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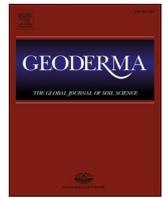
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Contribution of organic carbon to the total specific surface area of soils with varying clay mineralogy

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ABSTRACT

Soil specific surface area (SA) reflects the quantity and quality of the soil mineral and organic fractions. For soil samples that have similar clay mineral types, clay content and or organic carbon (OC) contents are good predictors of SA. However, the magnitude of the OC contribution to SA for different soil types is unclear, particularly since SA varies depending on which method or probe molecule is used to measure it. Consequently, we set out to (i) quantify the contribution of soil OC to total SA for soils with varying clay mineralogy, and (ii) assess the effect of probe molecule (EGME or H₂O) and water sorption direction on the contribution of OC to the total SA. We utilized 330 soil samples (clay = 1 to 89 %; silt = 2 to 78 %; OC = 0.03 to 34.9 %) that were grouped according to clay mineralogy and OC content. The total SA was measured using EGME adsorption (SA_E) and water adsorption and desorption (SA_{H₂O}). The contribution of OC to SA was examined using regression and partial correlation analyses that combined clay, silt, and OC as explanatory variables. Results showed that SA_E values were strongly correlated to SA_{H₂O}, except for OC-rich soils where SA_E was significantly lower than SA_{H₂O}. Apart from montmorillonite-rich samples, OC contribution to SA_E was smaller than for SA_{H₂O}. Organic carbon had a positive contribution to desorption SA_{H₂O} for all sample groups, except for montmorillonite-rich samples; OC contribution was 7.5, 10.7, and 13.9 m²/g per %C for illite-rich, kaolinite-rich and OC-rich samples, respectively. There was no significant effect of water sorption direction on the OC contribution to SA_{H₂O}. Partial correlation analyses that accounted for clay and silt contents confirmed a negative contribution of OC to SA_E or SA_{H₂O} for soil samples dominated by montmorillonite clay minerals. We can conclude that for the soil types investigated here (except montmorillonitic soils), OC has a positive contribution to total SA, and the magnitude of the contribution depends on the clay type.

1. Introduction

Specific surface area is an important soil property. It controls numerous physical and mechanical (e.g., soil swelling, water retention and infiltration), chemical (e.g., plant nutrient and contaminant adsorption and release) and biological (e.g., microbial decomposition) soil processes (Dolinar et al., 2007). For arable and natural soils with appreciable amounts of organic carbon, the total specific surface area (SA) is controlled by a combination of the particle size distribution (primarily clay and fine silt contents), clay mineralogy, organic matter

(OM) content, and iron and aluminium oxide contents (Kaiser and Guggenberger, 2003; Petersen et al., 1996). In general, the surface area available for sorption increases with increasing clay and fine silt contents (Karup et al., 2017; Petersen et al., 1996; Resurreccion et al., 2011). Clay mineralogy is another important determinant of SA. Soils dominated by kaolinite or illite clays have significantly lower SA than soils dominated by montmorillonite clay (Sivapullaiah et al., 2008). Further, the presence of metal (Fe, Al) oxides increases SA, and studies have shown that removal of these oxides from soil decreases the SA by as much as 50 % (Jiang et al., 2014; Kaiser and Guggenberger, 2003).

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However, the contribution of OM to the SA of soils is not entirely clear.

The relationship between SA and organic carbon (OC) seems to depend on the method used to estimate SA. Methods to estimate SA include (i) measurement of particle size and shape (Borkovec et al., 1993), (ii) adsorption of non-polar molecules like N₂ for external SA or CO₂ (de Jonge and Mittelmeijer-Hazeleger, 1996; Pennell, 2002), and (iii) sorption of polar molecules such as water (Farrar, 1963; Lu and Zhang, 2020), ethylene glycol (EG), methylene blue, or ethylene glycol monoethyl ether (EGME) (Cerato and Lutenecker, 2002; Pennell, 2002).

The contribution of OC to SA has been investigated by either (i) correlation and or regression analyses involving OC and SA for a set of soils (Bartoli et al., 2007; Kirschbaum et al., 2020; Petersen et al., 1996), (ii) comparison of SA measured before and after removal of OM (e.g., Bower and Gschwend, 1952; Kaiser and Guggenberger, 2003; Pennell et al., 1995), or (iii) manipulation experiments involving OM and OM-clay mineral complexes (Bu et al., 2019a).

When SA is measured via N₂ adsorption coupled with the BET equation (SA_{N2}), the contribution of OC to SA varies depending on the soil type. In the majority of cases, for soil samples with varying clay types (illite, kaolinite, montmorillonite, etc.), the removal of OM either by H₂O₂ or NaOCl treatment led to increased SA (e.g., Burford et al., 1964; Kaiser and Guggenberger, 2003; Sequi and Aringhieri, 1977; Theng et al., 1999). Other studies where the effect of OC on SA_{N2} was examined by correlation and or regression analyses showed negative relationships between OC and SA_{N2} for Andosols (Bartoli et al., 2007) and Oxisols, Alfisols and Chernozems (de Jong, 1999). The increased SA_{N2} after OM removal has been attributed to (i) removal of organic coatings from soil particles that increase the surface area available for N₂ sorption (Burford et al., 1964), or the increased SA of the clay fraction as it is broken up after removal of the OM that acts as a binding agent (Feller et al., 1992). Furthermore, it has been found that the reduction of SA_{N2} due to OC depends on the OM loading and the type of clay mineral present. The SA_{N2} of oxyhydroxides or phyllosilicates decrease with increasing OM loadings. (Kaiser and Guggenberger, 2003).

For SA determined by adsorption of EG, one of the earliest studies (Bower and Gschwend, 1952) reported that the removal of OM by H₂O₂ treatment decreased SA of four samples (SA range, 17 to 57 m²/g; OM range 0.4 to 5.2 %). Based on that study, the authors calculated the SA of OM to range from 558 to 803 m²/g. Later, Pennell et al. (1995) used four soils (SA range, 37 to 163 m²/g; OC range 0.08 to 44.6 %) in a similar experiment and confirmed the decrease in SA of the soil samples after OM removal. However, their estimates of the SA of OM were lower (65 to 481 m²/g). The authors noted that the estimated SA of OM was contingent on the quantity and quality of the initial OM and the effect of H₂O₂ on other soil properties, among others.

A regression study de Jong (1999) involving Oxisols, Alfisols, and Chernozems found that there was no effect of OC on the variations in SA determined by EGME (SA_E), whereas OC was positively correlated to SA determined by H₂O (SA_{H2O}). Similarly, Kirschbaum et al. (2020) showed that, for 292 soil samples with poorly interstratified hydroxyl interlayered vermiculate and mica-vermiculite clays from New Zealand, there was a strong positive correlation between OC and the SA determined from water adsorption at 42 % relative humidity. Based on these 292 samples, they estimated the contribution of OC to SA_{H2O} to be approximately 0.43 m² mg C⁻¹. Furthermore, manipulation experiments involving different types of OM and OM-mineral complexes reveal a strong contribution of OM to SA_E for mudrocks, but this also depends on the type of OM present (Zhu et al., 2020). Bu et al. (2019b) used two types of model organic molecules (tetramethylammonium bromide and dodecyl trimethyl ammonium bromide) and montmorillonite clay mineral to explore the effect of OM on SA_E. They concluded that both organic molecules lowered SA_E by occupying sorption sites in the interlayer and external surface of EGME.

