

Water vapour adsorption by soil aggregate fractions

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A b s t r a c t. Water vapour adsorption by soil aggregates of humus accumulating soil horizon (fractions ≤ 0.1 , $0.1-0.25$, ..., $5-10$, >10 mm) is found to be adequately described in the range of $0.1 \leq p/p_0 \leq 0.98$ by the equation $W = W_{mh}[(p/p_0)^6 - (p/p_0)^3 + (p/p_0)] + W_{res}$, where: W_{mh} – maximum hygroscopic moisture, W_{res} – residual water content or model fitting coefficient. The main parameter W_{mh} of the dependence $W=f(p/p_0)$ of aggregated part of soil is determined by soil type.

K e y w o r d s: water vapour adsorption, soil aggregates

INTRODUCTION

Interaction of water vapour and soil solid phase is important for the study of the thermodynamics of water sorption and the diffusion of water vapour in soils. In this case a unified mathematical expression of the relation between the content of adsorbed water and the equilibrium pressure of water vapour is required. To describe gas adsorption of solid surface many equations have been proposed, such as Langmuir, BET, Farrar, Harkins-Jura and Dubinin equations (Braunaer *et al.*, 1938; Farrar, 1963; Tarasevich and Ovcharenko, 1975). However, most of the equations proposed can be applied only to certain parts of isotherms and cannot describe isotherms in the range of relative pressure $0 < p/p_0 < 1$ because of the following processes: in most soils, a monomolecular layer of water is formed in the $0 < p/p_0 < 0.3-0.4$ range; the formation of an adsorption water layer with sharply changed properties is completed in the $0.4 < p/p_0 < 0.6$ range, and capillary condensation begins at $p/p_0 > 0.6$ (Voronin, 1984). When $p/p_0 \rightarrow 1$, both stable and metastable states of water film are possible (Deryagin and Churaev, 1984).

As shown by the authors previously (Kharitonova *et al.*, 2003), water vapour soil adsorption isotherms in the range $0.1 \leq p/p_0 \leq 0.98$ are described with the following equation:

$$W = W_{mh}[(p/p_0)^6 - (p/p_0)^3 + (p/p_0)] + W_{res}, \quad (1)$$

with mean determination coefficient $r^2=0.99$, where: W is moisture content, in % of dry soil weight, W_{mh} – maximum hygroscopic moisture, W_{res} – residual water content or model fitting coefficient. The independently defined constant W_{mh} characterizes air-dry soil capacity to adsorb water from the atmosphere, saturated with water vapour, at 20°C (Lozet, 1990). As equilibrium is obtained slowly, W_{mh} is commonly determined over K_2SO_4 saturated solution. W_{mh} is used to evaluate specific soil surface and wilting moisture (Vadunina and Korchagina, 1973).

Equation (1) has the following assumptions. Firstly, during adsorption, sorbent mass increase is directly proportional to its internal energy increase due to the energy of molecule interaction forces between the sorbent and the sorbate on the phase boundary. Secondly, relative water vapour pressure is inversely proportional to the average effective distance between gas phase interacting molecules and molecules of sorbent surface. Thirdly, 'solid phase – gas' interactions (active centers of soil particle surface – water molecules in gas phase) and 'liquid – gas' (adsorbed water surface films – water molecules in gas phase) are not differentiated. In both cases interaction occurs on the phase boundary and is determined by characteristics of solid phase surface. Sorbent mass increase in soil experiment practice is commonly expressed in percentages of solid phase weight (W). Then:

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$$W = A(p/p_0)^6 + B(p/p_0)^3 + C(p/p_0) + D \quad (2),$$

where: W – moisture, % of dry soil weight, A, B, C and D – calculation coefficients. The first equation member $(p/p_0)^6$ includes the effect of dispersion forces energy; the second member $(p/p_0)^3$ includes the effect of both orientation forces energy and hydrogen bonds formation energy; the third member (p/p_0) includes the effect of energy of ‘gravitation’ or central force which is an inverse square of the distance between interacting particles.

