

WATER VAPOUR SORPTION ON MIXTURES OF PODZOLIC SOILS WITH ORGANIC FERTILISER ROSAHUMUS

Kamil Skic, Zofia Sokołowska

Department of Physicochemistry of Agricultural Materials,
Institute of Agrophysics, Polish Academy of Sciences
Doświadczalna 4, 20-290 Lublin, Poland
e-mail: kskic@ipan.lublin.pl

Abstract. Water vapour sorption processes on mixtures of soil and organic fertiliser Rosahumus (RH) were investigated. Mixtures were prepared with Orthic Luvisol soil formed from loamy sand and Haplic Luvisol soil formed from loess. Samples contained different doses of fertiliser in the range from 1 to 50 weight percent. Differences in water vapour sorption on Rosahumus (RH) as well as the soils were observed. The properties of soil mixtures and organic material depended on the properties of both components and on the dose of Rosahumus. However, fertiliser was a dominant factor in sorption processes of investigated mixtures. Adsorption isotherms obtained by gravimetric method belonged to the same type II, in accordance to the BET classification. Significantly higher influence on the water vapour sorption was associated with fertiliser dose and was greater for mixtures with soil formed from loess. The increase of water vapour sorption was visibly higher for mixtures below 4% of Rosahumus content. On the other hand, greater concentration of RH resulted in similar amount of water vapour sorption and for Rosahumus dose of 50% the sorption was practically the same. Similar results were found for the maximum hygroscopicity (*Mh*) of mixtures. Strong correlation was observed between the *Mh* and the amount of added organic fertiliser with determination coefficient (R^2) from 0.997 to 0.998.

Key words: water vapour sorption, podzolic soil, organic fertiliser, maximum hygroscopicity

INTRODUCTION

From agronomic point of view one of the basic factors responsible for the fertility of soils is the content of organic material which improves not only the physicochemical properties of soils but also leads to the development of biological processes valuable for plants. It is well known that the intensification of agriculture leads inevitably to a decrease of organic matter content in soil. There are few commercial products in Poland that contain brown coal, humus or

humic acids from leonardite and have the certificate for use in plant growth and ecological agriculture (Sas Paszt *et al.* 2013). The humic acids extracted from lignite and leonardite are used as the organic and organo-mineral fertilisers (Aitken *et al.* 1964, Akinremi *et al.* 2000, Hoffman *et al.* 2010, Huculak-Mączka *et al.* 2010). Their applications lead to a significant increase in soil organic matter content and improve plant growth as well as crop yield (Asmaa and Magda 2010, Dudley *et al.* 2004, Dobrzański *et al.* 2008, Ece *et al.* 2007, Sanli *et al.* 2013, Verlinden *et al.* 2009).

Adsorption isotherm, i.e. the relationship between adsorbate pressure (p) and the amount of adsorbed substance, measured at constant temperature, is the most popular expression of adsorption data. The isotherm naturally starts at the coordinate origin and ends nearly at the point of saturated vapour (p_0). In the case of soils, the interpretation of the main part of the curve is difficult and usually applies to three regions of the adsorption process. A indicates only adsorption, A+CC – simultaneous adsorption and capillary condensation, while CC refers to capillary condensation and it is the dominant process. On the adsorption isotherm domain A is below the value $p \cdot p_0^{-1} \approx 0.4$, A + CC is from 0.4-0.5 to 0.7, and domain CC is above 0.7-0.8 (Kutilek and Nielsen 1994). The beginning part of the isotherm is used to obtain the surface energetic heterogeneity (average adsorption energy), the monolayer capacity and the surface area. The end part provides information about pore structure in the solid phase and surface geometric heterogeneity (fractal dimension). The volume of liquid which is adsorbed from a saturated vapour by 1 gram of adsorbent is called the pore volume of the adsorbent. From the adsorption isotherm the maximum hygroscopicity (Mh) or hygroscopic coefficient can be estimated (Kutilek and Nielsen 1994). The maximum hygroscopicity is equal to the amount of adsorbed water at the relative pressure, $p \cdot p_0^{-1} \approx 0.964$. The term hygroscopic coefficient should truly characterise only the hygroscopic properties of soils. The properties of soil mixtures and organic material depend on the properties of all components as well as on the composition of the mixture. Previous studies of mixtures of a brown organic soil and keratin-bark-urea (KBU) compost confirmed that significantly higher influence on the water vapour sorption, surface area, porosity, wettability and surface free energy of brown soil was associated with the properties and dose of compost (Sokołowska *et al.* 2002a, 2002b, Żurawska 2001).

