ABSTRACT

Soil-gas diffusivity plays a fundamental role on diffusion-controlled migration of climate impact gases from different terrestrial ecosystems including managed pasture systems. Soil-gas diffusivity has a strong bearing on soil type/texture and soil structure (e.g., density) and typically shows a depth-dependent behavior in subsurface. This study investigated the gas diffusivity in soils sampled from a managed pasture site at Ambewela, Sri Lanka at 0-5 cm depth range along a downgrading transect. The soils were pre-characterized for particle-size distribution, organic matter content, dry density and particle density. Soil-gas diffusivity was measured using one-chamber diffusion apparatus using N_2 and O_2 as experimental gases. The measured diffusivity, together with selected intact and repacked soil data from literature, were tested against the existing predictive gas diffusivity models. We used a generalized descriptive parametric two-region model to represent bimodal/two-region behaviour of selected soils which was able to statistically outperform the predictive models for both intact and repacked soils and hence demonstrated its applicability to better characterize site-specific greenhouse gas emissions with useful implications for pasture management. .

INTRODUCTION

Grazed pasture systems are predominant sources of greenhouse gases such as nitrous oxide (N_2O) which inevitably affect the climate resulting in global warming and climate shifts. For example, N_2O has 298 times global warming potential than that of CO_2 over a 100-year time frame (Myhre et al., 2013). Extensive applications of nitrogen fertilizer and increased stocking rates are the main factors contributing to enhanced pastoral emissions of N_2O. Primarily, pastorial N_2O is produced through nitrification and denitrification mechanisms as a result of microbially-mediated processes in the presence of anaerobic conditions in the soil. Once produced, the N_2O must be transported through the subsurface via the topsoil and emit across soil-atmosphere continuum in order to make an impactful climate effect. If the topsoil is sufficiently aerated, N_2O will be oxidized and emit to atmosphere as dinitrogen (N_2), an environmentally benign gas as compared to N_2O with no climate forcing effect. Thus, the pastoral topsoil (0 – 5 cm) becomes critically important in regulating the climate in local, regional and global contexts.

The migration of N_2O in pastoral topsoil (0-5 cm), and its emission to the atmosphere is predominantly diffusion-controlled, particularly in the absence of wind-induced pressure gradients. In addition, the soil textural and structural properties, as well as soil moisture status and soil density, play significant roles on N_2O emissions. Mitigation measures, therefore, are highly dependent on how well the diffusion-controlled gas transport processes in pasture topsoil is understood and how accurately they can be accounted in predictive numerical tools.

Gas diffusion in soil is commonly described by soil-gas diffusivity, D_p/D_o where

D_p (m^3 soil air m^{-1} soil s^{-1}) and D_o (m^2 air s^{-1}) are the soil-gas diffusion coefficients in soil and in free air, respectively. Measuring D_p/D_o is, however, experimentally intensive and instrumentally challenging due to the requirement of specific apparatus and tight control of boundary conditions. Hence, the predictive gas diffusivity models are widely used to predict soil-gas diffusivity from easily-measurable properties such as air-filled porosity ( ) and total porosity (Φ). In complex ecosystems such as managed pastures, however, complex soil physical and bio-geo-chemical heterogeneity makes the application of developed models questionable. Therefore, a careful revisit of existing predictive models, together with measured gas diffusivity data on a wide range of pasture topsoils, is a necessity to investigate their applicability.

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Generally, the pasture soils are considered to be well-structured aggregated soils, having both inter-aggregate pores (i.e., pores between the aggregates) and intra-aggregate pores (i.e., pores within the aggregates), resulting in a distinctive bimodal pore structure. The two pore regions are generally considered to be functionally analogous with respect to soil-moisture and soil-gas dynamics, and hence it is common to describe them in terms of two additive mathematical expressions in modeling soil-moisture retention (e.g., Durner, 1994) or soil-gas diffusivity (e.g., Resurreccion et al., 2008). However, compaction of soil due to animal treading and mechanical implements on pasture sites may alter soil pore structure (Jayarathne et al., 2019). Compaction essentially reduces the macropore domains and increases the micropore domains of soil, thus shifting the bimodal nature of soil. Although there are currently available predictive models to predict gas diffusivity in non-aggregated soils, these models cannot be used directly for aggregated soils as they may yield biased results due to the presence of two distinct pore regions. Therefore, various models have been modified and developed to predict the soil-gas diffusivity in well-structured aggregated soils (Jayarathne et al., 2019). Moreover, literature is abound with soil-gas diffusivity based investigations of pasture soils on both structurally intact and disturbed soils with little attention to their relative differences (Chamindu Deepagoda et al., 2018 and 2019).

