LEACHING TESTS: EQUILIBRIUM AND IMPACT OF DESORPTION KINETICS

In this chapter we combine the knowledge about sorption/desorption kinetics to analyze leaching tests where different time scales are involved. Leaching tests comprise batch shaking tests ("in a bottle") and column percolation tests; normally tests aim at equilibrium conditions, but time scales to reach sorption equilibrium depends on mass transfer mechanisms, solid to liquid ratios, particle sizes, sorption coefficients, etc... Initially leaching of pollutants in column tests often occurs in sorption equilibrium, while later slow desorption kinetics cause extended tailing of effluent concentrations.

1. INTRODUCTION

1.1 PHILOSOPHY OF LEACHING TESTS

End of the nineties last century, a shift in paradigm occurred for the assessment of the risk of water pollution from contaminated materials (soils, sediments, solid waste materials…): The concentration in water in contact with the waste material was considered relevant and not just the concentration in the solids. Aqueous concentrations in leaching tests depend on water/solid ratios, equilibration time and thus on the test type (e.g., column vs. shaking test), which is discussed in the following.

Elution (= leaching) tests are aimed to determine contaminant concentrations, which can be expected in water, that is in contact with the solid material under consideration. Crucial for this is the contact time of the water with the material, and the velocity of the mass transfer processes involved. Assuming sufficient contact time, equilibrium is reached between the concentration in the solids and in the water, that means, there is no more net mass transfer between the solids and the water. The equilibrium concentration may be influenced by other water constituents. In the case of nonionic organic contaminants this might be dissolved organic substances or colloids (see example box at the end of this document); in case of heavy metals additionally the pH and the redox conditions may play a role. In batch shaking tests, the equilibrium concentration may be a function of the ratio between water and the solids, due to dilution. Otherwise, the equilibrium concentration is a maximum concentration ('worst case') provided that sufficient time is available in laboratory tests or in the field to achieve equilibrium.

In the case of the standard elution tests column percolation methods, tank tests (with stagnant water), and shaking or stirred batch tests can be distinguished, where different volumes of water are brought into contact with the solids under consideration for varying time intervals. The results of the different tests can be compared, provided that distribution coefficients between solids and aqueous phase are known provided that equilibrium conditions are established (concentrations are the same in all tests if dilution is negligible). However, if equilibrium is not reached in the test, the kinetics of the mass transfer process have to be known. In the case of shaking tests, equilibrium conditions are usually assumed a priori (generally without proving it), while tank tests are intended to be conducted under non-equilibrium conditions (e.g., by exchanging the water several times). In column experiments, both conditions occur sequentially. Depending on the flow-velocity, grain sizes and contaminant release rates initially equilibrium concentrations are observed at the column

effluent - later the concentrations decrease indicating non-equilibrium (this means, that boundary conditions for mass transfer in a column experiment become the same as those in a tank test).

According to the German soil protection ordinance (BBodschV, 1999), column experiments are required for the elution of organic and inorganic contaminants ('Sickerwasserprognose') (see Grathwohl and Susset (2001) for details). Fig. 1.1 shows the principle of groundwater risk assessment with the "source" term and transport of the leached compounds to the point of compliance (POC) where they can undergo attenuation processes. In the following we focus on the source term and work out how the different leaching test methods and boundary conditions influence the contaminant concentrations in water. Basic principles can be found in Grathwohl (1998), Förstner et al. (2002) and Susset et al. (2011). Some examples showing the elution of different contaminants from soils can be found in Weiß et al. (1997), Grathwohl (2000), Grathwohl and Susset (2009, 10), Beyer et al. (2009), Grathwohl (2014), and Finkel et al. (2017). A sophisticated analysis of column leaching is provided by Liu et al. (2021).

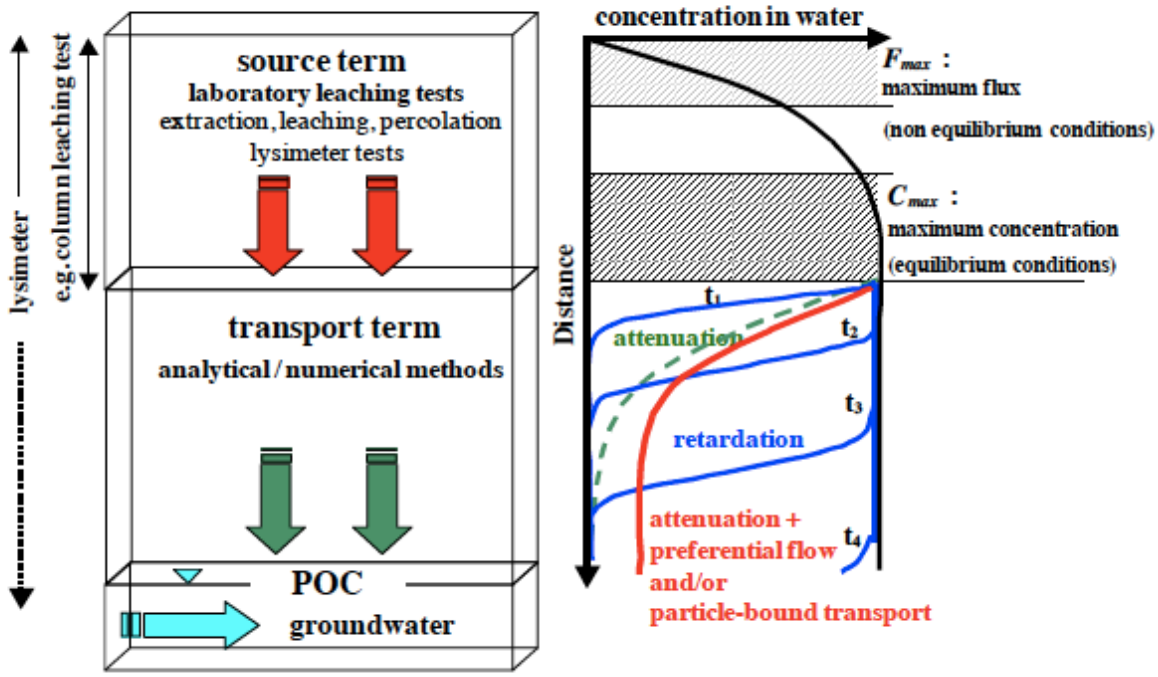


Fig. 1.1: Principles of groundwater risk assessment with leaching of contaminants from the source (solid water, recycling material, etc...) followed by transport to the point of compliance (POC), usually the groundwater table; during transport sorption causes retardation, biodegradation leads to decreasing concentrations and preferential flow leads to early arrival of a fraction of seepage water (avoiding attenuation).

1.2 EQUILIBRIUM TESTS: WATER/SOLID-RATIOS ARE RELEVANT

In practice, due to the more easy interpretation and transferability to the field scale, elution tests are preferred that imply equilibrium conditions. These tests are in coincidence with the concentrations to be expected in the field only, if also in the field equilibrium is reached and if,

e.g. in shaking tests, no dilution happens at high water/solid ratios and low sorption. Equilibrium conditions are defined by a distribution coefficient K_d:

$$K_d = \frac{C_s}{C_w} = \frac{(X_{tot} - X_w)}{m_d} \frac{V_w}{X_w} \tag{1.1}$$

where C_s and C_w are the contaminant concentrations on the solids (‚sorbed') and in water, respectively. X_{tot}, X_w, V_w and m_d are the initial (total) contaminant mass in the solids, the contaminant mass in water after equilibration, the volume of the water, and the dry mass of the solids. The equilibrium concentration in the water can be calculated from the initial concentration in the dry solids ($C_{s,ini}\ m_d = X_{tot}$):

$$C_{s,ini}\ m_d = C_w\ K_d\ m_d + C_w V_w \quad => \quad C_w = \frac{C_{s,ini}}{K_d + \frac{V_w}{m_d}} \tag{1.2}$$

How aqueous concentrations decrease with an increase of the liquid/solids-ratio ($LS = V_w / m_d$) is shown in Figure 1.2. Large liquid/solids-ratios along with small K_d values ($K_d < LS$) lead to a dilution resulting in low water concentrations, which would not necessarily be observed in the field due to the generally much smaller water/solids ratios there. The threshold, at which this dilution effect is significant, is dependent on the K_d value – for K_d values > 100, even water/solids ratios of 10 will not cause significant dilution of resulting aqueous concentrations. Note, LS corresponds to the water content (assuming a density of water of one); the inverse of LS is m_d/V_w and represents the concentration of solids in water e.g. in a soil slurry or the suspended sediment concentration in river water.

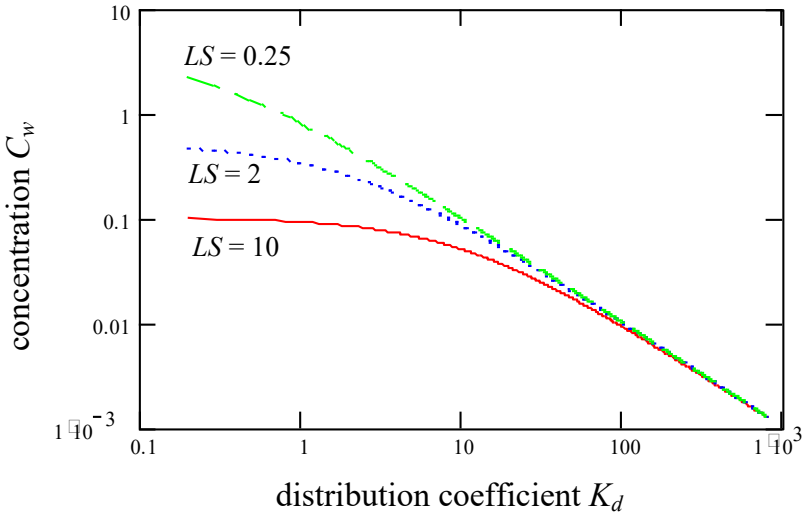


Fig. 1.2: Decrease in aqueous concentrations with increasing distribution coefficient K_d at different liquid to solids ratios (LS) starting at an initial concentration in the solids ($C_{s,ini}$) of 1 [mg/kg or µg/kg etc.]. The least dilution, meaning almost equal concentrations independent of LS are observed for K_d values > 100 (inverse linear relation between concentration and K_d independent on LS). The highest concentrations in water are observed for small LS ratios and low K_d values. LS = 0.25 represents approximately the conditions in a column experiment or a water saturated porous medium; LS then corresponds to the ratio of porosity and bulk density = n/ρ_{bulk}; under unsaturated conditions LS would be even lower and the liquid volume is given by the volumetric water content = θ/ρ_{bulk}.