Analysis of the base model for soil adsorption of water vapour (Kharitonova *et al.*, 2003) showed that adsorption isotherms of ground (1 mm) air-dry soil samples in $0.1 \leq p/p_0 \leq 0.98$ interval is described by the following polynomial, associated with Eq. (2):

$$W = A[(p/p_0)^6 - (p/p_0)^3 + (p/p_0)] + B. \quad (3)$$

Two polynomials $f(x)$ and $g(x)$ are associated, $f(x) \sim g(x)$, if $f(x)/g(x)$ is a unit. If $f(x) \sim g(x)$ polynomials $f(x)$ and $g(x)$ are of the same content and accepted as equal (Veil, 1941). Estimations showed that when the significant level $\alpha = 0.05$, coefficient A (Eq. (3)) is taken as numerically equal to the W_{mh} value. This equation has been calculated and its reliability proved only for the samples prepared by standard methods. They were triturated and sieved through a 1 mm sieve (Kharitonova *et al.*, 2003).

The tasks set were to test the proposed model for dry-sieved fractions of soil aggregates (fractions 0.1, 0.10-0.25, ..., 5-10, >10 mm) from humus accumulative horizon of different soil types, as well as to identify fraction size influence on model parameters. One of the main tasks of the present study was to validate the equation proposed for soil conditions and to prove the physical content of its parameters (Kutilek and Novak, 1998). That is why statistical arguments for the equation reliability were in the focus of attention.

OBJECTS AND METHODS

Soils that differ in genesis and grain composition were selected for research purposes. They included a soddy strongly-podzolic soil (Moscow Region), an ordinary chernozem (Kursk Region), a chestnut soil and a medium-columnar solonetz (Volgograd Region). To obtain soil aggregate fractions from A horizon, air-dry soil samples were sieved through a set of 0.1, 0.25, 0.5, 1, 2, 3, 5, 7, and 10 mm sieves.

Water vapour adsorption isotherms were obtained by the sorption equilibrium method at 20°C ($\pm 0.1^\circ\text{C}$). Soil samples were kept over saturated salt solutions and sulfuric acid solutions of given concentration (12 experimental points in the range of $0.1 \leq p/p_0 \leq 0.98$). Maximum hygroscopic moisture W_{mh} in the samples was defined as the final point of adsorption isotherm at $p/p_0 = 0.98$. Each experiment was repeated twice. Weight method (precision

± 0.1 mg) was used to determine moisture in the samples studied after they were dried at 110°C ($pF=7$, practically all the water removed). The basic physical and chemical characteristics of soil, the methods used to obtain adsorption isotherms, and the model calculations were previously described in full detail (Kharitonova and Vityazev, 2000; Kharitonova *et al.*, 2003).

RESULTS AND DISCUSSION

To decide whether Eq. (1) can be used to describe isotherms of water vapour adsorption by separate fractions of soil aggregates, complete statistical analysis of linear regression Eq. (3) has been applied to all the fractions. Equation (3) reliably describes adsorption isotherms of the soils studied. Regression statistical significance has been checked using the Fisher criterion $F_{reg} = s_R^2/s_{res}^2$, where s_R^2 is variance due to regression and s_{res}^2 is residual variance (Himmelblay, 1970). F ratio varies in the range of 480-1380, which is significantly higher than $F_{tab} = 3.76$ (for the significance level $\alpha = 0.05$).

The Fisher criterion $F = s_{res}^2/s_{\{y\}}^2$ has been used to test model adequacy, *ie* the provision that prediction accuracy should be comparable with experiment error margin. The variance of reproducibility $s_{\{y\}}^2$ for adsorption is taken from preliminary experiments. The Cochran criterion has been used to test dispersion homogeneity. F values, calculated for adsorption isotherms, are lower than F_{tab} ($F_{0.95} = 3.76$), which means that Eq. (3) adequately describes adsorption process for all soil aggregate fractions. It is worth noting that higher F values close to F_{tab} characterize the isotherms of chernozem aggregates, as compared to isotherms of the other soils studied (3.54 and 0.4-1.7 respectively). Montmorillonite composition of a clay fraction from chernozem A1 horizon might be the reason for this. Experimental points at $p/p_0 = 0.2$ and $p/p_0 = 0.485$, which are relevant to the area of formation, and stability of double-layer molecular structure of montmorillonite inclusions, are characterized by the biggest deviation from calculated moisture values (Fig. 1, arrows) and, thus, the biggest share in F and s_W .

The shape of adsorption curves $W = f(p/p_0)$, calculated for all soil aggregate fractions with Eq. (2) in the interval $0.1 \leq p/p_0 \leq 0.98$, coincides with the shape of estimated dependence plots. Index $|r|$, autocorrelation coefficient, is lower than the critical value of r_{cr} . Systematic model error may be neglected for all the isotherms. Model error function $\Delta = \bar{y} - Y$ (where: \bar{y} and Y denote measured and calculated values of moisture content) is independent of response function (Pachepsky, 1992).

