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Identifying the Origin of Soil Water Repellency at Regional Level Using Multiple Soil Characteristics: The White Carpathians and Myjavska Pahorkatina Upland Case Study

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Abstract

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This paper evaluates the relationship between water repellency and multiple characteristics of topsoil samples belonging to seven Reference Soil Groups, taken from the area of the White Carpathians and the Myjavska pahorkatina Upland. In order to quantify water repellency, the Water Drop Penetration Time test and the Molarity of an Ethanol Droplet test were performed on 210 soil samples. The water repellency data were confronted with a number of categorical and numerical soil variables. It was observed that the particular land-use type and the nature of soil parent material, both are related towards detected water repellency of soil samples. All samples taken from the agricultural (tilled) and grassland soils were wettable. On the contrary, all samples which exhibited water repellency, belonged to the group of forest soils, although, not all forest soils were water repellent. Samples which showed considerable repellency were soils developed either on consolidated sedimentary rocks (sandstones, limestone-dolomitic rocks, flysch) or unconsolidated sediments of aeolic or polygenetic origin. On the other hand, the great majority of soils developed on recent alluvial deposits were clearly wettable. Correlation and regression analyses showed that susceptibility of forest topsoil to exhibit water repellency generally increases with increasing sand and organic carbon contents, and with a simultaneous decrease of soil pH value. An interesting observation came out regarding $CaCO_3$ and water repellency relation. Although certain soils with higher $CaCO_3$ exhibited water repellency (Rendzic Leptosols and Cambisols), all soils that developed on loose sediments and contained $CaCO_3$ were wettable.

Keywords: land-use; molarity of an ethanol droplet (MED); soil organic carbon; soil reaction; water drop penetration time (WDPT); water repellency

DeBano (2000) documented that the interest in water repellency (WR) phenomena began well before the 20th century, although it was not identified as such; even if none of the pre-20th century publications used the term water repellency, it was obvious that many of scientists of that time were observing the WR phenomenon as we know it today. During the following decades, there was a growing interest in WR and its management implications which was documented by the number of papers on that phenomenon. Many scientists throughout the world were involved in the exploratory studies covering different topic areas and produced many research findings, which have improved the understanding of water repellent (WR) soils. In the field, the presence of WR is often not clearly noticeable, e.g. due to vegetation or when soil exhibits a particular water content level, although under wet conditions WR does occur, too (Jaramillo *et al.* 2000). However, surface storage of rain water in the plant litter on

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the forest floor (agricultural soils are less prone to repellency) may disguise the fact that infiltration and percolation are impeded. Consequently, WR soil may not be a problem until canopy and ground cover are removed during clear-felling, or as a result of fire. Once the surface storage capacity is removed and the soil is exposed to drying, the site is at risk of overland flow occurring during rainstorms, leading to soil erosion and reduced soil water replenishment (Scott 2000).

Although many studies have documented the occurrence of soil WR in various parts of the world, to our knowledge, the present study is the first to survey the phenomenon extensively over a continuous area of as many as 890 km^2 like is that of the White Carpathians and Myjavska pahorkatina Upland. This westernmost mountain range of the Carpathians located in western Slovakia is interesting in terms of very diverse geomorphology and high land cover diversity (Michalcová *et al.* 2014). Besides that, the area is known for the occurrence of gully erosion, which has been studied from different perspectives (Stankoviansky 2003; Dlapa *et al.* 2012). This proves that intense rainfall can have significant geomorphic consequences in the area, which makes soil and water interaction worth further studying. The contribution of this work resides in the complex analysis of soil WR over a large area with a relatively diverse soil cover. Its main goal is to explore the relationship between multiple soil characteristics and detected WR at a regional scale spreading over two specific geomorphic units. The studies which would confront soil wettability data with specific combination of multiple soil properties like presented herein (soil organic carbon (SOC) content, particle size distribution, soil reaction, $CaCO_3$ content, land-use, soil type, and nature of soil parent material) are lacking. We believe that some findings presented in this paper are not limited by regional scale of this work and may pertain to soils of different origin as well.

MATERIAL AND METHODS

Soil sampling. The main criterion for selecting representative soils was the assumption of soil WR occurrence. Selection of soils appropriate for the investigation of WR was made on the basis of soil map investigation. The soil survey followed the Handbook of field soil survey and soil mapping (Čurlík & Šurina 1998). For the purpose of this study, 210 disturbed samples of various soil types (depth interval 0–20 cm) were taken from the area of 890 km^2 (Figure 1), where the altitude of individual sampling points ranged from 175 up to 862 m a.s.l. Soil samples of ca.1–3 kg were obtained from digged soil pits exposing the soil profile as well as from drilled soil pits. Approximate sample spacing was one soil pit (i.e. one sample) per 4 km^2. The soils were classified according to WRB (2006).

Sample preparation and processing. All samples were dried at room temperature, then grinded, carefully sieved through a 2-mm mesh, gravel and large plant debris were discarded, and the remaining fine-earth fraction gently mixed until it appeared to be homogeneous. This homogenized fine soil was stored in clean dark polyethylene bags and prepared for further analyses.

