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Fractal analysis of soil water hysteresis as influenced by sewage sludge application

G. Ojeda [a,*], E. Perfect [b], J.M. Alcañiz [a], O. Ortiz [a]

[a] *Centre de Recerca Ecológica i Aplicacions Forestals (CREAF), Facultat de Ciències, Universitat Autónoma de Barcelona, 08193 Bellaterra (Barcelona), Spain*

[b] *Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN 37996-1410, USA*

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Abstract

The impact of three types of surface applied sewage sludge from the same lot (fresh, composted, and thermally dried) on the water retention properties of a loam soil (*Udic Calciustept*) and a loamy sand soil (*Typic Haplustalf*) from central Catalonia (NE Spain) was investigated using fractal analysis. First, we proposed a composite fractal model that covers both the low and high suction regimes. This model has four fitting parameters: D_1 (the pore-solid fractal dimension), D_2 (the surface fractal dimension), A_1 (a compound parameter that includes D_1, the density of water, bulk density, particle density, and the air/water displacement suction), and A_2 (a compound parameter that includes D_2, and the critical suction and water content separating the low and high suction regimes). This model was fitted to the main wetting and drying branches of soil water retention curves obtained from small-disturbed samples using the chilled mirror dew point method. The equation fitted the data extremely well with adjusted R^2 values ≥ 0.99 ($p < 0.0001$). Analysis of variance (ANOVA) was performed on the resulting parameter estimates. Few significant effects were observed for the loamy sand soil. In contrast, all of the model parameters, except D_1, were significantly affected by hysteresis and/or the sludge treatments for the loam soil. Values of A_1 and A_2 from the main drying branch were significantly higher than corresponding estimates from the wetting branch. This trend was reversed for D_2, indicating that pore surfaces are smoother after wetting, as compared to initially dry surfaces. The fresh, composted and thermally dried sludge treatments all significantly increased the A_1 parameter relative to the untreated loam soil, possibly by decreasing bulk density. The fresh and thermally dried sludge treatments also significantly increased the A_2 parameter. All three sludge types increased D_2 relative to the control when this parameter was determined from the main wetting branch of the water retention curve. In contrast, D_2 estimated from the main drying branch was not influenced by any of the sludge treatments. These analyses indicate that the effects of sewage sludge on hysteresis of the soil water retention curve were still present 2 years after surface application in the case of the loam soil.

1. Introduction

Continuous human population growth produces a great variety of organic wastes, one of which is sewage sludge. Application of sewage sludge to soil solves two problems: waste disposal and increased agricultural production (Aggelides and Londra, 2000). Controlled application of organic wastes can be an inexpensive initial source of organic matter and plant nutrients for soil rehabilitation purposes (Sopper, 1993). Application of sewage sludge to a degraded soil facilitates the establishment of a vegetation cover. Besides protecting the soil from erosion, this can stimulate C and N cycling, thereby reducing pollution by runoff and leaching (Albaladejo et al., 2000). As a result, this activity is becoming increasingly popular as a technical solution

* Corresponding author. Tel.: +34 93 5811465; fax: +34 93 5814151.
E-mail addresses: g.ojeda@creaf.uab.es (G. Ojeda), eperfect@utk.edu (E. Perfect).

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for restoring degraded soils and for encouraging the re-establishment of vegetation cover (Düring and Gäth, 2002).

It is generally acknowledged that organic matter has a positive effect on soil structure. Therefore, sewage sludge applications should improve soil aggregation (Albiach et al., 2001). Because of the biodegradability of sludges, however, it is uncertain how long such improvements last. The addition of sewage sludge to a degraded landscape results in a temporary modification of soil physical properties, and decreased risk of erosion (Sort and Alcañiz, 1999a; Bresson et al., 2001). These changes can occur as a result of improvements in bulk density, aggregate stability, and/or soil water retention (Sort and Alcañiz, 1999a; Aggelides and Londra, 2000; Caravaca et al., 2001).

Many authors have reported reductions in soil bulk density with increasing organic carbon and nitrogen levels (Schjonning et al., 1994; Mapa and Gunasena, 1995; Haynes and Naidu, 1998; Halvorson et al., 1999; Rawls et al., 2003). Organic matter can increase the cohesion of aggregates through the binding of mineral particles by organic polymers or through physical enmeshment of particles by fine roots and fungi (Tisdall and Oades, 1982; Dorioz et al., 1993; Chenu et al., 1994; Chenu et al., 2000). Organic matter can also decrease the wettability of soil aggregates, slowing down their wetting rate, and thus the extent of slaking (Chassin, 1979; Sullivan, 1990). Chenu et al. (2000) found that when soil organic carbon contents increase, the contact angle increases.

Soil water retention is a specific characteristic of each soil, being the result of several interacting factors, such as percentage and mineralogy of the clay fraction, percentage of organic matter, and soil structure/bulk density (Melo et al., 2004). The energy required for removing water from a hydrophilic soil matrix increases continuously with decreasing saturation. At intermediate-to-high saturations the water is held by capillary forces (Nitao and Bear, 1996). At low saturations, most of the water occurs in thin films which control flow and evaporative losses (Truong and Wayner, 1987; Nitao and Bear, 1996). There is evidence that adsorbed water films may have different transport and thermodynamic properties from those of regular capillary water (Parker, 1986; Nitao and Bear, 1996).

Many authors have reported increases in soil water retention by sewage sludge amendments (Kumar et al., 1985; Illera et al., 1999; Aggelides and Londra, 2000; Tsadilas et al., 2005). According to Rawls et al. (2003) the effect of organic carbon on soil water retention is meditated mainly through changes in bulk density, and its magnitude depends upon soil texture. Vigerust (1983), Clapp et al. (1986), and García-Orenes et al. (2005) stated that reductions in bulk density due to biosolid amendments were related to increases in soil aggregation and stability, as well as to the addition of less dense material. De Jong (1983) experimented with disturbed soil samples and found that increases in organic matter content gave higher water contents at all suctions investigated. Similar observations were made by several other authors cited by Rawls et al. (2003).

The relationship between the volumetric water content of a soil, θ, and its energy state or suction, ψ, differs depending upon whether the soil is wetting or drying; this path dependence is know as hysteresis. The $\theta(\psi)$ relationship can be characterized by a main drying curve and a main wetting curve. The water content at a given suction may lie anywhere between these two envelopes depending upon the sequence of wetting/drying events (Gardner et al., 1999; Whitmore and Heinen, 1999). Thus, a family of scanning loops, bounded by the main wetting and drying curves, is necessary to fully describe the $\theta(\psi)$ relationship (Mitchell and Mayer, 1998). Hysteresis in the water retention curve influences soil water movement, especially when frequent wetting and drying cycles occur (Milly, 1982; Hopmans and Dane, 1986; Feddes et al., 1988).

Hysteresis arises mainly from differences in the process of emptying and filling individual pores (Braddock and Parlange, 2001). Such differences can be caused by incomplete connectivity of pore spaces, shrink–swell phenomena, thermal gradients, the presence of entrapped air (Feddes et al., 1988), the "ink bottle" capillary effect (pore necks or throats prevent complete drainage of soil pores), and contact angle hysteresis. Araujo et al. (1995) and Ustohal et al. (1998) report differences in contact angles for wetting and drying conditions, with advancing menisci having a greater contact angle than receding ones.

