Density-Corrected Models for Gas Diffusivity and Air Permeability in Unsaturated Soil

Accurate prediction of gas diffusivity ($D_{w}/D_o$) and air permeability ($k_a$) and their variations with air-filled porosity ($\epsilon$) in soil is critical for simulating subsurface migration and emission of climate gases and organic vapors. Gas diffusivity and air permeability measurements from Danish soil profile data (total of 150 undisturbed soil samples) were used to investigate soil type and density effects on the gas transport parameters and for model development. The measurements were within a given range of matric potentials (~10 to ~50 cm H$_2$O) typically representing natural field conditions in subsurface soil. The data were regrouped into four categories based on compaction (total porosity $\Phi$ < 0.4 or >0.4 m$^3$ m$^{-3}$) and soil texture (volume-based content of clay, silt, and organic matter <15 or >15%). The results suggested that soil compaction more than soil type was the major control on gas diffusivity and to some extent also on air permeability. We developed a density-corrected (D-C) $D_{w}(\epsilon)/D_o$ model as a generalized form of a previous model for $D_{w}/D_o$ at ~100 cm H$_2$O of matric potential ($D_{w,100}/D_o$). The D-C model performed well across soil types and density levels compared with existing models. Also, a power-law $k_a$ model with exponent 1.5 (derived from analogy with a previous gas diffusion model) used in combination with the D-C approach for $k_a(\epsilon)$ (reference point) seemed promising for $k_a(\epsilon)$ predictions, with good accuracy and minimum parameter requirements. Finally, the new D-C model concept for gas diffusivity was extended to bimodal (aggregated) media and performed well against data for uncompacted and compacted volcanic ash soil.

Abbreviations: D-C, density-corrected; GMP, generalized macroporosity; MQ, Millington and Quirk; OM, organic matter; WLR, water-induced linear reduction.

The migration and emission of greenhouse gases such as CO$_2$, CH$_4$, and N$_2$O as well as other environmental impact gases (e.g., organic vapors at polluted sites) from terrestrial environments to the atmosphere causes increasing concern for climate, human, and ecosystem health. The enhanced atmospheric concentrations of the major greenhouse gases may potentially lead to significant regional and global climate shifts, with inherent regional and global environmental problems (Intergovernmental Panel on Climate Change, 2007). Terrestrial production of greenhouse gases occurs largely in natural systems (e.g., forest and peat lands), but rapidly expanding anthropogenic sources like agricultural fields, landfills, and constructed wetlands have also contributed significantly to increasing atmospheric concentrations (Bartlett and Harriss, 1993). For example, atmospheric CH$_4$ is a powerful greenhouse gas that contributes approximately 25% of the anticipated global warming (Mosier, 1998), and nearly one-third of global CH$_4$ emission stems from terrestrial soils (Smith et al., 2003). Landfills are a particularly large source, responsible for between 7 and 20% of global anthropogenic sources of CH$_4$ emissions (Poulsen et al., 2001), with the unsaturated final-cover soil layer being the main control of CH$_4$ migration, consumption, and emissions from landfills (Hamamoto et al., 2009b).

The uptake or emission of gases in soil systems is mainly controlled by the physical, chemical, and biological processes in the vadose zone and is strongly linked to soil physical properties such as soil texture and soil total porosity. Therefore, accurate prediction of gas movement in soils related to varying soil physical properties under natural field conditions is a prerequisite for realistic simulations of land type and management impacts on climate gas consumption or emission. Subsurface migration of gases through the soil air phase and subsequent emission across the soil–atmosphere interface occur predominantly by diffusion (Penman, 1940), and near-surface pressure fluctuations further accelerate the movement by advection (Poulsen et al., 2003).
The diffusive and advective movement of gases in soils is controlled by the soil gas diffusivity (the ratio of gas diffusion coefficients in soil and free air, $D_p/D_o$) and the soil air permeability ($k_a$), respectively. Measurements of these two gas transport parameters, however, require special equipment and are complicated to perform in situ with sufficient control of the initial and boundary conditions (Rolston et al., 1991; Rolston and Moldrup, 2002; Werner et al., 2004). Models, therefore, are frequently used to predict $D_p/D_o$ and $k_a$ as a function of easily measurable parameters such as air-filled porosity ($\varepsilon$) and total porosity ($\Phi$). Despite significant progress in developing and testing predictive models for $D_p/D_o$ and, to a lesser extent, $k_a$ during the last decade, the links between the gas transport parameters and basic soil physical properties such as texture and compaction level (as described by bulk density or total porosity) are still not well understood.

Compaction essentially decreases the pore space between soil particles, thereby decreasing the total porosity. Deleterious impacts to soil porosity may derive from long-term pedogenetic processes or from short-term anthropogenic activities (management). Dense soils are often encountered in both natural and engineered soil systems. They are also likely to occur in deep vadose zone profiles due to the weight of the overlying soil mass. In shallow urban soil profiles, compacted soils occur beneath building foundations due to the load of the superstructure and soil damage from construction activities. Traffic by heavy machinery in agricultural fields and forests creates soil compaction in the topsoil as well as in subsoil layers to $\sim$1-m depth. This consequently affects crop productivity and soil functions related to environmental quality (Schjønning et al., 2009). Modern landfill sites are often capped with extremely compacted soil liners to reduce water permeability and trace gas emissions (Poulsen et al., 2001). Although the effects of soil density on soil aeration are recognized in general, only a few studies have examined the direct effect of soil density on the gas transport parameters (Buckingham, 1904; Stepniewski, 1981; Currie, 1984; Xu et al., 1992; Shimamura, 1992; Fujikawa and Miyazaki, 2005). Different studies have come to contradictory conclusions with regard to the effect of compaction on gas transport parameters. For example, the studies by Stepniewski (1981) and Xu et al. (1992) on gas diffusion in differently textured soils found little effect of bulk density on the relationship between $D_p/D_o$ and $\varepsilon$. On the contrary, Fujikawa and Miyazaki (2005) and Hamamoto et al. (2009a) observed increased $D_p/D_o$ with increasing bulk density at a given $\varepsilon$. Furthermore, Currie (1984) concluded that no single curvilinear relationship, even for one given soil, can describe the change in $D_p/D_o$ with $\varepsilon$ when changes occur in bulk density.

