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# Determination of the gas diffusion coefficient of a peat grassland soil

A. BOON<sup>a,b</sup>, J. S. ROBINSON<sup>a</sup>, P. D. NIGHTINGALE<sup>c</sup>, L. CARDENAS<sup>b</sup>, D. R. CHADWICK<sup>b</sup> & A. VERHOEF<sup>a</sup>

<sup>a</sup>Department of Geography and Environmental Science, University of Reading, Whiteknights, PO Box 233, Reading RG6 6DW, UK,

<sup>b</sup>Rothamsted Research North Wyke, Okehampton, Devon EX20 2SB, UK, and <sup>c</sup>Plymouth Marine Laboratory, Prospect Pl, Plymouth, Devon PL1 3DH, UK

## Summary

Peatland habitats are important carbon stocks that also have the potential to be significant sources of greenhouse gases, particularly when subject to changes such as artificial drainage and application of fertilizer. Models aiming to estimate greenhouse gas release from peatlands require an accurate estimate of the diffusion coefficient of gas transport through soil ( $D_s$ ). The availability of specific measurements for peatland soils is currently limited. This study measured  $D_s$  for a peat soil with an overlying clay horizon and compared values with those from widely available models. The  $D_s$  value of a sandy loam reference soil was measured for comparison. Using the Currie (1960) method,  $D_s$  was measured between an air-filled porosity ( $\varepsilon$ ) range of 0 and 0.5 cm<sup>3</sup> cm<sup>-3</sup>. Values of  $D_s$  for the peat cores ranged between  $3.2 \times 10^{-4}$  and  $4.4 \times 10^{-3}$  m<sup>2</sup> hour<sup>-1</sup>, for loamy clay cores between 0 and  $4.7 \times 10^{-3}$  m<sup>2</sup> hour<sup>-1</sup> and for the sandy reference soil they were between  $5.4 \times 10^{-4}$  and  $3.4 \times 10^{-3}$  m<sup>2</sup> hour<sup>-1</sup>. The agreement of measured and modelled values of relative diffusivity ( $D_s/D_0$ , with  $D_0$  the diffusion coefficient through free air) varied with soil type; however, the Campbell (1985) model provided the best replication of measured values for all soils. This research therefore suggests that the use of the Campbell model in the absence of accurately measured  $D_s$  and porosity values for a study soil would be appropriate. Future research into methods to reduce shrinkage of peat during measurement and therefore allow measurement of  $D_s$  for a greater range of  $\varepsilon$  would be beneficial.

## Introduction

Peatland environments are estimated to cover 12% of UK land area and contain 43% of UK terrestrial carbon stocks (Falloon *et al.*, 2006). Land drainage is a major threat to the continued existence of these stocks as it increases loss as carbon dioxide (CO<sub>2</sub>) and also promotes the production of nitrous oxide (N<sub>2</sub>O), a potent greenhouse gas (Gorham, 1991; Regina *et al.*, 1996). Studies of greenhouse gas emissions from peat soils under drought conditions suggest that CO<sub>2</sub> and N<sub>2</sub>O fluxes increase after drought in response both to increased aeration (potential for aerobic microorganism activity) and a greater air-filled porosity, leading to increased gaseous transport through the soil profile (Freeman *et al.*, 1993; Knorr *et al.*, 2008). Studies have shown that greenhouse gas emissions are limited by the wettest soil layer (Turcu *et al.*, 2005; Pihlatie *et al.*, 2007) because diffusive transport of a gas through the air is 10 000 times more effective than through water (Fang & Moncrieff, 1999). For greenhouse

gases, this increased residence time can lead to the bubbling (ebullition) of large quantities of methane (CH<sub>4</sub>) through the water-filled porosity and therefore substantial episodic emissions (Kellner *et al.*, 2006), or to increased consumption of N<sub>2</sub>O by denitrifying bacteria adapted to anaerobic conditions (Firestone & Davidson, 1989). In order to understand the effect of drainage and related land-use changes on greenhouse gas emissions, in-profile processes of greenhouse gas production and transport must be accurately modelled under varying hydrological conditions for peatland soils. Models developed for this purpose rely on accurate physical parameters for the soils in question. The gaseous diffusion coefficient ( $D_s$ ) is an important parameter to estimate the transport of gases through soil, because most gas movement is by diffusion through the air or water-filled phases (Fang & Moncrieff, 1999).

