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Reconciliation of expressions for the modified
retardation factor and incorporation of non-linear
contaminant sorption to the stationary phase

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Reconciliation of expressions for the modified retardation factor and incorporation of non-linear contaminant sorption to the stationary phase

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Abstract

The retardation factor describes the average velocity of a sorbing contaminant in groundwater relative to the average velocity of groundwater. The modified retardation factor (R' or R^*) describes the average velocity of a sorbing contaminant relative to groundwater in the presence of a carrier that binds the contaminant and facilitates its transport. Dissolved organic matter and particulate colloids are examples of potential facilitating carriers. The modified retardation factor R' concerns the case when sorption of the carrier itself to the stationary phase is negligible, whereas R^* accounts for significant sorption of a facilitating carrier to the stationary phase, and so represents a magnitude less than R , but greater than R' . A well-cited expression for R^* is shown to differ in form and behavior relative to a lesser known expression for R^* , and the bounds of applicability of these expressions are examined. The lesser-known expression for R^* is shown to be more broadly applicable in its ability to describe situations where carrier sorption to the stationary phase is significant, and even rivals or exceeds that of the contaminant. The well-known expression for R^* is shown to be not applicable to situations involving significant sorption of the carrier. The derivation of the expression for R^* presented in this paper is given by two separate methods used to develop the previously published expressions, in order to relate the presented and

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previously published expression to each other. The expression is extended to include non-linear contaminant sorption to the stationary phase, and predictions from this expression are compared to a set of experimental data. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Groundwater; Retardation factor; Sorption

1. Introduction

In describing the transport of a contaminant in groundwater, the concept of retardation is used. Retardation results from interaction of the contaminant with the stationary phase, for instance, soil or sediment. Early models of contaminant transport regarded contaminant retardation as being determined solely by the strength of interaction of the contaminant with the porous media. More recently however, the ability of dissolved natural organic matter and colloidal material to bind, and facilitate the transport of, various contaminants has been recognized (Enfield et al., 1989; Magee et al., 1991; Corapcioglu and Jiang, 1993; Johnson and Amy, 1995). The decreased retardation of a contaminant due to facilitated transport was initially quantified as a function of the strength of contaminant association with the stationary phase and the carrier phase (Hutchins et al., 1985); the term carrier denotes mobile phases other than water. Later, the effect of interaction of the carrier with the stationary phase was also included (Magee et al., 1991). This latter form of the modified retardation factor (R^*) for facilitated transport of a contaminant is, however, limited in its range of applicability, as described below. In this paper, we introduce an expression for R^* which is applicable across all ranges of contaminant and carrier interaction with the stationary phase. We compare the predictions from this new expression to those from previously published expressions for R^* , and reconcile their differences. We also extend the new expression for R^* to include the case of a non-linear contaminant sorption isotherm (Langmuir or Freundlich) and compare predictions from this model to a set of laboratory data.

2. Background

The retardation factor of a contaminant in a given soil–water system represents the average transport velocity of the contaminant (v_{av}) relative to that of water (v_w). In the case where the contaminant obeys a linear isotherm, the retardation factor (R) is quantified directly from the observed strength of interaction of the contaminant with the stationary phase (K_{sed}^c), as shown below:

$$R = 1 + K_{sed}^c \frac{\rho_b}{\theta} \quad (1)$$

where ρ_b is the sediment bulk density (M_{sed}/L_{REV}^3), θ is the volumetric water content

$(L_w^3/L_{REV}^3) M_{sed}$ refers to the mass of the stationary phase (sediment in this case), and 'REV' refers to the representative elementary volume.

The retardation factor is therefore an equilibrium parameter, and is directly related to the equilibrium distribution coefficient for the contaminant between water and sediment, K_{sed}^c , defined as:

$$K_{sed}^c = \frac{M_s^c/M_{sed}}{M_w^c/V_w} \quad (2)$$

where M_w^c = mass of contaminant in the aqueous phase; M_s^c = mass of contaminant on the stationary phase; V_w = the volume of the aqueous phase.

The equilibrium constant for this interaction is often referred to as K_d ; however, for the sake of clarity, this convention is modified in this paper. The retardation of a contaminant is easily discerned in experiments that monitor the breakthrough of a contaminant in the effluent from a packed soil or sediment column to which the contaminant is continuously introduced. The value of the retardation factor for a contaminant in a given soil–water system is determinable by integration of the area above the breakthrough curve to a relative concentration (C/C_0) of unity (Nkedi-Kizza et al., 1987).

In a more complicated system, that includes soil, water, and dissolved organic matter or mobile colloids, binding of contaminant by the mobile carrier will reduce the retardation factor. Hutchins et al. (1985) account for this effect under the assumption that the mobile carrier travels at the same velocity as the groundwater. The resulting expression for the modified retardation factor under these conditions, denoted R' (Magee et al., 1991) is:

$$R' = 1 + \frac{K_{sed}^c \frac{\rho_b}{\theta}}{1 + K_{OM}^c [DOM]} \quad (3)$$

where K_{OM}^c is the equilibrium distribution constant for the contaminant between water and organic matter (OM):

$$K_{OM}^c = \frac{M_{OM,w}^c/M_w^{OM}}{M_w^c/V_w} \quad (4)$$

where $M_{OM,w}^c$ = mass of contaminant in OM, M_w^{OM} = mass of OM in the aqueous phase and where [DOM] is the aqueous concentration of the mobile carrier (dissolved organic matter in this case).

$$[DOM] = \frac{M_w^{OM}}{V_w} \quad (5)$$

Magee et al. (1991) recognized that dissolved organic matter itself may interact with the

Table 1
Experiment parameters from the work of Magee et al. (1991)

K_{sed}^{OM} (ml/g)	K_{sed}^c (ml/g)	K_{OM}^c (l/mg)	ρ_b/θ (g/ml)	[DOM] (mg/l)
0.6	16.0	0.0438	4.38	85.8

stationary phase, and that the degree of organic matter interaction with the stationary phase causes the observed retardation factor to change. The modified retardation factor which accounts for interaction of the carrier phase with the stationary phase is denoted R^* :

$$R^* = \frac{1 + K_{sed}^c \frac{\rho_b}{\theta} + K_{OM}^c [DOM]}{1 + K_{sed}^{OM} \frac{\rho_b}{\theta}} \quad (6)$$

where K_{sed}^{OM} is the equilibrium constant for distribution of organic matter between water and sediment:

$$K_{sed}^{OM} = \frac{M_s^{OM}/M_{sed}}{M_w^{OM}/V_w} \quad (7)$$

and M_s^{OM} = mass of OM on the sediment (stationary phase). The behavior of this latter expression (Eq. (6)) can be examined using data from Magee et al. (1991), as shown in Table 1. By modifying the value of K_{sed}^{OM} from zero (no interaction of organic matter with stationary phase) to twice that of K_{sed}^c (organic matter interaction with the stationary phase twice as strong as that for the contaminant), a non-linear dependence of R^* on carrier sorption is observed (Fig. 1). Note that when K_{sed}^{OM} is zero, R^* is equal to R' (maximum facilitation, no carrier interaction with sediment). When K_{sed}^{OM} is equal to