In this study, we compared soils that had reached a specific compactness through very different processes in time and space. We have chosen the term density for expressing the compactness. The ambition of this study expressed in general terms was to develop a simple and useful model for predicting $D_p/D_o$ and $k_a$ across soils with a range in density irrespective of the cause of that density. More specifically, the study investigated the effects of soil density and soil type on $D_p/D_o$ and $k_a$ based on data from vadose zone profiles across Denmark, including soils from urban, agricultural, and forest sites as well as a final landfill cover soil. Density-corrected model approaches were developed for both $D_p/D_o$ and $k_a$, with the models being applicable across different soil types and total porosities within the range of soil water matric potential mostly occurring under natural field conditions (between $-10$ and $-500$ cm H$_2$O).

**Materials and Methods**

**Soils and Data**

In this study, we used both unpublished and literature data on undisturbed soils from eight different locations with a wide geographical distribution and land uses spread across Denmark, representing a wide range of soil texture, horizons, and total porosities (we refer to each soil according to the sampling location). Measurements on a total of 150 undisturbed soil samples from the eight locations were considered. Metal rings with similar dimensions (0.034-m length, 0.061-m i.d., 100-cm$^3$ sample volume) were used for sampling at all locations. During sampling, the sharpened edge of the metal ring was carefully driven into the soil by means of a hammer and retrieved with the soil core, ensuring minimum disturbance. The end surfaces were trimmed and the edges were kneaded with a knife to prevent preferential air flow through the annular gap between the core and the sample. The samples were end-capped and stored at 2°C before measurements.

**Urban Soils**

The sampling site at Skellingsted was located adjacent to an unlined municipal landfill operated as a dump of municipal solid waste and industrial waste from 1971 to 1990. The landfill was covered with 80 cm of sand and 20 cm of topsoil at the final closure (Christoffersen and Kjeldsen, 2001). The lateral migration of trace landfill gases, however, caused a fatal explosion in a house near the landfill in 1991 (Poulsen et al., 2001). Samples were collected at 70-cm depth for measurements (data for both gas diffusivity and air permeability were partly presented by Poulsen et al. [2001]). Hjørring soils were sampled from a deep vadose zone profile from 4- to 5- and 6- to 7-m depths at a former municipal gas work site (gas diffusivity data were partly presented by Moldrup et al. [2000b]; air permeability data have not previously been published). The profile featured differently textured horizons including a less organic clay layer at the top (410-cm depth) and organic-matter-rich loamy soils toward the bottom of the profile.

**Agricultural and Forest Soils**

Three lysimeter soils (Rønhave, Foulum, and Jyndevad) and two agricultural field soils (Mammen and Gjorslev) from Kawamoto et al. (2006a,b) were also included. The lysimeter soils with different soil textures were excavated from the three locations into large
soil bins located at Aarhus University, the Faculty of Agricultural Sciences at Research Centre Foulum in 1993. The soils were air dried, crumbled to aggregates <20 mm, and then packed in the bins incrementally in 10-cm layers to the same dry bulk density as occurred in the field. For details on management and treatment practices of the soils before sampling, and on the packing procedure into the soil bins, see Kawamoto et al. (2006b) and Lamandé et al. (2007), respectively. The two agricultural field soils (Mammen and Gjorslev) have been in agricultural use for centuries.

Two medium-organic sandy layers collected in a natural mixed hardwood forest at Poulstrup, 10- to 15-cm depth (data from Kruse et al., 1996) and 15- to 20-cm depth (data from Moldrup et al., 1996) were considered. These soils showed high CH$_4$ consumption rates probably controlled by $D_p/D_o$ and its variation with ε (Kruse et al., 1996). The sampling depths, soil texture, and characteristics of each layer for the selected soils are given in Table 1.

We also used a sieved and repacked, microaggregated volcanic ash soil (Andisol) from Tsukuba, Japan (data from Osozawa, 1998) for testing a possible extension of the new gas diffusivity model to soils with bimodal pore-size distribution. We considered the soils at two compaction levels: uncompacted and uniaxially compacted at 200 kPa (Osozawa, 1998).

Table 1. The sampling locations, depths and soil physical characteristics.

