Implementation of Diffusion in GoldSim

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Introduction

This paper outlines how diffusion in air and water is to be implemented in GoldSim models that include diffusion in the unsaturated zone. The need for this discussion arises from the assumption in GoldSim that diffusion occurs only in saturated porous media. In the modeling of radioactive waste facilities, we have the definite need to include diffusion in both the air phase (e.g. diffusion of radon from buried wastes to the ground surface) and often in the water phase. These processes can be independently enabled or disabled by setting logical “switches” in the model.

We have tested diffusion-specific models built in GoldSim for consistency with analytical results, and have verified our interpretation of GoldSim’s internal calculations, and the appropriateness of our modifications to definitions of diffusive flux.

Diffusion Math

To introduce basic diffusive transport mathematics, we turn to Jury (1991), who provides the following 1-dimensional gas phase conservation (transport) equation:

$$\frac{\partial \theta_a C_g}{\partial t} = -\frac{\partial J}{\partial z} \qquad [1]$$

where

θ_a = volumetric air content (constant in space and time),
C_g = gas concentration in air,
t = time, and
z = the single spatial dimension,

and the diffusive mass flux J is given by

$$J = -D_g^s \frac{\partial C_g}{\partial z} \qquad [2]$$

where the effective diffusion coefficient D_g^s is

$$D_g^s = \tau_a \cdot D \qquad [3]$$

where

τ_a = tortuosity of the air phase and

D = free air molecular diffusion coefficient (also called the free air diffusivity).

Combining equations [1], [2], and [3], we find that

$$\frac{\partial \theta_a C_g}{\partial t} = \frac{\partial}{\partial z}\left(\tau_a \cdot D \frac{\partial C_g}{\partial z}\right) \qquad [4]$$

Diffusion in GoldSim

In the GoldSim modeling environment, the flux equation looks like (GoldSim CT manual p. B-4, Eq. B-3):

$$J = D_{cs}\left(C_i - C_j\right) \qquad [5]$$

where

J = diffusive mass flux,
D_{cs} = GoldSim's "diffusive conductance",
C_i = concentration in cell i in air (essentially C_g), and
C_j = concentration in cell j in air (essentially C_g).

Note that GoldSim uses the concentration difference, not the gradient, in the fluid medium in question. The gradient is the difference divided by the diffusive length (in GoldSim, this is the sum of the diffusive lengths defined in each adjacent cell). Diffusive conductance is defined as (GoldSim CT manual p. B-5, Eq. B-5):

$$D_{cs} = \frac{A_c}{\dfrac{L_{ci}}{f_{ms} \cdot d_{ms} \cdot t_{Pci} \cdot n_{Pci}} + \dfrac{L_{cj}}{f_{ns} \cdot d_{ns} \cdot t_{Pcj} \cdot n_{Pcj} \cdot K_{nms}}} \qquad [6]$$

where

A_c = the bulk cross-sectional area of diffusive mass flux link,
L_{ci} = diffusive length in cell i,
L_{cj} = diffusive length in cell j,
f_{ms} = available porosity for species s in medium m (i.e., the fraction of the pore volume of solid m that is accessible to species s),
f_{ns} = available porosity for species s in medium n (i.e., the fraction of the pore volume of solid n that is accessible to species s),
d_{ms} = diffusivity for species s for fluid m (in cell i),
d_{ns} = diffusivity for species s for fluid n (in cell j),
t_{Pci} = tortuosity for the porous medium in cell i ($t \leq 1$),
t_{Pcj} = tortuosity for the porous medium in cell j ($t \leq 1$),
n_{Pci} = porosity for the porous medium in cell i,
n_{Pcj} = porosity for the porous medium in cell j, and
K_{nms} = partition coefficient between fluid medium n (in cell j) and fluid medium m (in cell i) for species s.

This equation can be greatly simplified if we ignore the “available porosity” factors (let the equal 1) and assume no suspended solids, one porous medium (partition coefficients, porosities and tortuosities are the same) and one fluid medium (diffusivities are the same):

