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Comparison of Models for Predicting Pore Space Indices and their Relationships with CO₂ and N₂O Fluxes in a Corn-Soybean Field

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ABSTRACT

Several models predict soil pore space indices (the relative gas diffusion coefficient, D_s/D_o and the pore tortuosity, τ), but information is lacking on which models predicted indices better relate to soil processes. We compared pore space indices predictive models based on air-filled porosity (f_a) alone vs models using air-filled porosity and total pore space (Φ) ($f_a + \Phi$). We also assessed the relationships between these indices and CO_2 and N_2O . The study was conducted from 2011 to 2014 on a silt loam soil at Lincoln University. Soil samples were collected at 0-10 and 10-20 cm depth and oven dried at 105°C for 72 h. After drying, f_a and Φ were calculated, and later used in models for predicting D_s/D_o and τ . CO_2 and N_2O were measured with a Shimadzu Gas Chromatograph (GC) and a Photoacoustic Gas Analyzer (PSA). Results showed that D_s/D_o predicted using f_a alone (Marshall and Buckingham) was higher as compared to values predicted with models based on $f_a + \Phi$ (Sallam et al, Millington, and Jin and Jury) ($p < 0.001$). However, values of τ predicted with models based on f_a alone were lowest ($p < 0.001$). CO_2 and N_2O measured with GC better related with D_s/D_o and τ .

Keywords: Soil pore structure, diffusivity models, gas diffusion coefficient, pore tortuosity factor, greenhouse gases emissions

INTRODUCTION

Most climate scientists agree that the prime cause of the current global warming trend is the expansion of the greenhouse effect. It originates mainly from anthropogenic activities including land use and land use change in agricultural and forest systems, industrial development and urban expansion, among other sources (Lambin et al., 2003). It results into more emissions of greenhouse gases (GHGs) such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), troposphere ozone (O_3) and chlorofluorocarbons (CFCs) (Fletcher et al., 2012; IPCC, 2013). In soil, these GHGs are mainly emitted through soil pore under microbiological processes and their flux variations are regulated by processes which control microbial activities (Nkongolo et al., 2010a).

Porosity is an index of the relative pore space in a soil (Hillel, 1998; Negassa et al., 2015). The gas diffusion and the tortuosity properties of pore space are collectively called as soil pore space indices (Nkongolo et al., 2010a). The soil gas diffusion coefficient (D_s/D_o) and its dependency on air-filled porosity (f_a) govern most gas diffusion processes in soil (Ungureanu and Statescu, 2010), whereas the pore tortuosity factor (τ) is a quantity which characterizes the convoluted nature of the porous pathways followed by diffusing species (Hudson and Aharonson, 2008).

Gas diffusion in porous media is a fundamental topic and there are numerous predictive models that describe soil diffusivity processes for undisturbed soils in the vadose zone (Zheng et al., 2012). However, information is still lacking on which models' predicted indices relate better to soil processes. For instance, some models are based only air-filled porosity (f_a) and are linear in nature, some are a combination of air-filled porosity and total pore space ($f_a + \Phi$), and non-linear, some uses soil water curve, etc. Nkongolo et al (2010b) have predicted the relative gas diffusion coefficient (D_s/D_o) either as a function of air-filled porosity (f_a) alone:

$$D_s/D_o = f_a^{1.5} \text{ (Marshall, 1957)} \quad [1]$$

$$D_s/D_o = f_a^2 \text{ (Buckingham, 1904)} \quad [2]$$

or as a quotient of air-filled porosity (f_a) over total porosity (Φ):

$$D_s/D_o = f_a^{3.1}/\Phi^2 \text{ (Sallam et al., 1984)} \quad [3]$$

$$D_s/D_o = f_a^{3.33}/\Phi^2 \text{ (Millington, 1959)} \quad [4]$$

$$D_s/D_o = f_a^2/\Phi^{2/3} \text{ (Jin and Jury, 1996)} \quad [5]$$

In addition, Nkongolo et al (2010b) also predicted the pore tortuosity factor (τ) as either a function of air-filled porosity (f_a) alone:

$$\tau = 1/f_a^{0.5} \text{ (Marshall, 1957)} \quad [6]$$

$$\tau = 1/f_a \text{ (Buckingham, 1904)} \quad [7]$$

or as a quotient of total porosity (Φ) over air-filled porosity (f_a):

$$\tau = \Phi^2/f_a^{2.1} \text{ (Sallam et al., 1984)} \quad [8]$$

$$\tau = \Phi^2/f_a^{2.33} \text{ (Millington, 1959)} \quad [9]$$

$$\tau = \Phi^{2/3}/f_a \text{ (Jin and Jury, 1996)} \quad [10]$$

Besides soil temperature and moisture (Davidson and Trumbore, 2002), indices of N availability (Kim and Dale, 2008), only a few authors have focused on D_s/D_o and τ as potential controlling factors for GHGs emissions. Hence, the objectives of this study were (i) to compare pore space indices predictive models based on air-filled porosity (f_a) alone vs models using air-filled porosity and total pore space ($f_a + \Phi$), and (ii) to assess the relationships between pore space indices and greenhouse gas emissions (CO_2 and N_2O) in a corn and soybean field.

