UDC 631.43
DOI: 10.19047/0136-1694-2019-97-91-112

Cite this article as:
Matveeva N.V, Milanovsky E.Yu., Rogova O.B., The method of preparing soil samples for soil – water contact angle measurement using sessile-drop technique, Dokuchaev Soil Bulletin, 2019, V. 97, pp. 91-112, DOI: 10.19047/0136-1694-2019-97-91-112

THE METHOD OF PREPARING SOIL SAMPLES FOR SOIL – WATER CONTACT ANGLE MEASUREMENT USING SESSILE-DROP TECHNIQUE

© 2019 N. V. Matveeva[1,2*], E. Yu. Milanovsky[1,2], O. B. Rogova[1]

[1]V.V. Dokuchaev Soil Science Institute,
Russia, 119017, Moscow, Pizhevskiy per., 7, build. 2,
[*]e-mail: Nataliy_Matveeva@list.ru

[2]Lomonosov Moscow State University,
Russia, 119991, Moscow, Leninskie Gory, 1

Received 06.03.2019, *Revised* 01.04.2019, *Accepted* 28.05.2019

The method of soil samples preparation for measuring the (wetting) contact angle (CA) of the soil solid phase surface using membrane filters is proposed. The samples of kaolinite, a standard sample of chernozem and samples of agro-chestnut soil were taken for the experiment. The results of the CA measurements using two types of sample preparation for the analysis were compared. The first method of sample preparation was to apply a sample to a double-sided sticky tape; the second method involved the deposition of suspensions of the studied samples of certain concentrations on membrane filters. The advantages and disadvantages of each sample preparation method are described. The significant difference in the obtained CA values depending on the sample preparation for measurement was revealed. The method of sample preparation with the use of membrane filters developed by the authors made it possible to reduce the CA measurement error by more than 2 times. Reducing the variation of the CA value of a single sample will allow comparing similar soil samples, including soils of the same type, but involved in different land use systems.

Keywords: wettability, hydrophilicity, hydrophobicity, soil – water contact angle, sample preparation.

INTRODUCTION

Currently, researchers pay great attention to the work aimed at identifying functionally significant markers, compound groups, fractions and pools, which help to predict the resistance of soil organic matter and soils in general to anthropogenic effects and climatic changes. This leads to the search for methods and technologies to determine the integral indicators of changes in the properties of organo-mineral soil system with a minimum altering in its chemical composition and microaggregate structure. A change in the substantial soil composition, especially the properties of organic substance, is reflected in a change in physical properties, namely, the properties of solid phase surface, such as hydrophilicity and hydrophobicity of particles, which determines wettability and affects agronomic value of the soil structure as a whole (Milanovsky et al., 2005). Thus, the properties of solid soil phase surface are linked to infiltration, evaporation, resistance to water erosion and to hydrological soil balance in general. Soil water-repellent properties depend mainly on the organic components of various origin and structure (Doerr et al., 2000). Wettability increases with more and denser polar functional groups on the surface of solid soil phase, while non-polar functional groups on the surface of solid phase contribute to formation of moisture-repellant surface (Ellerbrock et al., 2005). Root excretions (Moradi et al., 2012), decomposition products of leaf and branch decay along with bacteria and fungi decay products in the soil (Doerr et al., 2000) can also affect soil wettability. All the indicators mentioned above are directly correlated with the method of soil treatment and use.

Several methods are used to determine the degree of soil wetting. These methods are usually selected based on their suitability for field or laboratory work, as well as time and resources (Papierowska et al., 2018). Afield the ability of soil to be wetted is often estimated by infiltration time (water drop penetration time, WDPT) (Bahrani et al., 1973; Doerr, 1998); in the laboratory it is determined by measuring the soil-water contact angle (CA) using any of two ways – by capillary rise method (CRM) (Adamson, 1990; Liu et al., 2016) or by sessile drop method (SDM) (Ryley, Khoshaim, 1977).