Most of the studies examining the contribution of OC to SA were limited to SA_{N2}, and in the few cases where SA_E or SA_{H2O} were measured, only a few soils were considered. Since the main sorbate in

soils is H₂O, it is crucial to investigate how OC affects the SA derived from the sorption of H₂O. In the last few years, several studies have utilized H₂O as the sorbent to determine SA (e.g., Akin and Likos, 2014; Arthur et al., 2013; Chen et al., 2021; Lu and Zhang, 2020) and have shown that SA determined from water sorption is comparable to SA_E. In a few cases where samples had large SA values or contained montmorillonite clay, SA_E and SA_{H2O} were different (Akin and Likos, 2014; Arthur et al., 2018). Additionally, since the majority of soil types exhibit significant sorption hysteresis (Arthur et al., 2020), it is necessary to consider the sorption direction when estimating SA from water sorption. To identify the effect of OC on SA, it is also essential to use a method to determine SA that is unaffected by high contents of OC in the sample. Derkowski and Bristow (2012) explored the limitations of the EGME method for a suite of OM-rich shales and mudstones and recommended that the EGME method should not be used for samples that have OM >3 %, and for samples with montmorillonite clay, the OM threshold was even lower. Similarly, Zhu et al. (2020) suggested an OC threshold of 1.5 %, above which the EGME method is not recommended for mudrock without OM removal. It is important to investigate these thresholds for soil samples that are rich in OM.

Based on the knowledge gaps identified above, we utilized a large dataset comprising soil samples with varying clay mineralogy, and a wide range of OC content to achieve the following objectives:

- (1) Quantify the contribution of soil organic carbon to the total specific surface area for soils with varying clay mineralogy.
- (2) Assess the effect of probe molecule (EGME or H₂O) and water sorption direction on the contribution of organic carbon to the total specific surface area.

2. Materials and methods

2.1. Investigated samples

In this study, we considered 330 soil samples from 29 countries distributed across five continents (Africa 56, Asia 42, Europe 140, North and Central America 76, and South America 16). The samples were selected to cover wide variations in clay mineralogy, soil textures, and OC contents. The samples were grouped into four categories based on the dominant clay mineralogy and OC content. The sample categories comprised (a) 36 kaolinite clay-rich samples, KAO, (b) 155 samples dominated by illite clay or mixed-clays, IL/MC, (c) 110 samples dominated by montmorillonite clays, MMT, and (d) 29 samples with large variation in OC content (coefficient of variation = 93 %) and dominated by illite clay minerals, ORG. The ORG samples were from the topsoil of two field sites in Denmark (Estrup and Obakker). The two sites exhibit a natural gradient in OC content: 2.73 to 8.42 %C in Estrup (average clay content = 9 %) and 1.57 to 34.8 %C in Obakker (average clay content = 7 %). To contrast with the ORG samples, the KAO, IL/MC, and MMT samples were denoted “mineral” samples. Further details about the clay, silt, sand, and OC contents of the sample groups are presented in Table 1.

2.2. Laboratory measurements

For the measurements described below, all samples were initially air-dried, crushed, and sieved to less than 2 mm particle size.

2.2.1. Particle size distribution, organic carbon, and clay mineralogy

The distribution of particle sizes was determined by a combination of wet sieving and the pipette or hydrometer methods after removal of OC and carbonates, where necessary. The standard methodology used follows that described by Gee and Or (2002). For total carbon determination, the 2-mm sieved samples were ball-milled before oxidization of the carbon at 950 °C using an elemental analyzer combined with a thermal conductivity detector (Thermo Fisher Scientific, Waltham, MA, USA). For samples containing calcium carbonate, OC was calculated as the

Table 1
Descriptive statistics of soil properties for the different soil sample categories.

Property	Min	Mean	Median	Max	SD	CV%	Skewness
<i>All mineral samples (n = 301)^a</i>							
Clay	1	36	31	89	20	56	0.57
Silt	2	30	27	78	16	54	0.58
Sand	0	31	26	96	23	75	0.54
OC	0.03	1.42	1.24	6.80	1.13	80	1.18
SA _E	6	137	102	445	109	80	0.87
SA _{T1}	6	125	99	373	89	71	0.87
SA _{T2}	7	139	111	402	96	69	0.81
<i>Kaolinite-clay rich samples (n = 36)</i>							
Clay	8	37	35	73	18	50	0.62
Silt	8	21	15	55	13	62	1.24
Sand	2	41	41	73	20	49	-0.14
OC	0.03	0.84	0.35	4.83	1.08	128	2.00
SA _E	16	49	45	100	21	42	0.69
SA _{T1}	12	57	48	151	33	57	1.19
SA _{T2}	15	67	59	178	37	55	1.19
<i>Illite-clay and mixed-clay samples (n = 155)</i>							
Clay	1	26	23	71	15	58	0.96
Silt	3	30	27	78	16	53	0.60
Sand	1	41	40	96	22	55	0.22
OC	0.06	1.58	1.46	4.02	0.98	62	0.46
SA _E	6	78	62	314	59	75	1.76
SA _{T1}	6	78	67	250	50	64	1.22
SA _{T2}	7	89	77	273	58	64	1.22
<i>Montmorillonite-clay rich samples (n = 110)</i>							
Clay	12	50	47	89	18	37	0.13
Silt	2	33	31	74	17	50	0.40
Sand	0	14	11	62	14	97	1.33
OC	0.06	1.39	1.13	6.80	1.27	91	1.72
SA _E	40	249	250	445	88	35	0.03
SA _{T1}	41	213	202	373	73	34	0.42
SA _{T2}	46	234	223	402	78	33	0.36
<i>Organic carbon-rich samples (n = 29)</i>							
Clay	2	8	9	13	2	31	-0.42
Silt	3	17	17	29	9	53	-0.16
Sand	5	54	56	92	20	38	-0.88
OC	1.57	10.86	6.16	34.88	10.11	93	1.43
SA _E	10	47	40	97	21	44	0.76
SA _{T1}	13	116	59	426	119	102	1.70
SA _{T2}	16	136	69	506	139	102	1.70

^a All mineral samples exclude the 29 samples with high organic carbon content. SD = standard deviation; CV = coefficient of variation; OC, soil organic carbon; SA_E, specific surface area (SA) determined by EGME; SA_{T1}, SA from water vapor adsorption; SA_{T2}, SA from water vapor desorption. Clay, silt, sand, and OC are in g 100 g⁻¹, SA_E, SA_{T1}, and SA_{T2} are in m²/g.

difference between total carbon and inorganic carbon computed from the percentage of calcium carbonate. The clay mineralogy of the samples was determined by X-ray Diffraction (XRD) analysis. The filter peel method (Drever, 1973) was applied to prepare oriented clay glass slides for X-ray Diffraction (XRD) analysis. To quantify the clay mineralogy based on the measured XRD diffraction patterns, the RockJock software package (Eberl, 2003), which performs a whole-pattern modified Rietveld-type refinement, was applied.

2.2.2. Soil specific surface area (SA)

2.2.2.1. EGME specific surface area (SA_E). The SA_E was determined from EGME retention at monolayer coverage as described in Pennell (2002) without pre-treatments (removal of OC or ion saturation). Briefly, the 2-mm sieved sample was mixed with EGME, and the mixture was sealed in an equilibration chamber under a high vacuum. After an equilibration period of between 12 and 72 h, depending on sample SA, we repeatedly weighed the samples in sealed weighing bottles until the

weight became constant. The average SA was calculated from the mass of EGME retained by three replicate samples for each soil.

