Soil pore surface properties in managed grasslands

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Abstract

Properties of pore surfaces control adsorption and transport of water and chemicals in soils. Parameters are needed to recognize and monitor changes in pore surfaces caused by differences in soil management. Data on gas adsorption in soils can be compressed into parameters characterizing (a) area available to a particular adsorbate, and (b) surface roughness or irregularity. Our objectives were to see (a) whether models of adsorption on fractal surfaces are applicable to water vapor adsorption in soils in the capillary condensation range, and (b) whether differences in long-term management of grasslands are reflected by soil pore surface properties. Water vapor adsorption was measured in Gray Forest soil (Udic Argiboroll, Orthic Greyzezem, clay loam) samples taken at four plots, where a long-term experiment on grassing arable land had been carried out for 12 years. The experiment had 2 × 2 design. Factors were ‘harvest–no-harvest’ and ‘fertilizer–no-fertilizer’. The hay was cut after over-seeding in harvested treatments every year. Ammonium nitrate, superphosphate, and potassium chloride were applied annually after the snowmelt to get the total amount of nutrients of 60 kg ha⁻¹. The monolayer adsorption capacity was estimated from the Brunauer–Emmett–Teller model. A fractal Frenkel–Halsey–Hill model of adsorption on a fractal surface, and a thermodynamic adsorption model were applied in the range of relative pressures from 0.7 to 0.98 and provided good fit of data. Values of the surface fractal dimension Ds were in the range from 2.75 to 2.85. Removal of carbohydrates resulted in increase of Ds. Differences in management practices did not affect values of Ds in the scale range studied, whereas the monolayer capacity was affected. Both fertilization and harvesting resulted in an increase of the monolayer capacity, with the largest increase observed in soil that was fertilized but not harvested. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Water vapor; Adsorption; Fractal surface; Grassland; Gray Forest soil

1. Introduction

Properties of pore surfaces control adsorption and transport of water and chemicals in soils. Parameters are needed to recognize and monitor changes in pore surfaces caused by differences in soil management. Once established, such diagnostic parameters can be used to quantify effects of management on soil functioning by means of land quality or soil quality indices (Singer and Ewing, 2000).

Data on gas adsorption in soils can be compressed into parameters characterizing (a) area available to a particular adsorbate, and (b) surface roughness or irregularity. Specific surface area is known to char-
acterize the ability of soil to retain and transport nutrients and water. Specific surface area of soils correlates with the sorptive capacity and ion exchange capacity (Jurinak and Volman, 1957; Ben-Dor and Banin, 1995), retention and release of chemicals (Rhue et al., 1988; Valverde-Garcia et al., 1988; Ong and Lion, 1991), swelling (Sapozhnikov, 1985), water retention (Kapilevich et al., 1987), dry-aggregate stability (Skidmore and Layton, 1992). Tester (1990) observed an increase in specific surface area parallel to the increase in organic matter content after compost application.

Pore surfaces in soils are irregular. Fractal models were found useful in the description of natural and man-made irregular surfaces. Fractal surfaces exhibit dependencies of their area $S$ on the resolution, or scale, $R$ at which the area is measured (Russ, 1994). These dependencies have a power law form

$$S \propto R^{2-D_s}$$

(1)

where $D_s$ is the surface fractal dimension. The surface fractal dimension characterizes the degree of roughness or disorder of the surface. Numerical values of surface fractal dimensions vary from 2.0 (perfectly smooth) to a maximum value of 3.0. The larger the value of $D_s$, the greater is the irregularity of the surface.

Theoretical studies of adsorption on fractal surfaces predicted the effect of the surface fractal dimension on diffusion-limited adsorption kinetics (Seri-Levy and Avnir, 1993; Giona and Giustiniani, 1996). Douglas (1989) showed that adsorption of polymers on rough surfaces should be affected by the surface fractal dimension. The increase in fractal dimensions should cause tighter binding of polymer with a surface. Surface fractal dimensions were studied with relation to technological parameters in production of ion-exchange fibers (Kutarov and Kats, 1992), carbon blacks (Darmstadt et al., 1995), cements (Niklasson, 1993), food products (Aguerre et al., 1996), and wood (Hatzikiriakos and Avramidis, 1994).