Sequential leaching or cascade tests. Occasionally such tests are used to check for the mobility or long-term behavior of contaminants in a sample. Initially the dry sample is suspended in a given volume of water, for sampling the water is separated from the solids and then this step is repeated several times with new batches of water (NEN 7349, 1995). Such sequential extractions (also called cascade test) rely on equilibrium at each step (which maybe questionable); the relative concentration decrease at each step is:

$$C/C_o = \left(1 + \frac{V_w}{K_d\, m_d}\right)^{-LS\frac{m_d}{V_w}}$$

or (1.3)

$$C/C_o = \exp\left[-LS\frac{m_d}{V_w}\ln\left(1 + \frac{V_w}{K_d\, m_d}\right)\right]$$

and because of $\ln(1 + V_w/(m_d\, K_d)$ for $V_w/(m_d\, K_d) << 1$ (e.g < 0.1) $\cong V_w/(m_d\, K_d)$:

$$C/C_o = \exp[-LS/K_d] \quad (1.4)$$

Here V_w/m_d denotes the liquid to solid ratio applied in each single leaching step and $LS/\square V_w/m_d\square$ denotes the number of leaching steps. The hypothetical initial concentration in water C_o here would equal C_s/K_d. The concentration after the 1st leaching step ($LS = V_w/m_d$) can be calculated according to Eq. 1.2. For $LS = K_d$, C/C_o is exp(-1) = 0.368 similar to a percolation experiment (column tests, see chap. 3.1).

2. TIME TO REACH EQUILIBRIUM CONDITIONS – COUPLED INTRAPARTICLE – FILM DIFFUSION

In leaching tests a major uncertainty concerns release kinetics of target compounds from solids or time needed to reach equilibrium (note the difference between complete release of solute from a solid *vs.* time needed for equilibration within a limited volume of water). In many cases, contaminant release kinetics depend on diffusion processes either in an aqueous boundary layer (film diffusion) or in the particle itself (diffusion in the intraparticle pore space of fragments of rocks, concrete, soil aggregates, etc. or solid diffusion, e.g., in plastic particles). Which of these two mass transfer mechanisms dominate depends on K_d, flow conditions, grain size and finally time. Typically, at short time periods film diffusion is dominant (because gradients in the particle are very steep at early times). At late time periods intraparticle diffusion may become more relevant (and mass transfer resistance shifts into the particle). In general, for strongly sorbing compounds film diffusion in the aqueous boundary layer is limiting mass transfer.

2.1 INTERNAL/EXTERNAL MASS TRANSFER SHIFTS: WHICH FILM LIMITS?

The two-film diffusion model can be easily derived by assuming that the mass transfer of a solute contaminants involves two films adjacent to the particle/water interface, where one film represents an external aqueous boundary layer and a second one is inside the particle (see Fig. 2.1). Here we

assume a porous particle, e.g. a rock fragment, granular activated carbon, soil aggregates etc... (see chap. 2.3 for solid particles such as natural organic matter or synthetic polymers e.g. microplastics).

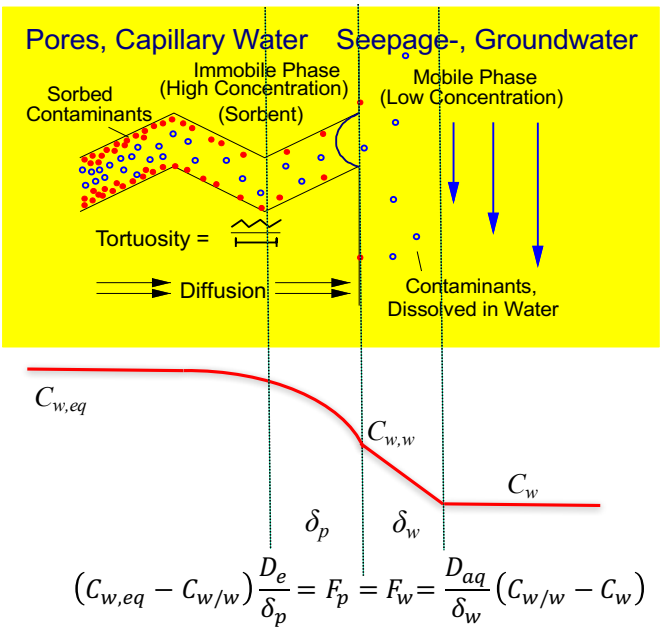


Fig. 2.1: Scheme of the two-film diffusion model for a desorption scenario (red lines indicate concentrations). Mass transfer across both films may be assumed to be controlled by Fick's 1st law. At the interface, concentrations are equal ($C_{w/w}$). $C_{w,eq}$ and C_w are the concentrations in equilibrium (initially in pore water) and in external water. δ_p and δ_w refer to the respective film thicknesses; note that δ_p may grow with time (see also Liu et al., 2021).

The fluxes per surface area in each film can be evaluated following Fick's 1st law for the aqueous boundary layer (film):

$$F_w = -\frac{D_{aq}}{\delta_w}(C_w - C_{w/w}) \tag{2.1}$$

and analogously in the particle:

$$F_p = -\frac{D_e}{\delta_p}(C_{w/w} - C_{w,eq}) \tag{2.2}$$

$C_{w,eq}$ and C_w are the concentrations in equilibrium in pore and bulk water; $C_{w/w}$ denotes the concentration at the interface between particle and water, respectively; D_e ($\approx D_{aq}\,\varepsilon^2$) and D_{aq} are the effective diffusion coefficient and aqueous diffusion coefficient. Under steady-state conditions the fluxes in both films have to be equal:

$$F_w = -\frac{D_{aq}}{\delta_w}(C_w - C_{w/w}) = -\frac{D_e}{\delta_p}(C_{w/w} - C_{w,eq}) = F_p \tag{2.3}$$

This can be easily solved for the unknown concentration at the interface:

$$\frac{D_{aq}}{\delta_w}C_{w/w} + \frac{D_e}{\delta_p}C_{w/w} = \frac{D_e}{\delta_p}C_{w,eq} + \frac{D_{aq}}{\delta_w}C_w \Longrightarrow C_{w/w} = \frac{\frac{D_e\,\delta_w}{\delta_p\,D_{aq}}C_{w,eq} + C_w}{1 + \frac{D_e\,\delta_w}{\delta_p\,D_{aq}}} \tag{2.4}$$

Eq. 2.4 then is inserted e.g. into eq. 2.1 and the flux is:

$$F_w = \frac{-D_{aq}}{\delta_w}\left(C_w - \frac{\frac{D_e\,\delta_w}{\delta_p\,D_{aq}}C_{w,eq} + C_w}{1+\frac{D_e\,\delta_w}{\delta_p\,D_{aq}}}\right)$$
$$= \frac{-D_{aq}}{\delta_w}\left(\frac{C_w + C_w\frac{D_e\,\delta_w}{\delta_p\,D_{aq}} - \frac{D_e\,\delta_w}{\delta_p\,D_{aq}}C_{w,eq} - C_w}{1+\frac{D_e\,\delta_w}{\delta_p\,D_{aq}}}\right) \quad (2.5)$$
$$= \frac{-D_{aq}}{\delta_w}\left(\frac{\frac{D_e\,\delta_w}{\delta_p\,D_{aq}}\left(C_w - C_{w,eq}\right)}{1+\frac{D_e\,\delta_w}{\delta_p\,D_{aq}}}\right) = -\frac{\frac{D_e}{\delta_p}\left(C_w - C_{w,eq}\right)}{1+\frac{D_e\,\delta_w}{\delta_p\,D_{aq}}}$$

Thus, the flux in both films is:

$$F = F_w = F_p = -\frac{1}{\frac{\delta_p}{D_e}+\frac{\delta_w}{D_{aq}}}\left(C_w - C_{w,eq}\right) \quad (2.6)$$

From that, we conclude that if D_e gets small, then mass transfer becomes limited by diffusion in the particle, provided that film thicknesses are similar.

In order to estimate film thicknesses empirical relationships may be used. δ_w may be calculated based on empirical Sherwood numbers (Sh), which describe how the mass transfer coefficient k [m s^{-1}] (= D_{aq}/δ_w) depends on diffusion coefficients, grain size (d) and δ_w:

$$\mathrm{Sh} = \frac{k\,d}{D_{aq}} = \frac{d}{\delta} \Rightarrow \delta = \frac{d}{\mathrm{Sh}} \quad (2.7)$$

A very simple relationship is proposed by Liu et al. (2014) which can be derived from mean square displacement and finally lead to a correlation of Sh to the Peclet number (Pe):

$$\mathrm{Sh} = \frac{k\,d}{D_{aq}} = \frac{d}{\delta} \approx 0.1\frac{d}{\sqrt{D_{aq}\frac{d}{v}}} = 0.1\sqrt{\frac{d\,v}{D_{aq}}} = 0.1\sqrt{\mathrm{Pe}} \quad (2.8)$$

d/v denotes the contact time of the water with the particle at a given flow velocity (v). δ_w thus is:

$$\delta_w = \frac{d}{\mathrm{Sh}} \approx \frac{d}{0.1\sqrt{\mathrm{Pe}}} = 10\sqrt{D_{aq}\frac{d}{v}} \quad (2.9)$$

Similarly, δ_p may be estimated based on mean square displacement for early time approximation of diffusion into a particle:

$$\delta_p \approx \sqrt{\pi\,D_a\,t} = 1.8\sqrt{D_a\,t} \quad (2.10)$$

The mean square displacement employs the apparent diffusion coefficient D_a (= D_e / (ε + $K_d\,\rho$)) and δ_p will grow with the square root of time. To elucidate the limiting mass transfer process, ratios of the (additive) mass transfer resistances in eq. 2.6 may be used:

$$\frac{\frac{\delta_w}{D_{aq}}}{\frac{\delta_p}{D_e}} \approx \frac{\frac{10\sqrt{D_{aq}\frac{d}{v}}}{D_{aq}}}{\frac{\sqrt{\pi\, D_a t}}{D_e}} \approx \frac{\frac{10\sqrt{D_{aq}\frac{d}{v}}}{D_{aq}}}{\frac{1.8\sqrt{\frac{D_{aq}\varepsilon^2}{(\varepsilon + K_d\,\rho_p)}t}}{D_{aq}\varepsilon^2}} \approx 5.6\;\varepsilon\sqrt{\frac{d}{v\,t}\,K_d\,\rho_p} \tag{2.11}$$

With increasing K_d and grain diameter (d) mass transfer gets limited by the aqueous boundary layer. With increasing time, the ratio of the mass transfer resistances drops below one, which indicates the point when intraparticle diffusion starts to limit sorption/desorption kinetics. For K_d values between 10 and 100, an intraparticle porosity of 5%, grain size of 1 mm and a flow velocity of about 1 m day^{-1} this takes between 4 – 40 hours. Similarly to the aqueous boundary layer thickness a fixed contact time can be assumed in special cases e.g. during initial flooding of a column, when water always encounters new particles which have the original concentration ($t = d/v$):

$$\frac{\frac{\delta_w}{D_{aq}}}{\frac{\delta_p}{D_e}} \approx \frac{\frac{10\sqrt{D_{aq}\frac{d}{v}}}{D_{aq}}}{\frac{\sqrt{\pi\, D_a \frac{d}{v}}}{D_e}} = \frac{\frac{10\sqrt{D_{aq}}}{D_{aq}}}{\frac{\sqrt{\pi\frac{D_e}{(\varepsilon + K_d\,\rho_p)}}}{D_e}} = \frac{10\sqrt{D_e(\varepsilon + K_d\,\rho_p)}}{1.8\sqrt{D_{aq}}} \tag{2.12}$$

$$\approx 5.6\sqrt{\frac{D_{aq}\varepsilon^2 K_d\,\rho_p\left(1+\frac{\varepsilon}{K_d\rho_p}\right)}{D_{aq}}} \approx 5.6\;\varepsilon\sqrt{K_d\,\rho_p}$$

Because the similar definition of both film thicknesses in this case the grain size drops out. Since diffusion in both films is in aqueous phase D_{aq} drops out in eqs. 2.13 and 2.14. This is only the case for this specific empirical relationship where Sh depends on the square root of the Peclet number ($Pe^{1/2}$); in other empirical correlations Sh is a function of the third root of D_{aq} ($Sh \propto Re^{1/2}\,Sc^{1/3}$) and then a slight dependency of the mass transfer ratios on D_{aq} is left over ($\propto D_{aq}^{1/6}$). If the intraparticle porosity becomes small, pore diffusion may limit mass transfer; for high K_d values again film diffusion becomes limiting (for an intraparticle porosity of 5%, film diffusion dominates for $K_d > 5$).