Measurement of the contact (wetting) angle (CA) is a common method to measure soil hydrophobicity (Burghardt, 1985; Shein, 2014; Kholodov et al., 2015); however, there are no universal methods for applying it to all types of soil samples (Bachmann, 2001). So, in the work (Shang et al., 2008) different methods of CA measuring were compared; the CA ranged from 10º to 40º. The authors noted the highest measurements replicability for finely dispersed minerals - kaolinite and illite, while the accuracy in the case of the sessile drop method was influenced by the thickness of test sample layer. Thus, the method of sample preparation for measurement plays a crucial role in obtaining replicable results. When preparing samples, the following requirements should be considered: the thickness of the sample layer should be minimal in order to exclude the absorption and let the drop spread over. In this case the sample particles should form the densest surface. In 2000, Bachmann (Bachmann et al., 2000) proposed to apply a powder sample onto a double-sided sticky tape fixed on a slide. In the work (Lamparter et al., 2010) it was proposed to place the sticky tape on a flexible fabric rather than on a hard surface so that the sample covers better the surface of the adhesive tape. However, this method also does not guarantee that the particles will be evenly and densely distributed on the tape surface. Moreover, the properties of the sticky tape itself, which is used as a support, can affect the results due to the fact that the particles on its surface are insufficiently densely packed (Goebel et al., 2004).

The aim of this work is to improve the existing methodology for soil samples preparation to determine the contact (wetting) angle in order to obtain more reliable measurement results. To obtain a uniform sample surface and to exclude any influence of sticky tape on measurement results, we propose to deposit a water suspension on a membrane filter. Reducing the variation in CA value of single sample would make it possible to compare soil samples with similar properties, including soils of the same type but of different land use systems.

MATERIALS AND METHODS

The experiments were carried out on the clay mineral kaolinite of Prosyanovskoye deposit, a standard sample of chernozem (Certificate SP-1 No. 901-90) and samples of agro-chestnut soil, which

were selected in 2013 on the fields of the FSBSI VNIIOZ, Volgograd Region from the upper layer of 0–25 cm. Air-dry soil samples were ground with a pestle with rubber top and sieved through a 1 mm sieve.

The evaluation of CA was carried out by sessile drop method (Ryley, Khoshaim, 1977), on a digital goniometer (Drop Form Analysis System, DSA100, Kruss, Germany) equipped with a video camera and a software. The method allows getting CA value directly, by constructing a tangent line at the interface point of three phases - water, soil, air – in contrast to the method of raising capillary rim, in which the CA is calculated by the curves of the change in soil weight when it is saturated with water.

Sessile drop method is to place a drop of water on a flat surface and to measure the angle of water-surface phase separation. The experiment is carried out according to the following scheme: a drop of distilled water of 1.5 μl is squeezed out from a vertically placed needle, the needle goes down so that the drop settles on the sample, then the needle rises. The whole process is recorded by video filming. The software allows us to analyze the drop shape on the sample surface and calculate CA values. Since the soil has a high absorptive capacity (Shang et al., 2008), CA is determined by the first clear shot at the time when the drop settles onto the sample and the needle is removed (Fig. 1).

To select the optimal conditions to measure CA we have tested two different methods of sample preparation for measuring.

The following were used as a basis for the sample application: double-sided sticky tape on a polypropylene basis with an acrylic adhesive system, the tape thickness is 1000 microns; Vladipor MFAS-OS-2 type membrane filters that is a microporous film material made on the basis of a mixture of cellulose acetates with a pore size of 0.45 microns and the total porosity of 80–85 %. The diameter of the filter is 47 mm.

The samples were applied on a double-sided sticky tape according to the method described in the literature (Bachmann et al., 2000b; Beatty, Smith, 2010). Seven identical squares of double-sided sticky tape were glued onto a slide with the size of (2.5 × 7 cm). Separation of sticky tape sections is necessary to prevent excessive liquid spreading during the experiment; this method made it possible to

record the number of CA measurement for each sample. The ground sample was evenly distributed on a slide covered with double-sided sticky tape and pressed with another slide for one minute with a force of about 100 g. Non-sticking particles were gently shaken off and the sample was pressed once again with a glass slide.

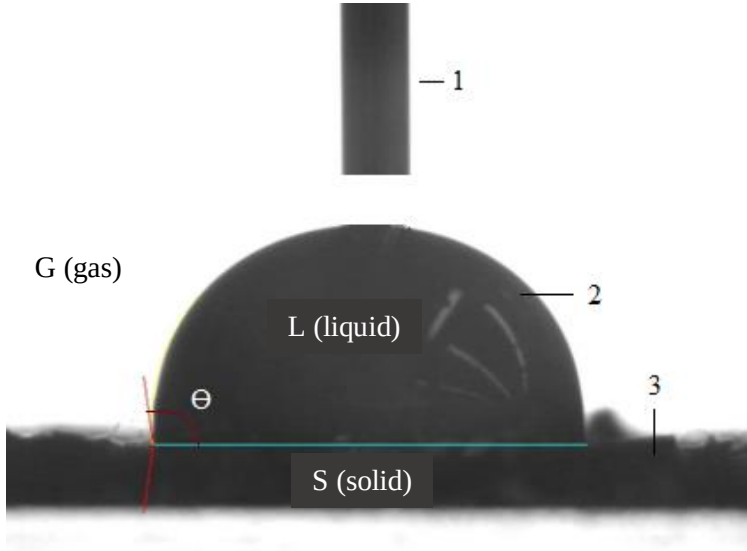

Fig. 1. Determination of contact angle. 1 – needle for drop delivery; 2 – a drop of liquid; 3 – the test sample; Θ – contact (wetting) angle.