Walczak *et al.* (2002) reported that for peat, sand and their mixtures the greatest changes in bulk density/total porosity, water retention and differential water capacity were observed in the range of 0.1-23% of organic matter content. In the case of perfectly modelled mixtures of sand and peat, the relation between the specific surface area, fractal dimension and the percentage of peat was almost linear with correlations coefficient higher than 0.99. This confirmed the final

conclusion that sand-peat systems can be treated as mechanical mixtures, with negligible interactions between the components (Sokołowska *et al.* 2009).

The main goal of this study was to investigate the influence of commercial organic fertiliser Rosahumus on water vapour sorption of two podzolic soils and to estimate the hygroscopic properties of its mixtures with organic fertiliser.

MATERIALS AND METHODS

The studies were conducted on soils formed from loamy sand (soil 1) and loess (soil 2), taken from 0-20 cm soil depth. Studied soils had different physicochemical properties. The Orthic Luvisol from loamy sand (in accordance with FAO soil classification system) had clay, silt and sand content equal to 2%, 7%, and 91%, respectively. The soil acidity measured in H₂O reached 5.4 of pH unit, and the organic matter content was 0.27%. The Haplic Luvisol from loess (in accordance with FAO soil classification system) exhibited clay, silt and sand content equal to 7%, 29%, and 64%, respectively. The soil acidity measured in H₂O reached 5.9 of pH unit, and the organic matter content was 1.15%. Soil pH was measured in 1:2.5 (v/v) suspensions of soil and water using a digital pH-meter. Soil organic matter was determined using the TOC Analytik Jena apparatus. The granulometric composition of soil samples was determined using the Casagrande-Prószyński method.

Commercial organic fertiliser Rosahumus (RH) from Rosier S.A. was isolated from leonardite and contained 85% of humus acids, 12% of K₂O and 0.6% of Fe (<http://rosahumus.pl/wp-content/uploads/2012/11/rosahumus-katalog-2012.pdf>) and had the certificate NE/133/2010 (www.iung.pulawy.pl/odpady/wykaz.htm).

The soil samples were air-dried and sieved through a sieve of 1 mm mesh. Series of samples were prepared by adding different doses of Rosahumus ranging from 1 to 50 weight percent.

The adsorption-desorption isotherms of water vapour were measured by the gravimetric method in accordance with Polish standard method (PN-Z-19019-1, 1997). Before the adsorption measurement soil samples were dried in a vacuum chamber with concentrated sulphuric acid until the weight of samples reached constant values. The soil sample of a weight equal approximately to 3 g was put into a glass vessel and was placed over sulphuric acid solution. The sample was equilibrated with water vapour during two days. The amount of adsorbed water vapour was computed as the difference between the weight of the sample with water and the dry sample (dried in an oven at 105°C). The relative water pressures were obtained from the density of sulphuric acid solutions. Twenty levels of relative pressure were selected in the range of 0.015 to 0.95. The adsorption measurements were replicated three times, keeping the temperature constant at $T = 20^{\circ}\text{C} \pm 0.5$. The variation in replicated data did not exceed $\pm 5\%$ at the lowest

vapour pressure and $\pm 1\%$ at the highest vapour pressure. The averaged values were used to prepare Figures.