Note, that empirical Sherwood correlations at low Reynolds numbers decrease for spheres to a minimum of 2 - then δ_w equals the particle radius, which is also the largest value we may assume for δ_p. Thus the mass transfer resistance would only depend on the ratio of D_e/D_{aq} and finally ε^2. Since ε is always smaller than 1, intraparticle pore diffusion tend to be the limiting factor on the long term (as soon as δ_p approaches the radius of the particle). For a more detailed discussion see Liu et al. (2021).

2.2 SORPTION/DESORPTION KINETICS IN THE FINITE BATH: SOLID/LIQUID RATIOS

Eq. 2.6 may be evaluated in terms of aqueous concentrations in finite and infinite bath boundary conditions. In the finite bath the concentration at the boundary changes with time while in case of an infinite bath (infinite volume of water) or a strong sorbent the concentrations at the interface

are fixed. Flux densities (from eq. 2.6) may be easily converted into changes of concentrations by introducing the specific area of the interface and volumes (here for water during desorption, V_w):

$$\frac{dC_w}{dt} = \frac{F}{V_w}\frac{m_d\,3}{\rho_p\,r} = -\frac{1}{\frac{\delta_w}{D_{aq}} + \frac{\delta_p}{D_e}}\frac{m_d\,3}{V_w\,\rho_p\,r}\left(C_w - \frac{C_s}{K_d}\right) \tag{2.13}$$

Unknown aqueous (C_w) and solid concentrations (C_s) in the finite bath (batch experiment) change over time which may be evaluated based on mass conservation:

$$C_s\,m_d + C_w V_w = C_{s,eq}\,m_d + C_{w,eq}V_w = C_{w,eq}\,K_d\,m_d + C_{w,eq}V_w \tag{2.14}$$

C_s thus is:

$$C_s = C_{w,eq}K_d + C_{w,eq}\frac{V_w}{m_d} - C_w\frac{V_w}{m_d} \tag{2.15}$$

and the concentration difference in eq. 2.16 becomes:

$$\begin{aligned} C_w - \frac{C_s}{K_d} &= C_w - C_{w,eq} - C_{w,eq}\frac{V_w}{m_d\,K_d} + C_w\frac{V_w}{m_d K_d} \\ &= C_w\left(1 + \frac{V_w}{K_d\,m_d}\right) - C_{w,eq}\left(1 + \frac{V_w}{K_d\,m_d}\right) \\ &= \left(1 + \frac{V_w}{K_d\,m_d}\right)\left(C_w - C_{w,eq}\right) \end{aligned} \tag{2.16}$$

Thus eq. 2.13 becomes (extended by the term in parenthesis):

$$\begin{aligned} \frac{dC_w}{dt} &= -\frac{1}{\frac{\delta_w}{D_{aq}} + \frac{\delta_p}{D_e}}\frac{m_d\,3}{V_w\,\rho_p\,r}\left(1 + \frac{V_w}{K_d\,m_d}\right)\left(C_w - C_{w,eq}\right) \\ &\approx -\frac{1}{10\sqrt{\frac{d}{D_{aq}v}} + \sqrt{\frac{\pi}{D_e\left(\varepsilon + K_d\,\rho_p\right)}t}}\frac{3}{r\,K_d\,\rho_p}\left(1 + K_d\frac{m_d}{V_w}\right)\left(C_w - C_{w,eq}\right) \end{aligned} \tag{2.17}$$

As we already saw in eqs. 2.6 and 2.9 at large values of K_d film diffusion dominates and K_d finally drops out (if $K_d < V_w/m_d$). If film diffusion dominates, kinetics slow down with increasing particle size $r^{3/2}$ while for intraparticle pore diffusion kinetics slow down with r^2 (because the time is then under the square root). The term before the concentration difference ($C_w - C_{w,eq}$) is a rate constant.. For discussion of characteristic times see scripts for film and intraparticle diffusion as well as Seidensticker et al. (2017) and the recent publication of Liu et al. (2022) on a first order approximation oof eq. 2.17. In contrast to many batch experiments, kinetics in columns are quite fast (because large values of m_d/V_w) and at least initially equilibrium conditions may be assumed (see Box 2). Therefore chap. 3. deals with equilibrium column leaching tests.

Box 1. General solutions to rate equations

The rate equations above follow the general form:

$$\frac{dC}{dt} = -\lambda\left(C - C_{eq}\right)$$

Solutions may be easily obtained by integration:

$$\int_0^{C_s} \frac{dC}{C - C_{eq}} = \int_0^t -\lambda\, dt$$

$$\ln\left(C - C_{eq}\right) - \ln\left(0 - C_{eq}\right) = \ln\left(-\frac{C}{C_{eq}} + 1\right) = -\lambda\, t$$

$$\frac{C}{C_{eq}} = 1 - \exp(-\lambda\, t)$$

C denotes either the concentration in water during a desorption experiment in a finite bath or the concentration in the solids for sorptive uptake (starting from a concentration of zero to the equilibrium concentration).

2.3 DIFFUSION IN SOLID PARTICLES AND FILM DIFFUSION

The two-film diffusion model can be easily derived for solid particles, e.g., natural organic particles or synthetic polymers (microplastics) by applying a partition coefficient at the particle/water interface.

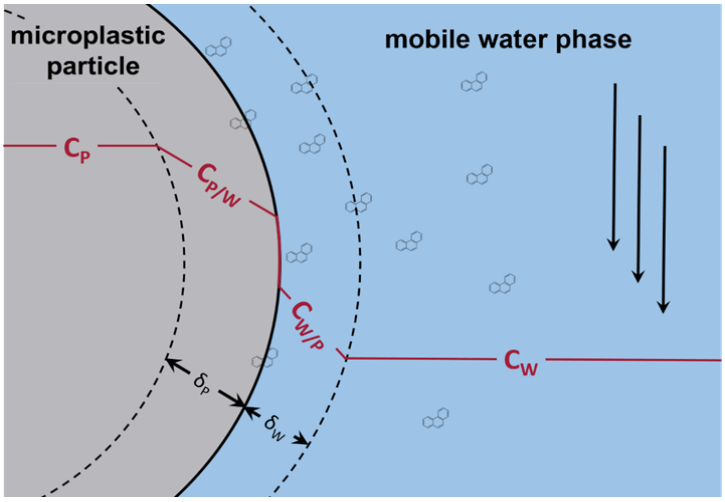


Fig. 2.2: Schematic view of the stagnant two-film model for a desorption scenario (red lines indicate concentration gradients) with a solid particle (e.g. microplastics). At the interface between both films "local equilibrium" is assumed and the partition coefficient between the particle and water applies ($C_{s/w} = K\, C_{w/s}$). δ_p and δ_w refer to the film thicknesses; C_s and C_w are the concentrations in the bulk particle and aqueous phase, respectively. (Figure: Sven Seidensticker)

The fluxes per surface area in each film can be evaluated following Fick's 1st law in each boundary layer (film). Under steady state conditions the fluxes in both films have to be equal:

$$F_w = \frac{-D_{aq}}{\delta_w}\left(C_w - C_{w/s}\right) = \frac{-D_s}{\delta_p}\left(C_{s/w} - C_s\right) = F_s \qquad (2.18)$$

C_w and C_s are the concentrations in water and in the solids; $C_{s/w}$, and $C_{w/s}$ denote the interfacial concentrations of the solute in the particle and the water, respectively; D_s and D_{aq} are the respective diffusion coefficients. The concentration in solids is volume based, which keep units consistent

(fluxes here come in mass per time per area = flux densities). The unknown concentration at one of the interfaces is found by introducing the partition coefficient of the compound between particle and water (K):

$$K = \frac{C_{s/w}}{C_{w/s}} \tag{2.19}$$

The partition coefficient in this case is volume based and thus dimensionless. The unknown concentration in one of the flux equations (here $C_{s/w}$) is:

$$\frac{-D_{aq}}{\delta_w}\left(C_w - \frac{C_{s/w}}{K}\right) = \frac{-D_s}{\delta_p}\left(C_{s/w} - C_s\right)$$

$$\text{thus} \quad C_{s/w} = \frac{C_s + \frac{D_{aq}\delta_p}{D_s\delta_w}C_w}{1 + \frac{D_{aq}\delta_p}{D_s\delta_w K_s}} \tag{2.20}$$

Eq. 2.20 then is inserted into eq. 2.18 and the flux is:

$$F_s = \frac{-D_s}{\delta_s}\left(\frac{C_s + \frac{D_{aq}\delta_p}{D_s\delta_w}C_w}{1 + \frac{D_{aq}\delta_p}{D_s\delta_w K}} - C_s\right) = \frac{-D_s}{\delta_p}\left(\frac{C_s + \frac{D_{aq}\delta_p}{D_s\delta_w}C_w - C_s - C_s\frac{D_{aq}\delta_p}{D_s\delta_w K}}{1 + \frac{D_{aq}\delta_p}{D_s\delta_w\, K}}\right)$$

$$= \frac{-D_s}{\delta_p}\left(\frac{\frac{D_{aq}\delta_p}{D_s\delta_w}\left(C_w - \frac{C_s}{K_s}\right)}{1 + \frac{D_{aq}\delta_p}{D_s\delta_w K}}\right) = -\frac{\frac{D_{aq}}{\delta_w}\left(C_w - \frac{C_s}{K}\right)}{1 + \frac{D_{aq}\delta_p}{D_s\delta_w K}} = -\frac{\left(C_w - \frac{C_s}{K}\right)}{\frac{\delta_w}{D_{aq}} + \frac{\delta_p}{D_s K}} \tag{2.21}$$

Thus, the flux in both films is:

$$F = F_w = F_p = -\frac{1}{\frac{\delta_w}{D_{aq}} + \frac{\delta_p}{D_s K}}\left(C_w - \frac{C_s}{K}\right) \tag{2.22}$$

From that we conclude that if K_p gets big, mass transfer becomes limited by diffusion in the aqueous boundary layer, provided that ratios of both diffusion coefficients and film thicknesses are similar. Again, ratios of the (additive) mass transfer resistances in eq. 2.22 may be used to find out which film limits, δ_p or δ_w:

$$\frac{\frac{\delta_w}{D_{aq}}}{\frac{\delta_p}{D_s K_p}} \approx \frac{\frac{10\sqrt{D_{aq}\frac{d}{v}}}{D_{aq}}}{\frac{\sqrt{\pi\, D_s \mathrm{t}}}{D_s K_p}} = \frac{10K_p\sqrt{D_p\frac{d}{v}}}{1.8\sqrt{D_{aq}\, t}} = 5.6\, K_p\sqrt{\frac{D_s\frac{d}{v}}{D_{aq}\, t}} \tag{2.23}$$

D_s represents the diffusion coefficient in the solid particle (e.g., a polymer diffusion coefficient). For large K_p mass transfer is initially limited by diffusion in the aqueous boundary layer, but as time increases, the ratio of the mass transfer resistances may drops below one and intraparticle diffusion starts to limit sorption/desorption kinetics. If D_s is much smaller than D_{aq} this may be much earlier than seen before for intraparticle pore diffusion. During first flooding of a column the time t

corresponds to d/v and the mass transfer resistance ratio only depends on square root of the diffusion coefficient ratios times 5.6 K_p (in this case mass transfer is limited by film diffusion for most compounds).