To obtain a sample film on a membrane filter a vacuum filtration unit with a porous glass base for a membrane filter was used. The unit consisted of a funnel of 250 ml and a Bunsen flask of 1 liter. The filtration area through the unit was 12.5 cm^2. The filtration unit was used in conjunction with a water-jet vacuum pump connected to the water supply system. Before the experiment the membrane filters were kept in distilled water for 24 hours so that their surface was evenly moistened, which would ensure equal filtration over the entire filter surface. Having checked that the filtration surface was of horizontal position at vacuum, the membrane filter was carefully placed on it avoiding the formation of air bubbles under the filter, pressed with the

funnel and fixed with a special clip. The waterjet pump was turned on and then several aliquots of distilled water were passed through the filter. The water and the samples suspensions were applied with a 5 ml dose-meter. After the water vaccum suction filtration the vacuum was turned off so that a small layer of the liquid could remain on the filter, the sample suspension was carefully applied dropwise, after that the pump was turned on. Wet filters with the sample were placed on the slide onto which a double-sided sticky tape had previously been glued; then dried at 40º in the drying oven.

The technique for CA measuring on a sticky tape was described in the work (Bachmann et al., 2000b) and suggested CA measuring of the samples at their application to a double-sided sticky tape. Before measurement the test samples were kept for 24 hours in the drying oven at the temperature of 40º, then they were ground in an agate mortar and sieved through a 100-micron sieve. As it is known, drying temperature affects water-repellent properties of soils; therefore, it should not be further increased (Dekker et al., 1998). The experiment was conducted on air-dried samples.

Methods of CA measuring on membrane filters. The work (Wu, 2001) described the procedure for samples preparation by putting aqueous suspensions on slides. The method was proposed to reduce the influence of the surface properties on CA value on which the sample is applied and also made it possible to reduce the amount of the sample, compared with the method described above. However, it is thus difficult to ensure the required thickness of the analyzed sample layer and to avoid the appearance of inhomogeneity during drying.

Our modification of the technique consists in uniformly applying soil suspension to the membrane filters rather than to the slide. For this, we placed in a test tube a dried, ground and sieved through d = 0.25 mm weighed portion of sample and added 25 ml of distilled water. The suspensions of the studied samples with 8 different concentrations from 0 to 5 mg/ml were exposed to Branson Digital Sonifier ultrasound at the power of 40 % for 5 min. Then, the entire suspension was transferred back to the tube at the same time being filtered through a sieve with d = 0.1 mm to ensure greater homogeneity. The residual

insignificant amount of coarse sand was collected separately and was not used in the analysis.

Statistical processing of the results was carried out in the STATISTICA10 program (StatSoft, RU). The normality of the distribution of CA values for each sample was checked with the Kolmogorov – Smirnov normality criterion (Lilliefors, 1967). The significance of pairwise differences was checked with t-test. The correlation between CA value and concentration of the deposited suspension on the membrane filter was checked by the Kruskal – Wallis (K–W) criterion (Kruskal, Wallis, 1952).

RESULTS AND DISCUSSION

Testing of the sample preparation method using sticky tape was carried out on kaolinite mineral and 16 samples of agro-chestnut of various land use systems. Measurements of kaolinite CA were carried out in three experimental replications each of which assumed seven analytical replicates. The average kaolinate CA value was 27º, the variation in the CA value for one experimental replication ranged from 1.5º to 8º, which is 28 % of the average value (Fig. 2).

Varying CA value at measurements on sticky tape corresponds to the variation obtained by other authors when studying the CA of minerals and soil samples prepared for analysis in the same way (Bachmann et al., 2013; Sofinskaya et al., 2016; Bachmann et al., 2009).

Table 1 shows the fluctuation limits of CA value measured for a single sample, illustrating the actual results according to a number of researchers. The obtained limits of indicator fluctuations are consistent with those presented in the table.