At low water contents, the distribution of a wetting fluid on a solid substrate is strongly influenced by the geometry of the underlying matrix (Sweeney et al., 1993). The effects of surface roughness on wetting behavior can be quantified in terms of contact angle (Morrow, 1975; Sweeney et al., 1993). de Gennes (1985a) identified three major causes of contact angle hysteresis: (i) surface roughness, (ii) chemical contaminants or heterogeneities on the solid surface, and (iii) solutes in the liquid (surfactants, polymers, etc.) which may deposit a film on the solid surface. The presence or absence of such films can lead to hysteretic effects.

Land application of sludge's can add a variety of organic chemicals to the soil–water system (Abu-Zreig et al., 2003). Detergents containing anionic and non-ionic surfactants account for the highest concentrations of organic chemicals found in sewage sludge (Wild et al., 1990; Abu-Zreig et al., 2003). Non-ionic surfactants are generally found in concentrations that are between five and ten times lower than those of anionic surfactants (Madsen et al., 1998; Kuhnt, 1993). In spite of their biodegradability, residual concentrations of surfactants have been detected in soils (Gejlsbjerg et al., 2003). These chemicals may influence hysteresis in sludge-amended soils. For example, Abu-Zreig et al. (2003) found that application of anionic surfactants to loam and loamy sand soils resulted in an increase in their contact angle and sorptivity.

The effects of sewage sludge application on hysteresis of the water retention curve have not been investigated previously. In this study, fresh, composted, and thermally dried sewage sludge from the same wastewater treatment plant was surface applied at a moderate rate (10 t ha^{-1} of dry matter) to field plots of loamy and loamy sand soils for the purpose of land rehabilitation. The main objective of this paper is to assess the effects of the different types of sewage sludge 2 years after application, on hysteresis of the water retention curve as related to the organic C and total N contents of both soils. To facilitate this objective we introduce a new-segmented fractal model to quantify the main wetting and drying branches of the soil water retention curve. This model is described below.

2. Model development

2.1. Low suction regime

In the low suction regime, pores empty and fill according to their effective neck and body sizes as described by the Young–Laplace capillary equation. Several fractal and prefractal models have been used to describe this regime (e.g. Tyler and Wheatcraft, 1990; Rieu and Sposito, 1991; Perfect et al., 2004). Recently Bird et al. (2000) proposed a new model for the low suction regime based on a pore-solid fractal formulation:

$$\left(\frac{\theta}{\theta_s}\right) = \left(\frac{\psi}{\psi_e}\right)^{D_1-3} \quad (1)$$

where θ is volumetric water content, θ_s is the water content at saturation, ψ is suction, ψ_e is the air/water entry suction, and D_1 is the pore-solid fractal dimension. Eq. (1) can be seen to be consistent with the empirical Brooks and Corey (1964) (assuming zero residual saturation) and Campbell (1974) power law functions that have been widely used to predict the water retention properties of soils.

Eq. (1) can be reformulated in terms of the gravimetric water content, w, as follows. The gravimetric and volumetric water contents are related by:

$$\theta = \frac{w\rho_b}{\rho_w} \quad (2)$$

where ρ_b is the soil bulk density and ρ_w is the density of water. Substituting Eq. (2) into Eq. (1) and assuming $\rho_w = 1$ g cm^{-3}, we have:

$$w = \frac{\theta_s}{\rho_b}\left(\frac{\psi}{\psi_e}\right)^{D_1-3} \quad (3)$$

or

$$w = A_1\psi^{D_1-3} \quad (4)$$

where

$$A_1 = \frac{\theta_s}{\rho_b\psi_e^{D_1-3}} = \left(1-\frac{\rho_b}{\rho_s}\right)\frac{1}{\rho_b\psi_e^{D_1-3}} = \left(\frac{1}{\rho_b}-\frac{1}{\rho_s}\right)\psi_e^{3-D_1} \quad (5)$$

and ρ_s is the particle density.

2.2. High suction regime

It is well established that surface irregularity can be quantitatively described in terms of fractal geometry using the surface fractal dimension, D_2 (Mandelbrot, 1982; Garcia-Ayuso et al., 1998). This parameter provides information about the surface morphology of pore structures. Furthermore, it may also influence the mechanics of phase separation (Mandelbrot, 1982; Katsaros et al., 1997). Surfaces can act as a mould or force field, thereby imposing on any adsorbate, intermolecular conditions that are intermediate between those in two- and three-dimensional assemblages. This suggests that the underlying surface irregularity should be naturally described by a parameter that takes a value between two and three (Pfeifer and Avnir, 1983). When $D_2 \rightarrow 3$ the surface will be highly irregular, with many asperities in pore walls that can trap capillary water. In contrast, when $D_2 \rightarrow 2$ the surface is smooth and less tortuous, so that water molecules are restricted to thin films (Pfeifer and Obert, 1989; Garcia-Ayuso et al., 1998).

At high suctions most soil pores will be partially desaturated. Under such conditions, water will be present as both trapped capillary structures and thin films, which provide hydraulic connectivity (Toledo et al., 1990), i.e.

$$\theta_h = \theta_t + \theta_f \tag{6}$$

where θ_h is the maximum volumetric water content associated with the high suction regime, θ_t is that component trapped in capillary structures, and θ_f is the volume fraction present in thin films. The trapped capillary phase can occur in the asperities of pore walls, in pendular rings between grains, in bridges between grains separated by small gaps, in pore throats between two larger (drained) pores, or in more complicated structures formed by some combination of these morphologies (Toledo et al., 1990; Bryant and Johnson, 2003; Turner et al., 2004).

de Gennes (1985b) showed that the water retention function for capillary structures trapped within the asperities of a surface fractal is given by:

$$\left(\frac{\theta_t}{\theta_h}\right) = \left(\frac{\psi}{\psi_c}\right)^{D_2-3} \tag{7}$$

where ψ_c is the suction that separates the region dominated by complete pore filling/emptying from that dominated by partial pore filling/emptying. If one assumes that the total volume of water in thin films is small compared to that trapped in capillary structures, one can write (Toledo et al., 1990):

$$\frac{\theta}{\theta_h} \approx \frac{\theta_t}{\theta_h} \tag{8}$$

It then follows from Eq. (7) that:

$$\left(\frac{\theta}{\theta_h}\right) \approx \left(\frac{\psi}{\psi_c}\right)^{D_2-3} \tag{9}$$

Eq. (9) has been successfully tested on partially saturated porous media by Davis (1989) and Toledo et al. (1990). Although it has exactly the same form as Eq. (1) it is important to note that the parameters in the two models are quite different.

Repeating the steps outlined for the low suction regime, it is also possible to express Eq. (9) gravimetrically, i.e.

$$w = A_2\psi^{D_2-3} \tag{10}$$

where

$$A_2 = \frac{\theta_h}{\rho_b}\psi_c^{3-D_2} = w_c\psi_c^{3-D_2} \tag{11}$$

and w_c is the maximum gravimetric water content associated with the high suction regime. Note that A_1 and A_2 are constants with different physical meanings, depending on which suction regime dominates the wetting or drying cycle.

2.3. Combined model

Based on Eqs. (4), (5), (10), and (11) we propose the following segmented fractal model to take into account both the low and high suction regimes:

$$w = A_1\psi^{D_1-3}; \qquad \psi_e \le \psi \le \psi_c \tag{12a}$$

$$w = A_2\psi^{D_2-3}; \qquad \psi_c \le \psi \le \infty \tag{12b}$$

Eqs. (12a)/(12b) indicates that the water retention curve is comprised of two distinct domains separated by the critical suction, ψ_c. Setting $\psi = \psi_c$ in both Eqs. (12a) and (12b), equating the resulting expressions, and then solving for ψ_c yields the following definition of the critical suction:

$$\psi_c = \left(\frac{A_1}{A_2}\right)^{\left(\frac{1}{D_2-D_1}\right)} \tag{13}$$

Since $A_1 \ge A_2$ it is possible to distinguish four cases from Eq. (13):

(i) if $A_1 = A_2$ and $D_1 = D_2$, then ψ_c does not exist
(ii) if $A_1 = A_2$ and $D_1 \ne D_2$, then $\psi_c = 1$ MPa
(iii) If $A_1 > A_2$ and $D_2 > D_1$, then $\psi_c > 1$ MPa
(iv) If $A_1 > A_2$ and $D_2 < D_1$, then $\psi_c < 1$ MPa

In case (i) the curve is symmetrical and the relationship between w and ψ can be described by a single power law model with no break point. For cases (ii), (iii), and (iv) a break point exists, and the relationship between w and ψ is described by a dual power law model.

