" A MICROPOROSITY STUDY OF A BLACK EARTH OF SOUTHERN SPAIN "

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INTRODUCTION.

The porosity is a main characteristic of structure and texture of soils to determine its degree of aeration, circulation and water retention. The great practical interest of these matters is obvious as shows the literature.

A detailed porosity study of Western Andalusia soils has been carried out by Arrue (1976). The above study make clear that in soils with a high clay content, the pores below 1 μm represent about 50-60 % of total porosity. According to this, we consider of interest the study of pore-size distribution below 1 μm because in this way it is possible to know what amount of water stored in soils is available by plants. We are interested in this subject because the special climatological factors in South Spain soils.

Pore-size differential distribution of clay mixture has been studied by Aylmore and Quirk (1967) and Sills, Aylmore and Quirk (1973) with conventional techniques.

In the present paper we have used a combination of Scanning Electron Microscopy, nitrogen adsorption-desorption isotherms and the moisture content study in the range of pF 3.7-5.6 to obtain a better knowledge of micropore volume and microstructure of the samples studied.

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MATERIAL AND METHODS.

The samples used in this work correspond to four depths of a black earth profile (Pelloxererts) which location and short description (Martin, Moreno and Arrue, 1976) are given as follow :

Black Earth (Pelloxererts). Situation: Utrera (30 Km. SE. Seville).

Ap	0-30 cm	10 YR 3/1 moist, 10 YR 6/1 dry. Clay. Weakly developed subangular blocky structure which breaks up into medium to fine crumby structure. Plactic, adhesive.
B_{21}	30-48 cm	10 Y R 4/1 moist, 10 YR 6/1 dry. Clay. Weakly developed angular blocky structure which breaks up into medium crumby structure. Very plastic and adhesive.
B_{22}	48-82 cm	Same colour and texture as above. Medium weakly developed angular blocky structure. Very plastic and adhesive.
C	$>$82 cm	10 YR 3/1 moist, 10 YR 6/1 dry. Clay. Medium and large, strongly developed angular blocky structure. Very plastic and adhesive.

All samples were sieved (aggregates $<$ 0.25 mm).

Scanning Electron Micrographs were obtained using a HITACHI HHS - 2R microscope, with secondary electron image and a accelerating voltage of 25 KV. Samples were coated by vacuum evaporation of a gold layer c. a. 30 nm thickness.

Moisture contents were determined by means of pres sure membrane cell (Richards 1947) on the pF range of. 3.7–4.2 and for pF larger than 4.2 was used the vapour pressure method with controlled relative humidity (De Boodt 1967).

Nitrogen adsorption–desorption isotherms were measured with a conventional micro-BET apparatus at 78 K using liquid nitrogen as crioscopic bath. All samples were heated at 105 º C under vacuum until the pressure remained 10^{-6} torr before measurements of adsortion-desorption isotherms. The calculation of pore-size distribution of samples was carried out from desorption isotherms (according to method described by Carrasco et al., 1971) by an UNIVAC 1108 computer , using a FORTRAN IV program.

RESULTS AND DISCUSSION.

Scanning Electron Micrographs of different depths of profile considered show aggregates of about 20–55 µm at low magnification (Fig. 1 A, 2 A, 3 A). At higher magnification (Fig. 1 B, 2 B, 3 B) the aggregates are revealed to be composed of particles which distribution in a parallel form gives rise to high amount of plate-shaped pores according to Martin, Moreno and Arrue (1976), in relation to montmorillonite and illite content in this soil. Fig. 1 B, 2B, 3B show some cylindrical pores about 0.5–2 µm diameter.

Comparison of Scanning Electron Micrographs of samples of different depths studied show a similar microstructure along the profile that suggests a high homogeneity in relation to this characteristic, This indicates that in the whole profile there are an important proportion of plate shaped pores and for this reason from now on we will use the equivalent plate separation parameter (d_e) instead of equivalent diameter (d) in order to characterization of pore size.

The results of moisture content in the range of pF 3.7-5.6 are given in Table 1. From these values the pore -size distribution has been calculated, Table 2, which pore-size range corresponding to equivalent plate separation of 600-8 nm.

