Conjunct Use of BTC and Batch Methods for Heavy Metal Transport

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Appendix

There are several methods to estimate the value of the *k* d parameter through experiments, 1) laboratory batch, 2) *in-situ* batch,3) laboratory flow-through (BTC) method, 4) field modeling, and 5) *k* oc method, with the *k* d parameter included in the retardation factor, R, <http://www.epa.gov/radiation/docs/kdreport/vol1/402-r-99-004a.pdf>,

R = (1)

R retardation factor = pore-water velocity/solute velocity, dimensionless

*k* d distribution coefficient. It is an expression of solute mobility in the porous medium

*via* dividing the adsorbed solute mass, S, by the residual solute mass, C, staying in solution at equilibrium. A high *k* d value means more adsorption, i.e., less mobility to groundwater, dimensionless

** dry bulk density of soil material, kg/m3

** volumetric soil moisture content, dimensionless
(** is a product of the gravimetric moisture content and the dry bulk density, **.)

For the non-linear equilibrium adsorption, the Freundlich isotherm, S = K *f* CN, and the Hashimoto derivative (Hashimoto, 1964), *k*d\_H = S/C, are used, and the R-parameter will be adequately expressed accordingly as R = 1 + (**/) K f NCN-1. The Freundlich isotherm turns into a linear isotherm, with *k* d = K *f*, only if N = 1.

The value *k* d = 0 (i.e., R = 1), Eq. 1, means that there is no reaction of the concerned solute with the sediment. A high *k* d value, in contrast, shows high adsorption of the solute on the solid phase. Each type of porous media, and all sets of concentrations, impose different values for the *k* d parameter for the studied system. That is why a detailed study should be conducted for each case. The *k* d values that may be picked from the literature can be misleading if generalized to other sites and conditions. The values for the *k* d parameter do not only vary between solutes, but also varies in function of the chemistry of the used aqueous solution, and the present solid phases (Delegard and Barney, 1983; Kaplan *et al.,* 1994a, and Kaplan and Serene, 1995).

The assumptions associated with the thermodynamically-defined *k* d parameter in the empirical linear equilibrium adsorption relationships are mostly violated in the computer codes used to estimate the *k* d value <http://www.epa.gov/radiation/docs/kdreport/vol1/402-r-99-004a.pdf>). The small difference between the “thermodynamic *k* d parameter as derived from ion-exchange,” and the “empirical *k* d used in solute transport formulas,” is usually omitted in the computer codes. Moreover, the reference given above indicates that a “conditional *k* d” values (Jenne, 1977) is usually used to identify the “experimentally-derived distribution coefficient” as a ratio between the adsorbed to the residual dissolved species The differences between the “true thermodynamic *k* d,” and the “conditional *k* d” are also usually omitted. The effect of the pH and ionic strength change, during the BTC experimental work, is moreover dropped out, whereas the so-called “parametric *k* d” and “mechanistic *k* d” are sparingly used in the computer models since they need detailed information that is costly or very complex to obtain and difficult to be installed in the solute-transport models.

The Péclet number, P, is a scale-dependent dimensionless expression of the ratio of solute transport by the relatively rapid convection (mass-flow by inertial forces with water in the macro-pores between the large-size particles and aggregates) to solute transport taking place by the relatively slow diffusion phenomenon (in the micro-pores between the fine-grained solid-phase particles and inside the small aggregates). When the diffusion process has a negligible impact (i.e., there is only mechanical dispersion), the P-parameter will solely depend on the type of the solid phase, not on the tracer.

Large P values indicate the supremacy of convection (product of average pore-water velocity, **x, and column length, L) over the effective hydrodynamic dispersion coefficient, DL, which includes molecular diffusion and controlled by tortuosity (CFITM and CFITIM codes, igwmc, 2001, and van Genuchten and Wierenga, 1986). The dominance of convection may be seen by obtaining small values for the longitudinal dispersivity (a scale-dependent length parameter that expresses soil non-homogeneity, which is referred to by the symbol  in the four-parameter models, or by the symbol  in two-parameter models) since P ≈ L/.

Practically, a significantly high P-value will mean high solute mobility from soil to the local groundwater. In contrast, a low P-value (i.e., high -value) will show the dominance of solute transport by slow diffusion and reflect substantial heterogeneity of the solid phase particle-sizes and arrangement (aggregation) on the microscopic level (Hussein, 2009).

The parameter  (dimensionless) is a rate constant known as the mass-transfer coefficient of solute exchange between the mobile and immobile moisture regions. It is expressed by dividing the hydrodynamic water residence-time, L/q, hr, (Damkohler II number) by the characteristic time, hr, of exchange (1/). Otherwise,  value is to obtain by multiplying Damkohler II number by the first-order kinetic rate coefficient, , hr-1. The parameter ** is instantaneous retardation, dimensionless, that has several expressions according to the sub-model in use, van Genuchten, Report No 119 (1981) in Table 6, p 36.

The solute-transport phenomenon is idealized through several conceptual models. These models may solve the second-order partial differential CDE equation by operational codes that describe solute transport with ion exchange or adsorption (where adsorption includes ion exchange) in a unique mobile water region (CfitM code) or may solve the CDE for mobile and immobile water regions (CfitIM code). These codes are processed, under the right initial and boundary conditions, to yield the specific analytical solution (that corresponds to a given experimental run). The values found by CfitM, or CfitIM, for the built-in parameters, are then used in the numerical simulation models for solving elaborate solute transport problems in the field conditions.