Laboratory analyses of selected physical and chemical soil properties. The persistence of WR was determined using the Water Drop Penetration Time (WDPT) test, which is the simplest and most common and practical method used to measure this parameter. WDPT is a measure of the time required for contact angle (α) to change from its original value, which was greater than 90°, to a value approaching 90° (Letey *et al.* 2000) (Figure 2). This procedure

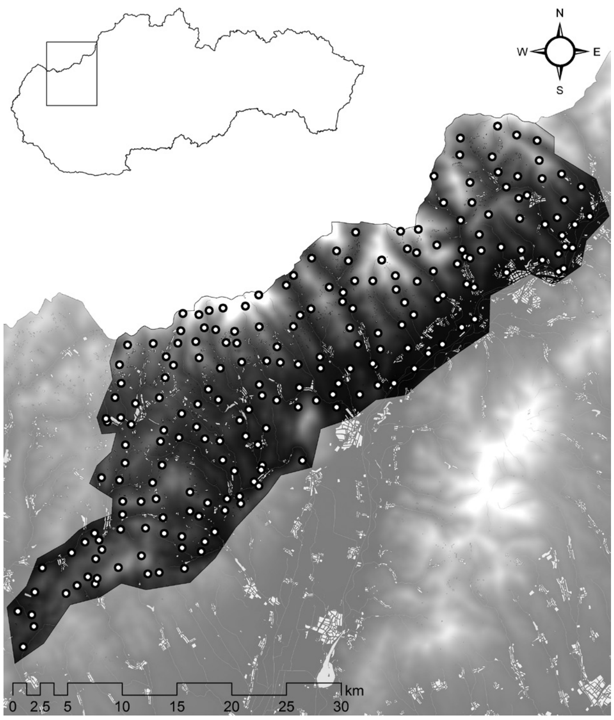

Figure 1. Soil map of the White Carpathians and Myjavska pahorkatina Upland with soil pits localization

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separates soils classified as WR (α > 90°) from those not WR (α < 90°).

The method involves placing several drops of distilled water from a standard medicine dropper on the smoothed surface of a soil sample, and recording the time taken for its complete penetration (Letey 1969). A soil is classified as WR, if a water droplet placed on the soil surface is not spontaneously soaked into the soil (it indicates that the surface tension of the soil surface is below that of the droplet) within particular time interval. In this study, ten drops of distilled water (20°C) were applied onto soil surface and the soil was considered to be WR if WDPT exceeded 5 s (Bisdom *et al.* 1993); the time required for infiltration of each drop was recorded and the mean penetration time was taken as representative of WDPT for each sample. The volume of water in a droplet was 0.05 ml. A standard droplet release height of approximately 10 mm above the soil surface was used to minimize the cratering effect on the surface (Wylie *et al.* 2001). According to the WDPT test, soils were classified into 5 repellency categories: < 5 s, wettable; 5–60 s, slightly; 60–600 s, strongly; 600–3600 s, severely; > 3600 s, extremely WR soils (Dekker & Ritsema 1995). Measurement carried out on dried samples was considered to be the most appropriate parameter for comparing soils with respect to their sensitivity to WR (Dekker & Ritsema 1994), because differences in water content were wiped out (Moral Garcia 1999).

The degree of WR was determined using the Molarity of an Ethanol Droplet (MED) test. It is an indirect measure of the surface tension of the soil surface γ_{sa}

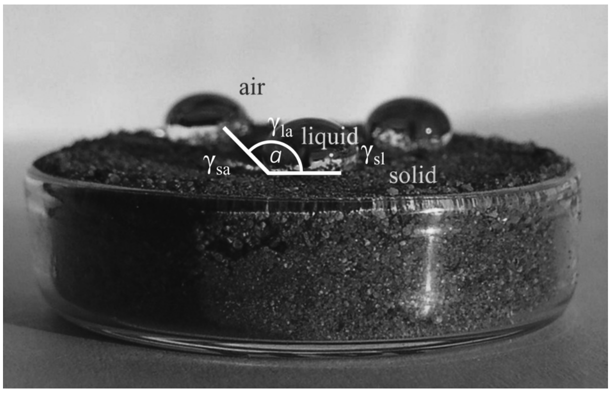

Figure 2. Water droplet on water repellent surface that remains as a drop of finite area; α – definite contact angle between the solid and liquid surface, γ_{sa} – surface tension of a solid/air interface, γ_{la} – surface tension of a liquid/air interface, γ_{sl} – surface tension of a solid/liquid interface

(Figure 2) and indicates how strongly a water drop is repelled by soil at the time of application (i.e. how strongly it "balls up") (Doerr 1998). An advantage of the MED test is its speed so that it is well suited to field investigations where long persistence times make WDPT technique impossibly laborious (Wallis *et al.* 1991). The MED test uses the known surface tensions of standardized solutions of ethanol in water, where the surface tension of solution increases with the decreasing concentration (molarity) of ethanol; completely wettable soil will be readily wet at zero molarity of ethanol. Drops of those dilutions are applied onto a smoothed soil surface using medical droppers (similarly to WDPT procedure) and their instant or short-term infiltration behaviour is observed (Watson & Letey 1970). A droplet with a lower surface tension (higher ethanol concentration) will infiltrate into the soil more rapidly than a droplet with a higher surface tension (lower ethanol concentration) which will remain on the soil surface for some time. Droplets are usually applied in increasing surface tension order until a droplet resists infiltration. The WR degree of 46 dried soil samples (previously found repellent on the basis of the WDPT test) was measured using increasing ethanol concentrations (0.5, 1, 2, 3, ..., 32% by volume). The volume of water in a droplet was 0.05 ml.