Millán and González-Posada (2005) proposed and tested a similar segmented fractal model for the soil water retention curve. However, they worked with θ rather than w, and only investigated the main drying branch. They also linearized their model by log-transformation. Furthermore, they treated the critical suction as an independent fitting parameter, resulting in a 5-parameter model. This is not necessary since Eq. (13) shows that ψ_c is defined by the other parameters in the model. In contrast to Millán and González-Posada (2005) we used a 4-parameter model, Eqs. (12a)/(12b), and then calculated ψ_c from the best estimates of A_1, A_2, D_1, and D_2 using Eq. (13). Hysteresis was evaluated by statistically comparing the parameter estimates obtained for the main wetting and drying branches of each water retention curve.

3. Materials and methods

3.1. Experimental sites

Two field sites (El Puig and La Vallmitjana) with contrasting soil types but similar climatic conditions were chosen in the center of Catalonia, Spain (Taradell municipality). The soils at El Puig are derived from marl, and are rich in carbonates. The A horizon contains a moderate amount of well-stabilized organic matter. The mineralogy of the clay fraction is dominated by illite and calcite, with no detectable amount of smectites present. The El Puig soils are classified as *Udic Calciustepts* (Soil Survey Staff, 1998). The soil types at La Vallmitjana are derived from conglomerates and sandstone, and have a slightly acidic pH. They contain relatively little organic matter and are classified as *Typic Haplustalfs* (Soil Survey Staff, 1998). Mica quartz and illite are the dominant clay minerals at this site, with some smectites present in the Bt horizon.

This study focussed on the A horizons of both soils. Table 1 shows the main physico-chemical properties of this horizon. Because of the differences in texture, we will refer to the El Puig and La Vallmitjana soils as loam and loamy sand, respectively, from now on.

The experimental plots were located on hillsides with a mean slope of 16% (Ojeda et al., 2003). Natural vegetation (scrub) was killed by mechanical crushing just before of application of the sewage sludge's. The resulting debris was left on the soil surface at La Vallmitjana, while at El Puig it was removed leaving the soil surface bare. The A horizons of both soils are well drained and accumulation of surface water was not possible due to topographic conditions. Soils were seeded without tillage with a mixture of *Lolium perenne*, *Dactylis glomerata* and *Festuca arundinacea* in order to introduce plants good for grazing.

Table 1
Physical and chemical properties of <2 mm fraction of the two soils studied

Property	La Vallmitjana	El Puig
Coarse sand (2–0.2 mm) (%)	68.31	4.85
Fine sand (0.2–0.05 mm) (%)	18.0	29.46
Silt (0.05 mm–0.002 mm) (%)	5.93	49.22
Clay (<0.002 mm) (%)	7.77	16.48
Texture	Loamy sand	Loam
pH (H_2O 1 : 2.5)	7.1	8.05
$CaCO_3$ (%)	0.0	27.4

Mean values for 0–20 cm depth samples from experimental plots (modified from Ojeda et al., 2003).

Table 2
Physicochemical properties of the three types of sewage sludge added to the surface of experimental plots (from Ojeda et al., 2003)

Property	Units	Fresh sludge (F)	Thermal sludge (T)	Composted sludge (C)
Dry matter	%	20.27	84.69	66.48
Loss on ignition at 560 °C	g kg^{-1}	668.9	674.6	643.0
Oxidize C	g kg^{-1}	489.8	497.9	427.4
Total N (Kjeldahl)	g kg^{-1}	46.6	44.5	33.6
C/N		10.5	11.2	12.7
Total P	g kg^{-1}	19.1	17.9	15.6
pH_w		8.3	7.0	7.35
E.C. (saturated paste) at 25 °C	dS m^{-1}	1.80	5.28	5.84
Total Cu	mg kg^{-1}	749.2	743.6	786.3
Total Zn	mg kg^{-1}	885.2	800.7	995.0
Total Cd	mg kg^{-1}	3.63	3.59	4.40
Total Pb	mg kg^{-1}	73.6	75.5	89.9
Total Ni	mg kg^{-1}	42.6	46.0	42.2
Total Cr	mg kg^{-1}	50.62	88.5	51.7
Total Hg	mg kg^{-1}	2.6	2.7	2.4

3.2. Sewage sludge applications

Three sludge treatments derived from the same batch of fresh anaerobically digested sewage sludge (20% dry matter) were applied to the soil plots in surface applications at both sites. The treatments were: fresh sludge (F), composted sludge (C), thermally dried sludge (T), and a control with no sludge (O). Detailed information about the properties of the different sludge treatments is given in Table 2. The biosolids were applied using available agricultural machinery: a seed drill for the composted and thermally dried sludge, and a manure spreader for the fresh sludge. The application rate was 10 t ha^{-1} (dry matter), which is equivalent to approximately 50 t ha^{-1} of fresh sludge, 14 t ha^{-1} of composted sludge, and 11 t ha^{-1} of thermally dried sludge. Heavy metal inputs were lower than the maximum annual limit values specified in Directive 86/278/EEC (European Council, 1986).

3.3. Soil sampling

In April 2001, 32 experimental plots (20-m long × 5-m wide) were established at the two sites. At El Puig there were three replications of the four sludge treatments (i.e., 12 plots), while at La Vallmitjana there were five replications of the four sludge treatments (i.e., 20 plots). Three soil cores (10 cm in diameter) were collected from the 0–5 cm depth of each plot in late May of 2003 at the two sites. In the laboratory, soil was extracted from the cores, pooled, air-dried, and passed through a 2-mm sieve to give 32 disturbed samples. The mean gravimetric water contents of the samples after air drying and sieving were 1.6% for the loam, and 1.3% for the loamy sand.

3.4. Organic carbon and nitrogen contents

Total organic carbon content (oxidizable carbon) was measured by the wet oxidation method. Total nitrogen content was measured by sulphuric digestion with a TECATOR 1015 block and a Büchi K-314 distiller using the Kjeldhal method. Both measurements were performed in triplicate for each field plot.

