A Linear Model to Predict the Soil-Gas Diffusion Coefficient of Undisturbed Unsaturated Volcanic Ash Soil

Toshiko KOMATSU*, Ken KAWAMOTO*, Augustus RESURRECCION*, and Per MOLDRUP**

The soil-gas diffusion coefficient, D_p, is needed when analyzing the transport of volatile organic chemicals in polluted soil sites which is mainly controlled by gas diffusion. In this report, a linear model was developed to describe the variation of the soil-gas diffusion coefficient with soil moisture conditions. This new model was tested against 48 natural intact field soil samples, and performed superior to the nonlinear gas diffusivity model commonly applied in numerical simulations studies.

Keywords: Gas diffusivity, Soil-air content, Predictive model, Penman-Call model

1. Introduction

The transport and fate of volatile organic chemicals (VOCs) in polluted soil sites is mainly controlled by gas diffusion in the vadose zone above the groundwater table. To evaluate the risk due to the migration of VOCs, for example, from leaks from underground gasoline storage tanks nearby household buildings, accurate description of the gas diffusivity D_p/D_o (where D_o is the gas diffusion coefficient in free air) and its dependency on soil moisture conditions (in terms of soil-air content, ε) are essential.

Several prediction models for $D_p(\varepsilon)/D_o$ have been proposed and used as input parameters when simulating the transport of VOCs. These $D_p(\varepsilon)/D_o$ models include the classical soil-type independent models and the more conceptual nonlinear soil-water retention based models to include effect of soil type.

In this study, we measured soil-gas diffusion coefficients on undisturbed volcanic ash soils (Andisols) and developed a linear gas diffusivity model to describe the variation of D_p with ε. We tested this new model against measurements on intact soil samples, and compared its performance against the widely-used nonlinear model and soil-water retention based models.

2. Materials and Methods

2.1 Soil-Gas Diffusivity Data Used

We considered a total of 48 undisturbed Andisols where 12 intact samples were taken at 5-10 cm depth from a cattle pasture site in Nishi-Tokyo, Japan, and 36 intact samples were collected from a forest site at Fukushima Prefecture at three depths (0 to 5-, 15 to 20-, and 55 to 60-cm; 12 samples at each depth) with a steep organic matter gradient. Soil gas diffusion coefficient (D_p) and soil-water retention were measured for each at soil water matric potentials of -10, -60, -100, -1000, -12600 cm H_2O, and for 19 (out of 48) samples at air- and oven-dry conditions. Other soil samples collapsed during the drying process and were not measured for D_p at air- and oven-dry conditions.

* Graduate School of Science and Engineering, Saitama University, 255 Shimo Okubo, Sakura-ku, Saitama, JAPAN
** Dept. of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Aalborg, DENMARK
原稿受付日：平成 19 年 4 月 16 日

2.2 Measurement Method

The soil-gas diffusion coefficient D_p was measured using the diffusion chamber (Fig. 1) developed by Currie (1960)[1] and recommended by Rolston and Moldrup (2002)[2]. Oxygen was used as the experimental (tracer) gas. The increasing concentration of oxygen inside the chamber is a result of diffusion from the atmosphere through the soil to the chamber initially filled with N_2 gas. From the measurements of the oxygen concentration inside the diffusion chamber at regular time intervals, the soil-gas diffusion coefficient D_p was calculated using the solution to the combination of Fick's law of diffusion and continuity equations given in Rolston and Moldrup (2002) [2]. The soil-gas diffusion coefficient, D_p, can be derived from the slope of the plot of the natural logarithm of the relative concentration versus time which becomes linear for a sufficiently large time.

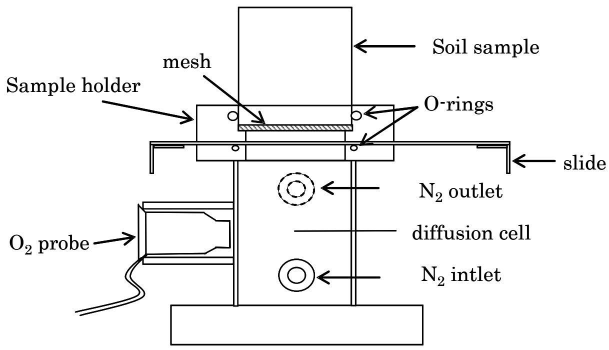

Fig. 1 Soil-gas diffusion apparatus.