Besides concentration of an ethanol droplet which penetrates into the soil within particular time interval (Dekker & Ritsema 1994), values obtained from the MED test are presented as a molarity – MED index (King 1981; Harper & Gilkes 1994), surface tension γ_{ND} of an ethanol droplet which wets the soil at 90° (Carrillo *et al.* 1999), and surface tension of a solid/air interface γ_{sa}. In this study, the time allowed for the drop to infiltrate was 3 s (Doerr 1998). According to the molarity (MED) of ethanol (M = mol/l), WR of soils was classified as follows (Doerr 1998): 0–0.85 M wettable, 0.85–1.45 M slightly, 1.45–2.22 M moderately, 2.22–3.07 M strongly, 3.07–6.14 M very strongly, > 6.14 M extremely WR soil.

Results of MED testing were used to calculate approximate values of a solid/air surface tension γ_{sa} which would also characterize wettability of measured soil samples.

In the first step, 90° surface tension γ_{ND} (mN/m) was calculated:

$$\gamma_{ND} = 61.05 - 14.75 \ln (M + 0.5) \quad (1)$$

where:

M – molarity value obtained via MED testing (King 1981)

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Subsequently values of γ_{ND} were approximated by means given by Carrillo *et al.* (1999) or Regalado & Ritter (2005) to obtain γ_{sa} (mN/m):

$$\gamma_{sa} = \gamma_{ND}/4\ \Theta^2 \quad (2)$$

where:

Θ – constant that varies with molecular properties of solid/liquid

It was found that for soils it equals approximately to 0.6 (Regalado & Ritter 2005).

Since the temperature and relative air humidity may affect results, WR of all samples was, in accordance with Dekker and Ritsema (1994), measured under controlled conditions at constant temperature (22.5 ± 2.5°C) and relative air humidity under 50%.

Soil samples were further analyzed to characterize soil texture (the percentage of sand, silt, and clay particles), pH, $CaCO_3$, and SOC. Soil texture was determined by pipette method as described by Fiala *et al.* (1999) and results were classified according to USDA-FAO texture triangle. Soil pH was measured potentiometrically in deionized water and in 1M KCl with a soil:solution ratio of 1:2.5; $CaCO_3$ content using Janko's calcimeter (Fiala *et al.* 1999); and SOC content by its rapid dichromate oxidation (Walkley & Black 1934).

RESULTS AND DISCUSSION

Regarding the relative content of particles of various sizes, eight textural classes (with n of samples in parentheses) were identified in the region under study: loamy sand (5), sandy loam (66), sandy clay loam (8), loam (73), silt loam (39), silty clay loam (1), clay (1), and clay loam (17). Although loam soils normally absorb water and store moisture well (Cañizares 2010), majority of WR samples had the sandy loam (30) and loam (11) texture. Nonetheless, loams have a wide range of compositions and even a wider range of physical properties (Handreck & Black 2002).

On the whole, the tested soils contained 9.32 to 86.60% of sand and 0.82–44.36% of clay. Content of particles < 0.05 mm ranged from 13.40 to 90.68%. There were no WR samples below 32.68% of sand. The number of repellent soils increased when the value of the sand content exceeded 40%. Four out of six extremely WR samples contained more than 60% of sand. The soil (Haplic Fluvisol) with the highest sand content was wettable, probably due to high $CaCO_3$ (11%) and low SOC (0.66%) content. Most of the WR soils (30 samples) had clay contents of less than 12.32%. Repellency did not occur in soils with the clay content higher than 22.28%. The most WR sample (Haplic Cambisol) contained 14.76% of clay. There were another two extremely WR samples, Cutanic Albic Stagnic Luvisol with 18.16% and Cambic Leptosol with 22.16% of clay, both not containing calcium carbonate, with strongly acid soil reaction and very high SOC content (7.1 and 15.03%, respectively). Some medium-textured soils, such as loam and sandy clay loam, were highly water repellent. From the results found in this study it can be generally assumed, in accordance with Jamison (1946), Roberts and Carbon (1971), Bishay and Bakhati (1976), and Dekker (1988) that coarse-textured soils with higher content of sand are more prone to repellency than clayey soils due to their lower specific surface area.

SOC content ranged from 0.52 to 20.94%. Leptosols showed the widest range of SOC content (1.17–20.94%), followed by Cambisols (0.91–19.76%). These soils belonged to those most affected by WR. Fluvisols, and Planosols with Stagnosols had a very narrow range of SOC content values (0.53–3.13%, 0.67–2.04%, respectively). SOC content varied with different land-use, forest soils showed higher values ranging between 0.66–20.94%, grasslands and ploughed soils had similar SOC contents ranging between 0.53–4.17% and 0.52–4.55%, respectively. Below 3.1% of SOC there were only two WR samples. Except one sample (Eutric Cambisol), all soils with SOC above 8.06% were found WR.

