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Gas diffusivity in *chinampas* soils in Mexico City

Difusión de gases en suelos de chinampas en la Ciudad de México
Difusão de gases em solos chinampas da Cidade do México

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ABSTRACT

In this laboratory experiment we measured soil gas diffusion coefficients (D) on undisturbed cores of anthropogenic *chinampas* soils and tested the validity of some classical gas diffusivity models for predicting the ratio of D to the gas diffusion coefficient in free air (D_0) as a function of the soil air-filled porosity (ε). The A1 horizon (0-7 cm) of *chinampas* soils had the highest gas diffusivity and a linear relationship between D/D_0 and ε, and thus, the Penman model gave an adequate prediction for this sub-horizon. The Millington-Quirk model was similar to the D/D_0 at all values of ε for the A2 sub-horizon (7-18 cm) and at $\varepsilon < 0.5$ cm^3 cm^{-3} for the A3 (18-30 cm) and A4 (30-50 cm) sub-horizons. Gas diffusivities in *chinampas* soils were lower than in mineral soils, as predicted by D/D_0 (ε) models, likely due to the high content of soil organic carbon. The predictive models could be used for the evaluation of greenhouse gases emission from *chinampas* soil.

RESUMEN

En este experimento de laboratorio, medimos los coeficientes de difusión de gas (D) en núcleos inalterados de suelos antropogénicos de chinampas y probamos la validez de algunos modelos clásicos de difusión de gases para predecir la relación de D con el coeficiente de difusión de gas en aire libre (D_0) como una función de la porosidad del suelo llena de aire (ε). El horizonte A1 (0-7cm) de los suelos de chinampas alcanzó la difusividad de gas más alta y una relación lineal entre D/D_0 y ε, y así, el modelo de Penman mostró una predicción adecuada para este subhorizonte. El modelo de Millington-Quick tuvo un D/D_0 similar en todo el rango de ε para el subhorizonte A2 (7-18 cm) y a la $\varepsilon < 0,5$ cm^3 cm^{-3} para los subhorizontes A3 (18-30 cm) y A4 (30-50 cm). La difusividad de gas en suelos de chinampas fue menor que en suelos minerales, como predijeron los modelos D/D_0 (ε), debido probablemente al contenido elevado de carbono orgánico del suelo. Los modelos predictivos podrían ser utilizados para la valoración de la emisión de gases de efecto de invernadero de los suelos de chinampas.

RESUMO

Neste ensaio laboratorial, mediram-se os coeficientes de difusão de gás do solo (D) em "cores" não perturbados de solos antropogénicos de chinampas e testou-se a validade de alguns modelos clássicos de difusividade de gás para prever a relação de D com o coeficiente de difusão do gás ao ar livre (D_0) como função da porosidade de arejamento do solo (ε). O horizonte A1 (0-7 cm) dos solos chinampas apresentaram a difusão de gás mais elevada e uma relação linear entre D/D_0 e ε e como tal, o modelo de Penman forneceu uma previsão adequada para este sub-horizonte. O modelo de Millington-Quirk foi semelhante ao de D/D_0 para todos os valores de ε para o sub-horizonte A2 (7-18 cm) e para $\varepsilon < 0.5$ cm^3 cm^{-3} para os sub-horizontes A3 (18-30 cm) e A4 (30-50 cm). As difusividades de gás em solos chinampas foram inferiores em solos minerais, como previsto pelos modelos D/D_0 (ε) provavelmente devido ao alto teor de carbono orgânico do solo. Os modelos preditivos poderão vir a ser usados para a avaliação da emissão de gases de efeito estufa do solo chinampas.