Using the Brunauer-Emmett-Teller (BET) method (Gregg and Sing 1978, Ościk 1982), the monolayer capacity (N_m) of the soil samples was evaluated from adsorption-desorption isotherms in the BET range of relative water vapour pressure $0 < p/p_0 < 0.35$, using the BET equation:

$$\frac{x}{N(1-x)} = \frac{1}{C_{BET} N_m} + \frac{(C_{BET} - 1)}{C_{BET} N_m} x$$

where $x = p/p_0$ is the relative pressure of water vapour, N is the amount of adsorbed water vapour, and C_{BET} is a constant.

RESULTS AND DISCUSSION

Figures 1 and 2 represent the experimental adsorption isotherms for mixtures of podzolic soils formed from loamy sand (soil 1) and from loess (soil 2) with Rosahumus. In general, the shapes of the isotherms were similar. In accordance to the BET classification (Gregg and Sing 1978, Ościk 1982), the adsorption isotherms belonged to the same class, namely to type II. However, the detailed course of the curves showed that isotherms for mixtures were shifted in relation to control as well that the amount of adsorbed or desorbed water vapour varied for individual samples. It was associated with the content of organic fertiliser in the samples. The water vapour sorption for mixtures of soil 2+RH was higher than for mixtures of soil 1+RH. The increase was more clearly visible for mixtures below 4% of Rosahumus content (Fig. 1A and 2A). For both soil mixtures, higher concentration of organic fertiliser resulted in a similar water vapour sorption which for the dose of RH = 50% was practically the same (Fig. 1B and 2B).

The maximum water vapour sorptions in mixtures were higher in comparison to control soils and varied from 0.012 to 0.31 g g⁻¹ and from 0.031 to 0.32 g g⁻¹ for soil 1 and 2, respectively. This effect was significantly correlated with the dose of Rosahumus, $R^2 = 0.997$ and $R^2 = 0.998$. For mixtures of soils with addition of RH, at the level of 20, 30, 50%, W_{max} was similar and ranged from 0.098 to 0.22 g g⁻¹ and from 0.11 to 0.23 g g⁻¹ for soil 1 and soil 2, respectively. The differences between W_{max} of soil mixtures are presented in Figure 3. In general, systematic changes of adsorption with the RH addition were observed. However, this influence was not directly proportional. A small amount of organic fertiliser, below 5%, did not change the W_{max} . In the range from 10 to 50% of RH dose W_{max} was higher. The increase was visibly connected with RH dose in the mixtures.

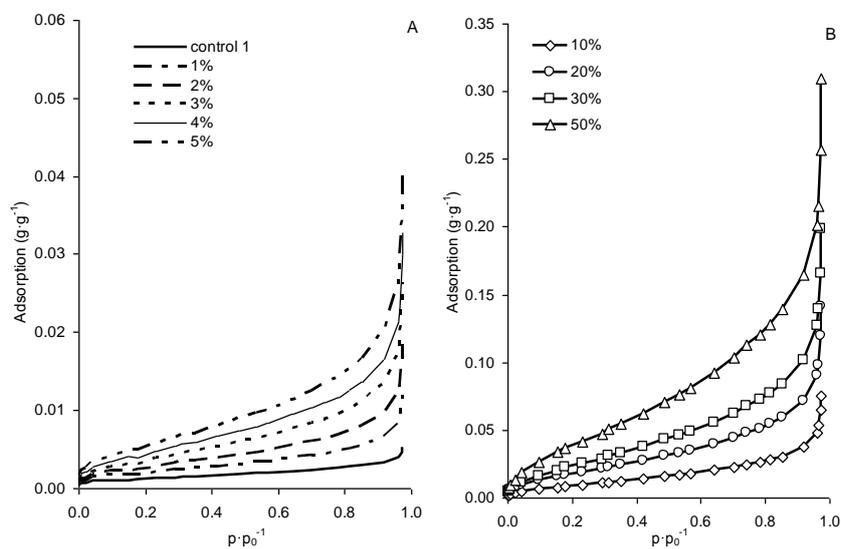


Fig. 1. Water vapour adsorption isotherms for mixtures of podzolic soil formed from loamy sand with organic fertiliser Rosahumus. Part A – dose of Rosahumus from 1 to 5%. Part B – dose of Rosahumus from 10 to 50%