The calcium carbonate contents ranged from 0 to 63%, and most soils (62%) contained no carbonates. All Fluvisols were rich in $CaCO_3$, Rendzic Leptosols contained 92% of carbonated samples. Haplic Leptosols and Cambic Leptosols, developed on the siliceous parent rock, Planosols and Stagnosols, were not carbonated. There were two WR samples with high $CaCO_3$ content of 50 and 51%, the repellency could be caused by high SOC content and a high proportion of the sand fraction. In contrast to Dekker and Jungerius (1990) claiming that WR degree is not dependent on $CaCO_3$ content, the largest proportion of WR soils (38 samples, representing 82.6%) contained no $CaCO_3$.

The soils exhibited reaction ranging from strongly acidic (0.95% of soils) to slightly alkaline (30% of soils). The variability of observed pH values may be attributed to high diversity of soil parent materials occurring in the area and also to varying altitude of

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individual sampling points. In the case of active soil reaction (measured in H_2O) detected values were between 3.46 and 8.31, with median being equal to 6.32. Cambisols were soils with the widest pH range. Fluvisols, Planosols, and Stagnosols had a narrow pH interval and were intensively agriculturally used, these soils also showed no or very weak WR. The most acidic soils were among Haplic Leptosols and Cambic Leptosols. Leptosols were also found most unattractive for agriculture. WR was observed within quite a large pH interval extending from 3.46 to 8.05. Above this value all samples were found wettable. There were no wettable samples below pH/H_2O of 4.1 and pH/KCl of 3.34. 72% of WR soils had pH/KCl values lower than 4.31. In contrast to Roberts and Carbon (1971) and Steenhuis *et al.* (2001) who suggested that WR does not appear under alkaline conditions, it was detected in 9% of alkaline soils. Furthermore, there was one slightly alkaline soil sample (Calcaric Cambisol, pH of 7.45, 19.8% of $CaCO_3$) classified as extremely WR; it contained 83.16% of sand. In accordance with Ritsema and Dekker (1998) and Hurrass and Schaumann (2006), in all soil reference groups containing repellent soils, rising pH improved the wettability.

Results of both types of repellency testing (WDPT and MED) were in a relatively close accordance and showed that a majority of 210 topsoil samples were not WR. Specifically, in the case of 46 samples, time required for the penetration of a water droplet exceeded 5 s; in the case of 21 samples more than 60 s was needed for the infiltration of a droplet. The concentration of ethanol in applied droplets, which did not enter the soil spontaneously (< 3 s), was above 0.85 mol/l in 26 cases, and in 19 cases of them the ethanol concentration exceeded 1.45 mol/l value. WR samples may be further divided into the categories of scale proposed by Dekker and Ritsema (1995): slightly (29 samples), strongly (6), severely (5), and extremely (6) WR samples. The longest time required for water penetration was 78 756 s (Haplic Cambisol) and the highest ethanol concentration used was 32% (Rendzic Leptosol). However, it should be noted that in the case of long penetration times, i.e. after elapsing of 12 h (43 200 s), the WDPT measurement is not very precise, because evaporation of water droplet is taking place. The MED test showed results similar to WDPT, although this trend did not pertain to all samples. The Pearson's coefficient of correlation calculated for the couple of two variables (WDPT and MED) was 0.937. Because the approximate surface tension values are derived from molarities of applied ethanol droplets, we may conclude that all three parameters describing soil WR were significantly correlated in the case of this study (although the statistical distributions of their respective values were different).

Determining various soil properties enabled us to investigate WR from different perspectives. Two types of variables were used in this study: categorical and numerical. In spite of limitations of categorical data, with respect to their use in quantitative analysis, certain trends can be extracted from confronting WDPT or MED data with type of land-use, soil type, and soil parent material. Since the nature of parent material is one of the factors that significantly affect formation of a particular soil type, it could be expected that the relationship between either soil type or soil parent material on the one hand, and WR on the other, would be similar. Specific types of pedogenic substrates occurring in the area of interest are listed in Table 1. Presented types of soil parent materials are recognized according to the classification system of soils used in Slovakia (Collective 2000). As it can be seen from Table 1, two major types may be distinguished: sediments and sedimentary rocks. Each of these units may be further divided into number of subgroups. Later unit (sedimentary rocks) was represented in the area by (1) various limestone-dolomite rocks largely of Mesozoic age, (2) Paleogene sandstones, and (3) Paleogene flyschoid rocks. These pedogenic substrates, typically located at higher altitudes (above ca. 200 m) are, in lower parts, surrounded by Quaternary unconsolidated sediments, mainly of deluvial, aeolic or fluvial origin. Soils developed on sandstones and/or flysch rocks were typically Cambisols or Leptosols. On the other hand, Rendzic Leptosols were found on limestone and dolomitic parent material. It can be seen from Table 2 that a substantial part of WR soils were Cambisols (27.5% of WR soils) and Leptosols (35.1% of WR soils), which were developed on consolidated sedimentary rocks. With respect to unconsolidated sediments, some of the WR soils were associated with deluvial or aeolic substrate. This concerned particularly Luvisols and Regosols. Not all samples from this group showed WR. The third group of samples, which stands out for its wettability, were Fluvisols developed on recent alluvial deposits. All Fluvisol samples (except for one) showed a wettable character during the repellency testing. It should be noted, that all the mentioned types of parent material