High values of the mean determination coefficient ($r^2 = 0.985$) of the adequate model indicate an almost perfect coincidence between the experimental and calculated values of moisture content in the considered range of relative

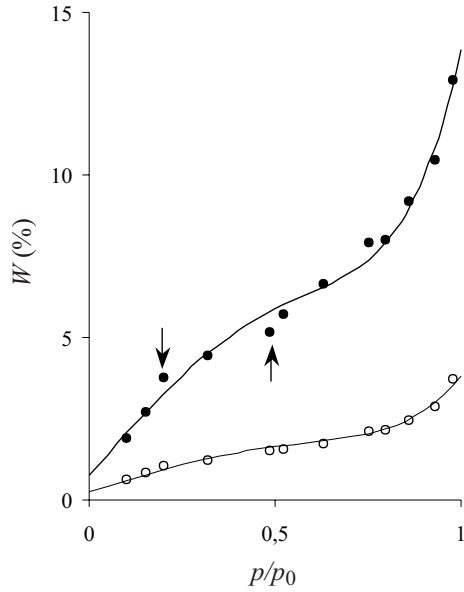


Fig. 1. Calculated and experimental data of water vapour adsorption by 3-5 mm aggregates from horizon A of soddy strongly-podzolic soil and ordinary chernozem (●, ○ - experimental points, respectively); solid line – data calculated from Eq. (1); arrows are explained in the text.

pressure 0.1 p/p_0 0.98 and the functional relationship $W = A[(p/p_0)^6 - (p/p_0)^3 + (p/p_0)] + B$ for the soil aggregate fractions studied. Statistical significance of factor sum $(p/p_0)^6$, $(p/p_0)^3$ and (p/p_0) contribution to the model is confirmed by calculated t -criterion values ($t_A > t_{0.95}$). As the determination coefficient for the sieved fractions is less than for the triturated ones (0.985 and 0.993 respectively), and

standard error s_W is higher (0.21 and 0.16 respectively), the Eq. (3) describes adsorption isotherms for the sieved fractions less accurately than for the triturated ones. Uniformity of the triturated samples might be the reason for this.

Table 1 presents estimation data for Eq. (3) coefficients and for maximum hygroscopic moisture in soil aggregate fractions of the soils studied. Coefficient A in the Eq. (2) nearly coincides with maximum hygroscopic moisture W_{mh} or $W_{0.98}$. Our estimates show 0.02 mean value for $W_{mh} - A$ and standard deviations $s_{W_{mh}} < s_{\Delta} < s_A$ for W_{mh} , A values being 0.18, 0.19 and 0.2 respectively. Thus, constant A in the Eq. (3) for separate soil aggregate fractions and for triturated soil samples (Kharitonova *et al.*, 2003) represents maximum hygroscopic moisture W_{mh} , which is related to hydrological soil constants (Michurin, 1975). Constant B in Eq. (3) is a model-fitting coefficient which is probably determined by quantity of water, not involved in adsorption in the range 0.1 p/p_0 0.98. Similar to (Kharitonova *et al.*, 2003), B coefficient will be called residual moisture or W_{res} . Thus, our statistical analysis indicates that equation type to describe relation $W=f(p/p_0)$ during absorption process does not depend on soil type, fraction dimensions in soil microaggregates (fractions 0.1, 0.1-0.25 mm) and macroaggregates (fractions 0.25-0.5, ..., 5-10, >10 mm). Besides, it does not depend on the tested methods used to prepare samples for analysis *ie* dry sieving without preliminary trituration or soil sample trituration to particle size 1 mm.

What do these equation parameters depend on? Soil adsorption capacity is known to depend to a great extent on particles <0.001 mm. They are also significant in soil

