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Porosity and pore size distribution of Ultisols and correlations to soil iron oxides

Sheng-Gao Lu *, Zaffar Malik, Dan-Ping Chen, Cheng-Feng Wu

Zhejiang Provincial Key Laboratory of Subtropical Soil and Plant Nutrition, Ministry of Education Key Laboratory of Environmental Remediation and Ecosystem Health, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, P. R. China

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ABSTRACT

The pore structure of soils greatly influences soil functions and processes. The Ultisols developed on Quaternary red clay in the subtropical China were collected to characterize the porosity and pore size distribution (PSD). Mercury intrusion porosimetry (MIP) and nitrogen adsorption/desorption (NAD) methods were used to quantitatively describe the PSD of soil in the range of equivalent pore diameter of 100–0.003 and 0.1–0.001 μm, respectively. The total MIP porosity of Ultisols ranged from 33.0% to 44.9% with a mean value of 36.5%. The soils exhibited three-modal PSDs with peaks at the pore diameter of about 0.01–0.05 μm, 0.1–2 μm, and >70 μm, indicating the heterogeneous nature of the pore system. The ultramicropores (0.1–5 μm) and cryptopores (<0.1 μm) were dominant pore classes representing an average of 35% and 30% of total pore fraction, respectively. Among the different land use types, bare land (BL) had significantly higher cryptopore (0.01–0.1 μm) volume compared with forest land (FL) and orchard land (OL). Higher volume of cryptopores under BL could be attributed to the higher iron oxide and low organic matter contents. The free iron oxide (Fed) and clay contents were positively and significantly correlated with crytoporosity (<0.1 μm) while negatively correlated with ultramicroposity. The pores with 0.001–0.1 μm diameter were mainly attributed to the pores associated with the structure of clay and iron oxides. The ultramicroporosity (0.1–5 μm) increased with increasing soil aggregation index: mean weight diameter (MWD) and geometric mean diameter (GMD). No significant correlation was observed between soil porosity and soil organic matter and macro-, meso-, and microporosity were independent of soil components. Our data suggest that high Fed and clay contents lead to increase <0.1 μm pore volume. The Fed and clay contents played an important role in determining the pore structure of Ultisols.

1. Introduction

Soil pore characteristics are important soil quality indicators. The total volume, size distribution, and shape of soil pore spaces determine many soil processes and functions, such as water storage and transmission, gas diffusivity, microbial activity and soil mechanical resistance to root penetration (Cameron and Buchan, 2006; Munkholm et al., 2012; Strong et al., 2004). Studies demonstrated that better descriptions of soil pore size distribution (PSD) are very helpful for understanding a number of soil processes occurring in soils, such as structural stability, water and solute movement, and organic carbon sequestration (Lipiec et al., 2006, 2012; Pagliai et al., 2004; Six et al., 2004; Strong et al., 2004). Therefore, studies on soil pore characteristics are extremely useful to evaluate soil structure and soil quality.

Soil pore structure is very sensitive to soil management practices and environmental changes. Previous studies indicated that land use, tillage, fertilization, and compaction could alter the total porosity, size distribution and functionality of soil pores and thereby affect the chemical, physical and biological processes in the soils (Bhattacharyya et al., 2006; Cameira et al., 2003; Cassaro et al., 2011; da Costa et al., 2014; Lipiec et al., 2006, 2012). Therefore, changes in pore volume, pore size distribution and/or pore shape pattern have been used to compare effects of conventional and zero tillage, organic matter waste, and land use on soil structure and quality (Cassaro et al., 2011; Deurer et al., 2009; Wairiu and Lal, 2006; Zhou et al., 2012, 2013). Soil tillage and compaction generally decrease soil macroporosity and altered pore size distribution (Cassaro et al., 2011; da Costa et al., 2014; Deurer et al., 2009; Lipiec et al., 2012). This preferential loss of larger pores can potentially change many important soil ecological functions. The quantification of size, shape and continuity of pores can help to understand the effects of management practices and environmental changes in soil quality.

