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Models for predicting the gas diffusion coefficient in undisturbed soil

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Abstract- Overall objective of this project is mathematical modeling of diffusion processes, functional status and numerical methods development. This paper includes qualitative study to estimate the gas diffusion coefficient (D_P/D_0) in undisturbed soils. Based on empirical and numerical models of Penman [1940], Millington and Quirk [1960], Millington and Quirk [1961] and Moldrup [1999] has determined diffusion coefficient variation for different types of soil taken in the study. It was found that soil type, texture, structure, porosity, apparent density are the main factors influencing the diffusion and gas transport in porous media. The project conducted fundamental research on both general diffusion models and analysis models particulare major in science and engineering.

Key words: gas diffusion, undisturbed soil, models, Penman-Millington-Quirk models.

1. INTRODUCTION

The gas diffusion coefficient in soil (D_P) and its dependency on soil physical characteristics, governs the diffusive transport of oxygen, greenhouse gases, fumigants and volatile organic pollutants in agricultural, forest, and urban soils. Accurate models for predicting D_P as a function of air-filled porosity (PT) in natural, undisturbed soil are needed for realistic gas transport and fate simulations.

Soil gaz diffusivity and its dependency on/and soil type (texture, structure, horizon, management) control gas transport and fate in natural, undisturbed soil system where diffusive gas transport is normally dominant compared with convective gas transport.

The soil gas diffusion coefficient (D_P) and its dependency on air-filled porosity (θ) govern most gas diffusion-reaction processes in soil. Accurate $D_P(\theta)$ prediction models for undisturbed soils are needed in vadose zone transport and fate models. The objective of this paper was to develop a D_P (θ) model with lower input parameter requirement and similar prediction accuracy as recent soil-type dependent models.

Numerous predictive - descriptive models for D_P as a function of θ are available and may be divided into six groups:

1. The first group consist of predictive $D_P(\theta)$ models based only on θ. The classical $D_P(\theta)$ models in the first group are the linear $D_P(\theta)$ models by Penman (1940), van Bavel (1952), Call (1957) and nonlinear by Marshall (1959) and Millington (1959).

2. The second group consists of simple, empirically, or mechanistically based, nonliniear $D_P(\theta)$ models that take into account both θ and soil total porosity (PT). These predictive models introduce a minor soil type effect through PT that is dependent on for example, soil texture and management. Among the numerous models within this group are the Millington and Quirk (1960) model, as re-introduced by Jin and Jury (1996), and the Millington and Quirk (1961) model that is almost universally accepted and applied in vadose zone transport and fate models to describe both and solute diffusivity. The frequent use of the Millington and Quirk (1961) model is noteworthy since the model has never been validated against gas diffusivity data for undisturbed soils representing a broad interval of soil types and porosities.

3. The models in the third group use the SWC (soil water curve) as an additional input to take into account soil type effects on gas diffusivity. Moldrup et al. (1996) introduced the Campbell SWC parameter b as the third model parameter, together with θ and PT, in D_P (θ) models.

4. The fourth group of models consist of generalized power law models that introduce additional, empirical model parameters and thereby can provide a good fit to $D_P(\theta)$ data within the θ interval where measurements are avaible. The most frequently used within this group is the Troeh et al. (1982) model where two additional fitting parameters are introduced. The Troeh et al. (1982) model was successfully used in several studies to fit and subsequently represent

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measured $D_p(\theta)$ data in gas transport and fate models (Petersen et al. 1994,1996).

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8. The sixth group of $D_P(\theta)$ models consist of macroscopic pore-size distribution models based on equivalent pore radius capillary tube, jointed tubes of different radii, or multidimensional capillary tube networks (Ball, 1981; Nielson et al., 1984; Steele and Nieber, 1994). The $D_P(\theta)$ models in this group at present have several empirical constants that must be fitted to actual $D_P(\theta)$ data for the soil and, hence, are not immediately applicable for predicting soil gas diffusivity.

We acknowledge that the above grouping of $D_P(\theta)$ models may be disputable since some models may arguably belong to more than one group. In general, the last three groups (IV-VI) are mainly descriptive, multiparameter $D_P(\theta)$ models that can accurately fit measured, detailed $D_P(\theta)$ data and thereby help in interpreting the data to better understand the gas diffusion process in unsaturated soil. However, the models are at present not useful for predicting $D_P(\theta)$. Looking at the first three groups (I-III) containing predictive, low-parameter $D_P(\theta)$ models, one can conclude that there is an obvious lack of simple, predictive models that on one hand take into account soil type differences for undisturbed soils but on the other hand do not require knowledge of the entire SWC (soil water curve).