Fractal scaling was demonstrated for soil pore surfaces. Sokolowska (1989) used a fractal model to analyze the soil particle surface heterogeneity with data on water vapor adsorption experiments. Toledo et al. (1990) showed that fractal dimensions of soil particle surfaces could be estimated from water retention data at low moisture contents. Bartoli et al. (1991) introduced the use of mercury porosimetry to estimate surface fractal dimensions in soils. Soil constituents, such as humus materials and clay minerals, were found to be surface fractals (Rice et al., 1999; Sokolowska and Sokolowski, 1999).

The management-related change in soil quality is a current topic of interest. Efforts were made to define soil quality and suggest a minimum set of analyses to aid in evaluating soil quality as affected by long-term management practices (Doran and Parkin, 1994). Long-term and short-term management effects on soil pore surface fractal dimensions were observed using soil thin sections (Pachepsky et al., 1996b; Giménez et al., 1997; Oleschko et al., 1998). Fractal dimension analysis provided additional information by describing the changes in pore shapes.

Adsorption isotherms of gases present an attractive source of data on surface roughness. Several theories of adsorption on a fractal surface were developed during last 15 years. Two types of adsorption data analysis have been used most often. One of them uses several different adsorbates and employs the mean radius of each adsorbate’s molecules as the resolution, or scale, $R$ in Eq. (1). The logarithmic transform of this equation and the subsequent regression ‘radius vs. specific surface’ in log–log scale provides the value of $D_s$ as the slope subtracted from 2 (Farin and Avnir, 1989). With this approach, data on adsorption at low relative pressures are used at which the monolayer coverage is known to occur. Another type of the adsorption data analysis employs the data at high relative pressures, where capillary condensation occurs so that micropores become filled with adsorbate. Then the micropore radius becomes a measure of scale $R$ in Eq. (1). Avnir and Jaroniec (1989) obtained a relationship between the adsorbed amount and vapor pressure by assuming the applicability of the Dubinin–Radushkievich equation to describe the adsorption in micropores, and assuming fractal pore volume distribution on the surface. The same equation was obtained by Neimark (1990) and Yin (1991) from the assumption that the capillary condensation was present. A different model was proposed by Neimark (1990). He did not assume validity of any adsorption isotherm equation, but used directly the scaling relationship (1) with the surface curvature radius as a scale measure. Although both models mentioned above were applied in experimental studies, no unambiguous way was
found to see which one is superior (Jaroniec et al., 1997).

Our objectives were to see (a) whether models of adsorption on fractal surfaces are applicable to water vapor adsorption in soils in the capillary condensation range, and (b) whether differences in long-term management of grasslands are reflected by soil pore surface properties.

2. Materials and methods

2.1. Soil sampling and analyses

Gray Forest soil (Udic Argiboroll) was sampled in April 1994 near Pushchino, Moscow Region, Russia. Samples were taken at a site, where an experiment on grassing arable land had been carried out since 1982 (Yermolayev and Shirshova, 1994). Grass mixture consisted of Festuca Pratensis, Huds., Phleum Pratense L., and Trifolium Pratense L. The experiment had 2 x 2 design. Factors were ‘harvest–no-harvest’ and ‘fertilizer–no-fertilizer’. The hay was cut after over-seeding in harvested treatments every year. Ammonium nitrate, superphosphate, and potassium chloride were applied annually after the snowmelt to get the total amount of nutrients of 60 kg ha\(^{-1}\). Area of each plot was 0.5 ha. The soil was in no-till, since 1982. The soil had the pH 6.3, a loamy texture with 45% particles less than 0.01 mm and 20% particles less than 0.001 mm, and contained illite, kaolinite, and smectites in its clay fraction. Sampling depth was 10–30 cm. Five samples were taken from each plot, and the mixed sample was used in adsorption measurements for each of the four combinations of factors.

Soil was air-dried and sieved, and aggregates less than 2 mm were used. Each sample was split, and carbohydrates were removed in one of the two subsamples. The oxidation of carbohydrates has been performed with 0.02 M NaIO\(_4\) solution (Cheshire et al., 1984).

Water vapor adsorption isotherms were measured with a vacuum microbalance technique. The temperature was kept within the range of 294±0.1 K. The adsorption isotherms were measured in duplicate at 14 relative pressure levels of 0.0217, 0.0902, 0.1246, 0.2142, 0.3008, 0.3404, 0.4112, 0.5324, 0.6075, 0.6533, 0.7320, 0.7727, 0.8680, 0.9826.

