

# Groundwater Hydraulics and Pollutant Transport

**Randall J. Charbeneau**

*The University of Texas at Austin*



Long Grove, Illinois



### Compositional Models

It is not difficult to develop compositional models for chemical leaching from contaminated soils, though the computational effort is significantly greater than that presented earlier. For each constituent, the mass balance relation Equation 5.4.3 and Raoult's law may be written as follows:

$$m_i = (\theta_w + \theta_a K_H + \rho_b K_d) c_{wi} + \theta_o c_{oi} ; c_{wi} = S_i \frac{c_{oi}/\omega_i}{\sum_j (c_{oj}/\omega_j)} \quad (5.4.21)$$

These relations may be combined to give

$$c_{oi} = \frac{m_i}{(\theta_w + \theta_a K_H + \rho_b K_d) \frac{S_i/\omega_i}{\sum_j (c_{oj}/\omega_j)} + \theta_o} \quad (5.4.22)$$

If the initial soil concentrations are known, then at any later time the magnitude of  $m_i$  and the other parameters are known for all constituents, and Equation 5.4.22 may be solved iteratively for the set of values  $c_{oi}$ . The left side is only slightly sensitive to the assumed values in the denominator of the right side, so convergence is fast. Once the composition set  $(c_{oi}, i=1, N)$  are found from Equation 5.4.22, the corresponding set of aqueous concentrations may be found from the first of Equation 5.4.21. Then, if the soil is contaminated over a depth  $L_o$ , mass conservation gives

$$L_o \frac{dm_i}{dt} = J_i = q_w c_{wi} ; L_o \frac{d\theta_o}{dt} = \sum_j \frac{J_j}{\rho_j} \quad (5.4.23)$$

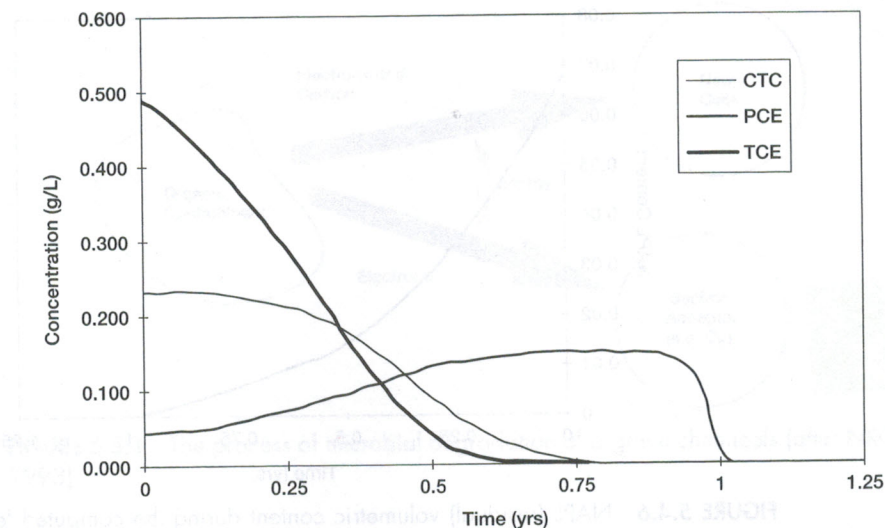
Together, Equations 5.4.21 to 5.4.23 provide the leachate and soil concentrations, and the NAPL content for a contaminated soil. One could also include mass loss through soil air diffusion for volatile chemicals.

#### EXAMPLE 5.4.4 Compositional Leaching Model

##### PROBLEM

A solvent solution to be used in a laboratory column leaching experiment consists of TCE, PCE, and CTC at initial concentrations 620, 465, and 465 g/L, respectively. The soil column is held vertically and has porosity 0.45, bulk density 1,460 g/L, fraction organic carbon 0.01, and average water saturation 0.5 during the test. The upper 5 cm section of the column retains residual solvent at an initial saturation 0.15. Water is introduced at the top of the column at volumetric flux (Darcy velocity) 4 cm/d. Estimate the leachate concentration and residual saturation as a function of time.





**FIGURE 5.4.5** Calculated leachate concentrations from a laboratory investigation

This problem is similar to that of Example 5.4.3, except that the compositional model will be used instead of constant partition coefficients. The properties of the three solvents are provided in Table 5.4.1. The initial bulk concentrations are estimated from  $m_i(0) = c_{oi}(0)\theta_o(0)$ . The initial solution concentrations were then used in Equation 5.4.22 to find the initial NAPL concentrations in soil. After 2 iterations, the results are 604.9, 461.7, and 442.3 g/L for TCE, PCE, and CTC, respectively. A simple direct-step computation of Equation 5.4.23 was then performed to find the solute concentrations and NAPL content. All calculations were performed using a spreadsheet. Figure 5.4.5 shows the leachate concentration as a function of time. TCE concentrations are initially largest and decrease most rapidly because of its greater solubility and initial concentration. Note that even initially, the TCE leachate concentration is significantly less than its solubility of 1.1 g/L. The solubility of CTC is somewhat less than that of TCE but much larger than that of PCE. CTC disappears shortly following TCE. The constant partition coefficient model would not predict the behavior of PCE in leachate. Its concentration is initially small because of its small solubility. As the other constituents are leached from the NAPL solution, however, its mole fraction increases, as does its solubility. Eventually the PCE leachate concentration reaches its aqueous solubility, corresponding to when it is the only NAPL present. This behavior is followed in the NAPL saturation history shown in Figure 5.4.6. The rate of decrease in saturation is greatest initially when TCE and CTC are at their largest concentrations in leachate. At a time of about 0.4 years, PCE is the dominant constituent in leachate, and because of its smaller solubility, the rate of decrease in NAPL saturation also decreases. If a solution contains constituents all with the same solubility (or a single