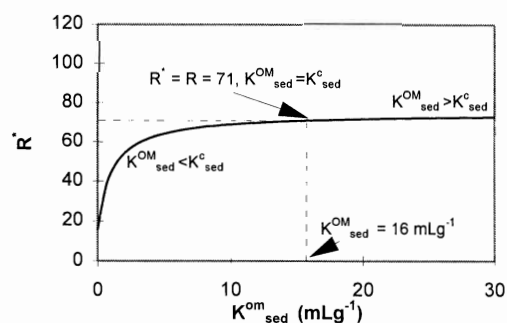


Fig. 1. Prediction of R^* by Eq. (6), using the data in Table 1, but varying the strength of carrier sorption to the stationary phase.

K_{sed}^c , then R^* is equal to R (no facilitated transport, carrier and contaminant average velocities are equal). Beyond the point at which carrier interaction with the stationary phase exceeds that of the contaminant, the value of R^* reaches a limiting value. The limiting value of R^* will be greater than or equal to R , depending upon the magnitude of the product $K_{\text{OM}}^c[\text{DOM}]$, and will be independent of the amount by which $K_{\text{sed}}^{\text{OM}}$ exceeds K_{sed}^c (the amount by which carrier sorption to sediment exceeds contaminant sorption to sediment). This asymptotic behavior is surprising in that it is difficult to explain why a carrier that interacts very strongly with the stationary phase would not further retard an associated contaminant. The purpose of this paper is to show that this asymptotic behavior indicates limitations in the applicability of the expression (Eq. (6)) for R^* . This paper will also describe an expression for R^* which is broadly applicable, and will reconcile the differences between the expressions.

3. Derivation of expressions for R^*

Corapcioglu and Jiang (1993) developed an expression for R^* from mass balance equations for contaminant transport in groundwater:

$$R^* = \frac{1 + k_5 C_c + \frac{\rho_b}{\theta} K_3 + \frac{\rho_b}{\theta} k'_6 k_4 C_c}{1 + k_5 C_c} \quad (8)$$

where C_c is the mass concentration of suspended colloids in the aqueous phase, and the parameters 'k' are equilibrium distribution coefficients: k_3 for interaction of dissolved contaminant with the stationary phase, k_4 for interaction of dissolved contaminant with immobile colloids, k_5 for interaction of dissolved contaminant with the mobile colloids, and k'_6 for interaction of colloids with the stationary phase, defined in terms of volumetric fraction of deposition. We must note that the dimensions of the parameter k_6 (from which k'_6 is developed) should have the units $L_{\text{water}}^3 L_{\text{colloid}}^3 / M_{\text{colloid}} L_{\text{REV}}^3$ rather than $L_{\text{water}}^3 / M_{\text{sediment}}$ (Corapcioglu and Jiang, 1996). To rectify the perceived dimensional inconsistencies on Eq. (8), as well as to resolve the limitations inherent in Eq. (6), we present an expression for R^* developed by two different means in Appendices A and B:

$$R^* = \frac{1 + K_{\text{sed}}^c \frac{\rho_b}{\theta} + K_{\text{OM}}^c [\text{DOM}] + K_{\text{OM}}^c K_{\text{sed}}^{\text{OM}} [\text{DOM}] \frac{\rho_b}{\theta}}{1 + K_{\text{OM}}^c [\text{DOM}]} \quad (9)$$

Appendix A derives this expression (Eq. (9)) using the method Magee et al. (1991) employed to derive Eq. (6). Appendix B derives the expression using the method employed by Corapcioglu and Jiang (1993) to develop Eq. (8). The expression given herein, and the expressions offered by Magee et al. (1991) and Corapcioglu and Jiang (1993) concern the introduction of a potential carrier (i.e., dissolved OM or particulate

colloids) to a system in which the carrier is not initially at steady state with respect to interaction with the stationary phase. Examples of such systems may include the introduction of dissolved exogenous OM to an aquifer, or the mobilization of colloids within an aquifer by infiltration of waste or low ionic strength water. In a system where the carrier is at steady state with respect to interaction with the stationary phase, transport of the carrier would not be retarded relative to groundwater, and Eq. (3) would apply. The effect of the carrier initially associated with the stationary phase is accounted for in the value K_{sed}^c . Sorption of introduced carrier, which is not at steady state with respect to interaction with the stationary phase, then provides additional stationary phase that binds the contaminant and is accounted for according to $K_{OM,s}^c$ in Eq. (10), which in Eq. (9) is assumed equal to $K_{OM,w}^c$. The use of single constants to describe contaminant interaction with the stationary phase and carrier, limits the applicability of these expressions to situations in which contaminant interaction with the stationary and carrier phases is quantifiable using a linear isotherm. This assumption often holds when the contaminant is a hydrophobic organic compound and the carrier is dissolved OM (Chiou et al., 1986; Backhus and Gschwend, 1990; Schlautman and Morgan, 1993; Mader et al., 1997). The use of a linear constant to describe carrier interaction with the stationary phase is only a rough approximation in the case of particulate colloids (Harvey and Garabedian, 1991; Johnson et al., 1996), and may apply only in cases of mild OM sorption to the stationary phase (Jardine et al., 1992; Gu et al., 1994). The use of equilibrium constants K_{sed}^c , K_{sed}^{OM} , $K_{OM,w}^c$, and $K_{OM,sed}^c$ requires that these mass transfer processes achieve local equilibrium. This assumption typically holds for the phase changes quantified by $K_{OM,w}^c$, and $K_{OM,sed}^c$ (Schlautman and Morgan, 1993; Johnson, 1997). Whether the local equilibrium assumption holds for the mass transfer processes quantified by K_{sed}^c and K_{sed}^{OM} depends upon properties of the contaminant, including its hydrophobicity (Schlautman and Morgan, 1993; Backhus and Gschwend, 1990), properties of the OM, including its molecular weight, charge, and aromaticity (Jardine et al., 1992; Dunnivant et al., 1992; Gu et al., 1994; McCarthy et al., 1996), the f_{oc} and intraparticle porosity of the stationary phase (Ball and Roberts, 1991), as well as the mineralogy and surface chemistry of the stationary phase (Murphy et al., 1990). Despite the many potential approximations made in utilizing linear equilibrium constants to describe phase changes in the system, the expression for R^* is a useful concept, and has been validated in experimental studies (Magee et al., 1991; Corapcioglu and Jiang, 1993; Johnson and Amy, 1995).