2.2.2.2. Water sorption specific surface area (SA_{T1} and SA_{T2}). To determine the SA from water vapor sorption (SA_{H2O}), the samples were air-dried at stable relative humidity (RH) of 0.45 before the measurement of sorption isotherms. Water vapor sorption and desorption isotherms covering the range 0.03 ≤ RH ≤ 0.93 with a resolution of 0.02 RH were measured for all samples at 25 °C with a vapor sorption analyzer (METER Group Inc., Pullman, WA, USA). After completion of the measurement, the samples were oven-dried for 48 h at 105 °C to determine the reference water content. Further details of the methodology are provided in Arthur et al. (2014).

The SA was estimated from the measured water sorption isotherms using the Tuller and Or (2005) model (TO model). The TO model relates the equilibrium soil water content, w (kg kg⁻¹) to matric potential ψ (m H₂O) and SA (m² kg⁻¹) as:

$$w = \sqrt[3]{\frac{A_{svl}}{6 \times \pi \times \rho_w \times g \times \psi}} SA \quad (1)$$

where A_{svl} (J) is the Hamaker constant for solid-vapor interactions through the intervening liquid, set to -6×10^{-20} J as reported by Tuller and Or (2005) and Macek et al. (2013), ρ_w is the density of water (1000 kg m⁻³) and g is the acceleration due to gravity (9.8 m s⁻²).

The model was parameterized with the sorption data (adsorption and desorption separately) by employing the Levenberg-Marquardt nonlinear least-squares algorithm implemented in the "minpack.lm" package (Elzhov et al., 2016) in R v4.0.2 (R Core Team, 2020).

The SA_{H2O} obtained from the adsorption and desorption data are denoted SA_{T1} and SA_{T2}, respectively.

2.2.3. Removal of OC

To evaluate the specific impact of OC on SA after the removal of OC, we selected 21 soil samples from Arizona. These samples were taken from different locations in Arizona and have soil textures ranging from coarse sand to clay, and the clay minerals present included kaolinite, illite/mica, and montmorillonite with traces of vermiculite. Firstly, we determined the three measures of SA (SA_E, SA_{T1}, SA_{T2}) for the non-treated samples (SA_{non}) as described earlier. Thereafter the samples were treated to remove OM and carbonates. To remove carbonates, 200 mL 1.0 M Na acetate (pH 5.0) was mixed with 20 g of soil. The solution was centrifuged for 10 min at 1500 rpm, and the supernatant was decanted and followed by washing the soil twice with deionized water. After carbonate removal, the remaining sample was air-dried and placed into a 300 mL beaker, and 200 mL of pH 9.5 NaOCl (Clorox bleach) were added and thoroughly mixed. The soil/bleach mixture was left to react for 1 h and then heated on a hot plate at 50 °C under frequent stirring until the reaction subsided. An automatic pipette was used to carefully remove the particle-free liquid off the top of the sample. After adding new pH 9.5 NaOCl and repeating the above procedure two more times the soil suspension was transferred to 100-mL centrifuge tubes. The samples were then centrifuged for 10 min at 1200 rpm and the supernatant was discarded.

Finally, SA_E, SA_{T1}, and SA_{T2} were determined for the treated samples (SA_{treat}). The percentage change in SA following OC and carbonate removal was determined as:

$$\% \text{ Change in SA} = \frac{SA_{\text{treat}} - SA_{\text{non}}}{SA_{\text{non}}} \times 100 \quad (2)$$

2.2.4. Data analyses and statistics

2.2.4.1. Correlation and multiple linear regression. To evaluate the relationships between the soil properties (clay, silt, sand, and OC) and the measures of SA (SA_E, SA_{T1}, SA_{T2}), we conducted correlation analyses for

all the samples together and separately within the four groups [KAO, IL/MC, MMT, ORG].

To evaluate quantitatively the contribution of OC to the three SA measures, we conducted multiple linear regression analyses (MLR) using the “lm” function in R for (i) ALL samples that comprised the KAO, IL/MC, and MMT samples, and (ii) the four sample categories separately. The MLR included clay content, OC, and silt content as explanatory variables, and SA (SA_E , SA_{T1} , or SA_{T2}) as the response variable. Silt content was included as it significantly contributes to surface areas in soils, particularly in soil samples with high fine silt contents (Karup et al., 2017). Despite the strong correlation between sand content and measures of SA (Table 2), sand content was not included in the MLR because sand content was collinear with clay content ($r = -0.70^{***}$ to -0.40^{***}).

The MLRs were of the general form:

$$SA = \beta_0 + \beta_1 \times \text{clay} + \beta_2 \times \text{OC} + \beta_3 \times \text{silt} \quad (3)$$

where β_0 is the intercept, and β_1 , β_2 , and β_3 represent the contribution of clay, OC, and silt, respectively. The first round of analyses revealed that the intercept term was not significant in most of the regressions, so the intercept was subsequently set to zero (regression through the origin, RTO), and the model reduced to Eq. (4):

$$SA = \beta_1 \times \text{clay} + \beta_2 \times \text{OC} + \beta_3 \times \text{silt} \quad (4)$$

The magnitude of the coefficients of the full model, also known as ordinary least squares regression, OLS (Eq. (3)) and the reduced model, RTO (Eq. (4)) were compared to evaluate the effect of removing the intercept.

The quantitative contributions of clay, silt and OC to SA were expressed as $\text{m}^2 \text{g}^{-1}$ per a 1 % increase in clay, silt, or OC.

2.2.4.2. Partial correlation analyses. To further clarify the impact of OC

Table 2

Pearson correlations among soil texture, organic carbon, and the three measures of specific surface area for the different sample categories.

Soil property	Sample category	SA_E	SA_{T1}	SA_{T2}
Clay <0.002 mm	ALL	0.80 ^{***}	0.85 ^{***}	0.85 ^{***}
	KAO	0.76 ^{***}	0.76 ^{***}	0.74 ^{**}
	IL/MC	0.85 ^{***}	0.92 ^{***}	0.92 ^{***}
	MMT	0.77 ^{***}	0.84 ^{***}	0.84 ^{***}
	ORG	0.39 [*]	0.17	0.18
Silt 0.002–0.05 mm	ALL	-0.04	-0.06	-0.06
	KAO	0.07	0.13	0.16
	IL/MC	-0.07	-0.02	-0.03
	MMT	-0.52 ^{***}	-0.59 ^{***}	-0.59 ^{***}
	ORG	-0.02	-0.29	-0.30
Sand 0.05–2.00 mm	ALL	-0.65 ^{***}	-0.68 ^{***}	-0.69 ^{***}
	KAO	-0.74 ^{***}	-0.80 ^{***}	-0.80 ^{***}
	IL/MC	-0.54 ^{***}	-0.62 ^{***}	-0.62 ^{***}
	MMT	-0.31 ^{***}	-0.33 ^{***}	-0.35 ^{***}
	ORG	-0.77 ^{***}	-0.88 ^{***}	-0.87 ^{***}
Organic carbon	ALL	-0.07	-0.02	-0.01
	KAO	-0.02	0.16	0.18
	IL/MC	0.33 ^{***}	0.37 ^{***}	0.39 ^{***}
	MMT	-0.44 ^{***}	-0.37 ^{***}	-0.35 ^{***}
	ORG	0.73 ^{***}	0.99 ^{***}	0.99 ^{***}