The relative diffusivity ( $D_s/D_0$ , with  $D_0$  the diffusion coefficient through free air) is often used instead of  $D_s$  when discussing diffusion, in order to remove the complicating factor of which gas was used to calculate  $D_s$ . However,  $D_s/D_0$  is rarely measured and is often predicted with models that were developed for mineral soils (Iiyama & Hasegawa, 2005; Li & Kelliher, 2005). Our study

Correspondence: A. Boon. E-mail: Alex.Boon@reading.ac.uk

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aimed to measure  $D_s$  and calculate  $D_s/D_0$  for a UK peatland site at a range of soil moisture contents to test the hypothesis that there is variation in  $D_s/D_0$  for different moisture contents and soil horizons. The soil of the study site consisted of a deep peat deposit overlain by a layer of alluvial clay. This study therefore presented the opportunity to measure  $D_s/D_0$  for both mineral and peat soil horizons and to compare these measured values with those calculated using models widely used for peat and mineral soils.

## Materials and methods

### Study site

The study site was a 2-ha field of wet grassland located in West Sedgemoor, Somerset ( $51^{\circ}01.26'N$ ,  $-2^{\circ}55.38'W$ ). This peatland site is managed for wetland bird conservation by the Royal Society for the Protection of Birds (RSPB) and forms part of the Somerset Levels and Moors Environmentally Sensitive Area (ESA). The peat is mainly black Altcar 1 series fen peat (Fibric Histosol), overlain by an alluvial deposit of silty clay resulting from historical flooding of the River Parrett (Findlay *et al.*, 1984). Additional information on the field site is given in Kechavarzi *et al.* (2007). For comparison, a sandy loam Crediton series soil (Dystric Cambisol) was extracted from a grassland site at Sampford Courtenay, Devon ( $50^{\circ}47.39'N$ ,  $-3^{\circ}56.56'W$ ).

### Soil collection and moisture setting

Intact soil cores were removed from a  $10 \times 2 \text{ m}^2$  area of the field using  $100 \text{ cm}^3$  (5-cm diameter) stainless steel bulk density cylinders. Eighteen samples were taken from each depth increment: 5–15, 20–30 and 30–40 cm. The 0–5-cm sample was excluded in order to exclude vegetation from the cores. Eighteen cores of the sandy loam reference soil were removed from 10 to 20-cm soil depth. All cores were stored in sealed bags in a  $5^{\circ}\text{C}$  cold room until required for the experiment. Information on the physical characteristics of the cores is given in Table 1.

The soil cores were saturated by standing in a tray of free water for 3 days prior to moisture setting using tension tables or air drying. The saturated mass of the cores was recorded for use in calculating the water-filled porosity. At the end of the experiment, the soil cores were dried in an oven at  $105^{\circ}\text{C}$  and weighed to provide information for the calculation of dry bulk density, and the moisture loss from saturation was used to calculate water-filled porosity after the methods described in Rowell (1994). The total porosity was calculated from the bulk density measurements and an assumed particle density of  $2.65 \text{ g cm}^{-3}$  for mineral cores,  $1.4 \text{ g cm}^{-3}$  for peat cores and  $1.57 \text{ g cm}^{-3}$  for cores containing the clay-peat boundary (Rowell, 1994).

