

Column Leaching Tests for Groundwater Risk Assessment: Concept, Interpretation of Results, and Reproducibility

Bernd Susset & Peter Grathwohl

Center for Applied Geoscience, Eberhard-Karls-University of Tübingen, Germany

Introduction

This paper describes a method for the assessment of groundwater risk due to pollutant emission from contaminated soils. The method is based on column tests which are commonly used for the determination of desorption or dissolution rates of contaminants from various materials (e.g. contaminated soils and sediments). In Germany, legal standards focus on the contaminant concentrations to be expected in the groundwater and not on the total contaminant concentration in soils or sediments (BBodSchG, 1996). The federal soil protection ordinance (BBodSchV, 1999) requires that sites where a risk for groundwater quality is suspected must be evaluated with respect to the contaminant concentrations to be expected in the seepage water and shallow groundwater. The point of compliance is the transition zone between unsaturated and saturated zone (Fig.1, left). According to BBodSchV (annex 1, 3.3) the prediction of contaminant concentrations in the seepage water can be carried out on the basis of material investigations in the laboratory. For organic compounds column leaching tests or lysimeter tests are suggested methods. Column tests represent an established method for research purposes to determine desorption and dissolution rates of contaminants in contaminated materials. They can be easily performed and they do not require costly equipment. As first results from round robin tests show, reasonable good reproducibility can be reached. Depending on the mass transfer rates either maximum concentrations (equilibrium) or maximum fluxes (non-equilibrium) are monitored in the aqueous column effluent. For some materials uncertainties still exist in interpretation of the results (especially the distinction between equilibrium or non-equilibrium). If equilibrium conditions are prevailing in the column, maximum (or equilibrium-) concentrations can be observed in the column effluent. The equilibrium concentration can be easily transferred to the point of compliance in the sense of a worst case approach. In the case of non-equilibrium conditions, the concentrations in the seepage water have to be calculated from the determined maximum fluxes. Whether equilibrium and non-equilibrium conditions prevail during the contaminant release, depends on the properties of the compounds and materials (intra-aggregate porosity, sorption capacity, surface to volume ratio etc.). The main objective of this contribution is to introduce the theory and typical results to be expected in column tests on leaching of organic compounds from various materials. The tests were performed according to the preliminary German Industrial Standard DIN V 19736.

Methodology

The column leaching procedure used in this study was published as a preliminary German Industrial Standard (DIN V 19736) and is described briefly in Fig. 1 (right). Water (degassed, contaminant-free, e.g. drinking water) is pumped from the storage tank through the column at a constant pumping rate e.g. using a peristaltic pump. The soil column and the storage tank are connected by a PE-(PVC)tubing, whereas the column and the glass-collection-bottle are connected by stainless steel tubing. The contaminated material is placed above a filter layer of quartz sand (distribution of flow). The column is percolated from the bottom to the top in

order to minimize the trapping of air bubbles. The flow velocity of water in the column is adjusted roughly to field conditions. In this study flow velocities in the column were about 1 m day^{-1} , which corresponds roughly to typical groundwater flow velocities in valley aquifers in Southern Germany.

The advantage of column tests compared to the usual shaking tests is that bulk density and the porosity of the sample are closer to field conditions, artifacts such as emulsions or suspensions are avoided and the change of effluent concentrations with time can be easily monitored (this allows the prediction of the long term decrease in contaminant release rates). Depending on the length of the mass transfer zone the concentration measured in the column effluent is either at equilibrium (which is the maximum possible concentration) or at non-equilibrium. If the column is operated far away from equilibrium conditions, then the contaminant release occurs at a maximum possible flux (Fig. 1, left).

The actual length of the mass transfer zone (X_s) depends on the contaminant release process (slow intraparticle or intra-aggregate diffusion *vs.* fast film transfer across an interface) and the flow velocity of the percolating water. X_s is usually very short (e.g. 1 cm - 10 cm) for the dissolution of organic contaminants from non-aqueous residual phase which is present in the porous media as dispersed blobs (e.g.: Miller et al., 1990; Grathwohl, 1998). X_s is usually not reached in laboratory column tests if the contaminant release rate is limited by slow desorption of contaminants from coarse grained or aggregated materials (because of slow aqueous diffusion and relatively long diffusion distances).

