

Numerical and Analytical Modelling of Organic Leaching in Column Tests: "A Priori" Prediction of Release Rates Based On Material Properties

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Abstract: Column tests are an important laboratory tool for groundwater risk assessment. Depending on the mass transfer rates either maximum concentrations (C_{max} , equilibrium) or maximum fluxes (F_{max} , non-equilibrium) are monitored in the aqueous column effluent. With the aim of understanding and determining the relationships between material characteristics, contaminant properties, hydraulic conditions and contaminant release rates several "numerical column experiments" were performed. This allowed to identify "effective parameters" which can be used in simple analytical solutions to predict how long leaching of a compound in a column test will occur under equilibrium conditions. The results show a good agreement of numerical and analytical calculated equilibrium leaching times based on known material and compound properties.

Introduction

Since the remediation of all of the contaminated sites in Europe is economically not feasible, it is an overall aim of GRACOS to develop practicable groundwater risk assessment procedures. With regard to the harmonisation of legal standards and assessment methodologies in the EU many activities are ongoing in the field of groundwater risk assessment (e.g. the research project "Sickerwasserprognose" of the German Federal Ministry of Education and Research). In Germany the soil protection ordinance focuses on the contaminant concentrations to be expected in the groundwater and not on the contaminant level in soils or sediments (BBodSchG, 1996 and BBodSchV 1999) which requires new methods in groundwater risk assessment (Rudek & Eberle, 2001). Column leaching tests are an important laboratory tool commonly used for the determination of desorption or dissolution rates of (mobile) contaminants from various materials (e.g. contaminated soils and sediments, construction materials, demolition waste etc.) which can be an important contaminant source for groundwater pollution when they are deposited above (e.g. artificial fillings in the unsaturated zone) or below the groundwater table (e.g. construction components in the saturated zone). For the interpretation of the column test results with respect to the prediction of in situ concentrations in seepage water in the field, it is crucial to distinguish whether equilibrium (C_{max}) or non-equilibrium conditions (F_{max}) prevailed during the contaminant release in the laboratory test. To understand the major release and transport processes laboratory column leaching tests with specific materials and model simulations were performed. Different scenarios represented by "numerical column experiments" are calculated with the process based numerical code SMART (Finkel et al., 1999) and the major "leaching effective parameters" were identified employing sensitivity analysis. With the numerical model the "equilibrium leaching time" - in the following defined as the time duration until the effluent concentration (C_w) drops to 50% of the equilibrium concentration ($C_{w, max}$) - and the long-term decrease of contaminant release rates (time periods of years) can be determined. More simple analytical solutions based on Fick's second law were tested to predict the numerical calculated equilibrium leaching times. First results show, that the time scales of equilibrium release for various scenarios can be approximated by simple and practicable analytical solutions based on the concepts of retarded transport of a dissolution/desorption front or the lengths of mass transfer zones.

Laboratory Investigations

Organic column leaching tests with selected “GRACOS-materials” (polluted top soil, bottom ash, harbour sludge, old road tar) and previous laboratory work on various materials (Weiß et al., 1997) show, that two principally different leaching scenarios can be distinguished (for more details see Susset & Grathwohl, 2002).

A: Equilibrium conditions, the saturation concentration or the maximum concentration (C_{max}) is observed in the effluent over an extended period of time depending on the contaminant reservoir in the column

Equilibrium conditions are usually reached when the contaminant is rapidly released from the solid into the percolating water. One example are dispersed droplets of a non-aqueous phase liquid. In this case the saturation concentration (= water solubility of the compounds from the mixtures, as expected from Raoult's law) can be observed in the column effluent until the contaminant is depleted from the NAPL. Other cases of fast mass transfer are fine grained contaminated materials e.g. fine particles of carbon, coke or soot. Under equilibrium conditions the length of the mass transfer zone is much shorter than the column.

B: Non-equilibrium conditions, the effluent concentration starts to decrease rapidly and shows extended tailing. Maximum contaminant release rates (F_{max}) independent on the flow velocity are determined

Non-equilibrium conditions commonly prevail when desorption of contaminants from porous soil aggregates/particles is limited by slow intraparticle diffusion. In column tests with e.g. coarse grained porous materials the contaminant concentration in the column effluent initially decreases with the square root of time, indicating that diffusion in the intraparticle pore space is the major mass transfer process.

