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APPLICATION OF IMAGE ANALYSIS FOR EVALUATION OF MERCURY INTRUSION POROSIMETRY RESULTS*

E. Kozak, M. Pezda

Institute of Agrophysics, Polish Academy of Sciences, Doświadczalna 4, 20-236 Lublin, P.O. Box 121, Poland

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A b s t r a c t. Analysis of images of a sample before and after mercury porosimetry measurement is a convenient and quantitative method of testing whether the sample is compressed during mercury intrusion. Application of the method to oven-dried soil samples revealed stability of their structure under mercury pressure up to 200 MPa.

K e y w o r d s: mercury porosimetry, image analysis, pore size distribution

INTRODUCTION

Mercury intrusion porosimetry is one of the most popular methods used for determination of pore size distribution of porous materials. The basis of this method rests on the principle that a non-wetting fluid will not spontaneously intrude the pores of a solid, but will do so if sufficient pressure is applied. It is assumed that the sizes of pores intruded by mercury are inversely proportional to its pressure. The modern mercury intrusion porosimeters allow usually for applying pressures up to 200 MPa, which corresponds to the equivalent pore size of 3.7 nm. In recent years, mercury intrusion porosimetry was frequently used in studies of porosity of soil materials. Gliński *et al.* [5] ascertained the ability of this method to evaluate the influence of various treatments of mechanical tillage on soil structure. Fies [4] applied it in studies of pore size distribution of artificially prepared mixtures of clay, silt and glass beads. Wierzchoś *et al.* [16] used mercury porosimetry to determine the influence of selective removal of organically bonded metals and organic matter on soil microstructure. Bruand *et al.* [3] applied it for examination of porosity in tilled loamy clay soils. Bartoli *et al.* [1,2] and Pachepsky *et al.* [12] used mercury intrusion to measure pore size distributions which were next used to calculate the fractional dimension of soil pore surface. Thompson *et al.* [15] applied mercury porosimetry to evaluate effects of drying methods on the porosity of soil samples. Keng *et al.* [7] used it in investigations of the effect of dimethyl sulfoxide on soil pore structure during freeze-drying. Guidi *et al.* [6] used this method in a study of modification of soil porosity in a rice soil puddled by different mechanical implements. Several other examples of the application of mercury intrusion porosimetry method in soil studies have been collected by Kozak *et al.* [8]. Rapidity and replicability of the results is the advantage of mercury porosimetry. However, these results may not reflect the true pore size distribution of a

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sample when it collapses during mercury intrusion. The collapse can be caused by the overall mercury pressure applied, and by the existence of areas of differential pressure within the sample. The possibility of sample collapse during mercury intrusion can be examined by comparing sizes of aggregates before and after porosimetric analysis. It can be done in a quantitative way by using methods of image analysis. The aim of this paper is to show the possibility of such an application of these methods.

MATERIALS AND METHODS

Mercury intrusion porosimetry analyses were performed on the aggregates obtained from four mineral soils. Their mechanical composition and organic carbon content are collected in Table 1. More detailed characteristics of these soils can be found in ealier paper [8]. Soil samples were fully water saturated and subsequently allowed to equilibrate at pF 2.7 on a suction plate. Then, some aggregates were separated from the samples, air-dried (for 7 days), and oven-dried at 105 °C (24 h). Next, the aggregates were outgassed (up to 1.3 kPa) and subjected to the porosimetric analysis. Carlo Erba Mercury Porosimeter Series 2000 was used. The maximum mercury pressure applied in it is 200 MPa. To check whether during mercury intrusion a collapse of the sample does occur, the images of aggregates were captured before and after porosimetric analysis and compared. Image Analyser IPS 512 (Imal Ltd.) was applied. It consist of a TV Camera (CCD), a Personal Computer with computer board for image acquisition and processing, a high resolution monitor and a printer. Images were prepared by placing aggregates on a mat plate, highlighted from the bottom. Greyscale histograms of such images were characterized by broad, distinct minima (see Fig. 1). As a result, binarization operation was easy to perform: pixels in the range of 0-95 were assigned to whiteness level, and the remaining ones (96-255) were assigned to blackness level. Surface areas, perimeters and average diameters of shapes of each aggregate were registered.

A similar comparison of sample sizes before and after porosimetric analysis can be found in papers of Sridharan *et al.* [14] and Murray and Quirk [11]. However, in the work of Sridharan *et al.* [14] a comparison was done only in a qualitative way, and the mercury pressure applied there was almost two times lower than the maximum pressure of our porosimeter, whereas Murray and Quirk [11] did not analyse any images, but they measured, before and after intrusion, diameters of cores formed from the original material of a sample.

Table 1. Some properties of the soils used in the study.

