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An evaluation of Sherwood–Gilland models for NAPL dissolution and their relationship to soil properties

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ABSTRACT

Predicting the longevity of non-aqueous phase liquid (NAPL) source zones has proven to be a difficult modeling problem that has yet to be resolved. Research efforts towards understanding NAPL depletion have focused on developing empirical models that relate lumped mass transfer rates to velocities and organic saturations. These empirical models are often unable to predict NAPL dissolution for systems different from those used to calibrate them, indicating that system-specific factors important for dissolution are not considered. This introduces the need for a calibration step before these models can be reliably used to predict NAPL dissolution for systems of arbitrary characteristics.

In this paper, five published Sherwood–Gilland models are evaluated using experimental observations from the dissolution of two laboratory-scale complex three-dimensional NAPL source zones. It is shown that the relative behavior of the five models depends on the system and source zone characteristics. Through a theoretical analysis, comparing Sherwood–Gilland type models to a process-based, thermodynamic dissolution model, it is shown that the coefficients of the Sherwood–Gilland models can be related to measurable soil properties. The derived dissolution model with soil-dependent coefficients predicts concentrations identical to those predicted by the thermodynamic dissolution model for cases with negligible hysteresis. This correspondence breaks down when hysteresis has a significant impact on interfacial areas. In such cases, the derived dissolution model will slightly underestimate dissolved concentrations at later times, but is more likely to capture system-specific dissolution rates than Sherwood–Gilland models.

1. Introduction

The presence of non-aqueous phase liquids (NAPLs) in the subsurface has long been recognized as a major threat to groundwater resources. This is primarily due to the persistence of these compounds when they exist as a separate phase, in which case they act as a source of long term groundwater contamination. Research on NAPL contamination has been ongoing for decades and has shown that NAPLs are amenable to several remediation technologies (e.g. surfactants, bioremediation, chemical oxidation). Many of these technologies are based on enhancing the dissolution of NAPLs in water. Therefore, to effectively design these remediation technologies and to accurately predict clean-up times, the process of dissolution and the factors affecting it should be better understood and adequately captured by numerical models.

To this end, experimental and modeling studies have been conducted under a variety of conditions, and have elucidated a number of important factors that impact NAPL dissolution. The once common assumption of local equilibrium has been shown to be invalid under a range of conditions, and especially for heterogeneous NAPL distributions (Frind et al., 1999; Grant and Gerhard, 2007a; Mayer and Miller, 1996;

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Nambi and Powers, 2003), rendering kinetic expressions necessary to predict dissolution rates. The architecture of NAPL source zones has been consistently described as the most important factor influencing dissolution rates and remediation metrics like NAPL depletion times, concentrations, and mass flux reductions (Christ et al., 2006; DiFilippo et al., 2010; Fure et al., 2006; Lemke and Abriola, 2006). In the field, complex NAPL architectures combined with soil heterogeneity are typical, and reliably predicting dissolution under these conditions remains a challenge that needs to be addressed.

Numerical predictions of contaminant mass flux from complex NAPL source zones are typically obtained using kinetic dissolution models that have been developed by fitting the coefficients of power-law empirical relationships to data from laboratory experiments. Most often used are models known as Sherwood–Gilland models that relate a modified Sherwood number (Sh') to NAPL saturation and a dimensionless form of aqueous velocity, via:

$$Sh' = \frac{K_L d_m^2}{D^*} = b \cdot Re^c \cdot S_N^d \tag{1}$$

where K_L $[1/T]$ is the overall mass transfer rate, $d_m[1/L]$ is the mean particle diameter, D^* $[\mathrm{L}^2/T]$ is the contaminant molecular diffusion constant in water, Re [-] is the Reynolds number ($Re = v_w \rho_w d_m / \mu_w$), v_w is the porewater velocity, ρ_w is the water density, μ_w is the water kinematic viscosity, S_N [-] is the NAPL saturation and b, c and d are empirical coefficients. Eq. (1) is used to obtain K_L at the numerical grid scale, which is then used to calculate the dissolution mass flux by the linear driving force model:

$$J = K_L \cdot (C_s - C_w) \tag{2}$$

where $J\,[ML^{-3}T^{-1}]$ is the mass flux from the non-aqueous to the aqueous phase, and $C_S[M/L^3]$ is the effective solubility of the NAPL, $C_w[M/L^3]$ is the bulk aqueous phase concentration, and $C_S - C_w$ is the difference in concentration between the NAPL–water interface and the bulk aqueous phase.

