Determination of Gaseous Diffusion Coefficients

Introduction

The rate at which binary mixtures of soil gases diffuse through soil may be described by a form of Fick's Law of Diffusion.

\[ J_g = -D_g^s \frac{dC_g}{dz} \]  

[Eqn. 1]

where \( J_g \) is the gaseous flux, \( D_g^s \) is the apparent diffusion coefficient of a gas through soil, \( C_g \) is the concentration of gas \( \left( \text{gas cm}^{-3} \text{ soil air} \right) \), and \( z \) is distance. The value of the apparent diffusion coefficient, \( D_g^s \), is dependent upon the soil gas, soil-water content or air porosity, soil temperature, and the continuity and tortuosity of pores.

Several investigators have measured apparent diffusion coefficients in soils and have related those values to air porosity, tortuosity, and the value of the diffusion coefficient in air, \( D_g^a \). A commonly accepted relationship between the apparent diffusion coefficient, \( D_g^s \), and the diffusion coefficient in air, \( D_g^a \), is:

\[ D_g^s = a \left( \frac{L}{L_E} \right)^2 D_g^a \]  

[Eqn. 2]

where \( a \) is the air content and \( \left( \frac{L}{L_E} \right)^2 \) is the tortuosity with \( L \) being the actual length of a soil column or core and \( L_E \) is the effective diffusion length. The value of \( L_E \) will be larger than that of \( L \). The value of the tortuosity has been determined to be in the range of 0.6 to 0.7 for most soils and water contents. However, for many purposes it is desirable to know values of the apparent diffusion coefficient, \( D_g^s \), more accurately than can be determined from Equation (2).

Taylor (1949) introduced a simple method for determining the apparent diffusion coefficient, \( D_g^s \). By placing an oxygen deficient chamber on one side of a soil column and measuring the increase in oxygen in the chamber by diffusion from an atmosphere of constant oxygen concentration on the other side of the soil column, the value of \( D_g^s \) could be easily calculated. We will change this approach slightly by using freon gas of a certain concentration in the chamber with no freon in the soil initially.

The solution to Equation (1) using the experimental boundary conditions described above is:

\[ \ln \left( \frac{C_g - C_o}{C_i - C_o} \right) = -\frac{D_g^s At}{VL} \]  

[Eqn. 3]

where \( \ln \) is the natural logarithm, \( C_g \) is the concentration of freon in the diffusion chamber at elapsed time \( t \), \( C_i \) is the initial concentration of freon in the diffusion chamber, and \( C_o \) is the
concentration of freon at the upper boundary of the soil core (zero), $D_g^s$ is the diffusion coefficient, $A$ is the cross-sectional area of the soil column, $V$ is the volume of the diffusion chamber, and $L$ is the length of the soil column.

By plotting the left-hand side of Equation (3), versus $t$, the value of $D_g^s$ can be calculated from the slope, $(D_g^s A)/(VL)$, of the resulting line. For the case of no soil in the sample holder, $D_g^s = D_g^a$. The diffusion coefficient, $D_g^s$, has units of cm$^2$ min$^{-1}$ (if the unit of time is minutes and the unit of distance is cm).

**Procedure**

1. Remove 2.0 mL of air from the chamber and then inject 2.0 mL of pure freon into the diffusion chamber with the slide closed and allow to equilibrate for at least 20 min.

2. Pack dry, sieved soil into an aluminum cylinder with a screen attached to one end. Weigh the empty cylinder and then the cylinder plus soil so that the bulk density can be determined.

3. Place the aluminum cylinder containing soil on the diffusion chamber and seal with sealing compound.

4. After equilibration to be sure that the freon is well mixed within the chamber, remove 50 µL of gas with a syringe and determine concentration by gas chromatography.

5. Slide the hole of the plastic slide over the hole of the diffusion chamber and record the time.

6. Measure the concentration of freon in the diffusion chamber every 15 minutes for at least 1 hour. Be sure to flush out the syringe and check for clogs after each injection.

7. Measure the length and inside cross-sectional area of the cylinder.

8. Plot $\ln \left(\frac{C_g - C_o}{C_i - C_o}\right)$ versus $t$ in minutes. Calculate the value of $D_g^s$ in cm$^2$ min$^{-1}$ and cm$^2$ s$^{-1}$.

9. Determine the ratio of the volume of soil air to volume of chamber air. Use Figure 10-1 to obtain a correction factor $K$. The $D_g^s$ from step 8 should be multiplied by $K$ in order to obtain the correct $D_g^{s*}$. **Note:** $K$ corrects for the fact that the solution of Fick’s Law presented by Equation 3 is not exact. When multiplied by $K$ the Taylor (1949) solution (eqn. 3) is converted to the exact solution (for large time) presented by Currie (1960). For a more detailed explanation see Rolston (1986). In Figure 10-1 $A$ is the cross-sectional area of the core, $V$ is the volume of the diffusion chamber, $l$ is the length of the soil core and $\alpha_1^2$ is factor from the exact solution of Currie.

**Questions** (where necessary use $D_g^a = 0.077$ cm$^2$/s)

1. What influence would water content have on the value of the diffusion coefficient, $D_g^s$?

2. Determine the value of the tortuosity $(L/L_E)^2$, for this particular soil and water content. How well does it compare to that given for a range of soils and conditions?
3. How would you expect the tortuosity to change with water content?

**Lab Report Point Distribution**

Abstract: 0.75  
Materials and Methods: 0.25  
Presentation of Results: 2.25  
Discussion: 4.5  
Conclusion: 0.5  
Overall Composition: 0.75  
Question 1: 0.25  
Question 2: 0.5  
Question 3: 0.25  
**Total:** 10

**Reference:**


Figure 11-1: Correction factor $K$ used in determination of soil diffusion coefficient (Rolston, 1986). $K = A / (Vl\alpha^2)$. $D_g^{*} = K D_g^s$