An extended expression that includes the effect of pore size exclusion, or charge exclusion, $R^{* *}$, is also included in Appendix A. Additionally, the derivation of Eq. (9) assumes that sediment sorbed organic matter has the same affinity for hydrophobic organic compounds (HOC) as does aqueous organic matter. This assumption was made in order to allow comparison with Eq. (6), however, it is not a necessary assumption. The assumption was made in the derivation of Eq. (6) (Magee et al., 1991) to simplify the system. More recent investigations of distribution constants for polycyclic aromatic hydrocarbons between water and dissolved humic substances (Schlautman and Morgan, 1993) indicate that distribution constants for PAH with sorbed humics are about one-half those for the dissolved form of the same humic substance. By differentiating between the equilibrium distribution constant for HOC between water and aqueous OM, $K_{OM,w}^c$,

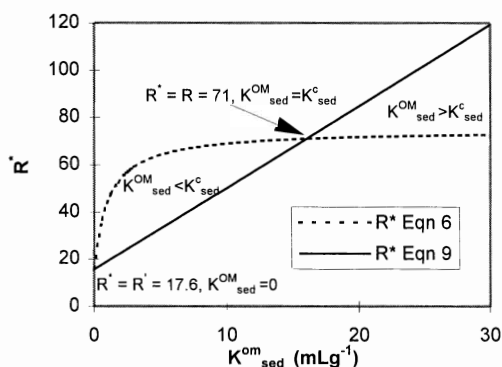


Fig. 2. Comparison of R^* predictions from Eqs. (6) and (9), using the data from Table 1, but varying the strength of carrier sorption to the stationary phase.

and the equilibrium distribution constant for HOC between water and sediment-sorbed OM, $K_{OM,s}^c$, a more general formula is obtained:

$$R^* = \frac{1 + K_{sed}^c \frac{\rho_b}{\theta} + K_{OM,w}^c [DOM] + K_{OM,s}^c K_{sed}^{OM} [DOM] \frac{\rho_b}{\theta}}{1 + K_{OM,w}^c [DOM]} \quad (10)$$

Eq. (10) allows the contaminant affinity to differ between aqueous OM and sorbed OM. Eq. (9), however, is the expression of interest presently since the assumption that $K_{OM,w}^c = K_{OM,s}^c$ was made by Magee et al. (1991) in deriving Eq. (6). Eqs. (9) and (10) may also be derived by back-substitution of equilibrium distribution constants into the series of kinetic equations that describe a system of sediment, water, contaminant, and dissolved organic matter as shown in Appendix B.

If one compares the predictions of R^* from Eq. (6), and the expression introduced above (Eq. (9)), significant differences are observed. Using the data in Table 1, and allowing carrier sorption to sediment, K_{sed}^{OM} , to vary (Fig. 2), shows that Eqs. (6) and (9) both predict facilitated contaminant transport when carrier sorption to sediment is less than contaminant sorption to sediment. Both equations predict that R^* will equal R

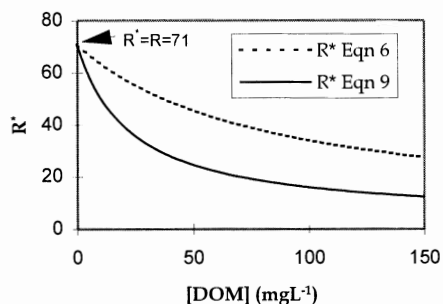


Fig. 3. Comparison of R^* predictions from Eqs. (6) and (9), using the data from Table 1, but varying the concentration of the carrier (dissolved organic matter, DOM).

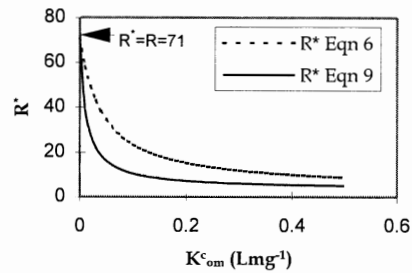


Fig. 4. Comparison of R^* predictions from Eqs. (6) and (9), using the data from Table 1, but varying the strength of contaminant sorption to the carrier.

(which is 71) when carrier and contaminant interactions with the stationary phase are equal ($K_{\text{sed}}^{\text{OM}}$ is equal to $K_{\text{sed}}^{\text{c}}$, or 16 ml/g). Both expressions also predict that R^* will equal R' (which is 17.6) when carrier does not sorb to sediment ($K_{\text{sed}}^{\text{OM}} = 0$). However, between the extremes of carrier interaction with the sediment being zero vs. being equal to that of the contaminant, the predictions of R^* from the two expressions diverge significantly. In this region, Eq. (9) predicts lower values of R^* relative to Eq. (6) for any given strength of carrier sorption to the stationary phase. Furthermore, when carrier interaction exceeds contaminant interaction with the stationary phase, that is when $K_{\text{sed}}^{\text{OM}}$ exceeds $K_{\text{sed}}^{\text{c}}$, Eq. (9) predicts that the carrier will further retard the contaminant, and R^* will actually exceed R to a value linearly dependent upon $K_{\text{sed}}^{\text{OM}}$. In contrast, Eq. (6) reaches a limiting value of R^* (only slightly greater than R , given the input data in Table 1) when $K_{\text{sed}}^{\text{OM}}$ exceeds $K_{\text{sed}}^{\text{c}}$. The limiting value of R^* predicted by Eq. (6) is difficult to explain physically, since binding of the contaminant by a strongly sorbing carrier should effectively anchor the contaminant to the stationary phase. In contrast, the ability of a strongly sorbing carrier to further retard the transport of a contaminant, as predicted by Eq. (9), seems physically reasonable. An example of a situation where sorption of a potential carrying phase is stronger than that of the contaminant is the use of cationic surfactants to retard the transport of an organic contaminant in the subsurface. The cationic head of the molecule effectively anchors the surfactant to the negatively charged solid matrix along with any hydrophobic contaminants associated with the hydrophobic tail of the surfactant (Burris and Antworth, 1992). The variation of

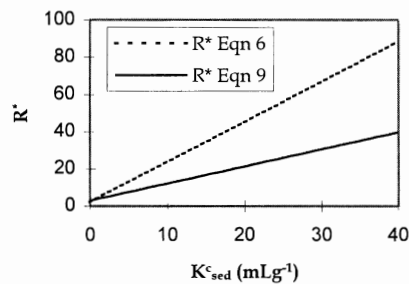


Fig. 5. Comparison of R^* predictions from Eqs. (6) and (9), using the data from Table 1, but varying strength of contaminant sorption to the stationary phase.

R^* under conditions where $K_{\text{sed}}^{\text{OM}} < K_{\text{sed}}^{\text{c}}$, has been simulated by Corapcioglu and Jiang (1996).

