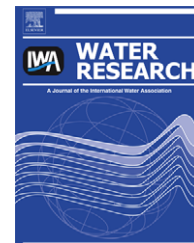


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Predicting organic carbon–water partitioning of hydrophobic organic chemicals in soils and sediments based on water solubility

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ABSTRACT

For predicting organic carbon–water partitioning of organic pollutants in soils and sediments, a simple empirical relationship is derived from Raoult's law and fitted to data sets of experimental organic carbon normalized partition coefficients (K_{oc}) and aqueous solubilities (S_i) of 64 hydrophobic organic chemicals (HOCs) from literature including mono- and polycyclic aromatic hydrocarbons, halogenated monoaromatic and alkyl hydrocarbons, and polychlorinated biphenyls. Although over 5 orders of magnitude are covered in sorptivity ($\log K_{oc}$), the new relationship ($\log K_{oc} = -0.85 \log S_i - 0.55$) predicts K_{oc} with an average absolute deviation of only 0.23 log units. The relationship between K_{oc} and S_i is inverse and slightly nonlinear. The product of K_{oc} times S_i ($= K_{oc}^*$, which indicates the theoretical maximum contaminant loading at its solubility limit per unit mass of organic carbon) is 0.098 kg kg^{-1} and 0.012 kg kg^{-1} for compounds with water solubilities of 1 g L^{-1} and $1 \mu\text{g L}^{-1}$, respectively.

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1. Introduction

Many organic chemicals occur ubiquitously because of their persistency in the environment. Hydrophobic organic compounds (HOCs) receive much attention because of their tendency to not only accumulate in the food chain, but in the soils and sediments as well, where strong sorption may limit their availability for biodegradation. HOCs of interest include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins, polybrominated flame retardants and other hydrocarbons. Hydrophobic chlorinated solvents (chlorinated C1–C2 alkanes) and monoaromatic

compounds (benzene, toluene, xylene, etc.) are relevant for subsurface and especially groundwater contaminations.

Fate and transport of these compounds strongly depend on their physicochemical properties (e.g., water solubility, vapor pressure, etc.) and the sorption capacity of soil and sediment solids (Schwarzenbach and Westall, 1981). Sorption determines the distribution of an organic chemical between the soil/sediment solids and water, and thus the retardation of a compound in diffusive and advective transport as well as its bioavailability (Allen-King et al., 2002; Chiou et al., 1979; Karickhoff et al., 1979; Moss et al., 2002). It is commonly agreed meanwhile, that sorption in soils often is due to both,

Abbreviations: HOC, Hydrophobic organic chemical; PAH, Polycyclic aromatic hydrocarbon; PCB, Polychlorinated biphenyl; LFER, Linear free energy relationship; op-LFER, One parameter linear free energy relationship; pp-LFER, Polyparameter linear free energy relationship; MAH, Monoaromatic hydrocarbon; X-MAH, Halogenated monoaromatic hydrocarbon; X-AH, Halogenated alkyl hydrocarbon; SLS, Subcooled liquid solubility.

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Nomenclature

K_{oc}	organic carbon normalized sorption coefficient [L kg ⁻¹]
K_{ow}	octanol/water partitioning coefficient
S_i	water solubility of the compound i [mol L ⁻¹], [g L ⁻¹], [kg L ⁻¹]
K_{om}	organic matter normalized partition coefficient
$K_{o/w}$	partitioning coefficient (organic solvent/water)
V_o	molar volume of the organic mixture [L mol ⁻¹]
$\gamma_{i,o}$	activity coefficient of the compound i in the organic mixture [-]
V_i	molar volume of the compound i [L mol ⁻¹]
M_i	molecular weight of the compound i [g mol ⁻¹]
ρ_i	density of the compound i in its liquid form [g L ⁻¹]
$C_{i,o}$	concentration of the compound i in the organic mixture [g kg ⁻¹]
$C_{i,wsat}$	aqueous concentration of the compound i at saturation [g kg ⁻¹]
$\chi_{i,o}$	mole fraction of the compound i in the organic mixture [-]
$f_{i,o}$	mass fraction of the compound i in the organic mixture [kg kg ⁻¹]
M_o	molecular weight of the organic mixture [g mol ⁻¹]
$C_{i,oc}$	concentration of the compound i in the organic carbon [g kg ⁻¹]
$C_{i,wt}$	concentration of the compound i in water [g kg ⁻¹]
b' (K_{oc}^*)	maximum loading of the compound i onto organic carbon at its solubility limit [kg kg ⁻¹]
a	empirical exponent in Eq. (8)
b	empirical coefficient in Eq. (8)
$ \Delta _{avg}$	average absolute deviation
R	correlation coefficient

