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METHODOLOGICAL ADVANCES USED TO ANALYSE MAXIMAL HYGROSCOPIC WATER IN SOILS OF DIFFERENT STRUCTURE

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Abstract. The paper presents principles of methods by Mitscherlich, Robinson and Nikolajew for the determination of maximal soil hygroscopicity (*MH*). Methods by the above-mentioned authors were modified and adapted for serial determinations. Modification of *MH* determination methods was found to simplify the course of investigations, increase repeatability of results and facilitate determinations of large sample series.

The paper presents the need and possibility for *MH* determination not only of air-dry powdered (sieved through 2 mm mesh) soil mass but also soil aggregates of natural and modelled structures, air-dry and wet samples. *MH* was determined in a vacuum chamber of vacuum drier over saturated K_2SO_4 solution. The use and applicability of the method was presented on 10 soils of diversified texture and structure.

Keywords: method, soil, aggregate, maximal hygroscopicity

INTRODUCTION

One of the important and typical physical properties of the soil proves to be its maximal hygroscopicity - *MH* (maximal molecular water capacity). The property is characteristic of the size of specific surface area of the soil and the area ability for physical sorption. It turns out to be an important characteristic feature of the soil moisture.

MH depends greatly on the particle size distribution, mineralogical composition, contents of organic matter as well as on chemical properties, structure of the soil mass, etc. In general, the biggest role is played here by the contents of the colloidal fraction. Due to such a diversified influence, the *MH* values reflect a wide complex of main physical and physicochemical properties of the soil mass. However, the *MH* values depend also to a cerain degree on the modifications used in methodology of *MH* determination. In the course of time, the modifications, which concerned various details in the analysis of *MH*, have slowly accumulated.

The theoretical foundations of *MH* determination were given by Radewald [8] and Mitscherlich [4] as early as the first decade of our century. At first *MH* was determined in a vacuum dessicator at about 22 °C in pressure conditions about 200 hPa (vacuum) and relative humidity about 94 %. Such relative humidity was settled in a dessicator over 10 % H_2SO_4. Thus determined maximal hygroscopicity was used to find the size (value) of specific surface area of particles contained in 1 g of soil mass [4]. However, the determination of specific surface area has since undergone methodological modifications, which were reviewed by Dechnik and Stawiński [2].

MH was also used to determine moisture of wilting point [12], to find the approximate limit between the soil water accessible to plants and soil water inaccessible to plants etc. Similar applications of *MH* are presented for instance by Rode [7] who discusses problems of soil water. *MH* has also been used to determine, e.g., the limit and moisture shrinkage of soil aggregates [11].

Thus there is a fairly wide range of potential applications of *MH* the low moisture level interval. These possibilities prove to be particularly useful because *MH* determination is simple, cheap and relatively fast, and at the same time offering very good repeatability of results.

In viev of the above-mentioned advantages and a wide applicability of *MH* results, the Department of Soil Science, Agricultural University (Poznań) embarked on some methodological research which started in the 1950's. The first priority was to improve and simplify determination methods used by Mitscherlich [4], Robinson [6], Nikolajew [5] as well as to adapt the method for serial determinations. The first stage of investigations ended in 1977. The most essential results were published by the Polish Society of Soil Science [9]. In the publication mentioned above, there is a comparison and evaluation of the findings obtained by the methods of Mitscherlich [4], Robinson [6] and Nikolajew [5]. Principles of these methods are generally similar whereas the differences concern more or less crucial methodological details.