The soil cores were placed on tension tables that were set up according to the method of Romano *et al.* (2002). The tension tables were  $100 \times 40 \times 7 \text{ cm}$  perspex trays with drainage channels cut into the base. A 2.5-cm depth layer of silica flour (grade HPF6) was used as the suction substrate. Suctions of 10 and

**Table 1** Average physical characteristics of cores extracted from West Sedgemoor and the reference soil

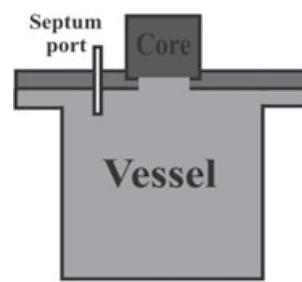
| Soil characteristic   | Soil location and depth |                  |                  |                  |
|---|-------------------------|------------------|------------------|------------------|
|   | West Sedgemoor          |                  |                  | Sandy loam       |
|   | 5–15 cm                 | 20–30 cm         | 30–40 cm         | 10–20 cm         |
| Texture   | Clay loam               | Loamy clay       | Peat             | Sandy loam       |
| Bulk density / g cm <sup>-3</sup>                               | $0.44 \pm 0.020$        | $0.40 \pm 0.040$ | $0.14 \pm 0.003$ | $1.39 \pm 0.020$ |
| Porosity ( $\phi$ ) / cm <sup>3</sup> cm <sup>-3</sup>          | $0.72 \pm 0.004$        | $0.75 \pm 0.008$ | $0.90 \pm 0.002$ | $0.48 \pm 0.009$ |
| $\varepsilon$ range attained / cm <sup>3</sup> cm <sup>-3</sup> | <0.01–0.36              | <0.01–0.38       | 0.06–0.32        | 0.13–0.66        |

120 cm were applied to the soils. Some cores were air dried for 2 and 5 days because, during preliminary trials, it was found that large suctions ( $>2 \text{ m}$ ) were required to drain the West Sedgemoor soils to an  $\varepsilon$  of  $0.2 \text{ cm}^3 \text{ cm}^{-3}$ . Moreover, 2 m was the limit of suction available on the tension tables used in this experiment. The four moisture treatments resulted in a range of  $\varepsilon$  values between 0 and  $0.40 \text{ cm}^3 \text{ cm}^{-3}$  for the West Sedgemoor soils and between 0.10 and  $0.67 \text{ cm}^3 \text{ cm}^{-3}$  for the reference soil (Table 1). Only values up to  $0.50 \text{ cm}^3 \text{ cm}^{-3}$  measured from reference soil cores were included in model comparison analysis because of the unavailability of corresponding large  $\varepsilon$  values for West Sedgemoor cores.

### $D_s$ measurement

$D_s$  was measured after the method developed by Currie (1960). Sulphur hexafluoride ( $\text{SF}_6$ ) was chosen as the tracer gas for this study because of its inertness, water insolubility, potential for measurement at small concentrations and negligible concentration in the atmosphere (Rudolph *et al.*, 1996; Nightingale *et al.*, 2000).

The chambers from the denitrification incubation system (DENIS) based at North Wyke Research, Devon (Cardenas *et al.*, 2003), were adapted for the purpose of this experiment to function



**Figure 1** Schematic of the Currie (1960) apparatus. The core is a  $100 \text{ cm}^3$  stainless steel bulk density container open at both ends. The vessel is a 2-litre capacity stainless steel container with a septum port for the introduction of a tracer gas. Once the soil core is inserted on to a shelf cut into the lid and sealed in place with silicone sealant, the only way for an introduced tracer gas to escape the vessel is through the soil core.

as the Currie apparatus (Figure 1). A hole of the same diameter as the soil core was cut into the stainless steel lids of the 2-litre capacity vessels with a narrow shelf on which the soil core could sit. A septum port was fitted into the lid through which the standard could be injected and samples removed. Silicone grease was used around the join between the soil core and the vessel lid in order to seal the cores into place and to ensure the seams were gas tight. The vessels were tested for leaks using helium prior to commencement of the experiment. The modified chambers were housed in a constant temperature room at 19°C.

