Column Experiment Design to Estimate Parameters for Modeling of Vapor Extraction/Bioventing Sequential Soil Treatment

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Abstract: Setting up accurate and user-friendly models of physical, chemical and biological processes is particularly useful for design and optimization of vapor extraction/bioventing (SVE/SBV) systems, and prediction of residual concentrations and remediation time. Despite improvment of model structures, the optimum experiments should be designed for model calibration. The feasibility of parameter estimation procedure was analyzed to obtain the input parameters of a model using first order kinetics to describe diffusion out of aggregates and biodegradation. Kinetic parameters in a non-equilibrium model were evaluated by inverse modeling of several column experiments which allowed for freedom in selection of the convective gas flux during SVE/SBV. To keep the experimental procedure simple, only measurements of hydrocarbon concentrations in effluent were used as input data. The procedure was sensitive to measurement errors which can be significant, particularly during the initial phases of SVE/SBV. In most cases this may be solved by increasing the time and frequency of sampling.

Volatilization of organic compounds during SVE/SBV is enhanced by an advective gas flow which is induced by withdrawing vapors and/or pumping air through wells screened in the unsaturated zone. Assuming that: (a) the gas phase is continuous and the only mobile phase, i.e. mass fluxes by advection and dispersion in other phases may be neglected, (b) the soil water content is unaltered, and (c) the effect of volatilization on gas flow is negligible, the macroscopic mass balance equations can be used to describe the process (Mercer and Cohen, 1990).

The gas flow is assumed steady-state because in permeable soils the vapor flow reaches steady-state in a very short time compared to SVE/SBV operation (Johnson et al., 1990). The contaminant mass flux in the gas phase caused by molecular diffusion and kinematic dispersion is assumed to obey Fick's Law. The distribution over 4 phases is required to define relative mobility of organics in soil. Strong adsorbing and less volatile components are less mobile, thus more difficult to remove. In case that all mass transfer reactions are fast, it may be assumed that equilibrium is reached instantaneously, and the system can be described with a reduced number of equations, which is known as the local equilibrium model (Rathfelder et al 1991). The contaminant partitioning is then completely described by Henry's constants, partial vapor pressures (Raoult's law) and adsorption isotherms. If not all reactions are fast, in case of slow desorption, for instance, mass transfer reactions have to be estimated. Consequently, only a partially reduced system may be obtained. In such a case the equilibrium partitioning between gas, water and NAPL phases, kinetic mass transfer between solid and water phases, and biodegradation rate are required. To solve such a partially reduced system the ECOSAT model was used (Keizer and van Riemsdijk, 1994) which is suited for multi-component transport, whereby the chemical equilibrium assumption can be combined with n-order reaction kinetics. The partially reduced system is numerically solved using the stream-upwind scheme for spatial discretisation of advective terms, central discretisation scheme for spatial discretisation of dispersive terms and the Euler method for time stepping.

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The possibility of model identification, which is prerequisite to solve the inverse problem (Kool and Parker, 1988) was examined for 2 series of hypothetical experiments with varied induced gas fluxes (Malina, 1999; Mous et al., 1994). The purpose was to calibrate a SVE/SBV model for toluene recovery by estimating of the mass transfer parameters $\kappa_{\alpha\beta}$ and $\lambda_{\alpha\beta}$ and the biodegradation factor μ_α. Since μ_α is orders of magnitude larger than $\kappa_{\alpha\beta}$ and $\lambda_{\alpha\beta,}$ logarithms were considered and a vector $\theta = (\ln(\kappa_{\alpha\beta}), \ln(\lambda_{\alpha\beta}), \ln(\mu_\alpha))$ was taken as a parameter. The parameters used in the simulations are given in Table 1. In the first series, the initial toluene spill was large and the NAPL phase was present. In the second series, only gas, water and adsorbed toluene phases were present. The averaged retention time for the first series was, therefore, much longer than for the second series.