Box 2. Equilibration during first flooding of a column (film diffusion)

During first flooding of a column (before a leaching test actually starts) the percolating water encounters always fresh particles until the equilibrium concentration ($C_{w,eq}$) is reached:

$$\frac{dC_w}{dt} = -\frac{D_{aq}}{\delta_w}\frac{m_d\ 3}{V_w\ \rho_p\ r}\left(C_w - C_{w,eq}\right) = -k\ A°\left(C_w - C_{w,eq}\right)$$

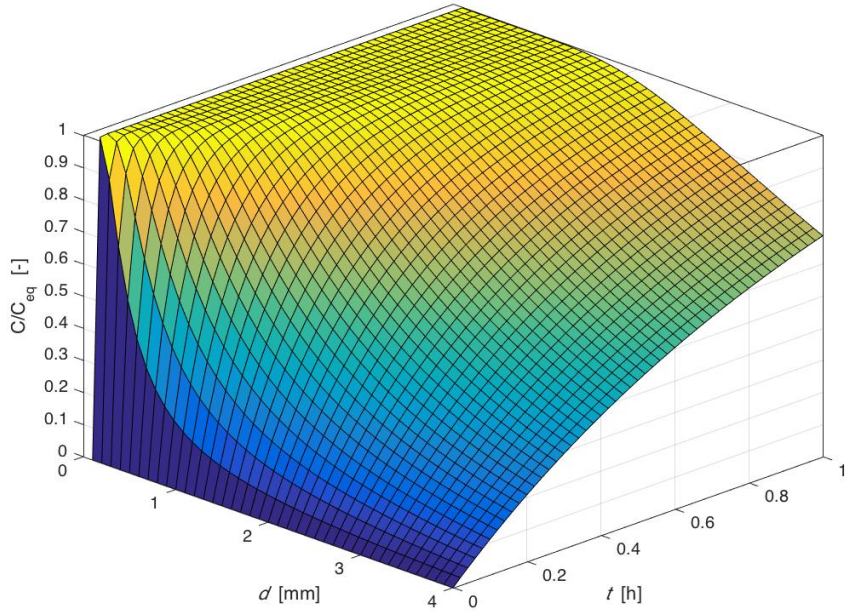
Realizing that m_d/ρ_p and V_w in a column correspond to volume of the solid particles (= 1-n) and the porosity n, resp. and calculating δ_w based on the empirical Sherwood relationship from Liu et al. (2014) results in:

$$\frac{dC_w}{dt} = -\frac{D_{aq}}{10\sqrt{D_{aq}\frac{d}{v}}}\frac{(1-n)\ 3}{n\ r}\left(C_w - C_{w,eq}\right) = -k\ A°\left(C_w - C_{w,eq}\right)$$

d/v here denotes the contact time with the particle. Integrating yields the well-known exponential function for the concentration increase in water during first flooding of the column:

$$\frac{C_w}{C_{w,eq}} = 1 - \exp\left(-0.1\sqrt{D_{aq}\frac{v}{2\ d}}\ \frac{(1-n)\ 3}{n\ r}\ t\right) = 1 - \exp(-k\ A°\ t)$$

This is fairly rapid (provided that desorption is limited by diffusion in the aqueous boundary layer) as shown below and independent on K_d. This is valid for homogenous samples - if only a fraction of the particles carries the contamination, m_d in the first eq. may be much smaller and equilibration is slower.



Only for large particles with diameters (d) > 3 mm, equilibrium is not reached within one hour.

If in contrast, the question is how long it takes to leach the contaminant more or less completely from the solids, a different boundary condition namely "the infinite bath" applies (the particle now is continuously purged with fresh water) and desorption slows down with increasing K_d:

$$\frac{C_s}{C_{s,eq}} = \exp\left(-0.1\sqrt{D_{aq}\frac{v}{d}}\ \frac{3}{K_d\ \rho_p\ r}\ t\right)$$

For a K_d of 10 and ρ_b of 2.5, the time scale is ca. 25 times longer than equilibration of pore water during the first flooding of the column (K_d times ρ_b). Note, that with increasing time, the mass transfer resistance may shift to the intraparticle domain which slows down kinetics even more (especially if large particles are concerned).

3. 1D COLUMN TESTS

3.1 ADVECTION DISPERSION EQUATION IN A COLUMN

Above we introduced shaking tests where the concentration in the water may be affected by dilution of the sample with more and more water (increasing *LS* ratio). Much closer to natural conditions and thus more relevant results are obtained by column leaching tests. Here the sample is packed into a column (a so-called "packed bed") and flooded with clean water usually from the bottom to the top (to avoid entrapped air). Conceptually a front of clean water ($C_w = 0$) then moves through the column (in a so-called "piston flow") displacing the contaminant. Initially steep concentration gradients between the solid and percolating water establish and thus at the beginning of the column test equilibrium concentrations are frequently observed in the effluent (i.e. the local equilibrium assumption is fulfilled at early times). Finally, the concentration will decrease (when the clean water front arrives at the column outlet) as described by the well-known advection dispersion equation:

$$\frac{\partial C}{\partial t} = \frac{D_l}{R}\frac{\partial^2 \mathrm{C}}{\partial x^2} - \frac{v}{R}\frac{\partial C}{\partial t} \tag{3.1}$$

D_l is the longitudinal dispersion coefficient [m² s^{-1}] (in x direction), v the flow velocity [m s^{-1}], x the distance or length of the column [m] and R denotes the retardation factor [-], defined as:

$$R = 1 + K_d\frac{\rho}{n} \tag{3.2}$$

ρ and n denote the dry bulk density [kg l^{-1}] and the (intergranular) porosity [-] of the packed bed. Note, the ratio n/ρ [l kg^{-1}] equals the liquid solid ratio (*LS*) in the column (which typically is smaller than in batch leaching test ca. 0.2 l kg^{-1} at a porosity of 0.35). A simple approximated analytical solution for the advection-dispersion equation (ADE) is given by:

$$\begin{aligned}\frac{C}{C_o} &= 1 - 0.5\ \mathrm{erfc}\left[\frac{x - \frac{v}{R}t}{2\sqrt{\frac{D_l}{R}t}}\right] = 1 - 0.5\ \mathrm{erfc}\left[\frac{x - \frac{v}{R}LS\frac{x}{v}\frac{\rho}{n}}{2\sqrt{\frac{D_l}{R}LS\frac{x}{v}\frac{\rho}{n}}}\right] \\ &= 1 - 0.5\ \mathrm{erfc}\left[\frac{x\left(1 - \frac{LS}{R}\frac{\rho}{n}\right)}{2\sqrt{\frac{D_l}{R}LS\frac{x}{v}\frac{\rho}{n}}}\right] = 1 - 0.5\ \mathrm{erfc}\left[\frac{\frac{n}{\rho} + K_d - LS}{2\sqrt{\frac{D_l}{x\,v}\left(\frac{n}{\rho} + K_d\right)LS}}\right]\end{aligned} \tag{3.3}$$

erfc denotes the complementary error function. Time t is also expressed based on *LS*:

$$t = LS\frac{x}{v}\frac{\rho}{n} \tag{3.4}$$

$C/C_o = 0.5$ in eq. 3.3 is reached if the term in in parenthesis becomes zero, which is given for $LS = K_d + n/\rho$. This solution assumes that initially the sample is equilibrated with the solids (which is a simplification, see below). C_o in this case is the initial equilibrium concentration in the column which has to be calculated based on mass balance considerations from the initial solids concentration $C_{s,ini}$ liquid to solid ratio in the column (see chap. 1):

$$C_o = \frac{C_{s,ini}}{K_d + \frac{n}{\rho}} = \frac{\frac{C_{s,ini}}{K_d}}{1 + \frac{n}{K_d\,\rho}} \tag{3.5}$$

Note, that $C_{s,ini}/K_d$ denotes the equilibrium concentration in water without dilution – half that concentration is achieved for $LS = K_d + n/\rho$. Eq. 3.3 is an approximation and only valid for small values of the dispersion coefficient (e.g. the dispersion length has to be shorter than the column length: $\alpha_L < 0.1\,x$). For more dispersion (or mixing) in the column an expanded solution is needed:

$$\frac{C}{C_o} = 1 - 0.5\left[\operatorname{erfc}\left(\frac{x - \frac{v}{R}t}{2\sqrt{\frac{D_l}{R}t}}\right) + \exp\left(\frac{xv}{D_l}\right)\operatorname{erfc}\left(\frac{x + \frac{v}{R}t}{2\sqrt{\frac{D_l}{R}t}}\right)\right] \tag{3.6}$$

In the literature often more simple equations are preferred instead of eq. 3.6 or 3.3 such as serial extraction (so-called cascade model, see chap 1.3) or continuous stirred-tank reactors (CSTR) which based on a mass balance are:

$$\begin{aligned} &V_w\frac{dC_w}{dt} + m_d\frac{dC_s}{dt} = \frac{dC_w}{dt}(V_w + m_d\,K_d) = -q\,C_w \\ &\Longrightarrow \frac{C_w}{C_{w,o}} = \exp\left(\frac{-q\,t}{V_w + m_d K_d}\right) = \exp\left(\frac{-LS}{\frac{n}{\rho} + K_d}\right) \end{aligned} \tag{3.7}$$

n/ρ here equals the liquid solid ratio (= V_w/m_d) in the reactor (n is the water filled intergranular pore space and ρ the dry mass of solids per unit volume = bulk density). If - as often the case - K_d is much larger than n/ρ, the argument in Eq. 3.7 simplifies to LS/K_d, which matches eq. 1.4 (cascade model). If LS equals ($K_d + n/\rho$) then C/C_o is exp(-1) = 0.368 in eq. 3.7. At this point LS and R are related as follows:

$$R = LS\,\frac{\rho}{n} = \left(\frac{n}{\rho} + K_d\right)\frac{\rho}{n} = 1 + K_d\,\frac{\rho}{n} \tag{3.8}$$

If this is inserted into eq. 3.3. then erfc becomes 1 (argument = 0) and C/C_o is close to 0.5 (LS at the breakthrough of the clean water front). This corresponds to the time after the pore volume in the column was replaced R-times. C/C_o at LS = ($K_d + n/\rho$) in eq. 3.6 also depends on the dispersion coefficient (decreases with increasing dispersion coefficient).