3.5. Water retention measurements

The main wetting and drying branches of the water retention curve were measured in the laboratory using a WP4 Dew Point PotentiaMeter (Decagon Devices, Inc. Pullman, WA). For the wetting curves, seven sub-samples of approximately 1 g of air-dry soil from each plot sample were oven dried at 105 °C for 24 h, and placed in sample cups (40 mm diameter × 10 mm high). One gram of air-dry soil resulted in a monolayer of aggregates that completely covered the bottom of the sample cups as recommended by the manufacturer. Each sub-sample was vapor wetted for a different length of time using an ultrasonic humidifier (Model 693-12/809996, Sunbeam Products Inc., Hattiesburg, MS). Wetting up times of 10, 15, 20, 30, 40 50, and 60 s were chosen to produce a series of approximately equally spaced suctions within the operating range of the WP4 (i.e. ~0.1–40 MPa). After wetting up, the samples were allowed to equilibrate for approximately 12 h. The suction was then measured with the WP4 instrument. At the end of each WP4 measurement, the samples were again oven dried at 105 °C for 24 h, and values of

Table 3
Organic carbon, nitrogen and C/N ratio for the different treatments (O = control; C = composted sludge; F = fresh sludge; T = thermally dried sludge) on both soils

Site	Sludge	Total Org. C (%)	Total N (%)	C/N
El Puig	O	0.9^a	0.06^a	15.6^a
	C	2.0^b	0.17^b	12.5^a
	F	1.8^b	0.17^b	10.8^a
	T	1.6^b	0.15^b	10.4^a
La Vallmitjana	O	1.8^a	0.10^a	18.3^a
	C	2.2^a	0.15^a	14.9^a
	F	3.1^b	0.22^a	16.2^a
	T	2.3^a	0.15^a	15.4^a

The same superscript letter within a column and site are not significantly different at $p<0.05$.

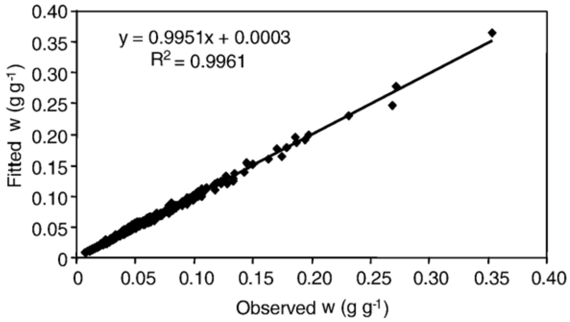

Fig. 1. Fitted gravimetric water contents from best fits of Eqs. (12a)/(12b) vs. observed values for both soils ($n=667$).

w were calculated. Seven paired measurements of w (gravimetric water content) and ψ (suction) were obtained in this way for each wetting branch.

For the drying curves approximately 1 g of air dry soil from each plot sample, was placed in a sample cup (sample and sample cup previously weighed) and saturated by capillarity for 6 h using two bands of filter paper in contact with a free water table approximately 5 mm above the soil surface. A balance and the WP4 Dew Point PotentiaMeter were then used to record w and ψ periodically over time, as the sample dried by evaporation (Perfect et al., 2004). Approximately 15–20 paired measurements of w and ψ were obtained in this way for each drying branch.

3.6. Statistical analyses

Eqs. (12a)/(12b) was fitted to the soil water retention data by segmented non-linear regression analysis with the break point, ψ_c, specified according to Eq. (13).

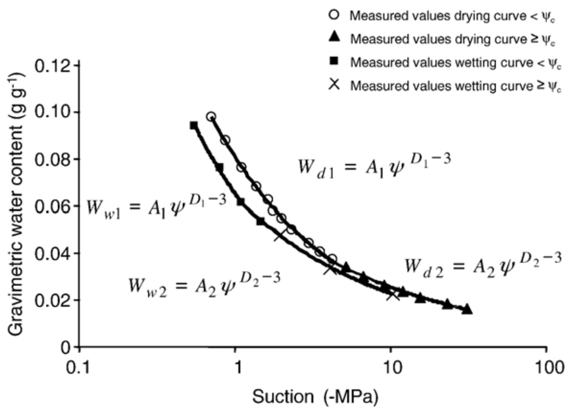

Fig. 2. Example of the segmented fractal model used to fit the main drying and wetting branches of the water retention curve applied to a sample from the loam soil (subscript d: drying state; w: wetting state; ψ_c: critical matrix potential).

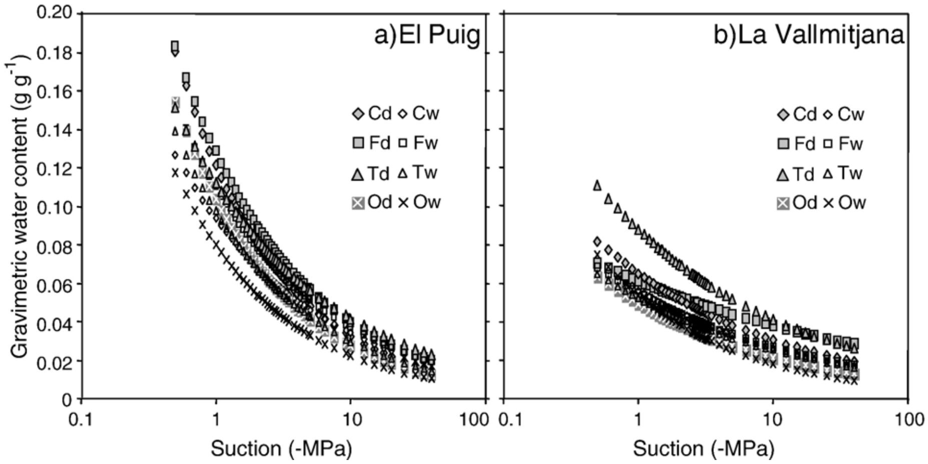

Fig. 3. Mean fitted water retention curves for all treatments (O = control; C = composted sludge; F = fresh sludge; T = thermally dried sludge), in both states (w: wetting; d: drying) and both soils.

The main wetting and drying branches were fitted separately. The fitting was done using PROC NLIN (Newton method) in the SAS/STAT® statistical software program (SAS Institute Inc., 1999). Convergence was achieved, according to the SAS/STAT® default criterion, in every case. This analysis yielded unique estimates of the A_1, A_2, D_1, and D_2 parameters for each branch of each water retention curve for each field plot (i.e. 4 parameters × 2 branches × 32 plots = 256 values). These values were then used to calculate ψ_c using Eq. (13), and the gravimetric water content at wilting point (w_{wp}) by setting ψ = 1.5 MPa in Eqs. (12a)/(12b), for both branches of each curve for each field plot. Treatment effects on the model parameters, calculated values, and total organic carbon and nitrogen contents were then evaluated by analysis of variance (ANOVA)

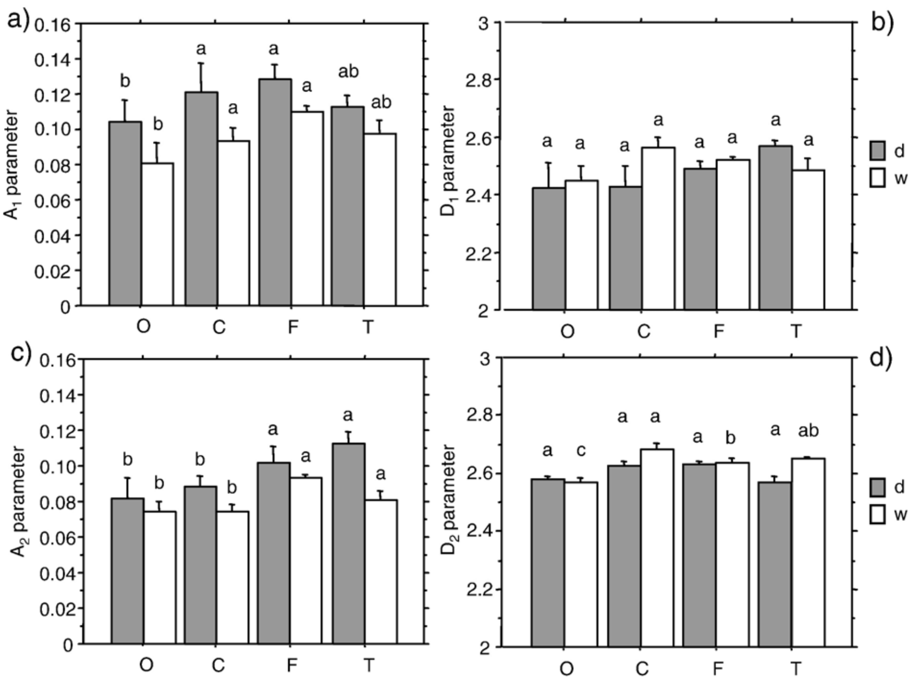

Fig. 4. Mean values of (a) A_1, (b) D_1, (c) A_2, and (d) D_2 for the different sludge treatments (O = control; C = composted sludge; F = fresh sludge; T = thermally dried sludge), in both states (w: wetting; d: drying) on the El Puig loam soil. Bars with the same letter are not significantly different at $p < 0.05$.

using PROC GLM in the SAS/STAT® statistical software program (SAS Institute Inc., 1999).

