Multifractal characterization of pore size distributions measured by mercury intrusion porosimetry

E. Vidal Vázquez[A], R. García Moreno[A], A.M. Tarquis[B], A. Saa Requejo[B], J.M. Mirás-Avalos[A] and **J. Paz-Ferreiro**[C]

[A] Facultad de Ciencias. Universidad de La Coruña- UDC, Spain
[B]CEIGRAM (Centre for Studies and Research on Agricultural and Environmental Risk Management), Universidad Politécnica de Madrid, Spain.
[C]Department of Biological Sciences, Lancaster University, Lancaster, United Kingdom, Email jpaz@udc.es

Abstract
The aim of this work was to assess the multifractal characteristics of pore size distributions measured by mercury injection porosimetry (MIP). Two pairs of soil samples were collected in plots with different topographic position and soil use, with each pair differentiated by distinct proportion of fine particles and organic matter contents. Macropore volume was higher on samples with higher clay and organic matter content. Mass exponent function, singularity spectra and generalized dimension spectra showed that multifractal distribution was a suitable model for mercury injection curves. Multifractal parameters extracted from singularity spectra and generalized dimension spectra reflected the main characteristics of the pore size distributions (PSDs). Therefore, it was concluded that multifractal analysis is useful for distinguishing between different patterns of pore size distributions obtained by Hg injection.

Key Words
Pore-size-distribution, indirect methods, multifractality, texture, organic matter content

Introduction
The pore size distribution (PSD) of a soil depends on the combined effects of texture and structure. The frequency distribution of soil pore sizes controls water and air storage and their transport into the profile. Greenland (1981) distinguished three pore size categories: i) transmission pores (>50 µm) responsible for water flow during drainage, ii) storage pores (50–0.5 µm) retaining most available water and iii) residual pores (<0.5 µm) where chemical reactions occur. These criteria show a rough correspondence with soil hydraulic properties. Frequently, PSDs are obtained by indirect methods, even if they provide little information on pore geometry. The water retention curve is the most widely used method to estimate PSDs. Mercury injection porosimetry (MIP) also has been recognized as an useful tool for characterizing the intra-aggregate porosity, from about 100 to 0.005 µm, which includes the so-called textural pore domain and the smaller classes of the structural compartment (e.g. Fiès, 1992).

Fractal models have been widely applied in soil science. Pore size distributions measured by MIP have been proven to be fractal in a limited range of scales (Bartoli *et al*., 1991). Interest has recently turned to multifractal analysis of porous media. The use of multifractal tools to understand soil porosity means that the PSD can be viewed as a singular statistical distribution and it is reasonable to explain it as a multifractal measure. Several authors carried out multifractal studies of PSDs obtained from image analysis (e.g. Posadas *et al*., 2003; Grau *et al*., 2006). Multifractal analysis of MIP data sets (Vidal Vázquez *et al*., 2008) is more recent. The aim of this study was to evaluate the performance of multifractal analysis for distinguishing between PSDs of soils with differences ~~i~~n both textural composition and organic matter content.

Methods
Two loam-silty soils were selected from Mabegondo (Coruña province) and Raigoso (Orense province), both located in Northwestern Spain, on the basis of differences in clay, silt and organic matter content. These soils will be next referred to as soil 1 and soil 2, respectively. Parent material was basic schist in Mabegondo and quaternary sediments in Raigoso. The soils were classified as Umbrepts according to the US Soil Taxonomy. Two different soil uses, grassland and cultivated were sampled on each site. Grassland plots were located at the footslope and exhibited hydromorphic features, whereas cropland plots were at the backslope.

Pore size distributions were estimated by MIP, which enables the measurement of both the pressure required to force mercury into the voids of a dry soil sample and the intruded Hg volume at each pressure. The pressure required to force Hg into soil pores is a function of the contact angle, size, and geometry of pores and surface tension. If the pores are cylindrical, then the relation between pressure, P (expressed in Pa), and equivalent pore diameter, d (expressed in mm), is given by the Young-Laplace equation:

$$P = -4\gamma\cos\theta/d \qquad (1)$$

where θ is the mercury-solid contact angle and γ is the surface tension of mercury. The values of θ and γ were taken as 140º and 0.480 Nm^{-1}, respectively (Fiès, 1992). The PSDs were determined using a "Thermaquest Pascal 440" porosimeter. The equipment operates from 10 kPa to 300 MPa, equivalent to pores with diameter, d, ranging from 150 μm to 0.005 μm, respectively.