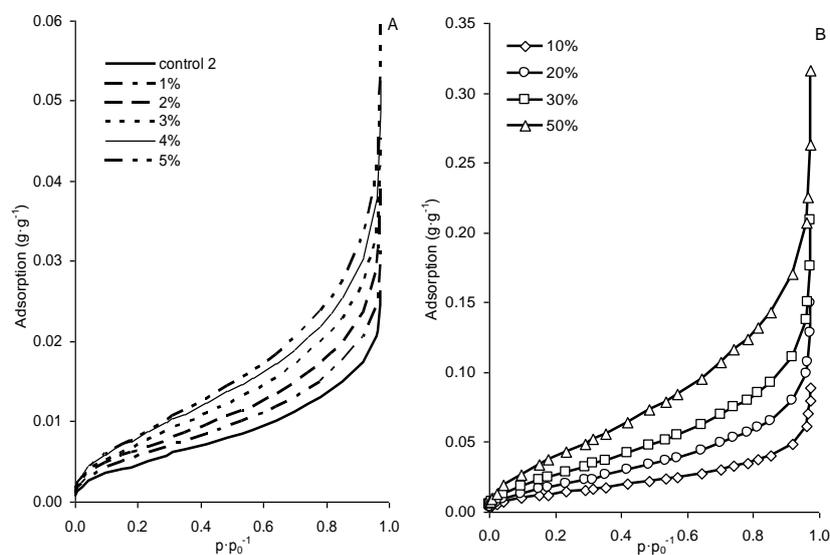


Fig. 2. Water vapour adsorption isotherms for mixtures of podzolic soil formed from loess with organic fertiliser Rosahumus. Part A – dose of Rosahumus from 1 to 5%. Part B – dose of Rosahumus from 10 to 50%

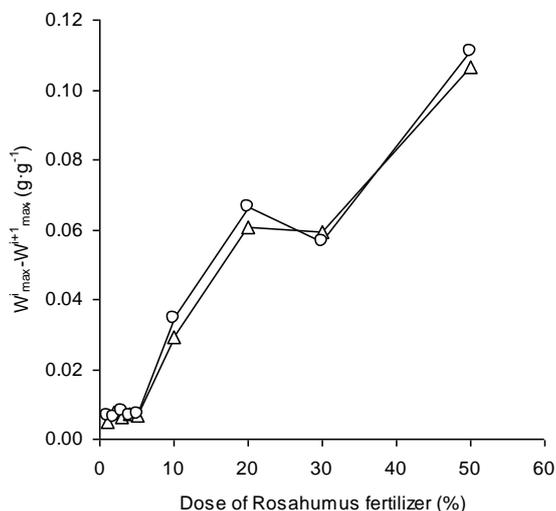


Fig. 3. Differences between ΔW_{max} of soils mixtures versus dose of Rosahumus fertiliser. Symbols: circle – podzolic soil formed from loamy sand, triangle – podzolic soil formed from loess

The experimental data were described using the BET equation. The values of the correlation coefficient, R^2 , indicate that the BET equation provides a good fit to experimental data in the range of relative water vapour pressure $0 < p/p_0^{-1} > 0.35$. In all cases the values of R^2 varied from 0.996 to 0.998. Generally, better fits were obtained for experimental desorption than for adsorption data.

The amount of water in monolayer (N_m) was calculated from the sorption/desorption isotherms using the BET equation. The differences between N_m values from the desorption and adsorption isotherms can show the amount of strongly bound monolayer water. The ΔN_m values for mixtures of soil 2 were five times higher in comparison with soil 1 mixtures (Fig. 4). The strongly bound monolayer water in soil 1+RH mixtures was positively correlated with Rosahumus content irrespectively from fertiliser dose ($R^2 = 0.993$). For soil 2+RH mixtures, the relation between RH dose from 1 to 50% was also high ($R^2 = 0.997$). However, the linear determination coefficient for all doses of RH was $R^2 = 0.979$ (Fig. 4).