In this study, a series of diffusivity measurements on a pasture soil as well as literature data were used to characterize gas transport behaviour in pasture topsoil (0-5 cm) in both structurally intact and disturbed soils. We used measured data from a Sri Lankan pasture site, together with additional supporting data from literature to represent a wide geographic origin including soils from Sri Lanka, Japan, United Kingdom, and New Zealand. An ensemble of soil-gas diffusivity models was tested against diffusivity data and a new generalized descriptive gas diffusivity model was presented to better characterize the pasture soils.

MATERIALS AND METHODS

Soils and Data

Undisturbed and disturbed soils from Ambewela pasture site (6.8693° N, 80.7957° E), Sri Lanka were collected at 0-5 cm depth from five locations, along a downgradient transect, which also showed a natural organic matter gradient. Located at the Central Hills of Sri Lanka at an elevation of 1847 m above mean sea level, the farm was initially established in 1942. The mean annual rainfall in this area has been recorded as 179.4 mm ranging from a minimum of 20.8 mm (February) to a maximum of 515.6 mm (December). The daytime ambient temperature in this area has been recorded as a mean of 20.5°C ranging between 16 – 25°C. The sampled area has not been used for grazing for about one year before sampling, and no agricultural machinery has been used at the site for the same period.

In addition to the unpublished data from Ambewela pasture site, Sri Lanka, a series of literature data on intact and repacked pasture topsoils (0-5 cm) from different countries were used to test the existing and proposed gas diffusivity models. Table 1 shows the considered soils from Sri Lanka (Ambewela and Peradeniya), Japan (Nishi-Tokyo), United Kingdom (Lexington), and New Zealand (Temuka, Templeton, Wakanui) with the names denoting the sampling location. Textural contrast and important soil physical properties of selected intact and repacked soils are also given in Table 1. For further details on the data from the literature, the reader is referred to the related literature mentioned in Table 1.

» Insert Table 1 «

Methods

The 100-cm^3 undisturbed soil samples were collected using metallic annular cores ensuring minimum disturbance to the soil. The retrieved samples, leveled and kneaded at both ends to remove redundant soil, were end-capped and wrapped with polythene to preserve ambient moisture before transferring to the Geotechnical Engineering laboratory for characterization. Repacked samples, on the other hand, were prepared from bulk soil sampled from 0-5 cm pasture layer, sieved to obtain 2-mm fraction and repacked to the same bulk density observed in the corresponding later.

The samples were first characterized following given standards for soil-moisture content (BS 1377: Part 2: 1990), particle density, bulk density (BS 1377: Part 2: 1990), particle size distribution (BS 1377: Part 2: 1990) and organic matter content (Loss on Ignition method).

The samples were then saturated for 72 hours and sequentially drained to intended moisture levels by stepwise evaporation. At each moisture level, the samples were kept closed for a sufficient time to reach the hydraulic equilibrium and moisture redistribution before diffusivity measurements.

Gas diffusivity was measured following the one-chamber method introduced by Taylor (1949) and developed by Schjønning (1985). The custom-fabricated PVC chamber is 20-cm in height and 3.4 cm in internal diameter, and provisioned with two values as inlet and outlet for priming. The chamber was checked for airtightness before the measurement campaign was initiated. For the measurements, the sample was mounted on top of the diffusion chamber and made it airtight. Then, the chamber was flushed with 99.99% N_2 gas to remove all the O_2 inside the chamber. The sample was then opened to the atmosphere by allowing the atmospheric O_2 to diffuse through the sample into the chamber. The increase of O_2 concentration inside the chamber was monitored continually with an O_2 sensor attached to the chamber wall. Calculation of D_p/D_o was performed following both Taylor (1949) and Currie (1960) methods as follows.

The Taylor (1949) method is founded on the Fick's first law and can be presented by the following equation.

$$\ln\left(\frac{C_t}{C_0}\right) = -\frac{D_p}{H_s H_c} t$$

where C_t is the change of concentration inside the chamber (gm^{-3}) ($C_t = C_{t=t} - C_{t=0}$), H_s is sample height (m), H_c is height of the chamber (m). D_p can be calculated from the gradient of the graph of ln (C_t/ C_0) vs time (t).

The Currie (1960) method on the other hand is founded on both the Fick's first law and the second law and the basic equation can be expressed as follows;

$$\ln\left(\frac{C_t}{C_0}\right) = -\frac{D_p \alpha_1^2}{\varepsilon} t + \ln\left(\frac{2h}{H_s\left(\alpha_1^2 + h^2\right) + h}\right)$$

where C_t is the change of concentration inside the chamber (gm^{-3}) ($C_t = C_{t=t} - C_{t=0}$), H_s is sample height (m), h is ε/H_c , ε is air filled porosity (m^3 m^{-3}), H_c is height of the chamber (m).