APPROACHING MODELS FOR PREDICTING THE GAS DIFFUSION COEFFICIENT

The most widely used of these one-parameter models is the Penman (1940) model:

$$D_P/D_0 = 0.66\theta \qquad (1)$$

where:

D_P = the gas diffusion coefficient in soil (cm^3 soil air cm^{-1} soil sec^{-1}),

D_0 = the gas diffusion coefficient in free air (cm^2 air sec^{-1});

θ = the soil air-filled porosity (cm^3 soil air cm^{-3} soil).

The next generation of D_P models also included soil-type effects in the form of the soil total porosity, PT (m^3m^{-3}) (Millington and Quirk, 1960, 1961).

The most widely used two-parameter model is that of Millington and Quirk (1960):

$$D_P/D_0 = \theta^2/PT^{2/3} \qquad (2)$$

and Millington and Quirk (1961):

$$D_P/D_0 = \theta^{10/3}/ PT^2 \qquad (3)$$

The model of Moldrup (1999) suggested that soil is dependent gas diffusivity:

$$D_P/D_0 = PT^2(\theta/PT)^{2+3/b} \qquad (4)$$

where:

PT corresponds to gas diffusivity in completey dry soil, following Buckingham (1904);

the term 2+3/b is a analog to Burdine (1953) - Campbell (1974), tortuosity model for describing unsaturated hydraulic conductivity (Moldrup et al. 1996).

These models was developed for 9 undisturbed soils with b values ranging from 2 to 11.

The D_P/D_0 value at low air - filled porosities may appear equal to zero in a nonlogarithmic scale plot but can actually be in the range ($D_P/D_0>10^{-4}$) where gas diffusion still dominates compared to solute diffusion.

Using SOILPARA program (Soil Parameter Estimator) was defined for each type of soil texture charts and have determined the main characteristics. SOILPARA (Soil Parameter Estimator) is based on statistical pore/particle size distribution models and can be used to estimate hydraulic parameters in the van Genuchten constitutive model for variably-saturated soils (Brooks-Corey parameters can be estimated from these).

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SOILPARA allows estimation of the unsaturated zone parameters:

1. From retention data and/or conductivity or diffusivity data (K or D vs. soil water content/pressure) based on the public domain RETC model by M. Th. van Genuchten et al., 1991) with a Windows native preprocessor that is easy to use and offers graphical output and extensive on-screen help;
2. From soil texture (based on the work of Shirazi and Boersma, 1984, and Campbell, 1985) by clicking on a soil texture diagram to return percentage sand, silt and clay within the pre-processor; or
3. By selection of USDA - recommended typical parameter values for various texture classes available in the SOILPARA database.

For a concrete approach to the studied models was considered 3 types of soil texture (coarse, medium, fine) with different apparent density values, resulting in 9 variants of calculation

Variants of soil types counted and their main properties are presented in table 1.

Table 1

Soil textural classification
and properties taken into account

Versions	Texture			DA (g/cm^3)	PT (%)
	A (%)	P (%)	N (%)		
0.1.1	12	30	58	1.28	52
0.1.2	12	30	58	1.35	50
0.1.3	12	30	58	1.42	47
0.3.1	30	28	42	1.28	52
0.3.2	30	28	42	1.35	50
0.3.3	30	28	42	1.42	47
0.5.1	40	35	25	1.28	52
0.5.2	40	35	25	1.35	50
0.5.3	40	35	25	1.42	47

The SOILPARA program determine the soil texture diagram, she requires only the fallowing input data, clay, silt and sand content (as a percentage) together with the dry density of the soil.

Once the program is run, the values of θ_w and θ_{aer}, the relationships between water content and suction and the relationship between suction and conductivity may be determined.