<table>
<thead>
<tr>
<th>Location</th>
<th>Depth</th>
<th>Texture†</th>
<th>Clay</th>
<th>Silt</th>
<th>Sand</th>
<th>Organic matter</th>
<th>Total porosity‡</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mammen</td>
<td>0.05–0.25</td>
<td>sandy clay loam</td>
<td>17.4</td>
<td>18.6</td>
<td>64.1</td>
<td>2.6</td>
<td>0.378 (0.015)</td>
<td>Kawamoto et al. (2006a,b)</td>
</tr>
<tr>
<td>Mammen</td>
<td>0.33–0.53</td>
<td>sandy clay loam</td>
<td>17.2</td>
<td>14.1</td>
<td>72.4</td>
<td>0.3</td>
<td>0.369 (0.008)</td>
<td></td>
</tr>
<tr>
<td>Mammen</td>
<td>0.80–1.00</td>
<td>sandy clay loam</td>
<td>19.3</td>
<td>19.1</td>
<td>61.6</td>
<td>0.2</td>
<td>0.338 (0.013)</td>
<td></td>
</tr>
<tr>
<td>Gjorslev</td>
<td>2.05–2.25</td>
<td>sandy clay loam</td>
<td>24.1</td>
<td>17.3</td>
<td>58.6</td>
<td>0.2</td>
<td>0.321 (0.006)</td>
<td></td>
</tr>
<tr>
<td>Gjorslev</td>
<td>3.50–3.70</td>
<td>sandy clay loam</td>
<td>22.8</td>
<td>17.0</td>
<td>60.1</td>
<td>0.3</td>
<td>0.291 (0.008)</td>
<td></td>
</tr>
<tr>
<td>Gjorslev</td>
<td>4.65–4.85</td>
<td>sandy clay loam</td>
<td>19.7</td>
<td>15.6</td>
<td>64.7</td>
<td>0.4</td>
<td>0.306 (0.037)</td>
<td></td>
</tr>
<tr>
<td>Rønhave</td>
<td>0.00–0.30</td>
<td>sandy clay loam</td>
<td>17.9</td>
<td>13.1</td>
<td>69.0</td>
<td>2.3</td>
<td>0.450 (0.025)</td>
<td></td>
</tr>
<tr>
<td>Rønhave</td>
<td>0.30–0.70</td>
<td>sandy clay loam</td>
<td>21.7</td>
<td>13.5</td>
<td>64.8</td>
<td>0.5</td>
<td>0.436 (0.012)</td>
<td></td>
</tr>
<tr>
<td>Foulum</td>
<td>0.00–0.30</td>
<td>sandy loam</td>
<td>11.8</td>
<td>11.3</td>
<td>77.0</td>
<td>2.3</td>
<td>0.539 (0.020)</td>
<td></td>
</tr>
<tr>
<td>Foulum</td>
<td>0.30–0.60</td>
<td>sandy loam</td>
<td>15.0</td>
<td>10.2</td>
<td>74.9</td>
<td>0.5</td>
<td>0.389 (0.017)</td>
<td></td>
</tr>
<tr>
<td>Jyndevad</td>
<td>0.00–0.30</td>
<td>loamy sand</td>
<td>5.9</td>
<td>2.1</td>
<td>91.9</td>
<td>1.9</td>
<td>0.469 (0.019)</td>
<td></td>
</tr>
<tr>
<td>Jyndevad</td>
<td>0.30–0.70</td>
<td>loamy sand</td>
<td>6.0</td>
<td>0.5</td>
<td>93.5</td>
<td>0.7</td>
<td>0.458 (0.010)</td>
<td></td>
</tr>
<tr>
<td>Jyndevad</td>
<td>0.70–1.40</td>
<td>loamy sand</td>
<td>5.2</td>
<td>0.7</td>
<td>94.1</td>
<td>0.2</td>
<td>0.438 (0.013)</td>
<td></td>
</tr>
<tr>
<td>Poulstrup</td>
<td>0.10–0.15</td>
<td>sand</td>
<td>3.7</td>
<td>3.1</td>
<td>93.2</td>
<td>3.7</td>
<td>0.519 (0.021)</td>
<td>Kruse et al. (1996)</td>
</tr>
<tr>
<td>Poulstrup</td>
<td>0.15–0.20</td>
<td>sand</td>
<td>4.3</td>
<td>2.6</td>
<td>93.1</td>
<td>4.1</td>
<td>0.539 (0.031)</td>
<td>Moldrup et al. (1996)</td>
</tr>
</tbody>
</table>

† Soil textures are classified based on the International Soil Science Society (ISSS) standard (Verhoyen and Ameryckx, 1984).
‡ Average values are given. Values in parentheses are standard deviations.
Measurement Methods
For all samples in this study, the desired soil water matric potentials were obtained following the method proposed by Klute (1986). The 100-cm³ undisturbed soil cores were first saturated inside sand boxes and subsequently drained to the intended matric potential (\(\psi\)) using either hanging water columns (for \(\psi > -100\) cm H₂O) or suction and pressure plate systems (for \(\psi < -100\) cm H₂O). The matric potentials were in the range of −10 to −500 cm H₂O (at least four different potentials for each sample).

For \(D_p/D_o\) measurements, the experimental setup initially suggested by Taylor (1949) and further developed by Schjønning (1985) was used. The gas diffusivity chamber was first made O₂–free by flushing with 100% N₂. Atmospheric air was then allowed to enter into the chamber through the soil sample by exposing the top surface of the soil core, and O₂ was measured by an electrode mounted on the chamber wall. The O₂ diffusion coefficient in soil (\(D_p\)) was calculated following Rolston and Moldrup (2002). The time taken for each measurement differed depending on the matric potential applied and was considered small enough to neglect the O₂ depletion due to microbial consumption (Schjønning et al., 1999).

For \(k_a\) measurements, a small air pressure gradient was established across the sample by applying a constant pressure difference at the ends, and the resulting air flow (which is proportional to the air permeability) was measured by means of a flow meter. The experimental setup and procedure were outlined by Moldrup et al. (1998) and Ball and Schjønning (2002).

Statistical Analyses
The performance of the proposed models for gas diffusivity and air permeability were evaluated and compared with existing predictive models by means of two statistical indices. To evaluate the model overall fit to the measured data, the RMSE was used:

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

where \(d_i\) is the difference between the observed and predicted values \((D_p/D_o\) or \(k_a\)) and \(n\) is the number of measurements in the data set.

The bias was used to assess the general overprediction (positive bias) or underprediction (negative bias) of the model compared with the observed data:

\[
\text{bias} = \frac{1}{n} \sum_{i=1}^{n} (d_i)
\]

When the statistical comparison is based on log-transformed values, Eq. [1] and [2] become \(\text{RMSE}_{\log}\) and \(\text{bias}_{\log}\), respectively, in which \(d_i\) now corresponds to the difference between the logarithms of the observed and predicted values.

