COMPARISON OF THREE TECHNIQUES TO ASSESS SURFACE HETEROGENEITY OF SOLIDS IN SOILS

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A b s t r a c t. Changes of surface adsorption energy distributions in soils can help to diagnose soil degradation. Techniques are needed to quantify the changes in the energy distributions. We used data on water vapor adsorption in three soils before and after simulated degradation caused by organic matter oxidation, cyclic wetting-drying, and silica acid treatment. To describe adsorption energy distributions we applied a technique that assumes lognormal distribution of adsorption energy and two techniques assuming the distribution function to be piecewise linear: (a) direct fit of the set of nonlinear equations to adsorption data and (b) a preliminary singular decomposition of the matrix of this set of equations. Parameters of the distributions and parameters of local adsorption isotherms were estimated together with their standard errors. Estimated parameters of the local adsorption isotherm were close for all three techniques. Piecewise linear energy distributions were bimodal. Singular decomposition technique provided the most detailed insight into adsorption energy distribution changes after simulated soil degradation.

K e y w o r d s: surface heterogeneity, soil, energy distribution function

INTRODUCTION

Heterogeneity of surfaces is a typical feature of soil particles. The heterogeneity of solid surfaces can be characterized by the statistical distribution of the energy of adsorption of gases. This approach has been successfully used in the surface chemistry of solids [6,18]. Recently, Sokołowska et al. [11,21] presented adsorption energy distributions from water vapor adsorption data on soils. They showed that the adsorption energy distributions are related to cation exchange composition and can be promising indicators of changes in soil surface properties caused by the simulated soil degradation.

Energy heterogeneity of an adsorbing surface is usually characterized by the so called energy distribution function $F(\varepsilon)$, defined in such a way that $F(\varepsilon)d\varepsilon$ gives the proportion of adsorbing sites having adsorption energies in the range from ε to $\varepsilon+d\varepsilon$ [18]. Adsorption equilibrium at a pressure p on particular adsorbing sites depends of the adsorption energy of the site. So the local adsorption is characterized by the local adsorption isotherm $\theta_L(p,\varepsilon)$ and the overall coverage of adsorbent is given by the following equation:

$$\theta(p) = \frac{n(p)}{n_m} = \int_{\varepsilon_{min}}^{\varepsilon_{max}} \theta_L(p,\varepsilon)F(\varepsilon)d\varepsilon . \quad (1)$$

Here $n(p)$ is the experimentally measured amount of the adsorbed gas g g^{-1}, n_m denotes the monolayer capacity of the adsorbent, i.e., the mass of adsorptive monomolecular layer covering the whole surface, g g^{-1}, ε_{min} is the lowest value of adsorption energy usually assumed

to be equal to the energy of condensation of the adsorbate ε_c, J mol^{-1}, ε_{max} is the highest existing energy of adsorption for the given adsorbent, J mol^{-1}. The evaluation of the distribution function $F(\varepsilon)$ from measured adsorption is based on the solution of Eq.(1).

The problem of the finding $F(\varepsilon)$ from Eq.(1) belongs to a class of ill-conditioned mathematical problems [6,18]. The mathematical nature of such problems is that small variations in data can cause large variations in the distribution density function [9]. A number of methods have been proposed to solve Eq.(1). Comprehensive reviews can be found in [6,9, 16,18]. The condensation approximation method [21] and a piecewise linear approximation of the function F [11] have been used in studies of water vapor adsorption on soils.

Methods of solving Eq.(1) differ in physical assumptions, in requirements to data sets, and in details of the surface heterogeneity they are able to reveal [18]. Data on water vapor adsorption in soils usually have a relatively small number of data points on isotherms. No comparison or assessment of techniques of solving Eq.(1) has been done for soils yet. Examples of comparison and assessment of such techniques for other adsorbents show that such a comparison can provide a useful information to select and distinguish methods [3,6]. The objective of this paper was to compare an applicability of techniques well-used for some adsorbents and adsorbates to characterize the surface heterogeneity of soil particles from water vapor adsorption data.