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Table 1. Number of soils developed on a particular type of soil parent material associated with type of land-use, and results of Water Drop Penetration Time (WDPT) testing

Type of soil parent material		Land-use			WDPT (s)	
		agricultural	grassland	forest	> 5	> 60
Sediments	deluvial/proluvial	11	8	12	7	0
	aeolian	13	2	4	1	1
	fluvial	19	2	7	1	0
	marine	1	1	1	0	0
	polygenetic and loess	15	5	8	6	3
	terrace	1	1	0	0	0
Sedimentary rocks	flysch (sandstones, schists)	5	4	10	1	1
	sandstones	5	9	27	20	9
	limestone-dolomite rocks	5	3	31	10	3

are not perceived here as a direct cause of neither wettable, nor WR character of the sample. However, there are certain aspects of topsoil genesis, e.g. in the case of Cambisols and Leptosols, which are probably related to the observed WDPT and MED values.

With respect to land-use, three soil types were distinguished within the studied area: forest, grassland and agricultural (tilled) soils. All samples exhibiting WDPT > 5 s were forest soils, and at the same time, none of the agricultural or grassland soils exhibited WR at all. There are several considerations which should be mentioned with respect to the explanation of these observations. Firstly, wettability of tilled agricultural soils is not surprising, mainly because of fertilizer application. Both the mineral and organic fertilizers act as wetting agents in the soil, due to their high solubility and polar nature. Besides that, agricultural soils exhibited neutral soil reaction (6.96), contained 2.17% $CaCO_3$ (on average), and their textural composition was according to FAO classified as loamy. Further on, regarding the soil humus type, it is probable that a majority of agricultural soils contained a substantial portion of humified organic matter (OM). It is highly probable that all the mentioned factors give an agricultural soil a predisposition to show the wettable character rather than WR. Apart from agriculturally utilized soils, all grassland soils showed the wettable character as well. White Carpathian semi-dry grasslands are famous for their extremely high plant diversity. There are locations, where more than 130 species of vascular plants per 100 m^2 could be found and for some plot sizes they hold world records in the number of vascular plant species (Merunková *et al.* 2012). The vegetation belongs to west Beskid Mts. flora (*Beschidicum occidentale*), including many calciphilous, orchid and fern species. Southeastern slopes are covered with unstocked areas grown with xerophytic grasses with a predominance of fescue and *Poa badensis* on rocks. In early studies (Prescott & Piper 1932) it was believed that essential oils from xerophytic vegetation caused soil WR. A decade later, this idea was dismissed by Jamison (1945) who indicated that the condition was merely a surface phenomenon, i.e. it is a property of the OM in the surface soil. Notwithstanding, there have been a great number of studies reporting WR on soils under grasslands (e.g. Dekker *et al.* 2000; Lichner *et al.* 2012; Martínez-Murillo *et al.* 2013). This is understandable since the association of a soil sample with particular land-use category does not give us any specific information about its water-related properties. There are more factors which have to be considered. The properties of grassland soils were in the case of this study relatively similar to those of tilled soils; the same (loamy) texture, neutral soil reaction (pH/H_2O = 6.4), $CaCO_3$ content of 1.89%, and a slightly higher SOC content (2.26%) in com-

Table 2. Number of individual soil types which exceeded particular threshold values in Water Drop Penetration Time (WDPT) and molarity of an ethanol droplet (MED) tests

Soil type (WRB 2006)	WDPT (s)		MED (mol/l)	
	> 5	> 60	> 0.85	> 1.45
Cambisols	22	5	12	7
Leptosols	13	7	8	7
Luvisols	7	6	3	2
Fluvisols	1	0	0	0
Regosols	3	3	3	3

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parison to agricultural soils (1.6%) do not indicate a significant difference. This can be partially attributed to land-use change that has been relatively common within the area of interest. It is probable, that some of the recent grasslands were in fact subjected to cultivation in the past. Besides that, grasslands in the area are often used as pastures, since it has been showed that moderate grazing has positive effect on soil properties (Li *et al.* 2011). This factor may support the wettable character of grassland soils as well.

