

# Applicability of the Guggenheim–Anderson–Boer water vapour sorption model for estimation of soil specific surface area

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## Summary

Soil specific surface area (SA) controls fundamental soil processes such as retention of water, ion exchange, and adsorption and release of plant nutrients and contaminants. Conventional methods for determining SA include adsorption of polar or non-polar fluid molecules with associated advantages and limitations. The Guggenheim–Anderson–Boer (GAB) sorption model accurately characterizes soil water vapour sorption isotherms and is posited as an alternate approach for the determination of SA from water vapour sorption. The present study investigates the GAB model as an alternative to other water sorption-based modelling approaches to determine SA. Measured water vapour adsorption and desorption isotherms for 321 soil samples were used to parameterize the GAB model, the Brunauer–Emmet–Teller (BET) equation and a film adsorption Tuller–Or (TO) model to estimate SA. For adsorption isotherms, the values of the GAB parameters varied depending on the water activity or relative humidity range of measured data (0.03–0.93 compared with 0.10–0.80), whereas the variation for desorption was minimal. For desorption isotherms, the average water activity value at which the GAB monolayer parameter was obtained was 0.24 for kaolinite-rich samples, 0.31 for illite-rich or mixed clay samples, 0.34 for smectitic samples and 0.30 for organic matter-rich samples, respectively. The GAB model provided reasonable estimates of SA (root mean squared error from 11.6 to 36.4 m<sup>2</sup> g<sup>-1</sup>), in particular for smectite-rich soil samples, when compared with SA measured by the ethylene glycol monoethyl ether (EGME) method. For kaolinitic samples, however, the BET equation provided the best estimate of EGME-SA. The SA estimates of the GAB model were comparable to those obtained by the TO adsorption model. Thus, the GAB model provides a good alternative to the TO model (applicable only to adsorption data) or the BET model, which fails when the fraction of swelling clay minerals increases.

## Highlights

- GAB, BET and film adsorption models were parameterized with water vapour sorption data.
- Water activity at GAB monolayer coverage depended on clay mineralogy.
- Soil organic matter did not affect water activity at monolayer coverage.
- Estimates of SA from GAB were in accord with EGME-measured SA.

## Introduction

The soil specific surface area (SA), expressed as the surface area per unit mass of soil (m<sup>2</sup> g<sup>-1</sup>), is a crucial basic soil property that governs numerous important soil characteristics and processes, including the retention of water, infiltration and drainage, ion

exchange, adsorption and release of plant nutrients and contaminants, heat transport and storage, structural soil development, microbial processes, soil swelling, plasticity, cohesion and soil strength. In arable soil, constituents such as clay minerals and organic matter are the primary contributors to SA. Typical values for soil range from less than 5 m<sup>2</sup> g<sup>-1</sup> in sandy soil to more than 200 m<sup>2</sup> g<sup>-1</sup> in smectitic soil. The SA of soil often comprises ‘external’ and ‘internal’ surfaces depending on the dominant clay mineral.

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The SA of kaolinite-rich soil is composed almost entirely of external surfaces, whereas soil with appreciable amounts of swelling clay minerals (e.g. smectite) has both internal and external surfaces.

In addition to the importance of SA for soil processes, it may be used to estimate other soil properties such as cation exchange capacity (CEC) (Yukselen & Kaya, 2006) and Atterberg limits (Dolinar *et al.*, 2007). The SA can be estimated by measurement of particle size and shape (Borkovec *et al.*, 1993) or by adsorption of non-polar probe molecules such as N<sub>2</sub> or CO<sub>2</sub> (Kim *et al.*, 2016) or polar molecules such as water (Cerato & Lutenecker, 2002), ethylene glycol, methylene blue (Hang & Brindley, 1970) or ethylene glycol monoethyl ether (EGME) (Cerato & Lutenecker, 2002). Large non-polar molecules such as N<sub>2</sub> cannot penetrate the internal soil surfaces, whereas EGME and water molecules can provide reliable estimates of both internal and external surface areas (Pennell, 2002). As a result, the EGME method is the preferred method in soil science and geotechnical engineering to determine SA (SA<sub>EGME</sub>). In addition to the tedious procedure of EGME measurement, other limitations such as challenges with monolayer coverage, inaccuracy of the commonly used smectite calibration, capillary condensation or effect of cation hydration energy have been discussed previously (Tiller & Smith, 1990; Quirk & Murray, 1999; Khorshidi *et al.*, 2017).