3. Gas Diffusivity Models

3.1 Soil-Type Independent Models

The proposed linear gas diffusivity model was compared to the soil-type independent models tested in this study. These classical models include Penman

(1940)[3] and Millington and Quirk (1961)[4] models. The Millington and Quirk model is noteworthy since it is almost universally applied to vadose transport studies but has not been yet tested thoroughly against undisturbed soils especially for volcanic ash soils.

The Penman model assumes a linear variation of gas diffusivity with ε using a constant tortuosity factor of 0.66, and is given as,

$$\frac{D_p}{D_o} = 0.66\varepsilon \qquad [1]$$

where ε is the soil-air porosity ($m^3\ m^{-3}$), D_p is the soil-gas diffusion coefficient (m^3 soil air m^{-1} soil sec^{-1}), and D_o is gas diffusion coefficient in free air (m^2 air sec^{-1}).

The Millington and Quirk model, derived assuming random cut and join of capillary tubes, is related to the soil-type through the soil total porosity (Φ, $m^3\ m^{-3}$), and is given as,

$$\frac{D_p}{D_o} = \frac{\varepsilon^{\frac{10}{3}}}{\Phi^2} \qquad [2]$$

3.2 Soil-Water Retention Based Models

Moldrup et al. (1999[5], 2000[6], and 2003[7]) found that soil-water-characteristic (SWC) based models using the Campbell (1974)[8] pore-size distribution (PSD) index b better predicted gas diffusivities for a variety of soils over a wide range of soil-water matric potentials, ψ, as compared to the soil-type independent models (Eq. [1] and [2]). The SWC-based models included the simple power-law Buckingham–Burdine–Campbell model (Moldrup et al., 1999[5]), and the macroporosity (taken as the soil-air content at ψ = -100 cm H_2O, ε_{100}) dependent model (Moldrup et al., 2000[6]). Recently developed models include the Penman-Call model, based on Call (1957[9]), that takes into account of the effect of inactive pore spaces (Moldrup et al., 2005[10]).

The Campbell (1974) soil-water characteristic (SWC) model [8], fitted to the soil-water retention data and used in the SWC-based D_p/D_o models, is given by,

$$\frac{\psi}{\psi_e} = \left(\frac{\theta}{\theta_s}\right)^{-b} \qquad [3]$$

where ψ is the soil-water matric potential (cm H_2O), ψ_e is the air-entry potential (cm H_2O), θ is the soil-water content ($m^3\ m^{-3}$), θ_s is the soil-water content at saturation, and b is the Campbell pore-size distribution parameter (b>0) which corresponds to the slope of the SWC curve in a log(-ψ) versus log(θ) plot.

The Buckingham-Burdine-Campbell (BBC) power-law model (Moldrup et al., 1999[5]) used the matching point reference value at air-filled saturation. The BBC model is given as,

$$\frac{D_p}{D_o} = \Phi^2\left(\frac{\varepsilon}{\Phi}\right)^{2+\frac{3}{b}} \qquad [4]$$

where the expression, Φ^2, is the Buckingham (1904) gas diffusivity at completely dry conditions[11]. Eq. [4] represents an analogue to the Burdine (1953)[12] capillary tube tortuosity model for unsaturated hydraulic conductivity.

Moldrup et al. (2000)[6] found a high correlation between the volumetric content of larger pores (macroporosity) taken as ε at ψ = -100 cm H_2O (ε_{100}, pore diameter > 30 μm) and the soil-gas diffusivity at ψ = -100 cm H_2O, $D_{p,100}/D_o$, which is

$$\frac{D_{p,100}}{D_o} = 2\varepsilon_{100}^{\ 3} + 0.04\varepsilon_{100} \qquad [5]$$

Using ψ = -100 cm H_2O as the matching point potential and using Eq. [5] to replace the Buckingham expression in the BBC model (Φ^2 in Eq. [4]), the ε_{100}-dependent gas diffusivity model becomes,

$$\frac{D_p}{D_o} = \left(2\varepsilon_{100}^{\ 3} + 0.04\varepsilon_{100}\right)\left(\frac{\varepsilon}{\varepsilon_{100}}\right)^{2+\frac{3}{b}} \qquad [6]$$