Data of Table 2 suggest that higher volume of pores in the four depths of profile corresponding to those in wich d_e are included between 72 and 16 nm. Also are important the pore size fraction of 16-8 nm and only in the 40-60 cm. and 60-80 cm depths, the pore fraction 600-21 nm has signification.

The pore-size distribution below 8 nm was also determined by nitrogen adsorption-desorption isotherms, which are plotted in Fig. 4. Samples (a) and (d) show hysteresis phenomena in the relative pressure (P/P_o) range studied. Therefore this is not important and in samples (b) and (c) are not present. The method used to obtain the pore size distribution has been applied to desorption isotherms in all samples. Fig. 5 shows the differential and cumulative form of results obtained for pore-size distribution. These results make clear that the samples content a high percentage of plate-shaped pores, which equivalent plate separation is 1.9 nm. Also are important the pore volume, which de is c.a. 2.7 nm. The high amount of pore volume in this samples in the range of pore-size studied can explain, if we take into account the high content of fine particles, especially clay fraction (montmorillonite and illite), c.a. 60% (Martin, Moreno and Arrue, 1976). In the same way, the results obtained for pore size below 8 nm agree with Aylmore and Quirk's (1967).

The specific surface area data of samples obtained from nitrogen adsorption isotherms (BET method) are included in Table 3. Samples (c) and (d) show a high value of S_{BET} according to their clay content (Martin et al., 1976). Cumulative surfaces and contribution percentage of pore-fraction below 8 μm to S_{BET} suggest that the most part of surface area is mainly due to the mentioned pores.

Values of C (constant of BET equation) included in Table 3 are related to the degree of interaction between nitrogen molecules and the solid. The higher values to (b) and (c) samples can be explained because in these cases the surface distribution is more accesible to nitrogen molecules and consequently the interaction is more effective between them. On the contrary, a particular plate microstructure of (a) and (d) samples must difficult the nitrogen molecules packing on solid surface. From the above considerations, it is obvious that the microporosity study of this soil only can be carried out with the association of different techniques, as here presented.

Results and considerations on microporosity of textural porosity of this black earth suggest an important property of this soil as the water storage by pores below 600 nm. If we take into account that this microporosity (below 600 μm) represents about 60 % of total porosity in this soil (Martin et al., 1976), it must be concluded that the majority of total water holding capacity is as no available or difficulty available water by plants.

This kind of pores is a fundamental contribution to specific surface area in this samples.

LEGENDS OF FIGURES.

Fig. 1. – Scanning Electron Micrographs of sample (a), depth : 0–20 cm; A, low magnification ; B high magnification.

Fig. 2. – Scanning Electron Micrographs of sample (b), depth : 20–40 cm; A low megnification; B high magnification.

Fig. 3. – Scanning Electron Micrographs of sample (c), depth 40–60 cm; A., low magnification; B high magnification.