D_p (soil-gas diffusion) can be derived from the slope of the plot of ln ($\frac{C_t}{C_0}$) versus time (t).

Soil-gas diffusivity modelling

Table 2 shows the array of descriptive-predictive models for soil-gas diffusivity that were tested against the measured pasture diffusivity data mentioned in Table 1.

» Insert Table 2 «

The two-region parametric soil-gas diffusivity model, which is proposed in this study to better characterize diffusivity measurements in pasture soils, takes the form of:

$\frac{D_p}{D_o} = A\left(- {}_o\right)^B + C(- i)$

wherein A is model scale factor, B is model shape factor, ${}_o$is threshold air content, i is inter-aggregate porosity, C is the gradient in the intra-aggregate region, assuming a linear increase of gas diffusivity. Setting $C = 0$ yields the classical power-law model explaining gas diffusivity in unimodal soils. In fact, all the existing models presented in Table 2 can be deduced from the Equation 3, provided suitable values/parameters are assigned for A,B and $_{o}$. Notably, $_{o}$ represents air-filled porosity below which the gas diffusivity is negligibly small due to extremely high moisture-induced tortuosity in soil-gas phase to yield a measurable gas diffusivity.

The gas-phase tortuosity (, dimensionless), can be described as the roundabout distance a gas molecule will travel in the gaseous phase between two predefined points which are a unit Euclidean distance apart. Based on this definition, can be deduced from soil-gas diffusivity data as presented by Ball (1980) as follows:

$\tau = \sqrt{\frac{\varepsilon}{\frac{D_p}{D_o}}}$

Statistical Analysis

Two statistical indices, RMSE and bias, were used to statistically analyze the model performance and compare the model predictions. The RMSE evaluates the overall model fit to the measured data.

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(d_i)^2}$$

The bias, on the other hand, evaluates whether a model overestimates (positive bias) or underestimates (negative bias) the observations.

$$Bias = \frac{1}{n}\sum_{i=1}^{n}(d_i)$$

where d_{i} is the difference between the observed and predicted diffusivity values, n is the number of diffusivity measurements in a data set.

The performance of the selected models and newly developed two-region model against the measured gas diffusivity data for intact soils and repacked soils expressed in terms of RMSE and Bias are shown in Table 3 and Table 4, respectively.

» Insert Table 3 «

» Insert Table 4 «

RESULTS AND DISCUSSION

Soil-gas diffusivity

Figure 1 shows the gas diffusivity against air-filled porosity for two-region descriptive model (Eq. 3) for six intact soils: Ambewela soil, three New Zealand soils, one UK soil and Peradeniya soil (Sri Lanka).

» Insert Figure 1 «

Pasture soils are often structurally aggregated and characterized by two distinct regions: the inter-aggregate pore region and the intra-aggregate pore region. As a result, typical D_p/D_o in pasture soils are expected to show non-linear behaviour with two distinct pore regions. However, for Ambewela pasture soil (0-5 cm), it showed a linear behaviour as shown in Figure 1(a) through 1(c). This is mostly due to the compacted behaviour of the soil due to frequent compaction by machineries and animal treading and trampling which result in an alteration to structural arrangement. The Ambewela topsoil (0-5 cm) further showed a cracked behaviour with visible cracks on the surface which also is attributable to the observed linear behavior of the soil. Note that the soil has only drained to -10 kPa, which may have not opened the intra-aggregate pores to distinguish the two-region behavior.

In Peradeniya pasture site, on the other hand, the use of livestock or agricultural implements is not extensive and therefore has gradually developed into a well-structured aggregated soil. Consequently, Peradeniya soil has exhibited a two-region behaviour (Figure 1(h)). The UK soil also showed a slight two-region behaviour due to its weakly-aggregated nature but was not so pronounced as the Peradeniya soil.

Figure 2 shows the measured gas diffusivity against air-filled porosity, together with predictions from the two-region model for six repacked soils: Two Peradeniya soils, one Japanese (Nishi-Tokyo) soil and three NZ soils. Among them, Peradeniya pasture soil (Figure 2(a), 2(b)) and Nishi-Tokyo pasture soil (Figure 2(c)) showed distinct two-region behaviour. But other soils showed a linear variation. Typically, since the sieving and repacking involves de-structuring of soil aggregates in repacked soils, they are expected to show less two-region behavior than intact soils. In Peradeniya repacked soils, the less-compacted soils (1.0 g cm^{-3}, Fig. 2a) have higher interaggregate pore volume than the highly-compacted soils (1.30 g cm^{-3}, Fig. 2b), implying a decrease in interaggregate pore space due to high compaction, with an overall decrease in $D_p/D_{o.}$

» Insert Figure 2 «

To reveal the behaviour of the peopoaws two-region descriptive model, its performance was compared with the classical and newly developed gas diffusivity models using scatterplot comparisons as shown in Figure 3 and Figure 4 for both intact soils and repacked soils, respectively.

