

Determination of soil specific surface area by water vapor adsorption

II Dependence of soil specific surface area on clay and organic carbon content

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Abstract. The specific surface area of 60 mineral soil samples estimated by water vapor adsorption at 20 % relative humidity ranged from 12.1 ± 3.6 to 225.1 ± 18.4 m²/g. Clay (range 1–72 %) and organic carbon content (0.7–14.6 %) together explained 84 % of the variation in the surface area. The regression equation predicting the specific surface area of soil was surface area (m²/g) = $2.69 + 1.23\text{clay-}\% + 8.69\text{org.C-}\%$.

Index words: water vapor adsorption, relative humidity, mineral soils

Introduction

Physical and chemical properties of soil are largely related to the specific surface area of soil. The ability to reserve available plant nutrients and the cation-exchange and buffer capacity of soil are ultimately derived from the surface area of soil particles. The surface area of soil is dependent on the content and mineral composition of clay fraction and on the content of organic matter and amorphous oxides.

Many methods used for the measurement of specific surface area are based on gas or liquid mono- or multilayer adsorption on soil surface. The number of molecules of gas

which will sorb onto surface at equilibrium depends on the partial pressure of the gas and the area of the surface. Water vapor adsorption isotherms are used in the estimation of the total surface area of soil. It is possible by the BET equation (BRUNAUER et al. 1938) to determine the amount of water at monolayer coverage, which gives the surface area when a standard value for the area covered by a molecule of water is known. If only comparative values of area are required and there is to be no isotherm analysis, use can be made of the fact that the water monolayer is complete for many soils and clays at the relative humidity, p/p_0 , corresponding approximately

to 0.20 (QUIRK 1955). It is therefore possible to obtain a rough estimate of the BET water area by a one-point determination at this relative humidity (GREENLAND and MOTT 1978). This one-point method has been applied eg. by PRITCHARD (1971), BASCOMB and THANIGASALAM (1978) and BORGGAARD (1982).

In many countries, the measurement of specific surface area is an essential soil analysis. In Finland, surface area measurement is mainly used for classification of till fractions by engineering geologists (LINDROOS 1976, NIEMINEN and KELLOMÄKI 1982). The aim of this study was to apply the one-point method of surface area measurement for arable soils and to study the relationship between water surface area and soil organic carbon and clay content.

Material and methods

The material was collected at 43 sampling sites, mainly locating in the southern part of Finland, and it consisted of 31 surface soil samples and 29 samples from deeper soil layer (Table 1). At 17 sampling sites, both surface and deeper layer samples were taken. The samples were air-dried and ground to pass a 2-mm sieve. The particle-size distribution of the inorganic matter in the soil was determined by the pipette method (ELONEN 1971). The organic carbon content was determined by a modified (GRAHAM 1948) ALTEN wet combustion method.

For estimation of the specific surface area of soil, 1 g of soil in a tared weighing bottle was placed in a desiccator over a saturated CH_3COOK solution at 20 % relative humidity. After 2 weeks of equilibration at +20°C the soil + weighing bottle was weighed. The water content of soil was determined by drying for 4 hours at +105°C (NISKANEN and MÄNTYLÄHTI 1987). In calculation of the specific surface area of soil, the cross-sectional area of 0.106 nm² (GÁL 1967) was assigned for a water molecule. Considering the water monolayer on soil surface complete at p/p_0 0.20,

the soil water content of 1 % corresponds to the surface area of 35.45 m²/g dry soil. The surface area measurement was carried out in quadruplicate.

Results and discussion

Soil water retention properties are largely related to the soil clay content. The surface adsorptive forces are effective on the water retention especially at high water tensions. Under these circumstances, the clay fraction with its large surface area is the principal contributing factor capable of water adsorption. Accordingly, clay has been reported to have strong influence on soil water retention especially at the wilting point pF 4.2 (PETERSEN et al. 1968), which is largely a function of the permanent negative charge of clay mineral particles. In the material of KIVISAARI (1971), the soil water content at pF 4.2 and clay content were highly correlated ($r=0.98^{***}$, $n=90$).

