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Review

# A framework for assessing the retardation of organic molecules in groundwater: Implications of the species distribution for the sorption-influenced transport

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## HIGHLIGHTS

- Assessment of (ionizable) organic compound retardation based on chemical character
- Compilation of existing concepts for the estimation of sorption coefficients
- Comprehensive guide for evaluating the retardation of arbitrary organic molecules

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## ABSTRACT

The pH-dependent molecule speciation (charge state) in solution strongly influences the transport of ionizable organic compounds in the aquatic environment. Therefore, the sorption behavior is complex and reliable predictions only based on physico-chemical sorbate, sorbent and solution properties are challenging. A short overview of underlying sorption processes causing retardation during the solute transport in aquifers is completed by a description of approaches for estimating respective sorption coefficients/retardation factors and discussed together with their limitations. Based on these initial considerations, a systematic framework is proposed, which allows the assessment of transport properties of organic molecule species by their chemical nature (neutral, acidic, basic, ampholytic). As a result, the transport properties of many (ionizable) organic molecules of interest can be assessed and even first presumptions for the sorption behavior of new and not yet investigated molecules can be derived.

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## 1. Introduction

Since the 1970s, the prediction of sorption and thus transport properties of non-ionizable compounds has already successfully been performed by using empirical correlations between the *n*-octanol water partitioning coefficient log $K_{OW}$ and the organic carbon normalized water partitioning coefficient log $K_{OC}$ (Chiou et al., 1979; Karickhoff et al., 1979). In the last years, however, especially ionizable and thus highly water soluble compounds, for which prediction is very complex, have gained more and more attention due to their ubiquitous occurrence in the aqueous environment (e.g., Csiszar et al., 2011; Fatta-Kassinos et al., 2011; Huntscha et al., 2012; Schaffer and Licha, 2014). It can be roughly assumed that around one half of all organic compounds are able to form ions under environmentally relevant pH conditions (Manallack, 2007, 2009; Franco et al., 2010). Since many physical, chemical, and physicochemical properties (e.g., hydrophilicity, water solubility, sorption affinity, volatility, reactivity) strongly depend on the ionic character and thus charge state of the considered molecule, a considerably different environmental fate can be expected compared to non-ionized molecules (Fatta-Kassinos et al., 2011; MacKay and Vasudevan, 2012; Schaffer and Licha, 2014; Schaffer et al., 2015). This applies, beside degradation/transformation, especially for sorption processes, such as partitioning, ion exchange, and complexation, which have substantial consequences for the retardation of such species during the transport in groundwater.

This article reviews current strategies for predicting sorption coefficients of organic molecules. Their limitations and implications for the transport in the subsurface are critically discussed. The synthesis of the reviewed literature with the systematic consideration of underlying processes led to a framework in form of a flowchart for the structure- and species-based assessment of sorption and transport properties of arbitrary organic compounds in porous (unconsolidated) aquifers. Common applications are river bank filtration sites, soil aquifer treatment and managed aquifer recharge systems, landfill leachates or industrial facilities. The framework has practical importance for cases where data on organic compounds are scarce. Due to the various and often unknown factors influencing biotransformation processes, degradation is not considered and the presented work only focuses on the sorption-influenced transport. Consequently, all molecules are assumed to be persistent in the following discussions.

## 2. Sorption as transport process leading to retardation

Sorption describes the net enrichment of chemical species from a fluid phase inside or onto the surface of a solid (or liquid) phase (Worch, 2012). Two main sorption processes can generally be distinguished by the type of attraction forces governing the sorption equilibrium: i) hydrophobic sorption onto uncharged sites of sorbent organic matter SOM; and ii) ionic (electrostatic) sorption onto variably or permanently charged surfaces of mineral phases, metal oxides or SOM.

Hydrophobic sorption is an entropy-driven process where the sorption of neutral (non-ionized) sorbates on hydrophobic surfaces is often explained by the occurrence of non-specific van-der-Waals interactions (dipole and/or induced-dipole interactions) (e.g., Goss and Schwarzenbach, 2001; Worch, 2012). Non-hydrophobic sorption, in contrast, can be mainly attributed to electrostatic sorption mechanisms where coulomb forces play a crucial role, such as ion exchange, surface complexation, electron donor–acceptor mechanisms (e.g. hydrogen bonding), ligand exchange, cation bridging, and charge-transfer processes (Senesi, 1992; Tolls, 2001; Kah and Brown, 2007; MacKay and Vasudevan, 2012). Hence, these processes strongly depend on the speciation (charge state) of the ionizable organic sorbate (bases, acids, ampholytes).