For intact soils, the statistical comparison of model performance for eight models based on two statistical indices (Table 3), showed that Buckingham (1904), MQ (1960), MQ (1961), WLR-Marshall and SWLR models underestimated the results while the Marshall (1959) and Millington (1959) models overestimated at higher air-filled porosities and underestimated at low air-filled porosities. The developed two-region model gave more accurate results for all the intact soils (Figure 3i). However, Penman (1940) model, typical upper-limit model describing soil-gas diffusivity, also accurately predicted the data for Ambewela soil as shown in Figure 3(b). That could be likely due to the cracked behaviour of

Ambewela soil as described before.

» Insert Figure 3 «

Similar to the intact soils, the scatterplot comparison of repacked soils is shown in Figure 4 using eight predictive models, together with the proposed two-region model which accurately described the measured data (Fig. 4i). Notably, Buckingham (1904) model made good descriptions for repacked soils while the WLR and SWLR models, which are originally developed for repacked soils, showed relatively poor performance for pasture soils.

» Insert Figure 4 «

Figure 5 shows, in log-transformed axes, the scatterplot comparisons of modelled and measured soil-gas diffusivities (D_p/D_o) for six intact soils: Peradeniya soil, Ambewela soil, UK soil and three NZ soils for nine models including the proposed descriptive two-region model. The generalized descriptive two-region model yielded better results than the other predictive models, suggesting the need of more generalized models to capture the unique behaviors in pasture topsoils.

As expected, in the dry region almost all models show an accurate prediction for all the soils. Generally, the behaviour of a soil at dry region or at low saturation can be predicted to a high accuracy. However, in the wet region or high moisture contents, it is comparatively difficult to find good predictions. As a result, the predictions vary considerably across the models in the wet region. Intrinsic variability and measurement difficulties at wet region are among the main reasons for the observed challenges in predictability. Intrinsic variability, which results from the random breakage/formation of water bridges between soil particles, creates differently tortuous pore network even at same air-filled porosity, yielding considerable variability in measured data even among replicate samples.

Diffusivity measurements in the wet region are harder than that in the dry region due to many practical challenges. When computing the air-filled porosity, the mass of water is typically measured in the soil samples, which is hard when the soil is at near saturation. In fact, the water retained in the filter paper, placed underneath the soil samples, is hard to be separated from water used for sample saturation which leads to some measurement uncertainties. In addition, it is practically hard to prevent draining water from the samples during transfer to the diffusion apparatus, causing additional uncertainties.

» Insert Figure 5 «

Figure 6 shows scatterplot comparisons of modelled and measured soil-gas diffusivities (D_p/D_o) for six repacked soils: two Peradeniya soils, Nishi-Tokyo (Japan) soil and three NZ soils. Predictions are shown from nine existing models, together with the proposed two-region descriptive model. The figure clearly demonstrates that the new descriptive two-region model could better characterize the measured data as compared to the commonly used models for each soil.

Notably, the conceptual development of the WLR-Marshall model, considering a linear reduction of water-induced effects on gas diffusivity, makes it better suited for repacked soils. As a result, the model is validated and recommended for diffusivity predictions for repacked soils (Moldrup et al., 2000). However, according to Figure 6(g), WLR-Marshall model has markedly underpredicted the observations in the wet region, thus demonstrating the modeling challenges in high-moisture soils. MQ (1961) model, on the other hand, yielded better results for intact soils than repacked soils (Chamindu Deepagoda et al., 2011). Nevertheless, MQ (1961) model has underpredicted the selected pasture intact soils markedly in the wet region (Figure 6f). The overall numerical analysis thus recognized the importance of a descriptive model with variable site-specific parameters to characterize the unique nature of the pasture topsoil since the existing predictive models may mischaracterize the gas diffusivity behavior, particularly in the wet region. The proposed descriptive empirical model thus demonstrated its applicability, provided few measurements could be carried out to estimate the model parameters.

» Insert Figure 6 «

Tortuosity

The predicted tortuosity for six intact pasture topsoils are shown in Fig. 7, together with calculated tortuosity from measured diffusivity and air-filled porosity data (Eq. 4). The Penman (1940) model, with a constant tortuosity across the total air-filled porosity variation, typically yielded a lower-limit tortuosity for all six soils as expected. The SWLR model, on the other hand, provides an upper limit for tortuosity for most of the soils except for the UK and Temuka (NZ) soils as shown in Figures 7(d) and 7(g). Buckingham, MQ (1960), MQ (1961), WLR-Marshall and SWLR models showed nonlinear variation with decreasing tortuosity as the air-filled porosity increases. Evidently, Marshall (1959) and Millington (1959) models showed constant value for high ε values and show only a limited non-linearity at high moisture regimes. The developed two-region model exhibited a good agreement with calculated tortuosity values for all the six soils.