The notations^{****}, ^{***}, and ^{**} indicate the statistical significance of the correlation at p-values less than 0.001, 0.01, and 0.05, respectively. OC, soil organic carbon; SA_E , specific surface area (SA) determined by EGME; SA_{T1} , SA from water vapor adsorption; SA_{T2} , SA from water vapor desorption. Clay, silt, sand, and OC are in $\text{g} \text{100 g}^{-1}$, SA_E , SA_{T1} , and SA_{T2} are in m^2/g . KAO, IL/MC, and MMT denote samples dominated by kaolinite, illite or mixed clays, and montmorillonite clay minerals, respectively. ORG, samples rich in organic carbon.

on the measures of the SA, the degree of association between OC and SA was determined using partial correlation coefficients (PC). The PC values were used to quantify the strength and direction of the effect of OC on the SA after accounting for the effect of clay and silt contents. The PC values were determined separately for all sample categories using the “pcor.test” function implemented in the “ppcor” package in R (Kim, 2015).

2.2.4.3. Model efficiency. The cross-validation of the models with and without the intercept was evaluated visually by scatter plots and quantitatively by the Nash-Sutcliffe model efficiency, NSE (Nash and Sutcliffe, 1970).

$$NSE = 1 - \frac{\sum_{i=1}^n (SA_o - SA_m)^2}{\sum_{i=1}^n (SA_m - \bar{SA})^2} \quad (7)$$

where SA_o is the observed SA values, SA_m is their corresponding modeled values and \bar{SA} is the mean of the observed values. The values of NSE can range from $-\infty$ to 1, with 1 indicating perfect agreement and numbers less than 0 indicating a model with lower predictive power than the mean of the observations.

3. Results and discussion

3.1. Comparing surface areas from EGME and water sorption

The investigated samples exhibited a very wide SA range. The SA for the mineral samples (KAO, IL/MC, and MMT) ranged from 6 to 445 m^2/g for SA_E , 6 to 373 m^2/g for SA_{T1} , and 7 to 402 m^2/g for SA_{T2} . For the ORG samples, SA_E ranged from 10 to 97 m^2/g , 13 to 426 for SA_{T1} and 16 to 506 m^2/g for SA_{T2} (Table 1). Water sorption hysteresis has been documented in several studies (Arthur et al., 2020; Lu and Khorshidi, 2015; Prunty and Bell, 2007), and this is evident when SA_{T1} and SA_{T2} are compared. For the mineral samples, SA_{T1} was approximately 90 % of SA_{T2} while for the ORG samples SA_{T1} was 85 % of SA_{T2} . The larger SA derived from desorption compared to adsorption is driven by mechanisms such as particle surface hydration and interlayer cation hydration (Lu and Khorshidi, 2015). These mechanisms are affected by the clay content and mineralogy, OC contents, and the interaction between the clay particles and OC (Arthur et al., 2020). Hysteresis is often larger in soils that have high clay and OC contents and appreciable amounts of 2:1 expandable clay minerals than in soils that have low clay and OC contents and 1:1 non-expandable clay minerals.

3.1.1. Mineral samples

There was a strong correlation between the SA_E and SA from water sorption (SA_{T1} and SA_{T2}) for the mineral samples. The relationship between the two SA measures, however, differed with clay mineralogy or organic matter content (Fig. 1). The SA_{T1} was about 1.2× larger than SA_E for the KAO samples. On the other hand, SA_E was comparable to SA_{T1} for the IL/MC samples. Similarly, Akin and Likos (2014) and Arthur et al. (2013) found that SA_{T1} and SA from water sorption derived from the BET equation were comparable to SA_E for samples with SA < 100 m^2/g . Further, Akin and Likos (2014) reported that SA from water sorption was about half the SA_E for clay mixtures with significant amounts of expandable clay minerals and subsequently large SA values (200 to 650 m^2/g). Although the investigated MMT samples did not exhibit such large SA values, SA_{T1} was ~85 % of SA_E . Reasons for this discrepancy are discussed in detail in Akin and Likos (2014) and include differences in surface tension and polar molar volume between EGME and H_2O , and the potentially higher surface retention by capillary condensation by EGME, and interlayer swelling of the samples during adsorption (Mooney et al., 1952).

3.1.2. Organic carbon-rich samples

In Figs. 1, 2, and S1, the SA data for samples from the two OC-

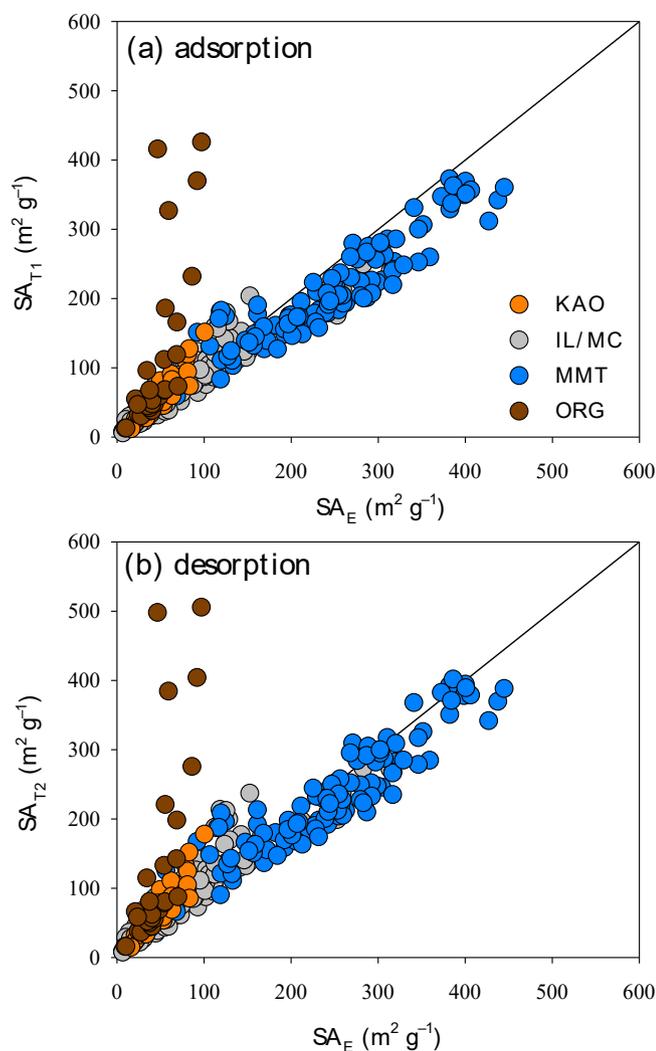


Fig. 1. Scatterplot depicting the relationship between the soil specific surface area determined by ethylene glycol monoethyl ether [SA_E] and by (a) water vapor adsorption [SA_{T1}] and, (b) water vapor desorption [SA_{T2}]. KAO, IL/MC, and MMT denote samples dominated by kaolinite, illite or mixed clays, and montmorillonite clay minerals, respectively. ORG, samples rich in organic carbon.

gradient fields are presented. For all samples, SA_E was smaller than SA_{T1} or SA_{T2} , and OC was more strongly correlated to SA_{T1} and SA_{T2} ($r^2 = 0.98$) than to SA_E ($r^2 = 0.52$). To examine if OC significantly affected the agreement or otherwise of SA_E to SA_{T2} , the ratio (%) of the two SAs and OC is presented in Fig. 2. Samples with similar SA_E and SA_{T2} will have a ratio % close to 100, and samples with large differences between SA_E and SA_{T2} will have values significantly lower than 100. There was no clear relationship between the ratio of SA_E to SA_{T2} for the Estrup field site that had a narrower OC range (2.73 to 8.42 %), but the SA_E averaged 72 % of SA_{T2} (Fig. 2a).