Multifractal analysis of PSDs supported on an interval I = [a,b] with a diameter L requires a set of different boxes or subintervals of I with equal length. A common choice is to consider dyadic scaling down (e.g. Vidal Vázquez *et al.*, 2008), which means successive partitions of the support in k stages (k=1,2,3…) that generate a number of cells $N(\delta) = 2^k$ of characteristic size length, $\delta = L \times 2^{-k}$, covering the initial interval I. The size interval of the experimental MIP curves ranged from 0.005 to 100 μm. Following this approach, the probability mass distribution, $p_i(\delta)$, for each box was estimated as a proportion according to:

$$p_i(\delta) = \frac{N_i(\delta)}{N_t} \qquad (2)$$

where $N_i(\delta)$ is the pore volume of the i^{th} box and N_t is the total volume of the system. To analyze the multifractal spectrum of the probability mass function the moment method was used which involves three functions: mass exponent, τ_q, singularity spectrum, f(α), and generalized dimension, D_q. First, the partition function $\chi(q,\delta)$ was estimated from the $p_i(\delta)$ values. The partition function scales with the box size, δ, as:

$$\chi(q,\delta) \propto \delta^{-\tau(q)} \qquad (3)$$

where τ(q) is the mass exponent or scaling function of order *q*. For multifractal measures, the probability mass function, $p_i(\delta)$, also scales with the box size, *δ*, as:

$$p_i(\delta) = \delta^{\alpha_i} \qquad (4)$$

where α_i is the *Hölder* or singularity exponent, characterizing the scaling property peculiar to each i^{th} box. On the other hand, the number $N_\delta(\alpha)$ of boxes of size δ, where the probability has singularity exponent values between α and $\alpha_i + d\alpha$, obeys a power law as:

$$N(\alpha) \propto \delta^{-f(\alpha)} \qquad (5)$$

where f(α) is a scaling exponent of the boxes with a common α, called the singularity exponent. A plot of f(α) versus α is called the singularity spectrum. Following Chhabra *et al.* (1989), the functions α and f(α) can be determined by Legendre transformation as:

$$\alpha(q) = \frac{d\tau(q)}{dq} \quad \text{and} \quad f(\alpha) = \alpha(q)q - \tau(q) \qquad (6)$$

Multifractal sets can also be characterized by their spectrum of generalized dimension, D_q, which can be introduced (for all $D_q \neq 1$) by the following scaling relationship:

$$D_q = \lim_{\delta \to 0} \frac{1}{q-1} \frac{\log[\chi(q,\delta)]}{\log \delta} \qquad (7)$$

For the particular case where *q*=1 equation (7) becomes indeterminate, so D_q is estimated by l´Hôpital's rule. The generalized dimension, D_q, is related to the other sets of multifractal exponents. Hence, D_q, is obtained from the relationship with mass exponent, τ_q, which can be defined as:

$$\tau(q) = (1-q)D_q \qquad (8)$$

The generalized dimensions, D_q for *q* = 0, *q* = 1 and *q* = 2, are known as the capacity, the information (Shannon entropy) and correlation dimensions, respectively.

Results

Table 1 lists general properties of the studied soil samples. Soil reaction was very strongly acidic in Mabegondo and extremely acidic in Raigoso. Organic matter content of the soil samples under cropland was lower than under grassland in the two soils. Also differences in finer particles between soil uses were large with greater silt and clay values under grassland than under cultivated land.

Table 2 shows the partial porosity values measured by MIP, for the equivalent diameter range from 100 to 0.005 μm (i.e. the total cumulative intrusion size range) and also for the 100 to 50 μm, 50 to 0.5 μm and 0.5 to 0.005 μm subintervals. On average the Hg volume injected over pore diameters between 100 and 0.005

μm was higher under grassland than under cultivated land and for soil 2 compared to soil 1. The smaller porosity of aggregates sampled in cultivated plots is an expected result owing to differences in silt + clay and organic matter content. Each pair of samples showed great volume differences in the pores size class 100-0.5 μm, whereas residual pore volume (< 0.5 μm) was little affected by soil use and fine particle content.
The three multifractal functions mass exponent, τ_q, (Figure 1) singularity spectrum, f(α), and generalized dimension, D_q (Figure 2) will be shown to be useful for describing multifractality. Mathematically, the multifractal property can be completely determined only by the entire fractal spectrum functions. Some characteristic values of these functions, however, portray the main characteristics of multifractality.

Table 1. Composition of samples of the two studied soils under grassland and cropland.