MATERIALS AND METHODS

Soil samples

Details of sampling and preparation of gray forest soil, ordinary chernozem soil, and dark chestnut soil have been reported elsewhere [11]. Air-dried soil samples were sieved, and the fraction 1 mm and smaller was further used.

Untreated and treated samples have been used to obtain isotherms of the water vapour adsorption. Treatments included partial removal of soil organic matter by boiling with a 10 % solution of hydrogen peroxide, cyclic wetting-drying with 10 cycles of the addition of 0.003 M solution of $CaCl_2$ and $MgCl_2$ and following drying in the laboratory during 2 days, and silica acid treatment which consisted in 10 cycles of wetting with the solution containing 80 mg L^{-1} H_2SiO_3, 5 mol L^{-1} $CaCl_2$ and 1 mol L^{-1} $MgCl_2$ and drying in the laboratory during 2 days.

Before water vapour adsorption measurements the soil samples were dried at T=378 K in vacuum (about 10^{-5} kPa) during 48 h. Adsorption was measured by using a vacuum microbalance technique [8]. During adsorption measurements temperature was kept constant within 0.1 K. Fifteen levels of relative pressure were selected in the range from 0.0485 to 0.875. The variations in replicated data did not exceed ± 5 % at the lowest vapor pressure and ± 1 % at the highest vapour pressure.

TECHNIQUES TO CHARACTERIZE THE SURFACE HETEROGENEITY

The local isotherm equation $\theta_L(p,\varepsilon)$ must be known prior to solving Eq.(1). A modified BET equation proposed in [2] can be successfully used as local isotherm equation describing multilayer adsorption of the water vapour on soils and clay minerals [11]. The need in modification follows from the fact that classical BET equation is for unlimited adsorption, and the actual number of layers of water molecules at saturation is usually less than five [8]. The modified equation can be written in the form:

$$\theta(p,\varepsilon) = \frac{1}{1-kx}\frac{Cy}{1+Cy}$$

$$x = \frac{p}{p_s}, \quad y = \frac{x}{1-kx}, \quad C = \exp\left(\frac{\varepsilon - \varepsilon_c}{RT}\right) \quad (2)$$

where R is the universal gas constant and T is Kelvin's temperature. Parameter k is related to the maximum number of molecular layers that can be formed at saturation when $p/p_0 = 1$. The larger is k the larger number of layers can be formed. Thus, value of k is a measure of the maximum adsorption capacity of the surface. With $k=1$, Eq.(2) is reduced to the classical BET equation with the infinite number of layers at

saturation. Brunauer *et al.* stated in [2] that k is a parameter which measures the attractive force field of the adsorbent. Authors of [11] pointed out that the value of k may reflect also the size of pores when the adsorption takes place in porous materials and the adsorbed water is confined between opposite pore walls.

The use of Eq.(2) in Eq.(1) means that constant parameters k and n_m have to be evaluated together with the function $F(\varepsilon)$ from experimental data on water vapour adsorption in soils. These unknowns are to be evaluated from measured adsorption $n(p_i)$ at several levels of pressure p_i, $i=1,2,...,N$. Further we used the dimensionless energy $\in = (\varepsilon - \varepsilon_o)/RT$ and replaced Eq.(1) by:

$$\theta(x) = \frac{n(x)}{n_m} = \int_0^{\in_\infty} \theta_L(x,\in)F(\in)d\in. \quad (3)$$

where $x=p/p_s$ and $\in_{max} = (\varepsilon_{max} - \varepsilon_c)/RT$, and $\varepsilon_c=10.5$ kcal mol^{-1} ≈44 kJ mol^{-1} was used [7]. Dependence of θ_L on x and $\in$ is expressed by Eq.(2). Since $F(\in)$ is a frequency distribution, it must satisfy the constraint:

$$\int_0^{\in_{max}} F(\in)d\in = 1. \quad (4)$$

We selected three well-used techniques to solve Eq.(1) that were known to work well with a relatively small number of experimental data points. Because k and n_m values had to be found together with $F(\in)$, we had to modify the techniques as described below. For all data sets and all techniques, we determined values of parameters that provided minimum lack-of-fit mean square which is known to be an unbiased estimator of the model's standard error [13]:

$$s_r = \sqrt{\frac{\sum_{i=1}^{N} m_i[n^c(x_i) - n(x_i)]^2}{N-P}}. \quad (5)$$

Here N is the total number of vapour pressure levels, m_i is a number of replications in the measurements at the ith vapour pressure, P is number of parameters

