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Soil texture effects on multifractal behaviour of nitrogen adsorption and desorption isotherms

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Nitrogen adsorption (NAI) and desorption (NDI) isotherms have been reasonably well described by multifractal analysis. This study aimed to assess effects of soil texture on the scaling heterogeneity of NAIs and NDIs. Contrasting medium textured and clayey soils, developed over parent materials with felsic or mafic compositions respectively, were sampled. These two soil groups also showed significant differences in specific surface area (SSA) and cation exchange capacity (CEC), but not in organic matter content (OMC). The scaling properties of all NAIs and NDIs studied exhibited a well-defined multifractal structure, which was assessed by generalised dimension, D_q , and singularity spectra, f (α), versus α functions. Width of D_q given by $(D_{-5}-D_5)$ and therefore scaling heterogeneity was significantly higher for NAIs than for NDIs. Also, the former was less evenly distributed than the latter. There was significant interaction between isotherm branch (NAI versus NDI) and texture (medium to heavy) for several indices obtained from Dq, namely D-5, D1 D2, D5 and $(D_{-5}-D_5)$, so that the values of these indices were greater for clayey soils during adsorption and for medium textured soils during desorption. Therefore, NAIs of clayey soils exhibited higher scaling heterogeneity and were more evenly distributed than those of medium textured soils and the reverse was true for their respective NDIs counterparts. Differences in multifractality of NAIs and NDIs were consistent with a wider hysteresis loop of the medium textured soils compared to that of the clayey soils; this is because features of this loop influenced the proportion of high and low values in the probability distribution of the isotherms. Multifractal analysis of N2 isotherms was useful to characterise soil types with contrasting textures, accounting for peculiar agronomical and environmental characteristics; therefore, it may help in assessing links between soil quality and inherent soil properties.

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1. Introduction

Soil quality is best defined in relation to the functions performed by soils (Doran & Parkin, 1994). The suitability of a soil for a given use depends on both inherent and dynamic soil properties (Carter et al., 1997; Lal, 1998). Inherent soil properties, such as particle size distribution, particle density, or soil mineralogy mainly depend on soil-forming factors. However dynamic soil properties, such as aggregate stability, water and nutrient status or bulk density, are changing in response to soil use and management (Carter et al., 1997), even if, to some extent, they may also depend on inherent soil properties. Several properties such as organic matter content, soil specific surface area (SSA) or bulk density may be considered as inherent properties for deep horizons, but have been shown to be dynamic, or use dependent, near the soil surface.

The soil mineral fraction is most frequently characterised by particle size analysis, because this is an inherent soil property, which greatly influences many physical and chemical processes controlling soil functions. However, several macro-scale physical and chemical soil properties and processes are closely related to other different grain-scale properties, such as SSA, porosity, pore size distribution or pore geometry (Hajnos, Korsunskaia, & Pachepsky, 2000; Petersen, Moldrup, Jacobsen, & Rolston, 1996), which are usedependent at least for the top soil horizons. In particular, the specific surface area (SSA) of a soil has been commonly considered to be strongly related to soil texture, clay type, reactivity of soil colloids and retention or release of chemicals (Feller, Shouller, Thomas, Rouiller, & Herbillon, 1992; Hepper, Buschiazzo, Hevia, Urioste, & Antón, 2006; Lado et al., 2013; Vidal-Vázquez & Paz-Ferreiro, 2012).

