

Title: Mass Transfer in Non-Aqueous Phase Liquid Contaminated Heterogeneous Porous Media  
Name: Panagiotis Nikolopoulos

## ABSTRACT

Dense Non-aqueous Phase Liquids (DNAPL) form a group of organic chemical compounds that are immiscible with water. When spilled in the subsurface environment, they cause long-term contamination due to their low aqueous solubility. The entrapment of DNAPLs in natural soils typically exhibits complex morphologies. This generates uncertainty both in the prediction of heterogeneity effect on the mass flux produced by their dissolution and in the effect of soil structure on their fate and transport.

Experimental investigation on the effect of dual-permeability structure on dissolution, fate and transport of a common DNAPL (Tetrachloroethylene) was conducted on natural and artificial physical dual-permeability models. Flow similarity with typical field-scale conditions was maintained by using a modified Péclet ( $Pe$ ) number. Fractured model theory was implemented. It was shown that although conservative flow demonstrated strong dual transport regime, the effect of dual structure on the DNAPL transport was masked by time-dependent sorption effects. However, at field-scale this time-dependence diminishes and equilibrium sorption models can apply. This can lead to dual flow regimes in the transport of dissolved NAPLs in real dual-permeability domains. In contrast, dual structure did not demonstrate an effect on pure-phase DNAPL dissolution either by sorption or by diffusion. Strong non rate-limited dissolution was confirmed in the dual NAPL source systems even for unrealistically high aqueous velocities.

Analytical 2-dimensional and 3-dimensional models were formulated for the calculation of mass flux from a single NAPL source under uniform and non-uniform flow conditions. Existing understanding on NAPL source dissolution was enhanced by the incorporation of rate-limiting effects in these models. A new flow by-pass factor,  $F_b$ , was developed to capture permeability contrast effects. The model was validated by numerical and experimental data for typical field conditions,  $Da_{source} > 10$ ,  $Pe_{source} > 1$  and  $0.5 < k_r < 2$  (error:  $\pm 15\%$ ). Typical mass flux from DNAPL was found strongly sensitive to the mean groundwater velocity,  $\bar{u}$ , to the source cross-sectional area,  $A_{source}$  and to the permeability ratio,  $k_r$ , that induced flow by-pass effects.

Field-scale heterogeneity effect on DNAPL source zone dissolution was examined by performing numerical simulations of DNAPL spill and dissolution in 2-dimensional  $50m \times 10m$  permeability fields of stochastic properties and by implementing a mass flux normalisation method by Soga et al. (2004). 4 heterogeneity groups of 10 cases each were investigated under 3 flow scenarios, in order to separate between field-induced and relative permeability-induced flow heterogeneity levels. Normalised mass flux was found to be relatively steady with source zone depletion ranging mainly between 0.5 and 1.0 for typical field heterogeneity. Mass flux reduction was observed in the heterogeneous compared to uniform flow scenario. This reduction was caused primarily by relative permeability effects rather than field heterogeneity itself.

The developed analytical model was up-scaled to describe mass transfer from a distributed NAPL source zone. Numerical field-scale simulations showed that this model can predict successfully field-scale mass flux. The field-scale by-pass factor,  $\hat{F}_b$ , was found to be the main parameter that controls normalised mass flux from a NAPL source zone.

**Keywords:** DNAPL, analytical solution, mass flux, heterogeneity, flow by-pass factor, dual domain