In this study, the water tension was essentially higher than pF 4.2. The pF value of water corresponding to 20 % relative humidity (R.H.) obtained from the equation (BOLT and FRISSEL 1960) $pF = 6.5 + \log(2 - \log R.H.)$ is 6.3. In the present material (Table 1), which included 25 clay soils (clay-% > 30) and 35 non-clay soils, the mean content of adsorption water was 2.45 % in the clay soil group and 1.46 % in the non-clay group.

The total surface area of soil determined by means of water vapor as an adsorbent not only depends on the clay content but to a great extent on the content of humus as well (DECHNIK and STAWINSKI 1970). The total surface area of soil increases with increasing clay and humus content (CURLIK 1973). According to BURFORD et al. (1964), organic matter present even in small amounts greatly affects the surface area. The values of the total soil surface area are higher in the presence of organic substances than after their removal (DOBRAŃSKI et al. 1972).

In the present material (Table 1), the effect of organic matter on soil water adsorption and

Table 1. Soil samples.

Soil sample No.	Locality	Sampling depth cm	Org.C, %	Particle-size distribution (μm), %			H ₂ O adsorbed % of dry soil *)	Surface area m ² /g dry soil *)
				<2	2-20	>20		
1a	Vaala	0-20	8.4	3	4	93	1.62 ± 0.10	57.4 ± 3.6
1b	»	20-40	1.3	1	3	96	0.85 ± 0.06	30.1 ± 2.1
2a	Viikki	0-20	9.2	3	7	90	1.96 ± 0.27	69.5 ± 9.6
2b	»	20-40	2.7	2	5	93	0.94 ± 0.21	33.3 ± 7.5
3a	Hyvinkää	0-20	12.5	6	11	83	3.37 ± 0.33	119.5 ± 11.7
3b	»	20-40	1.6	4	8	88	0.50 ± 0.08	17.7 ± 2.8
4a	»	0-20	3.7	15	24	61	1.76 ± 0.08	62.4 ± 2.8
4b	»	20-40	0.7	8	11	81	0.75 ± 0.08	26.6 ± 2.8
5a	Salo	0-30	3.1	20	31	49	1.86 ± 0.18	65.9 ± 6.4
5b	»	30-60	2.3	32	17	51	1.84 ± 0.06	65.2 ± 2.1
6a	Rajamäki	0-20	3.0	23	25	52	1.61 ± 0.13	57.1 ± 4.6
6b	»	20-40	1.0	49	19	32	2.61 ± 0.16	92.5 ± 5.7
7a	Imatra	0-20	5.5	24	43	33	2.03 ± 0.26	72.0 ± 9.2
7b	»	20-40	2.2	29	46	25	1.31 ± 0.22	46.4 ± 7.8
8a	Säkylä	0-30	3.2	25	41	34	1.88 ± 0.24	66.7 ± 8.5
8b	»	30-60	1.4	29	45	26	1.71 ± 0.19	60.6 ± 6.7
9a	»	0-30	3.1	27	42	31	1.74 ± 0.14	61.7 ± 5.0
9b	»	30-60	1.5	30	45	25	1.58 ± 0.27	56.0 ± 9.6
10a	Imatra	0-20	3.2	28	41	31	1.97 ± 0.24	69.8 ± 8.5