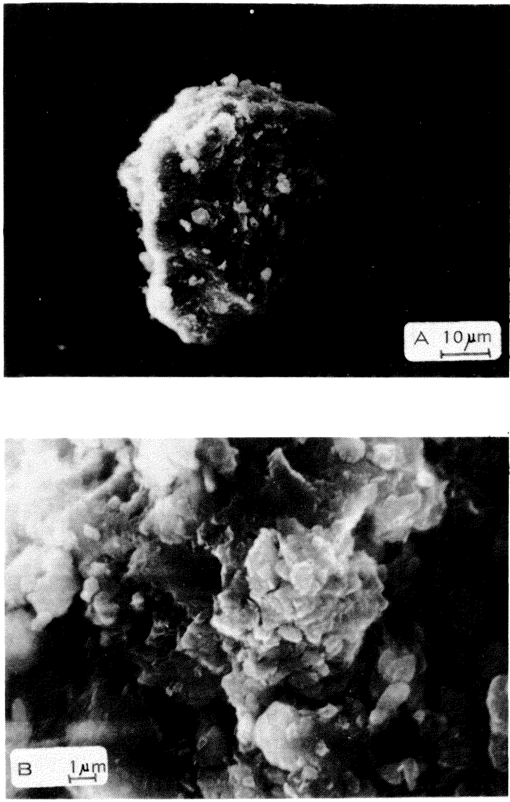


Fig. 1

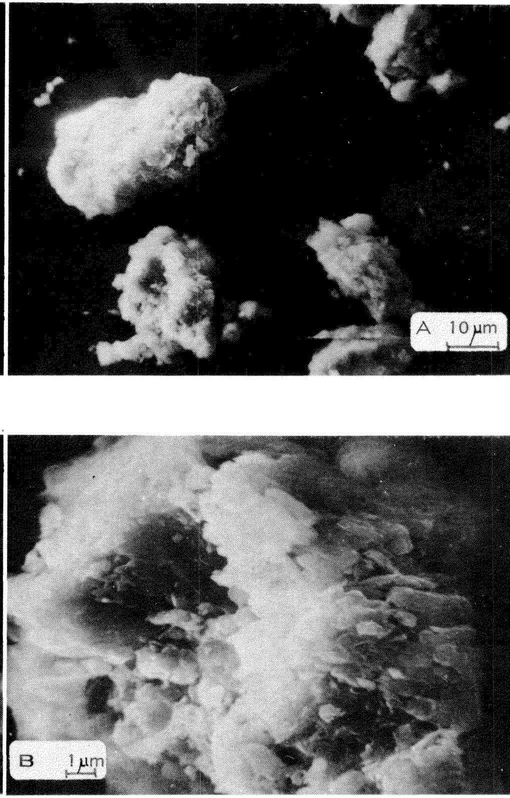


Fig. 2

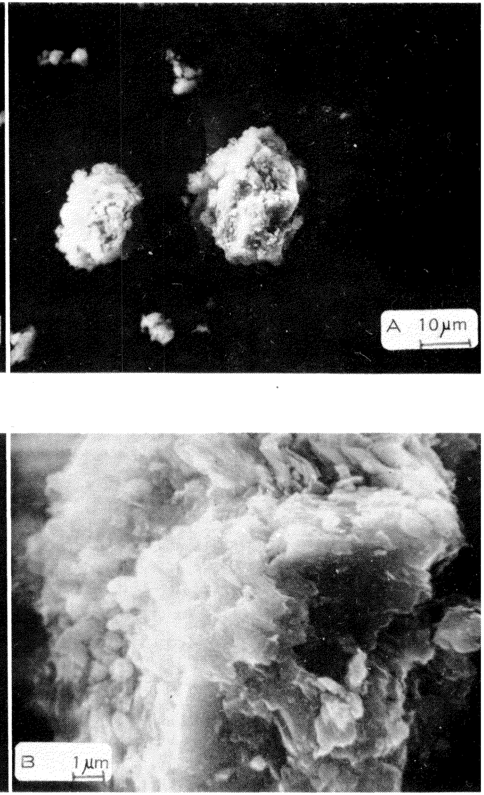


Fig. 3

Table 1

Moisture retention (weight %) in the range of pF 3.7-5.6

Sample	Depth (cm)	pF 3.7	pF 4.2	pF 4.6	pF 5.2	pF 5.6
(a)	0-20	22.0	21.5	20.7	12.9	10.6
(b)	20-40	22.1	21.6	20.5	13.4	10.7
(c)	40-60	23.8	21.6	20.3	13.2	10.7
(d)	60-80	24.2	22.0	21.5	13.6	10.7

Table 2

Pore Size Distribution on the range of 600-8 nm (cc g^{-1})