Gas Diffusivity Models from Literature
Buckingham (1904), in one of the earliest works on soil gas physics, empirically established the following relationship between soil \(D_p/D_o\) and \(\varepsilon\) using four different soils in varying states of compactness and moisture content:

\[
\frac{D_p}{D_o} = \epsilon^2
\]

From this, he concluded that the diffusion of gas in soils is not greatly affected by soil type. Similar single-parameter predictive models were developed later (e.g., Penman, 1940; Marshall, 1959; Millington, 1959) until the next generation of models started to incorporate some soil type and density effects through the soil total porosity (\(\Phi\)). Among commonly accepted soil-type-dependant models are the Millington and Quirk (MQ) (1960) model:

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

and the Millington and Quirk (1961) model:

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

with the latter (Eq. [5]) being almost universally accepted and recommended by the USEPA and Danish Environmental Protection Agency for risk assessment at polluted soil sites (USEPA, 1996; Danish Environmental Protection Agency, 2002). It is also frequently used for calculating climate gas emissions at different scales (from the field to a continent) and to infer gas fluxes from chamber measurements (e.g., Liu and Si, 2008; Perera et al., 2002).

The presence of water can significantly affect gas diffusion in soils. In wet soils, water held at bottlenecks (narrow pore throats between particles) can potentially create large tortuosity (prolonged pathways) for gas transport. The WLR–Marshall model (Moldrup et al., 2000a) takes this water blockage effect into account by assuming a water-induced linear reduction (WLR) of gas diffusivity:

\[
\frac{D_p}{D_o} = \epsilon^{1.5} \left( \frac{\varepsilon}{\Phi} \right)
\]

Rearranging Eq. [6] into the form used in this study yields

\[
\frac{D_p}{D_o} = \Phi^{1.5} \left( \frac{\varepsilon}{\Phi} \right)^{2.5}
\]

thereby making the WLR model mathematically analogous to the widely used model for relative electrical conductivity by Mualem and Friedman (1991).

Based on gas diffusivity measurements on 126 soils representing a broad range of soil texture, horizons, and management practices,
Moldrup et al. (2000b) observed a surprisingly high correlation ($r^2 = 0.97$) between the measured gas diffusivities at $-100$ cm H$_2$O of soil water potential ($D_{p,100}/D_o$) and the corresponding air-filled porosities at $-100$ cm H$_2$O, $\varepsilon_{100}$ (also called macroporosity), yielding

$$\frac{D_{p,100}}{D_o} = 2\varepsilon_{100}^3 + 0.04\varepsilon_{100}^3 [8]$$

Equation [8] (hereafter referred to as the macroporosity-dependent [MPD] relation) was successfully used in subsequent models (Moldrup et al., 2000b, 2004) as the reference-point gas diffusivity for $D_{p,100}/D_o$ models. It should be noted that the choice of $-100$ cm H$_2$O as the reference state is not an arbitrary value because the natural water content at field capacity is suggested as occurring at or close to $-100$ cm H$_2$O matric potential irrespective of soil texture (e.g., Schjønning and Rasmussen, 2000; Al Majou et al., 2008).

**Air Permeability Models from the Literature**

The effects of soil type, texture, and compactness and especially the effect of soil structure are more pronounced for air permeability than for gas diffusivity (Buckingham, 1904). Some widely used predictive models use a reference-point value, typically $k_{a,100}$ (i.e., air permeability at $-100$ cm H$_2$O of soil water potential, $\mu$m$^2$), together with a power-law function:

$$k_a = k_{a,100} \left( \frac{\varepsilon}{\varepsilon_{100}} \right)^\eta [9]$$

where the exponent $\eta$ represents the combined effects of tortuosity and connectivity of the air-filled pores (Kawamoto et al., 2006a). Moldrup et al. (1998) suggested $\eta = 2$ and Kawamoto et al. (2006a) proposed $\eta$ as

$$\eta = X - 1 [10]$$

where $X$ is an exponent related to the relative air saturation term ($\varepsilon/\Phi$) in an analogous power-law gas diffusivity model. For example, $X$ equals 2.5 in the WLR—Marshall model (Eq. [7]). For reference-potential air permeability, Kawamoto et al. (2006a) used the MPD relation for gas diffusivity (Eq. [8]) together with the classical nonjointed capillary tube model (Millington and Quirk, 1964; Ball, 1981) and with given assumptions on the equivalent diameter of conducting air-filled pores, yielding

$$k_{a,100} = 700(2\varepsilon_{100}^3 + 0.04\varepsilon_{100}^3) [11]$$

**Soil and Data Regrouping by Density and Texture Classes**

As discussed above, the selected soils were widely different with respect to texture and horizons and had a wide range of total porosities reflecting different states of compactness. To categorize the soils according to texture, we express the amount of fines in terms of a volume-based fraction of clay, silt, and organic matter (OM), denoted as CSOvol, and given by

$$CSOvol = \rho_b \left( \frac{\text{clay} + \text{silt} + \text{OM}}{2.7} \right) [12]$$

where CSOvol is the volume-based fraction of clay, silt, and organic matter ($\text{cm}^3\text{cm}^{-3}$); $\rho_b$ is the soil dry bulk density ($\text{g cm}^{-3}$); clay, silt, and OM are the gravimetric contents of clay, silt, and organic matter, respectively ($\text{g g}^{-1}$), and their denominators, 2.7 and 1, are the assumed particle densities for clay or silt and OM, respectively ($\text{g cm}^{-3}$) (Sumner, 2000). The value of CSOvol can range between 0 (for pure sand) and 1 (for organic soils or peat), with values in between for typical soils. A similar equation was introduced by Moldrup et al. (2007) taking into account only clay and organic matter, whereas Eq. [12] also considers silt particles as part of the finer particles potentially influencing the soil structure, pore networks, and gas transport.

Figure 1a illustrates the values of CSOvol plotted against the corresponding total porosities for the selected soils from each location.
To examine the effect of soil type and density on gas transport, we classified the soils having CSOvol > 0.15 as soils with high fines and those having CSOvol < 0.15 as soils with low fines. The two lines of demarcation, $\Phi = 0.40$ and CSOvol = 0.15, were selected arbitrarily and separated the soils into four groups in such a way that each soil belonged in one of the four groups with limited crossovers. The four new groups are denoted as A, B, C, and D as shown in Fig. 1b. The soils with low fines and those with high fines are shown with red circles and blue triangles, respectively, while the open and closed symbols represent less dense and dense soils, respectively. For the ease of distinction, the high-fines (clay) soil from Hjørring (at 410-cm depth) is denoted as D* and is symbolized by a yellow triangle (Fig. 1b).