Numerical Modelling, Conceptual Model

For reasonable process based forward modelling of organic leaching, retarded pore diffusion as the limiting process of slow sorption/desorption kinetics has to be taken into account accurately. Pore diffusion itself depends on the following major material properties: grain size (and grain shape), intraparticle porosity, organic carbon content or sorption capacity. In addition the release rates depend on the contaminant properties (diffusion coefficients, solubility etc.) and the mass and distribution of the contaminants in the particles. Whether at the column outlet and for what time period equilibrium concentrations are observed, depends on the contact time of the percolating water in the porous medium as function of flow velocity and column length. Solute diffusion into porous soil aggregates and into lithofragments in the sorptive uptake and desorption mode can be described by Fick's 2nd law in spherical coordinates, where C , t and r denote the aqueous concentration, time and the radial distance from the center of a spherical particle.

$$\frac{dC}{dt} = D_a \left[\frac{d^2C}{dr^2} + \frac{2}{r} \cdot \frac{dC}{dr} \right] \quad (1)$$

In water-saturated porous media the apparent diffusion coefficient D_a depends on the aqueous diffusion coefficient (D_{aq}), the intraparticle porosity (ϵ), the sorption coefficient (K_d); the bulk density of the particle (ρ_{bulk}) and the tortuosity factor (τ_f).

$$D_a = \frac{D_{aq} \mathbf{e}}{(\mathbf{e} + K_d \mathbf{r}_{bulk}) \mathbf{t}_f} = \frac{D_{aq} \mathbf{e}}{\mathbf{a} \mathbf{t}_f} \quad (2)$$

α denotes the capacity factor ($= \mathbf{e} + K_d \mathbf{r}_{bulk}$). In the presented modelling, \mathbf{t}_f is predicted directly from the intraparticle porosity based on Archie's law using an empirical exponent m ($= 2$):

$$\mathbf{t}_f = \mathbf{e}^{1-m} \quad (3)$$

The distribution coefficient $K_{d,eq}$ is the ratio of the contaminant concentration in solids and water at equilibrium conditions:

$$K_{d,eq} = C_s / C_{w,eq} \quad (4)$$

The process based numerical forward model SMART (Finkel et al., 1999) is coupled with a FD- solver for intraparticle diffusion ("BESSY", Jäger & Liedl, 2000). Spherical grains are divided in shells allowing precise resolution of the concentration gradients in the grain (non-equidistant nodes, decreasing shell thickness according to increasing concentration gradients in direction to the grain boundary) so that sorption/desorption kinetics with non-linear sorption isotherms (concentration dependent K_d) and time dependent concentration gradients can be modelled accurately. Heterogeneous grain mixtures are subdivided in fractions of different grain sizes and different lithocomponents with specific sorption and diffusion properties (mass percentages).

Figure 1 shows a simulation of a saturated organic column leaching test with 1D-saturated stationary flow for the same material but a different grain size (same initial solid concentration of phenanthrene, same column geometry, hydraulic and sorption properties).

The fine grained material of scenario A ($a = 0,1$ mm, bold lines in Fig. 1) with short diffusion distances allows fast mass transfer and thus the contact time of the percolating water (about 2,7 h) is sufficient to allow equilibration for 6 to 12 days depending on the column length (see Fig. 1 C, breakthrough curves, typically monitored in laboratory column experiments). Modelled concentration profiles in Fig 1 B (which are usually not measurable in the lab) show, that the length of the mass transfer zone (X_s , flow distance to reach the equilibrium concentration in the percolating water) is much shorter than the column length.

In scenario B, ($a = 1$ mm, thin lines in Fig. 1) slow diffusion along relatively long diffusion distances in the coarse porous material prevents a complete equilibration within the given contact time and the concentrations in the effluent start to decrease immediately (initially with the square root of time).