Isotherms of N2 are curves in a pressure-volume diagram at constant temperature, which may be obtained in both adsorption and desorption phases. Commonly an isotherm is represented by a graph showing the amounts of N2 adsorbed under vacuum conditions and relative pressure, i.e. p/p_0 , where p is the applied pressure and p_o is the atmospheric pressure. Determinations of either adsorption isotherms or adsorption-desorption isotherms are most frequently performed to estimate SSA and sometimes they are also used to evaluate various other surface properties (Bartoli, Poulenard, & Schouller, 2007; Hajnos et al., 2000; Jozefaciuk, Toth, & Szendrei, 2006; Lado et al., 2013; Paz-Ferreiro, da Luz, Lado, & Vidal Vázquez, 2013, Paz-Ferreiro, Wilson, & Vidal Vázquez, 2009; Petersen et al., 1996). Classical, non-fractal models are commonly employed to estimate SSA, from which the most conventional is the Brunauer-Emmett-Teller (BET) model (Brunauer, Emmett, & Teller, 1938). However, SSA is estimated using only the data contained in a limited range of p/p_0 , while NAIs and NDIs determinations can be easily performed over the entire range of relative pressure, $0 < p/p_o < 1$, providing additional information that is not employed in traditional assessments of soil surface properties.

Fractal-based models have been used in the past to describe soil NAIs (Hajnos et al., 2000; Jozefaciuk et al., 2006; Pachepsky et al., 1995). Also, the scaling properties of NAIs from soils (Paz-Ferreiro, Miranda, & Vidal Vázquez, 2010, 2009;

Vidal-Vázquez & Paz-Ferreiro, 2012) and artificial organoclays (Lado et al., 2013) have been reasonably well described by multifractal models. More recently, Paz-Ferreiro et al. (2013) performed multiscale analysis of the two isotherm branches, NAIs and NDIs. Indeed, comparison of results from the classical BET model and those from multifractal approaches is not straightforward. First, the BET model estimates the total surface area from adsorption isotherms in a limited range of relative pressure, (i.e., $0.05 < p/p_0 < 0.35$), while fractal and multifractal approaches use the information contained in the entire adsorption or desorption curve. Second, the BET method assumes that the soil pore-solid interface is not a fractal (Paz-Ferreiro, Wilson, & Vidal Vázquez, 2009). Nevertheless, it has been claimed that SSA and scaling analysis of N2 isotherms yield complementary information that may be useful for a better understanding of the geometry of soil surfaces and porous systems (Paz-Ferreiro et al., 2013).

Until now, multifractal analysis of adsorption isotherms has been carried out in Brazilian soils from Minas Gerais (Vidal-Vázquez & Paz-Ferreiro, 2012) and Santa Catarina states (Paz-Ferreiro et al., 2013). In this latter work, the studied soils had a wide range of soil organic carbon (SOC) content, but they were mostly clayey textured; therefore, the main focus was on the interaction between SOC and the scaling property of NAIs and NDIs. For the present study, medium and clayey textured soils developed over contrasting parent materials have been sampled in São Paulo state. In the study area, parent materials and topography have been shown to be the main soil-forming factors that explain soil distribution and soil properties at the local scale (Oliveira, Menk, & Rotta, 1979, p. 169; IPT, 1981, 1997). Moreover, the two contrasting textures are the result of the interaction between pedogenesis and morphogenesis across the landscape. The selected medium and clayey textured soil groups also are characterised by distinct physical, chemical and biological properties, and exhibit contrasting susceptibility to erosion and quality for agricultural uses (Weill & Sparovek, 2008).

We hypothesised that analysis of the complete information contained in NAIs or NDIs of these two main soil groups with contrasting texture using the multifractal formalism may be useful to further discriminate between them and also to provide indices of inherent soil quality. Therefore, the objectives of this work were: i) to examine and to compare the scaling property of NAIs and NDIs in soils with contrasting medium and heavy texture and ii) to evaluate the strength of associations between multifractal parameters obtained from nitrogen isotherms and general soil properties and their potential utility as indices of inherent soil quality.

2. Material and methods

2.1. Site characteristics and soil sampling

The study was conducted at the region of Campinas, São Paulo State, Brazil. Site altitudes ranged from 574 to 640 m above sea level. The local climate is a transition between two mesothermal types, according to Köppen, those with dry winter (Cwa) and hot summer (Cfa). Mean annual temperature is $22.4~^{\circ}\text{C}$, while mean annual precipitation is 1382~mm.

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