10b	»	20-40	1.1	33	39	28	1.81 ± 0.18	64.2 ± 6.4
11a	Viikki	0-20	2.4	29	30	41	1.46 ± 0.16	51.8 ± 5.7
11b	»	20-40	1.4	49	20	31	1.54 ± 0.19	54.6 ± 6.7
12a	Laukaa	0-30	2.6	32	55	13	1.46 ± 0.16	51.8 ± 5.7
12b	»	30-60	2.1	34	57	9	1.44 ± 0.08	51.1 ± 2.8
13a	Viikki	0-20	3.3	37	13	50	1.16 ± 0.21	41.1 ± 7.5
13b	»	20-40	0.8	39	6	55	0.76 ± 0.11	26.9 ± 3.9
14a	Hyvinkää	0-20	8.7	42	47	11	4.00 ± 0.22	141.8 ± 7.8
14b	»	20-40	6.5	38	52	10	3.39 ± 0.19	120.2 ± 6.7
15a	Viikki	0-20	3.4	43	33	24	2.55 ± 0.06	90.4 ± 2.1
15b	»	20-40	2.6	47	30	23	2.61 ± 0.37	92.5 ± 13.1
16a	Mietoinen	0-30	2.7	50	21	29	1.75 ± 0.21	62.0 ± 7.5
16b	»	30-60	2.4	54	21	25	1.67 ± 0.13	59.2 ± 4.6
17a	Imatra	0-20	10.7	70	18	12	5.91 ± 0.59	209.5 ± 20.9
17b	»	20-40	11.5	72	17	11	6.35 ± 0.52	225.1 ± 18.4
18	Hyvinkää	0-20	3.9	4	10	86	1.20 ± 0.21	42.5 ± 7.5
19	»	5-10	4.5	4	13	83	1.11 ± 0.18	39.4 ± 6.4
20	Viikki	0-20	1.5	4	16	80	0.51 ± 0.05	18.1 ± 1.8
21	Imatra	0-20	6.0	5	6	89	1.54 ± 0.11	54.6 ± 3.9
22	Tohmajärvi	0-20	3.7	6	19	75	1.55 ± 0.18	55.0 ± 6.4
23	Naantali	0-30	1.6	10	7	83	0.67 ± 0.13	23.8 ± 4.6
24	Viikki	0-20	4.4	10	7	83	1.49 ± 0.19	52.8 ± 6.7
25	Imatra	0-20	3.6	13	20	67	1.80 ± 0.16	63.8 ± 5.7
26	Hyvinkää	0-20	4.3	20	47	33	2.21 ± 0.25	78.4 ± 8.9
27	Imatra	0-20	3.8	22	31	47	1.67 ± 0.22	59.2 ± 7.8
28	Säkylä	0-30	14.6	25	43	32	3.76 ± 0.22	133.3 ± 7.8
29	Imatra	0-20	3.2	31	43	26	2.03 ± 0.29	72.0 ± 10.3
30	Viikki	0-20	4.7	36	8	56	1.59 ± 0.11	56.4 ± 3.9
31	Imatra	0-20	2.7	51	27	22	3.88 ± 0.33	137.6 ± 11.7
32	Vaala	20-40	1.0	1	2	97	0.34 ± 0.10	12.1 ± 3.6
33	Viikki	20-40	0.8	2	1	97	0.63 ± 0.10	22.3 ± 3.6
34	Tohmajärvi	30-50	1.1	2	20	78	1.01 ± 0.14	35.8 ± 5.0
35	Hyvinkää	20-40	2.3	3	4	93	0.65 ± 0.05	23.0 ± 1.8
36	Turenki	30-60	0.9	5	15	80	0.84 ± 0.11	29.8 ± 3.9
37	Imatra	20-40	3.7	14	19	67	1.62 ± 0.41	57.4 ± 14.5
38	Naantali	30-60	1.7	28	20	52	1.24 ± 0.33	44.0 ± 11.7
39	Hyvinkää	20-40	1.4	31	39	30	1.66 ± 0.21	58.9 ± 7.5
40	Viikki	20-40	1.7	45	19	36	1.96 ± 0.22	69.5 ± 7.8
41	Salo	30-60	1.3	45	27	28	1.93 ± 0.40	68.4 ± 14.2
42	Nurmijärvi	20-40	5.2	56	36	8	3.52 ± 0.16	124.8 ± 5.7
43	Mietoinen	30-60	2.0	70	23	7	2.16 ± 0.25	76.6 ± 8.9

*) means with the confidence limits at the 95 % level.

Table 2. Soil characteristics.