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1. Introduction

Diffusive transport is the major mechanism responsible for the movement of gases in soils and for gaseous exchange between soils and atmosphere (Kruse et al. 1996). Prediction of flow and transport processes in soil is crucial in many areas of soil and environmental sciences. The gas diffusion coefficient (*D*) is a widely used parameter for the evaluation of greenhouse gas emission from soil to atmosphere (Hashimoto and Komatsu 2006; Pingintha et al. 2010). Numerous models have been developed for the relative diffusion coefficient, defined as the ratio of the diffusion coefficient in the soil to that in free air (D_0), as a function of soil type and the air-filled porosity (ε). One of the classical $D(\varepsilon)$ models is the linear model by Penman (1940); other simple, nonlinear $D(\varepsilon)$ models take into account both ε and total porosity (Φ) (Buckingham 1904; Marshall 1959; Millington and Quirk 1961; Lai et al. 1976; Moldrup et al. 2000) (**Table 1**). The predictive models introduce a minor soil type effect through Φ that is dependent on, for example, soil texture and management (Moldrup et al. 2004).

KEY WORDS
Anthropogenic soils, air-filled porosity, predictive model, organic carbon content

PALABRAS CLAVE
Suelos antropogénicos, porosidad llena de aire, modelo predictivo, contenido de carbono orgánico

PALAVRAS-CHAVE
Solos antropogénicos, porosidade de arejamento do solo, modelos de previsão, teor de carbono orgânico

Table 1. Relative gas diffusion coefficient models

Equations	Reference
$D/D_0 = \varepsilon^2$	Buckingham (1904)
$D/D_0 = 0.66\ \varepsilon$	Penman (1940)
$D/D_0 = \varepsilon^{1.5}$	Marshall (1959)
$D/D_0 = \varepsilon^{10/3} / \Phi^2$	Millington and Quirk (1961)
$D/D_0 = \varepsilon^{5/3}$	Lai et al. (1976)
$D/D_0 = \varepsilon^{3/2} (\varepsilon / \Phi)$	Moldrup et al. (2000)

The existing data show that the soil gas diffusivity depends on soil type, and existing studies cover many of the natural groups of mineral soils (Moldrup et al. 2004; Kristensen et al. 2010) and organic soils (Iiyama and Hasehawa 2005). However, for some endemic soil groups, such as anthropogenic agricultural soils, the data regarding soil gas diffusivity are still insufficient. One such understudied soil type is the anthropogenic *chinampas* soil in Mexico City. Pre-Hispanic cultures in Mexico developed a specific technology for cultivating wetlands around the lakes in the Valley of Mexico by constructing elevated fields ("*chinampas*") for agricultural production (Ezcurra 1990; Ramos-Bello et al. 2011). Presently, the gas diffusion coefficient for *chinampas* soils has not been documented, which makes it difficult to predict the amount and the rate of gas transport and emission from this soil type.

Gas diffusion coefficients can be measured without removing soil from its natural location in field (Rolston et al. 1991) or in laboratory conditions which allow a varying soil water and evaluating *D* after establishing a steady state gas concentration (Hashimoto and Komatsu 2006). In this laboratory experiment, we determined the relative gas diffusion coefficient (D/D_0) in undisturbed samples of anthropogenic *chinampas* soils. The results were compared to existing $D(\varepsilon)$ models.

2. Material and Methods

2.1. Site description

Soil samples were collected at the grassland site located in the Xochimilco Ecological Park in Mexico City. The *chinampas* soil was classified as a Terric Anthrosol (IUSS Working Group WRB 2006) with a texture that varied from silty loam to clay (Ramos-Bello et al. 2011; Ikkonen et al. 2012). The morphology of the soil profile was relatively uniform (Ikkonen et al. 2012). Minor differences in colour, root density, texture and compaction allowed for division of the 50 cm thick topsoil into several layers, denoted A1, A2, A3 and A4, where A indicates a superficial humus-enriched horizon and the numbers indicate sub-horizons, distinguished by the layered morphology of the horizon. All the layers were soft and friable. The structure was weak subangular blocky. The highest root density was found in the A1 sub-horizon and decreased sharply with depth (Ikkonen et al. 2012). A high organic matter content throughout the topsoil and irregular vertical distribution of organic carbon (C) and bulk density has been reported for the area (**Table 2**). High salinity and sodicity have been described from *chinampas* soils (Ramos-Bello et al. 2011).