adsorption and partitioning, where at high concentrations the partitioning mechanism prevails and at very low concentrations adsorption is dominant (Allen-King et al., 2002; Kleineidam et al., 2002; Xia and Ball, 1999). Both mechanisms combined can be fitted very well by the Freundlich sorption model (Allen-King et al., 2002; Kleineidam et al., 2002; Xia and Ball, 1999). As outlined by Allen-King et al. (2002), in principle one measurement at low concentrations – in the adsorption domain – would be sufficient to characterize the Freundlich sorption isotherm provided that the partitioning part can be predicted independently. The latter is the focus of this study – partitioning is quantified by the K_{oc} -value, which is the ratio between the concentration of a chemical sorbed by the soil normalized to its organic carbon content and the respective equilibrium concentration in water. An accurate prediction of K_{oc} is essential for environmental risk assessment as well as for modeling the transport of pollutants. Although experimental data are always preferred, it is often difficult, time consuming and expensive to measure

sorption for different combinations of sorbate-sorbent systems.

The fact that organic carbon normalized sorption coefficients (K_{oc}) correlate well with other compound properties, such as the octanol/water partitioning coefficient (K_{ow}) and the water solubility (S_i), lead to the development of empirical correlations to describe partitioning of hydrophobic compounds into organic matter (Karickhoff et al., 1979; Chiou et al., 1979, 1983, 1989; Kenaga and Goring, 1980). The majority of these models are based on linear free energy relationships (LFERs) between K_{oc} and other experimental partition coefficients as physicochemical descriptors (Schwarzenbach et al., 1993; Leo et al., 1971), denoted here as one parameter correlations (op-LFER). In op-LFER, organic carbon or organic matter normalized partition coefficients (K_{oc} or K_{om}) are reported to correlate with K_{ow} (Chiou et al., 1979, 1983; Karickhoff et al., 1979; Moss et al., 2002; Briggs, 1969, 1981; Karickhoff, 1981; Brown and Flagg, 1981; Schellenberg et al., 1984; Sabljic, 1987; Lagas, 1988; Sabljic et al., 1995; Seth et al., 1999; Gerstl, 1990; Xia, 1998; Means et al., 1982) or S_i (Chiou et al., 1979, 1983; Briggs, 1969, 1981; Means et al., 1982). Sabljic (1987) noted that the diversity of these $K_{oc} - K_{ow}/S_i$ relationships is due to the low precision and wide variance of the experimental K_{ow} and S_i data. Therefore, he suggested excluding low precision K_{ow} and S_i data in developing correlations for predicting K_{oc} . Xia (1998) evaluated a large number of K_{oc} studies and selected 418 values for 53 HOCs from data published over the last several decades.

Additionally, polyparameter (pp) correlations were also developed, which take into account various parameters that describe chemical properties, such as H-bond donor/acceptor parameters, dipole-dipole interactions, polarizability, etc. Among several pp-relationships proposed (Nguyen et al., 2005; Park and Lee, 1993; Baker et al., 1997; Poole and Poole, 1999), Nguyen et al. (2005) presented a comprehensive data set of 353 K_{oc} -values for 75 different chemicals, including both HOC and more polar compounds. Even though they predict K_{oc} reasonably well, five chemical descriptors are needed compared to only one in op-LFERs. Also, many of these descriptors are still unknown for numerous environmentally hazardous chemicals.

The objective of this study is to show how a very simple op-LFER model can be derived from Raoult's law which predicts the partitioning behavior of a wide range of nonpolar HOCs in organic matter based on the compounds' water solubility. With that, we follow the proposal by Chiou et al. (2005) to estimate K_{ow} from S_i for the prediction of K_{oc} .

2. Theory

Partitioning is usually derived from Raoult's law for organic solvent mixtures (Chiou et al., 2005; Schwarzenbach et al., 2002):

$$K_{o/w} = \frac{1}{S_i V_o \gamma_{i,o}} \quad (1)$$

$K_{o/w}$, S_i , V_o , and $\gamma_{i,o}$ denote the partitioning coefficient, the water solubility [here in mol L⁻¹] of a solute i , the molar volume of the organic mixture [L mol⁻¹] and the activity

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