THE PRINCIPLE OF MITSCHERLICH'S, ROBINSON'S, NIKOLAJEW'S METHODS

The method according to Mitscherlich, for instance, [4, p. 69] boils down to the following procedure: 30-50 g air-dry soil (5-10 g for peat) is spread thinly (a layer of about 1 mm) in a flat weighing dish (12 cm diameter) placed in a vacuum dessicator on a porcelain stand. 100 ml 10 % H_2SO_4 should be found on the bottom of the dessicator where relative humidity is settled at 94 % (at 25 °C - 94.3 %). The dessicator contains also a small 'U' shaped mercury pressure gauge. Next the dessicator is connected to a water pump (aspirator) and the air is pumped out. The vacuum (negative pressure) reaches about 200 hPa. Then the dessicator is placed in a dark cupboard in order to eliminate temperature changes. After 2-3 days the vacuum is removed to exchange H_2SO_4 solution (1000 ml - 10 % H_2SO_4). Next the air is pumped out again and the dessicator is placed in the dark cupboard. After 3 days the vacuum is removed, the dish containing the soil is weighed, and then placed in a laboratory dryer (105 °C). After drying and cooling down, the dish is weighed again (in the orginal version, drying was performed in the vacuum dessicator over P_2O_5). The weight difference between the sample saturated with water vapour in the dessicator and the sample saturated with water vapour in the dessicator and the sample dried at 105 °C serves as the basis to calculate maximal hygroscopic water capacity *MH* in weight percentage - for soil mass.

In general terms, a similar principle for *MH* detrmination was used by Robinson [in 1, p. 35]. He suggested however 3.3 % H_2SO_4, over which relative humidity reaches about 98.2 % being slightly higher than that obtained in Mitscherlich's method.

Nikolajew [5] managed to achieve nearly the same level of relative humidity (about 98 % at 20 °C) over saturated K_2SO_4 solution. To determine *MH*, Nikolajew used relatively small weighing dishes of 30 or 50 mm diameter. Moreover, he used ordinary dessicators (non -vacuum). In the conditions of normal atmospheric pressure, the diffusion of water vapour was slower and thus *MH* determination usu-ally took about 30 days (maximum 49 days).

THE MODIFICATION OF MITSCHERLICH'S, ROBINSON'S, NIKOLAJW'S METHODS

Certain improvements and simplifications in the analysis have been introduced to compare and evaluate the three above mentioned methods. Instead of vacuum dessicators, a vacuum chamber of the vacuum dryer was used. The chamber, apart from its capacity (about 50 weighing dishes), ensures also temperature stabilization which plays a vital role in the investigations. The weighing dishes were 50 mm diameter and 30 mm height. The two-shelf vacuum chamber or fairly small diameters of weighing dishes enabled to determine *MH* in series of numerous samples.

The following questions had to be answered in order to methodologically evaluate the afore-mentioned improvements: (i) what is the effect of the soil layer thickness in the weighing dish on the result, (ii) does the location of the sample on the lower or upper shelf, or at the front or at the back of the shelf play a significant role in the obtained result, (iii) how is the time of determination influenced by the value of negative pressure (vacuum), (iv) what conditions should be met in order to obtain precise and repeatable results in serial determinations of *MH*.

Documented answers to such questions can be found in the cited publication which presents the following suggestions:

- vacuum chamber of preferable dimensions about 40x30x50 cm,
- chamber pressure - 200 to 250 hPa,
- thickness of sample layer - about 3 mm (± 1 mm), sample weight about 10 g,
- sample saturation time - 6 days for mineral soils of contents not exceeding 5 %. In the case of higher content of the organic substance, the weighted samples should be appriopiately smaller (*ca.* 5± 0.5 g) and the water vapour adsorption ought to last longer until the sample weight has settled (sample check following 6, 9, 12 etc. days).

During the determination of a large number of soil samples, the samples should be grouped into series of similar *MH*, namely a series of sandy soils, clayey soils, highly organic soils etc. Moreover, while removing the vacuum, the air inlet in the chamber should be secured (protected) so that soil particles are not blown off the dishes and the condensed water around the inlet opening does not fall into the dishes.

The methodological solutions and measurements presented above were used to carry out investigations aimed at comparing *MH* values obtained with 10 % H_2SO_4, 3.3 % H_2SO_4 and saturated K_2SO_4 solution. The investigations revealed highest *MH* in case of 3.3 % H_2SO_4, slightly lower *MH* for saturated K_2SO_4 solution, and lowest *MH* for 10 % H_2SO_4. The differences were relatively small - a few percent - as compared with maximal values (as 100 %). As a result, the use of 3.3 % H_2SO_4 was suggested to achieve the optimal comparability with results obtained in the West where this percentage of sulphuric acid was most frequently used.