At the Obakker field site, the SA_E to SA_{T2} ratio ranged from 9 to 65 % (average of 32 %) and was negatively correlated to the OC content (Fig. 2a). For the two sites together, SA_E was 53 % of SA_{T2} . This confirms that the EGME method it is not possible to accurately estimate the SA of samples rich in organic matter. On the one hand, EGME is reported to react with soil OM through partitioning in macromolecular compounds, resulting in artificially high SA_E (Chiou et al., 1990; Derkowski and Bristow, 2012). Conversely, Bu et al. (2019a) and Bu et al. (2019b) showed for some OM types, that EGME adsorption capacities and by extension SA_E , decreased after OM intercalation into the interlayer space of clay minerals. Moreover, when organic-rich soil samples have a high

amount of hydrophobic functional groups and are therefore water repellent, it is possible that SA_{H_2O} can be lower than expected, as the water sorbed will be lower.

Furthermore, the characteristics of the available sorption surfaces depend on whether it originates from the mineral fraction (clay and silt) or OC. For example, the influence of OC on SA_E is expected to be different for two samples that have the same OC content of 3 %, but significantly different clay contents (e.g., 5 % clay for sample 1 versus 50 % clay for sample 2). The clay/OC ratio (n), also known as the Dexter ratio (Dexter et al., 2008), has been applied to explain several soil physical processes, ranging from soil aggregation and structural stability (Jensen et al., 2019) to dynamics of soil SA (Resurreccion et al., 2011). For soils that have $n < 10$, all the clay particles are complexed by OC, and there is excess or non-complexed OC (Dexter et al., 2008), whereas for soils with $n > 10$, all there is no excess or non-complexed OC, but rather non-complexed clay with surfaces not covered by OC. Thus, for sample 1 with $n = 1.7$ (>10) and non-complexed OC, the sorption of H_2O or EGME will occur directly on OC rather than on clay. On the other hand, for sample 2 with a $n = 16.7$, the high clay content relative to OC means that H_2O or EGME will be sorbed on the surfaces of non-complexed clay rather than on OC. Based on this reasoning, we compared how the clay/OC ratio explained the variations in SA_E/SA_{T2} for the two field sites together (Fig. 2b). In Fig. 2b, n explained the trend in the SA_E to SA_{T2} ratio across the two field sites better than OC alone (Fig. 2a). Furthermore, the SA_E/SA_{T2} value increased as n increased. The clay mineralogy of the two sites in Fig. 2 is dominated by illite, and the relationships presented may not apply to soils with different clay mineralogy or OC type because OC-clay mineral surface and interlayer interactions are strongly affected by clay mineral type (Kleber et al., 2021).

3.2. Correlations among soil properties and soil specific surface area

In Table 2, the Pearson correlations among the three measures of SA and other soil properties (clay, silt, sand, and OC) are presented. For mineral soils, clay content was strongly correlated to all SA measures (Fig. S2). The strength of the correlation was in the order IL/MC > MMT > KAO. The water sorption-based SAs were more strongly correlated to clay content than SA_E . Soil clay particles, due to their small size, are the main contributor to soil SA in mineral soils that have average OC (0.2 to 2.5 %) contents (Petersen et al., 1996). The clay content of the ORG samples was poorly correlated to SA (Table 2). Due to the high SA_{H_2O} of OM, soils rich in OC tend to have a complex clay-SA relationship. The ORG samples had average clay content and OC of 8 % and 10.9 %, respectively, and this is likely why there was no clear relationship between SA and clay content.

Silt content did not show any significant correlation with SA for all groups except for MMT, although fine silt content is reported to contribute significantly to water sorption and consequently to SA_{H_2O} (Karup et al., 2017). Considering that the average silt content for MMT (33 %) is not markedly different from that of the IL/MC samples (30 %) it is unclear why silt was influential on the SA of MMT samples but not on the IL/MC samples. Sand contents exhibited a negative correlation with SA for all the sample groups. This is because of the sand's collinearity with clay content rather than a direct reducing effect on soil SA.

There was no correlation between OC and SA for all the mineral samples together or the KAO samples separately. The IL/MC and MMT samples showed significant negative correlations between SA and OC due to the higher average OC for the two groups (1.58 and 1.39 %) compared to the KAO samples (average OC of 0.84 %). The ORG samples exhibited a very strong correlation between SA and OC, particularly for SA_{T1} and SA_{T2} (Fig. S3). The stronger correlation of OC with SA_{H_2O} than with SA_E supports the suggestion that the EGME method is not capable of quantifying all available surfaces in soils rich in organic matter (Zhu et al., 2020).

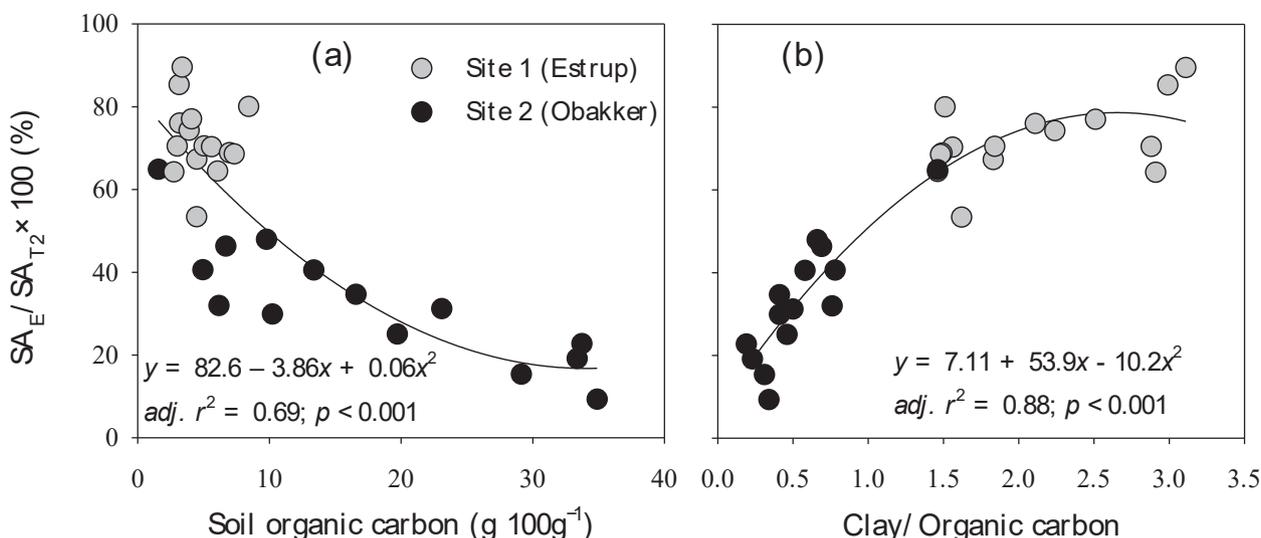


Fig. 2. Relationship between soil organic carbon and the ratio of the specific surface area determined by EGME (SA_E) to water vapor desorption (SA_{T2}) for the ORG samples differentiated by sampling site.