**Results, Model Development, and Tests**

### Effects of Density and Soil Type

To examine the effect of soil type and density on gas transport parameters, two representative gas diffusivity curves were selected from each group A, B, C, and D and presented together in Fig. 2a. The clay soil D* is also shown for comparison. No distinct effect of soil type could be observed, supporting the observations of Buckingham (1904) and Moldrup et al. (2001). Conversely, the two soils representing Group A are markedly separated from the soils representing Group B (placed on opposite sides of the Buckingham reference model ($\varepsilon^2$) shown by a dashed line in Fig. 2a), suggesting a clear effect of density. Similar observations were made when comparing Groups C and D soils (Fig. 2a).

The observed enhanced gas diffusivity in the dense soils compared with the less dense ones at a given air-filled porosity agrees with the results of some previous studies, for example Fujikawa and Miyazaki (2005), who attributed the effect to “preferential loss” of ineffective pore space in the gas flow regime following compaction. Taken at the same air-filled porosity, dense soils with relatively higher volumetric solids content hold less water (and hence exhibit less water bridging between particles and water-induced tortuosity), resulting in increased gas diffusivity.

A further comparison of gas transport parameter behavior at a given matric potential ($\psi$) will often be of more practical interest because the soil layers throughout a vadose zone profile under natural field conditions will typically stabilize at a given matric potential (allowing a sufficiently long time after infiltration and drainage). Figure 2b shows the gas diffusivities of the same soils as in Fig. 2a but now plotted against matric potential (expressed by $pF = \log[-\psi]$, where $\psi$ is in cm H$_2$O, following Schofield [1935]). At a given pF, the dense soils exhibited smaller gas diffusivities than the less dense soils, thus showing an opposite trend in gas diffusivity behavior compared with Fig. 2a. At a given matric potential, the reduced gas diffusivity in the dense soils can be ascribed to the decrease in air-filled porosity as a result of the increase in water retention (Currie, 1984). Consequently, the effect of soil type or texture (giving different water retention characteristics) becomes more pronounced. The corresponding trends for air permeability (not shown) are similar but less stringent due to the pronounced effects of the soil structure on the air permeability (Moldrup et al., 2001).

In summary, the effects of soil type (texture) seemed minor and the effects of soil density seemingly dominated the effects of soil type on relative gas diffusivity and to some extent also on air permeability when the two gas transport parameters were plotted as functions of air-filled porosity. Conversely, the effects of soil type dominated when the gas transport parameters were plotted as functions of pF due to the large differences in soil water retention characteristics between finer and coarser textured soils. Thus, to discuss the effects of soil density on gas transport parameters, it should be clearly distinguished whether the comparison is made at the same air-filled porosity ($\varepsilon$) or at the same soil water matric potential (for example, given as pF) because the effects will appear different: at the same $\varepsilon$, the $D_p/D_o$ will typically be greater for a dense soil than for a less dense soil, whereas the $D_p/D_o$ at a given matric potential will typically be smaller for a dense soil than for a less dense soil.

Fig. 2. Soil-gas diffusivities ($D_p/D_o$) as a function of (a) air-filled porosity ($\varepsilon$) and (b) pF (the negative logarithm of matric potential) for soil sample pairs selected to represent the four groups A, B, C, and D, and additionally the soil D*. The Buckingham (1904) model, Eq. [3], is also shown (black dashed line) as a reference in (a). Data from Poulsen et al. (2001), Moldrup et al. (2000b), and Kawamoto et al. (2006a,b).
Based on the above results, with more pronounced effects of density than of soil type at the same air-filled porosity, we focused on developing density-corrected models for both \( \frac{D_p}{D_o} \) and \( k_a \) as a function of air-filled and total porosities. The models can easily be transformed into functions also of the soil water matric potential (or pF) using an appropriate soil water retention model, for example the widely used van Genuchten (1980) or Campbell (1974) models.

### Density-Corrected Gas Diffusivity Model

We first confirmed the relatively good accuracy of the MPD relation (Eq. [8]) using gas diffusivity measurements for the soils in Groups A and B at pF 2.0 (−100 cm H₂O matric potential) (Fig. 3a). We further observed that the same model, when tested at pF = 2.7, still yielded promising results (Fig. 3b). Similar observations were made at pF = 1.7 as well (not shown). Based on this, we generalized the original MPD equation to yield a so-called generalized macroporosity-based (GMP) model:

\[
\frac{D_p}{D_o} = 2\varepsilon^3 + 0.04\varepsilon 
\]  

[13]

The GMP model, however, shows a tendency to underestimate data for the dense soils and overestimate for the less dense soils. This tendency was observed at all the considered pF values and was highly evident at pF = 2.7 (Fig. 3b). A modification to the GMP model, therefore, was necessary to take the effect of density into account. We observed that simply plotting the measured gas diffusivities against the normalized air-filled porosity (\( \varepsilon/\Phi \)) largely reduced the density-induced fluctuations in the measured data (Fig. 3c and 3d) and a new, density-corrected model analogous to the GMP model could yield more accurate predictions. The density-corrected (D-C) GMP model can be written as

\[
\frac{D_p}{D_o} = 0.1 \left[ \frac{\varepsilon}{\Phi} \right]^3 + 0.04 \left( \frac{\varepsilon}{\Phi} \right) 
\]  

[14]

The D-C GMP model retains the analogy to the GMP model except for the additional empirical scaling factor in front of the equation (set equal to 0.1) resulting from model fitting to the measured data for all 150 soil samples.