The average obtained values of kaolinite CA correspond to the published data (Shang et al., 2008; Leelamanie et al., 2010), however, the measurement error for the mineral turned out slightly higher than for soil samples according to the data (Beatty, Smith, 2010) and almost doubled that one obtained (Bachmann et al., 2000b) for a fine soil fractions.

Table 1. Variation of the contact angle of a single soil sample

Fluctuation limits, degree	Source
4–20	Beatty and Smith, 2010
2–13	Sofinskaya et al., 2016
2–15	Bachmann et al., 2000b
8–23	Bachmann et al., 2013
2–17	Bachmann et al., 2009

Note. CA was measured with sessile drop technique on sticky tape.

Given the uniformity of material composition of pure mineral and the size of its particles, such large differences can only be explained by the complexity of uniform and replicable sample application to the sticky tape.

The heterogeneity of real soil samples is obviously higher than that of a pure mineral. When analyzing CA value of similarly prepared samples of agro-chestnut soil, the average values for a single sample turned out to range from 17.1º to 27.6º, while the variation of this indicator for one sample was from 2.8º to 16.5º (Fig. 3).

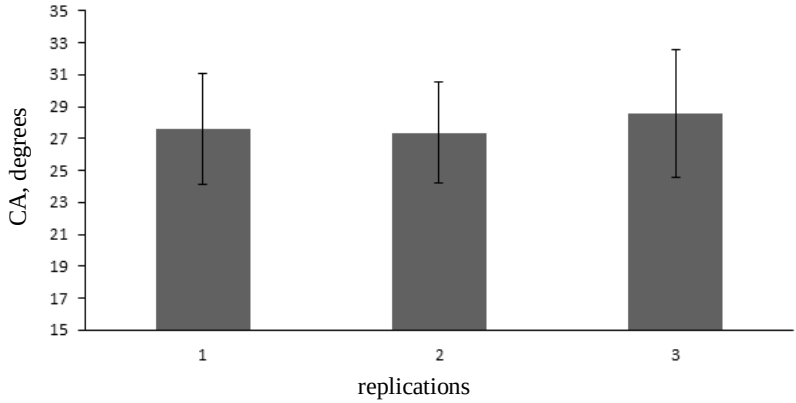

Fig. 2. Contact angle of kaolinite mineral. Standard deviation is calculated for 7 analytical replications. Measured on sticky tape.

Such variation leads to the fact that confidence intervals on the chart overlap by 1/3 or more. As is known (Grzhibovski, 2008), with

such a strong overlapping of confidence intervals we can observe the absence of a significant difference in relative values, i.e., such a significant variation in CA values measured for one sample makes it difficult to compare values obtained for different samples.

Therefore, we propose a different method of sample preparation with deposit of their suspensions on the membrane filters.

When determining CA with sessile drop method it is necessary to ensure a uniform, even, dense surface of the test sample and a sufficient thickness of its layer on the support so that the support material does not affect the obtained results. These conditions are satisfied when a quantity of the substance deposited on the filter is not less its certain amount, depending on the filter surface area.

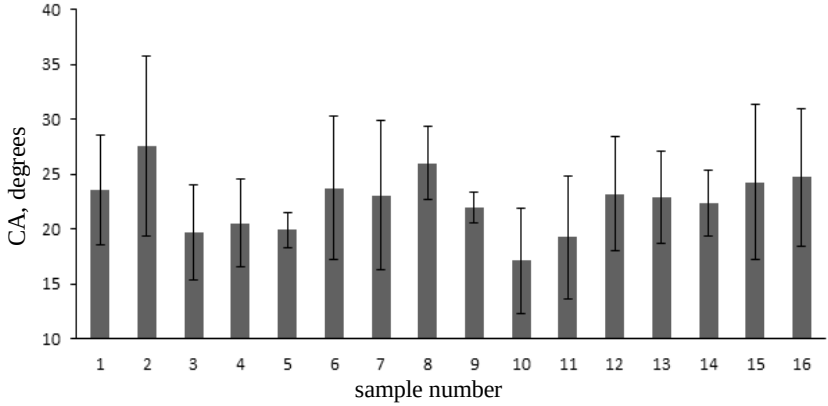

Fig. 3. Contact angle of agro-chestnut soil. Standard deviation is calculated for 7 analytical replications. Measured on sticky tape.