The values of the maximum hygroscopicity (Mh) for the mixtures of investigated soils with Rosahumus were estimated from the sorption isotherms and are showed in Figure 5. The Mh values for mixtures of soil 2+RH were two times higher in comparison with mixtures of soil 1+RH but only for Rosahumus dose below 5% (Fig. 5). Mh values for higher doses of RH were similar. The maximum hygroscopicity strongly correlated with the amount of organic fertiliser in mixtures. R^2 varied from 0.997 to 0.998 for soil 1 and 2, respectively.

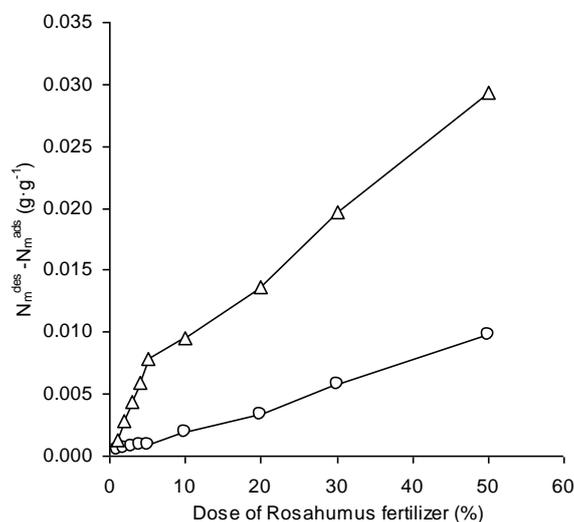


Fig. 4. Differences between N_m values from desorption and adsorption isotherms for soil mixtures versus the dose of Rosahumus fertiliser. Symbols: see Fig. 3

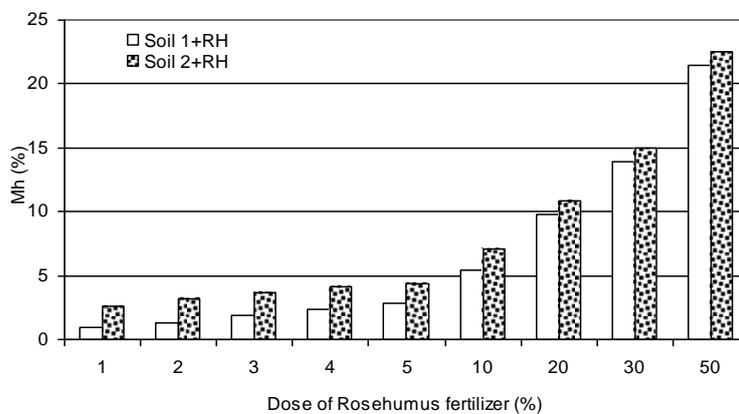


Fig. 5. Maximum hygroscopicity (Mh) for soil mixtures versus the dose of Rosahumus fertiliser. Legend: soil 1 – podzolic soil formed from loamy sand, soil 2 – podzolic soil formed from loess

It is well known that the adsorption of gases or vapours depends on the nature of the soil solids. Various kinds of polar and non-polar functional groups have been identified in mineral and organic soil constituents. The most important is the existence of functional groups containing oxygen, such as carboxyls, phenolics, and carbonyls. Several polar functional groups serve as sorption sites for water molecules.