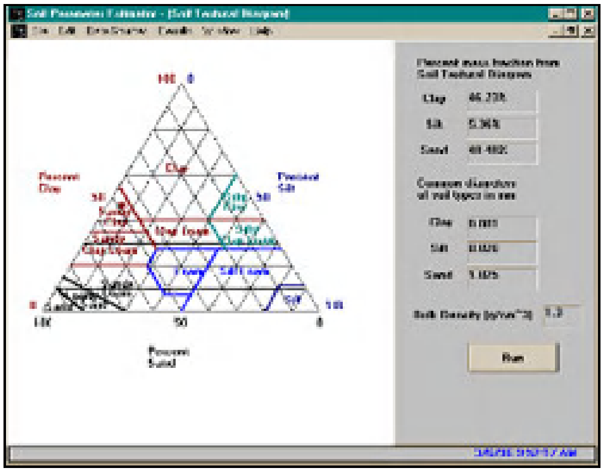


Fig. 1 The soil texture diagram

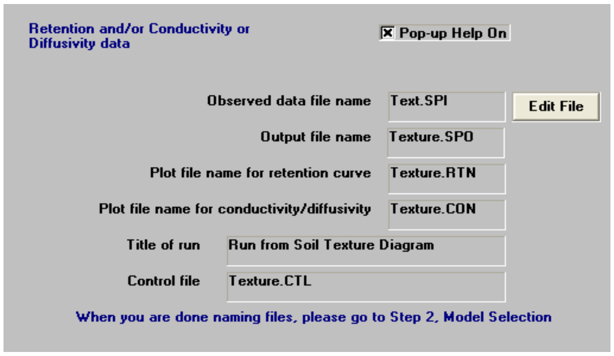
In the diagram of texture of soil on the left side is clay, increasing from bottom to top. On the the right is silt, increasing from top to bottom. On the bottom of the graph sand is increasing from left to right.

Soil texture classes include: sand, loamy sands sandy loams, loam, silt loam, silt, sandy clay, loam, clay loam, silty clay loam, sandy clay, silty clay and clay.

Apparent density must be less than 2,65 g/cm^3 (2,65 g/cm^3 being the density of solid rock material). This is needed to determine saturated conductivity for the soil using the method of Campbell (1985).

The soil water retention curve relates the soil water matric potential and the soil water content. When no significant changes occur in soil structure, the water retention curve can be considered as a soil physical characteristic.

Fig. 2 shows the input data which be taken to determine the retention curve.



Retention and/or Conductivity or Diffusivity data

☒ Pop-up Help On

Observed data file name: Text.SPI

Output file name: Texture.SPO

Plot file name for retention curve: Texture.RTN

Plot file name for conductivity/diffusivity: Texture.CON

Title of run: Run from Soil Texture Diagram

Control file: Texture.CTL

When you are done naming files, please go to Step 2, Model Selection

Fig. 2 Input data for determining the curve of water content and suction

For determine the retention curve is necessary through six steps:

1. File Name
2. Model Selection
3. Conductivity/Diffusivity
4. Program Controls
5. Parameter Estimation
6. Run Program

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These steps are used to plot the soil-water characteristic curve, the air entry value of matric suction can be determined. The air entry value of the soil is the matric suction when air starts to enter the largest pores in the soil. θ_w (expressed in percentages) is located at the point of maximum curvature on the curve, and is found by the intersection of two tangents.

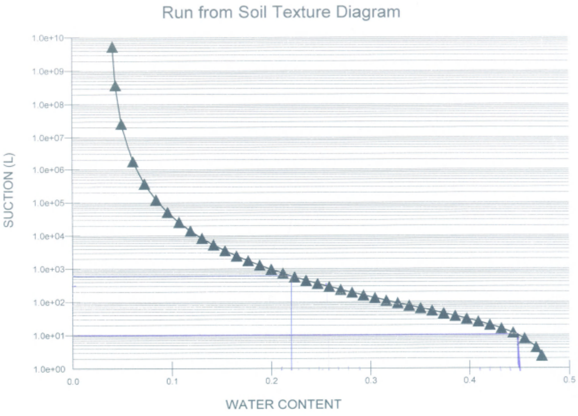

Fig. 3 The curve of water content and suction

In table 2 are presented values of θ_w (%) and θ_{aer} (%) for the nine variants of calculation.

$$\theta_{aer} = PT - \theta_w (\%) \qquad (5)$$

Table 2
Values of θ_w and θ_{aer} for variants of calculation

Variants calculation	θ_w (%)	θ_{aer} (%)
0.1.1	224	296
0.1.2	220	280
0.1.3	218	252
0.3.1	335	185
0.3.2	320	180
0.3.3	325	145
0.5.1	368	152
0.5.2	360	140
0.5.3	363	107

Looking the results, we can see in table 3, that the equation of Millington and Quirk model [1961] has high values, over the Penman model [1940], Millington and Quirk model [1960] and Moldrup model [1999], what have lower values.

Analyzing results after calculations we find that increasing porosity leads to intensification of gas diffusion in soil. We found that low values of apparent density influences growth in soil porosity.

Table 3
Predicting the gas diffusion coefficient (D_P/D_0) in undisturbed soil

Variants calcu-lation	D_P/D_0			
	0.66θ	$\theta^2/PT^{2/3}$	$\theta^{10/3}/PT^2$	$PT^2(\theta/PT)^{2+3/b}$
0.1.1	0.195	0.134	2.477	0.062
0.1.2	0.184	0.123	2.624	0.055
0.1.3	0.166	0.103	2.881	0.043
0.3.1	0.122	0.052	2.122	0.018
0.3.2	0.118	0.050	2.268	0.017
0.3.3	0.095	0.034	2.400	0.010
0.5.1	0.100	0.035	1.988	0.010
0.5.2	0.092	0.030	2.088	0.009
0.5.3	0.064	0.018	2.172	0.005

Compared with measured diffusivities close to phase saturation (soil-water and soil-air saturation for ion and gas diffusivity, respectively), the Penman (1940) model was superior to the Millington-Quirk models independent of diffusion type.

