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SUBJECT: PROPOSED MODIFICATIONS IN HYDRUS (1, 2/3D) SOFTWARE TO
            ENHANCE MODELING SOLUTE DIFFUSION AND GASEOUS DIFFUSION IN
            SOILS

INTRODUCTION

The Department of Pesticide Regulation (DPR) is currently working toward development of a numerical model for improving its fumigant risk assessment and management capabilities. Such a model should have the potential to combine all transport processes including volatilization of fumigants, be user friendly and cost effective. DPR has identified HYDRUS1-D and HYDRUS2/3D as state-of-the-art numerical multi-physics programs capable of simulating water, heat, and solute transport in one-, two-, and three-dimensional variably saturated porous media. The DPR is pursuing a contract to modify the HYDRUS models to make then more suitable for use in fumigant risk assessment and evaluation of agricultural fumigation practices. Several specialized modifications are needed to improve the solute and gaseous diffusivity sub-models that are currently used by HYDRUS.

The "natural" soil (sometimes called "undisturbed" soil) can refer to any soil that is in the field. It may be plowed, disked, rolled, furrowed, etc., but that still represents "undisturbed." The "repacked" soil represents any soil which is generally sieved and packed to a certain bulk density in a laboratory column. The repacked soil is sometimes called "disturbed" soil. This distinction is significant because we would like to compare HYDRUS to both field and laboratory column studies in which solute and gas diffusivity functions differ markedly. The proposed modifications will update the soil solute and gas diffusion sub models to reflect the most current and credible formulation. In addition, the new updates will facilitate model comparison to both field and laboratory diffusion studies, which is important in order to gain confidence in the ability of the model to describe soil diffusion processes. Laboratory column studies are conducted under controlled conditions and correctly simulating such studies is a first step towards model validation. Field studies are much more difficult to simulate because of (1) variability in soil properties, (2) dynamic temperature and moisture conditions, (3) unknown variation in pesticide application, and (4) inherent variation in the measurement of field level flux. Thus, the enhancements enable us

to use a tiered validation strategy which begins with the laboratory column studies, and after successful validation of laboratory column studies, moves on to comparison with field studies. The enhancements listed here and other enhancements (Spurlock, personal communication) to the HYDRUS software will allow us to properly simulate mitigation strategies such as the use of agricultural films (tarps), soil injection depth and post-application irrigations.

OBJECTIVE

The objective of this memo is to introduce new equations of gas and solute diffusivity for HYDRUS modifications.

REQUIRED MODIFICATIONS

HYDRUS predicts solute and gas diffusivity using equations introduced by Millington and Quirk (1960) which were based on unsaturated permeability functions in porous media. Soil gas diffusivity behaves significantly different in undisturbed (field) and repacked, sieved (laboratory column) soils. In contrast, solute diffusivity does not differ much between intact field soils versus repacked laboratory column soils. Consequently, unified solute diffusivity models will be proposed as HYDRUS modifications which can be used to simulate both field and laboratory column studies. Moreover, two soil gas diffusivity models will be discussed: one for use in undisturbed (field) soils and one for packed laboratory soil column studies.

Predicting Solute Diffusivity
The HYDRUS1D and HYDRUS2/3D use a solute diffusivity model given by Millington and Quirk (1960)

$$D_s = \theta D_w \frac{\theta^{7/3}}{\theta_s^2} \qquad (1)$$

where D_s effective diffusion coefficient of species in solute ($L^2\ T^{-1}$), D_w is molecular diffusion coefficient in free water ($L^2\ T^{-1}$), θ is volumetric water content ($L^3\ L^{-3}$), and θ_s is the saturated water content ($L^3\ L^{-3}$). Eq. (1) assumes that at saturated water content, all void space is full of water. An alternative to Eq. (1) is the soil type dependent model developed by Olesen et al. (1996) which applies to solute diffusivity in both disturbed and undisturbed soils

$$\frac{D_s}{D_w} = 0.45\,\theta \left(\frac{\theta}{\phi} \right)^{0.3b} \qquad (2)$$

where 0.45 is the mean value for the impact factor at water saturation, ϕ is porosity which can be treated as the saturated water content ($\phi = \theta_s$), and b is the pore size distribution parameter of the Campbell (1974) water characteristic model. Also $-b$ is the slope of the soil water characteristic curve in a log-log coordinate system ($b>0$) (Moldrup et al., 1997). It can also be obtained by nonlinear fitting the laboratory measured soil water characteristics to the Campbell (1974) model

using simple MicroSoft Excel nonlinear optimization method (Wraith and Or, 1998). Olesen et al. (1996) compared both models in Eqs. (1) and (2) and concluded that Eq. (2) estimated better the measured solute diffusivity values for soils with different textural types. This model (Eq. 2) can be used if a user wants to define diffusivity function from saturation to dry end of retention function assuming no discontinuity in liquid phase. To account for discontinuity of the diffusion pathways where solute diffusion ceases, Olesen et al. (2000 and 2001) developed a constant slope impedance factor model with soil water characteristic assuming linear relationship between impedance factor and water content,