Soil type	Locality	Depth (cm)	Aggregate code	C_{org} (%)	Mechanical composition (%)		
					Sand	Slit	Clay
Haplic Phaeozem	Werbkowice	0-20	wa	2.53	65.5	24.5	10
		69-95	wb1, wb2	2.02	58	25	17
		150-170	wc	1.45	59	25	16
Eutric Cambisol	Rudnik	0-20	ra	1.38	43	21	36
		30-60	rb1, rb2, rb3	0.28	34	16	50
Orthic Luvisol	Sobieszyn	0-20	gsa	1.02	69	14	17
		30-50	gsb	0.25	80	3	7
		180-200	gsc	0.11	92	3.5	4.5
Dystric Cambisol	Bukowina	0-16	ba	2.82	48.5	19	32.5
		16-46	bb	0.97	31	40.5	28.5
		46-80	bc	0.46	38.5	41.5	20

RESULTS AND DISCUSSION

Some images of aggregates obtained by using Image Analyser are shown in Fig. 2. A

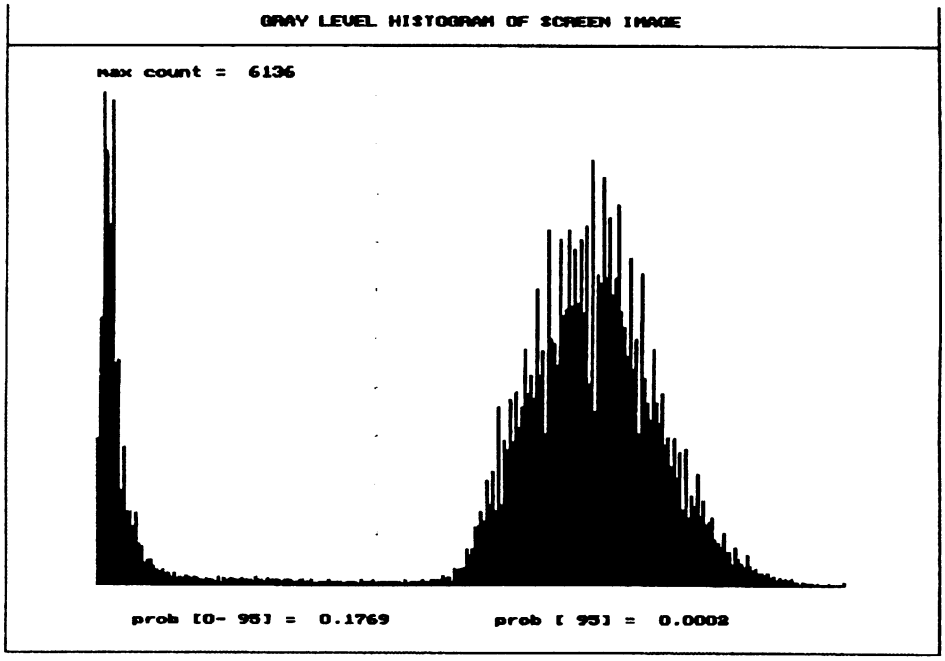

Fig. 1. Greyscale histogram of an image of soil aggregate placed on a mat plate, highlighted from the bottom.

couple of images represent the situation before and after mercury intrusion. Numerical results are collected in Table 2. Data presented there are averages from four replicate measurements. Statistical analysis of the results shows that surface areas, perimeters and average diameters of shapes of aggregates before and after mercury intrusion do not differ significantly (at significance level α=0.05). It suggests that sizes of oven-dried soil aggregates

T a b l e 2. Results of image analysis of soil aggregates before and after mercury intrusion up to the pressure 200 MPa

Aggregate code	Surface area (mm^2)			Perimeter (mm)			Average diameter (mm)		
	before	after	difference	before	after	difference	before	after	difference
wa	141.5±5.1	145.0±4.3	3.5	49.3±1.0	49.5±1.0	0.1	13.4±0.3	13.6±0.2	0.2
wb1	185.0±3.9	182.1±6.1	-2.9	61.2±1.8	58.8±1.3	-2.5	15.3±0.2	15.3±0.3	-0.1
wb2	166.8±5.8	171.0±5.4	4.2	53.4±1.4	55.6±1.5	2.2	14.6±0.3	14.7±0.1	0.2
wc	152.6±4.7	151.7±7.8	-0.9	51.2±1.3	50.6±1.6	-0.6	13.9±0.3	13.9±0.3	-0.1
ra	151.2±6.9	147.2±7.2	-4.0	52.5±1.8	50.6±1.6	-1.9	13.8±0.2	13.7±0.3	-0.2
rb1	119.4±5.5	119.3±7.0	-0.2	44.9±1.0	44.7±1.2	-0.2	12.3±0.4	12.3±0.4	-0.0
rb2	139.0±4.3	139.3±7.3	0.4	56.7±1.2	56.8±1.6	0.1	13.3±0.1	13.3±0.3	0.0
rb3	131.1±5.2	129.8±6.0	-1.2	49.3±1.1	48.7±1.1	0.7	12.6±0.2	12.6±0.3	-0.1
gsa	118.6±5.8	120.4±6.1	1.9	47.0±1.2	48.0±1.0	1.0	11.7±0.3	11.9±0.4	0.2
gsb	174.6±6.1	172.1±5.4	-2.5	58.2±1.8	59.5±1.7	1.3	14.9±0.2	15.2±0.2	0.4
gsc	143.3±4.8	130.7±6.7	-12.6	49.7±1.4	45.0±1.7	-4.8	13.5±0.2	12.5±0.3	-0.1
ba	132.4±6.1	129.8±6.6	-2.6	53.4±2.2	53.2±2.1	-0.1	12.9±0.3	12.8±0.3	-0.1
bb	155.0±5.5	155.4±6.5	0.4	52.5±1.4	52.3±1.1	-0.2	13.9±0.4	13.9±0.2	0.0
bc	139.9±4.5	140.3±5.4	0.4	53.2±0.9	53.5±1.1	0.3	13.2±0.2	13.3±0.2	0.1
		average:	-1.1		average:	-0.4		average:	0.0
		standard deviation:	4.0		standard deviation:	1.7		standard deviation:	0.3

