

determined for any pollutant/soil combination by performing preliminary batch and column experiments. These experiments can yield both the input parameters and insight into the degree of equilibrium achieved.

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{\rho_s}{\theta} K_F n C^{n-1} \frac{\partial C}{\partial t} \quad [4]$$

$$\frac{dq}{dt} = \frac{dq_f}{dt} + \frac{dq_s}{dt} \quad [5]$$

The second approach in solving equation 3 is to use a combination of equilibrium and first-order kinetics to describe the sorption process. In this approach, the sorption process is represented by two parts (equation 5) where q_f is the amount sorbed associated with the initial rapid phase and q_s is the amount sorbed associated with the later slow phase of sorption. Using this relationship, equation 3 is now modified as represented in equation 6.

$$\left(1 + \frac{\rho}{\theta} \frac{\partial q_f}{\partial C}\right) \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{\rho_s}{\theta} \alpha (q_{s,e} - q_s) \quad [6]$$

where

$$q_f = K_{F,f} C^{n_f}$$

$$q_s = K_{F,s} C^{n_s}$$

Lower case f in equation 6 represents parameters associated with the initial fast phase while s denotes those related to the second slow phase. The term α is an equilibrium/first-order rate constant and $q_{s,e}$ is the equilibrium pollutant mass associated with the solid phase normalized by the pollutant solid phase mass for the slow sorption- rate component. Miller and Weber (1988) more rigorously represent equation 6 and in their column reactor studies of the sorption of hydrophobic contaminants by aquifer materials, show its applicability to nitrobenzene transport.

Desorption, can also be an issue in contaminant migration through soil. For example, a sorbed pollutant can be released if the solution concentration in contact with the soil decreases (i.e. a rain event) or the concentrations of other constituents in solution change making it more favorable for mass transfer into the solvent. It is important to note that the rate of desorption and the rate of sorption can be quite different and hence the applicable equilibrium equations and values of parameters must be modified to account for this discrepancy. For example, although lead sorption

was shown to be greater than 95 % complete in less than 20 minutes by Eick *et al.* (1999), only 38% to 62% of lead had desorbed at 6.5 hours over the concentration range of 0.10-0.50 mM Pb. Weber, et al. (1991) have presented transport equations that include kinetic terms to account for the sorption and desorption, although these are first-order rates and may have limited applicability.

When soil freezing becomes a concern, both the driving forces and the processes of sorption, desorption, and transport of pollutants through unfrozen soil remain relevant, however the introduction of freezing brings into play other mechanisms that change the picture radically. The equations discussed above for unfrozen soil must, at a minimum, be modified due to the changes imparted to the soil and pollutant. The following sets out what we know and don't know about these processes and changes.

Fluid Transport In Freezing Soil

Consider the simplest case of a horizontal soil surface, with a homogeneous, fine grained soil profile saturated with uncontaminated water, and freezing temperatures above the soil surface that have persisted for some time. The thermal gradient and the phase changes associated with the freezing process generate a suction gradient that causes seepage of pore fluid toward the freezing soil. This upward flow can dominate and even reverse the direction of flow developed when the soil was unfrozen. Also the soil skeleton is no longer fixed, as is typically assumed in unfrozen soil, since the formation of ice causes the soil skeleton to expand.

Figure 3 shows the idealized soil profile undergoing cooling. T_f refers to the freezing temperature of the pore fluid; T_c and T_w , are the cold and warm side boundary temperatures. The role of the frozen fringe is especially important in seepage and freezing development because it controls the upward flow of water by its permeability which changes as ice forms in its pores. The whole system is changing with time, also, with the freezing process penetrating further into the soil, as long as T_c continues to decrease; and the upper portions of the soil are heaving upward as ice lenses continue to grow.

The pore fluid seepage velocity and quantity created by the freezing process depend on several factors, some of which are quite different from those controlling seepage in unfrozen soils. In soil with uncontaminated pore water, these include the following.

1) The availability of space into which that pore fluid can flow above the frozen fringe is governed by two factors: the thickness and degree of