Table 1. Constants (A, B) of Eq. (3) for dried-sieved soil aggregate fractions

Fractions (mm)	Soddy strongly-podzolic soil hor. A1 (2-10 cm)			Ordinary chernozem hor. A1 (20-30 cm)			Chestnut soil hor. A (5-15 cm)			Medium-columnar solonetz hor. A (0-10 cm)		
	A	B	W_{mh} (%)	A	B	W_{mh} (%)	A	B	W_{mh} (%)	A	B	W_{mh} (%)
<0.1	2.87	0.23	3.02	12.78	0.78	12.69	6.41	0.57	6.41	4.90	0.55	4.95
0.1-0.25	3.16	0.23	3.28	13.02	0.67	12.73	6.88	0.49	6.57	6.07	0.61	6.17
0.25-0.5	3.28	0.29	3.44	13.01	0.67	12.69	7.51	1.03	7.73	6.33	0.69	6.47
0.5-1	3.33	0.33	3.55	13.20	0.63	12.81	7.94	0.98	8.22	6.48	0.69	6.60
1-2	3.33	0.29	3.24	13.23	0.81	13.04	8.33	0.98	8.53	6.32	0.69	6.39
2-3	3.43	0.26	3.61	13.10	0.59	12.74	8.78	0.94	8.75	6.26	0.65	6.32
3-5	3.56	0.25	3.72	13.09	0.76	12.91	8.50	1.09	8.74	6.35	0.51	6.31
5-7	3.66	0.25	3.82	13.14	0.51	12.72	8.31	0.89	8.38	6.00	0.60	6.09
7-10	3.25	0.30	3.45	13.04	0.59	12.71	8.83	0.73	8.94	6.01	0.62	6.08
>10	2.90	0.23	3.09	13.10	0.77	12.93	7.15	0.76	7.27	6.15	0.56	6.13
Triturated soil, ≤1 mm	3.35	0.36	3.57	11.48	1.61	12.04	6.99	0.82	6.91	5.28	0.58	5.39
S	0.10	0.05	0.10	0.29	0.15	0.14	0.21	0.10	0.28	0.15	0.07	0.15

Note: S – standard deviation of parameters.

structure formation (Voronin, 1984). Our analysis of clay content in the soils studied has revealed that W_{mh} value is related to clay content in the samples from similar soil horizons. Thus, in humus accumulative horizons the more clay there is in the sample the higher is the W_{mh} value (Fig. 2). Therefore, maximum hygroscopic moisture W_{mh} ,

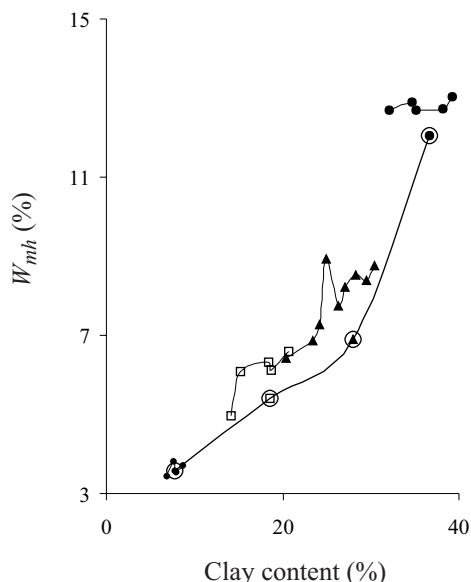


Fig. 2. Dependence of maximum hygroscopic moisture on clay content in soil aggregates (○ – experimental points for soddy strongly-podzolic soil, □ – medium-columnar solonetz, ▲ – chestnut soil, ● – ordinary chernozem); fine line – soil aggregate fractions (for clearness several experimental points are omitted); heavy line – trituated soil samples (≤ 1 mm), respective experimental points are circled.

the main parameter of Eq. (1), depends on clay content in the sample.

Relations between W_{mh} and clay content become more complex in soil micro- and macroaggregates of a separate soil horizon. Firstly, except for soddy strongly-podzolic soil, mean value of maximum hygroscopic moisture \bar{W}_{mh} for dry-sieved soils aggregates is higher than for trituated samples (particles ≤ 1 mm in size). It is 12.8 and 12.04% for ordinary chernozem, 7.98 and 6.91% for chestnut soil, 6.15 and 5.39% for medium-columnar solonetz, respectively. It seems to be connected with decomposition of not only soil macrostructure, but also its microstructure, when the samples were trituated. Secondly, W_{mh} strict increase because of clay content is not evident. Fig. 2 illustrates compact disposition of experimental points in soddy strongly-podzolic soil. In chernozem and solonetz (except the 0.1 mm fraction), the curve of W_{mh} dependence is parallel to the clay content axis. W_{mh} dependence on clay content for chestnut soil aggregate fractions is zigzag-shaped. Clay content influence in aggregates is mostly revealed through simbate changes of W_{mh} (min-max) intervals and relative fluctuation range of clay content in aggregates. The soils studied may be ranged as follows: ordinary chernozem < soddy strongly-podzolic soil < medium-columnar solonetz < and chestnut soil according to (min-max) interval data (0.24, 0.82, 1.65 and 2.53%, respectively) and relative fluctuation range of clay content in aggregates (20, 29, 36 and 42%, respectively).