### Test of Gas Diffusivity Models

Figure 4 shows scatterplot comparisons (in a log–log coordinate system) of predicted and measured \( \frac{D_p}{D_o} \) for the GMP model (Eq. [13]) and the D-C GMP model (Eq. [14]) together with two existing predictive models: the Buckingham (1904) model (Eq. [3]) and the MQ (1961) model (Eq. [5]). The model performances were evaluated using the RMSE (Eq. [1]) and bias (Eq. [2]) and the analogous log-transformed indices, RMSE log and bias log. Out of the four models shown, the widely accepted MQ (1961) showed a weak performance in terms of overall model fit (RMSE log = 0.77) and a tendency to slightly overpredict under relatively dry conditions and grossly underpredict under moist conditions, leading to a significant overall underprediction (bias log = −0.306). A similar behavior of the MQ (1961) model was also observed in some recent studies (Kawamoto et al., 2006b; Resurreccion et al., 2007), with some additional studies also implying a poor performance (Jin and Jury, 1996; Moldrup et al., 1996, 2003). Despite its simplicity, the Buckingham (1904) model performed remarkably well and outperformed the MQ (1961) model for most soils. A similar good performance of the classical Buckingham model was also recently observed by Resurreccion et al. (2008).
The statistical indices further suggest that the D-C GMP model performed best among the four models. The results of detailed statistical analysis, for each individual group A, B, C, and D (including D*) and overall, are given in Table 2 for six predictive models including also the MQ (1960) model (Eq. [4]) and WLR–Marshall model (Eq. [6]). The new D-C GMP model, with the lowest values for both statistical indices for the individual soil groups (except for biaslog in Groups A and B) as well as overall, seems to capture gas diffusivity behavior across soil texture and compaction levels accurately. Moreover, the new model is simple, with no additional input parameter requirements.

Applying independently measured data (i.e., data not utilized in developing the model) is an essential part of predictive model development. First, we considered measured $D_p/D_o$ data for two highly porous (and organic) topsoils sampled at 0- to 5- and 5- to 10-cm depths ($\Phi_{avg} = 0.72$) from Poulsstrup for model validation. When plotted together with the already used data for the two lower, less organic and less porous soil layers, Poulsstrup (10–15- and 15–20-cm depths, $\Phi_{avg} = 0.53$) and the very dense Skellingsted soil (70-cm depth, $\Phi_{avg} = 0.36$), three distinctly separated curves with respect to total porosity were obtained, implying a clear effect of soil total porosity and density (Fig. 5a). Predictions by the GMP model (dashed line) corresponds to a total porosity between 0.36 (dense) and 0.53 (less dense) and therefore probably represents only gas diffusivity of medium-dense soils. The separation in the measured data dramatically narrowed when plotted against the

Fig. 4. Scatterplot comparison of predicted and measured gas diffusivities ($D_p/D_o$) for four predictive models: (a) the generalized macroporosity (GMP) model, Eq. [13], (b) the density-corrected (D-C) GMP model, Eq. [14], (c) the Buckingham (1904) model, Eq. [3], and (d) Millington and Quirk (MQ) (1961) model, Eq. [5]. Calculated RMSE (Eq. [1]) and bias (Eq. [2]) and RMSElog and biaslog (calculated using log-transformed $D_p/D_o$ data) values are also given. Data from Poulsen et al. (2001), Moldrup et al. (1996, 2000b), Kawamoto et al. (2006a,b), Kruse et al. (1996), and this study.

Table 2. Test of predictive soil gas diffusivity models against measured data. For each predictive model, the two log-transformed statistical parameters, RMSElog and biaslog, are also given for individual categories A, B, C, and D (including D*) and overall.

<table>
<thead>
<tr>
<th>Model†</th>
<th>Equation‡</th>
<th>RMSElog</th>
<th>Biaslog</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Buckingham (1904)</td>
<td>$D_p/D_o = \varepsilon^2$</td>
<td>0.61</td>
<td>0.66</td>
</tr>
<tr>
<td>MQ (1960)</td>
<td>$D_p/D_o = \varepsilon^2/\Phi^{2/3}$</td>
<td>0.76</td>
<td>0.81</td>
</tr>
<tr>
<td>MQ (1961)</td>
<td>$D_p/D_o = \varepsilon^{10/3}/\Phi^2$</td>
<td>0.69</td>
<td>0.49</td>
</tr>
<tr>
<td>WLR-Marshall</td>
<td>$D_p/D_o = \varepsilon^{15/4}/\Phi$</td>
<td>0.61</td>
<td>0.55</td>
</tr>
<tr>
<td>GMP</td>
<td>$D_p/D_o = 2\varepsilon^3 + 0.04\varepsilon$</td>
<td>0.58</td>
<td>0.60</td>
</tr>
<tr>
<td>D-C GMP</td>
<td>$D_p/D_o = 0.1[2(\varepsilon/\Phi)]^3 + 0.04(\varepsilon/\Phi)$</td>
<td>0.53</td>
<td>0.40</td>
</tr>
</tbody>
</table>

† MQ, Millington and Quirk; WLR, water-induced linear reduction; GMP, generalized macroporosity-dependant model; D-C GMP, density-corrected generalized macroporosity-dependant model.
‡ $D_p/D_o$, soil gas diffusivity; $\varepsilon$, air-filled porosity; $\Phi$, total porosity.
normalized air-filled porosity (Fig. 5b), and the D-C GMP model produced accurate predictions for the five soil layers across a very wide range of total porosities.

Second, we used $D_p/D_o$ data for three differently textured intact soils from Freijer (1994): a sandy soil, Kootwijk C ($\Phi = 0.389$), and two silty loam soils, BeC ($\Phi = 0.452$), and EsC ($\Phi = 0.452$), all soils with 1.4 to 1.6% OM. Although the D-C GMP model was originally developed for undisturbed soils, we further tested its applicability for repacked soils using gas diffusivity measurements for the Hjørring sandy soil (9.3% clay, 4.8% silt, 86% sand, and 0.3% OM), sieved and repacked at three different bulk densities corresponding to total porosities of 0.42, 0.36, and 0.34 cm$^3$ cm$^{-3}$ (data from this study). Again, the GMP model failed to recognize the effect of density for both undisturbed and repacked soils (Fig. 6a), while the D-C GMP model yielded promising results (Fig. 6b) irrespective of the state of soil texture, structure (intact or repacked), or density.