For comparison purposes, we also used published data on water vapor adsorption on clay minerals (Mooney et al., 1952; Orchiston, 1954; Jurinak, 1963).

The BET equation (Adamson, 1967)

\[
N = N_0 \left( \frac{c(p/p_0)}{(1 - (p/p_0))(1 - ((c - 1)p/p_0))} \right)
\]

was fitted to the experimental isotherms in the range of relative pressures \(p/p_0\) between 0.02 and 0.34. Here and below \(N\) is the adsorbate amount, \(p/p_0\) is the relative pressure defined as a ratio of the actual pressure \(p\) to the saturation vapor pressure \(p_0\). The monolayer capacity \(N_0\) and thermodynamic constant \(c\) were adjusted to achieve the best fit.

3. Estimating fractal dimensions

Avnir and Jaroniec (1989) developed the fractal analogue of the Frenkel–Halsey–Hill (FHH) equation in the following form:

\[
\ln N = C - (D_s - 3) \ln \frac{p}{p_0}
\]

Here \(C\) is the intercept. The same equation was derived by Yin (1991) and Neimark (1990) by assuming the sequential filling of pores from small size to large, that is capillary condensation-type local adsorption isotherm. A similar equation was derived by Pfeifer and Cole (1990) by generalization of the classical FHH adsorption theory for the capillary condensation regime. Neimark pointed out that Eq. (1) should be used with data obtained for \(p/p_0>0.7\). Results of Pfeifer and Cole (1990) also indicate that Eq. (1) is valid at high \(p/p_0\) values when the capillary condensation is the dominant mechanism. We estimated the surface fractal dimension \(D_s\) from the slope of the regression given by Eq. (1) at relative pressures \(p/p_0\) in the range from 0.7320 to 0.9826.

Neimark (1990) and Neimark and Unger (1993) proposed a different model for calculating the fractal dimension \(D_s\) from the adsorption isotherm data. It was called the thermodynamic model. The model reflects the idea that during the adsorption on a fractal surface, the surface is smoothed by the adsorbate, and the surface of the adsorbent covered with an adsorbate is smaller than the surface of the uncovered adsorbent. The area of the 'condensed adsorbate–
vapor–equilibrium interface is obtained from the Kiselev equation

\[ S = \frac{RT}{\gamma} \int_{N}^{N_{\text{max}}} \left( -\ln \frac{p}{p_0} \right) dN \]  

(4)

Here \( N_{\text{max}} \) is the maximum adsorption, \( R \) the gas constant, \( T \) the Kelvin temperature, and \( \gamma \) is the surface tension of the liquid adsorbate. This area is related by the fractal scaling law (1) to the mean scaling radius of this interface \( R \) which is calculated from Kelvin’s equation

\[ R = \frac{2\gamma V_m}{RT(-\ln p/p_0)} \]  

(5)

where \( V_m \) is the molar volume of the liquid adsorbate.

The logarithmic transform of (1) with \( S \) from (4) and \( R \) from (5) results in the equation of the thermodynamic model:

\[ \ln S = a + (D_s - 2) \left( -\ln \frac{p}{p_0} \right) \]  

(6)

Here \( a \) is the intercept. We estimated the surface fractal dimension \( D_s \) from the slope of the regression given by Eq. (6) at relative pressure \( p/p_0 \) in the range from 0.7320 to 0.9826. The integral in the left-hand side of Eq. (4) was evaluated numerically with the trapezoid method. The maximum adsorbed amount was approximately equated to the adsorbed amount at \( p/p_0=0.9826 \).

Parameters of regression equations and their standard error estimates were found using the SigmaPlot Version 2 software package. The statistical significance of differences was tested with the \( t \)-test at the 0.05 significance level.