To study the effects of the size of aggregates and their clay content on the main parameter of the Eq. (1), group analysis of W_{mh} values for aggregate fractions was undertaken for each soil type (Table 2). W_{mh} (min-max) interval for each soil type has been divided into equal

Table 2. Influence of soil aggregates size on aggregate maximum hygroscopic moisture

Soil	Interval of W_{mh} (%)	Step of segmenting ΔW (%)	Significantly different groups of aggregate fractions (size, mm)	Intragroup \bar{W}_{mh} (%)	S_w	Mean clay content in the group (%)
Ordinary chernozem	12.69-12.90	0.14	all fraction	12.80	0.10	36.6
Soddy strongly-podzolic soil	3.02-3.82	0.10	$\leq 0.25; > 10$	3.13	0.14	6.5
			$0.25 < d \leq 10$	3.59	0.14	7.5
Medium-columnar solonetz	4.95-6.60	0.15	≤ 0.1	4.95	-	14.1
			> 0.1	6.28	0.18	18.9
Chestnut soil	6.41-8.94	0.28	≤ 0.25	6.64	0.33	21.9
			$0.25-0.5; > 10$	7.50	0.33	25.9
			$0.5 < d \leq 10$	8.59	0.27	28.4

Note: S – intragroup standard deviation of \bar{W}_{mh} .

$W = S_{W_{mh}}$ segments. Then W_{mh} data in the segments were grouped when standard deviation in the group was comparable with the analytic error of W_{mh} estimation.

W_{mh} value for ordinary chernozem does not depend on dry-sieved aggregate size, as standard deviation for W_{mh} value does not exceed standard deviation for the defined value (0.12 and 0.14%, respectively). Adsorption isotherms of water-resistant aggregates, 0.25-0.5, 0.5-1 and 1-2 mm in size, also coincide and may be described with Eq. (1). Mean \bar{W}_{mh} value for water-resistant aggregates is 12.89%. If $\sigma = 0.05$, it cannot be statistically differentiated from $\bar{W}_{mh} = 12.8\%$ of dry-sieved aggregates. This might be explained by high content of clay and its slight variation in all chernozem aggregates fractions (32-39%) which are mostly composed of montmorillonite.

Soddy strongly-podzolic soil aggregates have much less clay in them (6.4-8.6%) and smaller W_{mh} values as compared to chernozem. Their W_{mh} (min-max) interval is wider as compared with the one of chernozem (0.82 and 0.24%, respectively), thus allowing us to assume W_{mh} value dependence on aggregate size in soddy strongly-podzolic soil. W_{mh} (min-max) interval segmenting and fraction grouping have resulted in two fraction groups with statistically different \bar{W}_{mh} . Aggregates with small \bar{W}_{mh} values and low clay content (3.13 and 6.4-6.5%, respectively) compose the first group (fractions 0.25 and >10 mm). Aggregates with bigger \bar{W}_{mh} values and higher clay content (3.59 and 6.8-8.6%) are grouped into the second (fractions 0.25<d<10 mm). Differences in W_{mh} values within the group are statistically insignificant.

Clay content in dry-sieved aggregates of columnar solonetz is approximately twice as high as in aggregates of soddy strongly-podzolic soil (14.1-20.7%), as well as W_{mh} values (5-6.6%). In fraction <0.1 mm, minimal W_{mh} value of 4.95% corresponds to minimal clay content. Fraction 0.5<d<1 mm has the highest clay content (20.74%) and the maximum W_{mh} value. As for the remaining soil aggregates, clay content in the fraction and W_{mh} value, as well as clay content and effective specific surface value have simbate dependence. W_{mh} (min-max) interval for columnar solonetz is twice as wide as for soddy strongly-podzolic soil (1.65 and 0.82%, respectively). However, only one aggregate fraction

0.1 mm has been singled out after W_{mh} (min-max) interval segmenting and fraction grouping. This fraction differs with statistical confidence in W_{mh} value from other fractions, where group average $\bar{W}_{mh} = 6.28\%$ and standard deviation 0.18% is comparable with 0.15% analytic error of W_{mh} estimation.

