

Implementation of Diffusion in GoldSim

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While this paper has appeared in various forms a propos different projects in the past, this is the first version that is integrated into the Neptune document system. – JT, 3 Oct 2014 Made a minor modification in reference to GoldSim version 10 and subsequent versions. – JT, 6 Oct 2014		

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1.0 Introduction

This paper outlines how diffusion in air and water (or other fluids) is to be implemented in GoldSim models that include diffusion in unsaturated porous media. The need for this discussion arises from the way that GoldSim internally calculates diffusion in partially saturated porous media. In versions prior to GoldSim 10, these internal calculations worked correctly only for saturated media—that is, a porous medium with only one fluid phase.

At version 10, GoldSim modified its calculations for diffusion in partially saturated porous media through the use of a Diffusivity Reduction Formula (GTG, 2009). This formula, which is a property of a GoldSim Fluid element (e.g. Water or Air), allows the user to specify a formula that reduces the diffusion in an equivalent saturated porous medium as a function of the saturation of that medium. GoldSim internally calculates saturation for each fluid. While that approach is effective for simple systems that may involve a single Solid material, the complexity of environmental models, with multiple Solid definitions representing different layers of porous media makes the GoldSim adjustments to saturated diffusion non-ideal. Each fluid would have to be cloned within localized containers for Cells containing each different Solid in the model. And if a Cell has more than one Solid material within it, a proper calculation is not possible. Further, GoldSim still defines tortuosity as a Solid material property, though it is actually a property of both the porous medium and each of the Fluid phases within it. For these reasons, without the corrections outlined below, GoldSim cannot accurately simulate complex diffusive processes involving multiple fluids or porous media.

The approach outlined in this paper incorporates the corrections needed to program proper multi-fluid diffusion in porous media. By understanding what GoldSim is calculating internally, diffusive flux inputs can be modified to include corrections so that GoldSim properly accounts for partial saturation. Neptune has tested diffusion-specific models built in GoldSim for consistency with analytical results, and has verified GoldSim's internal calculations, and the appropriateness of our modifications to definitions of diffusive flux.

2.0 Diffusion Math

To introduce basic diffusive transport mathematics, we turn to Jury et al. (1991), which provides the following one-dimensional gas phase conservation (transport) equation:

$$\frac{\partial \theta_a C_g}{\partial t} = - \frac{\partial J}{\partial z}, \quad (1)$$

where

- J is the diffusive mass flux ($M \cdot T^{-1} \cdot L^{-2}$),
- θ_a is the volumetric air content (—),
- C_g is the gas concentration in air ($M \cdot L^{-3}$),
- t is the time (T), and
- z is the single spatial dimension (L),

and the diffusive mass flux J is given by

$$J = -D_g^s \frac{\partial C_g}{\partial z}, \quad (2)$$

where

the effective diffusion coefficient D_g^s is

$$D_g^s = \tau_a \cdot D, \quad (3)$$

where

τ_a is the tortuosity of the air phase (—) and
 D is the free air molecular diffusion coefficient ($L^2 \cdot T^{-1}$), also called the free air diffusivity.

Combining equations (1), (2), and (3), we find that

$$\frac{\partial \theta_a C_g}{\partial t} = \frac{\partial}{\partial z} \left(\tau_a \cdot D \frac{\partial C_g}{\partial z} \right). \quad (4)$$

3.0 Diffusion in GoldSim

In the GoldSim modeling environment, as documented in the *GoldSim Contaminant Transport Module User's Guide*, (GTG, 2014, p. 297), the flux equation is expressed as:

$$\text{diffusive mass rate} = \text{diffusive conductance} \times \text{concentration difference}. \quad (5)$$

Note that GoldSim uses the *concentration difference*, not the gradient, in the Fluid material 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).

In simple terms, *diffusive conductance* (GTG, 2014, p. 297) can be expressed as

$$\text{diffusive conductance} = (A d \tau n r) / L, \quad (6)$$

where

A is the mean cross-sectional area of the connection (L^2),
 D is the diffusivity in the Fluid ($L^2 \cdot T^{-1}$),
 n is the porosity of the Solid porous medium (—),
 τ is the tortuosity assigned to the Solid porous medium (—),
 r is a reduction factor, that varies with saturation (when saturated = 1), and
 L is the diffusive length (L).