3.3. Effect of organic matter removal on soil specific surface area

The 21 Arizona samples used to determine how the removal of OM affects SA had OC contents from 0.10 to 4.02 % (average of = 0.78 %), and average clay and silt contents of 19 % and 26 %, respectively. The SA_E , SA_{T1} , and SA_{T2} for the non-treated samples ranged from 7 to 158 m^2/g , 8 to 143 m^2/g , and 8 to 169 m^2/g , respectively. The change in SA after removal of OM depended on which measure of SA was considered (Fig. 3). There was a 2 to 66 % decrease in SA_E for 17 of the samples after OM removal. This supports earlier studies where OM removal led to a decrease in various measures of SA. Bower and Gschwend (1952) and Pennell et al. (1995) both used four samples and, respectively, found a 1 to 26 % and 9 to 22 % reduction in SA_E after OM removal from four soil samples. Similarly, Sanchez and Falasca (1997) revealed that removal of OM from nine soil samples dominated by illite and kaolinite led to decreased SA determined by ethyl glycol (5 to 57 %) in seven of the samples.

For SA_{T1} and SA_{T2} , only half of the samples showed a clear decrease after OM removal. For seven of the samples, OM removal led to significant increases (15 to 86 %) in SA_{T1} and SA_{T2} . Factors that may be

responsible for these observations include the clay mineralogy, clay content, and OC content of the samples. The dominant clay minerals were illite, kaolinite and smectite with traces of vermiculite. The sample (#2) that exhibited the largest decrease in SA_E had 76 % of the clay fraction dominated by kaolinite, while the sample with the largest increase in SA_{T1} and SA_{T2} (#8) was rich in montmorillonite (62 %). Thus, in montmorillonite-rich samples, increased SA after OM removal could be due to removal of organic coatings from the clay particles (Burford et al., 1964), modification of the internal SA or an increase in the SA of the clay fraction itself as they become more finely divided after OM removal (Feller et al., 1992).

3.4. Contribution of organic carbon to soil specific surface area

The quantitative contribution of soil constituents (clay, silt, and OC) on the different measures of SA was assessed by examining the MLR coefficients with and without an intercept (Fig. 4 and Table S1). The intercept in the MLR was not significant in the models for IL/MC, MMT and ORG, but significant for the ALL samples group and the KAO samples (Table S1). Generally, the inclusion of an intercept in MLRs is

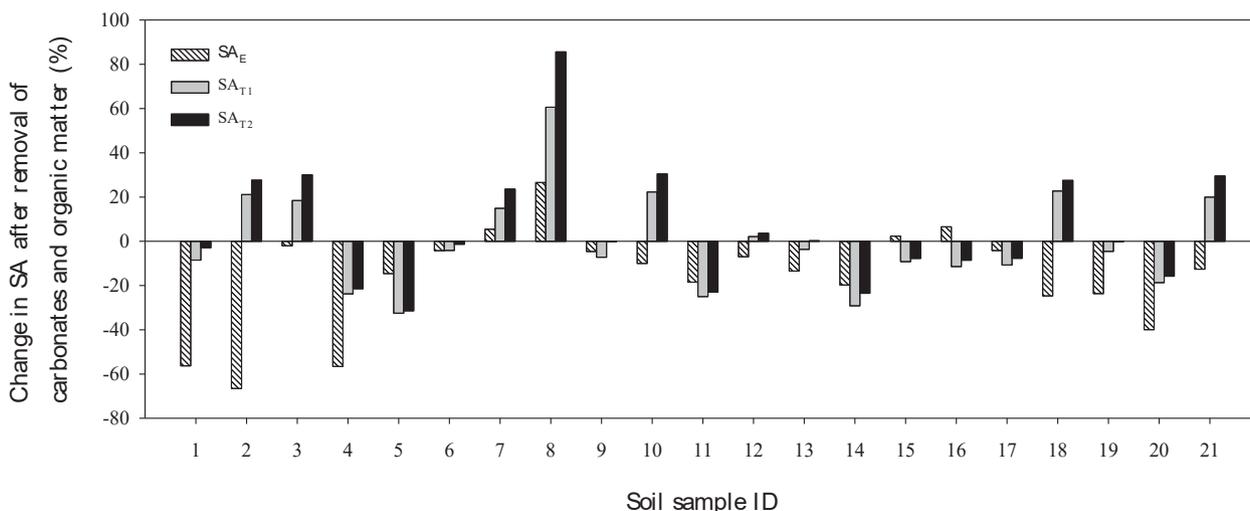


Fig. 3. Changes in soil specific surface area determined by ethylene glycol monoethyl ether (SA_E) and water vapor adsorption (SA_{T1}), and water vapor desorption (SA_{T2}) after removal of carbonates and soil organic matter for 21 Arizona samples.