In reality, the advection dispersion equations discussed above do not exactly apply to column tests. During the first flood of the column the infiltrating water always encounters “fresh” material and the solute is displaced from the inlet of the column leading to a different initial condition shown in Fig. 3.1. C_o in this case corresponds to $C_{s,ini}/K_d$. Note, as K_d decreases C_o increases and large concentrations are achieved at the outlet during the first flood for solutes such as “salts” which finally could lead to density driven flow especially if percolation is stopped (leading to more mixing in the column).

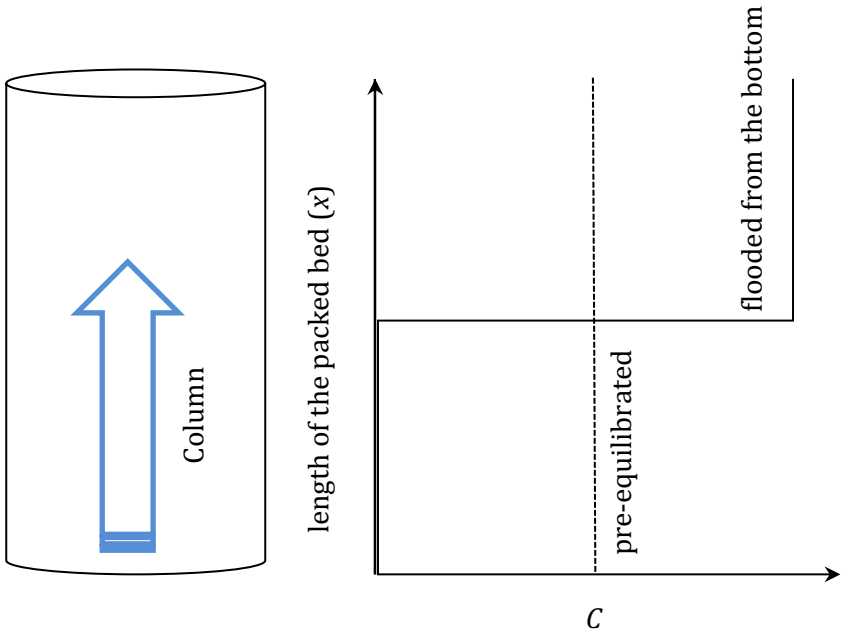


Fig. 3.1: Initial concentration profiles in a pre-equilibrated column and the more realistic case of a column flooded from the bottom

Therefore, in a real world up-flow column test the initial condition after first flooding has to be considered leading to:

$$\frac{C}{C_o} = 1 - 0.5\ \mathrm{erfc}\left[\frac{x - \frac{v}{R} - \frac{v}{R}t}{2\sqrt{\frac{D_l}{R}t}}\right] = 1 - 0.5\ \mathrm{erfc}\left[\frac{x(R-1) - \frac{v}{R}t}{2\sqrt{\frac{D_l}{R}t}}\right] \qquad (3.9a)$$

$$= 1 - 0.5\ \mathrm{erfc}\left[\frac{x(R-1) - t}{2\sqrt{D_l R\, t}}\right]$$

If we use again LS to replace time ($t = LS\frac{x}{v}\frac{\rho}{n}$) and use the longitudinal dispersivity α_l to calculate D_l (= $\alpha_l\, v$) we get:

$$\frac{C}{C_o} = 1 - 0.5\ \mathrm{erfc}\left[\frac{x(R-1) - v\, LS\frac{x}{v}\frac{\rho}{n}}{2\sqrt{\alpha_l v\, R\, LS\frac{x}{v}\frac{\rho}{n}}}\right] = 1 - 0.5\ \mathrm{erfc}\left[\frac{K_d - LS}{2\sqrt{\frac{\alpha_l}{x}\left(\frac{n}{\rho} + K_d\right)LS}}\right] \qquad (3.9b)$$

The difference to eq. 3.3 is only in the numerator of erfc where now just K_d – LS appears (n/ρ is "lost"). If K_d equals LS eq. 3.3 we obtain C/C_o = 0.5 (=> erfc (0) = 1) and in principle K_d could be determined directly from leaching curves (valid only at small dispersivities $\frac{\alpha_l}{x} < 0.1$). If LS goes to zero then erfc vanishes and C/C_o = 1. Eq. 3.9b is an approximation for small dispersivities, the more precise extended solution is:

$$\frac{C}{C_o} = 1 - 0.5 \left[\operatorname{erfc}\left(\frac{K_d - LS}{2\sqrt{\frac{\alpha_l}{\mathrm{x}}\left(\frac{n}{\rho} + K_d\right) LS}} \right) + \exp\left(\frac{x}{\alpha_l} \frac{1}{\left(\frac{n}{K_d\,\rho} + 1\right)} \right) \operatorname{erfc}\left(\frac{K_d + LS}{2\sqrt{\frac{\alpha_l}{\mathrm{x}}\left(\frac{n}{\rho} + K_d\right) LS}} \right) \right] \quad (3.10a)$$

If we assume α_l being a function of the distance travelled, e.g., = 0.1 x, then x drops out and if $K_d > n/\rho$ (which typically is 0.4/1.6 = 0.25), we finally get a simple approximation:

$$\frac{C}{C_o} = 1 - 0.5 \left[\operatorname{erfc}\left(\frac{K_d - LS}{2\sqrt{0.1\,K_d\,LS}} \right) + \exp\left(\frac{1}{0.1\left(\frac{n}{K_d\,\rho} + 1\right)} \right) \operatorname{erfc}\left(\frac{K_d + LS}{2\sqrt{0.1\,K_d\,LS}} \right) \right] \quad (3.10b)$$

For $K_d = LS$ (=> erfc(0) = 1) and K_d values > n/ρ), C/C_o is between 0.4 (α/x =0.1) and 0.25 (α/x = 1). This would allow an easy determination of K_d from leaching curves which would simple correspond to LS after C/C_o dropped to approx. 1/3 (0.4 - 0.25). Only the first term in erfc is needed for very small dispersivities (α/x << 0.1, see also eq. 3.9b).

Neglecting dispersion but accounting for mass transfer limitations (e.g., film diffusion) the Bohard-Adams approximation (Myers et al., 2023) may be used to describe the leaching behavior:

$$\frac{C}{C_o} = 1 - \frac{1}{1 + \exp\left(k\,A^\circ\,\frac{x}{v}\frac{\rho}{n}(K_d - LS) \right)} \quad (3.11)$$

This agrees very well with eq. 3.9b for fast kinetics (small grain sizes) and low dispersivities ($k = D_{aq}/\delta_w$; $A^\circ = (1\text{-}n)/n$ 3/radius; see also Box 2).

In Figs. 3.2 - 3.4 the different equations are compared for small and large values for the longitudinal dispersivity. At small dispersivities eq. 3.9 and 3.10 (and 3.6 pre-equilibrium case) agree, while at large dispersivities eq. 3.10 and 3.6 show a faster decline. Fig. 3.2 shows how real data fit to this simple equilibrium models.

Results from leaching tests are often shown in cumulative form, sum of the solute mass released vs. LS. The integral also allows to check mass balances of the different equations employed. This is shown in Fig. 3.3 for the cases shown in Fig. 3.1. For all column models besides the approximate case (eq. 3.9) the mass balance is achieved. Again, at small dispersivities eq. 3.9 and 3.10 (and 3.6) agree very well while at large dispersivities the approximation (eq. 3.9) shows large deviations. All models agree at low LS ratios (i.e. $LS < 0.1\ K_d$), because at this point the solute is not yet depleted from the solids ($C_s \approx C_{s,ini}$).

_LS_ in real time vs. cumulative sampling:

LS in the analytical solutions for the advection dispersion equation refers to a specific time point. In column tests typically water is sampled from the effluent over extended time (e.g., until 1 liter is obtained) and this has to be considered in assigning the correct *LS* (e.g., if one sample is obtained between *LS* = 1 and *LS* = 2, then the corresponding time point would be in the middle *LS* = 1.5).

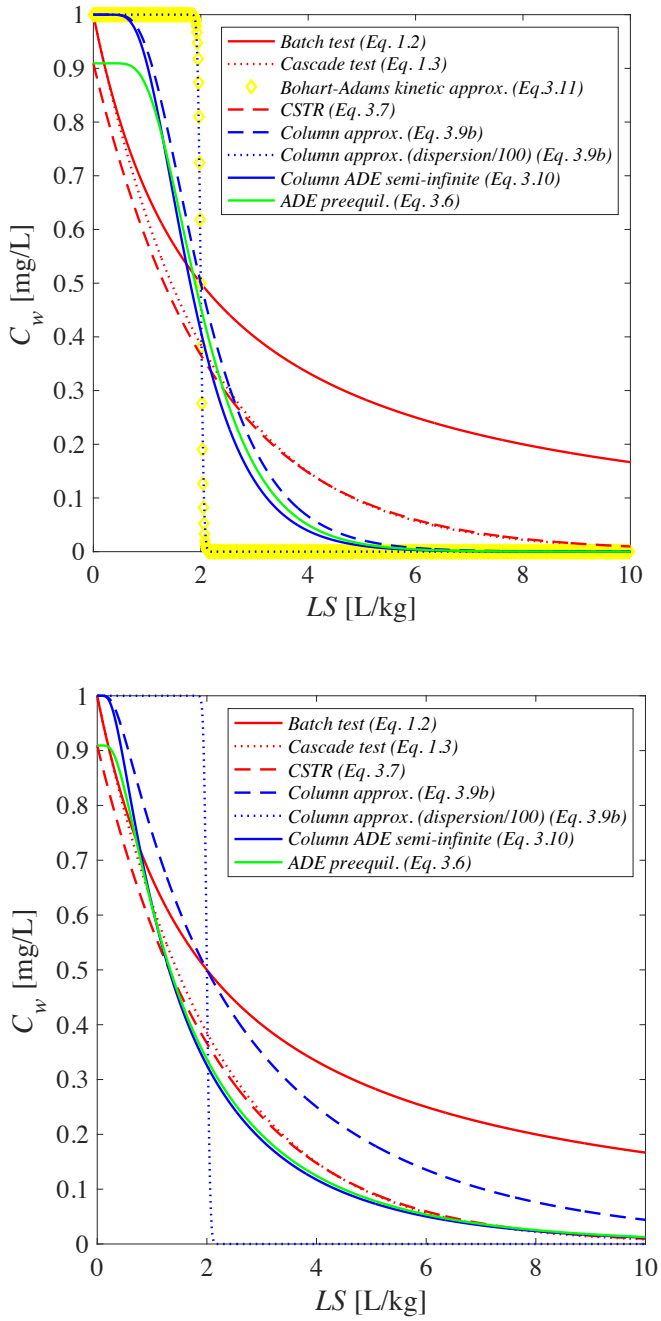


Fig. 3.1: Comparison of leaching curves from different leaching models *vs.* the liquid solid ratio; top: α = 10% of column length; bottom: 50% (ADE: Advection Dispersion Equation, CSTR: Continuous Stirred Tank Reactor; $C_{s,ini}$ = 2 mg kg^{-1}; K_d = 2, n = 0.35; d_s =2.7 kg l^{-1}; ρ = 1.775 kg l^{-1}; column length = 20 cm, v_a = 1 m day^{-1})