A technique which assumes a formula of the dependence of F on $\in$ was introduced by

Ross and Oliver [17] and later on used by several authors, e.g., in [4,5]. The method consists in the use of preselected formulas for $\theta(p, \in)$ and $F(\in)$ with unknown parameters. The parameters' values that provide minimum deviations between measured and calculated from Eq.(1) adsorption, have to be found.

Since $F(\in)$ must be 0 for $\in <0$ and must approach 0 for $\in \to \infty$ [6], we assumed that the energy distribution is lognormal:

$$F(\in) = \frac{1}{\sqrt{\pi} \sigma \in} \exp\left[-\frac{(\ln \in - \ln \overline{\in})^2}{\sigma^2}\right]. \quad (6)$$

This equation was substituted into Eq.(3) and nonnegative values of n_m, k, $\overline{\in}$, and σ were found to minimize s_r in the Eq.(5) with $P = 4$ for this case. The value of $\in_{max}$ was set to infinity as recommended for analytically expressed distribution functions [6].

A piecewise linear distribution of energies and the direct fit of Eq.(3) to data was introduced for the virial isotherm equation and later utilized in the algorithm CAEDMON [19]. The energy range is subdivided to several intervals and the frequency distribution $F(\in)$ is assumed to be constant over each interval, i.e.:

$$F(\in) = \begin{cases} 0, & \in \le \in_o \\ F_j, & \in_{j-1} \le \in < \in_j, j = 0,1,2,..., M \\ 0, & \in \ge \in_M \end{cases} \quad (7)$$

where M is the total number of intervals, $\in_o = 0$, $\in_M = \in_{max}$.

Values of $n_p(x_i)=n_i^c$ can be found from Eq.(3) with the local isotherm (2) and $F(\in)$ from (7) as:

$$n_i^c = \sum_{j=1}^{M} F_j a_{i,j}, i = 1,2,..., N; j = 1,2,..., M \quad (8)$$

where

$$a_{i,j} = n_m \int_{\in_{j-1}}^{\in_j} \theta_L(x_i,\in)d\in =$$

$$n_m \ln \frac{1 - kx_i + x_i \exp(\in_j)}{1 - kx_i + x_i \exp(\in_{j-1})}. \quad (9)$$

Nonnegative values of n_m, k, F_j, $j=1,2,...$

M have to be found to provide minimum lack-of-fit mean square in (5) with *P=M+2*.

In general, the more intervals one has the better will be a description of the distribution. On the other hand, to obtain reliable results in regression, one has to have the number of coefficients which is at least two times less than the number of data points (11). Having 15 data points, we first selected number of intervals *M* equal to 12. Twelve F_j values together with n_m and *k* gave 14 coefficients to be determined. However, we could not obtain stable results in fitting (3) to data and encountered numerous local extremums. Then we diminished *M* and had five F_j values to be found together with n_m and *k*.

The usual recommendation for the selection of $\in_{max}$ value is to use so called condensation approximation method [6]. The estimate is dependent on the lowest vapour pressure in measurements. The condensation approximation method provided the value $\in_{max}=3$ for the presented data sets [11]. The authors of [11] used $\in_{max}=6$ as a safe upper estimate. Values $\in_1=1$, $\in_2=2$, $\in_3=3$, $\in_4=4.5$, $\in_5=6.0$ were selected as some boundaries of energy intervals in (6).