The use of water vapour sorption to estimate SA from single-point measurements (Puri & Murari, 1964; Newman, 1983) or a combination of water vapour sorption isotherms and modelling approaches is gaining traction in recent studies (e.g. Tuller & Or, 2005; Arthur *et al.*, 2013; Akin & Likos, 2014; Leão & Tuller, 2014; Khorshidi *et al.*, 2017). The Tuller–Or (TO) approach that applies a thermodynamic scaling relationship between adsorbed water film thickness, matric potential and SA, works well for soils with SA values ranging from 5 m<sup>2</sup> g<sup>-1</sup> to about 200 m<sup>2</sup> g<sup>-1</sup>. (Arthur *et al.*, 2013; Maček *et al.*, 2013). Some challenges associated with the TO approach are the estimation of a realistic value for the apparent Hamaker constant (Or & Tuller, 1999; Tuller & Or, 2005) and inability of the model to describe accurately the drier parts of the adsorption isotherms (Resurreccion *et al.*, 2011). Khorshidi *et al.* (2017) proposed a new method of SA estimation, which postulates that the hydration of swelling clays and soil occurs on three distinct surfaces (exchangeable cation, inter-crystalline and external particle surfaces) in sequential order. For swelling clays and soil, their method produced more realistic estimates of SA than the traditional EGME procedure.

Monolayer or single-point methods for estimating SA are challenged by the identification of complete monolayer cover by water molecules on soil and clay surfaces. Quirk (1955) noted that polar molecules (water and EGME) tend to adsorb around cation exchange sites on the clay surfaces. The degree to which this corresponds with a monolayer depends on the surface density, invalidating the assumption of hexagonal close packing of the molecules on the surfaces. Because the standard EGME and Brunauer–Emmet–Teller (BET) approaches still use the monolayer approach to obtain SA, its applicability is still relevant. The BET equation (Brunauer *et al.*, 1938), frequently used to estimate

SA from N<sub>2</sub> adsorption, is one approach for estimating SA from water sorption (Quirk, 1955). In general, the SA from BET modelling (SA<sub>BET</sub>) of water sorption data is similar to SA<sub>EGME</sub> for non-swelling soil (e.g. Akin & Likos, 2014). For swelling soil, however, SA<sub>BET</sub> is smaller than SA<sub>EGME</sub> because the relative humidity or water activity ( $a_w$ ) range used for the BET model (0.1 to 0.4) does not reflect the effects of clay minerals that swell. Studies have reported widely varying values of  $a_w$  for monolayer completion. For example, Quirk (1955) and studies cited therein reported monolayer  $a_w$  values of between 0.20 and 0.25 for soil primarily dominated by kaolinite. Later, Newman (1983) suggested that for swelling clays, the monolayer is completed at  $a_w = 0.47$ , whereas for non-swelling soil, this corresponds to the water content at  $a_w = 0.47$  divided by a correction factor of 1.7 ( $w_{0.47/1.7}$ ). This was evaluated by Akin & Likos (2014) for natural clayey materials and artificial clay mixtures and they observed that BET monolayer water content was similar to water content at  $a_w = 0.20$  and  $w_{0.47/1.7}$  for soil with SA < ~150 m<sup>2</sup> g<sup>-1</sup>. Quirk & Murray (1999) also confirmed that the monolayer is completed in the range of  $a_w$  from 0.19 to 0.21.