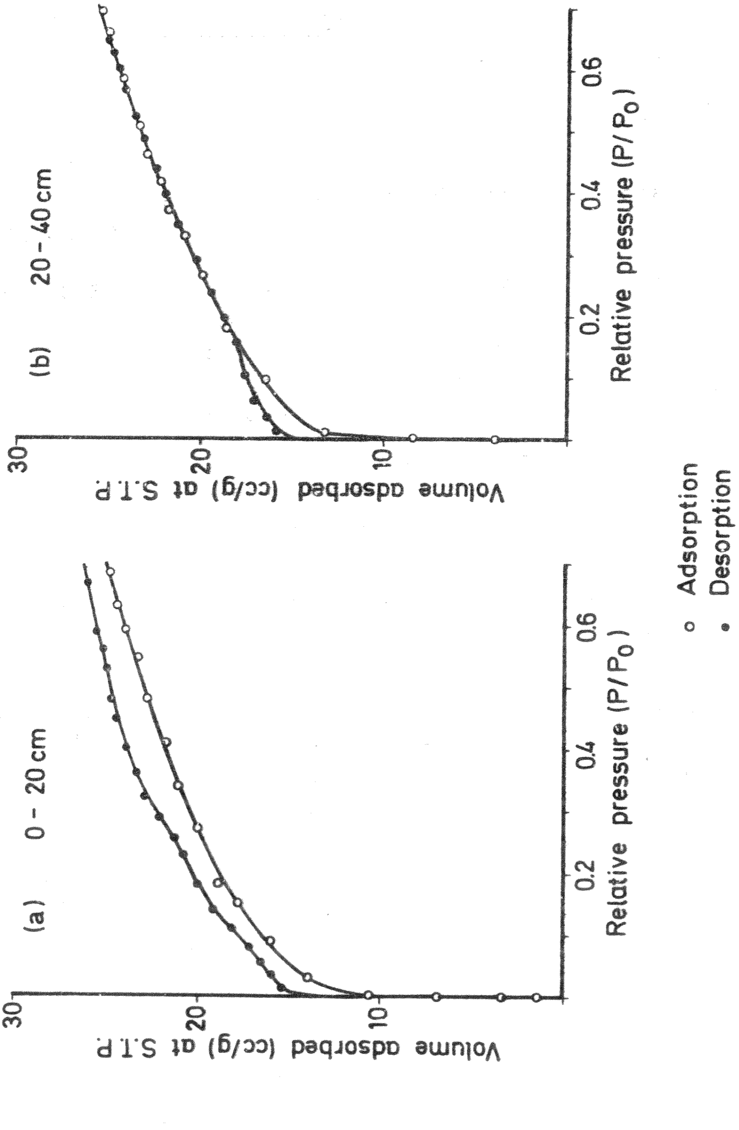
d_e (nm)	Sample and depth (cm)			
	(a) 0-20	(b) 20-40	(c) 40-60	(d) 60-80
600-210	0.005	0.005	0.022	0.022
210- 72	0.008	0.011	0.013	0.005
72- 16	0.078	0.071	0.071	0.079
16- 8	0.023	0.027	0.025	0.029

d_e = Equivalent plate separation

Table 3

Specific surface area (S_{BET}), cumulative surface area (S_c), contribution percentage of <8 nm pore-fraction to S_{BET} and C values of BET-equation

Sample	Depth(cm)	S_{BET} ($m^2 g^{-1}$)	S_c ($m^2 g^{-1}$)	% S_{BET}	C
(a)	0-20	60.4	44.1	73.0	90.0
(b)	20-40	64.0	42.8	66.9	271.0
(c)	40-60	68.0	50.4	74.1	258.0
(d)	60-80	65.7	45.6	69.4	87.6


(a) 0 - 20 cm
(b) 20 - 40 cm
Volume adsorbed (cc/g) at S.T.P
30
20
10
Relative pressure (P/P$_0$)
0.2
0.4
0.6
○ Adsorption
● Desorption