A singular decomposition technique was introduced in [23] and was utilized in their algorithm CAESAR. It also uses a piecewise constant approximation (6) of the frequency of the distribution. Unlike the previous technique, however, this one allows to control the precision of results. The set of Eqs(8) is presented in [23] in matrix form:

$$\vec{n}^c = [A]\vec{f} \qquad (10)$$

where $\vec{n}^c = \{n_1^c, n_2^c, ..., n_N^c\}, [A]=\{a_{ij}\}, f = \{F_1, F_2, ..., F_M\}$, *N* is number of relative pressure levels in measurements, *M* is number of intervals in (6). Using the singular decomposition algorithm the authors decompose the matrix [A] to three multiplier matrixes one of which contains singular values. For preselected rank value *r* the smallest *M-r* values of singular values are replaced by some large number *Q*. Then multipliers are composed back into the

altered matrix [A] which is substituted into (10) instead of [A]. Nonnegative values of F_j, *j=1,2,...,M*, are found to provide a minimum of the lack-of-fit mean square s_r in (5) with *P=M+2*.

Value of the rank governs the precision of results. In general, the larger rank is the better precision can be achieved. When the rank increases, however, results become less reliable. The optimal rank value is the minimum rank value that makes statistically insignificant a difference between standard errors of model estimates and standard errors of data. We evaluated the standard errors of estimates as s_r values and estimated standard error of data as a mean square pure error [11]:

$$s_e = \sqrt{\frac{\sum\limits_{i=1}^{N}\sum\limits_{j=1}^{m_i}[\bar{n}(x_i)-n_j(x_i)]^2}{\sum\limits_{i=1}^{N}m_i - N}} \qquad (11)$$

where *n* is an average adsorption and n_j is the *j*th replication, m_i is the number of replications at the ith level of $x=p/p_i$, *i=1,2,...,N*. For this data the optimal rank value was 5. We used the same algorithm of the singular decomposition as Vos and Koopal did in [23]. The *Q* value was equal to the largest singular value as recommended by WanLum and White [9].

The technique requires a preselection of the number of intervals *M* and value of $\in_{max}$. We selected *M=12* to have minimum acceptable *N-P=1* value in (5). Equal intervals $\in_j-\in_{j-1}=0.5$ were selected.

A modified Marquardt algorithm was used in all cases to obtain nonnegative parameter values that minimized s_r in (5)*. We used a version of the algorithm presented in [22]. This version proved to be very efficient in multi-parametric nonlinear optimization. To avoid local minimums of (5), we made 100 runs for every sample with random selections of initial parameter estimates. The algorithm provides not only estimates of parameters but also standard errors of these estimates.

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*Computer programs available upon request from the corresponding author[2].

It allowed us to test the statistical significance between average values of the same parameter for different samples. Student's t- statistic has been calculated as:

$$t = \sqrt{\frac{|p_1 - p_2|}{\sqrt{(s_{p,1})^2 + (s_{p,2})^2}}} \qquad (12)$$

where p_1 and p_2 are estimates of average of a parameter p to be compared, $s_{p,1}$ and $s_{p,2}$ are estimates of standard error of p_1 and p_2, respectively. The critical value of the t-statistic is $t_{N-P,1-\alpha/2}$, where N is the number of measurements, P is the total number of parameters, and α is the significance level.

RESULTS AND DISCUSSION

Data on adsorption are presented in Table 1 and calculated frequency of energy distributions are shown in Fig. 1. Some general parameters of distribution functions and local isotherms are collected in Table 2. Below we abbreviate the assumed lognormal distribution technique, piecewise linear distribution technique with the direct fit to data, and singular decomposition technique to LD, DF, and SD techniques, respectively.

Table 2 also contains mean square lack-of-fit values s_r computed according the Eq.(6).

These values show that the application of the Eq.(1) with the local isotherm (2) provides a good fit of the measured adsorption. we have not found a significant difference between standard errors of estimates s_r and standard error of measurements s_e for all three methods of energy distribution estimation.