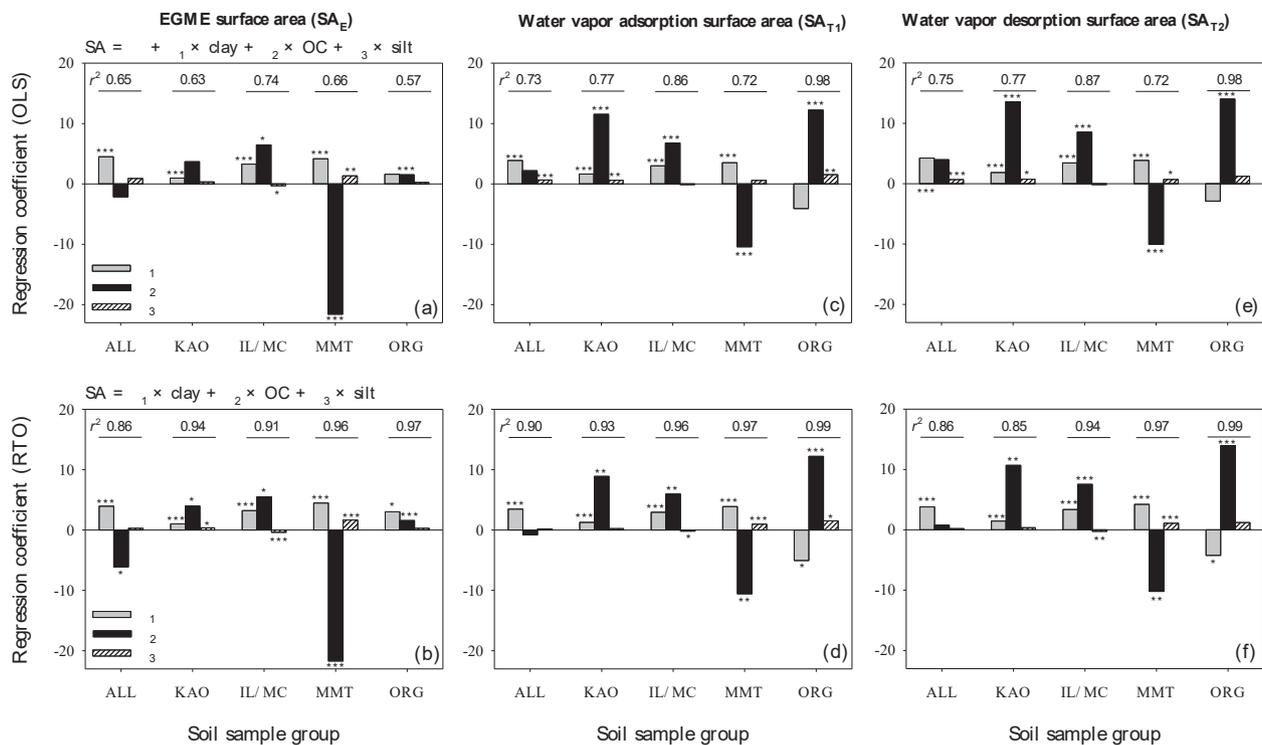


Fig. 4. Overview of multiple linear regression coefficients [by ordinary least squares regression, OLS, and regression through the origin, RTO] of clay, organic carbon (OC) and silt for soil specific surface area (SA) determined by (a, b) EGME, (c, d) water vapor adsorption, and (e, f) water vapor desorption modelled by the Tuller-Or (2005) model, for different sample categories. ALL, all investigated mineral samples; KAO, IL/MC, and MMT denote samples dominated by kaolinite clay, illite or mixed-clay, and montmorillonite clay minerals, respectively. ORG, samples rich in organic carbon. The numbers on the top of the bars indicate the adjusted r-squared values of the regression. The notations “****”, “***”, “**”, and “*” indicate the statistical significance of clay, silt, or OC at p-values less than 0.001, 0.01, and 0.05, respectively. For the values of β_0 , please see supplementary Table S1.

necessary to be able to account for unknown factors that may influence the independent variable (SA in this case). It can be assumed that for a soil sample with zero clay, silt and OC contents, the SA will be negligible or close to zero. If this is so, then the coefficients and standard errors of OLS and RTO should be similar. A visual examination of the coefficients revealed this to be true in most cases (Fig. S4). Discrepancies were observed in the clay coefficients for the ORG samples and the silt coefficients for the ALL, KAO and MMT samples. The coefficients for OC for the KAO, IL/MC, MMT and ORG samples were close enough to discount the intercept (Fig. S4b).

The coefficients obtained from the OLS and RTO MLR regressions were used to estimate SA_E , SA_{T1} and SA_{T2} for the sample groups and compared with the measured values (Fig. S5). Except for the KAO samples, there was no clear discrepancy between the SA values estimated from the OLS or RTO regressions. The models accurately estimated SA for the MMT, IL/MC and ORG samples, while showing some scatter for the KAO samples. In all cases, estimations of SA_E were less accurate with $0.58 \leq NSE \leq 0.75$ compared with the estimations of SA_{T1} and SA_{T2} where the NSE values ranged from 0.72 to 0.99. These observations support the earlier discussion on the removal of the intercept. Consequently, subsequent discussions will be based on the regressions without an intercept (Fig. 4b, d and f).

3.4.1. Effect of probe molecule (EGME and H_2O) on OC-SA interactions

The SA of soil is primarily contributed to by the clay and fine silt particles, and OC (Karup et al., 2017; Petersen et al., 1996; Resurreccion et al., 2011). Since the estimates of SA_E and SA_{H_2O} can be markedly different for different soil types, we estimated the contribution of these variables to the different measures of SA separately for the different sample groups.

3.4.1.1. EGME specific surface area. Clay and silt contents contributed

significantly to SA_E for all the sample groups, except in the case of ALL and ORG samples where silt was not significant. Clay contribution to SA_E ranged from $1.02 \text{ m}^2/\text{g}$ per %clay for the KAO samples to $4.47 \text{ m}^2/\text{g}$ per %C for the MMT samples. This is because kaolinite clay exhibits significantly smaller SA (36 to $50 \text{ m}^2/\text{g}$) than expandable clay minerals like montmorillonite (645 to $800 \text{ m}^2/\text{g}$) (Newman, 1983; Ugochukwu, 2017). Aside from the MMT samples, the contribution of silt to SA_E was less than $0.4 \text{ m}^2/\text{g}$ per %silt (Fig. 4b).

The contribution of OC to SA_E was negative for the MMT samples and ALL samples together, but positive for the KAO, IL/MC, and ORG samples. The positive OC contribution to SA_E for the ORG samples was relatively small ($1.58 \text{ m}^2/\text{g}$ per %C) compared to the other sample groups; 3.97 and $5.49 \text{ m}^2/\text{g}$ per %C for the KAO and IL/MC samples, respectively (Table S1). Due to the smaller SA of kaolinite clay compared to illite clay, the OC contribution to SA_E was expected to be larger for the KAO samples relative to the IL/MC. The discrepancy between the two sample groups is probably due to how EGME sorbs unto the different clay minerals and interacts with the OM present as well as the type of OM. For low-activity clay soils such as the KAO samples, OM has a much larger SA than the kaolinite clay, and coverage of the clay mineral by OC results in an increased SA_E . The same occurs for the IL/MC samples, but to a lesser degree as the illite clay mineral has a much larger SA compared to kaolinite. One advantage of the EGME method relative to gas adsorption methods to estimate SA is its ability to penetrate both the internal surface of OM (Heister, 2014) and the interlayer of clay minerals, except for illite clays where cations like Ca, Mg and K inhibit the entrance of polar molecules into the crystal structure (Varma, 2017). Furthermore, EGME reacts with OM by partitioning it into macromolecular compounds (Chiou et al., 1990), and this reaction is dependent on the type of OM, clay mineralogy or dominant exchangeable cation present (Derkowski and Bristow, 2012; Tiller and Smith, 1990). The strong negative contribution of OC to SA_E for the MMT samples (-21.6

m^2/g per %C) can be explained by the interaction between the OM functional groups, its location of the clay-OM complexes and the interaction with EGME. In a study by Bu et al. (2019a), two model OM types (lauric acid [LA] and 12-aminolauric acid [ALA]) were complexed with MMT clay either in the interlayer (ALA) or on the external surface (LA), and the effect on SA_E was investigated. They found that when non-ionic organic functional groups like LA sorb onto the external surface of clays, they clog the interlayer entrance pores and restrict the entry of EGME and subsequently decrease SA_E . For the easily protonated organic groups such as ALA that penetrate the interlayer of clay minerals, their bulky nature means they occupy a significant fraction of the interlayer space, reducing the sorption sites for EGME. Consequently, EGME sorbs onto the OM functional groups that have a lower SA than the MMT clay mineral, and subsequently reduce SA_E .

3.4.1.2. Water sorption specific surface area (SA_{T1} and SA_{T2}). The trends for the effect of the different soil constituents on $\text{SA}_{\text{H}_2\text{O}}$ were similar for both sorption directions [SA_{T1} and SA_{T2}] but with slightly larger coefficient values for SA_{T2} relative to SA_{T1} (Fig. 4c to 4f). The larger coefficient values arise from the hysteretic nature of water sorption, where $\text{SA}_{T2} > \text{SA}_{T1}$ for all investigated samples. Considering ALL samples, clay content contributed to $\text{SA}_{\text{H}_2\text{O}}$ by $3.46 \text{ m}^2/\text{g}$ per %clay, with negligible effects of silt and OC on SA (Fig. 4df). This observation is in stark contrast to the rest of the mineral-differentiated sample groups. Clay content contribution to SA_{T1} and SA_{T2} was 1.27 & 1.46, 2.96 & 3.37, and 3.89 & $4.22 \text{ m}^2/\text{g}$ per %clay for the KAO, IL/MC and MMT samples, respectively. Conversely, for the ORG samples, clay content contributed negatively to $\text{SA}_{\text{H}_2\text{O}}$ by -5.05 and $-4.23 \text{ m}^2/\text{g}$ per %clay, for the SA_{T1} and SA_{T2} , respectively. This negative contribution of clay to SA for MMT could be partly due to the interaction of clay and OM.