$$\frac{D_s}{D_w} = 0.11\,\theta\,(\theta - \theta_{th}) \quad \text{for} \ \ \theta > \theta_{th}$$

$$\frac{D_s}{D_w} = 0 \quad \text{for} \ \ \theta \le \theta_{th}$$
$$(3)$$

where θ_{th} is the threshold water content value ($L^3\,L^{-3}$) where solute diffusion ceases. This model gives more realistic approach to physics of the phase continuation and its effect on diffusion coefficient. However, the determination of the threshold water content is difficult to accomplish. Thus, Olesen et al. (1996) suggested a linear correlation between θ_{th} and the Campbell (1974) pore size distribution parameter, b, resulting in

$$\theta_{th} = 0.020\,b \quad (4)$$

In case of unavailable b parameter information, θ_{th} can be estimated using several measured physical properties since the parameter b is strongly influenced by these properties,

$$\theta_{th} = 0.81CF - 0.90CF^2 - 0.07SF - 0.6\rho_b + 0.22\rho_b^2 + 0.42 \quad (5)$$

where CF is the clay fraction (M M^{-1}), SF is the silt fraction (M M^{-1}), and ρ_b is the oven dry bulk density (M L^{-3}). The Eq. (5) is obtained from 23 soils having different textures (Olesen et al., 2001). However, Olesen et al. (2001) found that Eqs. (4) and (5) produce similar accuracy in prediction of θ_{th}. Moreover, they derived another expression for θ_{th} in case of known soil water characteristic curve parameter b and soil physical properties, yielding,

$$\theta_{th} = 0.035b - 0.001b^2 - 0.063CF - 0.023SF + 0.51\rho_b - 0.25\rho_b^2 - 0.26 \quad (6)$$

Olesen et al., (2001) argued that combination of parameter b and soil physical parameters as in Eq. (6) resulted better prediction of θ_{th} and eventually for solute diffusivity.

Predicting molecular diffusion coefficient in free water
Diffusion coefficient in free water is another parameter required to define the diffusion process in the liquid phase. Although diffusion coefficients in liquids are about ten thousand times slower than those in dilute gases (Cussler, 1997), determination of the diffusion coefficient is crucial to modeling efforts. I propose to implement estimation of molecular diffusion coefficient in free water into HYDRUS to ensuring correctness of D_w values submitted by registrants. The diffusion

coefficient can be estimated using Stokes-Einstein equation assuming the solute radius is larger than solvent radius and a rigid solute sphere diffusing in a continuum of solvent (Cussler, 1997; Flury and Gimmi, 2002)

$$D_w = \frac{k_B T}{6\pi\mu r_0} \quad (7)$$

where k_B is the Boltzmann constant (M L^2 T^{-2} K^{-1}) ($k_B = 1.380 \times 10$-23 J K^{-1}), T is the absolute temperature (K), μ is dynamic viscosity of the liquid (M L^{-1} T^{-1}) and r_0 is the solute radius (L).

Predicting Gas Diffusivity
The HYDRUS programs use an equation similar to Eq. (1) for predicting gas diffusivity by replacing θ with a_v

$$D_{a_v} = a_v D_g \frac{a_v^{7/3}}{\theta_s^2} \quad (8)$$

where D_{av} is effective diffusion coefficient of species in soil gas phase (L^2 T^{-1}), respectively, and D_g is the molecular diffusion coefficient in free air (L^2 T^{-1}), a_v is air content (L^3 L^{-3}), and θ_s is the saturated water content (L^3 L^{-3}) which is assumed equal to the total void space (porosity). In addition to this model, we would like to add to HYDRUS more contemporary expressions for gas diffusivity. These are more recent gas diffusivity models, which distinguish between repacked and undisturbed (natural) soils. This distinction is crucial because the soil gas diffusivity as a function of air filled porosity differs significantly between these two soil conditions (Moldrup et al., 2005; Rolston, and Moldrup, 2002).

Predicting gas diffusivity in natural (undisturbed) soil conditions
Sensitivity of gas diffusion to soil structure is profound. Models should describe gas diffusivity adequately as a function of natural soil conditions in order to better model volatilization of fumigants. The Millington-Quirk (1960) formula (Eq. 8) has been improved for more accurate gas diffusivity characterization. Moldrup et al., (1999) developed the Buckingham-Burdine-Campbell gas diffusivity model for predicting diffusion in natural soil state

$$\frac{D_{a_v}}{D_g} = \phi^2 \left(\frac{a_v}{\phi}\right)^{2+\frac{3}{b}} \quad (9)$$