If parameters from Table 1 are again used for prediction, but DOM concentration is varied (Fig. 3), it is seen that Eq. (6) predicts higher R^* relative to Eq. (9) for all [DOM] values. Hence, Eq. (9) predicts a stronger effect of DOM on facilitated transport relative to Eq. (6). Allowing contaminant sorption to OM, K_{OM}^{c} , to vary (Fig. 4) shows this same effect. Varying contaminant sorption to sediment, shows that both expressions allow R^* to vary directly with $K_{\text{sed}}^{\text{c}}$ (Fig. 5).

4. Reconciliation of the expressions for R^*

The above calculations illustrate major differences in the values of R^* predicted from the two expressions. The two equations cannot be reconciled algebraically, at least not directly unless $K_{\text{sed}}^{\text{OM}} = 0$ (the carrier has no affinity for the sediment). Fortunately, they are reconcilable when the term [DOM] in Eq. (6) is further considered. A review of the derivation of Eq. (6) (Magee et al., 1991) reveals that substitution of the term [DOM] into Eq. (6) was made to replace the term $(M_{\text{OM}})/(V_w)$ with a conventional parameter. However, the numerator of this term, M_{OM} , was defined in the derivation to represent all organic matter in the system, whether free in the aqueous phase, or sorbed onto the stationary phase. This definition would be most appropriate when DOM sorption is low, and would not serve well when a significant fraction of an organic carrier is sorbed. The term $(M_{\text{OM}})/(V_w)$ therefore does not equate with the conventional definition of [DOM], but instead represents, in the terminology used herein: $(M_w^{\text{OM}} + M_s^{\text{OM}})/(V_w)$. Making this substitution into Eq. (6) gives:

$$R^* = \frac{1 + K_{\text{sed}}^{\text{c}} \frac{M_{\text{sed}}}{V_w} + K_{\text{OM}}^{\text{c}} \left(\frac{M_w^{\text{OM}} + M_s^{\text{OM}}}{V_w} \right)}{1 + \frac{K_{\text{OM}}^{\text{c}} \left(\frac{M_w^{\text{OM}} + M_s^{\text{OM}}}{V_w} \right)}{1 + K_{\text{sed}}^{\text{OM}} \frac{M_{\text{sed}}}{V_w}}} \quad (11)$$

Recalling that $M_s^{\text{OM}} = K_{\text{sed}}^{\text{OM}} M_w^{\text{OM}} (M_{\text{sed}})/(V_w)$ and substituting:

$$R^* = \frac{1 + K_{\text{sed}}^{\text{c}} \frac{M_{\text{sed}}}{V_w} + K_{\text{OM}}^{\text{c}} \left(\frac{M_w^{\text{OM}} + K_{\text{sed}}^{\text{OM}} M_w^{\text{OM}} \frac{M_{\text{sed}}}{V_w}}{V_w} \right)}{1 + \frac{K_{\text{OM}}^{\text{c}} \left(\frac{M_w^{\text{OM}} + K_{\text{sed}}^{\text{OM}} + M_w^{\text{OM}} \frac{M_{\text{sed}}}{V_w}}{V_w} \right)}{1 + K_{\text{sed}}^{\text{OM}} \frac{M_{\text{sed}}}{V_w}}} \quad (12)$$

Multiplying through the parentheses, incorporating unity into the denominator, reducing the denominator to a product of two sums, and canceling redundant terms gives:

$$R^* = \frac{1 + K_{\text{sed}}^c \frac{M_{\text{sed}}}{V_w} + K_{\text{OM}}^c \frac{M_w^{\text{OM}}}{V_w} + K_{\text{OM}}^c K_{\text{sed}}^{\text{OM}} \frac{M_w^{\text{OM}}}{V_w} \frac{M_{\text{sed}}}{V_w}}{1 + K_{\text{OM}}^c \frac{M_w^{\text{OM}}}{V_w}} \quad (13)$$

And finally, substituting the conventional parameters gives:

$$R^* = \frac{1 + K_{\text{sed}}^c \frac{\rho_b}{\theta} + K_{\text{OM}}^c [\text{DOM}] + K_{\text{OM}}^c K_{\text{sed}}^{\text{OM}} [\text{DOM}] \frac{\rho_b}{\theta}}{1 + K_{\text{OM}}^c [\text{DOM}]} \quad (14)$$

By reconciling Eqs. (6) and (9) we have shown the reason for the different predictions obtained from these two expressions. We have also shown that Eqs. (9) and (10) are more broadly applicable for predicting facilitated transport in situations where the binary interactions can be described by linear equilibrium distribution constants. Furthermore, we have seen that, in this system, increased carrier sorption increases R^* linearly (with all other parameters held constant), such that R^* may, hypothetically, greatly exceed R if carrier interaction greatly exceeds contaminant interaction with the sediment.

5. Accounting for non-linear sorption isotherms

While Eqs. (9) and (10) are applicable for predicting facilitated transport when interactions between contaminant and sorbent can be described using a linear expression, it is less useful for predicting facilitated transport in more complex systems with non-linear sorptive interactions. The derivation of Eq. (9), given in Appendix A, can be modified to include non-linear interactions between contaminant and sorbent that can be modeled using either a Langmuir or Freundlich isotherm. The resulting R^* expressions are shown here (derivations are given in Appendix A): for Langmuir-type sorption of contaminant to the stationary phase,

$$R^* = \frac{1 + K_{\text{sed}}^c b_{\text{sed}}^c \frac{\rho_b}{\theta}}{1 + K_{\text{sed}}^c C} + K_{\text{OM}}^c [\text{DOM}] + K_{\text{OM}}^c K_{\text{sed}}^{\text{OM}} [\text{DOM}] \frac{\rho_b}{\theta} \quad (15)$$

for Freundlich-type sorption of contaminant to the stationary phase,

$$R^* = \frac{1 + K_{\text{sed}}^c C^{N_{\text{sed}}-1} \frac{\rho_b}{\theta} + K_{\text{OM}}^c [\text{DOM}] + K_{\text{OM}}^c K_{\text{sed}}^{\text{OM}} [\text{DOM}] \frac{\rho_b}{\theta}}{1 + K_{\text{OM}}^c [\text{DOM}]} \quad (16)$$

where b_{sed}^c is a constant that relates to the binding capacity of the sediment, N_{sed}^c is a constant related to the affinity of the sediment for the contaminant, and C is the concentration of the contaminant in solution.

In addition to the parameter dependencies in Eqs. (9), Eqs. (15) and (16) show a dependence of R^* on contaminant concentration. Because contaminant concentration varies with position in contaminant transport through porous media, the above expressions are difficult to apply to experimental column data. However, for three-component (contaminant/carrier/sorbent) static *equilibrium* experiments, these expressions can be used to predict the effective sorption isotherm of a contaminant in the presence of a carrier molecule.