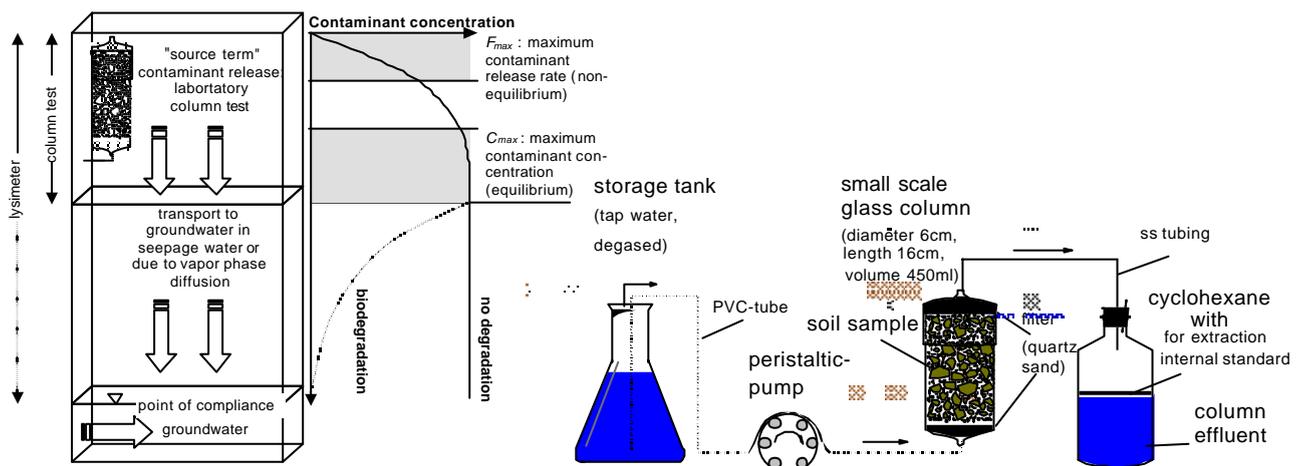


Figure 1, Left: Groundwater risk assessment procedure divided into the source term (material investigation) and the transport part (to the point of compliance). The presented column leaching tests cover only the source term whereas lysimeters may include the deeper reactive transport. The diagram shows the increase of the contaminant concentrations in seepage water. Initially maximum release rates are present (non-equilibrium: F_{max}). After longer flow distances maximum concentrations can be reached (C_{max} : equilibrium concentration during desorption or the solubility of the contaminants during dissolution from residual phase). During further transport to the groundwater table biodegradation may lead to decreasing contaminant concentrations in the seepage water. Right: schematic experimental setup for column leaching tests.

Results and Discussion

Figure 2 shows examples of column effluent concentrations of polycyclic aromatic hydrocarbons from a sandy sample containing coal tar in residual phase and diffusion limited-desorption of PAHs from contaminated material.