The optimal concentration of the suspension deposited on the membrane filter was determined with a kaolinite mineral, a standard sample of chernozem (SP-1) and a sample of agro-chestnut soil. The volume of suspension aliquot deposited on the membrane filter was 5 ml, thus, on the filter we received the concentrations of 0, 2, 4, 8, 10, 15, 20 and 25 mg/filter, respectively. The filtration part area was 12.5 mg/cm^2. Thus, when recalculating the concentration of deposited suspension per 1 cm^2, we obtained a range from 0 to 2 mg/cm^2.

Three filters were prepared for each concentration (four filters for zero concentration) and each analytical filter had six analytical replications of the CA measurements. By analyzing kaolinite and soil samples we were able to determine optimal concentration of the substance necessary for the study. The results are presented in Figure 3. It is clearly seen that in the case of kaolinite the contribution of the surface properties of the filter itself to CA value disappears at lower concentrations compared with the soil sample. Due to the homogeneity and small particle size of the mineral even at low concentrations of the suspension deposited on the filter we obtained values corresponding to the published data – 27.8º (Shang et al., 2008; Leelamanie et al., 2010).

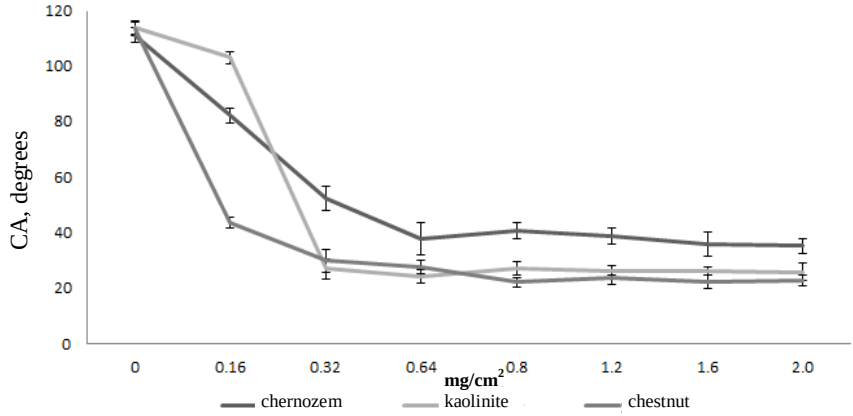

Fig. 4. Contact angle for different concentrations of kaolinite, chernozem and agro-chestnut soil. The mean values with standard deviations are shown. Measured on membrane filters.

Also, Figure 4 clearly shows a decrease in the standard deviation of the obtained CA values compared with the first method. Our proposed method of material sample preparation allowed us to reduce the range in CA value for one sample to 2º–5º for kaolinite and to 2º–8º for soil samples. A comparison of the data obtained for a standard chernozem sample with the available published ones (Kholodov et al., 2015) revealed their comparability. So, Kholodov et al. determined average CA values for chernozems aggregates of the mowing steppe as 64º–

70º, arable land as 14º–26º depending on water resistance. Our final CA values for SP-1 made of Kursk chernozem material are 33º–38º, which may be associated with a partial transformation of organic substance during storage.

The dependence between CA values on the concentration of deposited suspensions was determined with the Kruskal – Wallis criterion (Kruskal, Wallis, 1952). The suspension concentration acted as a grouping variable, CA value – as a dependent variable. Table 2 shows levels of significance (***p***) for different samples and ranges of suspension concentration changes.

Table 2. Evaluation of the significance of suspension concentration effect on the value of contact angle using the Kruskal – Wallis criterion

Concentration ranges, mg\cm^2	**Level of significance *p***		
	Kaolinite	**Cernozem**	**Chestnut soil**
0–2	0.0147	0.0027	0.0033
0.16–2	0.0372	0.0090	0.0119
0.32–2	0.0907	0.0223	0.0324
0.64–2	0.1507	0.0345	0.1241
0.8–2	0.1207	0.0729	0.8629
0.12–2	0.1184	0.0665	0.8371
0.16–2	0.8273	0.8273	0.8273

Note. $p > 0.05$ values are highlighted.

The results show that over the entire range of curves (Fig. 3) there is a significant correlation between the suspension concentration and the CA value, as evidenced by the level of significance of $p < 0.05$. CA value on suspension concentration dependence disappears, starting from a concentration of 0.32 mg/cm^2 for kaolinite, 0.8 mg/cm^2 for chernozem and 0.64 mg/cm^2 for a chestnut soil sample. We suppose that the minimum suspension concentration sufficient to obtain a uniform layer on the membrane filter surface depends on the particles size and on the structural features of the sample. So, the most finely dispersed sample of the studied ones is kaolinite, therefore, to obtain a

homogeneous thin layer less suspension concentration is required. The structure of soil samples is more complex, including both the mineral part and organic components. The highest concentration of suspension was required for chernozem – from 0.8 mg/cm^2, which may be associated with a high content of organic substance.