To develop an equilibrium isotherm from R^* expressions recall that:

$$R = 1 + K_{\text{sed}}^c \frac{\rho_b}{\theta} \quad (17)$$

where

$$K_{\text{sed}}^c = \frac{M_s^c/M_{\text{sed}}}{M_w^c/V_w} \quad (18)$$

or, substituting conventional parameters:

$$K_d = \frac{S}{C} \quad (19)$$

where S is the mass of contaminant sorbed per mass of sorbent and C is the concentration of contaminant in solution (including that bound to a suspended or dissolved carrier, if present) in solution. This K_d is an 'effective' K_d . That is, it is a single linear distribution coefficient, that can be used to describe the outcome of complex three-component interactions. For the case of facilitated transport with non-linear contaminant sorption, a different effective K_d can be determined at any solution concentration by setting Eqs. (15) and (16) equal to $R = 1 + K_d(\rho_b/\theta)$, and then solving for K_d . For example, the resulting expression for Freundlich-type sorption is:

$$K_d = \frac{\frac{\theta}{\rho_b} + K_{\text{sed}}^c C^{N_{\text{sed}}^c - 1} + K_{\text{OM}}^c [\text{DOM}] \frac{\theta}{\rho_b} + K_{\text{OM}}^c K_{\text{sed}}^{\text{OM}} [\text{DOM}]}{1 + K_{\text{OM}}^c [\text{DOM}]} - \frac{\theta}{\rho_b} \quad (20)$$

Then, substituting S/C for K_d , gives an expression for S in terms of C . The resulting equilibrium isotherm for Freundlich-type contaminant sorption is:

$$S = C \times \left(\frac{\frac{\theta}{\rho_b} + K_{\text{sed}}^c C^{N_{\text{sed}}^c - 1} + K_{\text{OM}}^c [\text{DOM}] \frac{\theta}{\rho_b} + K_{\text{OM}}^c K_{\text{sed}}^{\text{OM}} [\text{DOM}]}{1 + K_{\text{OM}}^c [\text{DOM}]} - \frac{\theta}{\rho_b} \right) \quad (21)$$

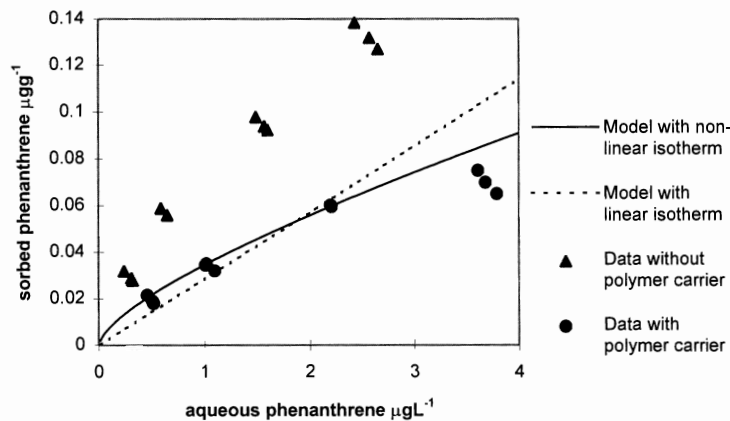


Fig. 6. R^* prediction of the effect of a carrier on non-linear contaminant sorption an aquifer sand (after the work of Cabral, 1996).

Fig. 6 shows an example of the use of this expression to determine the distribution of the polynuclear hydrocarbon, phenanthrene between the aqueous phase and an aquifer sand in the presence of a bacterial polymer carrier. The predictions of the model are compared to experimental measurements. The parameters used in the model equation were measured in independent experiments by Cabral (1996) and are given in Table 2. Comparison to the isotherm validates the inclusion of non-linear sorption in the expression for R^* . However, this comparison does not indicate the ability of the expression, which is based on equilibrium constants, to predict contaminant breakthrough. The agreement of model calculations and experimental observations shows that the modified three component model serves as a good predictor for phase distribution in cases where the contaminant sorption isotherm in the absence of the carrier is non-linear.

Table 2

Experimental parameters from the work of Cabral (1996)

K_{sed}^{OM} (ml/g) ^a	K_{sed}^c (ml/g) ^b	N^b	K_{OM}^c (l/mg) ^c	ρ_b/q (g/ml) ^d	[DOM] (mg/l) ^e
8.8	73	0.63	0.0076	0.02	180

^aDetermined from a linear fit to sorption data for ^{14}C radiolabelled extracellular polymer (obtained from a bacterium isolated from soil after growth on ^{14}C radiolabelled glucose) to an aquifer sand from an aqueous phase containing 5 mM $CaSO_4$ electrolyte and 0.25% sodium azide as a bacterial inhibitor (Cabral, 1996).

^bDetermined from a Freundlich isotherm fit to sorption data for ^{14}C radiolabelled phenanthrene to an aquifer sand from an aqueous phase containing 5 mM $CaSO_4$ electrolyte and 0.25% sodium azide as a bacterial inhibitor (Cabral, 1996). The isotherm data for phenanthrene in the absence of polymer are shown in Fig. 7.

^cCalculated from the reported value from the work of Dohse and Lion (1994) for $K_{OM}^c = 24,350$ ml/g TOC and value of 0.31 mg carbon/mg polymer reported by Chen et al. (1995).

^dBased on experimental conditions of 1 g aquifer material per 50 ml of solution.

^eEquilibrium dissolved extracellular polymer concentration for the experiment shown in Fig. 7.

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Appendix A. Derivation of Eq. (9) from mass fraction equations and extension to non-linear sorption of contaminant to the stationary phase

This derivation follows from that given in the work of Magee et al. (1991). In this approach, the average velocity of the contaminant in the presence of dissolved organic matter and sediment is:

$$v_{av} = f_w^c v_w + f_{OM,w}^c v_{OM,w} \quad (A1)$$

where f_w^c = the fraction of contaminant in the water phase; v_w = the velocity of water; $f_{OM,w}^c$ = the fraction of contaminant in the aqueous OM; and $v_{OM,w}$ = the velocity of OM in the aqueous phase. Assuming the average velocity of the OM equals the average velocity of water:

$$v_w = v_{OM,w} \quad (A2)$$

then:

$$v_{av} = f_w^c v_w + f_{OM,w}^c v_w \quad (A3)$$

therefore:

$$R^* = \frac{1}{f_w^c + f_{OM,w}^c} \quad (A4)$$

$$R^* = \frac{1}{\frac{M_w^c}{M_w^c + M_s^c + M_{OM,w}^c + M_{OM,s}^c} + \frac{M_{OM,w}^c}{M_w^c + M_s^c + M_{OM,w}^c + M_{OM,s}^c}} \quad (A5)$$