4. Results and discussion

Adsorption data are shown in Fig. 1. Shapes of the curves are similar. At the same relative pressure values, the adsorbed amount is the highest in soil from the non-harvested, fertilized plot, and is the lowest in soil from the non-harvested, non-fertilized plot. Intermediate values of adsorbed water amounts

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Organic carbon content (%)</th>
<th>Treatment</th>
<th>Surface fractal dimensions</th>
<th>Parameters of the BET equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fractal FHH model</td>
<td>Thermodynamic model</td>
</tr>
<tr>
<td>No harvest, no fertilizer</td>
<td>1.92</td>
<td>Original sample</td>
<td>2.77±0.01(^a)</td>
<td>2.75±0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbohydrates removed</td>
<td>2.79±0.01(^b)</td>
<td>2.79±0.08</td>
</tr>
<tr>
<td>No harvest, 60 kg NPK</td>
<td>1.76</td>
<td>Original sample</td>
<td>2.78±0.00(^c)</td>
<td>2.76±0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbohydrates removed</td>
<td>2.78±0.01(^d)</td>
<td>2.83±04</td>
</tr>
<tr>
<td>Harvested, no fertilizer</td>
<td>1.68</td>
<td>Original sample</td>
<td>2.78±0.00(^e)</td>
<td>2.78±0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbohydrates removed</td>
<td>2.78±0.01(^f)</td>
<td>2.85±0.03</td>
</tr>
<tr>
<td>Harvested, 60 kg NPK</td>
<td>1.64</td>
<td>Original sample</td>
<td>2.78±0.00(^g)</td>
<td>2.74±0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbohydrates removed</td>
<td>2.78±0.01(^h)</td>
<td>2.85±0.05</td>
</tr>
</tbody>
</table>

\(^a\) Standard errors are shown after the ‘±’ sign.
\(^b\) Not determined.
are found in soils from harvested plots. These effects of treatments are reflected in values of the monolayer capacity $N_0$ found from the BET equation (Table 1). The monolayer capacity did not correlate with the organic carbon content in this study. This could be related to the differences in composition of organic matter formed in soil under different management in this experiment (Yermolayev and Shirshova, 1988; Shirshova and Yermolayev, 1990).

Removal of carbohydrates caused a small decrease of the monolayer capacity of water adsorption in soil from all but non-harvested, fertilized plots. Feller et al. (1992) observed that partial removal of carbon by treatments with $\text{H}_2\text{O}_2$ increased the surface area of clay-sized organo-mineral complexes while surface areas of silt and sand were less affected. Oades (1984) suggested that clays were embedded in a matrix of soil organic matter. Therefore, in our study, differences in composition of soil organic matter could be related to the type of particles to which it was bounded.

Application of the fractal FHH model to data on soil minerals is shown in Fig. 2. The FHH model provides a reasonably good fit to the adsorption data. Surface fractal dimensions increase in the sequence ‘illite–Li-kaolinite–Na-montmorillonite’. The values of $D_s$ are 2.49, 2.62, and 2.74, respectively.

Application of both the fractal FHH model and the thermodynamic model to soil data is shown in Fig. 3. The dependencies between transformed data are very close to linear ones as predicted by both models. Estimated values of surface fractal dimensions are given in Table 1. The standard errors of the fractal dimension estimates are larger for the thermodynamic model than for the fractal FHH model. Estimated values of $D_s$ range from 2.73 to 2.78 for untreated samples and from 2.78 to 2.85 in samples, where carbohydrates were removed. Our data do not indicate that either of the two compared models is superior.

Fig. 2. Fractal scaling of pore surface from data on water vapor adsorption on clay minerals; $N$ is the adsorbed amount, $p$ the actual vapor pressure, and $p_0$ is the vapor pressure at saturation; (○) Na-montmorillonite (Mooney et al., 1952), (●) Li-kaolinite (Jurinak, 1963), (△) illite (Orchiston, 1954).

Fig. 3. Fractal scaling of the pore surface demonstrated with two models of vapor adsorption on fractal surfaces: (a) fractal Frenkel–Halsey–Hill model, (b) thermodynamic model; $N$ is the adsorbed amount, $N_{\text{max}}$ the maximum adsorbed amount, $p$ the actual vapor pressure, and $p_0$ is the vapor pressure at saturation; (●) no harvesting, no fertilization, (■) no harvesting, 60 kg NPK annually, (▲) harvested, no fertilization, (▼) harvested, 60 kg NPK annually.
The values of fractal dimensions are close for both models applied to the same sample, and no statistically significant differences are encountered. This might be expected since we used data in the range of relative pressures, where the capillary condensation was a dominating adsorption process. Jaroniec (1995) had shown that the Eq. (6) can be derived from the FHH equation under the assumption of the condensation approximation validity. Sahouli et al. (1996) observed the equivalence in results of application both the fractal FHH equation and the thermodynamic model (6) when the adsorption process was dominated by the capillary condensation in carbon black. Darmstadt et al. (1995) applied both the fractal FHH model (3) and the thermodynamic model (6) to data on N₂ adsorption on carbon blacks. They found the fractal dimensions from both models to be very close in three of four samples. Their fourth sample had much lower fractal dimensions than the other three. It was suggested that this sample had mesopores where the capillary condensation occurred which led to over-compensating the reduced adsorption due to the fractal surface.