Data in Table 2 show a close similarity in estimates of adsorption isotherm parameters obtained by different techniques for the same samples. Differences among values of monolayer capacity were close to 6 % only in one case and were below 4 % in all other cases. Similarly, differences in values of k exceeded 4 % in one case and were below 2 % in all other cases. All techniques show the same trend in changing of the isotherm parameters due a particular treatment.

Both LD and DF techniques have the number of parameters significantly less than the number of the measurements. Therefore the meaningful estimates of the standard deviations could be calculated for both parameters of isotherms and for parameters of the distributions. These estimates represent an essential complement to the estimates of the parameters itself, since the statistical hypotheses on equality of parameters before and after treatments could be tested. Results of such

T a b l e 1. Water vapour adsorption, mg g^{-1}, in soil samples

p/po	Untreated			Organic matter oxidized			Cyclic drying-wetting			Silica acid treatment	
	GFS[1]	Chz	Chs	GFS	Chz	Chs	GFS	Chz	Chs	Chz	Chs
0.0485	6.3	19.0	15.9	4.1	9.8	9.4	6.3	20.0	16.2	17.2	14.2
0.0812	7.6	22.7	19.4	5.1	12.7	12.2	7.6	23.7	19.6	20.5	17.2
0.1020	8.2	24.2	20.7	5.7	13.9	13.3	8.2	25.2	20.9	21.8	18.5
0.1271	8.8	26.5	22.8	6.1	15.6	15.1	8.8	27.5	23.2	23.9	20.0
0.1869	10.6	32.1	27.8	7.7	20.1	19.3	10.7	33.1	28.0	30.0	25.1
0.2703	12.8	38.1	32.9	9.2	24.6	23.6	12.9	39.2	33.3	35.2	30.1
0.3748	15.5	46.3	39.7	11.2	30.7	29.2	15.7	47.4	40.3	43.4	37.4
0.3945	15.7	47.2	40.6	11.6	31.9	29.9	16.1	48.4	41.3	44.4	38.2
0.4836	17.8	53.7	46.3	13.3	37.3	33.4	18.2	54.9	47.1	51.3	44.5
0.5349	19.1	57.4	49.5	14.7	40.8	37.2	19.6	58.7	50.5	55.3	48.0
0.6202	21.7	65.3	56.3	17.1	47.7	42.3	22.3	66.7	57.7	64.1	55.7
0.6787	23.6	70.9	61.1	19.0	53.4	47.6	24.3	72.4	62.9	70.6	61.5
0.7498	25.9	77.4	66.7	21.5	60.1	53.2	26.8	79.2	68.9	79.1	69.1
0.8407	30.9	90.3	77.5	26.6	73.8	63.2	32.3	93.0	81.5	98.2	86.1