» Insert Figure 7 «

A similar pore tortuosity analysis was also done for repacked pasture soil data as shown in Figure 8. The Penman (1940) model-based constant tortuosity across the total air-filled porosity variation, yileded a lower-limit tortuosity for all six soils same as intact soils while the MQ (1961) model provides an upper limit for tortuosity for all six soils. Buckingham, MQ (1960), MQ (1961), WLR-Marshal and SWLR models showed nonlinear variation with decreasing tortuosity as the air-filled porosity increases. On the other hand, Marshall and Millington models showed constant value for high ε values and showed slight non-linear variation at high moisture contents as shown in Figure 8(a), 8(b), 8(c). However, for the three NZ soils both models showed constant tortuosity across all ε values as shown in Figures 8(d), 8(e), 8(f). In comparison, the proposed descriptive two-region model exhibited a good agreement at all the ε values for NZ soils. For two Peradeniya soils and Nishi-Tokyo soil, the developed two-region model showed a slight non-linear variation with decreasing tortuosity as the air-filled porosity increases.

» Insert Figure 8 «

The numerical characterization/parameterization of soil-gas diffusivity using the proposed two-region model (Equation 3) is given in Table 5. All soils did not exhibit a notable water blockage with increasing air-filled porosity (i.e., $_{\mathrm{p}} = 0$).

» Insert Table 5 «

CONCLUSIONS

This study characterized measured soil-gas diffusivity and diffusivity-based gas phase tortuosity for pasture topsoils (0-5 cm) sampled from a pasture site in Ambewela, Sri Lanka together with literature measurements from other Sri Lankan, Japanese, New Zealand, and UK pasture topsoils. The measured diffusivity data, for both structurally intact and repacked samples retrieved from pasture sites, were compared against eight recognized soil-gas diffusivity predictive models together with a proposed generalized two-region descriptive model. The existing models mischaracterized the two-region behavior in some pasture soils and also yielded poor overall performance particularly in the wet region. The proposed generalized descriptive model, with best-fit parameters to the measured data statistically outperformed the classic diffusivity models and provided a good agreement for both intact and repacked soils. The pore tortuosity analysis also demonstrated that most existing models highly overpredicted the tortuosity in the wet region while the generalized two-region model best described it. The overall numerical analysis thus highlighted the importance site-specific characterization of gas diffusivity and pore tortuosity in order to make better description of soil-gas emissions which is a prerequisite to take pasture management strategies in relation to mitigation of greenhouse gases.

It should be noted that the all measurements involved have been carried out in laboratory-controlled environments where natural environmental complexities (e.g., temperature, evaporation, wind speed and humidity) were eliminated. Such additional environmental factors were out of the scope of this study but must be accounted when making more realistic conclusions. Results, therefore, must be compared against field-measured data with caution.

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REFERENCES

Ball, B.C. 1981. Modeling of soil pores as tubes using gas permeabilities, gas diffusivities, and water release. J. Soil Sci. 32:465–481. doi:10.1111/j.1365-2389.1981.tb01723.x.

Buckingham, E. (1904). Contributions to our knowledge of the aeration of soils. Bur. Soil Bull (Vol. 25). Washington, DC: U.S. Gov. Print. Office.

Chamindu, D., Møldrup, P., Schjønning, P., de Jonge, L. W., Kawamoto, K., & Komatsu, T. (2011). Density-Corrected Models for Gas Diffusivity and Air Permeability in Unsaturated Soil. Vadose Zone Journal, 10(1), 226-238. https://doi.org/10.2136/vzj2009.0137

Chamindu Deepagoda, T.K.K. T.J. Clough, J.R.R.N. Jayarathne, S. Thomas, and B. Elberling. 2019. Soil-Gas Diffusivity and Soil-Moisture effects on N2O emissions from Repacked Pasture Soils.Soil Sci. Soc. Am. J. DOI: 10.2136/sssaj2019.04.0118

Chamindu Deepagoda, T.K.K. T.J. Clough, S. Thomas, and N. Balaine. 2019. soil-gas diffusivity and soil-moisture effects on N2O emissions from intact pasture soils.. Soil Sci. Soc. Am. J. DOI: 10.2136/sssaj2018.