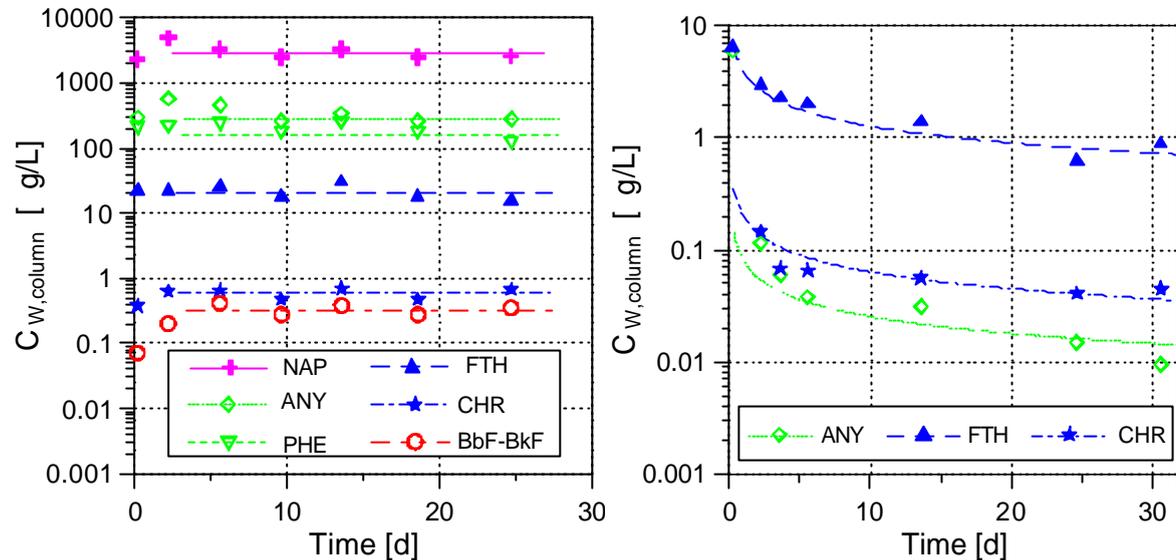


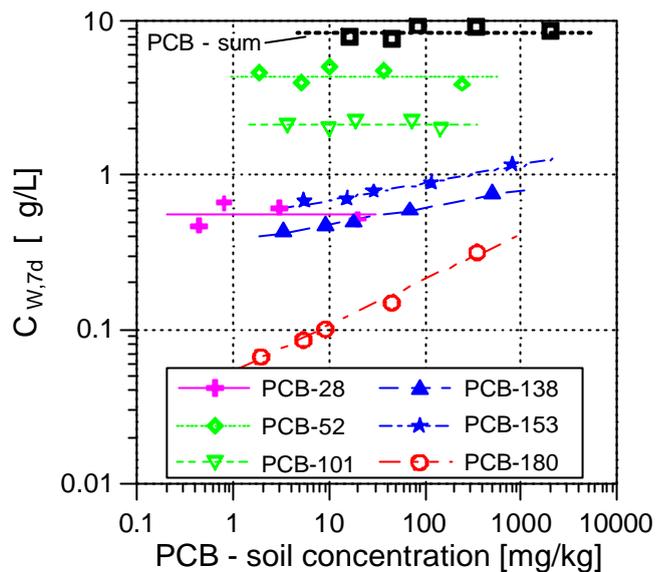
Figure 2: Column effluent concentrations of PAH from a sample containing coal tar in residual phase (left: equilibrium conditions) and for desorption which is limited by slow diffusion (right: non-equilibrium conditions, from Weiß et al., 1997). NAP: Naphthalene, ANY: Acenaphthene, PHE: Phenanthrene, FTH: Fluoranthene, CHR: Chrysene; BbF-BkF: Benz(b)-, Benz(k)fluoranthene.

Under equilibrium conditions the saturation concentration (= water solubility of the compounds from the mixtures, as expected from Raoult's law) was observed in the column effluent over the whole period of leaching time. As the sample contains non-aqueous residual phase (taroil), which is present in the porous media, dissolution of organic contaminants from the residual phase and dispersed blobs is the major mass-transfer process. The time period in which the saturation concentration can be observed depends on the contaminant mass (= reservoir) present in the sample.

Under non-equilibrium conditions the contaminant concentrations in the column effluent decreased with the square root of time. As the sample had a very low content of organic contaminants (no residual phase) slow aqueous diffusion and intra-particle diffusion was the major mass-transfer process.

For complex organic mixtures the saturation concentration can be calculated from Raoult's law, provided that the composition of the residual organic phase is known. In this case the contaminant concentration in the effluent depends on the composition of the residual phase and not on the concentration of the organic compound in soil as shown for PCBs in Fig. 3

Figure 3: Concentrations of polychlorinated biphenyls (PCBs) determined after 7 days in the column effluent ($C_{w,7d}$) vs. their concentration in 5 different soil samples. $C_{w,7d}$ of the relevant PCBs (PCB-sum) is independent of the concentration in the soil as expected from Raoult's law (the saturation concentration depends on the composition of the residual organic liquid and not on the amount of residual phase in the sample; Weiß et al., 1997).