In soil science, many methods like mercury intrusion porosimetry (MIP), nitrogen adsorption/desorption (NAD), X-ray micro-computed tomography (μCT) and soil water retention curve (SWRC) are widely used to characterize soil pore structure (Echeverria et al., 1999; Hajnos et al., 2006; Pires et al., 2008; Sasanian and Newson, 2013). Previous studies have demonstrated that MIP is a useful tool for soil porosity quantification and PSD in a wide range of pore diameter and

* Corresponding author. Tel.: +86 571 88982061.
E-mail address: lusg@zju.edu.cn (S.-G. Lu).

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characterization of PSD in response to soil tillage and fertilization (Cassaro et al., 2011; Dal Ferro et al., 2012), land use types (Deurer et al., 2009; Hajnos et al., 2006; Wairiu and Lal, 2006), and compaction (Lipiec et al., 2012). In some studies the PSD derived from the MIP method was used as a reference for the PSD from the water retention curve (Hajnos et al., 2006). The pore range measured by NAD is from nanometers to tens of nanometers. Therefore, NAD could provide valuable information about nano-scale pore in the soils.

Ultisols widely cover the subtropical and tropical regions of the world and thus presents one of the most common soil types to be used in crop production. The abundant iron oxides in Ultisols determine the pore structure and its response to soil management (Zhang and Horn, 2001; Zhou et al., 2013). However, there is limited information available about the use of MIP for analyzing the PSD of Ultisols, and also little is known about how iron oxides affect the pore structure of Ultisols. In the present work, the MIP was combined with NAD analyses to evaluate the porosity, pore size distribution and pore sizes characteristics of Ultisols. The main objective of this study was to quantitatively describe the soil pore characteristics of Ultisols under different land use and to evaluate the effect of soil constituents (especially iron oxides) on the pore structure of soils.

2. Materials and methods

2.1. Soil samples

A total of 20 Ultisols samples developed on Quaternary red clay were collected from the western part of Zhejinag Province, Eastern China. The soils were classified as typical clayey Plinthudults according to USAD Soil Taxonomy (Soil Survey Staff, 2006). These soils are generally distributed on low hilly areas with a relative elevation of 30–80 m, covering over 10% of total land area of Eastern China (Zhou et al., 2013). The sampling sites were selected based on different land uses. Four land use types, bare land (BL), crop land (CL), orchard land (OL), and forest land (FL), were chosen for the study. CL were covered with maize (*Zea mays*), sesame (*Sesamum indicum*), and soybean (*Glycine max*); OL with orange (*Citrus reticulata Banco*) and tea (*Camellia sinensis (L.) O. Kuntze*), while FL was composed of sparse forest dominated by Chins fir (*Cunninghamia lanceolata (Lamb.) Hook*) and bamboo (*Bambusoideae*). The 3–5 undisturbed soil cores (100 cm^3) at each sampling sites were taken from the 6 to 10 cm layer of soil by inserting steel cylinders gently into the soil. The soil cores were trimmed from both ends, coated with plastic film, and transported to laboratory. Further, 3–5 kg disturbed soil samples were taken from 5 to 15 cm layer for physical and chemical analysis.

2.2. Soil analyses

Undisturbed soil cores were used for analysis of soil bulk density and total porosity (Blake and Hartge, 1986). Soil water contents were determined by oven-drying at 105 °C for 24 h. The bulk density (g cm^{-3}) of the sample was estimated from the mass of the dry soil and the core volume. The total porosity was calculated from the measured bulk density by assuming a particle density of 2.65 g cm^{-3}. The aggregate stability was determined on disturbed soils by the wet sieving method (Kemper and Rosenau, 1986). Briefly, 50 g dried homogenized soil samples were sieved using a set of sieves with opening of 5, 3, 1, 0.5, 0.25, and 0.05 mm. The mass retained on each sieve was weighed, recorded and the percentage mass of each fraction was calculated. Aggregate stability was expressed as mean weight diameter (MWD) and geometric mean diameter (GMD).