Chantigny, M. H., Rochette, P., Angers, D. A., Bittman, S., Buckley, K., & Masse, D. (2010). Soil nitrous oxide emissions following band-incorporation of fertilizer nitrogen and swine manure. Journal of Environment Quality, 39, 1545–1553. https://doi.org/10.2134/jeq2009.0482

Clough, T. J., Sherlock, R. R., & Rolston, D. E. (2005). A review of the movement and fate of N2O in the subsoil. Nutrient Cycling in Agroecosystems, 72, 3–11. https://doi.org/10.1007/s10705-004-7349-z

Currie, J.A. (1960). Gaseous diffusion in porous media. Part 2. Dry granular materials. British Journal of Applied Physics, 11, 318–324

Currie, J. A. (1984). Gas diffusion through soil crumbs: The effects of compaction and wetting. Journal of Soil Science, 35, 1–10.

Ding, F., Sun, W., & Huang, Y. (2019). Net N2O production from soil particle size fractions and its response to changing temperature. Science of The Total Environment, 650(1), 97–104.

Fujikawa, T.,&Miyazaki, T. (2005). Effects of bulk density and soil type on the gas diffusion coefficient in repacked and undisturbed soils. Soil Science, 170, 892–901.

Hamamoto, S., P. Moldrup, K. Kawamoto, and T. Komatsu. 2009. Effect of particle size and soil compaction on gas transport parameters in variably saturated, sandy soils. Vadose Zone J. 8:986–995.

Jayarathne, J.R.R.N., Chamindu Deepagoda, T.K.K., Clough, T.J., Nasvi, M.C.M., Thomas, S., Smits, E.B., K., 2019. Gas-Diffusivity Based Characterization of Aggregated Agricultural Soils. Soil Sci. Soc. Am. J. https://doi.org/10.1002/saj2.20033.

Moldrup, P., T. Olesen, T. Komatsu, P. Schjønning, and D.E. Rolston. 2001. Tortuosity, diffusivity, and permeability in the soil liquid and gaseous phases. Soil Sci. Soc. Am. J. 65:613–623.

Myhre, G., D. Shindell, F.-M. Breon, W. Collins, J. Fuglestvedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G.

Stephens, T. Takemura, and H. Zhang. 2013. Anthropogenic and natural radiative forcing In: T.F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, and P.M. Midgley, editors, Climate change 2013: The physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge Univ. Press, Cambridge, U.K.

Pelster, D. E., Chantigny, M. H., Rochette, P., Angers, D. A., Rieux, C., & Vanasse, A. (2012). Nitrous oxide emissions respond differently to mineral and organic nitrogen sources in contrasting soil types. Journal of Environment Quality, 41, 427–435. https://doi.org/10.2134/jeq2011.0261

Rolston, D.E., and P. Moldrup. 2002. Gas diffusivity. p. 1113–1139. In J.H. Dane and G.C. Topp (ed.) Methods of soil analysis. Part 4. SSSA Book Ser. 5. SSSA, Madison, WI.

Schjønning, P. (1985). A laboratory method for determination of gas diffusion in soil. (In Danish with English summary.) Rep. S1773. Danish Inst. of Plant and Soil Sci., Tjele.

Schjønning, P., Thomsen, I. K., Møberg, J. P., de Jonge, H., Kristensen, K., & Christensen, B. T. (1999). Turnover of organic matter in differently textured soils: I. Physical characteristics of structurally disturbed and intact soils. Geoderma, *89*, 177–198.

Taylor, S. A. (1949). Oxygen diffusion in porous media as a measure of soil aeration. Soil Science Society of America Journal, 14, 55–61

FIGURE AND TABLE CAPTIONS

Figure 1: Measured soil- gas diffusivity against air-filled porosity for intact pasture topsoil, together with proposed descriptive two-region model (Equation 3).

Figure 2: Measured soil- gas diffusivity against air-filled porosity for repaked pasture topsoil, together with proposed descriptive two-region model (Equation 3).

Figure 3: Scatterplot showing the measured D_p/D_o and modelled D_p/D_o for intact pasture topsoils

Figure 4: Scatterplot showing the measured D_p/D_o and modelled D_p/D_o for repacked pasture topsoils

Figure 5: Scatterplot showing the measured D_p/D_o and modelled D_p/D_o for intact pasture topsoils in log-transformed axes.

Figure 6: Scatterplot showing the measured D_p/D_o and modelled D_p/D_o for repacked pasture topsoils in log-transformed axes.