Twelve soil cores (three of each soil type), subjected to the same moisture-setting procedure of 10-cm suction on a tension table, were weighed and placed on the vessel lids simultaneously. The vessels were aligned in two rows of six and the soil cores were arranged at random. At the start of the experiment, 120 ml 2% SF<sub>6</sub> in N<sub>2</sub> was injected into each vessel via the septum port to achieve an approximate target starting concentration of 1400 µl l<sup>-1</sup>. Two to three minutes later two 10-ml gas samples were taken from the vessel headspace and analysed. The average of these two samples represented the t=0 concentration for that diffusion vessel. The vessel headspaces were then sampled at intervals that were dependent upon the moisture treatment. The 10-cm suction and 150-cm suction cores were sampled once daily for 5 days. The 2-day air-dried cores were sampled twice daily for 1 day then daily for 4 days. The 5-day air-dried cores were sampled twice daily for 2 days. No more than 3% of the total volume of the vessel was removed by the end of the experimental period. Each sample was immediately manually injected into the gas chromatograph (GC): a Shimadzu GC-8A (Shimadzu, Colombia, USA) fitted with a thermal conductivity detector (TCD) and connected to a Spectra-Physics SP4290 integrator (Newport, Spectra-Physics Ltd, Harwell, UK). The GC was calibrated daily with an assumed linear relationship between ambient air (with a negligible SF<sub>6</sub> content), 0.2 and 2% SF<sub>6</sub> in N<sub>2</sub> (British Oxygen Company Gases, Guildford, UK). A 0.2% standard was also injected at the start and completion of each sampling time.

Three additional cores subjected to the same moisture treatment as the experimental cores were placed alongside the vessels. These were weighed twice daily to determine moisture loss from the experimental cores. A volume of water equal to the moisture loss calculated was added to the surface of the experimental cores to maintain initial moisture content. Where soils shrunk before the experiment, silicone sealant was inserted into the cracks and the soil re-weighed. Dry masses were taken with and without the added silicone to ensure accuracy.

The natural logs of the concentrations of SF<sub>6</sub> in the vessel were plotted against time for each moisture treatment.  $D_s$  was then calculated from the slope of the linear portion of this depletion curve after the method described by Rolston & Moldrup (2002). The  $D_0$  value for SF<sub>6</sub> was taken to be 0.093 cm<sup>2</sup> s<sup>-1</sup> (Rudolph *et al.*, 1996).

### $D_s/D_0$ modelling

For the purpose of comparison, the calculated  $D_s/D_0$  values were compared with values calculated with the three widely used models of Millington & Quirk (1961), Campbell (1985) and Moldrup *et al.* (1999). The Campbell (1985) model is given as:

$$D_s/D_0 = a(\varepsilon^b), \quad (1)$$

where  $\varepsilon$  is the air-filled porosity (cm<sup>3</sup> cm<sup>-3</sup>) and  $a$  and  $b$  are coefficients for pore tortuosity and pore size distribution, respectively. Commonly used values for  $a$  and  $b$  are 0.9 and 2.3, respectively (Campbell, 1985; Price *et al.*, 2004; Li & Kelliher, 2005). The Millington & Quirk (1961) model is:

$$D_s/D_0 = \varepsilon^{10/3}/\varphi^2, \quad (2)$$

where  $\varepsilon$  is the air-filled porosity (cm<sup>3</sup> cm<sup>-3</sup>) and  $\varphi$  is the total porosity (cm<sup>3</sup> cm<sup>-3</sup>). Finally, the Buckingham-Burdine-Campbell (BBC) model (Moldrup *et al.*, 1999) is:

$$D_s/D_0 = \varphi^2(\varepsilon/\varphi)^{(2+3/b)} \quad (3)$$

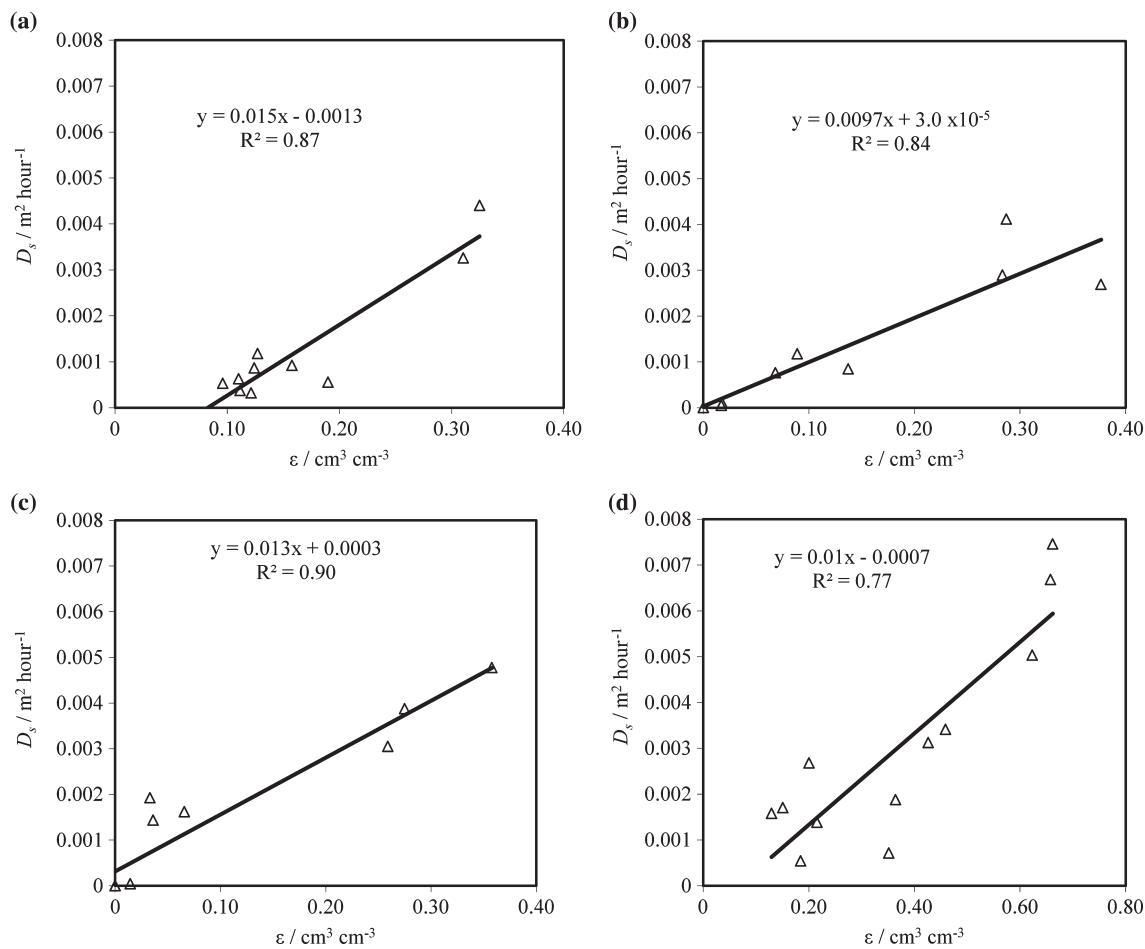
### Statistical analyses

All statistical analyses were carried out using Genstat (13th edition, 2010). In order to calculate the linear portion of the SF<sub>6</sub> depletion curve a 'line plus exponential' model was fitted to the data. In some saturated cores, a model could not be fitted because SF<sub>6</sub> in the vessel was not depleted. In these cases  $D_s$  was assumed to be 0. Genstat was also used to calculate  $D_s$  and generate the standard error for both the calculation and the model fit. Where the generated standard error from the calculation was greater than 10%, this  $D_s$  value was not used in further calculations. Lin's concordance (Lin, 1989, 2000) analyses were used to examine the agreement between measured and modelled values of  $D_s$  after techniques described by Dhanoa *et al.* (1999).