The experimental design is considered optimal if the smallest singular value is maximum, which means that all parameters in a single experiment have to be estimated with a certain minimum accuracy. The analysis of singular values and vectors (the direction of $\kappa_{\alpha\beta}$, $\lambda_{\alpha\beta}$ and $\mu_{\alpha,}$ in the parameter space) in individual experiments of the first series showed that the object function, corresponding to the first experiment with q_{air} = 0.1 l/hour, is very sensitive to μ_α and almost insensitive to $\kappa_{\alpha\beta}$. All experiments have one large and two small singular values. The large singular value correspond to either μ_α (biodegradation) or $\lambda_{\alpha\beta}$ (slow desorption). Sensitivity of concentration in the effluent gas to both parameters strongly depends on the sampling time with respect to rapid concentration decrease when no NAPL phase is present anymore. An increase in biodegradation speeds up the rapid concentration decrease, whereas an increase of the ad/desorption partitioning coefficient has the opposite effect. It makes the object function only sensitive to one parameter and, therefore, this experiment can only be used to estimate biodegradation when kinetic parameters $\kappa_{\alpha\beta}$ and $\lambda_{\alpha\beta}$ are well defined. In the second series, also one large singular value was present. This large value corresponds to the sensitivity of the object function to $\lambda_{\alpha\beta}$. At a moderate gas flux the object function is also sensitive to $\lambda_{\alpha\beta}$ and $\mu_{\alpha,}$. However, the object function is insensitive to $\lambda_{\alpha\beta}$ when the gas flux is low and to μ_α when it is high. The contribution of biodegradation to the removal of toluene increased exponentially as the gas flux decreased. So, as expected, sensitivity of the object function is correlated to contribution of biodegradation to the overall removal. Since sensitivity to $\lambda_{\alpha\beta}$ increases with decreasing gas flux, the optimum experimental design was found at q_{air} = 0.5 l/hour.

Inverse modeling of a SVE/SBV column experiment allows for freedom in choosing the optimal advective gas flux. Good experimental results could be obtained at a moderate gas flux of 0.5 l/hour, and no NAPL initially present. In the case NAPL is present, contaminant concentration is insensitive to kinetic parameters during the first phase of the remediation process. Only during the second phase, when NAPL is not present anymore, concentration in the effluent becomes sensitive to kinetic effects. On the other hand, the duration of the first part of the remediation process is very sensitive to kinetic effects. However, it is only possible to estimate biodegradation effects if ad/desorption effects are determined with sufficient accuracy.

Although the sensitivity of the parameter estimation to measurement errors has not been studied in details, this procedure is expected to be very sensitive to errors, especially during the initial phase. Generally, in such modeling measurement errors can be significant, however, increasing the sampling time and number of samples should suffice because the second term of the Hessian matrix becomes asymptotically negligible as the number of measurements goes to infinity. The

size of the numerical error in the sensitivity matrix $\varepsilon = |\Delta X(\theta)| / |X(\theta)|$ must be smaller than the smallest singular value (Mous, 1993) which requires small discretisation steps Δx and Δt.

Table 1. Parameters used in simulation of column experiments

Physical parameter			
Parameter	Unit	Value	
porosity, n	-	0.5	
air saturation degree, S_{air}	-	0.7	
water saturation, S_{water}	-	0.3	
advective gas flow, q_{air}	$dm^3 \cdot h^{-1}$	0.1-1.0	
diffusivity of toluene in air, D_{air}	$m^2 \cdot h^{-1}$	0.001	
column height, H_k	cm	45	
column diameter, D_k	cm	9.6	
temperature, T	^oC	20	
Chemical parameters			
Parameter	Unit	Toluene	Oxygen
initial concentration, C_0	$mol \cdot dm^{-3}$	0.084-0.422	0.00857
vapor pressure, p_v	$mg \cdot dm^{-3}$	110	
specific density, ρ	$g \cdot dm^{-3}$	867	
Henry constant log (H)	-	0.72	2.9
exchange constant ($\kappa_{\alpha\beta}$)	-	3.5	
partitioning constant ($\lambda_{\alpha\beta}$)	-	0.75	
biodegradation rate factor log(μ_α)	-	10.0	11.25

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