4. Results

4.1. Organic carbon and nitrogen contents

Total organic carbon and nitrogen contents in the control at La Vallmitjana were higher that those in the control at El Puig (Table 3). This result was likely due to the accumulation of partially decomposed plant debris in the 0–5 cm layer, and can be attributed to the different methods of site preparation. Shrubs were shredded and left on the soil surface at La Vallmitjana, while at El Puig plant debris was removed leaving the surface bare. This also explains the relatively high C/N ratio for the La Vallmitjana soil. Runoff and soil loss at La Vallmitjana were lower than at El Puig during the first year after sludge amendment (Ojeda et al., 2003), so it is also likely that fewer biosolids were lost to erosion at La Vallmitjana than at El Puig.

The sludge applications increased soil organic carbon and total nitrogen levels at both sites (Table 3). As a result, mean C and N contents were strongly positively correlated with each other ($r=0.878$, $p<0.0001$ and $r=0.866$, $p<0.0001$ for El Puig and La Vallmitjana, respectively). At La Vallmitjana, the fresh sludge treatment produced a significant increase in C relative to the control. At El Puig all three sludge treatments gave significant increases in C relative to the control. In terms of total nitrogen, the effect of sludge application was only significant at the El Puig site, where all three sludge treatments had higher soil N levels compared to the control (Table 3). Although the C/N ratios differed between El Puig and La Vallmitjana, there were no significant treatment effects on this property at either site (Table 3).

It is possible that some of the differences in topsoil organic matter content observed between the treatments could have been induced by variations in runoff associated with differences in slope. However, the first five runoff events immediately following the sludge amendments were the by far the biggest, after which soil loss and runoff gradually decreased over time due to the developing vegetation cover (Ojeda et al., 2003). We found no significant differences in soil particle size distribution between the plots at either site, suggesting that slope effects on runoff were not an important factor in this study.

It is probable that the initial effects of the sludge on C and N levels were larger earlier in the experiment, and diminished over time. Table 3 indicates that organic matter from the sewage sludge applications persisted for at least 2 years on both soils. This persistence may be explained in two ways. Firstly, the organic matter may have been directly stabilized by the calcareous nature of the soil (especially in the case of El Puig). The Ca probably acted as a bridge linking organic components to clay particles. This process is known to form aggregates that are physically, chemically, and biologically stable (Oades, 1988). Secondly, the sludge applications increased the vegetation cover, thereby indirectly contributing to the soil organic matter pool, and improving soil physical properties. During the experiment the vegetation cover was always lower in the control plots than in the sludge amended treatments on both soils (Ojeda et al., 2003).

4.2. Water retention curves

Measured values of w and ψ for the El Puig site (loam soil) ranged from 0.02 to 0.35 g g^{-1}, and 0.10 to

Table 4
Mean and standard error of mean (S.E.M.) of the fractal parameter estimates for the El Puig loam soil ($n=3$)

Parameter	State	Sludge	Mean	S.E.M.
A_1	Drying	O	0.103	0.004
		C	0.121	0.006
		F	0.128	0.009
		T	0.112	0.012
	Wetting	O	0.080	0.006
		C	0.094	0.022
		F	0.110	0.020
		T	0.097	0.015
A_2	Drying	O	0.081	0.008
		C	0.088	0.011
		F	0.102	0.009
		T	0.112	0.010
	Wetting	O	0.073	0.015
		C	0.074	0.005
		F	0.093	0.016
		T	0.081	0.017
D_1	Drying	O	2.424	0.010
		C	2.425	0.019
		F	2.489	0.018
		T	2.568	0.037
	Wetting	O	2.446	0.038
		C	2.560	0.056
		F	2.521	0.050
		T	2.486	0.063
D_2	Drying	O	2.579	0.008
		C	2.626	0.004
		F	2.629	0.014
		T	2.568	0.011
	Wetting	O	2.568	0.015
		C	2.682	0.007
		F	2.637	0.008
		T	2.650	0.015

39.8 MPa, respectively. In contrast, w and ψ ranged from 0.01 to 0.19 g g^{-1} and from 0.33 to 40.0 MPa, respectively for the La Vallmitjana samples (loamy sand soil). Since the data were collected at suctions well in excess of the air entry values, an increase in ψ always resulted in a decrease in w, and vice versa. Eqs. (12a)/(12b) fitted the experimental data for the main wetting and drying branches of the water retention curves extremely well. Fitted versus observed water contents for the entire data set (both soils combined) are shown in Fig. 1. Overall the water content values predicted by Eqs. (12a)/(12b) were very close to the observed water contents. Linear regression analysis indicated only minimal deviations from a 1 : 1 relationship.

Main wetting and drying branches of a representative $w(\psi)$ curve are shown in Fig. 2 along with the corresponding predicted relations from Eqs. (12a)/(12b). Because of the different experimental protocols employed, less data were available for fitting the main wetting branch as compared to the main drying branch. Note that over most of the range of suctions considered there are two gravimetric water contents associated with each suction value due to hysteresis. The magnitude of this effect varied with both soil type and sludge treatment, as can be seen in Fig. 3.

4.3. Fractal parameter estimates

Estimates of the A_1 parameter in Eqs. (12a)/(12b) ranged from 0.07 to 0.15 for the loam soil, and from between 0.04 to 0.20 for the loamy sand soil. Since A_1 subsumes both ρ_b and ψ_e this parameter should be sensitive to soil structure, including any shrink/swell phenomena. This appears to be the case for the loam soil (Fig. 4a and Table 4), but not for the loamy sand soil (Fig. 5a and Table 5). Analysis of variance (ANOVA) indicated significant sludge and hysteresis effects on A_1 (with no significant interaction) at El Puig (Table 6). At this site, A_1 was higher for the main drying branch as compared to the main wetting branch, and all of the sewage sludge treatments had values of A_1 greater than the control treatment (Fig. 4a). At La Vallmitjana, in contrast, no significant sludge or hysteresis effects were observed for the A_1 parameter (Table 6). Assuming particle density is a constant, Eq. (5) indicates that an increase in A_1 can occur as a result of a decrease in ρ_b, a decrease in ψ_e, or decreases in both of these properties. Thus, the sludge effects on A_1 can probably be explained in terms of organic matter induced changes in bulk density, and/or diameter of the largest pores present which determine ψ_e.