Explanations: [1]GFS - gray forest soil, Chz - chernozem soil, ChS - chestnut soil; data represent average over 3 replications.
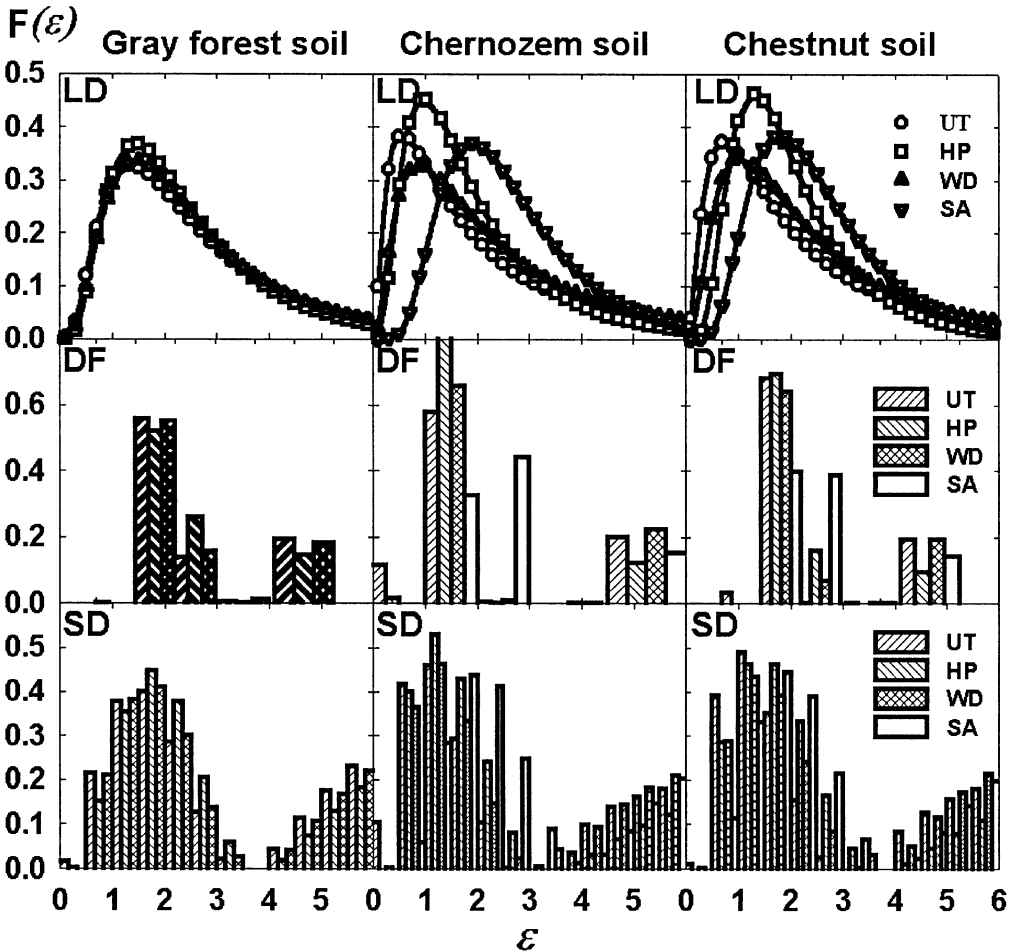
Fig. 1. Frequencies of adsorption energy distribution of water vapour in soils calculated using lognormal distribution (LD), direct fit of the isotherm based on piecewise-linear distribution (DF), and singular decomposition (SD) techniques; UT - untreated soil, HP - soil after organic matter oxidation, WD - after cyclic wetting-drying, SA -after silica acid treatment.

testing are shown in Table 3. Both LD and DF techniques have lead to similar results. Changes in values of the monolayer capacity n_m are statistically significant only after organic matter oxidation and silica acid treatments. The same is true for the value of k, but this value also increases significantly after wetting-drying treatment in the chestnut soil. It can be explained by the fact that this soil is found in semiarid region [1] and cyclic wetting-drying is very unusual regime for it. Average adsorption energy undergoes significant changes only after organic matter oxidation in chernozem and chestnut soils.

Differences among the techniques are related to their ability to show details of the energy distributions. Both DF and SD techniques demonstrate that the interval of energies between 3 and 4 is not represented by any significant number of adsorption sites in most of cases. The energy distributions are at least bimodal. The distribution function value in the range of the largest energies accounts both for energies in this range and for larger energies [3]. Therefore the distribution functions may have other peaks in the range of $\varepsilon > 6$; however the range of observed adsorptions precludes detecting these additional peaks.

T a b l e 2. Parameters of the adsorption energy distributions for soil samples as estimated by three techniques