$$D_{cs} = \frac{A\,n\,D\,\tau}{L} \qquad [7]$$

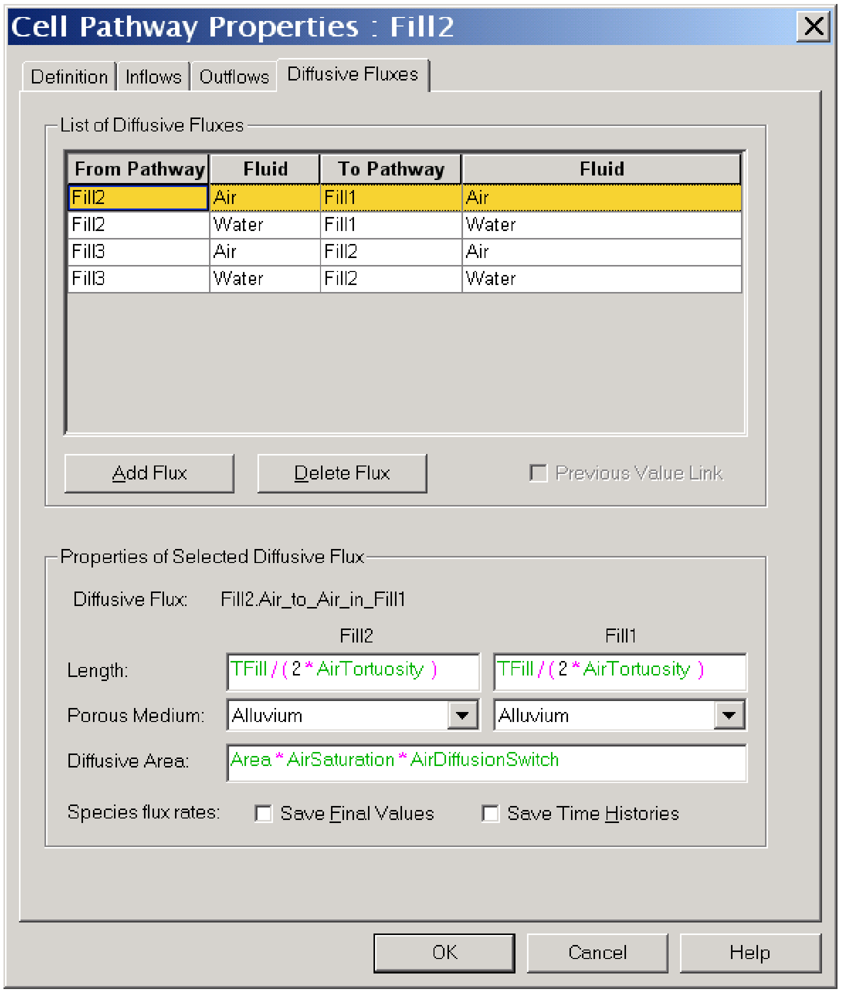
where

A = diffusive area, or bulk cross-sectional area of the porous medium,
n = total porosity of the porous medium,
D = free air diffusivity (same as D above),
τ = tortuosity of the entire pore space in the porous medium, and
L = the sum of the diffusive lengths in adjacent cells i and j.

It is useful to determine at this point exactly where each of these values comes from in GoldSim. The diffusive area and diffusive lengths are provided explicitly to GoldSim in the definition of each diffusive flux link, using Diffusive Fluxes tab in the Cell Pathway Properties dialog box shown in Figure 1.

Diffusion in Partially-Saturated Porous Media

This dialog box also provides for the definition of the porous medium, in this example “Alluvium”, which has the properties of porosity and tortuosity as part of its definition as a solid material. It is important to note that the values of porosity and tortuosity used in GoldSim’s calculation of diffusive flux are taken from the definition of the solid material, and *GoldSim assumes that the porous medium is saturated with respect to the fluid through which diffusion is occurring*. This assumption is violated for unsaturated conditions. In the current example, we wish to allow diffusion in both Water and Air fluids, so some corrections have to be applied to the values for porosity n and tortuosity τ. Instead of using the Alluvium’s defined n and τ, we need to use values appropriate for the fluid of interest. For example, for air, we want to use volumetric air content θ_a instead of n, and air-phase tortuosity τ_a instead of a generalized τ. Since GoldSim is hard-coded to apply the n and τ for the solid material (Alluvium), we need to account for the differences carefully.



From Pathway	Fluid	To Pathway	Fluid
Fill2	Air	Fill1	Air
Fill2	Water	Fill1	Water
Fill3	Air	Fill2	Air
Fill3	Water	Fill2	Water

Diffusive Flux: Fill2.Air_to_Air_in_Fill1

	Fill2	Fill1
Length:	TFill / (2 * AirTortuosity)	TFill / (2 * AirTortuosity)
Porous Medium:	Alluvium	Alluvium

Diffusive Area: Area * AirSaturation * AirDiffusionSwitch

Species flux rates: ☐ Save Final Values ☐ Save Time Histories

Figure 1. The definition of diffusive flux in GoldSim

In order to use volumetric air content instead of porosity, we insert a multiplicative factor into the definition of the Diffusive Area, so that we get the cross-sectional area of the fluid of interest, rather than the entire porous medium (see Figure 1). GoldSim internally multiplies the Diffusive Area times the Alluvium porosity n, so we must multiply that by the Air phase saturation, S_a, to get

$$D_{cs} = \frac{A S_a n D \tau}{L} \qquad [8]$$

so that GoldSim ends up working with the cross-sectional area of just the Air phase, which is $A\theta_a$:

$$D_{cs} = \frac{A \theta_a D \tau}{L} \qquad [9]$$

An alternative approach would be to define the porosity of the Alluvium to be unity, and correct the Diffusive Area by θ_a rather than by S_a. This approach, however, has unintended consequences since other processes (such as retardation) use the porosity value defined for Alluvium.