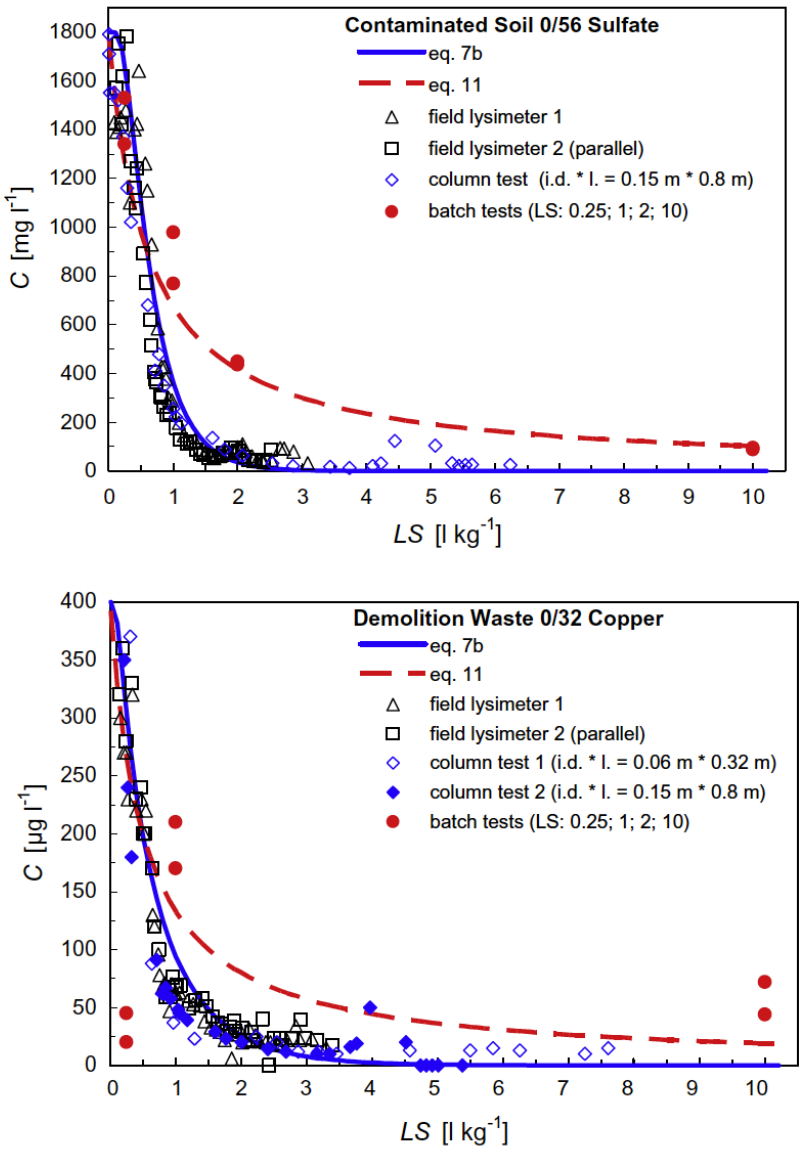


Fig. 3.2: Comparison of leachate concentrations from field lysimeters (natural infiltration of rain, layer thickness 0.5 m, partly in parallels), from columns of different inner diameters (i.d.) and lengths (l.) and batch tests with different *LS* with analytical solutions (for details see Grathwohl and Susset, 2009)

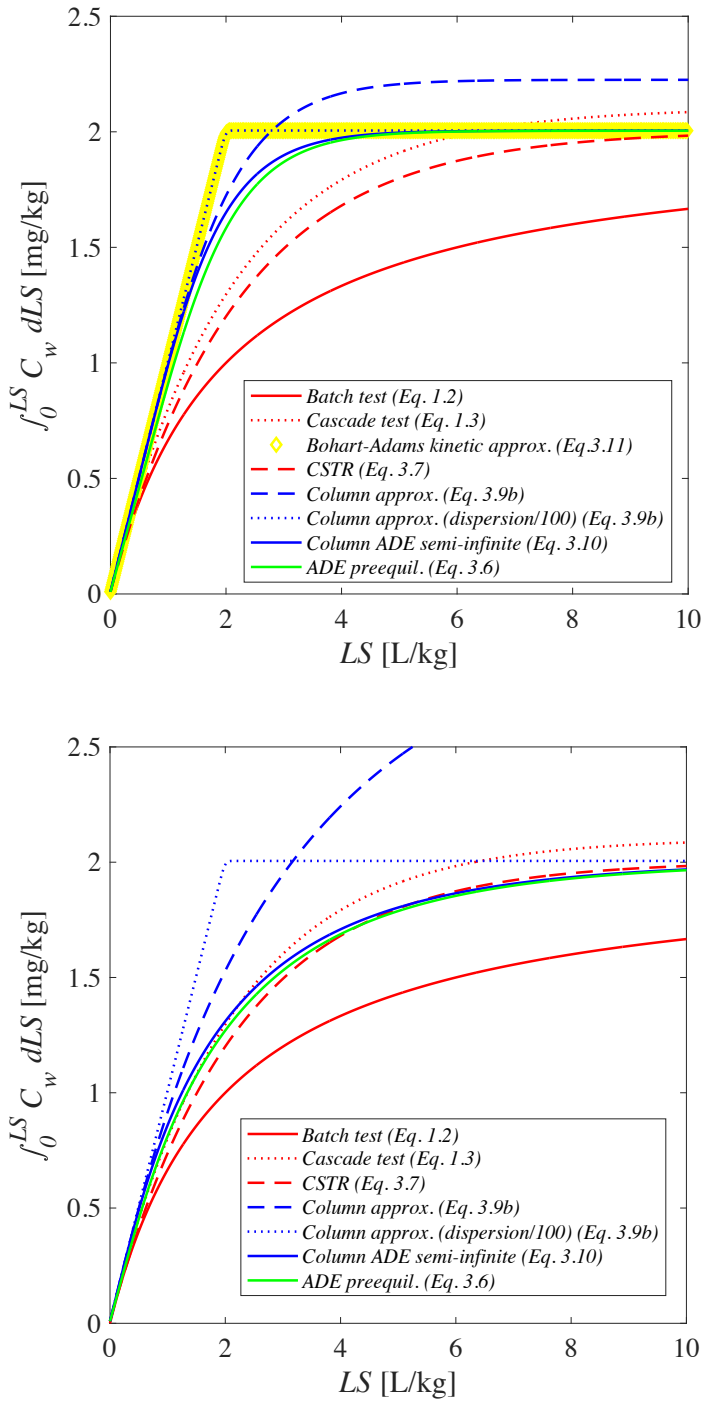


Fig. 3.3: Comparison of cumulative leaching curves from different leaching models *vs.* the liquid solid ratio; top: α = 10% of column length; bottom: 50% (ADE: Advection Dispersion Equation, CSTR: Continuous Stirred Tank Reactor; $C_{s,ini}$ = 2 mg kg^{-1}; K_d = 2, n = 0.35; d_s =2.7 kg l^{-1}; ρ = 1.775 kg l^{-1}; column length = 20 cm, v_a = 1 m day^{-1})

3.2 HOW LONG IS EQUILIBRIUM OBSERVED IN THE COLUMN EFFLUENT

From the mass transfer analysis explained above and data observed we may conclude that column tests initially start at or close to equilibrium conditions. At a given time, however, the clean water front arrives at the end of the column and we observe a more or less rapid decrease in concentrations followed by long tailing which is dominated by slow desorption processes (mostly intraparticle diffusion). If equilibrium conditions prevail, this equilibrium time scale (t_{eq}) may simply be calculated by how often the pore volume has to be displaced to "push out" the contaminated water:

$$t_{eq} = \frac{x_{col}}{v} R \tag{3.12}$$

X_{col} is the distance (length of the column, v the flow velocity [m s^{-1}], x the distance or length of the column [m] and R denotes the retardation factor. If we consider the first flooding of the column the distance to be displaced and thus the time will be shorter:

$$t_{eq} = \frac{x_{col} - x_{clean}}{v} R = \frac{x_{col} - x_{col}/R}{v} R = \frac{x_{col}}{v} K_d \frac{\rho_b}{n} \tag{3.13}$$

If desorption is slow then the length of the mass transfer zone (X_S) may be considered (see Box 3):

$$t_{eq} = \frac{x_{col} - X_S}{v} R = \frac{x_{col} - x_{col}/R}{v} R = \frac{x_{col}}{v} (R-1) = \frac{x_{col}}{v} K_d \frac{\rho_b}{n} \tag{3.14}$$

Depending on the definition this is defined as the time when the leading front of the mass transfer sone arrives at the end of the column. See Box 3 for the definition of mass transfer zones.

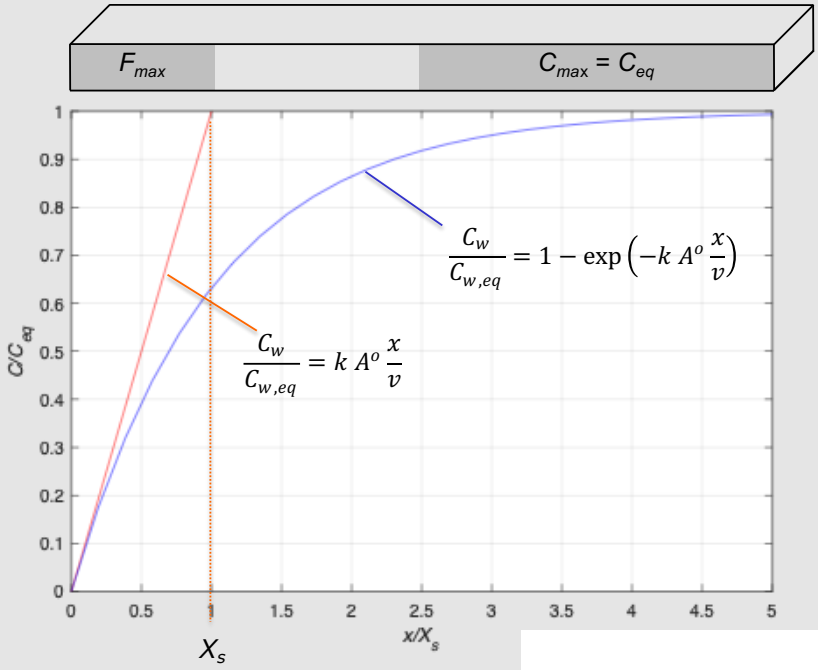
Box 3. The length of the mass transfer zone (see also Box 2)

If desorption is slow, then concentrations in the column slowly approach equilibrium conditions ($C_{w,eq}$) is reached. For simple first order mass transfer this follows:

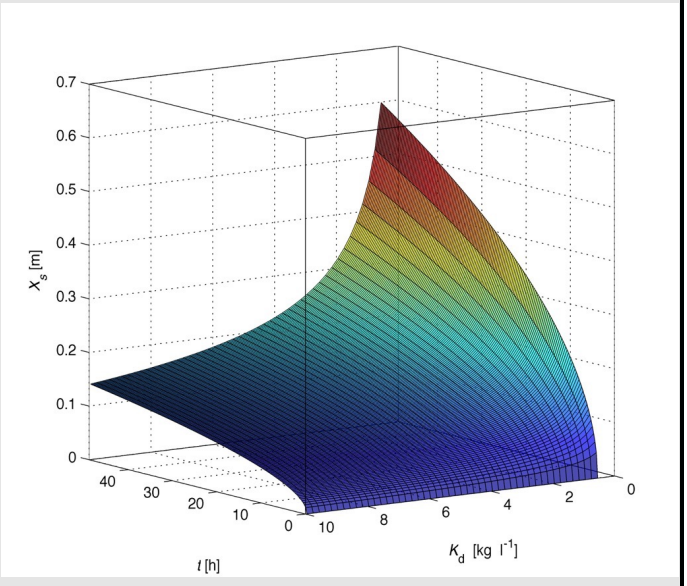
$$\frac{C_w}{C_{w,eq}} = 1 - \exp\left(-k\,A^o\,\frac{x}{v}\right) = 1 - \exp\left(-\frac{D_{aq}}{\delta}\,\frac{m_d\,6}{V_w\,\rho_p\,d}\,\frac{x}{v}\right) \approx 1 - \exp\left(-\frac{D_{aq}}{\delta}\,\frac{(1-n)\,6}{n\,d}\,\frac{x}{v}\right)$$

x/v denotes travel time in the column, k and $A°$ are the mass transfer coefficient and the surface to volume (of water) ratio (of the reactive particles). The right equation is only valid for homogeneous samples; if only a fraction of the material is reactive, equilibration is slower. The length of the mass transfer zone may be defined when 63% of the equilibrium concentration is achieved (the argument of the exponential function becomes 1):

$$X_s = \frac{v}{k\,A^o} = \frac{v}{\frac{D_{aq}}{\delta}\,\frac{m_d\,6}{V_w\,\rho_p\,d}} \approx \frac{v}{\frac{D_{aq}}{\delta}\,\frac{(1-n)\,6}{n\,d}} = \frac{v\,n\,d^2}{Sh\,D_{aq}(1-n)\,6}$$



For intraparticle diffusion the length of the mass transfer zone during leaching increases with time because the concentration gradients inside the grains become flatter and flatter.
It increases with the square root of time and is short for high K_d values. This does not apply for the first flooding of a column because here the time scale is related to the grain size (d/v) and equilibration becomes very fast.



3.3 NONLINEAR SORPTION IN LEACHING AND BREAKTHROUGH

While breakthrough of a nonlinearly sorbing solute with a Freundlich exponent $1/n < 1$ causes a self-sharpening front during column leaching this cause extended tailing as illustrate in the figure. For the self-sharpening front retardation factors can be simply derived based on mass balance considerations (by calculating the water volume $V_{w,BTC}$ a given inlet concentration $C_{w,in}$ needed to cover all sorption sites and the pore volume V_w in the column):

$$\begin{aligned} C_{w,in}\, V_{w,BTC} &= C_{w,in}\, V_w + C_s\, m_d = C_{w,in}\, V_w + K_{Fr} \left(C_{w,in}\right)^{1/n} m_d \\ V_{w,BTC} &= V_w + m_d\, K_{Fr} \left(C_{w,in}\right)^{1/n-1} \\ R_d &= \frac{V_{w,BTC}}{V_w} = 1 + \frac{m_d}{V_w}\, K_{Fr} \left(C_{w,in}\right)^{1/n-1} \end{aligned} \tag{3.15}$$

$V_{w,BTC}/V_w$ denotes the number of pore volumes (= PV) which need to be displaced until breakthrough occurs (this is the retardation factor: R_d = total capacity of the system/mobile fraction). In principle, this also holds for leaching (desorption) of a solute from a column after initially equilibrium was achieved. However, with non-linear sorption the concentration profiles look very different for breakthrough and leaching. In leaching (desorption) extended tailing (i.e. spreading front or dispersive wave) will develop and the leading edge has now less retardation, which follows the derivative of the Freundlich sorption isotherm:

$$R_d = 1 + K_{Fr}\, \frac{\rho_b}{n}\, 1/n\, {C_{w,in}}^{1/n-1} \tag{3.16}$$

$C_{w,in}$ is now the initial equilibrium concentration at the start of leaching. This allows to calculate the retardation of concentrating smaller than the initial concentration (or C_w as a function of PV):

$$\begin{aligned} R_d = PV &= 1 + K_{Fr}\, \frac{\rho_b}{n}\, 1/n\, {C_w}^{1/n-1} \\ PV - 1 &= 1/n\, K_{Fr}\, \frac{\rho_b}{n}\, {C_w}^{1/n-1} \\ \left(\frac{PV-1}{1/n\, K_{Fr}\, \frac{\rho_b}{n}}\right)^{1/(1/n-1)} &= C_w \end{aligned} \tag{3.17}$$

Example: $\left(\frac{10-1}{0.5\ 9}\right)^{1/(0.5-1)} = \left(\frac{9}{4.5}\right)^{-1/0.5} = \left(\frac{4.5}{9}\right)^{2} = 0.25$

See Fig. 3.4 for illustration of breakthrough and leaching curves.

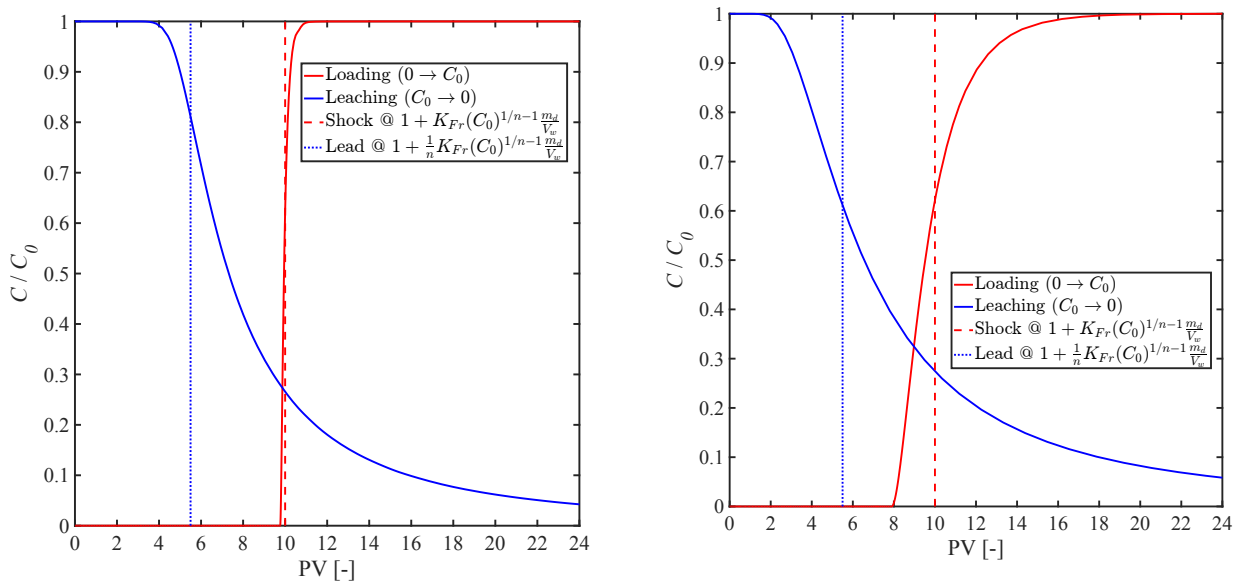


Fig. 3.4: Impact of non-linear sorption on leaching curves in blue compared to breakthrough (red); left: small dispersivity = $x/100$; right: $x/10$; PV: number of displaced pore volumes = "time"; Freundlich exponent = 0.5. The self-sharpening front ("shock wave": red, dashed) moves with a retardation factor of $1 + K_{Fr}\frac{\rho_b}{n}\left(C_{w,in}\right)^{1/n-1}$, while the leading edge (blue, dashed) of the leaching curve moves with $1 + \frac{\rho_b}{n} 1/n\, K_{Fr}\frac{1}{n}\left(C_{w,in}\right)^{1/n-1}$ (here: 1+9 $1^{-0.5}$ = 10 and 1+0.5 9 $1^{-0.5}$ = 5.5; the concentration in the tailing (trailing edge) drops with $(0.5\ 9)^2/(\text{PV-1})^2$, e.g. at PV=10: $(4.5/9)^2 = 0.25$); the centers of mass move with $1 + K_{Fr}\ \frac{m_d}{V_w}\left(C_{w,in}\right)^{1/n-1}$ (the areas above and under the curves are the same: mass conservation). For an example with no dispersion see lecture notes about "Nonlinear sorption". Note, in a leaching test PV has to be transferred to LS ("time") = $(\text{PV-1})n/\rho_b$.

Box 4. C_w is not always a function of C_s

In leaching tests aqueous concentrations (C_w) observed in batch or column experiments (or determined with passive samplers) are not always a function of the concentration determined in the solids. This is obvious for the example shown in the Figure, where the contamination of the soil sample is due to spilled transformer oil containing PCBs (polychlorinated biphenyls). C_w in this case is determined by Raoult's law and thus the composition of the oil and not the amount of oil in the sample is decisive. This applies for all mixed samples where the contamination is carried by a minor component of the sample, e.g., black carbon in sediments, soot in top soils, chars in industrial soils, demolition and other solid waste materials, etc... This may be illustrated by assuming that only the organic carbon fraction carries the contaminant:

$$C_w = \frac{C_s}{K_d} = \frac{C_{oc}\, m_{oc}}{K_d\, m_d} == \frac{C_{oc}\, f_{oc}}{K_{oc}\, f_{oc}}$$

m_{oc} and m_d denote the mass of organic carbon and dry mass of solids in the sample (m_{oc} / m_d = f_{oc}); finally, C_w only depends on the contaminant concentration in organic carbon (C_{oc}) and the organic carbon distribution coefficient (K_{oc}). C_w of course increases if C_{oc} increases, but the amount of organic carbon in the sample (f_{oc}) drops out, large amounts of contaminated organic carbon would appear as high C_s but not influence C_w. This is a simplified approach, in reality pollutants entering soils or sediments on particles will be redistributed between the various sorbent pools present (e.g. PAHs entering with soot particles from atmospheric deposition will get redistributed among the various natural soil organic matter phases). Note, that the amount of pollutant carrying particles may also be relevant for the redistribution kinetics especially if only a minor particle fraction is relevant.

