



Release and transport of hydrophobic contaminants from aged multicomponent NAPL in the subsurface - jump up and run or sit back and relax?

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Aged multicomponent NAPLs such as tar-oil or crude oil can be found frequently in the subsurface in industrialized countries. They pose a continuing threat to soil and groundwater quality and challenge our ability for risk assessment and reclamation of contaminated sites. Depending on the characteristics of the NAPL phase and on their physico-chemical properties, several processes contribute to non-textbook-like behaviour of such phases. We will review release and transport processes of polycyclic aromatic hydrocarbons (PAH) and petroleum hydrocarbons (PH) in the subsurface. Among others, this review is based on a large number of percolation experiments conducted by our group employing different soil materials contaminated with multicomponent NAPL in the field and in the laboratory.

We found several indications for carrier facilitation of the transport of hydrophobic contaminants. The carrier transport behaviour is decisively different from dissolved compounds and in particular single weather events can contribute predominantly to the mobility of this fraction in the unsaturated zone. As a consequence, much larger concentrations of contaminants can be observed in the pore water than would be expected from equilibrium dissolution. However, the significance and extent of this process seems to be highly dependent on NAPL phase properties, such as viscosity and melting point, and on properties of the pore water, such as ionic strength. Apart from carrier facilitation, also the process of cosolvation requires consideration. Release of organic constituents from multicomponent NAPL can reduce the surface tension considerably to enhance the concentration of hydrophobic contaminants in the aqueous phase beyond the amount expected from dissolution equilibrium.

The evaluation of risk emanating from such multicomponent phases is additionally complicated by "aging" processes. Most literature investigating release kinetics deals with fresh NAPL, which show rapidly very high contaminant concentrations in the water. In contrast, aged phases, in particular those, which are rigid at temperatures $<20^{\circ}\text{C}$, obviously pose a much lower threat, because they neither release considerable amounts of contaminants by dissolution nor by carrier facilitation. Due to the complex interdependencies of the processes and the lack of appropriate models at present, it is impossible to estimate the mobility of hydrophobic contaminants without proper experimental data. In particular percolation experiments are a valuable tool for this task as they offer the unique possibility to observe carrier transport behaviour under quasi natural conditions. Our results show that it is crucial to consider the special properties of aged NAPL, changes of the physico-chemical and hydraulic gradients in the subsurface and the effect of mobile particles to be able to evaluate the risk emanating from such phases.