The recently developed Penman-Call linear $D_p(\varepsilon)/D_o$ model, modified from Penman (1940)[3] and Call (1957)[9] D_p/D_o models, considers the effect of inactive pore spaces (threshold soil-air content, ε_{th}) below which soil-gas diffusivity becomes negligible. The general Penman-Call linear $D_p(\varepsilon)/D_o$ model proposed by Moldrup et al. (2005)[10] is,

$$\frac{D_p}{D_o} = C(\varepsilon - \varepsilon_{th}) \quad \text{if} \quad \varepsilon \ge \varepsilon_{th} \qquad [7a]$$

$$\frac{D_p}{D_o} = 0 \quad \text{if} \quad \varepsilon < \varepsilon_{th} \qquad [7b]$$

where C is the slope of the linear model and ε_{th} is the threshold soil-air content. Call (1957)[9] used C = 0.66 (Penman slope) with ε_{th} equal to 0.1 $m^3\ m^{-3}$.

3.3 Proposed Linear Model

In order to use the Penman-Call model as a predictive model, expressions for the parameters of Penman-Call model (model slope C and threshold soil-air content, ε_{th}) were developed linking D_p/D_o to the soil total porosity and soil-water retention. The threshold soil-air content, ε_{th}, is estimated as 20 percent of the total pore space in soil (total porosity, Φ) following Dracos (1991)[13],

$$\varepsilon_{th} = 0.2\Phi \qquad [8]$$

The slope C of the Penman-Call model can be defined from the gas diffusivity at maximum air-filled porosity, $D_p(\varepsilon = \Phi)/D_o$, by,

$$C = \frac{1}{(\Phi - \varepsilon_{th})}\frac{D_p(\varepsilon = \Phi)}{D_o} \qquad [9]$$

Two equations were suggested to estimate $D_p(\varepsilon = \Phi)/D_o$ in Eq. [9]. Following a general power-law $D_p(\varepsilon)/D_o$ model for completely dry conditions, the gas diffusivity is given as,

$$\frac{D_p(\varepsilon = \Phi)}{D_o} = \Phi^X \qquad [10]$$

where X is the tortuosity-connectivity factor for the soil-air phase at $\varepsilon = \Phi$. We assumed X = 3.8 based on the data for repacked Andisol (Osozawa, 1998[14]). The slope C is derived combining Eq. [8], [9], and [10] with X = 3.8,

$$C = 1.25\Phi^{2.8} \qquad [11]$$

Another expression for the model slope C was derived using the classical Buckingham (1904) D_p/D_o model[11] assuming independent contributions on gas diffusivity from the inter-aggregate and intra-aggregate pore space regions. Applying the Buckingham model at each region yields,

$$\frac{D_p(\varepsilon = \Phi)}{D_o} = (\varepsilon_{inter})^2 + (\varepsilon_{intra})^2 \qquad [12]$$

where ε_{inter} and ε_{intra} are the inter- and intra-aggregate porosity, respectively. The separation between inter- and intra-aggregate pores takes place at ψ = -1000 cm H_2O, as shown for an Andisol by Kawamoto et al. (2004)[15]. Combining Eq. [8], [9], and [12] and setting $\varepsilon_{inter} = \varepsilon_{1000}$ and $\varepsilon_{intra} = \Phi - \varepsilon_{1000}$ yields for C,

$$C = \frac{1.25}{\Phi}\left((\varepsilon_{1000})^2 + (\Phi - \varepsilon_{1000})^2\right). \qquad [13]$$

4. Results and Discussion

The D_p/D_o data for the intact samples from Nishi-Tokyo and Fukushima as shown in Fig. 2 suggested a linear increase in gas diffusivity with soil-air content. It is apparent that the widely-used Millington and Quirk (1961) model[4] underestimated the D_p/D_o data for pF < 4.1 (where pF = log(-ψ, cm H_2O)), and overestimated measurements at air-and oven-dry conditions.

The BBC model slightly underestimate D_p/D_o between pF 2 and pF 4.1 for all soils, as illustrated in Fig. 2 for three soil samples. The slight underestimation of the BBC model is likely due to the less tortuosity in the well-developed aggregated structure of Andisols as compared to normal mineral soils (Moldrup et al., 2003[7]) that would give slightly higher measured D_p/D_o than predicted by the BBC model. However at pF > 3, the soil aggregates start to dry out and the tortuous pathways through the soil aggregates will reduce soil-gas diffusivity. The enhanced tortuosity inside the relatively stable soil aggregates likely counter-balanced the low inter-aggregate tortuousity causing much lower gas diffusivities at air-dry and oven-dry conditions than predicted by the BBC model. This would explain the apparent linear behavior of the measured D_p/D_o up to the oven-dry conditions.

