varied from 1 day to 5 months, and observed desorption rates were from 1 to 3 orders of magnitude smaller than previously measured or predicted. If equilibrium were obtained during the desorption, typically over 82–99% of the adsorbed pollutant would have been desorbed, but generally only 30–50% of the adsorbed pollutant could be desorbed. These desorption results could not be explained by commonly invoked kinetic models or artifacts of the procedure. The possibility and consequences of such adsorption and desorption behavior being the result of either hysteresis or irreversible adsorption is discussed.

Introduction

Adsorption/desorption is often an important mechanism in the fate and transport of neutral hydrocarbon pollutants in the environment. In modeling pollutant transport, the adsorption/desorption process is often simplified by assuming what might be called ideal conditions of instantaneous equilibrium, isotherm linearity and desorption reversibility (1). However, many field and laboratory data deviate from that predicted by this simple model approach; as a consequence, the assumption of ideal behavior has been challenged by numerous researchers (1–7) and is the primary focus of the present paper.

Adsorption/desorption behavior, which does not conform to such a simple idea, has been attributed to several different factors, including the following: (a) varying adsorption energies, leading to isotherm nonlinearity (i.e., a Freundlich isotherm, see refs 1 and 5–6); (b) failure to attain equilibrium in either the adsorption or the desorption directions due to slow kinetics in either step (3, 4, 8–10); (c) chemisorption of the pollutants to various components of the soil matrix, causing apparently irreversible adsorption (1); (d) either biotic or abiotic degradation of the pollutant being studied, again causing an apparently irreversible adsorption (11, 12); (e) adsorption/desorption hysteresis (1, 13, 14); and (f) experimental procedures, such as centrifugation versus dilution (15). Only those ideas directly related to this research paper will be reviewed herein, but refs 1–4, 8, and 16–18 are recommended for further reading.

Adsorption nonlinearity has been studied extensively (1, 5, 11, 19), and the effect of this nonlinearity on pollutant transport has been investigated by several researchers (8, 9, 20). Adsorption nonlinearity is commonly fit to a Freundlich isotherm, with an exponent less than unity, although numerous other nonlinear isotherms are feasible (21, 22). If the true adsorption mechanism is such that it is correctly described by a Freundlich isotherm with an exponent less than one, the consequences concerning batch adsorption kinetics, transport, and fate can be substantial. For example, the leading edge of a pollutant breakthrough in groundwater will be substantially retarded versus that which would be predicted using a linear isotherm (8, 9). Similarly, the trailing edge of the flush-out curve would be much longer than that predicted using a linear isotherm. There would be a corresponding concentration-dependent effect upon several types of kinetics equations, e.g., those which depend upon the partition coefficient \( K_p \) and pore diffusion models. In practice, along with mechanistic considerations, the use of a Freundlich isotherm instead of a simple linear isotherm often causes the mathematics associated with the kinetics or with the transport modeling to be considerably more difficult. Also, there is no generally accepted procedure to estimate either the exponent or the partition coefficient for Freundlich isotherms as there is for linear isotherm partition constants. Therefore, there is a commensurate reluctance to use such a mathematical description, unless its use can be justified strongly (23).

With hydrocarbon pollutants and sediments, it is often observed in the laboratory that the desorption isotherm is not the same as the adsorption isotherm, and this difference is the basis for suggesting the existence of hysteresis. This type of hysteresis has been reported for several classes of compounds, including polycyclic aromatic hydrocarbons, chlorinated benzenes, pesticides, phenols, surfactants, halogenated aliphatic hydrocarbons, and PCBs (6, 7, 13, 17, 24, 25). Several authors have suggested that such reports of hysteresis are in fact generally a consequence of slow adsorption or desorption kinetics (1, 3, 4, 10). Karickhoff and Morris (26) used a two-compartment model, with equal adsorption intensity in each compartment, to account for the observed slow approach to equilibrium from either direction (portions of this model will be used later in the Results and Discussion section of this paper). Several empirical correlations have been used to relate rate constants to the partition coefficient (28–28). Models of radial pore diffusion have also been used to account for the slow kinetics. These radial diffusion models typically differ in the way they treat the effective diffusion coefficient, the porosity, and the tortuosity of the sediment particles (2–4, 8–10, 29). Adsorption and desorption time of minutes to years are predicted using these various kinetic approaches. To date, too few sediment/hydrocarbon systems have been studied experimentally over a sufficient range of variables, such as OC content and type, soil types and states of aggregation, pH and redox potential, temperature, and ionic strength and composition, to mention a few. In addition, changes in these parameters might affect the

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