Sherwood–Gilland models have been developed for a variety of systems and conditions (e.g. Imhoff et al., 1994; Miller et al., 1990; Nambi and Powers, 2003; Powers et al., 1994b; Saba and Illangasekare, 2000). The wide range of fitted empirical coefficients reported for these various systems indicates that these coefficients are specific to the calibration conditions. As a result, even though Sherwood–Gilland models can accurately capture dissolved concentrations for the experiments used to fit the coefficients, their predictive ability for different systems has been found to be poor (Grant and Gerhard, 2007a; Nambi and Powers, 2003; Powers et al., 1994b). This may be because Eq. (1) does not include system-specific parameters that are important for dissolution. For example, one known source of error is that the empirical Sherwood–Gilland models do not explicitly consider the NAPL–water interfacial area. This limitation can be overcome, by using the complete linear driving force model:

$$J = k_{la} \cdot a^n (C_s - C_w) \tag{3}$$

where k_{la} $[L/T]$ is the mass transfer coefficient per unit normalized interfacial area, and a^n $[1/L]$ is the effective normalized NAPL–water interfacial area. The mass transfer coefficient, k_{la}, is known to be related to aqueous phase velocities (Pfannkuch, 1984; Powers et al., 1994a). Interfacial areas can be calculated by geometric models (Lemke and Abriola, 2006; Powers et al., 1994a), or using thermodynamic theory (Grant and Gerhard, 2007a; Morrow, 1970). The thermodynamic theory for interfacial areas is based on the principle that work done during NAPL drainage and imbibition translates to the formation or destruction of NAPL–water interfaces. This explicitly links interfacial areas to capillary pressure–saturation constitutive relationships, and renders the thermodynamic model suitable for REV-scale multiphase models, without requiring geometric assumptions or parameter calibration. Furthermore, dissolution models that incorporate thermodynamically-based interfacial areas have been shown to accurately predict dissolution rates and effluent concentration for complex NAPL source zones, without calibration and for a range of aqueous velocities (Grant and Gerhard, 2007b; Kokkinaki et al., 2013).

Employing the thermodynamic dissolution model enables the detailed consideration of the processes driving the dissolution of complex NAPL source zones. While in theory such a detailed model can be applied for field-scale problems, the soil and source zone characterization required is often difficult to obtain in real field-scale situations. As a result, Sherwood–Gilland (SG) empirical relationships will likely remain the model of choice in regulatory practice guidance and research efforts. Given the prediction uncertainty associated with such empirical relationships, it would be highly instructive to understand the sources of error and the limits of applicability of these models. This is possible through comparison to the thermodynamic dissolution model. Such a comparison can also elucidate parameters important to dissolution that empirical SG models do not consider. Finally, if an analogy between the empirical and thermodynamic dissolution models exists, the comparison could provide some guidance for the use of empirical models. This comparison has not yet been presented in the literature.

In this paper, the dissolution of two complex dense non-aqueous phase liquid (DNAPL) source zones is simulated using five published Sherwood–Gilland models. The effectiveness of the five empirical models is evaluated by comparison to experimental data and predictions of the thermodynamic dissolution model, and the limitations of the Sherwood–Gilland approach are discussed. A theoretical comparison between the functional forms of the Sherwood–Gilland model and the thermodynamic dissolution model is presented, and conditions under which the two models converge are given. Under these conditions, the Sherwood–Gilland model coefficients are shown to be related to measurable soil properties. The derived dissolution model with coefficients calculated from these soil properties is evaluated under non-hysteretic and hysteretic conditions. The advantages of utilizing the derived dissolution model over Sherwood–Gilland models are shown, and potential limitations of the proposed approach are discussed.

2. Modeling methods

2.1. DNAPL dissolution experiments and multiphase model

The prediction of DNAPL dissolution is most challenging in heterogeneous aquifers, where the spatial distribution of