Figure 1 C includes the elution curves for the same conditions but double column length (dashed lines). Under equilibrium conditions the same effluent concentration is observed over twice the time period (twice the PHE-mass has to be leached out). Under non-equilibrium conditions the increased column length results in twice the effluent concentration in the tailing part. These relationships were observed as well in laboratory column experiments with varied flow velocities (Weiß, 1998). Under equilibrium conditions a decrease in the flow velocity results in a corresponding increase of the equilibrium leaching time period and under non-equilibrium conditions a corresponding increase of the effluent concentration in the tailing part was observed.

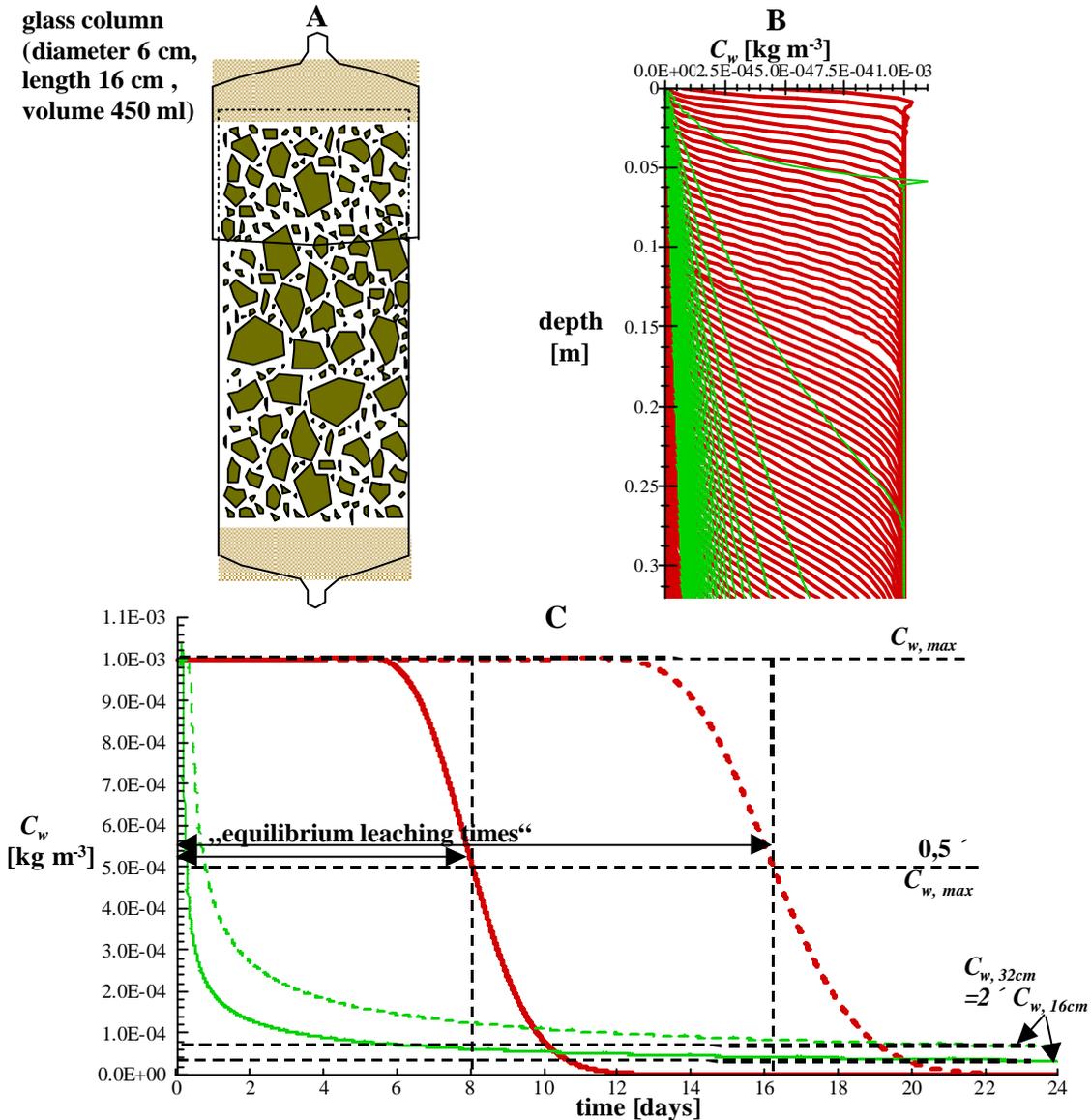


Figure 1: “Numerical column experiment” (1D-saturated flow, same hydraulic/ sorptivity): 1 A experimental setup, 1 B numerical concentration profiles in the column (time steps 5h), 1 C numerical determined concentrations in the column effluent versus time, scenario A (bold lines) silt (grain radii = 0,1 mm), scenario B (thin lines) coarse sand (grain radii = 1 mm); solid lines: column length of 16 cm, dashed lines: column length of 32 cm.

Analytical approximations

For a variety of initial and boundary conditions analytical solutions are available which allow to estimate how long it will take in a column test until the concentration in the effluent drops below 50% of the equilibrium concentration based on the local equilibrium assumption. Depending on "how far from equilibrium a certain experiment is", different analytical solutions are necessary to predict these arrival times of a desorption/dissolution front.

Scenario I: Equilibrium conditions, retardation:

During equilibrium sorption/desorption the retardation of the solutes can be expressed by a constant equilibrium retardation factor R_{eq} calculated with $K_{d,eq}$, n and ρ_{col} denote the flow effective porosity and the dry bulk density in the column. The equilibrium leaching time

(defined as time until $C_w = 0,5 * C_{eq}$) can be calculated from the retarded moving velocity of the solutes ($v_c = v_a/R$) and the column length L_{column} :