$$R^* = \frac{M_w^c + M_s^c + M_{OM,w}^c + M_{OM,s}^c}{M_w^c + M_{OM,w}^c} \quad (A6)$$

$$R^* = \frac{1 + \frac{M_s^c}{M_w^c} + \frac{M_{OM,w}^c}{M_w^c} + \frac{M_{OM,s}^c}{M_w^c}}{1 + \frac{M_{OM,w}^c}{M_w^c}} \quad (A7)$$

where M_w^c = mass of contaminant in the aqueous phase; M_s^c = mass of contaminant on the stationary phase; $M_{OM,w}^c$ = mass of contaminant in aqueous OM; $M_{OM,s}^c$ = mass of

contaminant in sorbed OM; M_s^{OM} = mass of OM on sediment; M_w^{OM} = mass of OM in the aqueous phase. Defining:

$$K_{sed}^c = \frac{M_s^c/M_{sed}}{M_w^c/V_w} \rightarrow M_s^c = K_{sed}^c M_w^c \frac{M_{sed}}{V_w} \quad (A8)$$

$$K_{sed}^{OM} = \frac{M_s^{OM}/M_{sed}}{M_w^{OM}/V_w} \rightarrow M_s^{OM} = K_{sed}^{OM} M_w^{OM} \frac{M_{sed}}{V_w} \quad (A9)$$

$$K_{OM}^c = \frac{M_{OM,w}^c/M_w^{OM}}{M_w^c/V_w} \rightarrow M_{OM,w}^c = K_{OM}^c M_w^c \frac{M_w^{OM}}{V_w} \quad (A10)$$

where M_{sed} is the mass of the stationary phase (sediment), and V_w is the volume of the aqueous phase.

Assuming that aqueous OM and sediment-sorbed OM have the same affinity for contaminant (this assumption is not necessary, but is made for comparison to Magee et al., 1991):

$$K_{OM}^c = \frac{M_{OM,s}^c/M_s^{OM}}{M_w^c/V_w} \rightarrow M_{OM,s}^c = K_{OM}^c M_w^c \frac{M_s^{OM}}{V_w} \quad (A11)$$

Substituting Eqs. (8)–(11) into Eq. (7), and recognizing that $M_w^{OM}/V_w = [DOM]$, and $M_{sed}/V_w = \rho_b/\theta$, in conventional terms, gives:

$$R^* = \frac{1 + K_{sed}^c \frac{\rho_b}{\theta} + K_{OM}^c [DOM] + K_{OM}^c K_{sed}^{OM} [DOM] \frac{\rho_b}{\theta}}{1 + K_{OM}^c [DOM]} \quad (A12)$$

Alternatively, one can include the effect of pore size exclusion or charge exclusion rather than assume $v_w = v_{OM,w}$. In this case, we return to the original expression:

$$v_{av} = f_w^c v_w + f_{OM,w}^c v_{OM,w} \quad (A13)$$

which, following the above derivation, gives:

$$R^{**} = \frac{1}{\frac{M_w^c}{M_w^c + M_s^c + M_{OM,w}^c + M_{OM,s}^c} + \frac{M_{OM,w}^c}{M_w^c + M_s^c + M_{OM,w}^c + M_{OM,s}^c} \frac{v_{OM,w}}{v_w}} \quad (A14)$$

which, following the remainder of the above derivation, results in:

$$R^{**} = \frac{1 + K_{sed}^c \frac{\rho_b}{\theta} + K_{OM}^c [DOM] + K_{OM}^c K_{sed}^{OM} [DOM] \frac{\rho_b}{\theta}}{1 + K_{OM}^c [DOM] \frac{v_{OM,w}}{v_w}} \quad (A15)$$

The following modifications to the above derivation can be made to account for non-linear sorption of the contaminant to the stationary phase (i.e., sediment). Replace:

$$M_s^c = K_{\text{sed}}^c M_w^c \frac{M_{\text{sed}}}{V_w} \text{ in the above derivation,}$$

with:

$$M_s^c = \frac{K_{\text{sed}}^c b_s^c M_w^c \frac{M_{\text{sed}}}{V_w}}{1 + K_{\text{sed}}^c \frac{M_w^c}{V_w}} \text{ for Langmuir-type contaminant sorption,}$$

or:

$$M_s^c = K_{\text{sed}}^c \left(\frac{M_w^c}{V_w} \right)^{N_s^c} M_{\text{sed}} \text{ for Freundlich-type contaminant sorption.}$$

Then, repeating the above derivation, the expression for retardation is (for Langmuir-type sorption):

$$R^* = \frac{\frac{1 + K_{\text{sed}}^c b_s^c \frac{\rho_b}{\theta}}{1 + K_{\text{sed}}^c C} + K_{\text{OM}}^c [\text{DOM}] + K_{\text{OM}}^c K_{\text{sed}}^{\text{OM}} [\text{DOM}] \frac{\rho_b}{\theta}}{1 + K_{\text{OM}}^c [\text{DOM}]} \quad (\text{A16})$$

and, for Freundlich-type sorption the expression for retardation is:

$$R^* = \frac{1 + K_{\text{sed}}^c C^{N_s^c - 1} \frac{\rho_b}{\theta} + K_{\text{OM}}^c [\text{DOM}] + K_{\text{OM}}^c K_{\text{sed}}^{\text{OM}} [\text{DOM}] \frac{\rho_b}{\theta}}{1 + K_{\text{OM}}^c [\text{DOM}]} \quad (\text{A17})$$

Appendix B. Derivation of Eq. (9) from transport equations

The expression for R^* published by Corapcioglu and Jiang (1993) (Eq. 8 of text) was developed from the mass balance equations describing contaminant transport. It is, therefore, useful to also use this approach here to develop Eqs. (9) and (10), in order to relate them to the expression published in the work of Corapcioglu and Jiang (1993), and in order to show that discrepancies between the published expressions are not the result of the two different derivation methods employed. The approach used here is to build the governing equation describing transport of a hydrophobic contaminant in the presence of dissolved organic matter one component at a time, in order to allow the reader to understand where from the equilibrium expressions which are substituted into the governing equation were obtained.

For transport of a dissolved contaminant through sediment in the absence of dissolved organic matter, the mass balance equation for contaminant in the aqueous phase is:

$$\frac{\partial C_w^c}{\partial t} \theta = -v_c \frac{\partial C_w^c}{\partial x} \theta + D_c \frac{\partial^2 C_w^c}{\partial x^2} \theta - k_{w-sed}^c \rho_b C_w^c \theta + k_{sed-w}^c \theta C_{sed}^c \rho_b \quad (B1)$$

where C_w^c is the mass of contaminant per volume of water; C_{sed}^c is the mass of contaminant per mass of sediment; k_{w-sed}^c and k_{sed-w}^c are the mass transfer coefficients (MTCs) for contaminant transfer from water to sediment, and back, respectively; ρ_b is the mass of sediment per representative elementary volume; θ is the volume of water per representative elementary volume; v_c and D_c are the interstitial velocity and hydrodynamic dispersion coefficients for contaminant, respectively.