The disturbed soil samples were air dried and small aggregates of 0.25–2 mm in size were obtained by dry sieving. These small aggregates were used for PSD analysis by MIP and NAD methods by following specific sample preparation. Another portion of air-dried disturbed soil was ground and passed through a 2-mm sieve for physical and chemical analyses. The analysis was performed according to standard procedure (Zhang and Gong, 2012). Soil particle size distribution was determined by a combination of wet sieving and pipette method. Organic carbon of soil was determined by dichromate oxidation method. The pH of soil was determined potentiometrically with a pH meter in soil-water suspensions (ratio of 1:2.5). Total iron (Fet) was determined on dissolution extracts obtained by acid digestion with a mixture of $HClO_4$:HNO_3:HF. Free iron oxide (Fed) was extracted by dithionite–citrate–bicarbonate (DCB) solution (Mehra and Jackson, 1958) and amorphous iron oxide (Feo) by the acid ammonium oxalate method (Schwertmann, 1973). The iron contents of the extracted solutions were determined colorimetrically.

2.3. Mercury intrusion porosimetry (MIP)

MIP is a widely-used technique for pore structure characterization, especially for the pore size analysis. Mercury intrusion porosimetry measures the volume of mercury forced into a porous sample over a range of applied pressures. Due to its high surface tension, mercury behaves as a non-wetting liquid when in contact with most solids. Consequently, it only enters into pores under applied pressure. The pressure (p) required to intrude into porous material is a function of the contact angle (θ) of mercury, its gas/liquid surface tension (r_{Hg}) and pore radius (r). If the pores are cylindrical then the relationship between pressure (p) and equivalent pore diameter (d) could be determined by Washburn equation:

$$p = 4\gamma_{Hg}\cos\theta/d \quad (1)$$

where p is the external pressure applied in the vacuum chamber, γ_{Hg} is the surface tension of mercury (0.47 N m^{-1}), θ is the contact angle of mercury and soil (140°), and d is the pore diameter (m).

The soil samples were freeze dried in liquid nitrogen and vacuumed for 24 h before mercury intrusion. An AutoPore IV 9510 mercury porosimeter (Micrometrics, USA) was used to determine pore size distribution in the range of equivalent diameter from 100 to 0.003 μm. The equipment operates in step-wise pressure increments in the range from 0.001 to 450 MPa. This wide range allows the detection of diverse soil pore classes along the PSD curve. The results were plotted in two graphical forms: the cumulative pore volume (cm^3 g^{-1}) and logarithmic differentiation dV/dlogd. Computer software attached to the instrument was used to determine the volume of the pores. It has been reported that the soil structure is not affected during the high pressure intrusion during MIP test (Lawrence, 1978).

Pore structure parameters, including porosity, pore surface area, and bulk density, were obtained from the intrusion data directly through the instrument software (AutoPore IV 9500 V1.09). Porosity was derived from the ratio of the total intruded volume of mercury injected at the highest pressure (450 MPa) to the total volume of a sample. Average pore diameter (4 V/A) was obtained by assuming that all pores are right cylinders; thus, when the volume ($V = \pi r^2 L$) is divided by the pore area ($A = 2\pi rL$), the average pore diameter (d) is equal to 4 V/A. The median pore diameter, based on surface area or intrusion volume estimation, stands for the size value at 50% accumulated surface area or 50% accumulated intrusion volume. In order to gain more insight into the pore size distribution of soils, the pores in the soils are divided into 5 size categories: macropores (100–75 μm), mesopores (75–30 μm), micropores (30–5 μm), ultramicropores (5–0.1 μm), and cryptopores (0.1–0.01 μm and 0.01–0.003 μm), according to Cameron and Buchan (2006).

2.4. Nitrogen adsorption/desorption (NAD)

The TriStar II3020 surface area and porosity analyzer (Micromeritics Instruments Co., USA) was used to obtain the nitrogen adsorption/desorption isotherms at standard 77 K. The nitrogen gas used was