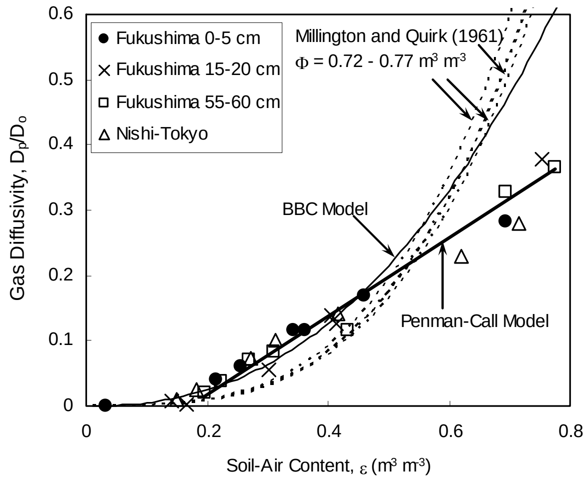

Fig. 2 The variation of the gas diffusivity with soil-air content of four intact samples. The widely used Millington and Quirk (1961) and the BBC model, and the proposed Penman-Call linear gas diffusivity model are also shown.

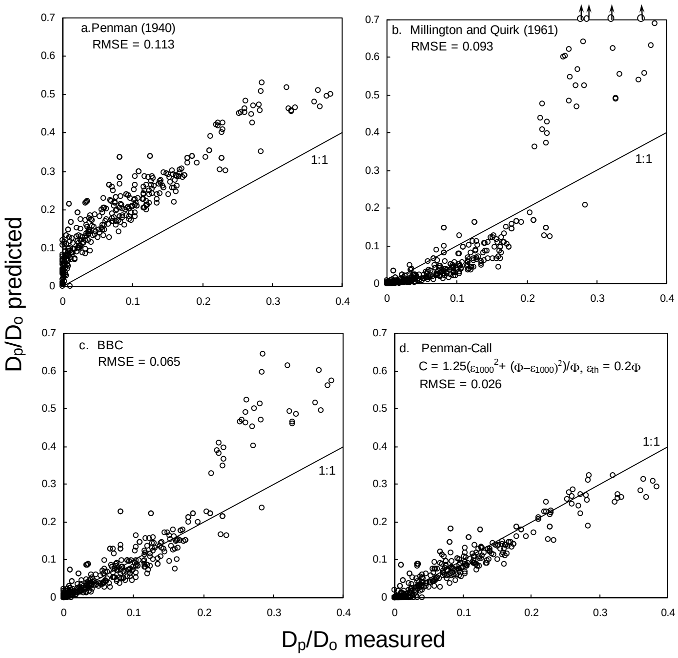

Fig. 3 Scatterplot comparison between measured and predicted gas diffusivity values.

The soil-type independent Penman (1940)[3], Eq. [1], and MQ (1961)[4], Eq. [2], models performed poorly in predicting D_p/D_o (Fig. 3a and 3b). The widely-used MQ model has already been reported to perform poorly on volcanic ash soils (Moldrup et al., 2003[7]) and on other mineral soils (Moldrup et al., 1999, 2000[5),6)]; Kawamoto et al., 2006[16)]). Both the BBC model (Eq. [4]) and the ε_{100}-dependent model (Eq. [6]) underestimated D_p/D_o between pF 2 and 4.1 and largely overestimated D_p/D_o at dry conditions (Fig. 3c).

The Penman-Call model (Eq [7]) using the developed expressions for ε_{th} (Eq. [8]) and C (Eq. [11]) significantly reduced the prediction error at very high soil-air content, and performed well on the total range of soil-air contents. However, when Eq. [13] for the slope C was used, the Penman-Call model gave a far superior performance as compared to the other models, especially at dry conditions (Fig. 3). This shows that the $D_p(\varepsilon)/D_o$ behavior of volcanic ash soils can be described as the sum of the D_p/D_o in the inter- and intra-aggregate porosities. When only the soil total porosity is known, Eq. [11] can be used instead of Eq. [13] to predict C. In perspective, additional data for volcanic ash soils are needed to test the Penman-Call model together using the developed expressions for the model slope C and ε_{th} especially when data for Andisols from outside Japan become available.