The combined use of the Penman model to predict the diffusivity at phase saturation together with a general Millington-Quirk model to predict relative decrease in diffusivity with decreasing phase content was labeled the Penman-Millington-Quirk (PMQ) model.

The PMQ (Penman - Millington - Quirk) model predicted gas diffusivity in sieved and undisturbed soil well, but a soil-type dependent model was superior for predicting ion diffusivity.

The new models seem promising for more accurately predicting gas and ion diffusion and, therefore, for improving simulations of diffusion-constrained chemical and biological reactions in soils.

Figure 1 shows the graphic representation of ec. 1, 2 and 4 for the 9 variants of the studied computing. Comparing diagrams obtained, one can observe a uniform distribution of the diffusion coefficient, satisfactory results being provided by eq. 4.

Is found that a clay soil with low porosity values of the diffusion coefficient is lower than a sandy soil with a high porosity.

The Penman [1940] and the Millington and Quirk [1960] model overpreticted D_P in the whole θ interval. The Moldrup [1999] model is applied to determine gas diffusion in dry soils.

The three models lead to similar results for different soil types (clay, sand and dust).

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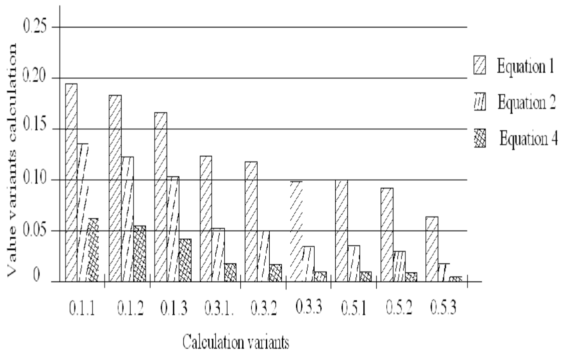

Fig. 1 Value variants calculation for eq. 1,2,4

The soil gas diffusion calculated with Millington and Quirk [1961] model, represented in fig. 2 shows very high compared to other models applied.

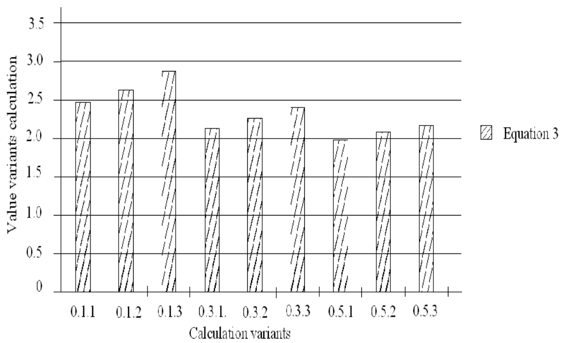

Fig. 2 Value variants calculation for eq. 3

This was expected since the model was originally derived for a porous medium with randomly distributed particles of uniform size, thus, mostly resembling coarse sandy soils. The model showed increasing tendency for underprediction at higher soil total porosities.

Overall, the Penman [1940] and Millington and Quirk [1960] models are not recommended for use in gas transport and fate models representing natural, undisturbed soil system. The Millington and Quirk [1961] may often provide reasonable predictions for more sandy and lower porosities soils but cannot be trusted across soil types and porosities.

The main soil-gas transport parameters, gas diffusivity and air permeability, and their variations with soil type and air-filled porosity play a key role in soil-gas emission problems including volatilization of toxic chemicals at polluted sites and the production and emission of greenhouse gases.

CONCLUSIONS

Evaluating and comparing the results shown, we can say that model Millington and Quirk [1961], often used in practice, could not provide satisfactory conclusions on this issue. Only models of Penman [1940], Millington and Quirk [1960] and Moldrup [1999] have led to realistic results on gas diffusion in undisturbed soil.

Recent models of gaseous diffusion in soils have taken account of the effects of soil structure, and explain the development of anaerobic zones within aggregates.

Aggregate sizes commonly fit log-normal distribution.

In clayey soils anaerobic conditions persist for long periods in the larger aggregates, but quantitative assessment of anaerobic volumes is complicated by uncertainty about the value of the diffusion coefficient for oxygen in wet soils.

Diffusion processes in the soil water and air phases often govern transport and fate of nutrients, pesticides and toxic chemicals in the vadose zone.

Knowledge of diffusion coefficient is critical to developing accurate predictive models for gas flow in porous media and to improving our understanding of the basic transport processes involved.

Thus gas diffusivity measurements on diferent sample sizes and evaluation of spatial variability and scale dependency is an important scope of diffusivity research.

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