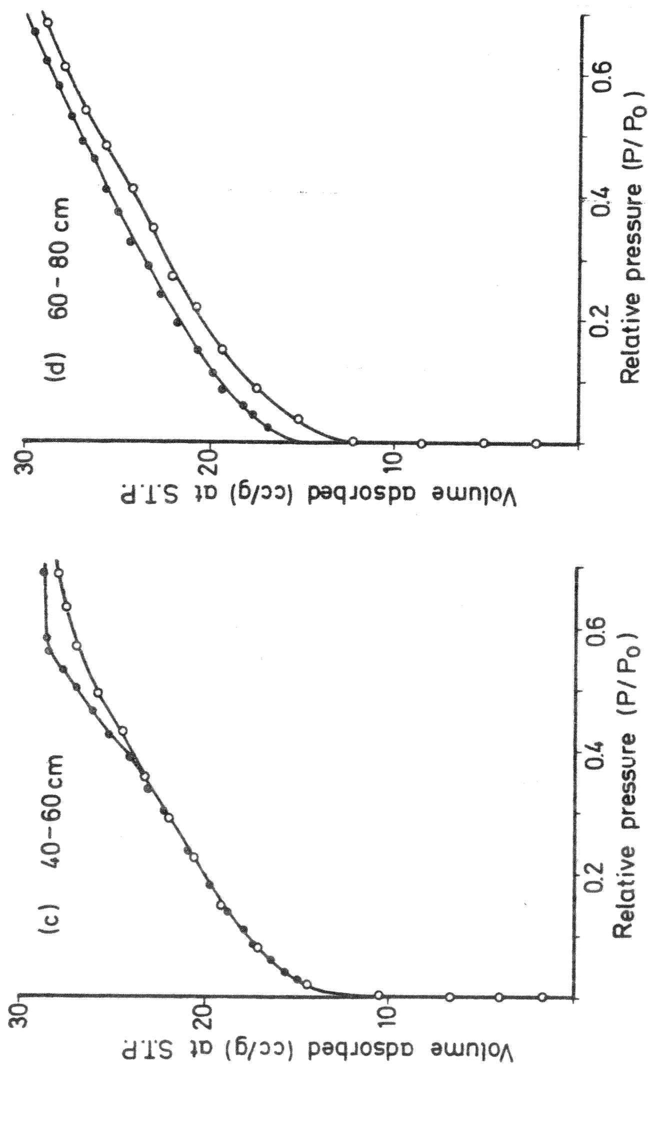
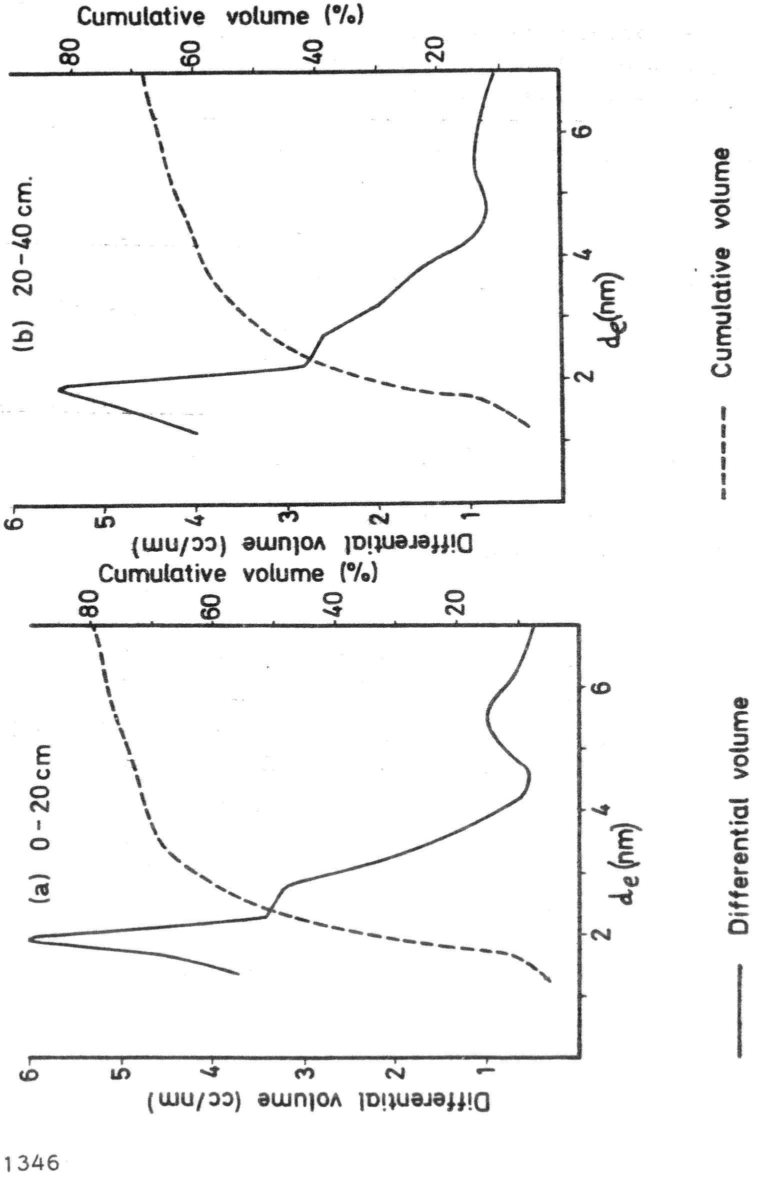