MATERIALS AND METHODS

Experimental field

The study was conducted from 2011 to 2014 at Freeman farm of Lincoln University of Missouri (Fig. 1) on a Waldron silt loam soil (Fine, smectitic, calcareous, mesic Aeric Fluvaquents) with an average slope of 2 percent. The coordinates of the experimental site are 38°34'55.8"N, 92°06'26.9"W. The average annual temperature and precipitation of those 4 years during the crop growing season were given in Fig. 2 and Fig. 3 respectively.

The experiment field consisted of 16 plots of 12.19 m width by 21.34 m length for each, arranged in randomized complete block with 3 replicates for a total of 48 experimental units. The treatments were (i) tillage at 2 levels (no tillage vs conventional tillage), (ii) cover crop at 2 levels (rye vs no-rye) and (iii) cropping sequence or rotation at four levels (continuous corn, continuous soybean, corn-soybean and soybean-corn rotations). All the plots received 26.31: 67.25: 89.67 kg/ha NPK. Additional nitrogen in the form of urea was applied to all corn plots at the rate of 201.75 kg/ha

Soil sampling and greenhouse gases measurements

Soil sampling and GHGs measurements protocols for this study were reported in Klavdivko et al. (2014). Basically, soil samples were collected at two depths (0-10 and 10-20 cm) at 3 locations in the field, using a core sampler with a volume 384.65 cm³ for a total number of 288 samples. They were collected after planting and full emergence of the seeds. After drying (105°C for 72 h), bulk densities (BD), air-filled porosity (f_a) and total pore space (Φ) were calculated. The relative gas diffusion coefficient (D_s/D_o) and the pore tortuosity factor (τ) were thereafter predicted using diffusivity models described earlier. CO₂ and N₂O were measured using a

Shimadzu Gas Chromatograph (GC-2014) in 2011 and 2012 while a Photoacoustic Gas Analyzer (PSA) was used in 2013 and 2014. For GC-2014 measurements (2011 and 2012), soil air samples for gas analysis were collected using 48 individual PVC static and vented chambers of 30 cm height and 20 cm diameter. Chambers were installed in each plot throughout the growing season and air samples were collected during every two weeks using a 60 ml syringe and stored in a 200 ml Tedlar bag. The concentrations of CO₂ and N₂O from air samples were measured using a GC-2014 within 2 hours of collection. For the photoacoustic method (2013 and 2014), CO₂ and N₂O were measured only in 16 plots belonging either corn-soybean rotation or soybean-corn rotation (Fig.1). Seven measurements were taken from each plot with a two minutes interval between each measurement and the concentration (average from 7 measurements) was recorded in database. The data was then transferred into an Excel data sheet where the gas concentrations were converted to a flux value (e.g. mg C- CO₂ m⁻² h⁻¹).

Statistical analysis

Statistix 10.0 software was used to analyze data. Log10 transformation was applied to 2014 soil for diffusivity models. Treatments effect on measured variables were tested by analysis of variance (ANOVA), and comparisons among treatment means were made using the least significant difference (LSD) multiple range test calculated at $p < 0.05$. Factorial AOV was used to assess the relationship between treatment combinations, compared using Means and Standard error functions, and later plotted on graphs. Pearson correlation and linear regression analysis were used to assess the relationship between soil pore space indices and greenhouse gas fluxes.

RESULTS

Pore space indices predictive models

Relative gas diffusion coefficient (D_s/D_o)

The summary of statistics (Table 1) for the relative gas diffusion coefficient (D_s/D_o) measured from 2011 to 2014 showed that the Marshall model predicted the highest D_s/D_o values for all the 4 years of this study. The Marshall model also had the lowest coefficient of variation (CV) in 2011 and 2014. The Jin and Jury model was next with high values of D_s/D_o and low CV in 2012 and 2013. A pair wise comparison for D_s/D_o (Table 2) showed that all diffusivity models were significantly different regardless of the predictive model ($p < 0.001$).

Pore tortuosity factor

Overall, the summary statistics for τ showed lowest mean values in Marshall (Table 3). However, the highest mean was observed in the Millington model. A pair wise comparison of models (Table 4) showed that all diffusivity models were significantly different for the pore tortuosity factor (τ) predicted using either f_a alone or a combination of $f_a + \Phi$ models ($p < 0.0001$).