Para-meter[§]	Grey forest soil			Chernozem soil				Chestnut soil			
	OR[¶]	HP	WD	OR	HP	WD	SA	OR	HP	WD	SA
Technique assuming lognormal energy distribution											
$n_m\ 10^2$	1.41	1.00	1.41	4.79	3.04	4.60	3.60	4.08	2.79	3.87	3.12
k	0.68	0.77	0.70	0.63	0.74	0.66	0.78	0.63	0.74	0.70	0.78
$<\varepsilon>$	2.84	2.56	2.78	2.99	2.05	3.06	2.77	2.75	2.10	2.78	2.77
σ	0.99	0.88	0.94	1.50	1.00	1.29	0.70	1.33	0.79	1.14	0.71
$s_r\ 10^3$	0.25	0.13	0.28	0.53	0.34	0.64	1.03	0.40	0.34	0.52	0.94
Technique using piecewise linear energy distribution											
$n_m\ 10^2$	1.39	0.99	1.40	4.53	2.94	4.44	3.59	3.91	2.75	3.88	3.13
k	0.69	0.77	0.70	0.64	0.75	0.66	0.78	0.64	0.74	0.68	0.78
$<\varepsilon>$	2.67	2.58	2.73	2.57	2.17	2.75	2.80	2.54	2.20	2.65	2.80
$s_r\ 10^3$	0.26	0.14	0.30	0.53	0.35	0.65	1.12	0.41	0.36	0.53	1.01
Singular decomposition technique											
$n_m\ 10^2$	1.43	0.99	1.44	4.78	3.02	4.61	3.65	4.03	2.80	3.87	3.20
k	0.68	0.77	0.70	0.63	0.75	0.65	0.77	0.63	0.73	0.67	0.78
$<\varepsilon>$	2.67	2.55	2.65	2.38	2.26	2.60	2.77	2.43	2.19	2.56	2.65
$s_r\ 10^3$	0.35	0.16	0.39	0.82	0.53	0.91	1.41	0.56	0.50	0.71	1.15

Explanations:[§]n_m is a monolayer capacity, g g^{-1}; k is a measure of the maximum adsorption capacity; $<\varepsilon>$ is an average reduced adsorption energy of the surface defined as $<\varepsilon> = \int_0^\infty \varepsilon\, F(\varepsilon)d\varepsilon$ [20]; σ is a variance of the lognormal energy distribution; s_r is a lack-of-fit mean square, g g^{-1}; [¶]OR - original samples; HP - hydrogen peroxide treatment; WD - wetting-drying treatment; SA - silicate acid treatment.

T a b l e 3. Student's t-statistics to test the hypothesis on equality of adsorption parameters before and after treatments

Parameter	Organic matter oxidized			Cyclic drying-wetting			Silic acid treatment	
	GFS[¶]	Chz	ChS	GFS	Chz	ChS	Chz	ChS
LD technique								
n_m	5.6	6.8	6.7	0.0	0.6	0.9	4.1	4.2
k	7.9	6.1	7.0	0.9	1.3	3.7	7.3	7.9
$<\varepsilon>$	1.1	3.4	2.8	0.2	0.2	0.1	0.7	0.1
DF technique								
n_m	7.1	12.2	10.4	0.1	0.5	1.6	5.4	4.1
k	5.2	9.0	8.3	0.5	1.4	3.0	8.4	4.1
$<\varepsilon>$	0.6	2.9	2.5	0.3	1.4	0.8	0.5	0.3

Explanation: [¶]GFS - gray forest; Chz - chernozem, and ChS - chestnut soils; [§]n_m is a monolayer capacity; gg^{-1}; k is a measure of the maximum adsorption capacity; $<\varepsilon>$ is an average reduced adsorption energy of the surface defined as $<\varepsilon> = \int_0^\infty \varepsilon\, F(\varepsilon)d\varepsilon$ [20].

The bimodality of surface energy distributions was earlier demonstrated for soils [11,21]. Of course, there probably exist a finer structure of the distributions, but much more dense measurements are needed to reveal it.

Using singular decomposition, we could double number of intervals for which the energy distribution density has been found. This kind of results is typical in solving ill-conditioned problems by means of optimization [15].

All three techniques reflect the changes in the surface energy distribution after treatments in a similar way. All treatments resulted in the loss of low-energy adsorption sites in the range of the $\in$ from 0 to 1 (ε from 44 to 46.5 kJ mol^{-1}). The maximum of the distributions shifts towards larger energies. The LD technique reflected these changes by the shift of the peak towards larger energies. The DF technique has shown the disappearance of the energy sites in the range from 0 to 1 after treatments. The SD technique have shown a complete disappearance of sites with energies in the range from 0 to 1 and a decrease of the number of sites in the range from 0.5 to 1 after some treatments for some soils.