Assessment of the significance of suspension concentration effect on CA value by the Kruskal – Wallis test allowed us to determine at what minimum suspension concentration of the test sample the dependence between CA and concentration disappears. However, this analysis does not make it possible either to evaluate replicability between the experimental replicates or to speak about uniformity of the sample thin layer deposited on the membrane filter.

Therefore, we evaluated the significance of the differences between the measurements for various concentrations as well as for one concentration between experimental replicates. Since the verification by the Kolmogorov-Smirnov criterion (Lilliefors, 1967) confirmed the normal distribution of the property, the pairwise comparison of CA values was carried out with calculation of the Student t-criterion: for kaolinite samples significant differences between the replicates for one and for different concentrations disappear at the concentration of 0.8 mg/cm^2 and higher.

At lower concentrations of the suspension deposited on the membrane filter there are significant differences for various concentrations, while there are no significant differences in replicates for one concentration. For soil samples significant differences disappear at the suspension concentration of 0.8–1.6 mg/cm^2. At the lower concentration of 0.32 mg/cm^2 the average values of the contact wetting angle for chernozem is significantly different from those corresponding to other concentrations and between replicates for this concentration. This is due to the fact that a soil sample at such a low concentration is more difficult to apply to the membrane filter in order to obtain a uniform layer, compared with the finely dispersed mineral kaolinite.

Thus, according to the results of our experiment, the minimum suspension concentration of the test sample sufficient for replicable results and confirmed by the Kruskal – Wallis criterion is 0.8 mg/cm^2. T-criterion made it possible to determine the range of optimal

concentrations to determine the CA of the studied samples – from 0.8 to 1.6 mg/cm^2.

Comparing kaolinite and agro-chestnut soil CA for different sample preparation methods (Table 3) it should be noted that the average CA values obtained on membrane filters in the selected range of suspension concentration fit the CA values measured on the double-sided sticky tape, at which case a scatter of values was significantly smaller.

Table 3. Comparison of the contact angle values of kaolinite and agro-chestnut soil, measured by two different methods

Kaolinite CA					
On sticky tape			**On membrane filters**		
Repli-cants	Average	Mean deviation	Suspen-sion con-centra-tion, mg\cm^2	Average	Mean deviation
1	27.6	3.5	0.8	27.5	2.4
2	27.4	3.2	1.2	27.5	1.5
3	28.6	4.0	1.6	26.6	1.8
Agro-chestnut soil CA					
1	23.8	6.6	0.8	21.1	1.5
2	24.7	6.2	1.2	22.0	1.4
3	22.9	4.2	1.6	22.4	1.8

Verification of these samples by t-criterion did not reveal significant differences. It then follows that the proposed method of sample preparation with membrane filters makes it possible to obtain reliable results of CA measurements with less variation, which will enable us to compare soil samples and their components that are close in properties or origin.

Comparing the two methods it should be noted: the CA measurement of the samples deposited on a double-sided sticky tape

has a simpler sample preparation, however, at the same time it gives a greater variation in the contact angle which is associated with the heterogeneity of the soil particles and the difficulty in their uniform appliance to the sticky tape. Such a technique requires a larger amount of studied material, which is not always possible in the study of hardly extractable soil fractions. CA measurement on membrane filters supports reducing by half the variation of analysis results and minimize the weighted portion of the test sample. This method of sample preparation has some disadvantages associated with the difficulty of sample uniform application on the membrane filter: determining the optimal concentration of the suspension which is necessary for deposition on the membrane filter; observing the same filtration rate in all parts of the filter.

CONCLUSIONS

When analyzing and comparing the results of CA measuring, it is necessary to consider both the measurement method (Bachmann et al., 2003; Papierowska et al., 2018) and the sample preparation before the measurement. We proposed a method of sample preparation with membrane filters that made it possible to reduce by half the variation in CA value for a single sample. We suggest considering a concentration of 0.8 to 1.6 mg/cm^2 optimal for soil suspension in the study of chernozems and chestnut soils. It should be noted that before measuring CA of other soil types with the proposed method it is necessary to verify the correctness of the chosen concentration of the soil suspension deposited on the membrane filter.