In chestnut soil, strict correlation and linear dependence between W_{mh} and clay content ($r^2 = 0.986$) has been found only in fractions 0.5 and >10 mm. As for 0.5<d<10 mm macroaggregates, W_{mh} value does not constitute a linear function of clay content and macroaggregate size. W_{mh} value standard deviation ($\bar{W}_{mh} = 8.59\%$) in 0.5<d<10 mm macroaggregates is 0.27% and does not exceed 0.28% error

of W_{mh} estimation. W_{mh} (min-max) interval segmenting and fraction grouping have indicated three groups with statistically different W_{mh} values and clay content (I group – 0.25 mm fractions; II group – 0.25-0.5 and >10 mm, III group – 0.5<d<10 mm).

The following explanation of the results obtained seems most appropriate. Macroaggregates usually contain elementary particles in proportions close to the ones in soil as a whole. It means that macroaggregates are similar to the soil in terms of their particle-size, mineralogical and chemical compositions and respective characteristics, such as effective specific surface and cation exchange capacity. Microaggregates (<0.25 mm) contain more sand and dust and less clay and hence have less water adsorption ability as compared to the soil as a whole. Compared to macroaggregates (0.25<d<10 mm), clay depletion in aggregate fractions 0.25 mm and in nonstructured part of soil mass of fraction d>10 mm may be the result either of aggregation processes or the method of soil splitting into aggregates. When dry sieved, elementary soil particles of sand and dust size, which are not firmly surface tied in 0.25<d<10 mm macroaggregates, separate and become the 0.25 mm fraction. Relative accumulation of elementary soil particles of sand and dust size in a nonstructured part of soil mass (soil separates >10 mm) is due to proportion diminishing between surface area and soil separates volume.

If the amount of elementary soil particles of sand and dust size, tied in some macroaggregates, is calculated as $V/S \cdot r/3$, where: \propto – proportionality symbol, V – volume, S – surface area, r – radius of a macroaggregate (ball shaped, minimum mass volume) and the number of elementary soil particles of sand and dust size, which are loose on the aggregate surface, is calculated as $S/V \cdot 3/r$, then the integral accumulation of elementary soil particles of sand and dust size inside some macroaggregates may be calculated with the following formula:

$$\int_{r_1}^{r_2} (V/S - S/V) dr = (1/6r^2 - 3 \ln r) \Big|_{r_1}^{r_2} \quad (4)$$

Our estimations of Eq. (4) result in positive values for macroaggregates 1 and >5-7 mm and in negative values for 1<d<5-7 mm, thus leading us to the conclusion that certain clay accumulation occurs in macroaggregate fraction of 1 to 7 mm. We shall call these fractions ‘an aggregated part of soil mass’. Compared to soil, an aggregated part contains more clay and hence less elementary soil particles of sand and dust size, aggregate fractions with higher content of elementary soil particles of sand and dust size 1 and >5-7 mm, nonaggregated part of soil mass. However, Eq. (4) ignores fractal dimension of aggregate volume and surface (Mandelbrot, 1978) which depend on particular soil characteristics (particle-size, mineralogical and chemical composition, amount and nature of organic substance). So lower and upper boundaries for aggregate size of an

aggregated part of soil mass depend on the soil type. Thus, for soddy strongly-podzolic soil, the lower and upper boundaries for aggregate size of an aggregated part of soil mass are $0.25 < d < 10$ mm and for chestnut soil they are $0.5 < d < 10$ mm. Only the lower boundary, *ie* aggregates > 0.1 mm has been determined in the case of columnar solonetz. No boundaries are determined for chernozem by this approach. All the fractions have similar W_{mh} values and clay content, which indicates high-level aggregation of humus accumulating horizon in chernozem.

CONCLUSIONS

1. Water vapour adsorption of dry sieved aggregates (fractions from 0.1, 0.1-0.25, ..., 7-10, >10 mm) obtained from humus accumulation horizons of soddy strongly-podzolic soil, ordinary chernozem, chestnut soil and columnar solonetz is described in $0.1 < p/p_0 < 0.98$ interval of relative pressure with the equation $W = W_{mh}[(p/p_0)^6 - (p/p_0)^3 + (p/p_0)] + W_{res}$, where: W_{mh} is maximum hygroscopic moisture and W_{res} determines the quantity of bound water that is not engaged in adsorption.

2. Analysis of soils with different clay content (from 8 to 39%) indicates that the main equation parameter W_{mh} depends on the clay content in soil.

3. Moreover, as for W_{mh} and clay content, dry sieved soil fractions can be grouped into aggregated and non-aggregated parts (soil type determines aggregate size boundaries).

4. Compared to the non-aggregated, the aggregated part of soil mass is characterized by bigger clay content and W_{mh} group values.

5. W_{mh} in the aggregated part of certain soils does not depend on aggregate size.

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