	All soils (n = 60)			Surface soils (n = 31)			Deeper layers (n = 29)		
	\bar{x}	s	range	\bar{x}	s	range	\bar{x}	s	range
Org.C, %	3.6	3.0	0.7—14.6	4.6	3.0	1.5—14.6	2.3	2.2	0.7—11.5
Clay (<2 μm), %	26	19	1—72	23	16	3—70	29	22	1—72
Silt (2—20 μm), %	24	15	1—57	25	15	4—55	23	16	1—57
Coarser fractions (>20 μm), %	50	29	1—97	51	26	1—86	48	32	7—97
H ₂ O adsorbed, % of dry soil	1.87	1.15	0.34—6.35	2.04	1.10	0.51—5.91	1.70	1.20	0.34—6.35
Surface area, m ² /g dry soil	66.3	40.8	12.1—225.1	72.3	39.0	18.1—209.5	60.3	42.5	12.1—225.1

surface area was particularly clear when topsoil and corresponding deeper layer samples of non-clay soils were compared. The values of water adsorption and surface area of topsoil samples 1a-4a and 7a were much higher than those of the corresponding deeper layer soils. The mean values of water adsorption and surface area of all deeper layer soils were 83 % of those in the topsoil group (Table 2).

The relationship between water adsorption at p/p_0 0.20 and clay and organic carbon content was more accurately studied by the regression analysis. When clay and organic carbon contents were used as independent variables, together they explained 84 % of the variation in the water content of the whole material ($n = 60$), the regression equation being $\text{H}_2\text{O-}\% = 0.076 + 0.035\text{clay-}\% + 0.245\text{org.C-}\%$. Using the silt content as an additional independent variable in the regression analysis showed that silt content was an insignificant explainer. The partial correlation coefficients for the relation between water content (1), clay content (2) and organic carbon content (3) were as follows: $r_{12.3} = 0.82^{***}$
 $r_{13.2} = 0.84^{***}$

Expressing the water adsorption as surface area, the regression equation takes the form: surface area (m²/g) = 2.69 + 1.23clay-% + 8.69org.C-%.

SILLANPÄÄ (1982) has used for the expression of soil texture as a single figure a texture index $\text{TI} = 1.0 \times \% \text{ of fraction } < 2 \mu\text{m} + 0.3 \times \% \text{ of fraction } 2-60 \mu\text{m} + 0.1 \times \% \text{ of fraction } 60-200 \mu\text{m}$.

When this texture index and organic carbon content were used as independent variables in the regression analysis, together they explained 84 % of the variation in the surface area, the regression equation being surface area (m²/g) = -14.69 + 1.22TI + 8.89 org.C-%.

The disadvantage of using a polar molecule like water in the determination of surface area is that it is more strongly adsorbed on specific sites on the surface, and thus not uniformly distributed (GREENLAND and MOTT 1978). Water molecules are attracted to the bare exchangeable cations and are clustered around them, which implies overlapping of the monolayer and multilayer processes. In addition, the geometry of clustering depends on the exchangeable ion, so that e.g. Ca²⁺ ion attracts water more strongly than K⁺ (STAWIŃSKI 1978). However, exchangeable cations in Finnish arable soils largely consist of divalent cations Ca²⁺ and Mg²⁺ (KAILA 1972, NISKANEN and JAAKKOLA 1986), and thus exchangeable cation composition is probably not a very important source of uncertainty in the determination of surface area.

Despite various uncertainties involved in the measurement of surface area, we still agree with HILLEL (1971) who claims that the measurement of soil specific surface area may eventually prove a more significant and pertinent index for characterizing a soil than the particle-size distribution.

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SELOSTUS

Maan ominaispinta-alan määrittäminen vesihöyryn adsorption avulla

II Maan ominaispinta-alan riippuvuus saveksen ja orgaanisen hiilen pitoisuudesta

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Maan ominaispinta-alan määrittämistä 20 % suhteellisessa kosteudessa tapahtuvan vesihöyryn adsorption

avulla tutkittiin 60 kivennäismaanäytteellä. Ominaispinta-alan vaihteluväli oli 12.1 ± 3.6 — 225.1 ± 18.4 m²/g. Savek-

sen (1—72 %) ja orgaanisen hiilen pitoisuus (0.7—14.6 %) selittivät yhdessä 84 % maan ominaispinta-alan vaihtelusta. Maan ominaispinta-ala riippui saveksen ja orgaanisen hiilen pitoisuudesta seuraavan regressioyhtälön mukaisesti: ominaispinta-ala (m^2/g) = $2.69 + 1.23\text{saves-\%} + 8.69\text{org.C-\%}$.