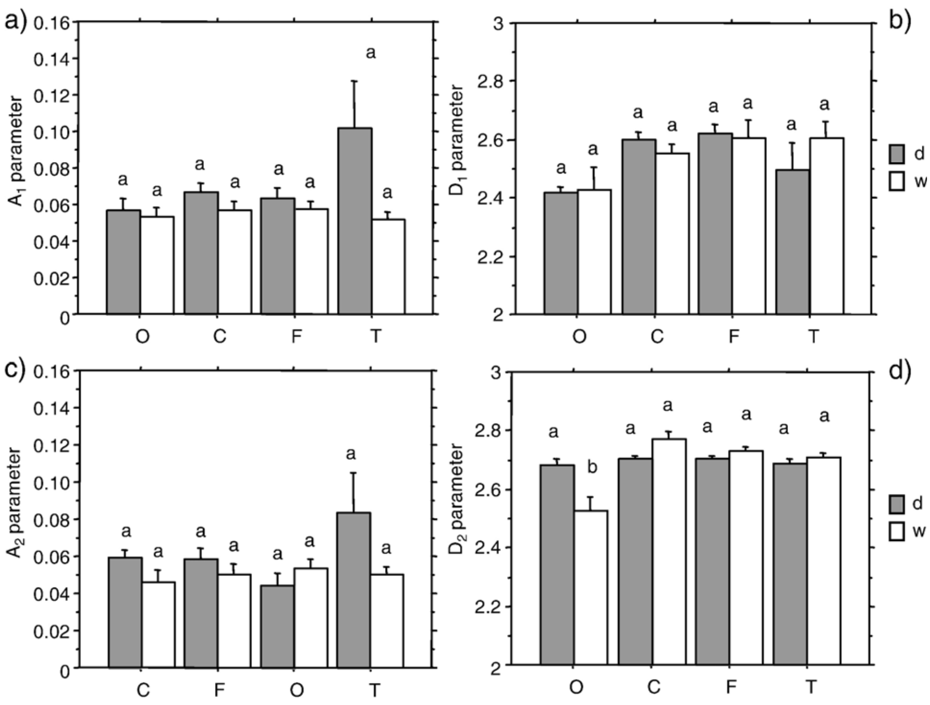

Fig. 5. Mean values of (a) A_1, (b) D_1, (c) A_2, and (d) D_2 for the different sludge treatments (O = control; C = composted sludge; F = fresh sludge; T = thermally dried sludge), in both states (w: wetting; d: drying) on the Vallmitjana loamy sand soil. Bars with the same letter are not significantly different at $p < 0.05$.

Table 5
Means and S.E.M. of the fractal parameter estimates for the Vallmitjana sandy loam soil ($n=5$)

Parameter	State	Sludge	Mean	S.E.M.
A_1	Drying	O	0.057	0.008
		C	0.067	0.006
		F	0.063	0.007
		T	0.101	0.008
	Wetting	O	0.053	0.005
		C	0.056	0.009
		F	0.057	0.011
		T	0.052	0.002
A_2	Drying	O	0.044	0.008
		C	0.059	0.006
		F	0.058	0.007
		T	0.084	0.006
	Wetting	O	0.053	0.027
		C	0.046	0.022
		F	0.050	0.037
		T	0.050	0.020
D_1	Drying	O	2.416	0.024
		C	2.601	0.014
		F	2.620	0.034
		T	2.497	0.036
	Wetting	O	2.426	0.017
		C	2.552	0.018
		F	2.605	0.030
		T	2.603	0.008
D_2	Drying	O	2.684	0.008
		C	2.706	0.006
		F	2.701	0.007
		T	2.690	0.006
	Wetting	O	2.524	0.033
		C	2.772	0.028
		F	2.731	0.032
		T	2.706	0.022

For the loam soil at El Puig, significant correlations were found between the A_1 parameter and soil organic carbon contents ($r=0.579$, $p<0.05$ and $r=0.736$, $p<0.01$ for the main drying and wetting branches, respectively) and total nitrogen ($r=0.646$, $p<0.05$ and $r=0.727$, $p<0.01$ for the main drying and wetting branches, respectively). Similar, albeit less pronounced, correlations were observed for A_1 from the main wetting branch ($r=0.531$, $p<0.05$ and $r=0.530$, $p<0.05$ for organic carbon and total nitrogen, respectively) of the loamy sand soil at La Vallmitjana. All these relationships indicate that A_1 increases with increasing soil organic carbon or total nitrogen contents.

Estimates of the pore-solid fractal dimension, D_1, ranged from 2.26 to 2.60 for the loam soil, and from 2.15 to 2.74 for the loamy sand soil. No sludge or hysteresis effects were observed on this parameter for either soil (Table 6 and Figs. 4b and 5b). The D_1 values for the drying and wetting branches of the water retention curve were not significantly correlated with organic carbon or total nitrogen contents for the loam soil. Some significant positive correlations were found between D_1 and organic carbon and total nitrogen levels for the loamy sand soil. However, these relationships explained less than 30% of the total variation in D_1.

Estimates of the A_2 parameter ranged from 0.64 to 0.12 for the loam soil and from 0.03 to 0.16 in the loamy sand soil. In the case of the loam soil, significant non-interactive sludge and hysteresis effects were observed on A_2 (Table 6). The fresh and thermally dried sludge treatments had significantly higher values of A_2 than the control (Fig. 4c). The A_2 parameter from the drying curves of the loam soil was positively correlated with both organic carbon ($r=0.629$, $p<0.05$) and total nitrogen content ($r=0.680$, $p<0.05$). In contrast, this parameter estimated from the wetting curve was only correlated with the total nitrogen content ($r=0.583$, $p<0.05$). Eq. (11) indicates that an increase in A_2 can

Table 6
Summary of analyses of variance (ANOVA) for the fractal parameter estimates

Site	*F* value					R^2
	Parameter	Model	Sludge	Hysteresis	Interaction	
El Puig	A_1	5.68	4.92	17.26	NS	0.785
	D_1	NS	NS	NS	NS	0.356
	A_2	10.04	10.82	23.13	NS	0.866
	D_2	6.73	11.36	10.73	4.28	0.812
	ψ_c	NS	NS	NS	NS	0.558
	w_{wp}	10.37	10.99	27.76	NS	0.870
La Vallmitjana	A_1	NS	NS	NS	NS	0.403
	D_1	NS	NS	NS	NS	0.422
	A_2	NS	NS	NS	NS	0.399
	D_2	6.72	13.06	NS	9.57	0.725
	ψ_c	NS	NS	NS	NS	0.449
	w_{wp}	NS	NS	NS	NS	0.405

All values are significant at $p<0.05$ except for those denoted by NS.

occur as result of increases in either or both of w_c and ψ_c. We show later that there were no significant treatment effects on ψ_c. Thus, an increase in w_c implies that the sludge additions increased the amount of capillary water trapped at high suctions, possibly due to changes in the wetting angle and/or film connectivity.

For the loamy sand soil, neither sludge, hysteresis, nor their interaction, had any significant impact on the A_2 parameter (Table 6 and Fig. 5c). Only estimates of A_2 from the main wetting branch of this soil were positively correlated with nitrogen content ($r=0.457$, $p<0.05$). Although significant, this correlation was low and strongly influenced by a single "outlier" value for total nitrogen. The absence of any clear relations between organic matter and the A_2 parameter for the La Vallmitjana site may well be related to the coarse texture of this soil. Because of its definition, the A_2 parameter is most likely to be influenced by micro-structural changes involving silt and clay-sized particles. Such changes are difficult to identify when the silt and clay fractions make up less than 15% of the total soil mass (Table 1).

Estimates of the surface fractal dimension, D_2, varied between 2.53 and 2.70 for the loam soil and between 2.41 and 2.86 for the loamy sand soil. In most cases, the mean D_2 values were lower for the loam soil than for their loamy sand counterparts (Tables 4 and 5). On both soil types there were significant differences in D_2 between the treatments (Table 6 and Figs. 4d and 5d) including a significant interaction between sludge application and hysteresis. The sludge treatments generally increased D_2, and at the same time decreased differences between the wetting and drying estimates, relative to the control.