## Results and discussion

### Measured values for $D_s$ and $D_s/D_0$

Values of  $D_s$  for the peat cores (30–40 cm) ranged between  $3.2 \times 10^{-4}$  and  $4.4 \times 10^{-3}$  m<sup>2</sup> hour<sup>-1</sup>, for the peat/clay cores (20–30 cm) ranged between 0 and  $4.1 \times 10^{-3}$  m<sup>2</sup> hour<sup>-1</sup> and for the loamy clay cores (5–15 cm) ranged between 0 and  $4.7 \times 10^{-3}$  m<sup>2</sup> hour<sup>-1</sup>. The sandy reference soil had values of  $D_s$  between  $5.4 \times 10^{-4}$  and  $3.4 \times 10^{-3}$  m<sup>2</sup> hour<sup>-1</sup> for  $\varepsilon$  up to 0.5 cm<sup>3</sup> cm<sup>-3</sup>, and  $D_s$  up to  $7.4 \times 10^{-3}$  m<sup>2</sup> hour<sup>-1</sup> at  $\varepsilon$  up to 0.7 cm<sup>3</sup> cm<sup>-3</sup> (Figure 2). The  $D_s$  values were within similar ranges for all cores at  $\varepsilon$  up to 0.5 cm<sup>3</sup> cm<sup>-3</sup> and increased with increasing  $\varepsilon$ . The  $D_s/D_0$  values between 0 and 0.16 (Figure 3) were within ranges previously found in the literature (Rudolph *et al.*, 1996; Caron & Nkongolo, 2004; Iiyama & Hasegawa, 2005).



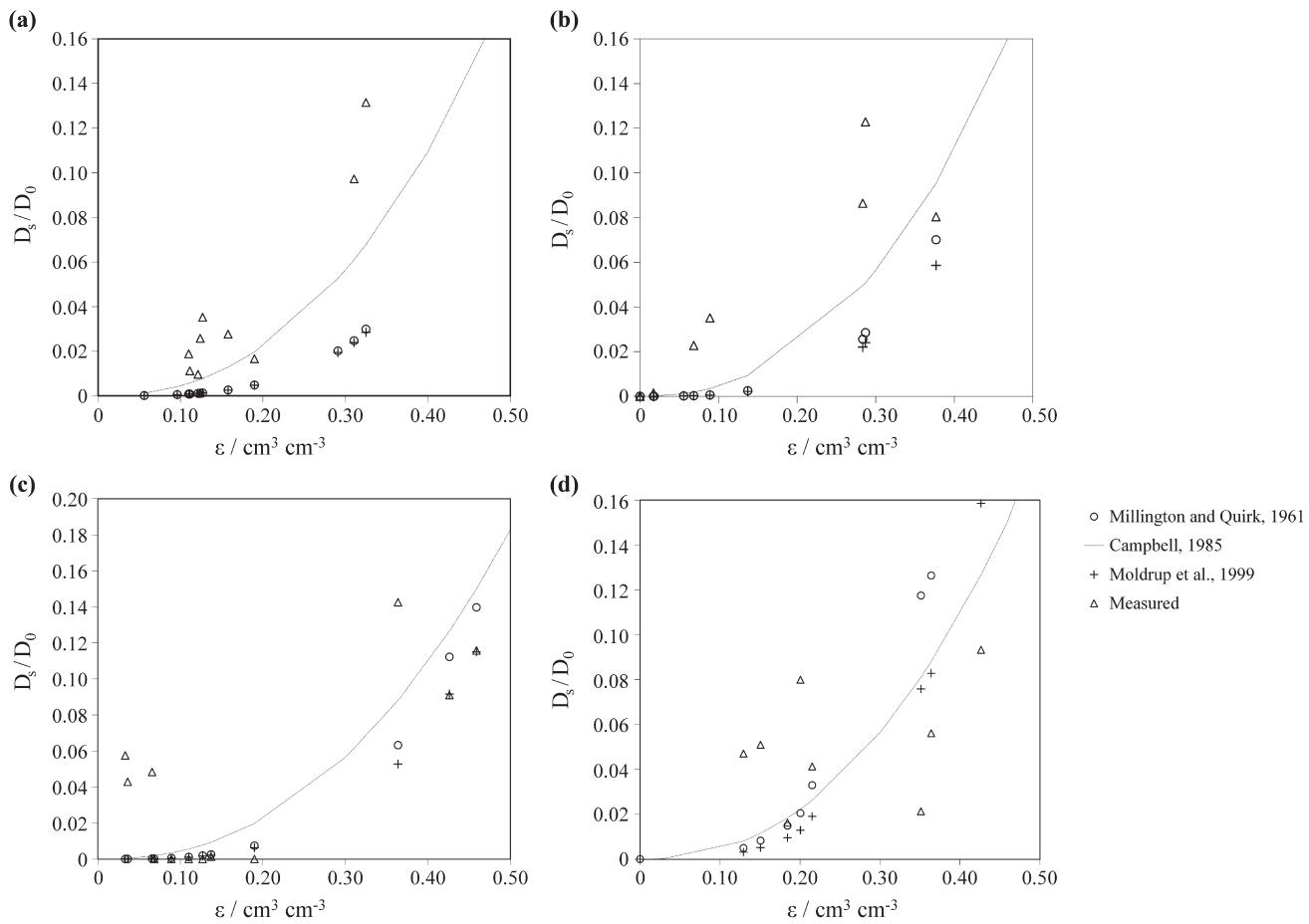
**Figure 2** Triangles represent measured  $D_s$  values ( $\text{m}^2 \text{ hour}^{-1}$ ) for (a) 30–40 cm peat, (b) 2–30 cm clay/peat, (c) 5–15 cm clay loam and (d) the sandy loam soil plotted against  $\epsilon$ . A best-fit linear regression line is also shown in the figures.