The second stage of our research programme has begun recently, which is aimed at further improvement and development of *MH* determination methods. However, saturated K_2SO_4 solution was finally regarded as the best choice for the following reasons: (i) it is harmless and safe to use, (ii) it does not need to be exchanged frequently, as it does not change its concentration, (iii) it has relatively good buffering which is reflected in its ability for absorption and desorption of water vapour from soil samples, (iv) it enables *MH* determination for air dry and wet samples. Moreover, preparation of this solution is fast and easy. Potassium sulphate is dissolved in hot water. After cooling down, the excess of K_2SO_4 undergoes crystallization on the walls of the container and close to the surface of the solution.

The basic aim of the second stage of our investigations was to solve the problem of *MH* determination for samples of natural and modelled structure and not only for powdered samples, as it had been practised before. In many cases it is necessary to use *MH* determinations expressed in volumetric percentage. The investigations were also aimed at *MH* determination of wet samples not concentrating only on the air-dry ones. The following problems were successfully solved in the course of our investigations.

METHODS AND OBJECT OF INVESTIGATION

Soil samples of natural structure were collected by the use of a 1 cm sampler which belongs to the Litwinow Field Laboratory Kit PL-9 used to investigate mechanical properties of the soil [3]. A suitable figure and description of the sampler is also included in the publication [10, p. 10] which deals with modelling and physical properties of soil aggregates. Sampling was mainly carried out from the humus horizon of 56 arable soils which represent the most typical soil types in Poland. The samples were taken after soil moisture had reached field water capacity. These samples represented the structure of the arable layer at its highest and relatively even compaction. It usually occurs at the end of the vegetation period before autumn ploughing. These samples were also treated as models of soil aggregates of a definite shape (cylindrical), size (1 cm^3), bulk density and moisture. In order to determine *MH*, the samples or soil aggregates were first led to the air-dry condition. Some of the samples for *MH* determination had their moisture close to field water capacity. 5-7 soil aggregates (about 10 g of naturally structured soil) were placed in the weighing bottles. *MH* was expressed in weight and volumetric percentages.

For naturally compacted soil samples, the *MH* analysis revealed the following question: Are the *MH* values dependent on soil compaction or porosity, and if so, to what extent? Answers to these questions were found in suitable investigations on soil samples or aggregate models of different bulk density. The so-called 'tempering effect' was used in the conditions of the consolidating effect of consolidating water. The soil texture of various bulk density and porosity was formed by different additions of water in a slightly lower range than the low and high ranges of plasticity acc. to Atterberg. The consolidating factor was water, as it is in the natural conditions. More comprehensive explanation of modelling and investigating soil textures can be found in the publication cited above [10].

Samples for *MH* determination were collected using a sampler from a water-consolidated soil. Five models of air-dry aggregates were placed in the vacuum chamber. Table 1 and Fig. 1 present the most significant findings.

RESULTS AND CONCLUSIONS

Table 1 shows *MH* results for soil samples of various bulk density (column 8) and for air-dry samples sieved through a 2 mm sieve, the apparent volume of the sample was 5 cm^3. The soils were ranked according to the growing amount of clay (column 2).

The most significant general conclusions which can be drawn from the data in the table are as follows: (i) *MH* expressed as weight percentage proves to be generally similar both in samples of modelled structure as well as in samples of powdered structure, (ii) considerable changes are found in values expressed as volumetric percentages (columns 10, 12), (iii) *MH* does not however depend greatly on bulk density or soil sample porosity, (iv) the well known rule has been confirmed which says that *MH* values increase quite regularly just as the clay percentage goes up, (v) in order to express *MH* values as volumetric percentages, soil sample shrinkage should be considered. This issue is presented in Fig. 1.

Figure 1 presents the significant differences between *MH* determined for the air-dry samples state and for that of the wet state. *MH* for air-dry samples proves to be considerably lower than for the wet samples. The phenomenon of hysteresis is found in the difference. Another finding is the fact of considerably higher *MH* values (vol. %) for naturally structured or modelled samples, or for soil aggregates in comparison to *MH* obtained from powdered soil material. The differences are relatively big amouting to 50-60 %. The size of these differences can be described by for instance the soil aggregate *MH*: powdered soil mass *MH* ratio (Table 1, column 11). In case of the investigated soils the ratio was ranged from 1.11 (soil number 20) to 1.76 (soil number 48).

