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Trends in soil fractal parameters caused by accumulation of soil organic matter as resulting from the analysis of water vapor adsorption isotherms

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ABSTRACT

The experimental adsorption isotherms are used to evaluate the specific surface area and the surface fractal dimensions of several samples containing organic matter. The aim of the investigations has been to search for correlations between specific surface area and geometrical heterogeneity, as characterized by the surface fractal dimension and the content of organic matter. Besides natural organic soils (peats, forest humuses and brown coal from mines) we also investigate controlled systems obtained by adding humic acids to kaolin and quartz, organic compost to soils and by mixing sandy soil and peat at different ratios. The aim of the investigations of controlled systems was to discover some general trends in the dependencies of the specific surface area and the surface fractal dimension on the content of organic matter.

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1. Introduction

Fractal geometry (Mandelbrot, 1982) has been widely used to describe heterogeneity in a wide range of natural processes. In particular, the fractal approach to study soil structure, its dynamics, and numerous physical phenomena occurring in soils appears to be a useful tool to develop a more complete description that is practically impossible by conventional methods based on Euclidean geometry (Anderson et al., 1998; Pachepsky et al., 1999; Young et al., 2001; Bird and Perrier, 2003; Millán et al., 2003; Fedotov et al., 2005; Guber et al., 2005; Blair et al., 2007).

According to fractal approach, the shape and density of the individual objects within the distribution is assumed to be scale invariant. In particular, in the case of adsorption phenomena a fractal adsorbing surface has the same structural features at length scales that are comprised between the inner, r_{min}, and the upper, r_{max}, cut-off limits (Pfeifer, 1984). The surface irregularity is described by the surface fractal dimension, D that characterizes geometry of the gas–solid dividing surface (Sokołowska et al., 1989). Low values of D indicate that the dividing surface is close to a plane, whereas the values approaching 3 mean that the adsorbed phase effectively fills the entire three-dimensional space. The fact that the complexity of an adsorbing surface can be captured by a single number is extremely convenient and appealing, and allows for a great simplification of the theoretical description of adsorption phenomena. Several methods have been developed to evaluate D from adsorption measurements, mercury porosimetry data, scanning electron microscopy and from X-ray and neutron scattering data (Avnir, 1989; Robbins et al., 1991; Senesi, 1994; Perfect and Kay, 1995). The approaches based on adsorption measurements are the simplest and perhaps the most convenient, because they require only one adsorption isotherm curve to determine D (Pfeifer et al., 1989; Neimark, 1990; Pfeifer and Lui, 1997).

Soil organic substances comprise a wide class of ubiquitous organic materials typically characterized by a large physical and chemical heterogeneity and a lack of discrete structure and order in the molecular organization (Stevenson, 1994; Orlov, 1990). Also, organic substances present in mineral soils are usually bonded to the “mineral skeleton” by strong forces, so their breaking requires drastic treatments. Obviously, the bonding of organic substances by mineral soil components changes their structure. Moreover, due to the existence of functional groups containing oxygen, such as carboxyls, phenolic, and carbonyls the exposed surfaces of organic substances may chelate metals and form with them complexes of different stability. Consequently, soil organic matter is one of the important factors determining surface properties of soils as, e.g., adhesion, wettability, aggregate stability (Schnitzer and Khan, 1978; Orlov, 1990; Piccolo, 2002; Zsolnay, 2003; Margherita et al., 2006; Khan et al., 2007). The soil organic matter can also change energetic characteristics of adsorption and the value of the specific surface area. However, the effect of the soil organic matter on both energy of adsorption and the specific surface area is not unequivocal in general (Sokołowska and Sokołowski, 1999;

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Sokołowska et al., 2000). All the above briefly listed properties of the soil organic matter and the organo-mineral complexes formed with soil minerals cause that such systems appear to be highly susceptible of a fractal description. Indeed, several previous investigations indicated that the structure and the changes in the structure of soils and of soil organic matter can be described through the *D* value and that those systems can be decomposed in parts where each one is "a copy" of the "whole" (Rice and Lin, 1994; Senesi et al., 1996; Senesi, 1999; Mendonca et al., 2004; Zhuang et al., 2008).

The objective of this work is to perform studies aiming at the investigations of the dependence between the content of organic matter and the surface fractal dimension of samples. The values of the surface fractal dimension are calculated from the adsorption isotherms of water vapor. We start with the studies of model systems, containing controlled amount of organic matter. Two basically different approaches have been used to develop such systems. One involves the gradual removal of the humus from the soil, and comparative investigation of the residual samples (Pachepsky et al., 1995; Sokołowska et al., 1998; Nordborg, 2001; Blagoveshchenskii and Samsonova, 2001; Józefaciuk and Sokołowska, 2003). The other is to model interactions between purified inorganic and organic soil constituents by using special techniques, which simulate the formation of humic coatings on clay surfaces in the laboratory (Kretzechmar et al., 1993; Józefaciuk et al., 1995; Wershaw et al., 1996; Sokołowska et al., 1997, 1999; De Las Cuevas, 1997; Wagner et al., 2007). We have applied the second method below and report the results of investigation of samples of kaolin and quartz modified by addition of different amount of humic acid (HA). Moreover, we have also studied controlled systems obtained by mechanical mixing sandy soil with peat and by adding a known amount of compost to soil. The studies of controlled systems should be helpful to establish trends on both the specific surface area and the surface fractal dimension as functions of the organic matter content. Then, we proceed to study more complex systems, i.e. peats and moorshes, as well as brown coals from opencasts.