The units of the MTCs used here are not $1/T$, but instead are second-order, as shown below for the last two terms in Eq. (1):

$$-\frac{1}{T} \frac{M_{sed}}{L_{REV}^3} \frac{M_{cont}}{L_{water}^3} \frac{L_{water}^3}{L_{REV}^3} + \frac{1}{T} \frac{L_{water}^3}{L_{REV}^3} \frac{M_{cont}}{L_{water}^3} \frac{L_{water}^3}{L_{REV}^3} \quad (B2)$$

where REV denotes representative elementary volume. The corresponding mass balance equation for contaminant on the sediment is:

$$\frac{\partial C_{sed}^c}{\partial t} \rho_b = +k_{w-sed}^c \rho_b C_w^c \theta - k_{sed-w}^c \theta C_{sed}^c \rho_b \quad (B3)$$

At equilibrium mass transfer in both directions is equal:

$$\rho_b \theta k_{w-sed}^c C_w^c = \rho_b \theta k_{sed-w}^c C_{sed}^c \quad (B4)$$

defining:

$$K_{sed}^c \equiv \frac{C_{sed}^c}{C_w^c} = \frac{k_{w-sed}^c}{k_{sed-w}^c} \quad (B5)$$

re-arranging and differentiating gives:

$$\frac{\partial C_{sed}^c}{\partial t} = K_{sed}^c \frac{\partial C_w^c}{\partial t} \quad (B6)$$

Likewise, for dissolved organic matter transport through sediment in the absence of contaminant (assuming a linear isotherm applies):

$$\frac{\partial C_w^{OM}}{\partial t} \theta = -v_{OM} \frac{\partial C_w^{OM}}{\partial x} \theta + D_{OM} \frac{\partial^2 C_w^{OM}}{\partial x^2} \theta - k_{w-sed}^{OM} \rho_b C_w^{OM} \theta + k_{sed-w}^{OM} \theta C_{sed}^{OM} \rho_b \quad (B7)$$

$$\frac{\partial C_{sed}^{OM}}{\partial t} \rho_b = +k_{w-sed}^{OM} \rho_b C_w^{OM} \theta - k_{sed-w}^{OM} \theta C_{sed}^{OM} \rho_b \quad (B8)$$

where: C_w^{OM} is the mass of OM per volume of water; C_{sed}^{OM} is the mass of OM per mass of sediment; k_{w-sed}^{OM} and k_{sed-w}^{OM} are the MTCs for OM transfer from water to sediment, and back, respectively; v_{OM} and D_{OM} are the interstitial velocity and hydrodynamic dispersion coefficients for OM, respectively. At equilibrium:

$$k_{w-sed}^{OM} \rho_b C_w^{OM} \theta = k_{sed-w}^{OM} \theta C_{sed}^{OM} \rho_b \tag{B9}$$

Defining:

$$K_{sed}^{OM} \equiv \frac{C_{sed}^{OM}}{C_w^{OM}} = \frac{k_{w-sed}^{OM}}{k_{sed-w}^{OM}} \tag{B10}$$

Gives:

$$\frac{\partial C_{sed}^{OM}}{\partial t} = K_{sed}^{OM} \frac{\partial C_w^{OM}}{\partial t} \tag{B11}$$

The mass balance equation for contaminant associated with aqueous OM is:

$$\begin{aligned} \frac{\partial C_{OM,w}^c C_w^{OM}}{\partial t} \theta = & -v_{OM} \frac{\partial C_{OM,w}^c C_w^{OM}}{\partial x} \theta + D_{OM} \frac{\partial^2 C_{OM,w}^c C_w^{OM}}{\partial x^2} \theta \\ & - k_{OM,w-w}^c \theta C_{OM,w}^c C_w^{OM} \theta + k_{w-OM,w}^c C_w^{OM} \theta C_w^c \theta \end{aligned} \tag{B12}$$

where $C_{OM,w}^c C_w^{OM}$ is the product of the mass of contaminant per mass of dissolved OM times the mass of dissolved OM per volume of water (mass of contaminant which occurs in dissolved OM per volume of water). The terms $k_{w-OM,w}^c$ and $k_{OM,w-w}^c$ are the MTCs for contaminant transfer from water to dissolved OM, and back, respectively. At equilibrium:

$$k_{w-OM,w}^c C_w^{OM} \theta C_w^c \theta = k_{OM,w-w}^c \theta C_{OM,w}^c C_w^{OM} \theta \tag{B13}$$

in terms of units:

$$\frac{1}{T} \frac{M_{OM}}{L_{water}^3} \frac{L_{water}^3}{L_{REV}^3} \frac{M_c}{L_{water}^3} \frac{L_{water}^3}{L_{REV}^3} = \frac{1}{T} \frac{L_{water}^3}{L_{REV}^3} \frac{M_{cont}}{M_{OM,w}} \frac{M_{OM,w}}{L_{water}^3} \frac{L_{water}^3}{L_{REV}^3} \tag{B14}$$

Defining:

$$K_{OM,w}^c \equiv \frac{C_{OM,w}^c}{C_w^c} = \frac{k_{w-OM,w}^c}{k_{OM,w-w}^c} \tag{B15}$$

Thus:

$$\frac{\partial C_{OM,w}^c}{\partial t} = K_{OM,w}^c \frac{\partial C_w^c}{\partial t} \tag{B16}$$

Likewise, the equation for contaminant in sediment-sorbed OM,

$$\frac{\partial C_{OM,s}^c C_{sed}^{OM}}{\partial t} \rho_b = +k_{w-OM,s}^c C_{sed}^{OM} \rho_b C_w^c \theta - k_{OM,s-w}^c \theta C_{OM,s}^c C_{sed}^{OM} \rho_b \quad (B17)$$

where $C_{OM,s}^c C_{sed}^{OM}$ is the product of the mass of contaminant per mass of sediment-sorbed OM times the mass of OM per mass of sediment (mass of contaminant which occurs on sediment-sorbed OM per mass of sediment). The terms $k_{w-OM,s}^c$ and $k_{OM,s-w}^c$ are the MTCs for contaminant transfer from water to sediment-sorbed OM, and back, respectively. At equilibrium:

$$k_{w-OM,s}^c C_{sed}^{OM} \rho_b C_w^c \theta = k_{OM,s-w}^c \theta C_{OM,s}^c C_{sed}^{OM} \rho_b \quad (B18)$$

in terms of units:

$$\frac{1}{T} \frac{M_{OM}}{M_{sed}} \frac{M_{sed}}{L_{REV}^3} \frac{M_c}{L_{water}^3} \frac{L_{water}^3}{L_{REV}^3} = \frac{1}{T} \frac{L_{water}^3}{L_{REV}^3} \frac{M_c}{M_{OM,w}} \frac{M_{OM,w}}{L_{water}^3} \frac{M_{sed}}{L_{REV}^3} \quad (B19)$$