Very strong correlations were observed between D_2 estimated from the main wetting branch and both organic carbon ($r=0.882$, $p<0.0001$) and total nitrogen ($r=0.863$, $p<0.001$) contents for the loam soil. No significant correlations were found for this soil in the case of D_2 estimated from the main drying branch. For the loamy sand soil, the only significant correlation was between organic carbon content and D_2 for the wetting curve ($r=0.490$, $p<0.05$). These relations indicate an increase in apparent pore surface roughness with increasing organic matter content. The fact that this effect was only manifested during wetting up of the soil suggests that the sludge treatments

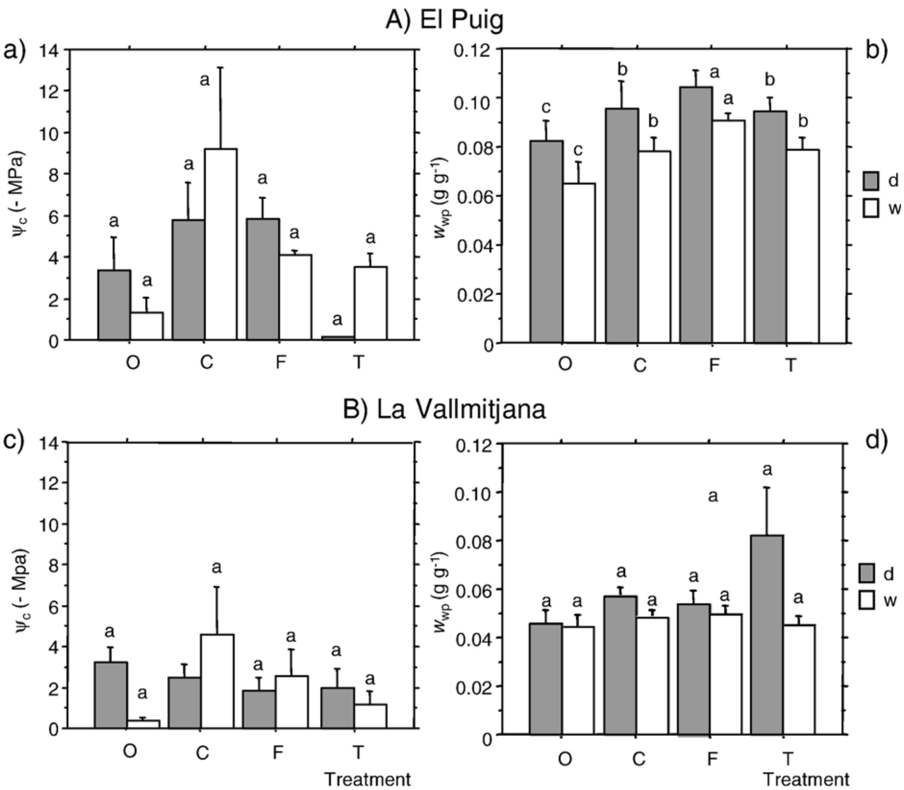

Fig. 6. Mean values of ψ_c (a, c) and w_{wp} (b, d) for the different sludge treatments (O=control; C=composted sludge; F=fresh sludge; T=thermally dried sludge), in both states (w: wetting; d: drying) and both soils. Bars with the same letter are not significantly different at $p<0.05$.

combined with oven drying may have induced a certain degree of hydrophobicity. Hydrophobicity, which is common with various kinds of dry organic amendments, often reduces the rate of water penetration into sludge-amended soil. This effect can persist for a long period of time following sludge application (Agassi et al., 1998). An increase in hydrophobicity may cause an apparent increase of surface roughness by differentially changing the contact angle in large versus small pores.

4.4. Critical suction and water content at wilting point

Analysis of variance indicated no significant effects of hysteresis or sludge application on the critical suction dividing the high and low suction regimes (Table 6 and Fig. 6). The mean values of this parameter were 4.14 and 2.26 MPa for the loam and loamy sand soils, respectively. The ψ_c was weakly positively correlated with organic carbon content for the wetting state of the loam soil (r=0.509, p>0.05), and weakly negatively correlated for drying state of the loamy sand soil (r=−0.383, p>0.05).

The soil water content at wilting point, w_{wp}, can be accurately estimated using the chilled mirror dew point method since ψ=1.5 MPa falls well within the range of suctions measured by the WP4 instrument. Because of hysteresis, w_{wp} was always higher when calculated from the drying curves as compared to the wetting curves (Fig. 6). Analysis of variance indicated significant effects of hysteresis and sludge addition on w_{wp} for the loam soil (Table 6 and Fig. 6b), but not for the loamy sand soil (Table 6 and Fig. 6d). In the former case, the soil water content at wilting point in the control treatment was significantly lower than in any of the sludge treatments.

There was a strong positive correlation between w_{wp} and the A_1 parameter from Eqs. (12a)/(12b) (Fig. 7), suggesting that these two quantities are directly linked in some way. As mentioned above, A_1 can be theoretically related to both the bulk density and the diameter of the largest pores present. Since it is highly unlikely that the gravimetric water content at wilting point was influenced by macropores, Fig. 7 implies that the variations in A_1 were mainly the result of changes in bulk density.

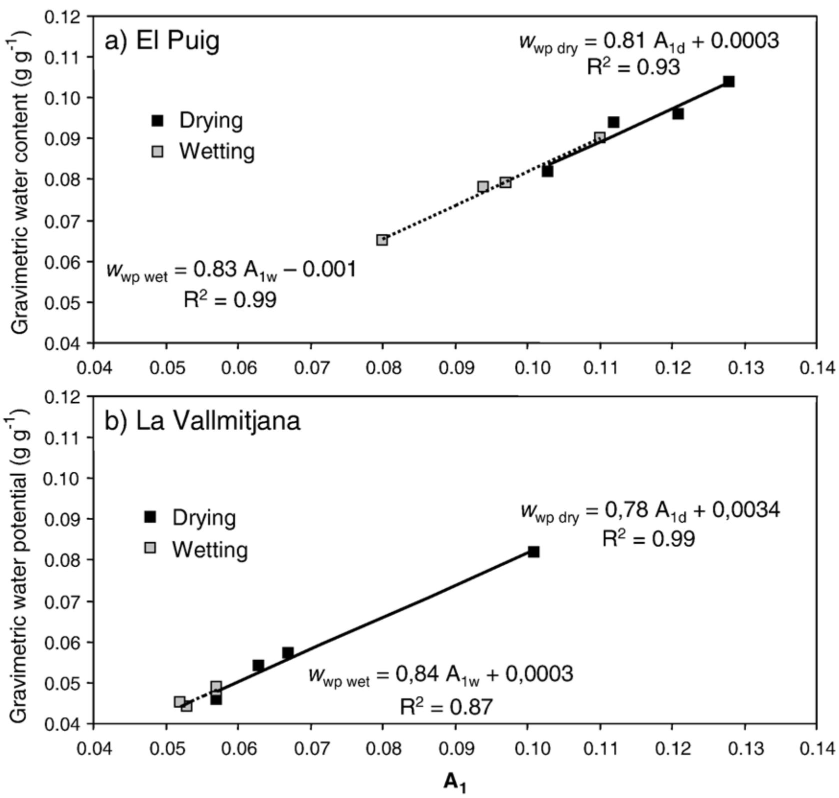

Fig. 7. Relationships between mean gravimetric water content at wilting point (ψ=1.5 MPa) and the A_1 parameter for the different sludge treatments on the two soils. Drying and wetting refer to the main drying and wetting branches for the water retention curve, respectively.