where $\phi = \theta_s$. Rolston and Moldrup (2002) suggested that in case it is necessary to estimate the Campbell pore-size distribution parameter, b, the clay fraction can be used as an estimator for this parameter. Based on data from a total of 1845 soils, a high correlation between clay fraction and pore size distribution parameter gives the following:

$$b = 13.6\,CF + 3.5 \qquad 0 < CF < 1 \quad (10)$$

Predicting gas diffusivity in sieved repacked soil conditions
For estimating gas diffusivity in repacked soils, especially the case in laboratory column studies, Moldrup et al. (2000) developed Water-induced Linear Reduction model which contains a model by Marshall (1959) to take into account solid induced tortuosity,

$$\frac{D_{a_v}}{D_g} = a_v^{1.5} \left(\frac{a_v}{\phi} \right) \tag{11}$$

However, Moldrup et al. (2005) found that the Water-induced Linear Reduction model (Eq. 11) can underestimate gas diffusivity at high porosity values from 0.54 to 0.76 ($L^3 \, L^{-3}$). This is particularly valid condition when studies are conducted on volcanic or organic soils. To solve this problem, they introduced a simple porosity correction term to account for high gas connectivity at high porosity values. This becomes

$$\frac{D_{a_v}}{D_g} = \frac{a_v^{3-\phi}}{\phi} \tag{12}$$

where the correction term $a_v^{0.5-\phi}$ accounts for increase in pore connectivity at high porosity values.

Predicting molecular diffusion coefficient in free air
To ensure validity of molecular diffusion coefficient in free air submitted by registrant and for user conveniences, I propose adding to HYDRUS a formulation for capability of calculation of molecular diffusion coefficient in free air. The diffusion coefficient in free air for can be calculated quite accurately using empirical equations. The most commonly used equation is developed by Fuller et al. (1966)

$$D_g = \frac{10^{-3} T^{1.75} \left(\dfrac{1}{M_A} + \dfrac{1}{M_B} \right)^{0.5}}{P \left[\left(\sum V_A \right)^{1/3} + \left(\sum V_B \right)^{1/3} \right]^2} \tag{13}$$

where D_g is the binary diffusion coefficient in air ($L^2 \, T^{-1}$), P is the absolute pressure ($M \, L^{-1} \, T^{-2}$), T is temperature in degree Kelvin, M_A, M_B, $\sum V_A$ and $\sum V_B$ are molar mass of air ($M \, mol^{-1}$) and the pesticide in gas phase ($M \, mol^{-1}$), values of summed atomic diffusion volumes of air ($L^3 \, mol^{-1}$) and pesticide in gas phase ($L^3 \, mol^{-1}$), respectively.

SUMMARY

The DPR has potentially identified HYDRUS1-D and HYDRUS2/3D as state-of-the-art numerical multi-physics programs capable of simulating water, heat, and solute transport in one-, two-, and three-dimensional variably saturated porous media for improving its fumigant risk assessment and management capabilities. Due to its extensive use world-wide by scientist's expert on vadose zone hydrology and providing active support services, the DPR decided to pursue a contract to modify the HYDRUS models to make then more suitable for use in fumigant risk assessment and evaluation of agricultural fumigation practices. Several specialized modifications are needed for improved modeling of solute diffusion, volatilization and gaseous diffusion in soils. I proposed adding the following capabilities to HYDRUS (1, 2/3D):

1. Eq. (2) predicts solute diffusivity from saturation to dry end of soil water retention curve assuming no discontinuity in the soil liquid phase.
2. Eq. (3) predicts solute diffusivity within liquid phase continuity until certain threshold water content value, θ_{th} where solute diffusivity ceases.
3. Eq. (4) estimates the threshold water content value, θ_{th}, in Eq. (3) using pore size distribution parameter, b, of Campbell (1974) soil water retention function.
4. Eq. (5) estimates the threshold water content value, θ_{th}, in Eq. (3) using measured soil physical properties. It yields similar accuracy as Eq. (4) in prediction of θth but it is useful when there is no available b parameter value.
5. Eq. (6) estimates the threshold water content value, θ_{th}, in Eq. (3) using measured soil physical properties and pore size distribution parameter, b, of Campbell (1974) soil water retention function. The Eq. (6) yields best results in estimating the threshold water content value, θth and eventually solute diffusivity.
6. Eq. (7) estimates molecular diffusion coefficient of species in free water.
7. Eq. (9) estimates gas diffusivity for natural soil conditions (undisturbed) where status of soil sample represents current soil condition in the field.
8. Eq. (10) estimates the pore size distribution parameter, b, of Campbell (1974) soil water retention function when there is no available pre-determined b value.
9. Eq. (11) estimates gas diffusivity for sieved and repacked (disturbed) soils used in laboratory studies where value of porosity is lower than 0.56.
10. Eq. (12) estimates gas diffusivity for sieved and repacked (disturbed) soils where value of porosity is between 0.56 and 0.74.
11. Eq. (13) estimates molecular diffusion coefficient of species in free air.

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