Soil	Soil use	pH	O.M. (g kg^{-1})	Sand (g kg^{-1})	Silt (g kg^{-1})	Clay (g kg^{-1})
1 Mabegondo	Grassland	5.0	75.5	111	680	208
1 Mabegondo	Cultivated	5.1	34.7	235	601	164
2 Raigoso	Grassland	4.0	79.6	125	665	210
2 Raigoso	Cultivated	4.3	20.4	204	625	171

A comparison between the moment scaling function, τ_q, of all the studied PSDs and the scaling function of the simulated monofractal type is shown in Figure 1. The slope of the τ_q functions for q < 0 were different from that of q > 0, which means a multiple scaling nature, so that low and high density regions of the studied variable, the soil porosity, scale differently.

Table 2. Pore volume in different diameter size classes of the two studied soils. Total pore size is 100-0.005 μm.

Soil	Soil use	100-0.005 μm (cm^{3}kg^{-1})	100-50 μm (cm^{3}kg^{-1})	50-0.5 μm (cm^{3}kg^{-1})	<0.5 μm (cm^{3}kg^{-1})
1 Mabegondo	Grassland	326	5	219	102
1 Mabegondo	Cultivated	272	5	155	112
2 Raigoso	Grassland	502	22	339	141
2 Raigoso	Cultivated	365	7	222	136

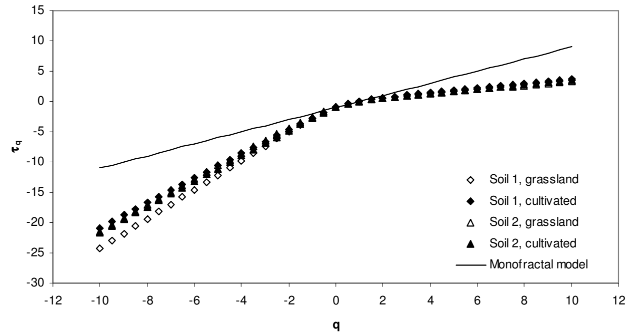


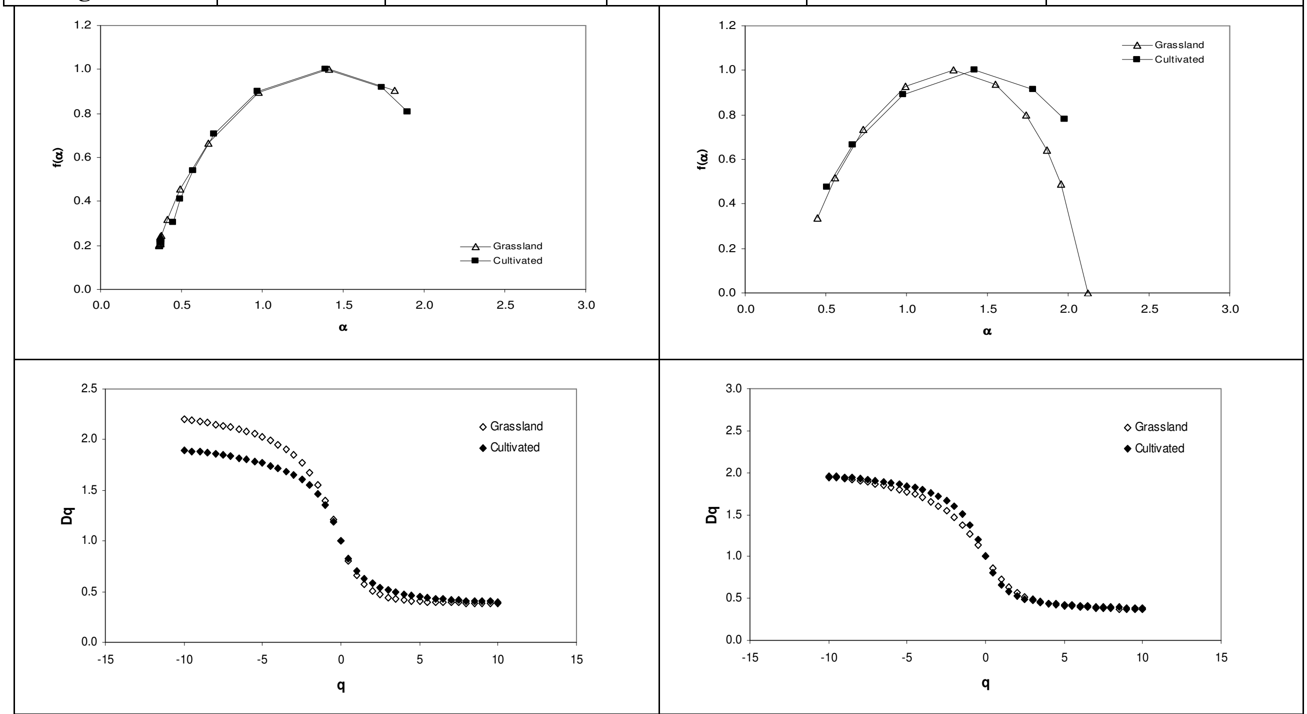
Figure 1. Mass exponent function τ_q, versus *q* for the studied pore size distributions.