5. Conclusions

In this study, the linear Penman-Call type $D_p(\varepsilon)/D_o$ model (Moldrup et al., 2005[10)]) to predict the variation of gas diffusivity with soil-air content was proposed. The performance of this new linear model was compared to the existing traditional nonlinear models. This linear Penman-Call type $D_p(\varepsilon)/D_o$ model, with the model slope C and threshold air content ε_{th} related to soil-water contents at saturation and pF 3 better predicted gas diffusivity across soil moisture conditions, as compared to frequently used non-linear models.

Acknowledgment

This study was made possible by a grant from the Innovative Research Organization, Saitama University and by a grant from the Japanese Ministry of Education, Science, Sports, and Culture (Monbukagakusyo: Research No. 18360224).

References

1) Currie, J. A. 1960. Gaseous diffusion in porous media: Part 1. A nonsteady state method. Br. J. Appl. Phys. 11:314–317.

2) Rolston, D. E., and P. Moldrup. 2002. Chapter 4.3. Gas Diffusivity. *In*: J. H. Dane and G. C. Topp (eds.). Methods of Soil Analysis, Part 4, SSSA Book Ser. 5, ASA and SSSA, Madison, WI, pp. 1113-1139.

3) Penman, H. L. 1940. Gas and vapor movements in soil: The diffusion of vapors through porous solids. J. Agric. Sci. 30:437-462.

4) Millington, R. J. and J. M. Quirk. 1961. Permeability of porous solids. Trans. Faraday Soc. 57:1200-1207.

5) Moldrup, P., T. Olesen, T. Yamaguchi, P. Schjønning, and D. E. Rolston. 1999. Modeling diffusion and reaction in soils: IX. The Buckingham-Burdine-Campbell equation for gas diffusivity in undisturbed soil. Soil Sci. 164:542-551.

6) Moldrup, P., T. Olesen, P. Schjønning, T. Yamaguchi, and D. E. Rolston. 2000. Predicting the gas diffusion coefficient in undisturbed soil from soil water characteristics. Soil Sci. Soc. Am. J. 64: 94-100.

7) Moldrup, P., S. Yoshikawa, T. Olesen, T. Komatsu, and D. E. Rolston. 2003. Gas diffusivity in undisturbed volcanic ash soils: Test of soil-water-characteristic based prediction models. Soil Sci. Soc. Am. J. 67: 41-51.

8) Campbell, G. S. 1974. A simple method for determining unsaturated conductivity from moisture retention data. Soil Sci. 117:311-314.

9) Call, F. 1957. Soil fumigation: V. Diffusion of ethylene dibromide through soils. J. Sci. Food Agric. 8:143–150.

10) Moldrup, P., T. Olesen, S. Yoshikawa, T. Komatsu, A. M. McDonald, and D. E. Rolston. 2005. Predictive-descriptive models for gas and solute diffusion coefficients in variably saturated porous media coupled to pore-size distribution: III. Inactive pore space interpretations of gas diffusivity. Soil Sci. 170:867-880.

11) Buckingham, E. 1904. Contributions to our knowledge of the aeration of soils. USDA. Bur. Soil Bul. 25. U.S. Gov. Print. Office, Washington, DC.

12) Burdine, N. T. 1953. Relative permeability calculations from pore-size distribution data. Trans. AIME. 198:71-78.

13) Dracos, Th. 1991. Multiphase flow in porous media. *In*: Bear, J., and J. M. Buchlin (ed). Modeling and applications of transport phenomena in porous media. Kluwer, Dordrecht, the Netherlands, pp.196-220.

14) Osozawa, S. 1998. A simple method for determining the gas diffusion coefficient in soil and its application to soil diagnosis and analysis of gas movement in soil (in Japanese with English summary). DSc. Dissertation No. 15 (March 1998) Natl. Inst. of Agro-Environmental Sci., Ibaraki, Japan.

15) Kawamoto, K. and B. Aung. 2004. Experimental study on soil water repellency of volcanic ash soils: Effects of organic matter content and initial water content. Trans. of JSIDRE. 230:75-83.

16) Kawamoto, K., P. Moldrup, P. Schjønning, B. V. Iversen, T. Komatsu, and D. E. Rolston. 2006. Gas transport parameters in the vadose zone: Gas diffusivity in field and lysimeter soil profiles. Vadose Zone J. 5:1194-1204.