The difference in the physical properties of the investigated mixtures of soil + Rosahumus depended on the properties of each component as well as on the composition of the mixture. The mineral components of both soils and the organic component were characterised by different properties. The maximum water vapour sorption for control soil 1 (W_{max}^1) was 0.005 g g^{-1} , for soil 2 (W_{max}^2) was 0.026 g g^{-1} whereas for RH – 0.623 g g^{-1} . Moreover, the values of Mh for the control soils were lower in comparison to Rosahumus. Maximum hygroscopicity of soil 1, soil 2 and RH were 0.4%, 2.13% and 44.4%, respectively. Rosahumus contained 85% of humus acids. It is known that humic acids are the most reactive and widely distributed components of humus substances. They contain polar groups that are adsorption centres for water molecules (Stevenson 1994). The effect of the Rosahumus fertiliser on water vapour sorption was related with the polar functional groups content. The influence of RH was the dominant factor in the sorption processes of investigated mixtures of both soils.

CONCLUSIONS

1. Water vapour sorption for mixtures of soil 2 + RH was higher than for mixtures of soil 1 + RH. This increase of sorption was more clearly visible for mixtures below 4% of Rosahumus content. In the case of higher concentration of organic fertiliser in soil material, the amount of water vapour sorption was similar and for the dose of RH = 50% was practically the same.

2. Shapes of the isotherms were similar for both soils. In accordance to the BET classification the adsorption isotherms belong to the same type II.

3. Maximum water vapour sorption of mixtures varied from 0.012 to 0.31 g g^{-1} and from 0.031 to 0.32 g g^{-1} for soil 1 and 2, respectively, and was linearly correlated with RH dose.

4. Maximum hygroscopicity values for mixtures of soil 2 + RH were two times higher in comparison to mixtures of soil 1+RH, for Rosahumus dose below 5%. Higher dose of RH resulted in similar values of Mh . Maximum hygroscopicity was associated with the amount of organic fertiliser in prepared mixtures.

5. Influence of Rosahumus on water vapour sorption was the dominant factor in sorption process of investigated mixtures and was observed for both tested soils.

REFERENCES

- Aitken J.B., Acock T.L., Senn T.L., 1964. The characteristics and effect of humic acids derived from leonardite. S. Carolina Agric. Exp. Stn. Tech. Bull., 10015, 28.
- Akinremi O.O., Janzen R.L., Lemke R.L., Larney F.J., 2000. Response of canola, wheat and green beans to leonardite additions. Can. J. Soil Sci., 80, 437-443.

- Asmaa M., Magda H., 2010. Increasing productivity of potato plants (*Solanum tuberosum* L.) by using potassium fertiliser and humic acid application. *Int. J. Acad. Res.*, 2, 83-88.
- Dobrzański A., Anyszka Z., Elkner K., 2008. Response of carrots to application of natural extracts from seaweed (*Saragassum* SP.) – algaminoplant, and from leonardite – humiplant (in Polish). *J. Res. And Applications in Agricultural Engineering*, 53, 53-58.
- Dudley J.B., Pertuit A.J., Toler J.E., 2004. Leonardite influences zinnia and marigold. *Hort Sci.*, 39, 251-255.
- Ece A., Saltali K., Erigid N., Uysal F., 2007. The effect of leonardite applications on climbing bean (*Faseolus vulgaris* L) yield and some soil properties. *J. of Agronomy*, 6, 480-483.
- Gregg S. J., Sing K. S. W., 1978. Adsorption, surface area and porosity. Acad. Press, New York, USA.
- Hoffman K., Popławski D., Huculak-Mączka M., Hoffman J., 2010. Influence of the fineness on efficiency of obtaining humic acids from lignite (in Polish). *Proceedings of ECOpole 4*, 377-382.
- Huculak-Mączka M., Hoffman K., Skut J., Hoffman J., 2010. Estimate of contents of humic substance in selected raw materials and wastes (in Polish). *Proceedings of ECOpole 4*, 383-387.
- Kutilek M., Nielsen D.R., 1994. *Soil hydrology*. Catena Verlag.
- Ościk J., 1982. *Adsorption*. PWS Ellis Horwood Ltd. Publish. Chichester.
- Polish Standard PN-Z-19010-1, 1997. *Soil Quality. Determination of specific surface area of soils by water sorption (BET)* (in Polish).
- Sanli A., Karadogan T, Yonguc M., 2013. Effects of leonardite applications on yield and some quality parameters of potatoes (*Solanum tuberosum* L.). *Turkish J. of Field Crops*. 18, 20-26.
- Sas Paszt L., Głuszek S., Grzyb Z.S., 2013. Possibility to use of brown coal for eco-agriculture (in Polish). *Eko Tech Produkt Newsletter*, 16.
- Sokołowska Z., Hajnos M., Boguta P., 2002a. Porosity of mixtures of a loess-like soil with keratin-bark-urea compost (in Polish). *Acta Agrophysica*, 2011, 18, 457-467.
- Sokołowska Z., Sokołowski S., Warchulska P., 2009. Trends in soil fractal parameters caused by accumulation of soil organic matter as resulting from the analysis of water vapor adsorption isotherms. *Ecological Complexity*, 6, 254-262.
- Sokołowska Z., Żurawska E., Hajnos M., Wolski T., 2002b. Influence of keratin-bark-urea compost on wettability of a brown soil formed from loess (in Polish). *Acta Agrophysica*, 70, 305-315.
- Stevenson F.J., 1994. *Humus Chemistry. Genesis, Composition, Reaction*. 2nd ed. Wiley, New York, USA.
- Verlinden G., Pycke B., Mertens J., Debersaques F., Verheyen K., Baert G., Bries J., Haesaert G., 2009. Application of humic substances results in consistent increases in crop yield and nutrient uptake. *J. Plant. Nutr.*, 32, 1407-1426.
- Walczak R., Rovdan E., Witkowska-Walczak B., 2002. Water retention characteristics of peat and sand mixtures. *Int. Agrophys.*, 16, 161-165.
- Żurawska E., 2001. Influence of keratin-bark-urea compost on selected physicochemical properties of soil (in Polish). Master Thesis, IA PAS Lublin, Poland.