Singularity spectra, f(α) versus α, shown on Figure 2 have a strongly marked asymmetric concave down parabolic shape, also indicative of multifractal behavior. These are a powerful tool for charcaterize the simililarity and/or differences between the scaling properties of the measure and also enable us to examine the local property of the studied variable. The wider the spectrum (i.e. the greater the α_{max}-α_{min} value) the higher is the heterogeneity in the local scaling indices of the variable and vice versa. Moreover, dominance of extremely high or extremely low data values is related to the left- (q>>1) and right-hand (q<<-1) sides of the f(α) spectrum, respectively.
The generalized dimension, D_q, would be a constant in the case of scale-invariant distributions but changes with *q* for multifractal measures, so that $D_0 > D_1 > D_2$. The capacity or box-counting dimension, D_0, was not significantly different from 1.00, which correspond to an Euclidean support. Results for D_1 and D_2 (Table 3) clearly support the hypothesis of singular behavior of relative pore volume distributions. The entropy or information dimension, D_1, of the individual PSDs varied between 0.757 and 0.866 for the initial surface and between 0.656 and 0.727, whereas D_2 ranged from 0.508 to 0.580. The R^2 fits leading to a Dq spectrum were higher than 0.925 in the range of q moments -10 < q <10. Results of the generalized dimension analysis are

in agreement with observations from the mass exponent function τ_q presented above.

Table 3. Mean values and standard deviation of selected multifractal parameters from D_q spectra.

Soil	Soil use	D_1	D_2	D_{-10}	D_{10}
1 Mabegondo	**Grassland**	0.656 ± 0.024	0.508 ± 0.012	2.197 ± 0.625	0.386 ± 0.001
1 Mabegondo	**Cultivated**	0.700 ± 0.036	0.580 ± 0.059	1.896 ± 0.452	0.401 ± 0.056
2 Raigoso	**Grassland**	0.727 ± 0.043	0.569 ± 0.056	1.948 ± 0.235	0.367 ±0.072
2 Raigoso	**Cultivated**	0.663 ± 0.075	0.525 ± 0.102	1.961 ± 0.483	0.385 ± 0.101



Soil nº 1 (Mabegondo)	**Soil nº 2 (Raigoso)**

Figure 2. Singularity spectra f(a) and generalized dimensions, D_q, versus q for the studied PSDs.

Conclusion
Mercury intrusion analysis showed an increase of storage and transmission pore categories with increasing clay + silt and organic matter contents, whereas no changes were detected in residual porosity. The scaling properties of PSDs measured by MIP could be fitted reasonably well with multifractal models. Multifractal analysis allowed discrimination between different patterns of pore size distributions.

Acknowledgements
This work was supported by Spanish Ministry of Education and Science (project AGL2005-08219-C02-01/HID) and by Xunta de Galicia (project INCITE08PXIB 162169PR).

References

Bartoli F, Philippy R, Doiresse M, Niquet S, Dubuit M (1991). Structure and self-similarity in silty and sandy soils: the fractal approach. *Journal of Soil Science* **42,** 167-185.

Grau J, Méndez V, Tarquis AM, Díaz MC, Saa A (2006) Comparison of gliding box and box-counting methods in soil image analysis. *Geoderma* **134,** 349-359.

Fiès JC (1992). Analysis of soil textural porosity relative to skeleton particle size, using mercury porosimetry. *Soil Science Society of America Journal* **56,**1062-1067.

Greenland DJ (1977). Soil damage by intensive arable cultivation. Temporary or permanent? *Philosophical Transactions of the Royal Society Series B* **281,** 193-208.

Posadas AN, Giménez DD, Quiroz R., Protz R. (2003) Multifractal characterization of soil pore systems. *Soil Science Society of America Journal* **67,** 1361-1369.

Vidal Vázquez E, Paz Ferreiro J, Miranda JGV, Paz González A (2008) Multifractal analysis of pore size distributions as affected by simulated rainfall. *Vadose Zone Journal* **7,** 500-511**.**

1 – 6 August 2010, Brisbane, Australia. Published on DVD.