**Density-Corrected Air Permeability Model**

Following the same approach as for gas diffusivity, we first tested the performance of the macroporosity-based air permeability relation (Eq. [11]) for the soils in Groups A and B under pF 2.0 conditions. We note that at pF 2.0, the $k_a$ values for the soils in Groups C and D were mostly low and highly scattered. The model predictions are in good agreement with the measured data for Groups A and B (Fig. 7a), but the data again showed a tendency to differentiate between dense and less dense soils, as also observed for gas diffusivity (Fig. 3a). Following the same D-C approach as adopted for gas diffusivity, the density-induced differences could be reduced by plotting the observed air permeabilities against the normalized air-filled porosity (Fig. 7b). Modifying Eq. [11] as a function of relative air-filled porosity and assuming the same empirical scaling factor (0.1) as found in the case of gas diffusivity (Eq. [9]) yielded a D-C reference point air permeability model:

$$k_{a,100} = 70 \left( \frac{\varepsilon_{100}}{\Phi} \right)^{0.3} + 0.04 \left( \frac{\varepsilon_{100}}{\Phi} \right)^{0.53}$$  \hspace{1cm} [15]

To obtain a model for $k_a$ valid not only at pF 2.0, we further assumed the validity of the general power-law model for $k_a(\varepsilon)$, Eq. [9]. Correct estimation of the power-law exponent $\eta$ (Eq. [9]) is essential for accurate predictions of air permeability as a function of air-filled porosity (Kawamoto et al., 2006a). Using the observed reference-point air permeability ($k_{a,100}$) values, we tested the performance of two power-law exponents: $\eta = 2$ as suggested by Moldrup et al. (1998), and $\eta = 1.5$, which can be derived from the analogous gas diffusivity exponent $X = 2.5$ (Eq. [7]) in

![Fig. 5. Measured gas diffusivities ($D_p/D_o$) for two high-porosity and high-organic-matter (OM) soils from Poulstrup at depths of 0 to 5 and 5 to 10 cm (average total porosity $\Phi_{avg} = 0.72$) together with soils used in density-corrected model development: Poulstrup (10–15- and 15–20-cm depths, $\Phi_{avg} = 0.53$) and Skellingsted (70-cm depth, $\Phi_{avg} = 0.36$). Measured $D_p/D_o$ values are shown (a) as a function of air-filled porosity ($\varepsilon$) together with generalized macroporosity (GMP) model (Eq. [13]) predictions (dashed line), and (b) as a function of relative air-filled porosity ($\varepsilon/\Phi$) together with density-corrected (D-C) GMP model (Eq. [14]) predictions (solid line). Data from Kruse et al. (1996), Moldrup et al. (1996), and Poulsen et al. (2001).](image)

![Fig. 6. Tests of new gas diffusivity ($D_p/D_o$) models against two independent data sets: (i) Hjørring soils, repacked at three bulk densities with corresponding total porosities of $\Phi = 0.42, 0.36,$ and $0.34$ and (ii) three soils from Freijer (1994): Kootwijk C ($\Phi = 0.389$), BeC ($\Phi = 0.452$), and EsC ($\Phi = 0.459$). The observed $D_p/D_o$ data are shown (a) as a function of air-filled porosity ($\varepsilon$) together with generalized macroporosity (GMP) model (Eq. [13]) predictions (dashed line) and (b) as a function of relative air-filled porosity ($\varepsilon/\Phi$) together with density-corrected (D-C) GMP model (Eq. [14]) predictions (solid line).](image)
The results revealed that the power-law model with the newly derived exponent ($\eta = 1.5$), however, $k_a$ predictions were significantly improved. Figure 8 further revealed that the power-law $k_a$ model (Eq. [9]) with $\eta = 1.5$ yielded more accurate results when used with measured $k_{a,100}$ values (Fig. 8a) than the predicted $k_{a,100}$ values using the D-C MP model (Fig. 8b). We therefore recommend using measured $k_{a,100}$ whenever possible, in Eq. [9]. In the absence of measured $k_{a,100}$ data, however, the D-C MP model can still yield reasonably accurate estimates of $k_{a,100}$.

Finally, we note that advective air flow in soils may preferentially occur through continuous macropores, for example in the presence of continuous structural cracks or wormholes, which cannot generally be explained by the above predictive models. The measurement scale is of great importance in describing such preferential air flow conditions in soils [Iversen et al., 2001] and often cannot be detected at the 100-cm$^3$ sample scale. Thus, macropore and upscaling effects on air permeability are not included in the D-C model and need to be further investigated.

**Extension of New Gas Diffusivity Model to Bimodal Soils**

The new models discussed so far are developed for, and hence limited to, relatively structureless (unimodal) soils; however, the occurrence of variably compacted and highly aggregated (bimodal) soils with distinct interaggregate (Region 1) and intraaggregate (Region 2) pore spaces is not uncommon, especially for cultivated high-clay soils. We therefore extended our analysis to two-region soils by testing the new gas diffusivity models (GMP and D-C GMP) against measurements for a sieved and repacked, microaggregated Andisol at two compaction levels (uncompacted and compacted at 200 kPa) (data from Osozawa, 1998).