Conclusions

Column tests can be used for the determination of desorption or dissolution rates of contaminants from various materials. First practical experience shows that column tests are easy to perform and do not require costly equipment.

Column tests allow the determination of either the contaminant saturation concentration in the effluent (equilibrium conditions) or the maximum contaminant release rate (non-equilibrium conditions: maximum concentration gradients between immobile and mobile phase).

The saturation concentration of the contaminant species is obtained in the column effluent until the contaminant species is dissolved if mass-transfer is fast, for example with dispersed residual tar oil blobs present in the sample. This saturation concentration is independent from the flow velocity. Especially for PAH (in tar oil) with low solubilities the dissolution lasts very long and the concentrations can be constant for several weeks and month. High soluble compounds can be leached out of residual phase very fast – the concentrations in the column effluent then decrease exponentially after a short equilibrium period (e.g. benzene leaching out of gasoline).

If the contaminant release is dominated by diffusion processes (slow, diffusion limited desorption) in the pore space and matrix (aggregated materials, rock and construction fragments), usually no equilibrium conditions in the column are reached. In this case the maximum flux, which is independent of the flow velocity, is obtained in the column effluent. Ideally the contaminant concentrations in the column effluent decrease with the square root of time (2nd Fick's law). Here, the observed concentrations in the column effluent depend on the flow velocity (increasing flow velocities cause increasing "dilution" of the concentrations).

With the concept of maximum concentration or maximum flux, determined in the column experiments, the prediction of the in situ concentration in soils or groundwater is relatively simple:

1. Dissolution from dispersed blobs of residual phase or fast desorption from small particles (e.g. < 100 μm): The saturation concentration (= equilibrium) is reached in-

situ after a short flow distance and equals the concentration determined in the column effluent.

2. Slow desorption (limited by intraparticle diffusion from porous grains/aggregates): The in-situ concentration can be estimated from the maximum flux determined in the column experiment, the groundwater or seepage water flow velocity and the total mass of contaminated material.

For some materials uncertainties still exist in the interpretation of the results (distinction between non-equilibrium/equilibrium) with respect to the prediction of in situ concentrations in the seepage water in the field. If the contaminants are associated with fine particles of carbon, coke or soot etc., a period of equilibrium leaching can precede the long-term diffusion limited contaminant release in the column. The “a priori” prediction of release rates based on material, contaminant and hydraulic properties with analytical and numerical tools is the objective of an ongoing GRACOS-project (for more details see Susset & Grathwohl, 2002).

The reproducibility of the column leaching test presented in this study is reasonably good as shown in Tab. 1. It should be noted that most of the uncertainty of a leaching test is due to sampling in the field. The most severe problem in all contaminated site investigations is to obtain a representative sample - or to know for which area the sample investigated is representative.

Table 1: Results from round robin column tests with a taroil-contaminated sample from a former gasworks site. Coefficients of variation (% , bold) of spiked water samples and column leachates sampled after 24 and 48 hours (VI_{dot} ; VI 24 h, VI 48 h), respectively. C_{avg} : average PAH concentrations (from TZW, 1998)

	Nap	Any	Ace	Fln	Phe	Ant	Fth	Pyren
VI_{dot} (0,048 µg/l) ^a	14,5	12,7	24,4	18,6	17,6	16,4	22,1	16,0
VI 24 h	61,6	30,5	33,2	30,5	44,8	28,0	25,1	46,9
VI 48 h	97,2	30,8	34,8	31,7	50,3	32,5	30,6	27,1
C_{mittel} [µg/l] 24h	686	888	373	555	414	84	96	57
C_{mittel} [µg/l] 48h	880	763	337	506	383	78	85	50

^a spiked concentration of each compound

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