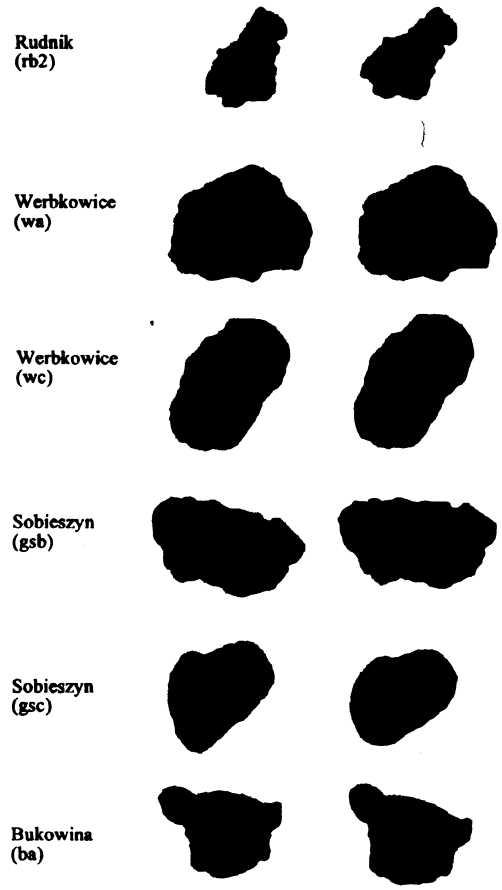

Fig. 2. Images of oven-dried soil aggregates before (column on the left) and after mercury intrusion up to the pressure of 200 MPa (column on the right).

do not change under mercury pressure up to 200 MPa. The greatest difference between the parameters characterizing the shape of aggregate before and after porosimetric analysis was observed for the aggregate 'gsc' obtained from C horizon of Orthic Luvisol from Sobieszyn. This sample was rich in sand and poor in clay. A decrease in its surface area and linear dimensions of about 10 % is attributed here rather to damage of aggregate during manual operations than to a collapse during mercury intrusion.

The lack of changes of the external size of a sample is not sufficient evidence of stability of its structure, because some internal changes may occur. We consider below the methods proposed for the examination of this possibility.

The obvious way is to measure some parameters characterizing the internal structure of a sample twice: for the virgin sample and after removing mercury intruded into the sample during porosimetric analysis. Most often, the method applied for obtaining the corresponding results was just mercury porosimetry. Porosimetric analysis was performed twice for the same sample. After the first intrusion the intruded mercury was removed from the sample by heating under vacuum. On the basis of such measurements Sarakhov [13] stated that some charcoal samples are destroyed under high mercury pressure, and Winslow [17] showed the lack of changes of the structure of some porous aluminas. The possibility of destruction of soil samples during mercury intrusion was examined in this way by Lawrence [9]. He found no sample volume and pore size distribution changes greater than the experimental error limits. The experiment was performed on samples taken from three soils, air- and oven-dried from the field moisture state and freeze-dried after equilibrating at pF 1 on a suction plate. Maximum mercury pressure was 245 MPa.

Another method, applied recently for the examination of sample structure before and after mercury intrusion, was nitrogen adsorption. This method was applied by Minihan *et al.* [10] in studies of possibility of compression of a number of silicas. After mercury porosimetry analysis the samples were washed free of mercury by using nitric acid and freeze-dried. There were no published similar studies on soil samples.

The methods of examination of internal sample structure before and after porosimetric analysis are much more complicated and labour-consuming than the analysis of the image of a sample. The main problem is the necessity of removing the intruded mercury.

The other way of verification of mercury intrusion porosimetry results is their comparison with the results of another method. For this purpose two methods are usually taken into account: nitrogen sorption and water desorption method. However, the range of

pore sizes common for nitrogen sorption and mercury intrusion method is rather narrow. On the other hand, there is a possibility of a continuous change in the volume of pores during water desorption, when some swelling materials are present in the sample. It limits the possibility of a valuable comparison of the methods.

CONCLUSION

The analysis of the image of a sample before and after mercury porosimetry measurement is a simple, convenient way of quantitative examination, whether the sample is damaged or not during mercury intrusion. Application of this method seems to be necessary in all cases where samples subjected to mercury intrusion are of relatively weak and delicate structure. In particular this concerns soil samples dried from a high moisture content by using more sophisticated methods than oven-drying (critical point-drying, freeze-drying, etc.), and most biological materials.

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