For use in computations, diffusive conductance between two GoldSim Cell Pathway elements, for a given GoldSim contaminant Species s , is defined in GTG (2014, p. 298, Eq. B-6) as:

$$D_s = \frac{A}{\frac{L_i}{f_{ms} \cdot d_{ms} \cdot \tau_{Pi} \cdot r_m(\theta_m) \cdot n_{Pi}} + \frac{L_j}{f_{ns} \cdot d_{ns} \cdot \tau_{Pj} \cdot r_n(\theta_n) \cdot n_{Pj} \cdot K_{nms}}}, \quad (7)$$

where

- D_s is the diffusive conductance for Species s in the mass flux link ($L^3 \cdot T^{-1}$),
- A is the bulk cross-sectional area of the diffusive mass flux link (the area shared between two adjacent Cells i and j , containing porous media m and n , respectively) (L^2),
- L_i is the diffusive length in Cell i (L),
- L_j is the diffusive length in Cell j (L),
- f_{ms} is the available porosity for Species s in Solid material m (i.e., the fraction of the pore volume of Solid m that is accessible to Species s) (—),
- f_{ns} is the available porosity for Species s in Solid n (i.e., the fraction of the pore volume of Solid n that is accessible to Species s) (—),
- d_{ms} is the diffusivity for Species s for the Fluid m (in Cell i) ($L^2 \cdot T^{-1}$),
- d_{ns} is the diffusivity for Species s for Fluid n (in Cell j) ($L^2 \cdot T^{-1}$),
- τ_{Pi} is the tortuosity for Solid m in Cell i (≤ 1) (—),
- τ_{Pj} is the tortuosity for Solid n in Cell j (≤ 1) (—),
- $r_m(\theta_m)$ is the diffusive reductive formula for Fluid m (in Cell i) to account for saturation with respect to Fluid m (—),
- $r_n(\theta_n)$ is the diffusive reductive formula for Fluid n (in Cell j) to account for saturation with respect to Fluid n (—),
- n_{Pi} is the porosity for the Solid m in Cell i (—),
- n_{Pj} is the porosity for the Solid n in Cell j (—), and
- K_{nms} is the partition coefficient between Fluid n (in Cell j) and Fluid m (in Cell i) for Species s (L^3 in medium m / L^3 in medium n).

This equation can be greatly simplified if we ignore the “available porosity” factors (let them equal 1, representing 100% availability for porosity) and assume no suspended solids, a single Solid (so that partition coefficients, porosities, and tortuosities are the same), and one Fluid material (making diffusivities the same). We also assume that the diffusive reduction formula equals 1 for each fluid, so that we can account for unsaturated conditions in each Fluid and Solid combination. In a GoldSim model, this means that the definition of “Tortuosity” within Solid materials should always be set to 1, and the definition of “Diff. Reduction Formula” within Fluid materials should also be set to 1. These properties are accounted for elsewhere, as discussed below.

With these assumptions, the equation for diffusive conductance D_s for Species s can be simplified to:

$$D_s = \frac{AnD\tau}{L}, \quad (8)$$

where

- A is the diffusive area; the bulk cross-sectional area shared between adjacent Cells (L^2),
- n is the total porosity of the Solid porous medium (—),
- D is the free air diffusivity (same as D above) ($L^2 \cdot T^{-1}$),
- τ is the tortuosity with respect to a chosen Fluid within the Solid (—), and
- L is the sum of the diffusive lengths in adjacent cells i and j (L).

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 the Diffusive Fluxes tab in the Cell Pathway Properties dialog box shown in Figure 1.