Fig. 4. -Nitrogen adsorption-desorption isotherms (78 K), samples (a), (b), (c) and (d).


(a) 0 - 20 cm
(b) 20 - 40 cm.
Cumulative volume (%)
80
60
40
20
Differential volume (cc/nm)
6
5
4
3
2
1
d_e (nm)
2
4
6
Differential volume
Cumulative volume

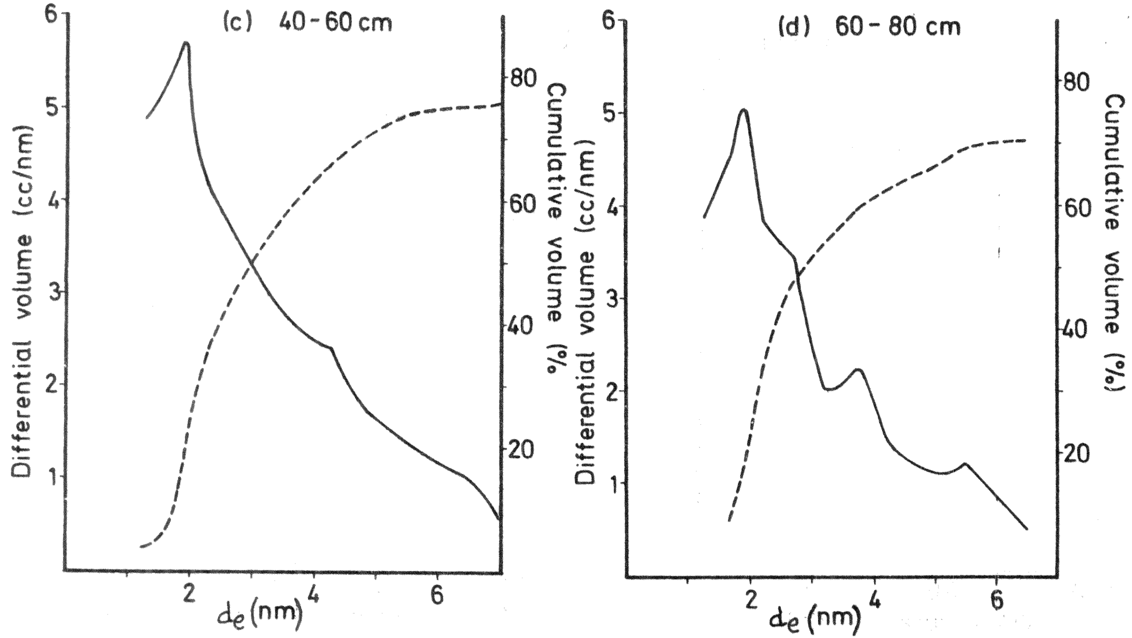


Fig. 5. - Differential and cumulative pore-size distribution, samples (a), (b), (c) and (d). d_e = equivalent plate separation.

SUMMARY

Cualitative and cuantitative study of microporosity of a black earth has been carried out by association of - Scanning Electron Microscopy, pF determinations and micro-BET nitrogen sorption.

Pore size distribution are related with water stored by the soil and use of this water by plants.

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