REFERENCES

1. Grzhibovskii A.M., Analiz kolichestvennykh dannykh dlya dvukh nezavisimykh grupp (Analysis of quantitative data for two independent groups), *Ekologiya cheloveka*, 2008, No. 2, pp. 54–60.
2. Milanovsky E.Yu., Shein E.V., Rusanov A.M., Zasypkina D.I., Nikolaeva E.I., Anilova L.V., Pochvennaya struktura i organicheskoe veshchestvo tipichnykh chernozemov Predural'ya pod lesom i mnogoletnei pashnei (Soil structure and organic matter of typical chernozem of the Pre-Urals under forest and perennial arable land), *Vestnik Orenburgskogo gosudarstvennogo universiteta*, 2005, No. 2, pp. 113–117.

3. *Svidetel'stvo na standartnyi obrazets (CO) SP-1 (kurskii chernozem) № 901-90 (OOKO152) po gosudarstvennomu reestru mer i izmeritel'nykh priborov SSSR (razdel standartnye obraztsy)*. Certificate for a standard sample (CO) SP-1 (Kursk black soil) No. 901-90 (OOKO152) according to the state register of measures and measuring devices of the USSR (section standard samples),1990.
4. Shein Ye.V., Milanovskiy Ye.Yu., Khaydapova D.D., Dembovetskiy A.V., Tyugay Z.N., *Novye pribory dlya izucheniya fizicheskikh svoistv pochv: 3D-tomografiya, reologicheskie parametry, kontaktnyi ugol* (New instruments for studying soil physical properties: 3D tomography, rheological properties, contact angle), Vestnik AGAU, 2014, No. 5 (115), pp. 44–48.
5. Kholodov V.A., Yaroslavtseva N.V., Yashin M.A., Frid A.S., Lazarev V.I., Tyugai Z.N., Milanovskii E.Yu., Kontaktnye ugly smachivaniya i vodoustoichivost' pochvennoi struktury (Contact angles of wetting and water resistance of the soil structure), *Pochvovedenie*, 2015, No. 6, pp. 693–693, DOI: 10.7868/S0032180X15060064.
6. Adamson A., Physical chemistry of surfaces 5th edn, New York: NY John Wiley & Sons Inc, 1990, 757 p.
7. Bachmann J., Contact angle and surface charge of wettable and hydrophobic silt particles, *J. Soil Sci. Plant Nutr*., 2001, No. 1, pp. 26–33.
8. Bachmann J., Ellies A., Hartge K.H., Development and application of a new sessile drop contact angle method to assess soil water repellency, *Journal of Hydrology*, 2000a, No. 231, pp. 66–75.
9. Bachmann J., Goebel M.O., Woche S.K., Small-scale contact angle mapping on undisturbed soil surfaces, *Journal of Hydrology and Hydromechanics*, 2013, No. 61 (1), pp. 3–8.
10. Bachmann J., McHale G. Superhydrophobic surfaces: a model approach to predict contact angle and surface energy of soil particles, *European Journal of Soil Science*, 2009, No. 60 (3), pp. 420–430.
11. Bachmann J., Horton R., Van Der Ploeg R.R., Woche S., Modified sessile drop method for assessing initial soil-water contact angle of sandy soil, *Soil Science Society of America Journal*, 2000b, No. 64 (2), pp. 564–567, DOI: 10.2136/sssaj2000.642564x.
12. Bachmann J., Woche S.K., Goebel M.O., Kirkham M.B., Horton R., Extended methodology for determining wetting properties of porous media, *Water Resources Research*, 2003, Vol. 39, No. 12, 14 p., DOI: 10.1029/2003WR002143.
13. Bahrani B., Mansell R.S., Hammond L.C., Using infiltrations of heptane and water into soil columns to determine soil-water contact angles, *Soil Science Society of America Journal*, 1973, No. 37 (4), pp. 532–534, DOI: 10.2136/sssaj1973.03615995003700040020x.