Independent from the nature and type, however, all sorption processes have in common that they lead to a retardation of the sorbates relative to the groundwater flow and non-sorbing (conservative) solutes, respectively, during their migration in the subsurface. This sorption-influenced transport (without degradation) can mathematically be described for saturated porous media based on mass conservation considerations by the advection-dispersion-equation (ADE) including a sorption term on the right-hand side:

$$\frac{\partial c}{\partial t} = -\overline{v} \cdot \vec{\nabla} c + \vec{\nabla}\left(D\vec{\nabla} c\right) - \frac{\rho}{\theta_e} \cdot \frac{\partial q}{\partial t} \tag{1}$$

where $c$ is the solute concentration, $t$ is the time, $\overline{v}$ is the mean pore water velocity, $D$ is the hydrodynamic dispersion tensor (including hydromechanical dispersion and molecular diffusion), $\rho$ is the bulk density, $\theta_e$ is the effective porosity and $q$ is the sorbent loading (solid phase concentration). All sorption processes are usually summarized and a retardation factor $R$ can be defined:

$$R\frac{\partial c}{\partial t} = -\overline{v} \cdot \vec{\nabla} c + \vec{\nabla}\left(D\vec{\nabla} c\right). \tag{2}$$

This factor represents the ratio of $\overline{v}$ and the apparent solute transport velocity of the concentration front. Assuming a local sorption equilibrium (instantaneous sorption), the sorption rate $\partial q/\partial t$ in Eq. (1) can be expressed by means of sorption isotherm models resulting in different formulations for $R$ (Table 1).

In contrast to Eq. (3) (Henry isotherm), $R$ is concentration-dependent for the non-linear isotherms (Freundlich and Langmuir isotherms) in Eqs. (4) and (5) and, therefore, also time- and space-dependent as a consequence of dispersive effects. The respective breakthrough curves generally show a stronger tailing/fronting or front sharpening (e.g., Langmuir or Freundlich isotherms with $n \neq 1$) than breakthrough curves underlying linear sorption (Bürgisser et al., 1993; Appelo and Postma, 2005) and can usually only be modeled numerically. The same applies for transport problems where the sorption kinetics cannot be neglected (Worch, 2004; Rahman and Worch, 2005). Due to this increasing complexity, sorption is mostly assumed to be linear and in equilibrium (Eq. (3), use of $K_d$) in the considered concentration range (low concentrations) for practical purposes, especially when analytical solutions of the ADE are intended to be used. Consequently, the proposed framework (see Section 4; Fig. 1) is tailored for the application in porous

**Table 1**
Expressions of $R$ for common sorption isotherm models.

| Sorption model | Isotherm equation | Sorption rate $\partial q/\partial t$ | Retardation factor $R$ | Eq. |
|---|---|---|---|---|
| Henry | $q = K_d \cdot c_{eq}$ | $\frac{\partial q}{\partial t} = K_d \cdot \frac{\partial c_{eq}}{\partial t}$ | $R = 1 + \frac{\rho}{\theta_e} \cdot K_d$ | (3) |
| Freundlich | $q = K_F \cdot {c_{eq}}^n$ | $\frac{\partial q}{\partial t} = K_F \cdot \frac{\partial c^n}{\partial t}$ | $R = 1 + \frac{\rho}{\theta_e} \cdot K_F \cdot n \cdot {c_{eq}}^{n-1}$ | (4) |
| Langmuir | $q = \frac{K_L \cdot q_{\max} \cdot c_{eq}}{1+K_L \cdot c_{eq}}$ | $\frac{\partial q}{\partial t} = \frac{K_L \cdot q_{\max}}{1+K_L \cdot c_{eq}} \cdot \frac{\partial c_{eq}}{\partial t}$ | $R = 1 + \frac{\rho}{\theta_e} \cdot \left[\frac{K_L \cdot q_{\max}}{\left(1+K_L \cdot c_{eq}\right)^2}\right]$ | (5) |

$c_{eq}$ = equilibrium concentration, $K_d$ = distribution coefficient, $K_F$ = Freundlich sorption coefficient, $K_L$ = Langmuir sorption coefficient, $n$ = Freundlich exponent, $t$ = time, $q$ = sorbent loading, $q_{\max}$ = maximal sorbent loading, $R$ = retardation factor, $\rho$ = bulk density, $\theta_e$ = effective porosity.