In addition to the area correction to account for partially-saturated media, we need to use an appropriate value for tortuosity. What we want is the tortuosity of the phase in which diffusion occurs, but again, GoldSim assumes saturation and is hard-coded to use the bulk tortuosity defined for the porous medium, Alluvium. In this case, it is simplest to effectively remove the porous medium tortuosity by setting it equal to 1 in the definition of the Alluvium, and to apply fluid-specific tortuosities in the definition of the Diffusive Flux. The logical parameter to modify is the Diffusive Length, since the concept of porosity is one of increased distance of travel that a diffusive species must travel due to its tortuous path through the partially-saturated porous medium. Fortunately, no other processes in GoldSim use the tortuosity value specified for Alluvium, so defining it as unity does not affect other parts of the model.

We have adopted the definition of tortuosity as the straight-line path between points A and B in the porous medium divided by the actual path through the fluid, tortuosity values are always between 0 and 1, with lower values implying more tortuous paths. The corrected Diffusive Length, therefore, is L / τ_a (for Air in this case). This correction can be seen in Figure 1. In effect, GoldSim is then solving the equation (for Air)

$$D_{cs} = \frac{A\theta_a D\tau_a}{L} \qquad [9]$$

For the water phase, the analogous equation is found by substituting θ_w and τ_w for θ_a and τ_a. While values for θ_w and θ_a are simple in concept and derivation, the fluid-specific tortuosities are not. Their derivation is the subject of a discussion below.

Grappling with Tortuosity

Jury (1991) discusses models for estimating air-phase tortuosity from other material properties, such as water content and porosity. In Jury's Table 6.1, the following three models are presented:

Table 1. Air phase tortuosity equations.

equation for air phase tortuosity	**reference**
$\tau_a = \frac{\theta_a^{10/3}}{n^2}$	Millington and Quirk (1961)
$\tau_a = 0.66^{\theta_a}$	Penman (1940)
$\tau_a = \theta_a^{3/2}$	Marshall (1959)

At air contents and porosities typical of arid sites, however, these models give markèdly different results. If we assume a porosity of 0.39 and a water content of 0.06, then we have an air content of 0.30. The three models return values for air phase tortuosity of 0.12, 0.88, and 0.16, respectively, showing wide variation in their estimates. Which model is most appropriate for a given material is a matter of site-specific investigation.

Also undetermined is an appropriate model for water phase tortuosity.

Modeling with GoldSim vs FEHM

The solution to GoldSim's unsaturated diffusive flux problem was originally developed while modeling the Radioactive Waste Management Sites (RWMSs) at the Nevada National Security Site (NNSS, formerly the Nevada Test Site). Since the issues surrounding the migration of water in the unsaturated zone at the NNSS were addressed by practitioners at Los Alamos National Laboratory (LANL) using the FEHM modeling program, we examined the implementations of diffusive flux in GoldSim and in a FEHM-based unsaturated zone model developed by Walvoord, Wolfsberg and Stauffer. This is important for consistency between the GoldSim and FEHM models of the unsaturated zone at the RWMSs.

Returning to the simplified version of GoldSim's equation for Diffusive Flux modified for a single fluid phase (equation [9]), we can substitute that equation into the mass balance equation (GoldSim CT manual p. B-2, Eq. B-1), giving

$$\frac{\partial m}{\partial t} = \frac{A}{L}\theta_a \tau_a \cdot D\left(C_i - C_j\right) \qquad [10]$$

We can convert mass to concentration (in air, rather than bulk concentration) since $m = C_g \theta_a V$, and rearrange to look more like the equation from Jury (Eq. 4)

$$\frac{\partial \theta_a C_g}{\partial t} = \frac{A}{VL}\left[\theta_a \tau_a \cdot D\left(C_i - C_j\right)\right] \qquad [11]$$

where V is the volume of the cell. Dividing through by θ_a gives

$$\frac{\partial C_g}{\partial t} = \frac{A}{VL}\left[\tau_a \cdot D\left(C_i - C_j\right)\right] \qquad [12]$$

The key is seeing that the definition of D_g^s in the Jury text does not explicitly include volumetric air content. From Eq. 11, we can see that GoldSim *does* explicitly include volumetric air content (or rather, porosity) in the definition of D_g^s (or D_{cs}), so that D_g^s is defined as

$$D_g^s = \theta_a D \tau_a$$

Note that FEHM, like GoldSim, includes volumetric air content explicitly.

Thus we must be careful when we define the air phase tortuosity τ_a in our model in order to understand how D_g^s is defined in the literature that the various tortuosity equations come from. For example, Jury (1991) writes the Millington-Quirk (1961) equation for air phase tortuosity as $\frac{\theta_a^{10/3}}{n^2}$ (where n is porosity) and in GoldSim we need to use $\frac{\theta_a^{7/3}}{n^2}$ for tortuosity.

References

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Marshall, T.J., 1959. “The diffusion of gas through porous media.” *Journal of Soil Science* (10) pp. 79-82

Millington, R.J., and J.P. Quirk, 1961. “Permeability of porous solids.” *Trans. Faraday Society* (57) pp. 1200-1207

Penman ----1940 -----(referenced in Jury 1991)