$$R_{eq} = 1 + \frac{K_{d,eq} \mathbf{r}_{col}}{n} \quad (5)$$

and

$$T_{btr,C/C_{eq}=0,5} = \frac{L_{column} R_{eq}}{v_a} \quad (6)$$

Scenario II : Non-equilibrium conditions, length of the mass transfer zone:

The length of the mass transfer zone (in our case the flow distance after which equilibrium conditions are reached) depends on the contaminant release process (slow intraparticle diffusion or dissolution), on material and contaminant properties and on the flow velocity of the percolating water (contact time). If the column is operated far away from equilibrium conditions, then the contaminant release occurs at a maximum possible flux. Scenario B (thin lines in Fig. 1 B) shows that then the length of the mass transfer zone is much longer than the column. At $x = X_s$ the contaminant concentration in the water reaches 63,2% of C_{max} . As desorption proceeds the effective diffusion distances (in spherical grains) increase (with the square root of time for short time periods) and the release rates decrease correspondingly (because concentration gradients decrease). X_s therefore also becomes time dependent. For diffusion limited desorption from spherical particles the length of the mass transfer zone X_s can be defined as (Grathwohl, 1998):

$$X_s = \frac{v_a n a \sqrt{t p}}{3 \sqrt{D_e a}} \quad (7)$$

If $L_{column} \ll X_s$, non-equilibrium conditions prevail in the column and contaminant release with maximum flux occurs. By setting X_s equal to the column length the time duration until the effluent concentration drops to $0,63 \times C_{max}$ can be calculated from eq. 8:

$$T_{btr,C/C_{eq} \geq 0,5} = \frac{9 D_e a L_{column}^2}{v_a^2 n^2 a^2 p} \quad (8)$$

Comparison of Analytical Predictions with Numerical Results

For sensitivity analysis various leaching scenarios with varied material parameters (a , e , n), sorption coefficients (K_d), hydraulic parameters (pumping rate Q or v_a) and column lengths (L_{column}) were investigated with SMART. The equilibrium leaching times (time duration until the concentrations in the effluent drop to 50% of equilibrium concentration) were determined from the numerical elution curves and compared to the analytical approximations (equations 6 and 8) in Figure 2.