The spread of  $D_s$  values for a similar  $\epsilon$  may indicate that the Currie method will not allow an accurate detection of small  $D_s$  values (Figure 2). This is particularly an issue for the sandy soil (Figure 2d). This may be because a moisture gradient inside the soil core forms or there is shrinkage associated with drying of peat soils whilst on the diffusion apparatus and therefore the difficulty of accurately estimating  $\epsilon$  for the whole core (Rolston & Moldrup, 2002; Allaire *et al.*, 2008). Attempts were made to reduce the effects of moisture loss on  $\epsilon$  by adding water during the experiment; cores lost between 2 and 23% (typically 8%) of their starting moisture content during the course of the experiment. The greatest amount of moisture was lost from the saturated sandy soil cores. Caron & Nkongolo (2004) proposed that accurate measurements of soil moisture within a core (in their case using TDR probes) with a suitable model for  $D_s/D_0$  may be more useful than  $D_s/D_0$  measurement. Improvements to  $D_s$  measurement methodology that targets the prevention of moisture gradient formation would be beneficial. In order to prevent a moisture gradient forming, the core would have to be on the apparatus for less time and therefore a two-chamber

approach would be required with the soil core closed to the atmosphere and a system in place to ensure rapid flow of tracer gas through the core from the injection chamber to the measurement chamber (Bonroy *et al.*, 2011). Alternatively, humidified air could be passed continually over the surface of a core open to the atmosphere (Rolston & Moldrup, 2002), although this would require careful monitoring to ensure that the humidity is suitable. Complementary measurements to characterize the distribution of tracer gas inside a larger core with an established moisture gradient (Allaire *et al.*, 2008) would provide useful information on how gases move within soils that is applicable to field conditions.

#### Comparison of measured and modelled $D_s/D_0$

The agreement between measured and modelled values of  $D_s/D_0$  varied with soil type (Figure 3). At air-filled porosities close to zero, the measured  $D_s/D_0$  values for all soils were often larger than those predicted by modelling, perhaps as a result of the difficulties with drying during these experiments. For all soils the best fit was with the Campbell (1985) model (Table 2).



**Figure 3** Modelled and measured  $D_s/D_0$  values for (a) 30–40 cm peat, (b) 20–30 cm clay/peat, (c) 5–15 cm clay loam and (d) the sandy loam soil plotted against  $\varepsilon$ .