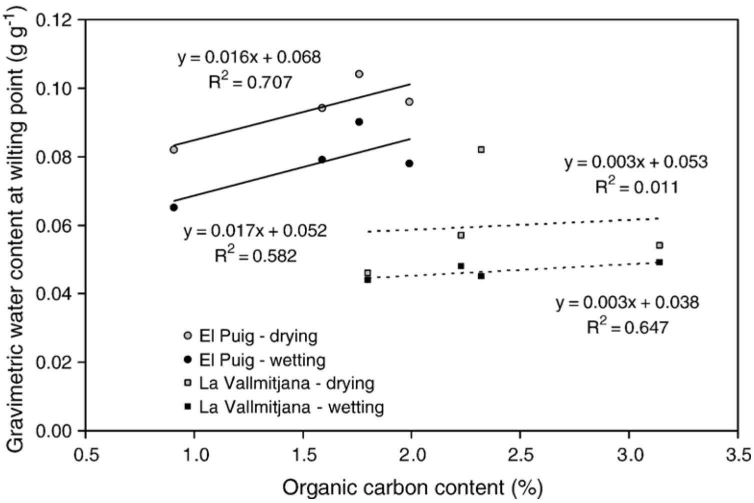

Fig. 8. Relationship between mean gravimetric water content at wilting point (ψ = 1.5 MPa) and mean organic carbon content for the different sludge treatments on the two soils. Drying and wetting refer to the main drying and wetting branches for the water retention curve, respectively.

The sludge amendments increased organic carbon levels on the two soils, and the w_{wp} was positively correlated with these increases (Fig. 8). A similar correlation was reported by Perfect et al. (2004) for a loam soil in which organic carbon levels had been changed by long-term tillage and fertilization management practices. The direct effects of sewage sludge on w_{wp} can be explained in terms of organic matter induced changes in soil structure. The addition of sewage sludge increased soil organic carbon and nitrogen levels (Table 3). These constituents can alter the pore-size distribution through soil aggregation, and thus influence w_{wp}. Organic matter is also known to modify the adsorption of water onto clay minerals (Cristensen, 1996; Rawls et al., 2003). However, any direct effects of sludge on water retention are hard to justify since organic matter in the biosolids had already undergone significant transformations prior to application. It is much more likely that the effects of the sewage sludge on w_{wp} were indirectly mediated through increased vegetation cover and improved biochemical cycling in the amended treatments (Ojeda et al., 2003).

5. Discussion and conclusions

The existence of hysteresis was confirmed for the loam soil by the presence of significant differences between model parameters determined from the wetting and drying curves. For this soil, values of A_1 and A_2 for the main drying branch were higher than the corresponding values for the main wetting branch. The D_1 did not exhibit any hysteretic behavior. In contrast, D_2 from the wetting curve was higher than the corresponding value from the drying curve. The loamy sand soil did not produce any significant differences between the drying and wetting states with respect to A_1, A_2 or D_1, although D_2 was sensitive to the interaction between sludge type and hysteresis in a similar way to that observed for the loam soil. It is likely that soil at the La Vallmitjana site was too coarse to be strongly influenced by either hysteresis or the sludge applications.

The main wetting and drying branches of the water retention curves were determined under very different conditions. In order to measure the main drying branch it was necessary to start with saturated soil. Saturation was achieved by slowly wetting up air dry samples by capillarity in order to minimize slaking. Some aggregate collapse was observed during this process, and it is possible that differences in soil strength induced by the sewage sludge treatments may have influenced the pore-size distributions, and thus the drying curves. Wet-aggregate stability measurements by the Le Bissonnais (1996) method (data not presented) indicated a higher stability for all of the sludge treatments as compared to the control on the loam soil. Increased wet aggregate stability is known to reduce micro-cracking of samples during wetting. It is also possible that the sludges reduced the wetting rate, and thus minimized slaking, through their effects on aggregate hydrophobicity (see below). Following saturation, the soil was allowed to dry by evaporation. In order to use Eqs. (12a)/(12b) we assumed that any shrinkage during drying had a negligible effect on ρ_b. This assumption appears to be reasonable given the very low clay content at La Vallmitjana, and the absence of smectites at El Puig.

In order to determine the main wetting branch of the water retention curve, soil samples were first oven-dried. Little is known about the irreversible alterations that occur due to drying soil to an extent that rarely happens in the field (Bruand and Prost, 1987; Bachmann and van der Ploeg, 2002). Mitchell and Mayer (1998) suggested that the impact of hysteresis tends to be more important near the soil surface where extreme wetting and drying events frequently occur. Due to the surface sludge applications, we concentrated our sampling efforts on the 0–5 cm depth. Dekker et al. (1998) indicated that the degree of potential water repellency changes with different drying regimes, and that drying samples at temperatures higher than 25 °C can increase the water repellency of some soils, but not others. Thus, it is possible that the sludge effects observed on the wetting branch data collected in this study could have been magnified by the oven drying pre-treatment. Slowly rewetting the soil from an oven dry condition may also have induced some aggregate breakdown due to small-scale differential swelling (Bruand and Prost, 1987; Le Bissonnais, 1996).

We hypothesize that the organic matter from sewage sludge amendments on the loam soil probably stabilized aggregates against slaking, mechanical breakdown, and differential swelling during wetting. The increases in organic matter could have resulted in changes in the pore-size distribution, aggregate stability, and possibly hydrophobicity through modification of the contact angle. These changes could be responsible for the different hysteretic water retention curves obtained for the sludge treatments as compared to the control. For the loamy sand soil, the observed increase in surface fractal dimension, D_2, could also be associated with changes in the contact angle. Any increase in surface roughness would decrease water flow, and thus could be interpreted as an apparent increase in hydrophobicity.

A basic question arises as to what is the relationship between D_2 and the physicochemical structure of adsorbed water in porous media (Pfeifer and Avnir, 1983; Li et al., 2000). Yehoda and Messier (1985) demonstrated that the surfaces of thin films are themselves fractal in nature. However, Cheng et al. (1989) found that the film–vapor interface is smoother than the fractal substrate surface. The wetting fluid essentially "defractalizes" the porous medium at smaller length scales, effectively giving a new lower scaling limit corresponding to the size of the largest water filled pores. Thus, the response of the wetting phase saturation to changes in capillary pressure can be used as a probe of pore space roughness, independently of the disjoining pressure behavior (Davis et al., 1990).

In contrast to the results for D_2, Table 6 and Figs. 4 and 5 suggest that the capillary component of the soil water retention curve (as quantified by D_1) was not subject to hysteresis. According to Sort and Alcañiz (1999b), fresh sludge should have increased the proportion of pores >50 μm. After 2 years, however, it is possible that this increase was lost due to changes in the organic matter pool over time, or that vegetation development in the control plots increased the proportion of pores >50 μm to a level similar to that in the sludge amended plots.

In conclusion, the effects of sewage sludge amendment on the main wetting and drying branches of the soil water retention curve were still discernable 2 years after application. This observation is consistent with studies by Kumar et al. (1985) and Joshua et al. (1998) that showed improvements in the water holding capacity and other physical properties of soils to which sewage sludge had been added. Aggelides and Londra (2000) also reported an increase in soil water retention through the use of composted sludge. In the present study, only small differences were observed between the three types of sludge applied (composted, fresh, and thermally dried), and these differences were only detected on the loam soil. Our analyses also suggest that the effects of the sludge were mainly due to changes in surface adsorption properties rather than capillary drainage phenomena. Further research employing alternative experimental methods and covering a wider range of suctions is needed to confirm this observation.

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