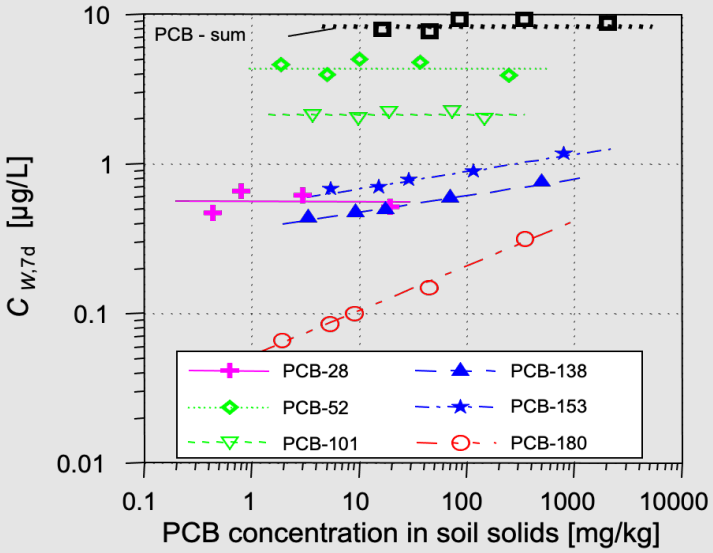


Figure. Effluent concentrations (C_w) of PCBs vs. concentration in solids (C_s) after a 7 day column leaching test. C_w of the sum of PCBs is independent on C_s, due to contamination by transformer oil. C_w depends on the composition of the oil (Raoult's law) and not on the amount of oil in the sample. Increasing concentrations of PCB-138-180 are due particles released from the sample (particle facilitated transport of strongly sorbing compounds).

4. INFLUENCE OF DOC (AND PARTICLE FACILITATED TRANSPORT)

Concentrations of many compounds, especially heavy metals, often depend strongly on pH and dissolved organic carbon DOC (e.g., natural occurring humic and fulvic acids). Besides the complexation of heavy metals, DOC also causes solubilization of organic compounds which decreases the sorption coefficients and increases leaching. The solubilization factor (corresponding to the decrease in sorption or K_d) is given by mass balance considerations:

$$C_{w,tot} = X_{tot}/V_w = (C_w V_w + C_w K_{DOC} f_{DOC})/V_w$$
$$S' = C_{w,tot}/C_w = 1 + C_{DOC} K_{DOC} \approx 1 + f_{DOC} K_{DOC} \quad (4.1)$$

f_{DOC} and K_{DOC} denote the fraction of dissolved organic carbon in the aqueous phase and the organic carbon normalized distribution coefficient (l kg^{-1}). Fig. 4.1 and 4.2 show the influence of increasing DOC values on relative concentrations and distribution patterns of polycyclic aromatic compounds (PAHs) leaching from demolition waste. Low solubility compounds are affected most but they do not contribute much to the sum of the 16 EPA PAHs, if the DOC concentration stays below 30 mg/l. It should be noted that in both cases - heavy metals and organic compounds - DOC can cause significantly enhanced leaching and in many field cases is probably more important than particle facilitated transport. In contrast to suspended particles, DOC cannot be filtered (in the lab or in the field) and therefore is an important parameter if present in sufficient concentrations (> 30 mg L^{-1}).

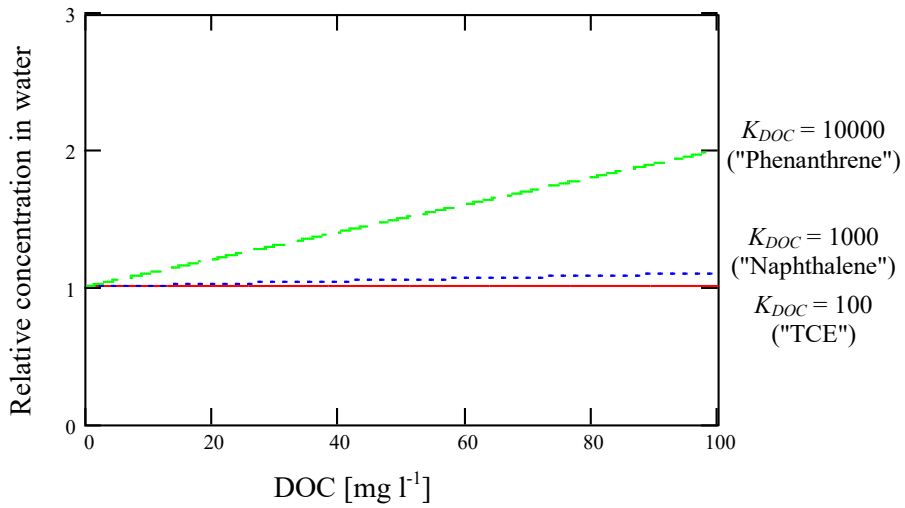


Fig. 4.1: A significant influence (> factor 1,5) appears only for highly hydrophobic compounds (K_{oc} > 10000, e.g. 3ring PAHS) and DOC concentrations above 50 mg l^{-1}. K_{oc}s of 100, 1000 and 10000 would be roughly representative for trichloroethene (TCE), naphthalene and phenanthrene, respectively.

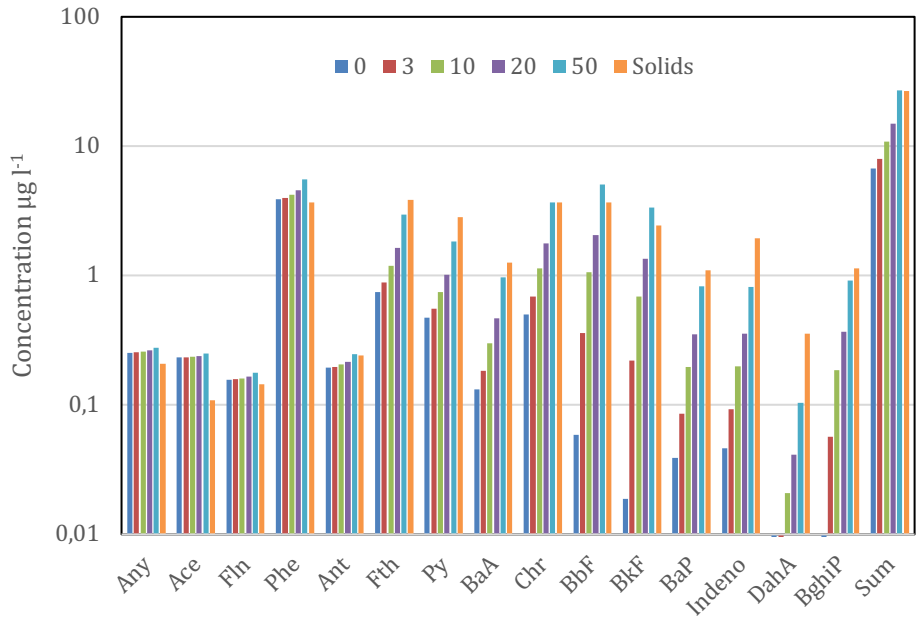


Fig 4.2: Distribution pattern of 16 EPA PAHs in aqueous leachate concentrations of soils. With increasing DOC (0 - 50 mg l^{-1}) total aqueous concentrations shift towards the distribution pattern of the solids (right bar for each PAH). Note, that low molecular weight PAHs up to anthracene (Ant) are not much affected and that more than 20 mg l^{-1} are needed to cause a significant increase in the sum of the 16 EPA PAHs.

5. REFERENCES

BBodSchV: Bundes-Bodenschutz- und Altlastenverordnung vom 16. Juli 1999. Bundesgesetzblatt Jahrgang 1999, Teil I Nr.36, S. 1554-1682

Beyer, C., Konrad, W., Rügner, H., Bauer, S., Liedl, R., Grathwohl, P. (2009): Model-based prediction of long-term leaching of contaminants from secondary materials in road constructions and noise protection dams. Waste Management, 29, 839–850; doi:10.1016/j.wasman.2008.06.025

DIN V 19736 (1998): Ableitung von Konzentrationen organischer Stoffe im Bodenwasser. Beuth, Berlin

Finkel, M., Grathwohl, P. (2017). Impact of pre-equilibration and diffusion limited release kinetics on effluent concentration in column leaching tests: Insights from numerical simulations. Waste Management. 63, 58–73, http://dx.doi.org/10.1016/j.wasman.2016.11.031

Förstner, U., Grathwohl, P., Dahmke, A. (2002): Ingenieurgeochemie.- Springer

Grathwohl, P. (1998): Diffusion in Natural Porous Media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics. Kluwer Academic Publishers, Boston, 224 p.

Grathwohl, P. (2000): Elemente der Sickerwasserprognose zur Gefahrenbeurteilung "Grundwasser" bei kontaminierten Böden/Materialien/Altlasten. Handbuch Bodenschutz, BoS. Lfg. V/00, 40 S.

Grathwohl, P., Susset, B. (2001): Sickerwasserprognose für organische Schadstoffe: Grundlagen und Stand der Forschung. altlastenspektrum, 6, 285-293

Grathwohl, P., Susset, B. (2009): Comparison of percolation to batch and sequential leaching tests: Theory and data. Waste Management, 29, 2681-2689, doi:10.1016/j.wasman.2009.05.016

Grathwohl, P., Susset B. (2010): Reply to the comment by D. Guyonnet, on "Comparison on percolation to batch and sequential leaching tests: Theory and data". Waste Management, 30, 1748-1751

Grathwohl, P. (2014): On Equilibration of Pore Water in Column Leaching Tests. Waste Management, 34, 908 - 918 http://dx.doi.org/10.1016/j.wasman.2014.02.012

Liu, Y. Illangasekare, T.H., Kitanidis, P.K. (2014): Long-term mass transfer and mixing-controlled reactions of a DNAPL plume from persistent residuals. J. Cont. Hydrol., 157, 11–24

Liu, B., Finkel, M., Grathwohl, P. (2021): Mass transfer principles in column percolation tests: Initial conditions and tailing in heterogeneous materials. Materials, 2021, 14, 4708. https://doi.org/10.3390/ma14164708

Liu, B., Finkel, M., Grathwohl, P. (2022): First order approximation for coupled film and intraparticle pore diffusion to model sorption/desorption batch experiments. J. Hazardous Materials, rev.

Myers, T.G., Cabrera-Codony, A., Valverde, A. (2023): On the development of a consistent mathematical model for adsorption in a packed column (and why standard models fail). International Journal of Heat and Mass Transfer 202, 123660, https://doi.org/10.1016/j.ijheatmasstransfer.2022.123660

NEN 7349:1995 (nl). Leaching characteristics of solid earthy and stony building and waste materials - Leaching tests - Determination of the leaching of inorganic components from granular materials with the cascade test (withdrawn)

Rügner, H., Kleineidam, S., Grathwohl, P. (1999): Long-term sorption kinetics of phenanthrene in aquifer materials. Environ. Sci. Tech., 33, 10, 1645 - 1651

Seidensticker, S., Zarfl, C., Cirpka, O., Fellenberg, G., Grathwohl, P. (2017). Shift in Mass Transfer of Wastewater Contaminants from Microplastics in the Presence of Dissolved Substances. Environ. Sci. Technol., 51, 12254–12263

Susset B., Leuchs, W., Grathwohl, P. (2011): Leaching standards for mineral recycling materials - a harmonized regulatory concept upcoming German Recycling Decree. Waste Management, 31, 201 – 214 (doi:10.1016/j.wasman.2010.08.017)

Weiß, H., Eberhardt, C., Grathwohl, P. (1997): Säulenversuche zur Grundwassergefährdungs-abschätzung an kontaminierten Standorten. TerraTech 5, 52-55