Table 2. The organic carbon content, bulk density and total porosity in *chinampas* soils of the Xochimilco study area (Ikkonen et al. 2012)

Top soil sub-horizon	Depth (cm)	C (g kg^{-1})	Bulk density (g cm^{-3})	Porosity (%)
A1	0-7	148.2	0.29	86.7
A2	7-18	66.3	0.63	71.5
A3	18-30	27.3	0.78	63.1
A4	30-50	68.3	0.72	64.3

2.2. Soil gas diffusivity measurements

Soil cores (D = 8 cm, length = 5 cm) were excavated from soil sub-horizons of a soil profile at depths of 0-7, 7-18, 18-30, 30-50 cm with cylindrical chambers (25 soil cores from each soil sub-horizon), according to soil sub-horizons. The chambers with the soil cores were brought into the laboratory with high soil moisture and stored at room temperature for 2-6 weeks to redistribute the soil water content. Some chambers were covered with a polyethylene sheet in order to keep the high soil water content in the soil cores. The gaseous diffusion coefficients of undisturbed soil cores were measured using the method described by Richter (1987) using CH_4 as the diffusing gas. This laboratory method is based on establishing a high initial gas concentration within a single diffusion chamber for a soil core. A digital pressure meter was used to monitor the pressure inside the gas chambers and care was taken to minimize any extra pressure buildup inside the chambers. The decrease of the gas concentration was followed over time by the regular withdrawal of gas samples from the chamber's headspace through a hole sealed with silicon septa (Corning System, USA) with a gas-tight 100 µL syringe (Hamilton Company). The decrease in the amount of gas in the chamber was expressed as the product of the decrease in the concentration with time and the volume of soil core and chamber. The gas samples were analyzed using a gas chromatograph (HP Agilent, 6890 GC System, GMI, USA), with the temperature of the column of 35 °C and temperature of the detector of 300 °C, using N_2 as carrier gas.

In the course of a preliminary three day experiment we detected no methane consumption in *chinampas* soils (unpublished results), and so the methane consumption in the soil cores was considered negligible during the measurement periods (minutes to a few hours depending on water content of the soil cores). The weighing of the diffusion chambers with the soil cores before and after measurements showed that there was negligible change in the soil water content during the measurements period for each core. At the end of each experiment, the soil cores were placed in an oven to determine their volumetric water content and air-filled porosity. To determine the soil moisture content the soil samples of known volume were weighed before and after drying at 105 °C for 24 h. The air-filled porosity of soil cores was calculated using the values for the total porosity (**Table 2**) and the soil moisture content.

Where appropriate, the D/D_0 data under different ε values were fitted with a non-linear function by means of a Statgraphics program (StatPoint Technologies, Inc.).

3. Results and discussion

The relative diffusion coefficient (D/D_0) increased with increasing air porosity for all soil sub-horizons (**Figure 1**). The A1 sub-horizon (0-7 cm) demonstrated a linear relationship between D/D_0 and air-filled porosity (ε), whereas for the A2-A4 sub-horizons the relationship was non-linear. The relative gas diffusivities for A2-A4 sub-horizons did not vary significantly within the air porosity range from 0 to 0.25 $m^3\ m^{-3}$, but with the increase of air-filled pore space the D/D_0 increased significantly and the highest measured relative gas diffusion coefficient values were determined at the highest ε. Moldrup et al. (2001) showed that pore size has little effect on gaseous diffusion, which is instead controlled by pore tortuosity and connectivity. At low air-filled porosity transport occurs only in pores with low tortuosity (Kristensen et al. 2010), whereas at high ε values some small and tortuous pores are drained and contribute non-linearly to gas diffusivity (Moldrup et al. 2001). When the soil is wet, the water causes a change in the pore shape and configuration of air-filled pores, which leads to increased tortuosity and lower pore connectivity for gas transport (Moldrup et al. 2000).