ADSORPCJA PARY WODNEJ NA MIESZANINACH GLEB PSEUDOBIELICOWYCH I NAWOZU ORGANICZNEGO ROSAHUMUS

Kamil Skic, Zofia Sokołowska

Zakład Fizykochemii Materiałów Porowatych
Instytut Agrofizyki im. Bohdana Dobrzańskiego PAN
ul. Doświadczalna 4, 20-290 Lublin
e-mail: kskic@ipan.lublin.pl

Streszczenie. Badano proces sorpcji pary wodnej na mieszaninach gleby i nawozu organicznego Rosahumus (RH). Mieszanki sporządzono z gleby pseudobielicowej wytworzonej z piasku gliniastego i z lessu. Próbkę mieszanin zawierały dawki nawozu od 1 do 50% wagowych, zgodnie z definicją stężenia procentowego. Badane gleby i Rosahumus wyraźnie różniły się zachowaniem wobec pary wodnej. Właściwości badanych mieszanin zależały od właściwości obu składników i wielkości dawki Rosahumusu. Jednakże nawóz był dominującym komponentem, który determinował właściwości mieszanin w procesie sorpcji. Izotermy sorpcji pary wodnej, otrzymane metodą grawimetryczną, zaliczono do grupy II według klasyfikacji BET. Stwierdzono, że ilość zasorbowanej pary wodnej zależała od wielkości dawki nawozu i była większa dla mieszanin gleby wytworzonej z lessu niż piasku gliniastego. Wyraźne zróżnicowanie w ilości zasorbowanej wody było widoczne dla mieszanin zawierających do 4% Rosahumusu. Dla wyższych dawek RH, różnice w ilości zasorbowanej pary wodnej były małe, a dla dawki 50% praktycznie zanikły. Podobne zależności stwierdzono dla maksymalnej higroskopijności mieszanin, gdzie obserwowano silne zależności pomiędzy Mh i dodatkiem Rosahumusu, R^2 od 0,997 do 0,998.

Słowa kluczowe: sorpcja pary wodnej, gleby pseudobielicowe, nawóz organiczny, maksymalna higroskopijność