2. Materials and methods

2.1. Materials

All the results reported below were obtained analyzing adsorption isotherms of water vapor on different samples. They included kaolin (Pontedra, Spain) and quartz (Szklarska Poręba, Sudety Region, Poland) modified by humic acids, soils prepared by mixing sand and peat, brown soils with added compost, peats and samples of brown carbon.

2.1.1. Preparation of kaolin and quartz samples

Humic acids were extracted with water from an Ah horizon of an acidic sandy forest soil (pH < 3.63, clay content $<1\%$, organic carbon content of 2.45% and fulvic to humic acids ratio equal to 1.42), taken from the Gunewald experimental plot (Berlin city region). The extracts were filtered by G4 glass bed, coagulated with HCl, washed with distilled water by centrifuging and peptized in water. Finally the suspensions of HA concentration $c_0 = 8$ g/dm^3 was obtained. The ash content of the HA was 3.3% of dry mass, its surface area was about 745 m^2/g and the negative charge at pH = 8.2 was 4.72 mequiv./g. The final suspension of HA (of the concentration of $c_0 = 8$ g/dm^3) was diluted with distilled water to the concentrations 1, 1/2, 1/4, 1/8,...,1/512 of c_0. These suspensions were added to quartz and kaolin at the ratio 1:1, dried in room temperature and mildly ground in a mortar. To reach the value of $c = 2c_0$, a double amount of the suspension at the concentration c_0 was added to the mineral samples. The consecutive samples of modified minerals are abbreviated with the symbols: 2, 1, 1/2,..., 1/512. We should emphasize here that the analysis of adsorption isotherms of water vapor on modified kaolin samples was reported in our previous work (Sokołowska and Sokołowski, 1999). We have included these results here for the sake of completeness.

Quartz samples contained grains of the size < 2 mm were obtained from crystalline quartz mineral by siphoning and centrifuging. They were washed with boiling HCl and distilled water. The surface area of the resulting material, calculated from a granulometric composition, was equal to about 2 m^2/g. Kaolin contained grains of the size lower than 2 mm. The sample consisted of 70% kaolinite, 12% quartz and 18% mica. The BET surface area obtained from water vapor adsorption isotherm was 22.5 m^2/g. The percent of the mineral surfaces covered by HA can be determined by performing measurements of the contact angles of drops of some selected substrates (Józefaciuk et al., 1995).

2.1.2. Preparation of model soils by mixing sand and peat

Peats, being potentially fertile, have several adverse properties. An increase of their utility can be mainly achieved by physical methods of optimizing water–air and heat conditions (Walczak et al., 2002). To improve agricultural properties and to protect cultivated peat soils from rapid destruction and degradation, method of land improvement known as the German method (Kuntze, 1987) of sand admixture is widely used. The German method consists of the addition of sand to arable horizons of peat soils. On the other hand, an introduction of peat to poor sandy soils also improves their quality. Therefore, the model systems studied by us were obtained by mixing at different ratios forest sandy soil (taken from Koepenick, Berlin region, composed of the following fractions: 76.6% of sand, 18.9% of silt and 4.5% of clay, its pH was 7.3 and the content of organic carbon was 0.8%) and peat soil (Grunewald, Berlin region, pH = 3.8, belonging to H1-2 class, according to van Prost classification (Myślińska, 2001) and containing 47.1% of organic carbon). The specific surface area of the peat obtained from water vapor isotherm was 219.1 m^2. The preparation of the samples was carried out as follows. Air-dry samples were stirred in a mortar, sieved through a sieve of 1 mm mesh and mixed at required weight proportion. They were mixed together in a wet state, dried and stirred again in a mortar.

2.1.3. Loess modified with keratin–bark–urea compost

The next series of samples was prepared from loess by adding different doses of keratin–bark–urea (KBU) compost (commercial product, HIMAL, Łódź, Poland). This sort of compost is obtained from wastes of furniture industry and egg-poultry farms and has been proved to be a good fertilizer that is a source of several important elements and organic matter. Also, its addition to soils improves soil structure and air–water conditions (Wegner et al., 1993).

The KBU compost is produced by mixing plumage, bark and urea in the ratio 1:1:2. The mixture is heated in water steam under pressure up to 100 °C to obtain a jelly-like mass. After drying the mass is granulated. It contains about 25% of keratin, 35% of urea and 35% of modified bark. The content of organic carbon is 33%. Moreover, the compost contains about 28% of nitrogen, about 0.05% of phosphorus, 0.2% of potassium, 0.18% of calcium and 0.01% of magnesium.

The air-dry samples of brown soil formed from loess (containing about 17% of clay, 24% of silt and 59% of sand fractions and 0.4% of organic carbon) were mixed with the compost at the doses 5, 10, 20 and 50 wt.%. The mixtures were stirred in a mortar and sieved though the sieve of 1 mm mesh. The samples prepared in such a way were next used in adsorption experiments.

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