The effective longitudinal hydrodynamic dispersion coefficient, DL, (cm2 hr-1), is built in the Péclet number, P, (Eq. 2). It is clear, in this equation, that short columns and fine-grained soil materials will produce small P values, and *vice versa*,

P = = ≈ (2)

DL = (3)

DL = (4)

DL ≈ **x (5)

 ≈ (6)

where

P ratio of convective mass-flow **x L to hydrodynamic-dispersion coefficient, DL

**x Mean effective pore-water velocity, cm/hr

L Column length, cm; the product (**x L) is the advective solute-transport

DL Effective longitudinal hydrodynamic-dispersion coefficient, cm2/hr

D\* Molecular diffusion coefficient, cm2/hr (often dropped since negligibly small)

d10 Particle-size 10% finer by weight in the semi-log cumulative dry-sieving plot

q Darcy velocity, cm/hr

** volumetric soil moisture content, dimensionless

** Longitudinal dispersivity, cm (****** in models where all water is considered as mobile)

The application of different analytical sub-models, corresponding to different boundary conditions, will produce somewhat different values for R and P (van Genuchten, 1981, Report No 118), and this will result in some deviation of the obtained values for DL and *k* d parameters. These deviations could be minimized by using longer columns (30 to 50 cm in length).

The convection-dispersion solute-transport process taking place during 1-D steady-state water flow is expressed by the following second-order partial differential equation (CDE) known as Fick’s 2nd order law (van Genuchten M. Th., 1981, Reports No. 118 and 119),

 = (7)

When solute decay is also considered, the sink-term, S, is introduced to express chemical and/or biological “kinetic reactions” responsible for such decay (Eq. 8a to 8e).

 = (8a)

This formula is used for reactive and non-reactive solute transport in the CfitM code. Other forms of that equation may be written as following,

 = (8b)

 = (8c)

 = (8d)

 = (8e)

These forms are obtained by manipulation of the retardation factor, R, formula,

R = 1 + ** *k* d/**

R = 1 + ** (S/CL)/**

(R-1) = (S/CL) **/**

**/** = (R-1) (CL/S)

where

** volumetric soil moisture content, dimensionless

** bulk density, kg m-3

CL solute concentration in solution, ppm, i.e., mg l-1

DL *effective* hydrodynamic-dispersion coefficient, cm2/hour
It includes the (D\*) term (the effective molecular diffusion coefficient, *cm2/hour*)

z depth, negative downward, cm

q Darcy velocity (flux), negative downward, *cm/hr*

** pore-water velocity, cm/hr

S adsorbed solute, gsolute/kg soil(S = K *f* CN in Freundlich isotherm*, with* K *f* capacity coefficient and N sorption intensity exponent)

*k* or *k* d distribution coefficient,

m3soluion/kg soil (with *k* d = N S/CL. i.e. *k* d = K f = S/CL if N =1)

L column length, *cm*

The 2-parameter code CfitM code is used for transport of non-reactive and reactive solutes, assuming that all soil moisture content is mobile, and all adsorption sites are freely accessible. However, the 4-parameter MIM codes (e.g., CfitIM) were introduced (Nkedi-Kizza, 1979 and Nkedi-Kizza, et al., 1983) to consider the more practical problems where soil moisture is subdivided into mobile (macro-porosity) and immobile (micro-porosity) regions. Transport takes place by convection and dispersion in the mobile region, while in the immobile region, it is presumed as being a diffusion-controlled process (proportional to concentration differences between the two regions). Gao et al., (2009) stated that the MIM codes consist of a conventional CDE for solute transport in the mobile region coupled with a term, , (Eq 9) describing solute mass-transfer between the mobile and the immobile regions with (Eq 10) expressing solute transfer flux as proportional to the concentration difference between these two regions. The one-dimensional CfitIM code for reactive solute transport (van Genuchten and Wierenga 1976, and van Genuchten, 1981, Report no 119) is expressed by Eq. 9 and Eq. 10 (with N = 1). Eq. 9 is a reduced form of Eq. 12 in van Genuchten and Wierenga (1976), and it is the same as Eq. 25 in van Genuchten (1981) Report No 119, page 15.

 = (9)

 = = (10)

The equations from 11 to 21 show the terms and parameters used in the CfitIM code.

q = **m **m (11)

**m = (12)

m = (13)

 = **m + **im (14)

P = = (15)

 = = (16)

 = (17)

Rm = (18)

Rim = (19)

R = (20)

** = (21)

S = f Sm + (1 -f) Sim (22)

where

q Darcy velocity, cm/hr

**m Pore-water velocity in the mobile water region, cm/hr

m Ratio of mobile moisture, m, to total moisture, 

 Mass-transfer coefficient of solute exchange between the mobile and immobile regions expressed as a rate constant, dimensionless

** First-order kinetic rate coefficient for solute exchange between mobile and immobile regions, hr-1

** instantaneous retardation that may have several expressions, Table 6, van Genuchten (1981), page 36, dimensionless

S Total adsorption, g/kg soil

** m Mobile moisture, dimensionless

**im Immobile moisture, dimensionless

f Adsorption sites available. expressed as mass fraction of the solid phase

The dimensionless forms of Eq 9 and 10 include the parameters R, P, ** and ,

(with T as the pore-volume)

 = (23)

 = (24)

The following dimensionless variables are used in the physical non-equilibrium sub-model B in the CfitIM code.

, , ,