The A1 sub-horizon exhibited higher relative gas diffusivities compared with the A2-A4 sub-horizons at the same air porosities. This could

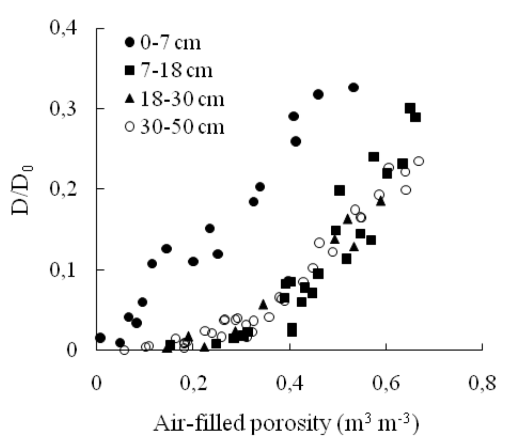

Figure 1. Measured gas diffusivities (D/D_0) in the soil cores selected from the A1 (0-7 cm), A2 (7-18 cm), A3 (18-30 cm), and A4 (30-50 cm) sub-horizons of *chinampas* soils.

be explained by the differences in soil properties between these horizons since soil type, texture, structure and management have been shown to control gas transport in natural undisturbed soils (Moldrup et al. 2004). The A1 sub-horizon had the highest organic carbon content and total soil porosity and the lowest bulk density across all investigated horizons (**Table 2**). Hamamoto et al. (2009) showed that higher gas diffusion coefficients were observed in soils with larger particle sizes and pore diameters due to rapid gas diffusion through the less tortuous large-pore networks. The higher D/D_0 values of the A1 sub-horizon may therefore be associated with lower pore tortuosity values. Furthermore, as was shown by Lange et al. (2009), the higher D/D_0 values of the A1 sub-horizon could be associated with macropores such as cracks. These authors noted that while D/D_0 variability within a soil profile could not be explained solely by the variability in bulk density and total soil porosity, the soil macroporosity and layering greatly influenced variability of gas movement.

Figure 1 shows that while there were no major discrepancies between the relative gas diffusion coefficients of the A2-A4 sub-horizons, the D/D_0 values of the A4 sub-horizon when compared with A2 and A3 sub-horizons tended to be higher at ε from 0.2 to 0.3 cm^3 cm^{-3} and lower at $\varepsilon > 0.6$ cm^3 cm^{-3}.

All measured relative gas diffusion coefficients were optimized and presented as a function of air-filled porosity. Comparisons of the gas diffusivity models with measured data are shown in **Figure 2**. The Penman model gave a similar and adequate prediction for the soil of the A1 sub-