14. Beatty S.M., Smith J.E., Fractional wettability and contact angle dynamics in burned water repellent soils, *Journal of Hydrology*, 2010, Vol. 391, No. 1–2, pp. 99–110, DOI: 10.1016/j.jhydrol.2010.07.007.
15. Burghardt W., Determination of the wetting characteristics of peat soil extracts by contact-angle measurements, *Zeitschrift Fur Pflanzenernahrung Und Bodenkunde*, 1985, Vol. 148, No. 1, pp. 66–72, DOI: 10.1002/jpln.19851480108.
16. Dekker L.W., Ritsema C.J., Oostindie K., Boersma O.H., Effect of drying temperature on the severity of soil water repellency, *Soil Science*, 1998, No. 163 (10), pp. 780–796, DOI: 10.1097/00010694-199810000-00002.
17. Doerr S.H., On standardizing the 'water drop penetration time' and the 'molarity of an ethanol droplet' techniques to classify soil hydrophobicity: A case study using medium textured soils, *Earth Surface Processes and Landforms*, 1998, Vol. 23, No. 7, pp. 663–668.
18. Doerr S.H., Shakesby R.A., Walsh R.P.D., Soil water repellency: its causes, characteristics and hydro-geomorphological significance, *Earth-Science Reviews*, 2000, Vol. 51, Issue 1, pp. 33–65, DOI: 10.1016/S0012-8252(00)00011-8.
19. Ellerbrock R.H., Gerke H.H., Bachmann J., Goebel M.O., Composition of organic matter fractions for explaining wettability of three forest soils, *Soil Science Society of America Journal*, 2005, Vol. 69, Issue 1, pp. 57–66.
20. Goebel M.O., Bachmann J., Woche S.K., Fischer W.R., Horton R., Water potential and aggregate size effects on contact angle and surface energy, *Soil Science Society of America Journal*, 2004, Vol. 68, Issue 2, pp. 383–393.
21. Kholodov V.A., Yaroslavtseva N.V., Yashin M.A., Frid A.S., Lazarev V.I., Tyugai Z.N., Milanovskiy E.Y., Contact angles of wetting and water stability of soil structure, *Eurasian Soil Science*, 2015, Vol. 48, Issue 6, pp. 600–607, DOI: 10.1134/S106422931506006X.
22. Kruskal W.H., Wallis W.A., Use of ranks in one-criterion variance analysis, *Journal of the American statistical Association*, 1952, Vol. 47, Issue 260, pp. 583–621.
23. Lamparter A., Bachmann J., Woche S.K., Determination of small-scale spatial heterogeneity of water repellency in sandy soils, *Soil Science Society of America Journal*, 2010, Vol. 74,Issue 6, pp. 2010–2012.
24. Leelamanie D.A.L., Karube J., Yoshida A., Clay effects on the contact angle and water drop penetration time of model soils, *Soil Science and Plant Nutrition*, 2010, Vol. 56, Issue 3, pp. 371–375, DOI: 10.1111/j.1747-0765.2010.00471.x.
25. Lilliefors H.W., On the Kolmogorov-Smirnov test for normality with mean and variance unknown, *Journal of the American statistical Association*, 1967, Vol. 62, Issue 318, pp. 399–402.

26. Liu Z., X. Yu, Wan L., Capillary rise method for the measurement of the contact angle of soils, *Acta Geotechnica*, 2016, Vol. 11, Issue 1, pp. 21–35, DOI: 10.1007/s11440-014-0352-x.
27. Moradi A.B., Carminati A., Lamparter A., Woche S.K., Bachmann J., Vetterlein D., Vogel H.J., Oswald S.E., Is the rhizosphere temporarily water repellent? *Vadose Zone Journal*, 2012, Vol. 11 (3), 8 p.
28. Papierowska E., Matysiak W., Szatylowicz J., Debaene G., Urbanek E., Kalisz B., Lachacz A., Compatibility of methods used for soil water repellency determination for organic and organo-mineral soils, *Geoderma*, 2018, Vol. 314, pp. 221–231.
29. Ryley D.J., Khoshaim B.H., New method of determining contact-angle made by a sessile drop upon a horizontal surface (sessile drop contact-angle), *Journal of Colloid and Interface Science,* 1977, Vol. 59, Issue 2, pp. 243–251.
30. Shang J., Flury M., Harsh J.B., Zollars R.L., Comparison of different methods to measure contact angles of soil colloids, *Journal of Colloid and Interface Science*, 2008, Vol. 328, Issue 2, pp. 299–307, DOI: 10.1016/j.jcis.2008.09.039.
31. Sofinskaya O.A., Kosterin A.V., Kosterina E.A., Contact angles at the water-air interface of hydrocarbon-contaminated soils and clay minerals, *Eurasian Soil Science*, 2016, Vol. 49, Issue 12, pp. 1375–1381, DOI: 10.1134/S1064229316120115.
32. Wu W.J., Baseline studies of the clay minerals society source clays: colloid and surface phenomena, *Clays and Clay Minerals*, 2001, Vol. 49, No. 5, pp. 446–452.