Figure 7: Pore tortuosity against air-filled porosity for intact soils

Figure 8: Pore tortuosity against air-filled porosity for repaxked soils

Table 1: Soils and data from literature and their physical properties

Table 2: Selected predictive soil-gas diffusivity models used in this study

Table 3: Statistical analysis on model performance using RMSE (Eq. 5) and Bias (Eq. 6) for intact soils

Table 4: Statistical analysis on model performance using RMSE (Eq. 5) and Bias (Eq. 6) for repacked soils

Table 5: Numerical parameterization of soil-gas diffusivity in selected pasture soils based on the proposed generalized two-region descriptive model (Eq. 3)

@ >p(- 18) * >p(- 18) * >p(- 18) * >p(- 18) * >p(- 18) * >p(- 18) * >p(- 18) * >p(- 18) * >p(- 18) * >p(- 18) * @ Soil & Sampling depth & Soil Type & Soil Texture & Bulk

density & Organic matter & Total

porosity & Reference & &
& (cm) & & Sand (%) & Silt (%) & Clay (%) & Mg m^{-3} & (kg kg^{-1}) & (cm^{3} cm^{-3}) &
Intact soils & & & & & & & & &
Ambewela, SL & 0-5 & Sandy loam & 54.1 & 39.5 & 6.3 & 0.72 (0.02) & 0.07 & 0.70 & This study
Peradeniya, SL & 0-10 & Sandy loam & 72.1 & 25.1 & 2.8 & 133 (0.05) & 0.096 & 0.46 & Jayarathne et al. (2019)

Wakanui, NZ

& 0-5 & Sandy loam & 70.6 & 25.4 & 4.0 & 0.95 (0.07) & 0.09 & 0.64 & Deepagoda et al. (2019)

Temuka, NZ

& 0-5 & Sandy loam & 64.4 & 32.3 & 3.3 & 1.14 (0.05) & 0.10 & 0.57 &

Templeton, NZ

& 0-5 & Loamy sand & 80.1 & 18.4 & 1.4 & 1.19 (0.18) & 0.09 & 0.55 &

Lexington, UK

& 0-5 & Silt loam & 7.3 & 67.3 & 25.4 & 1.51(0.06) & 0.05 & 0.43 & Kreba (2013)
Repacked soils & & & & & & & & &
Wakanui, NZ & 0-5 & Sandy loam & 70.6 & 25.4 & 4.0 & 0.95 (0.07) & 0.09 & 0.64 & Deepagoda et al. (2019)
Temuka, NZ & 0-5 & Sandy loam & 64.4 & 32.3 & 3.3 & 1.14 (0.05) & 0.10 &

0.57 &
Templeton, NZ & 0-5 & Loamy sand & 80.1 & 18.4 & 1.4 & 1.19 (0.18) & 0.09 & 0.55 &
Peradeniya-1, SL & 0-10 & Sandy loam & 72.1 & 25.1 & 2.8 & 1.10 (0.05) & 0.10 & 0.57 & Jayarathne et al. (2019)
Peradeniya-2, SL & 0-10 & Sandy loam & 72.1 & 25.1 & 2.8 & 1.30 (0.05) & 0.10 & 0.57 & Jayarathne et al. (2019)
Nishi-Tokyo, JP & 0-5 & Silt loam & NA$^{\pm}$ & NA & NA & 0.62 (0.05) & NA & 0.74 & Deepagoda et al. (2011)

SL: Sri Lanka; NZ: New Zealand; UK: United Kingdom; JP: Japan

$^{\pm}$ NA: Not available

D_p/D_o Model	Equation
Buckingham (1904)	$\frac{D_p}{D_o} = \varepsilon^2$
Penman (1940)	$\frac{D_p}{D_o} = 0.66\varepsilon$
Marshal (1959)	$\frac{D_p}{D_o} = \varepsilon^{\frac{3}{2}}$
Millington (1959)	$\frac{D_p}{D_o} = \varepsilon^{\frac{4}{3}}$
MQ (1960)	$\frac{D_p}{D_o} = \frac{\varepsilon^2}{\emptyset^{\frac{2}{3}}}$
MQ (1961)	$\frac{D_p}{D_o} = \frac{\varepsilon^{\frac{10}{3}}}{\emptyset^2}$
WLR-Marshall	$\frac{D_p}{D_o} = \varepsilon^{1.5}(\frac{\varepsilon}{\emptyset})$
SWLR	$\frac{D_p}{D_o} = \varepsilon^{(1+C_m\emptyset)}\left(\frac{\varepsilon}{\emptyset}\right)$

MQ, Millington and Quirk; WLR, Water-induced Linear Reduction; SWLR, Structure-dependant Water-induced Linear Reduction