Defining:

$$K_{OM,s}^c \equiv \frac{C_{OM,s}^c}{C_w^c} = \frac{k_{w-OM,s}^c}{k_{OM,s-w}^c} \quad (B20)$$

Gives:

$$\frac{\partial C_{OM,s}^c}{\partial t} = K_{OM,s}^c \frac{\partial C_w^c}{\partial t} \quad (B21)$$

Combination of all of the above mass transfer processes describes the transport of the aqueous contaminant through sediment in the presence of organic matter:

$$\begin{aligned} \frac{\partial C_w^c}{\partial t} \theta = & -v_c \frac{\partial C_w^c}{\partial x} \theta + D_c \frac{\partial^2 C_w^c}{\partial x^2} \theta - k_{w-sed}^c \rho_b C_w^c \theta + k_{sed-w}^c \theta C_{sed}^c \rho_b \\ & - k_{w-OM,w}^c C_w^{OM} \theta C_w^c \theta + k_{OM,w-w}^c \theta C_{OM,w}^c C_w^{OM} \theta \\ & - k_{w-OM,s}^c C_{sed}^{OM} \rho_b C_w^c \theta + k_{OM,s-w}^c \theta C_{OM,s}^c C_{sed}^{OM} \rho_b \end{aligned} \quad (B22)$$

Eqs. (B3), (B7), (B8), (B12), (B17) and (B22) can be solved simultaneously to simulate the kinetic system (Johnson, 1997). Alternatively, the expressions relating mass transfer to time (Eqs. (3), (8), (12) and (17)) can be substituted to result in:

$$\begin{aligned} \frac{\partial C_w^c}{\partial t} \theta = & -v_c \frac{\partial C_w^c}{\partial x} \theta + D_c \frac{\partial^2 C_w^c}{\partial x^2} \theta - \frac{\partial C_{sed}^c}{\partial t} \rho_b - \frac{\partial C_{OM,w}^c C_w^{OM}}{\partial t} \theta \\ & + v_{OM} \frac{\partial C_{OM,w}^c C_w^{OM}}{\partial x} \theta - D_{OM} \frac{\partial^2 C_{OM,w}^c C_w^{OM}}{\partial x^2} \theta - \frac{\partial C_{OM,s}^c C_{sed}^{OM}}{\partial t} \rho_b \end{aligned} \quad (B23)$$

Applying the chain rule:

$$\frac{\partial C_{OM,w}^c C_w^{OM}}{\partial t} = \frac{\partial C_{OM,w}^c}{\partial t} C_w^{OM} + \frac{\partial C_w^{OM}}{\partial t} C_{OM,w}^c \quad (B24)$$

$$\frac{\partial C_{OM,s}^c C_{sed}^{OM}}{\partial t} = \frac{\partial C_{OM,s}^c}{\partial t} C_{sed}^{OM} + \frac{\partial C_{sed}^{OM}}{\partial t} C_{OM,s}^c \quad (B25)$$

Because C_w^{OM} and C_{sed}^{OM} change slow relative to contaminant concentrations in the above phases, the right-most terms in Equations 24 and 25 are negligible, substituting:

$$\begin{aligned} \frac{\partial C_w^c}{\partial t} \theta = & -v_c \frac{\partial C_w^c}{\partial x} \theta + D_c \frac{\partial^2 C_w^c}{\partial x^2} \theta - K_{sed}^c \frac{\partial C_w^c}{\partial t} \rho_b - \frac{\partial C_{OM,w}^c}{\partial t} C_w^{OM} \theta \\ & + v_{OM} \frac{\partial C_{OM,w}^c}{\partial x} C_w^{OM} \theta - D_{OM} \frac{\partial^2 C_{OM,w}^c}{\partial x^2} C_w^{OM} \theta - \frac{\partial C_{OM,s}^c}{\partial t} C_{sed}^{OM} \rho_b \end{aligned} \quad (B26)$$

If local equilibrium holds for all mass transfer processes, then the equilibrium expressions (6, 11, 16, 21) can be substituted to give:

$$\begin{aligned} \frac{\partial C_w^c}{\partial t} \theta = & -v_c \frac{\partial C_w^c}{\partial x} \theta + D_c \frac{\partial^2 C_w^c}{\partial x^2} \theta - K_{sed}^c \frac{\partial C_w^c}{\partial t} \rho_b - K_{OM,w}^c \frac{\partial C_w^c}{\partial t} C_w^{OM} \theta \\ & + v_{OM} K_{OM,w}^c \frac{\partial C_w^c}{\partial x} C_w^{OM} \theta - D_{OM} K_{OM,w}^c \frac{\partial^2 C_w^c}{\partial x^2} C_w^{OM} \theta \\ & - K_{OM,s}^c \frac{\partial C_w^c}{\partial t} K_{sed}^{OM} C_w^{OM} \rho_b \end{aligned} \quad (B27)$$

Re-arranging gives:

$$\begin{aligned} & \left(1 + \frac{\rho_b}{\theta} K_{sed}^c + K_{OM,w}^c C_w^{OM} + \frac{\rho_b}{\theta} K_{OM,s}^c K_{sed}^{OM} C_w^{OM} \right) \frac{\partial C_w^c}{\partial t} \\ & = - (v_c + v_{OM} K_{OM,w}^c C_w^{OM}) \frac{\partial C_w^c}{\partial x} + (D_c + D_{OM} K_{OM,w}^c C_w^{OM}) \frac{\partial^2 C_w^c}{\partial x^2} \end{aligned} \quad (B28)$$

Assuming that in the aqueous phase $v_c = v_{OM}$ and $D_c = D_{OM}$, and re-arranging gives:

$$\frac{\left(1 + \frac{\rho_b}{\theta} K_{sed}^c + K_{OM,w}^c C_w^{OM} + \frac{\rho_b}{\theta} K_{OM,s}^c K_{sed}^{OM} C_w^{OM} \right)}{\left(1 + K_{OM,w}^c C_w^{OM} \right)} \frac{\partial C_w^c}{\partial t} = -v_c \frac{\partial C_w^c}{\partial x} + D_c \frac{\partial^2 C_w^c}{\partial x^2} \quad (B29)$$

The term applied to $\delta C_w^c / \delta t$ is the modified retardation factor, R^* , developed by the mass fraction approach in Appendix A.

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