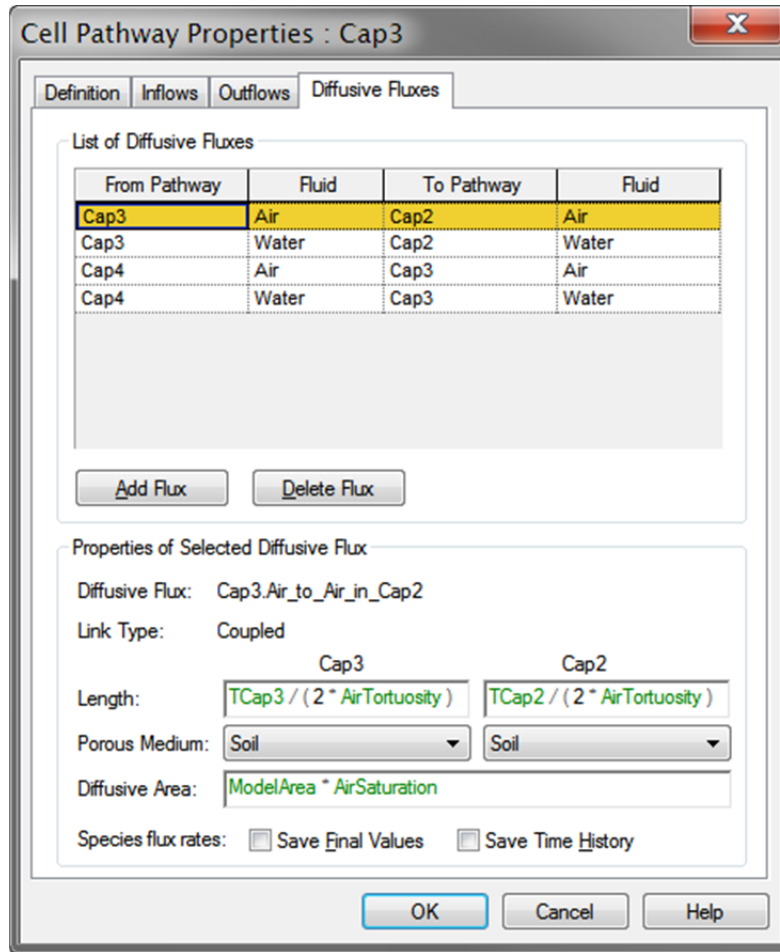


Figure 1. The definition of diffusive flux in GoldSim

4.0 Diffusion in Partially Saturated Porous Media

Figure 1 also provides for the assignment of a porous medium to either side of the diffusive link, choosing from Solid materials present in the respective Cells. In this example, “Soil,” 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 that when the diffusivity reduction formula is set equal to 1, *GoldSim assumes that the porous medium is saturated with respect to the fluid through which diffusion is occurring*. This assumption is invalid for unsaturated conditions, so corrections need to be made. With GoldSim version 10, the Fluid property “~Saturation” was introduced (see GTG 2014, p. 133 et seq.). This property is available to the Diffusion Reduction Formula, if one desired to employ it, but Neptune found it too restrictive as a way to handle unsaturated effects. In particular, it does not allow for more advanced definitions of tortuosity.

Neptune developed a workaround before GoldSim version 10, and it still applies. This involves changes in the definitions of flux links in order to account for partial saturation. 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 Soil’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 (Soil), we need to account for the differences carefully.

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 that of the entire porous medium (see Figure 1). GoldSim internally multiplies the Diffusive Area times the Soil porosity n , so we must multiply that by the Air phase saturation, S_a , to get

$$D_s = \frac{AS_a n D \tau}{L}, \quad (9)$$

so that GoldSim ends up working with the cross-sectional area of just the Air phase, which is that bulk area times the air content: $A \cdot \theta_a$, implemented here:

$$D_s = \frac{A \theta_a D \tau}{L}. \quad (10)$$

An alternative approach would be to define the porosity of the Soil 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 Soil.

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 full saturation and is hard-coded to use the “tortuosity” defined for the Solid porous medium, Soil. The problem here is that *the tortuosity with respect to*

a given Fluid is dependent on the partial saturation with respect to that Fluid, and is not merely a property of a Solid porous medium. Further, there are many models for the definition of tortuosity, and we prefer to leave the choice of which tortuosity model to use to the model developer. This is the topic of Section 5.0 below.

In this case, it is simplest to effectively remove the porous medium “tortuosity” by setting it equal to 1 in the definition of the Soil, and to apply fluid-specific tortuosities, defined elsewhere in the model, in the definition of the Diffusive Flux. The logical parameter to modify is the Diffusive Length, since the concept of tortuosity is one of increased distance of travel that a diffusive species must undergo due to its tortuous path through the partially saturated porous medium. Fortunately, no other processes in GoldSim use the tortuosity value specified for Soil, so setting it to 1 in the definition of a Solid 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 therefore 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)

$$D_s = \frac{A \theta_a D \tau_a}{L} \quad (11)$$

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 the discussion below.

5.0 Grappling with Tortuosity

Jury et al. (1991) discusses models for estimating air-phase tortuosity from other material properties, such as water content and porosity. In Jury et al.’s Table 6.1 (Table 1 below), the following three models are presented:

Table 1. Summary of 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 markedly different results. If we assume a porosity of 0.39 and a water content of 0.09, 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.

6.0 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 (Wolfsberg and Stauffer, 2003). 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 (11)) and assuming diffusion is the only transport mechanism, we can substitute that equation into the diffusive flux equation (GTG, 2014, p.297, Eq. B-4). Then the diffusive flux of Species s from Cell i into Cell j , which GoldSim annotates as $f_{s,i \rightarrow j}$, can be used in the mass balance equation (GTG, 2014, p. 294, Eq. B-1). When simplified (e.g., by assuming no radioactive decay, adsorption, or particulate diffusion), this gives

$$\frac{\partial m}{\partial t} = \frac{A}{L} \theta_a \tau_a \cdot D (C_i - C_j) \quad (12)$$

We can convert mass to concentration (in air, rather than bulk concentration) since $m = C_g \theta_a V$, and rearrange it to look more like the equation from Jury et al. (1991) in equation (4) above:

$$\frac{\partial \theta_a C_g}{\partial t} = \frac{A}{V L} [\theta_a \tau_a \cdot D (C_i - C_j)] \quad (13)$$

where

V is the volume of the cell.

Dividing through by θ_a gives

$$\frac{\partial C_g}{\partial t} = \frac{A}{V L} [\tau_a \cdot D (C_i - C_j)] \quad (14)$$

The key is seeing that the definition of D_g^s in the Jury et al. (1991) text does not explicitly include volumetric air content. From equation (12), we can see that GoldSim *does* explicitly include

volumetric air content (or rather, as porosity) in the definition of Jury et al.'s D_g^s (or, using this paper's notation, D_s), so that D_g^s is defined as

$$D_g^s = \theta_a D \tau_a \quad (15)$$

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 et al. (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.

7.0 References

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