Moreover, Fig. 1 presents volumetric changes of soil samples undergoing drying and wetting. Significant volumetric changes which were observed, occurred under the influence of a three-axial shrinkage. The shrinkage has to be taken into consideration while calculating volumetric percentages of *MH*. The shrinkage was found to reach sometimes big values (Table 1, soil number 9, shrinkage *ca.* 42 %) when sampling moisture was equal

T a b l e 1. Maximal hygroscopic water (*MH*) of modelled soil aggregates and powdered soil mass

No. of soil	Content of fractions (%)			Organic matter (%)	Water consolidated soil aggregates			Maximal hygr. water of soil aggregates (%)		Maximal hygr. water of powdered soil mass (siewed 2 mm)			Ratio *MH*: powd. soil
	clay	silt	sand		water (%)		bulk dens.			(%)		bulk dens.	
					(w/w)	(v/v)	(g/cm^3)	(w/w)	(v/v)	(w/w)	(v/v)	(g/cm^3)	
1	2	3	4	5	6	7	8	9	10	11	12	12	14
20	3	13	84	2.58	12.87	18.02	1.426	4.29	6.12	4.88	6.13	1.257	1.11
					14.66	19.88	1.395	4.65	6.49				
					16.56	27.30	1.583	4.63	7.32				
					20.14	29.67	1.654	4.36	7.21				
					24.62	36.19	1.596	4.41	7.04				
44	4	18	78	1.47	11.27	17.60	1.562	3.16	4.94	3.14	4.22	1.345	1.21
					13.02	32.27	1.673	2.99	5.00				
					14.22	23.97	1.765	3.00	5.30				
					15.95	27.67	1.830	2.85	5.22				
					18.56	31.81	1.845	2.76	5.09				
41	5	45	50	3.08	10.56	15.51	1.469	3.88	5.70	3.88	4.71	1.214	1.32
					15.83	24.47	1.546	3.93	6.08				
					18.4	28.92	1.618	4.17	6.75				
					23.55	35.23	1.583	3.83	6.06				
					29.00	42.66	1.619	3.81	6.16				
1	11	31	58	1.98	9.18	13.27	1.446	4.90	7.09	4.91	6.01	1.225	1.31
					12.90	19.26	1.563	5.17	7.88				
					14.11	22.90	1.696	4.90	8.31				
					17.43	28.79	1.825	4.73	8.63				
					21.98	35.34	1.848	5.10	9.42				
31	14	67	19	4.78	8.73	13.07	1.499	6.06	9.09	5.86	6.43	1.098	1.55
					16.58	25.83	1.617	6.26	10.12				
					20.75	31.48	1.632	6.22	10.15				
					27.16	40.55	1.655	6.31	10.44				
					31.70	42.67	1.593	6.27	9.99				

Table 1. Continuation

1	2	3	4	5	6	7	8	9	10	11	12	13	14
5	16	51	33	2.40	16.01	22.51	1.489	7.29	10.85	7.17	8.09	1.129	1.62
					18.59	28.58	1.604	7.64	12.25				
					21.77	34.33	1.893	7.30	13.82				
					25.45	37.34	1.827	7.33	13.39				
					32.12	43.30	1.739	7.69	13.37				
48	24	56	20	1.65	16.22	25.95	1.688	7.35	12.40	7.99	7.29	0.913	1.76
					18.60	29.02	1.729	7.47	112.92				
					21.62	33.68	1.777	7.42	13.15				
					26.48	40.72	1.786	7.40	13.22				
					31.78	43.57	1.703	7.31	12.46				
50	26	24	50	3.17	14.68	22.87	1.673	9.18	15.35	8.25	9.86	1.195	1.66
					20.10	30.73	1.776	9.45	16.77				
					23.97	36.00	1.832	9.39	17.20				
					28.53	41.74	1.831	9.15	16.74				
					34.55	48.13	1.768	9.19	16.24				
9	35	38	27	4.00	22.39	29.38	1.618	14.70	23.78	13.71	16.61	1.21	1.64
					28.00	39.39	1.866	14.97	27.92				
					32.55	43.31	1.927	15.10	29.09				
					39.14	49.04	1.916	14.63	28.03				
					46.68	54.94	1.880	14.78	27.79				
56	71	25	4	0.00	18.50	28.79	1.847	16.20	29.92	17.13	21.58	1.260	1.52
					25.96	38.68	1.990	16.57	32.97				
					31.98	40.01	1.950	16.85	32.86				
					38.13	39.05	1.944	17.52	34.06				
					45.17	45.31	1.930	17.60	33.97				