Greenhouse gases fluxes

Tables 5 and 6 show that emissions of CO_2 and N_2O from experimental plots were highest in 2011 and 2012 than rest of the years. CO_2 fluxes were highest in 2011 while N_2O fluxes in 2012. The highest emissions of CO_2 ranged from $62.67 \text{ mg C- CO}_2 \text{ m}^{-2}\text{h}^{-1}$ (conventional tillage, rye crop, corn- soybean rotation) to $457.9 \text{ mg C- CO}_2 \text{ m}^{-2}\text{h}^{-1}$ (conventional tillage, no rye crop, continuous soybean). N_2O emissions in 2012 ranged from $25.33 \text{ } \mu\text{g N-N}_2\text{O m}^2 \text{ h}^{-1}$ (continuous

tillage, no rye crop, soybean-corn rotation) to $302.72 \mu\text{g N- N}_2\text{O m}^{-2}\text{h}^{-1}$ (conventional tillage, no rye crop, corn-soybean rotation).

Relationship between pore space indices and CO_2 and N_2O fluxes

In 2012, there was a positive correlation between CO_2 and D_s/D_o ($r = 0.49$, $p < 0.05$) as showed in Fig. 4 while Fig. 5 shows that CO_2 was negatively correlated with τ ($r = -0.42$, $p < 0.05$). In 2013, however, this trend changed with CO_2 negatively correlating with D_s/D_o ($r = 0.51$, $p < 0.05$) and τ positively correlating with CO_2 ($r = 0.55$, $p < 0.05$). In 2012, N_2O was significantly correlated with D_s/D_o ($r = 0.36$, $p < 0.05$) (Fig. 6) and τ ($r = 0.32$, $p < 0.05$) (Fig. 7). There was no significant correlation between N_2O and D_s/D_o and τ in 2013 and 2014.

DISCUSSION

The Marshall diffusivity model (based on f_a) predicted both the highest D_s/D_o and lowest tortuosity. This is understandable as this model is linear and uses a lower power to compute D_s/D_o and τ from f_a . There was less emission of CO_2 in 2011 as compared to 2012, 2013 and 2014. One possible reason behind less emissions of CO_2 in 2011 is the increase in N fertilization which generally decreases soil CO_2 emissions (Halvorson et al. 2002; Micks et al. 2004; Wilson and Al-Kaisi, 2008).

N_2O emissions were also highest in 2012. The possible reason for higher emissions in 2012 than rest of the other years could be due to the drought. In fact, in 2012, temperature was up to 29.2°C during crop growing period. Soil temperature and moisture strongly influence not only the N_2O production by the activity of microorganisms (Signor and Cerri, 2013), but also its diffusion to the atmosphere (Davidson and Swank, 1986). Liu et al. (2011) reported that N_2O emissions

exponentially increased with increasing soil temperatures (0-50°C). This explains the existence of a close relationship among seasonal variation of N₂O flux and soil and air temperatures (Wolf and Brumme, 2002; Zhang and Han, 2008).

In 2011 and 2013, negative N₂O fluxes were also observed which means uptake or consumption of N₂O. Low mineral N and large moisture contents have sometimes been found to favor N₂O consumption. Generally, the conditions interfering with N₂O diffusion in the soil seem to enhance N₂O consumption (Lydie et al., 2007). Pore space indices were correlated with greenhouse gases, however the nature of the relationship changed from year to year as it was the case for CO₂ vs D_s/D_o which correlated positively in 2012, but negatively in 2013. Weltecke and Gaertig (2010) and Nan et al (2016) also reported negative correlations between CO₂ and the gas diffusion coefficient (D_s/D_o). Nan et al (2016) found a significant negative correlation between CO₂ concentrations and the diffusion gas coefficient from 0 to 20 cm and a significant positive correlation from 40 to 100 cm depth of soil. They attributed this phenomenon to more rapid production and efflux of soil CO₂ from 0 to 20 cm. In fact, it has been suggested that CO₂ transport may be limited due to a decrease in the effective diffusion coefficient with increasing soil moisture (Jassal et al., 2004; Fang and Moncrief, 1999). Obviously, the 40-100 cm soil layer had more moisture. In our study, we noticed that D_s/D_o generally decreased from 2011 to 2014, but also CO₂ emissions decreased from 2012 to 2013. This might have caused the shift in the direction of the relationship between CO₂ and D_s/D_o. Other authors have also reported the existence of the relationships between pore space indices and greenhouse gases emissions (Nkongolo et al., 2010b) and hence inclusion of D_s/D_o and τ in predictive models will certainly improve our understanding of the dynamics of greenhouse gas fluxes from soil.

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