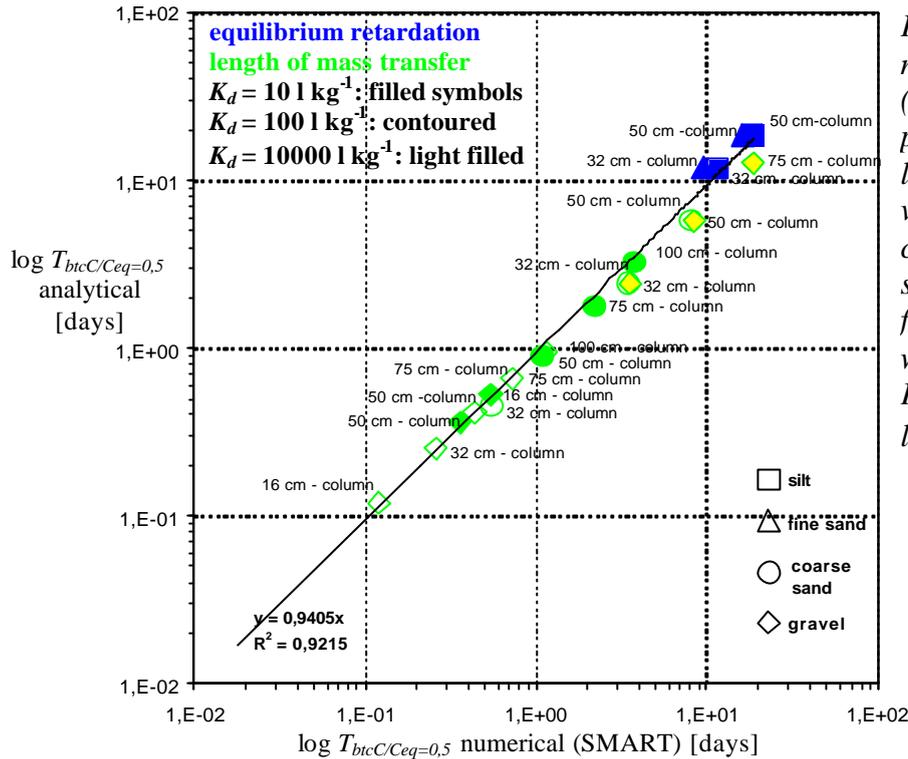


Figure 2: Comparison of numerically modelled (SMART) and analytical predicted equilibrium leaching times for a variety of column conditions (saturated, stationary 1D advective flow, $v_a = 1,39 \text{ m day}^{-1}$, with different grain sizes, K_d s, v_{as} and column lengths).

Fine grained materials, high distribution coefficients and long residence times (long columns) result in extended equilibrium leaching periods which can be predicted very well by v_a and retardation factors based on the local equilibrium assumption. For coarse grained materials, short columns, high flow velocities and small sorption capacities concentrations decrease rapidly which can be predicted from the length of mass transfer zone. For the most “experimental conditions” the analytical approximation methods agreed very well with numerically predicted arrival times.

The dimensionless Damköhler number $D^\#$ allows to distinguish between the two scenarios. It is defined as the ratio of transport time-scale to reaction time-scale (Weerd et al., 1998, Jennings & Kirkner, 1984).

$$D^\# = \frac{L_{column} D_a}{v_a a^2} \quad (9)$$

First calculations show, that for Damköhler numbers $\gg 1$ (contact time is relatively high in comparison with the diffusion/reaction time) the equilibrium retardation concept gives a good agreement of numerical and analytical predicted equilibrium times. For non-equilibrium conditions $D^\#$ decreases below about 0,1 (contact time is relatively short compared with reaction times) and the length of mass transfer concept (eq. 7 and 8) fits well with the numerical data.

Conclusions

Relationships between material properties, contaminant characteristics, hydraulic column conditions and contaminant release rates were developed in laboratory column investigations and extensive numerical model simulations (SMART) allow to identify the “leaching effective parameters”. These “effective parameters” (used as input for analytical

approximations) allow to predict accurately whether the contaminant concentrations at the column outlet are at equilibrium or not.

The Damköhler number allows the determination of validity areas of the two analytical approaches (retardation based on local equilibrium assumptions or considerations of the length of the mass transfer zone) for the prediction of equilibrium leaching times depending on column length, flow velocity, grain size, sorption and diffusion coefficients.

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