Relationships between the measured soil variables and detected WDPT and MED values were analyzed by correlation and regression analysis. These were performed using the whole set of 210 soils, and also smaller groups of samples, divided according to their categorical attributes. Before performing the correlation and regression analyses, the distribution of individual variables was checked by the Kolmogorov-Smirnov test. It was found that distribution of several variables differed significantly with respect to normal (Gaussian) distribution. For instance, in the case of whole data set (n = 210), only the values of sand and silt particle fractions were distributed normally. Whereas in the case of basic soil characteristics the application of simple transformation techniques (logarithm, n^{th} root, etc.) often led to normal distribution of data (not in the case of $CaCO_3$ content), in the case of WR values (WDPT, MED, surface tension) the application of common mathematical operations did not resolve the problem. Due to the presence of wettable soils, soil WR data contained many zero values, which resulted in a highly skewed distribution. This pertained also to some smaller groups of samples, e.g. soils when divided into two categories: $CaCO_3$-free samples (n = 130) and soils with some $CaCO_3$ content (n = 80). Analyzing the relationships between variables, whose distribution does not approximate a normal distribution by correlation or regression analysis, is problematic and results may be misleading. Therefore our analysis was aimed predominantly at the groups of samples, in which the values of particular properties were approaching normal distribution. Normality of WR data (MED values) was achieved in the case of forest soils (n = 99), and also $CaCO_3$-free forest soils (n = 69), by applying cube and square roots, respectively. As it was already indicated, the content of $CaCO_3$ was a variable with problematic distribution as well. Majority of the data were zeros or low contents (similarly as in the case of WR values). Only after $CaCO_3$ containing soils were separated in standalone group, normality of $CaCO_3$ contents was achieved by logarithmic transformation. This group, consisting of 80 samples, contained 8 soils exhibiting WDPT > 5 s, and from these, the time of droplet penetration exceeded 60 s only in 3 cases. On the other hand, soils in which $CaCO_3$ was absent, showed WDPT > 5 s in 37 cases, and in 14 cases WDPT was > 60 s. From this comparison it follows that in a majority of soils the presence of $CaCO_3$ may be associated with their wettable character.

Matrix of correlation coefficients (Pearson's) calculated for the group of 99 forest soils is presented in Table 3. The relation between particular soil variables was proved to be significant in several cases. Throughout this work mainly MED values are being presented as WR representative, since these values were most easily transformed onto normally distributed scale. It can be seen that WR varied positively with SOC and sand fraction contents, and at the same time, negatively with soil reaction and amount of silt fraction. Except for the correlation between WR and silt fraction, significance of all other correlations exceeded 0.001 error probability level. Repellency (MED) was negatively correlated also with clay content, which was significant at a 0.05 level. This suggests that wettability of topsoil in the area of interest is controlled by a number of

Table 3. Matrix of correlation coefficients (Pearson's) calculated for particular couples of variables of forest soils (n = 99)

	$MED^{1/3}$	$C_{org}^{1/4}$	pH_{H_2O}	Sand	Silt	$Clay^{1/2}$	$CaCO_3$
$MED^{1/3}$	1						
$C_{org}^{1/4}$	0.52***	1					
pH_{H_2O}	–0.351***	–0.231*	1				
Sand	0.338***	0.024	0.145	1			
Silt	–0.275**	–0.111	–0.215*	–0.863***	1		
$Clay^{1/2}$	–0.217*	0.169	–0.025	–0.659***	0.201*	1	
$CaCO_3$	0.094	–0.072	0.546***	0.272**	–0.229*	–0.198*	1

MED – molarity of an ethanol droplet, C_{org} – organic carbon; *, **, ***statistical significance at the 0.05, 0.01, and 0.001 level

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Table 4. Equations obtained by multiple regression analysis and selected statistics characterizing each model

Equation	R^2	F	P	df
Forest soils (n = 99)				
$MED^{1/3} = 0.0719\ C_{org} - 0.202\ pH_{H_2O} + 0.0134\ Sand + 0.0199\ CaCO_3 + 0.4762$	0.503	23.778	$3.834\ 10^{-40}$	94
Calcite-free forest soils (n = 69)				
$MED^{1/2} = 0.0872\ C_{org} - 0.2559\ pH_{H_2O} + 0.0148\ Sand - 0.0081\ Silt + 0.9106$	0.527	17.834	$2.836\ 10^{-24}$	64

MED – molarity of an ethanol droplet; C_{org} – organic carbon; R^2 – coefficient of multiple determination; F – observed value of F statistics; P – error probability value of F statistics; df – degrees of freedom

environmental variables. The observed correlation can be interpreted as follows: the statistically significant correlation between WR and the content of SOC is probably related to higher content of accumulated raw OM, which is an inherent property of many forest soils. This non-humified fraction, which is present in the soil in form of particulate matter or organic coatings, is composed of non-polar or amphiphilic organic substances such as waxes, fatty acids, their esters and salts, phytanes, phytols, and sterols (Morley *et al.* 2005). If these compounds are present in soil in higher amounts, or if they are particularly oriented or distributed in soil matrix, they impede the water which contacts the soil from entering its pore system. In spite of that we did not perform any specific analysis aimed at the quality of the soil OM, the negative correlation, which was observed in the case of WR and soil reaction, suggests that reduced wettability of topsoil is somehow related to the raw-acidic humus type. In forest soils, various organic acids are released either from living biomass or decomposing plant and microbial residues. As a result, with increasing content of SOC, (organic) acidity of topsoil increases as well, as it was suggested here by a significant correlation of two mentioned variables. Increased WR of forest topsoil as a partial consequence of raw-acidic humus type (moor) was previously reported from the High Tatras Mts. (Šimkovič *et al.* 2009). With respect to textural fractions, WR was positively correlated with sand, and negatively with silt and clay. This is related to two factors. Firstly, it is a known fact that sand particles have smaller specific surface and hence, less OM is needed in order to cover its (generally) hydrophilic surface (Mashum & Farmer 1985). Secondly, soils occurring in a moderate climatic zone which contain substantial portion of finer textural fractions (silt, clay), are often richer in quality (humified) OM in comparison to sandy soils (Galantini *et al.* 2004). This has been recently attributed to the catalytic effect of soil clay minerals on humification processes (Hardie *et al.* 2010). If humification proceeds at higher rate, the extent of accumulation of raw OM in topsoil is inherently lower.