Soil OC had a significant positive effect on $\text{SA}_{\text{H}_2\text{O}}$ for the KAO, IL/MC, and ORG samples. Due to the relatively small surface area of kaolinite clay, the effect of OC on SA_{T1} and SA_{T2} (8.89 & $10.7 \text{ m}^2/\text{g}$ per %C) was relatively large for the KAO samples. For IL/MC, OC contributed 5.96 & $7.53 \text{ m}^2/\text{g}$ per %C to SA_{T1} and SA_{T2} , respectively. Kirschbaum et al. (2020) determined the OC contribution to apparent SA (determined from water sorption at $RH = 0.42$) using New Zealand soil samples collected from different depths that were characterized by poorly interstratified hydroxyl interlayered vermiculites and mica-vermiculite clays, with a minor contribution of kaolinite, quartz, and feldspar. They found that OC contributed approximately $0.43 \text{ m}^2/\text{mg C}^{-1}$, which translates to $4.3 \text{ m}^2/\text{g}$ per %C. According to Kirschbaum et al. (2020), this estimate of OC contribution ranges from 5.06 (Poeplau et al., 2015) to $7.1 \text{ m}^2/\text{g}$ per %C (Parfitt et al., 2001). The differences between the cited studies and the present work can be attributed to the differences in clay content, clay mineralogy (as can be seen from the different soil groups here), and the hydrophilic or hydrophobic nature of the OC present (Hermansen et al., 2019). Soil OC tended to reduce $\text{SA}_{\text{H}_2\text{O}}$ (-10.6 & $-10.2 \text{ m}^2/\text{g}$ per %C) for the MMT samples, probably due to the much larger surface area of montmorillonite clay relative to OC or a decrease of interlayer cation hydration caused by the high OC. Thus, when the clay mineral surfaces are covered by organic matter, water molecules will sorb to the organic matter coating rather than directly onto the clay mineral surface, with a resultant decrease in $\text{SA}_{\text{H}_2\text{O}}$. Also, the OM could aggregate fine clay particles and lead to a lower SA than for the unaggregated particles (Feller et al., 1992).

For the ORG samples, the contribution of OC to $\text{SA}_{\text{H}_2\text{O}}$ was larger than all the other sample groups (12.2 & $13.9 \text{ m}^2/\text{g}$ per %C) due to the high OC contents relative to clay or silt contents for this sample group (Table 1). Any potential for hydrophobicity arising from the high OC contents was likely overshadowed by the high-water sorption capacity of OC for these samples.

As described earlier, the OM in soils may be partitioned into amorphous and morphological forms that have different effects on SA depending on whether the OM is adsorbed on the interlayer of clay

minerals (ALA) or as particulate OM (LA) on the external mineral surfaces (Bu et al., 2019a; Zhu et al., 2014). The proportion of the two OM forms as well as the hydrophobic or hydrophilic nature of soil OC may determine whether OC contributes positively or negatively to $\text{SA}_{\text{H}_2\text{O}}$. The presence of hydrophobic OM on the external surfaces of soil minerals can significantly reduce the sorption of water (Hermansen et al., 2021), and by extension $\text{SA}_{\text{H}_2\text{O}}$. However, aside from the ORG samples, the effect of hydrophobicity on the $\text{SA}_{\text{H}_2\text{O}}$ was considered negligible due to the relatively large clay and silt contents and the low OC contents.

The MLR approach provides a robust way to quantify the exact contribution of OC in the presence of clay and silt. The partial correlation approach helps to quantify the strength and direction of the OC-SA relationship while excluding the confounding effects of clay and silt contents. Based on the PC values, there was no effect of OC on SA for all mineral soils together ($PC < 0.10$) regardless of the probe molecule used for SA determination (Table 3). There was no significant correlation between OC and SA_E for the KAO and IL/MC samples, but the strength of the positive correlation between OC and $\text{SA}_{\text{H}_2\text{O}}$ was about twice that between OC and SA_E for the two sample groups (KAO and IL/MC). Conversely, OC was negatively correlated to all estimates of SA for the MMT samples (PC values from -0.27 to -0.44), confirming the MLR-based observations that OC tends to decrease SA in soil that contains montmorillonite clay minerals. Soil OC was almost perfectly correlated to $\text{SA}_{\text{H}_2\text{O}}$ for the ORG samples ($PC \geq 0.98$) but less for the OC- SA_E relationship.

4. Conclusions

We utilized datasets comprising soil samples with varying clay mineralogy and a wide range in organic carbon content (OC) to quantify the contribution of OC to soil specific surface area (SA) determined either by ethylene glycol monoethyl ether (EGME) or by water sorption. The SA measured by EGME (SA_E) was strongly correlated to the SA measured by water sorption ($\text{SA}_{\text{H}_2\text{O}}$) regardless of the dominant clay mineralogy of the sample. Conversely, samples with large OC contents exhibited significantly larger $\text{SA}_{\text{H}_2\text{O}}$ than SA_E , and the magnitude of the difference between the two SA measures depended on the interaction between clay and OC contents. Based on OC removal, and regression analyses, it was concluded that the clay mineralogy and OC content of soil samples significantly affected the magnitude of OC contribution to SA. For samples dominated by kaolinite or illite clay mineral, OC contributed positively (3.97 to $10.7 \text{ m}^2/\text{g}$ per %C) to SA; the contribution was larger for $\text{SA}_{\text{H}_2\text{O}}$ compared to SA_E . The OC contribution to SA for samples rich in montmorillonite clay was strongly negative ($-10.2 \text{ m}^2/\text{g}$ per %C for $\text{SA}_{\text{H}_2\text{O}}$). The inability of EGME to properly quantify the SA of OC-rich samples was shown by the very low contribution of OC to SA_E ($1.58 \text{ m}^2/\text{g}$ per %C), whereas for $\text{SA}_{\text{H}_2\text{O}}$, there was a significant

Table 3

Partial correlation (PC) coefficients between soil organic carbon (OC) and soil specific surface area (SA) determined by ethyl glycol monoethyl ether (SA_E), water vapor adsorption (SA_{T1}), or water vapor desorption (SA_{T2}) for different soil sample categories. The PC value is the correlation between OC and SA, controlling for clay and silt contents.

Category	Partial correlation coefficient		
	SA_E	SA_{T1}	SA_{T2}
ALL	-0.05	0.05	0.09
KAO	0.30	0.62***	0.63***
IL/MC	0.15	0.33***	0.37***
MMT	-0.44***	-0.30**	-0.27**
ORG	0.69***	0.99***	0.98***

ALL, all investigated mineral samples; KAO, IL/MC, and MMT denote samples dominated by kaolinite clay, illite or mixed-clay, and montmorillonite clay minerals, respectively. ORG, samples rich in organic carbon. The notations '***', '**', and '*' indicate the statistical significance of the degree of the association at p-values less than 0.001, 0.01, and 0.05, respectively.

positive contribution of OC to SA (13.9 m²/g per %C).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2022.116314>.

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