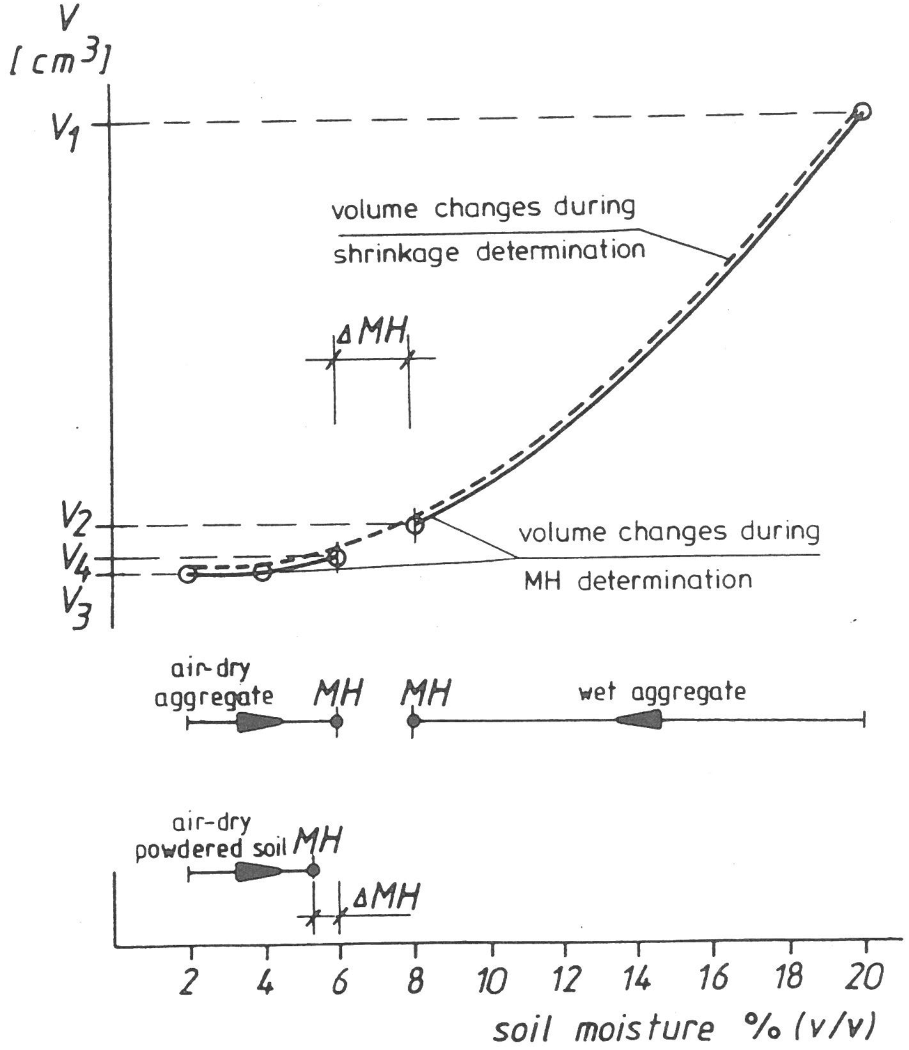

Fig. 1. The volume changes of air-dry and wet soil samples during *MH* and shrinkage detemination.

to field water capacity.

The upper part of Fig. 1 presents an example of a wet soil aggregate shrinkage in the vacuum chamber (solid line) and the same aggregate reaching air-dry state, which was then placed in the vacuum chamber (broken line). During water sorption from air-dry state to *MH* state, a minimal three-axial swelling can be observed along the section from shrinkage point to *MH*. The problem of shrinkage, determination method, calculation and interpretation of results are presented in the next publication [11].

Findings presented in Table 1 and complexity of *MH* determination and interpretation form only a part of more comprehensive investigations to be published in the future. The present paper focuses mainly on showing our method of *MH* determination and on presenting *MH* determination possibilities for natural and modelled structures, for air-dry and wet samples as well as for powdered structure (sieved through a 2 cm sieve). Results included in the paper should be treated as examples which mainly explain complexity of the problems concerning *MH* determination method.

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