Regression analysis performed on 99 forest soils showed that approximately one half of the variability observed within the MED data can be explained by applying the multiple linear approach. The multilinear equation and associated statistics, including coefficient of determination, observed value of F statistics, probability of F value, and degrees of freedom are presented in Table 4. The relationship between observed and predicted data is visualized in Figure 3. It can be seen that not all the variables, which were significantly correlated with WR, were also successfully tested as partial predictors of MED data (and *vice versa*). For instance, the negative relationship between content of finer textural fractions (silt, clay) and WR, which was observed in simple correlation analysis, was not confirmed in multilinear regres-

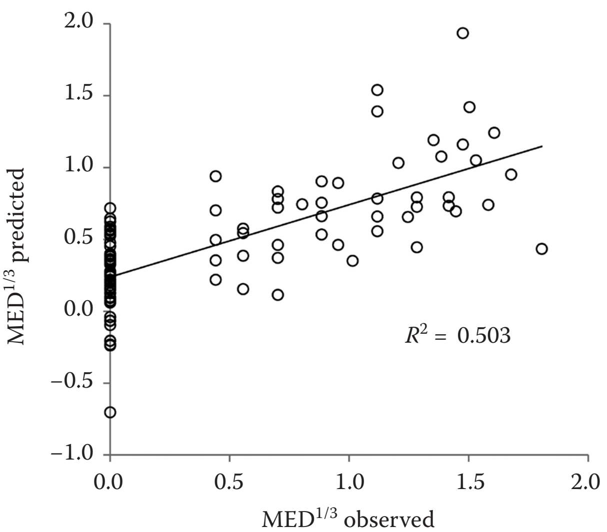

Figure 3. Relationship between observed water repellency data and those predicted according to equation presented in Table 4; MED – molarity of the ethanol droplet

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sion. On the other hand, the content of $CaCO_3$ was successfully tested as a partial predictor of WR in multilinear approach. The positive value of partial regression coefficient suggests the positive effect of $CaCO_3$ content in the equation predicting the MED value. We however do not perceive $CaCO_3$ as a cause of WR in spite of the regression outcome. The observed positive relationship between $CaCO_3$ and MED values does not prove that $CaCO_3$ is in fact the component of soil responsible for WR. In the case of forest samples, higher $CaCO_3$ content is often associated with higher sand content, and at the same time also higher concentration of SOC. Both properties are known to support susceptibility of soil to become repellent. In the data analysis, higher $CaCO_3$ content could in fact reflect higher amount of the two mentioned constituents (sand, SOC). There are several aspects regarding $CaCO_3$ and WR relationship which are worth mentioning at this point. $CaCO_3$ itself is generally considered as hydrophilic, and also after its dissolution and reaction of Ca^{2+} with dissociated organic ligands, the products (Ca-complexes) are not expected to be of hydrophobic nature. Moreover, there are some information sources available, in which authors report that additions of carbonate material into the soil caused distinct alleviation of WR. This was observed either in the case of liming of agricultural soils in the field (Orfánus *et al.* 2014) or in the laboratory experiments (Šimkovic *et al.* 2005). In the field conditions, added $CaCO_3$ is gradually washed away from the topsoil, and a similar process proceeds also in the upper part of soils which inherited $CaCO_3$ from their parent material. For instance, in Rendzic topsoil, microscopic calcite is usually absent since it has been dissolved and leached away. Remaining proportion of $CaCO_3$ is present in form of macroscopic limestone (or dolomite) sand particles, whose surface does not come into contact with water droplet, when WDPT or MED tests are performed. Another aspect which is related to the effect of $CaCO_3$ on WR is that in various soils different forms of $CaCO_3$ occur. These differ for example in a particular crystalline form, spatial distribution of particles in soil matrix, and also in surface area available for water penetration into the soil matrix. One may expect that $CaCO_3$ present in the loess material (or in soils developed on loess) would differ in all of the mentioned characteristics from $CaCO_3$ occurring in Rendzic Leptosols or Rendzinas, which are developed on limestone and dolomitic sedimentary rocks. The results observed here as well as the literary data (e.g. Mataix-Solera *et al.* 2007), both suggest that even the soil containing a significant amount of $CaCO_3$ may exhibit WR, but the reason for this observation probably resides in a higher content of raw OM, which (at small spatial scale) is preventing water from contacting the mineral particles.