After the organic matter oxidation treatments, the energy distributions are much more narrow than in untreated soils. These treatments seem to eliminate high-energy adsorption sites. This effect is not so strong in the gray forest soil, but in the chernozem and especially in the chestnut soil it is very pronounced. The LD technique reflects these changes by the higher position of the peak and the smaller variance of the distribution. The DF technique shows that the increase of the distribution density occurs in the range of the $\in$ from 2 to 3 for the gray forest and chestnut soils and in the range of $\in$ from 1 to 2 for the chernozem soil. The SD technique displays more complex changes of the distribution density. For example, for gray forest soil and chestnut soil, the average distribution density is not affected by the organic matter oxidation in the range from 1 to 2. However, distribution density decreases in the range from 1 to 1.5 and increases in the range from 1.5 to 2. Ap-

plication of each of the techniques resulted in the decrease of the average adsorption energy, as can be seen in the Table 2. The LD technique suggested larger changes than DF and SD techniques.

The cyclic wetting-drying does not significantly change the surface energy distribution for the gray forest soil and results in the shift of the distribution towards larger energy range for the gray forest soil and for the chernozem soil. The DF technique gives a rough sketch of the changes: complete loss in the {0,1} range, increase in the range {1,3} and the absence of changes in the range {4.5,6}. The SD technique reveals details of the increase in the ranges {1.5,2}, {2,2.5}, {2.5,3} and small but visible increase in the range {4.5,6} for chernozem and chestnut soils. The frequent cyclic drying-wetting is the natural regime of gray forest soils [14] and it may be a reason of the absence of changes in the energy distribution after this treatment.

The silica acid treatment causes the most significant changes in the surface energy distributions. The LD technique shows the decrease of the peak heights. The DF technique shows that the range of energies {2,3}, where original samples did not have energy sites, gets the largest frequency of energy sites. At the same time the relative importance of the range {1,2} diminishes. The new energy sites in the range of $\in$ from 2 to 3 (i.e., ε from 49 to 51.5 kJ mol^{-1}) seem to be created due to precipitation of the silica compounds. To test this assumption, we used the data on adsorption of water on silica gel [10]. We assumed the energy distribution function to be a delta-function $F(\in) = \sigma (\in - \in_s)$. In this case (3) reduces to:

$$\theta(x) = \frac{1}{1 - kx} \frac{y}{y + \exp(-\in_s)} \qquad (13)$$

We fit this equation to the data on water adsorption on silica gel and found the reduced energy of silica gel $\in_s$ equal to 2.35. This value is within the range of energies where we observed a significant increase in the

frequency of the energy distribution after silica acid treatment. Precipitating silica compounds could cover mineral surfaces that provided sites with energies form 1 to 2 thus diminishing their relative input in energy distributions after silica acid treatment.

SUMMARY

The sensitivity of the adsorption energy distribution to particular treatments of soils can be important for diagnosing soil degradation [11]. To quantify this sensitivity, we used lognormal and piecewise adsorption energy distributions combined with the modified BET equation for the local adsorption isotherm. Both direct fit to data and singular regularization were used for the piecewise linear distribution. The experimental data set consisted of water vapour adsorption on three soils before and after removal of organic matter, cyclic wetting-drying, and silica acid treatment. The technique using the lognormal distribution is able to provide the right vales of the local isotherm parameters but fails to show the bimodality of the energy distribution. Both techniques based on piecewise distribution indicated the bimodality of the adsorption energy distribution, and results of their application were in broad general agreement. The technique based on lognormal distribution gave the same parameters of the local isotherm as two other techniques. Estimates of standard errors of parameters were derived for the parameters of the distribution functions and for parameters of the local isotherm. These estimates were useful in evaluation of the significance of the observed changes in parameter values resulting from soil treatments.

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