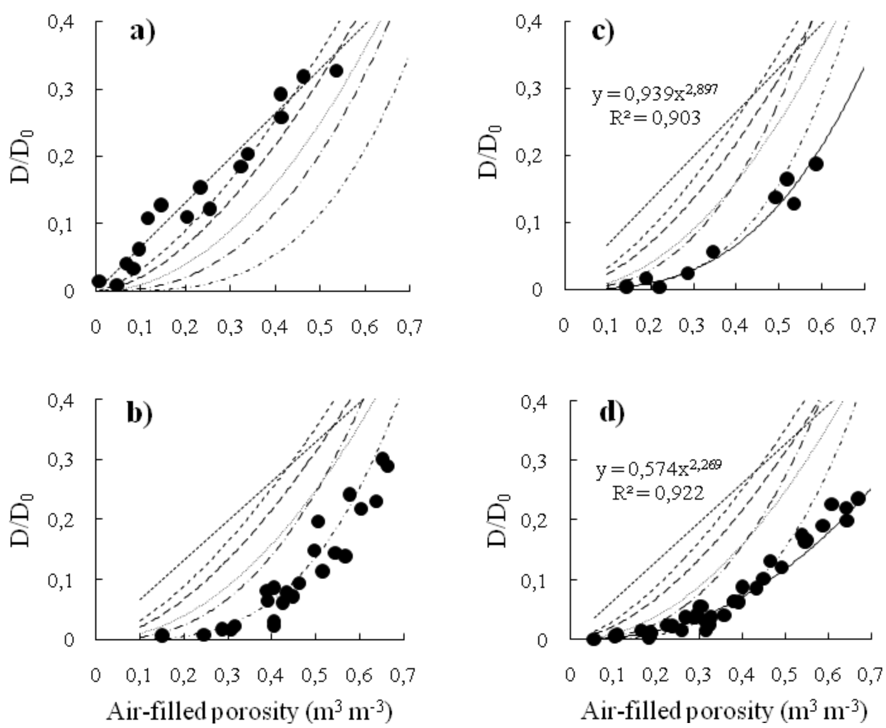

Figure 2. Comparison of predicted (Buckingham (1904); Penman (1940); Marshall (1959); Millington and Quirk (1961); Lai et al. (1976); Moldrup et al. (2000); non-linear function) and measured (black dots) gas diffusivities in the soil cores from the A1 (**a**), A2 (**b**), A3 (**c**) and A4 (**d**) sub-horizons.

horizon, while the Marshall model was similar to the measured data at ε lower than 0.5 $cm^3\ cm^{-3}$ and the Lai model provided an approximate upper limit for most measuring points (**Figure 2a**). The other models underestimated the diffusivities of the A1 sub-horizon. For the A2 sub-horizon the Millington-Quirk model provided the best overall fit over the entire range of ε while the other models largely overestimated measured D/D_0 (**Figure 2b**). For the A3 and A4 horizons the Millington-Quirk model gave fairly accurate estimates of gas diffusivities at low ε ($\varepsilon < 0.5$ $cm^3\ cm^{-3}$), but at higher ε this model overestimated the measured D/D_0 values (**Figure 2c, d**). The gas diffusion coefficient is better described by $D/D_0 = 0.939\varepsilon^{2.897}$ and $D/D_0 = 0.574\varepsilon^{2.269}$ for the A3 and A4 horizons respectively.

For A2-A4 sub-horizons the classical predicted models generally predicted a higher gas diffusivity than the measured data (**Figure 2b-d**), probably because the predicted models were based on D/D_0 measurements in mineral soils, while *chinampas* soils, as was shown by Ramos-Bello et al. (2011) and Ikkonen et al. (2012), have a high organic carbon content resembling that of organic soils. Gas diffusion has been shown to be lower in organic soils than mineral soils (Ikkonen and Tolstoguzov 1996; Iiyama and Hasegawa 2005; Lange et al. 2009). Organic compounds exhibit a high affinity for water and the chances of forming inter-particle water films are higher in soils with a higher organic matter content (Pokhrel et al. 2011). Soil gas diffusivity in organic soils has been suggested to decrease with the increase of soil organic carbon content (Iiyama and Hasegawa 2005).

4. Conclusions

In the *chinampas* soils the Penman and Millington-Quirk models offered the best prediction of gas diffusivity in the A1 and A2 sub-horizons, respectively. For the A3 and A4 sub-horizons, the Millington-Quirk model gave a similar prediction at $\varepsilon < 0.5$ $cm^3\ cm^{-3}$. At $\varepsilon > 0.5$ $cm^3\ cm^{-3}$ the D/D_0 values were best described by $D/D_0 = 0.939\varepsilon^{2.897}$ for the A3 sub-horizon, and $D/D_0 = 0.574\varepsilon^{2.269}$ for the A4 sub-horizons. The chosen predictive models could be used for evaluation of emission of greenhouse gases from *chinampas* soils to atmosphere.

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