This model provided the best fit despite the reliance on standard coefficients for  $a$  and  $b$ ; however, the model is widely used in the literature (Dunfield *et al.*, 1995; Price *et al.*, 2004; Li & Kelliher, 2005). The poor fit with the Millington & Quirk (1961) and Moldrup *et al.* (1999) models may have resulted from the difficulties associated with calculating an accurate porosity for peat and clay soils. This supports the use of the Campbell (1985) model for these soils in the absence of accurate porosity values.

The use of models to provide the  $D_s/D_0$  of a soil is widespread in the literature, particularly as interest has developed in the use of Fick's Law:

$$F = -D_s (dx/dz), \quad (4)$$

where  $F$  is the gaseous flux ( $\text{mg m}^{-2} \text{ day}^{-1}$ ),  $D_s$  is the diffusion coefficient of study soil ( $\text{m}^2 \text{ day}^{-1}$ ),  $x$  is the measured or estimated concentration of target gas ( $\text{mg m}^{-3}$ ) and  $z$  is the soil depth (m) for greenhouse gas flux determination (Li & Kelliher, 2005; Pingintha *et al.*, 2010). Many such studies suggest that reliance on modelled  $D_s/D_0$  is a potential source of significant error in their gradient calculations (Jassal *et al.*, 2005; DeSutter *et al.*, 2008). These are

**Table 2** Lin's concordance coefficient<sup>a</sup> for each modelled  $D_s/D_0$  compared with the measured  $D_s/D_0$

| Soil (depth)         | Model                     |                              |                 |
|----------------------|---------------------------|------------------------------|-----------------|
|                      | Millington & Quirk (1961) | Moldrup <i>et al.</i> (1999) | Campbell (1985) |
| Loamy clay (5–15 cm) | 0.75                      | 0.70                         | 0.79            |
| Clay/peat (20–30 cm) | 0.40                      | 0.35                         | 0.62            |
| Peat (30–40 cm)      | 0.30                      | 0.29                         | 0.71            |
| Sandy loam           | 0.31                      | 0.49                         | 0.52            |

<sup>a</sup>Lin's concordance coefficient is a measure of the degree of agreement between two continuous variables that takes into account both correspondence between the two variables and divergence from the 1:1 agreement line. A value of 1 indicates perfect agreement and a value of 0 indicates an absence of concordance.

strong cases for providing, at the very least, a benchmark soil-specific  $D_s$  with which to compare modelled values before using the gradient method. The  $D_s$  values generated by our research provide such information for a UK lowland peatland environment. Although there was uncertainty as a result of drying and shrinkage,

the Currie method provides a simple and inexpensive approach to attaining measurements and informing the choice of model for such environments. In order to verify the use of  $D_s/D_0$  models at  $\varepsilon$  greater than 0.5, some of the difficulties associated with providing cores at larger values of  $\varepsilon$  would need to be addressed. The future of  $D_s$  measurement is likely to lie in two-chamber methods with automated systems in place to ensure accuracy and provide measurements more quickly, reducing the possibility of moisture gradient formation in the soil core (Bonroy *et al.*, 2011).

## Conclusion

This study reported values of  $D_s$  and  $D_s/D_0$  for the West Sedgemoor study soil within the ranges reported for other soils. The Currie method was a successful method for  $D_s$  determination; variability in the results may be explained by moisture losses during the experiment or difficulties in attaining an accurate porosity value for clay and peat. The results of this experiment suggest that the Campbell (1985) model is reliable in predicting  $D_s/D_0$  within a  $\varepsilon$  range of 0 to  $0.5\text{ cm}^3\text{ cm}^{-3}$ ; however, further research using a closed chamber, automated system for  $D_s/D_0$  measurement (Bonroy *et al.*, 2011) would be useful to determine the accuracy of models for  $\varepsilon$  outside of this range. This would be particularly useful for peat and clay soils as the shorter time required for measurement would reduce difficulties associated with moisture loss and shrinkage. Further research into the importance of soil type as a control of gas movement through the profile of peatland soils, conducted at a greater range of air-filled porosities, would be useful to further clarify the findings of the present study. Such research will provide valuable information for use in studies examining transport of greenhouse gases through peatlands and inform the development of models to estimate greenhouse gas loss in future climates.

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