The observed gas diffusivities as a function of air-filled porosity (Fig. 9) clearly exhibited two-region behavior at both compaction levels, as also implied by the bimodal behavior of the soil-water retention curves (not shown). The predictions of the D-C GMP model (Eq. [14]) based on total porosity failed to capture the dual-porosity characteristics of the observed gas diffusivities and hence could not yield accurate results (shown as a dashed-dotted line in Fig. 9). Therefore, in the case of highly aggregated soils with clear bimodal behavior (e.g., judged from the soil water retention curve),
we suggest that only the D-C models to be used for the predictions in Region 1, using the interaggregate porosity in place of the total porosity. The interaggregate porosity is here considered to be the air-filled porosity at pF 3.0 near which the transition from inter- to intraggregate pore space occurs on draining (Resurreccion et al., 2010). For the predictions in Region 2, we suggest a Buckingham (1904) type model with no additional input parameters. Thus, the GMP and D-C GMP models extended for the predictions of two-region soils can be written as follows:

For Region 1:

GMP model: \[ \frac{D_p}{D_o} = 2\varepsilon^3 + 0.04\varepsilon \quad (pF \leq 3.0) \] \[ \text{[16]} \]

D-C GMP model:

\[ \frac{D_p}{D_o} = 0.1 \left( \frac{\varepsilon}{\Phi_1} \right)^3 + 0.04 \left( \frac{\varepsilon}{\Phi_1} \right) \quad (pF \leq 3.0) \] \[ \text{[17]} \]

For Region 2:

\[ \frac{D_p}{D_o} = \frac{D_p}{D_o \mid pF=3.0} + (\varepsilon - \Phi_1)^2 \quad (pF > 3.0) \] \[ \text{[18]} \]

where \( \Phi_1 \) is the interaggregate porosity assumed equal to the air-filled porosity measured at pF 3.0 and \( D_p/D_o \mid pF=3.0 \) is the predicted gas diffusivity at pF = 3.0 using either the GMP model (Eq. [16]) or the D-C GMP model (Eq. [17]). With this bimodal approach, the performance of both models significantly improved and the D-C GMP model in particular showed promising results at both compaction levels (Fig. 9a and 9b). A similar two-region extension of the new D-C air permeability model was not examined due to the lack of appropriate data and is therefore a prospect for future research.

**Evaluation of the Density-Corrected Generalized Macroporosity Model Scaling Factor**

The 150 soils used to develop the D-C models had total porosities ranging between 0.27 and 0.58 cm\(^3\) cm\(^{-3}\) and the independent tests of the D-C GMP gas diffusivity model showed slight underprediction for the highly porous Poulstrup top layer (0–10 cm, \( \Phi = 0.72 \) cm\(^3\) cm\(^{-3}\); Fig. 5) as well as for uncompacted aggregated soils (\( \Phi = 0.76 \) cm\(^3\) cm\(^{-3}\); Fig. 9). Furthermore, for the Poulstrup soils, the very high OM content (average OM = 17%) while the maximum OM content in the soils used to develop the DC model was 4.1%) also probably influenced the observed deviation between the model and the data. This implies that the D-C gas diffusivity model scaling factor (taken as 0.1 in Eq. [14] and [17]) may in reality be a function of the total porosity or the OM content.

Therefore, we examined whether a variable D-C GMP model scaling factor could yield improved D-C GMP model predictions. We assumed the scaling factor to be a linear function of \( \Phi \) or OM content, or both, thereby including additional density and soil type effects in the overall model performance. We note that \( \Phi \) and OM content are often not independent parameters because highly organic soils typically will have lesser densities and greater total porosities. Making the scaling factor a function of \( \Phi \) alone, OM content alone, or both \( \Phi \) and OM content did not yield overall improvements in the D-C GMP model performance for the 150 soils. We therefore conclude that using a constant scaling factor of 0.1 in Eq. [14] and [17] seems generally applicable across a wide range of soil types and densities for fairly accurate predictions of \( D_p(\varepsilon) \) from only air-filled and total porosities.

For a given soil or soil profile, however, like the differently compacted aggregated Andisol or the Poulstrup soil profile representing a natural depth gradient in OM, an improved site-specific \( D_p(\varepsilon) \) model can probably be obtained by making the scaling factor a function of compaction level (\( \Phi \)), OM content, or both. Because this could allow more accurate predictions of, e.g., climate gas emissions or uptake from vadose zone profiles containing layers of very different densities, textures, and OM contents, it should be further investigated when additional detailed \( D_p(\varepsilon) \) and \( k(\varepsilon) \) data for soil profiles and soil transects representing natural gradients in density, OM content, and clay and silt content become available.
Conclusions

This study investigated the effect of soil type and density on gas diffusivity and air permeability under typically occurring subsurface moisture conditions (matric potentials between −10 and −500 cm H$_2$O). A significant effect of soil density on both gas transport parameters was observed, together with a less marked effect of soil type. Two D-C models were introduced for gas diffusivity and air permeability, respectively, which performed well across different soil types and density levels compared with existing predictive models.

The D-C approach for air permeability resulted in only a minor improvement in model performance at pH 2.0 (reference point); however, the new D-C-based $k_g$–$ε$ relation at pH 2.0 used in combination with a simple power-law model (developed in analogy with a recent gas diffusivity model) produced improved and reasonably accurate $k_g(ε)$ predictions.

The new D-C gas diffusivity model was derived and successfully validated for undisturbed soils but adequately described data also for sieved and repacked soil at different compaction levels. The D-C gas diffusivity model was further extended for highly aggregated (two-region or bimodal) media with promising results for an uncompacted and compacted Andisol.

The new predictive D-C models represent a step toward a unified model concept for gas diffusivity and air permeability in undisturbed, variably saturated soils with differing densities and are useful in predicting the subsurface migration and fate of climate gases. In perspective, the new model needs to be tested against data for a wider range of soil water matric potentials and soil types, including peat, forest, and reclaimed wetland soils with typically greater OM contents and thus different soil pore structures and architecture (de Jonge et al., 2009).

Acknowledgments

This study was made possible by the project Gas Diffusivity in Intact Unsaturated Soil (GADIUS) and the large framework project Soil Infrastructure, Interfaces, and Translocation Processes in Inner Space (Soil-it-is), both from the Danish Research Council for Technology and Production Sciences. We gratefully acknowledge the assistance of the Innovative Research Organization of Saitama University, Japan.

References