Fractal dimension values did not differ between the experimental treatments. The soil surface irregularity remained the same. The intercepts in graphs of Fig. 2 show differences among the treatments. Soil in harvested plots displayed similarities in parameters of both fractal models. For non-harvested plots, the intercepts are different from each other and from the harvested plots. The differences in intercepts reflect the difference in film surface area at the same capillary radius value. The larger the intercept, the larger is the film surface area. Therefore, within the studied radii range from 3 to 60 nm, the number of pores of any given radius is the largest in the soil of the non-harvested fertilized plot. As the radius changes, this number scales in a similar manner in all plots.

Several fractal models of pore surfaces were successfully used to distinguish effects of tillage and compaction on soil structure (Perfect and Kay, 1995). Scales in these studies corresponded to the aggregate sizes in dry sieving, i.e. 0.3–30 mm (Giménez et al., 1997), or to the recognizable features in soil thick and thin sections, i.e. 0.008–3 mm (Pachepsky et al., 1996b; Oleszko et al., 1998). In the above studies, the authors measured soil structure directly using variants of the box-counting method. Scales were much smaller in this study, and the resolution was defined indirectly by converting pressures to the radii. Different sensitivity of fractal parameters to long-term soil management and laboratory treatments was found in different ranges of scales (Pachepsky et al., 1996a; Giménez et al., 1997). The absence of differences in fractal dimensions in the capillary condensation region does not imply that the grassland management does not affect surface roughness at all. The differences are absent in the specific range of pore radii from 3 to 60 nm, but it is possible that differences in surface roughness exist in other ranges of radii.

Carbohydrate removal had an effect on the values of fractal dimensions estimated with the thermodynamic model but not with the fractal FHH (Table 1). No statistically significant differences were found between the fractal dimension estimates in original samples and samples with removed carbohydrates. The increase in surface fractal dimension values was expected since the irregularity of the surface should increase after the removal of structure-forming organic compounds. Removal of organic matter caused an increase in surface fractal dimensions measured with the mercury porosimetry in three soils studied by Pachepsky et al. (1996a).

Compared with pure minerals in Fig. 2, the soil in this study had larger values of surface fractal dimensions. Mixed mineral composition and the presence of organic matter are probable reasons for that. Application of other fractal models to quantify irregularity of soil composition and structure also resulted in obtaining high, close to three, values of mass and fragmentation fractal dimensions for fine textured soils (Perfect and Kay, 1995).

A caution has to be exercised in interpreting values of fractal dimensions obtained with water adsorption because of specific interactions of water molecules with surfaces. Niklasson (1993) has found that data on nitrogen adsorption tend to give larger values of surface fractal dimensions than data on water adsorption. This author observed a close correspondence between fractal dimensions obtained from water adsorption and from small-angle neutron scattering. Pachepsky et al. (1996b) used mercury porosimetry to measure the surface fractal dimension under developing barley crop for the same soil as in this study but in agricultural use. In samples taken during spring, they found
values of $D_s=2.87\pm0.10$ which did not differ significantly from the values in Table 1.

Fractal scaling presents additional parameters to characterize soil pore surfaces. Specific surface area was shown to be related to various physical and chemical properties of soil (Petersen et al., 1996). The region of relative pressures between 0.05 and 0.3 is used to find the specific surface area (Adamson, 1967; Kutilek and Nielsen, 1994). Fractal scaling parameters as defined in this paper give information about different range of relative pressures, and therefore, different range of pore radii. There is a growing interest in competitive adsorption of volatile organic compounds and water in soils as related to soil bioremediation and fate of fumigants (e.g. Pennell et al., 1992; Poulsen et al., 1998). Fractal parameters of pore surfaces may find applications in this field.

In conclusion, the models of adsorption on fractal surfaces appear to be applicable to water adsorption in soil in this study. Differences in long-term management of the grassland did not affect surface fractal dimensions, although the surface area was affected.

References