The regression (obviously) provided different results in certain aspects when analysis was performed on forest soils in which $CaCO_3$ was absent. This group of 69 soils was composed predominantly of Cambisols (43), Leptosols (10), and Luvisols (9). Regression analysis showed that WR within this group was affected positively by SOC content and sand fraction and at the same time it varied negatively with increasing soil reaction and silt content. Regression equation and statistics describing its significance are presented in Table 4 and associated scatter plot of observed vs predicted WR data is presented in Figure 4. The results were in a relative accordance with the outcome of simple correlation analysis and their interpretation is fairly straightforward. The effect of individual terms (variables) on resulting MED value can be described similarly as it was in the case of the simple correlation analysis. Raw OM with acidic character accumulated in topsoil is favouring its WR, and prevalence of sand fraction in textural composition is supporting it, since mineral surfaces of coarse particles are being covered more easily with organic coatings in comparison to finer ones (silt, clay). The observed negative effect of silt content on WR may be in fact related also to the ef-

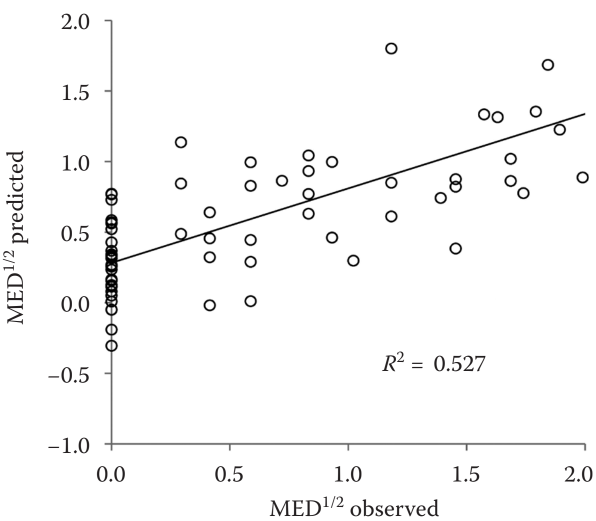

Figure 4. Relation between observed water repellency data and those predicted according to equation presented in Table 4; MED – molarity of the ethanol droplet

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fect of loam structure of soil on soil wettability. Soils with loamy structure are commonly characterized by a relatively uniform distribution of organic and mineral particles in the soil matrix, and at the same time, by the presence of more humified soil OM. The mentioned characteristics may be perceived as factors which decrease susceptibility of soil to exhibit WR.

Regression analysis in general did not elucidate much of the WDPT or MED variances (> 40% of the variability remained unexplained). On the other hand, the data analysis helped identify important aspects of WR origin in the soils of the investigated area. It is possible that results of the regression analysis could be better (higher R^2) if some characteristics, related somehow to soil water regimen, were tested in the analysis as WR predictors. However, the samples were gathered during a relatively long time period, in various weather conditions, and in different parts of the year. It is probable that soil moisture levels, which would have been detected in the field, would not be very helpful as regards explanation of variability within WDPT and/or MED data. Moreover, both types of measurements were performed on air-dried soils.

CONCLUSIONS

Exploratory analysis of the detected laboratory data together with results of regression and correlation analysis suggest that in soils within the area of interest, different mechanisms may be governing susceptibility of soil to become water repellent. In the group of soils, which are actively utilized for the purpose of plant breeding, none of the samples exhibited water repellency. In this case, type of land-use is an important factor supporting wettable character of respective soils. Fertilizers, added into soil on the yearly basis, are in general composed of highly soluble chemicals, which act in soil as wetting agents. The factor, which is also (at least partially) related to this type of land-use, is the relative absence of accumulated particulate fraction of soil organic matter in agricultural soils. We conclude that the agricultural arable soils could be high probably expected wettable, which is a useful expert knowledge by arrangement of any regional mapping of soil WR.

The results of the performed data analysis suggest that a higher content of OM found in forest soils that are known to contain substantial proportion of raw-accumulated carbon, is a factor significantly increasing susceptibility of soil to exhibit water repellency. Coarse-textured forest soils with a lower soil reaction value, which at the same time contained a higher amount of organic carbon, were most prone to water repellency.

Besides the effect of the mentioned factors, there are certain predispositions of the soil parent material as regards susceptibility of soil to exhibit water repellency. We observed that a significant number of water repellent samples were among soils developed on either consolidated sedimentary rocks (31) or unconsolidated sediments (14) of aeolic, deluvial (proluvial) or polygenetic origin. On the other hand, soils developed on recent fluvial deposits showed in almost all 28 cases (except one slightly water repellent) a clearly wettable character.

An interesting finding is related to samples which contained $CaCO_3$. Regarding these 80 soils, water repellency was detected in eight cases; in seven of which the soils were developed on consolidated carbonate sedimentary rocks. Soils that were developed on unconsolidated sediments and at the same time contained $CaCO_3$ were wettable (almost) in all cases. From the mentioned data it follows that if soil from the area of interest is developed on unconsolidated sediments, and at the same time, its topsoil contains $CaCO_3$, it is highly probable that its material will be wettable, while when developed on limestone and/or dolomitic rocks, microscopic calcite is usually leached away from the topsoil and higher contents of $CaCO_3$ remain in form of macroscopic sand particles, which have small contact surfaces for water and do not alleviate soil WR.

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