D_p/D_o Model	Ambewela, SL RMSE	Peradeniya, SL Bias	UK RMSE	Temuka, NZ Bias	Wakanui, NZ RMSE	Templeton, Bias
Buckingham (1904)	0.04614	-0.03958	0.0671	-0.0579	0.035573	-0.02826
Penman (1940)	0.023595	0.002422	0.0394	0.0215	0.024989	0.020301
Marshal (1959)	0.028525	-0.01897	0.0451	-0.0048	0.017649	-0.00935
Millington (1959)	0.028418	-0.00685	0.0575	0.0221	0.014408	0.003467
MQ (1960)	0.041263	-0.03503	0.0615	-0.0139	0.027648	-0.02123
MQ (1961)	0.062527	-0.0515	0.0816	-0.0511	0.042827	-0.03472
WLR-Marshall	0.053144	-0.04504	0.0679	-0.0425	0.03749	-0.03026
SWLR	0.066403	-0.05381	0.0872	-0.0768	0.042875	-0.03466
Two Region	0.018149	-0.00478	0.0012	-0.0007	0.015097	0.003122

MQ, Millington and Quirk; WLR, Water-induced Linear Reduction; SWLR, Structure-dependant Water-induced Linear Reduction

@ >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * >p(- 24) * @ D_p/D_o Model & Peradeniya-1, SL

d = 1.0 g cm^{-3} & Peradeniya-2, SL

d = 1.3 g cm^{-3} & Nishi-Tokyo, JP & Temuka, NZ & Wakanui, NZ & Templeton, NZ & & & & & &
& RMSE & Bias & RMSE & Bias & RMSE & Bias & RMSE & Bias & RMSE & Bias & RMSE & Bias
Buckingham (1904) & 0.0437 & -0.0290 & 0.0594 & -0.0468 & 0.0804 & 0.0083 & 0.0110 & -0.0088 & 0.0179 & -0.0137 & 0.00384 & -0.00270
Penman (1940) & 0.0534 & 0.0462 & 0.0418 & 0.0365 & 0.0815 & 0.0749 & 0.0351 & 0.0288 & 0.0173 & 0.0085 & 0.03979 & 0.03550
Marshal (1959) & 0.0454 & 0.0324 & 0.0293 & 0.0127 & 0.1160 & 0.0751 & 0.0121 & 0.0052 & 0.0083 & -0.0057 & 0.01424 & 0.01064
Millington (1959) & 0.0738 & 0.0615 & 0.0522 & 0.0421 & 0.1401 & 0.1063 & 0.0230 & 0.0149 & 0.0098 & -0.0001 & 0.02517 & 0.02033
MQ (1960) & 0.0569 & 0.0244 & 0.0392 & -0.0014 & 0.1228 & 0.0431 & 0.0085 & -0.0058 & 0.0155 & -0.0122 & 0.00352 & -0.00001
MQ (1961) & 0.0755 & -0.0133 & 0.0697 & -0.0468 & 0.1489 & -0.0122 & 0.0189 & -0.0146 & 0.0234 & -0.0169 & 0.00997 & -0.00761
WLR-Marshall & 0.0504 & -0.0072 & 0.0525 & -0.0337 & 0.1195 & 0.0072 & 0.0145 & -0.0116 & 0.0206 & -0.0154 & 0.00650 & -0.00524
SWLR & 0.0499 & -0.0122 & 0.0545 & -0.0367 & 0.1127 & -0.0123 & 0.0156 & -0.0124 & 0.0214 & -0.0158 & 0.00715 & -0.00572
Two Region & 0.0165 & 0.0023 & 0.0115 & 0.0010 & 0.0168 & 0.0036 & 0.0034 & 0.0009 & 0.0046 & -0.0021 & 0.00419 & 0.00108

MQ, Millington and Quirk; WLR, Water-induced Linear Reduction; SWLR, Structure-dependant Water-induced Linear Reduction

@ >p(- 10) * >p(- 10) * >p(- 10) * >p(- 10) * >p(- 10) * >p(- 10) * @ Soil & Soil-gas diffusivity

Eq. (3) & & & &
& A & B & $_o$ & $Ø_{int}$ & C
Intact soils & & & & &
Ambewela, SL & 0.580 & 1 & 0 & 0 & 0
Peradeniya, SL & 1.40 & 1.5 & 0 & 0.21 & 0.32

Wakanui, NZ

& 0.235 & 1 & 0 & 0 & 0

Temuka, NZ

& 0.280 & 1 & 0 & 0 & 0

Templeton, NZ

& 0.145 & 1 & 0 & 0 & 0

Lexington, UK

& 0.465 & 1 & 0 & 0 & 0
Repacked soils & & & & &
Wakanui, NZ & 0.39 & 1 & 0 & 0 & 0
Temuka, NZ & 0.25 & 1 & 0 & 0 & 0
Templeton, NZ & 0.145 & 1 & 0 & 0 & 0
Peradeniya-1, SL & 1.50 & 2 & 0 & 0.424 & 0.4
Peradeniya-2, SL & 2.0 & 2 & 0 & 0.325 & 0.4
Nishi-Tokyo, JP & 1.40 & 2 & 0 & 0.392 & 0.4