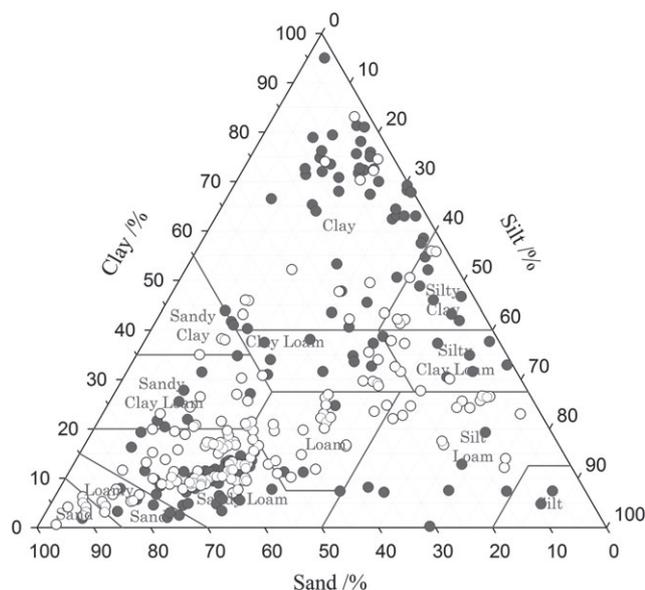
As mentioned above, the BET approach with water vapour sorption data works quite well for non-swelling soil, but fails for soil with large amounts of swelling clay minerals (Khorshidi *et al.*, 2017). The European Cooperation in Science and Technology (COST) 90 recommended the Guggenheim–Anderson–Boer (GAB; van den Berg & Bruin (1981)) equation for modelling isotherms of food products because of its greater flexibility when compared with the BET approach. The GAB equation is similar to the BET equation, but with an additional parameter to account for difference in the properties of the multilayer molecules relative to the bulk liquid. Further details on the model are provided later in the methodology section. Timmermann (2003) suggested, based on experimental sorption data and mathematical analyses, that the BET equation may be replaced with the GAB equation to estimate monolayer water content and also the SA of soil from water sorption. Recent research indicates that the GAB equation accurately describes water sorption isotherms ( $a_w$  from 0.03 to 0.93 or 0.95) for a wide range of natural (Arthur *et al.*, 2016) and swelling soils (Akin & Likos, 2017), in particular desorption data.

Based on the considerations above, the present study investigates the GAB equation as an alternative to other water sorption-based modelling approaches (BET and TO models) and the EGME method to determine the SA for a global collection of soil samples. An additional objective was to evaluate the water activity corresponding to the GAB monolayer water content for different soil groups (kaolinite-rich, illite-rich and mixed clay samples, smectite-rich and organic soil samples).

## Methodology

### *Soil samples investigated*

The study considered a total of 321 soil samples with geographical origins in Northern Europe (149), North America (59), South & Central America (39), Africa (42), Greenland (15), Asia (10) and New Zealand (7). Fifteen of the soil samples with organic carbon



**Figure 1** Textural classification of soil samples ( $n = 321$ ). Open symbols represent samples with  $SA_{EGME}$  data ( $n = 162$ ).

**Table 1** Summary of properties of soil samples investigated ( $n = 321$ , for  $SA_{EGME}$  data,  $n = 162$ )

Property	Minimum	Maximum	Mean	CV / %
Clay / %	0.2	95	26	82
Silt / %	3	87	30	54
Sand / %	0.4	96	44	59
Organic carbon / %	0.03	30.9	2.0	131
$SA_{EGME} / m^2 g^{-1}$	6	437	56	103

contents ranging from 2.5 to 30.9% (from Greenland, Denmark and New Zealand) were grouped as organic matter-rich soil. The particle-size distributions and summaries of the soil organic carbon and  $SA_{EGME}$  are presented in Figure 1 and Table 1. The clay mineralogy of the soil samples comprised smectite, illite–mica, kaolinite, vermiculite and chlorite minerals in various proportions (Table S1, Supporting Information).

### Measurements

The measurements described below were carried out with air-dried soil samples that had been passed through a 2-mm sieve. The particle-size fractions (texture) of the soil samples were obtained by a combination of wet sieving and the pipette or hydrometer methods. In all cases, organic matter and carbonates (when present) were removed prior to determination of the particle-size fractions. The method applied is described in Gee & Or (2002). For the majority of samples, soil organic carbon was determined on milled subsamples by oxidizing the carbon at 1800°C and measuring soil organic carbon (OC) content with an organic elemental analyser coupled to a thermal conductivity detector (Thermo Fisher Scientific, Waltham,

MA, USA). For samples containing carbonates, OC was estimated as the difference between total carbon and inorganic carbon calculated from the percentage of  $CaCO_3$ . For 44 samples, OC was determined by the Walkley–Black method described in Nelson & Sommers (1996).

The soil specific surface area used as the reference was determined from EGME retention at monolayer coverage as described in Pennell (2002) with no pre-treatments (removal of OC or ion saturation). Briefly, we mixed 2-mm sieved samples with EGME and sealed them in an equilibration chamber under vacuum. After an equilibration period of between 12 and 72 hours, depending on sample SA, we weighed the samples in sealed weighing bottles until the weight became constant. The SA was calculated from the mass of EGME retained by the sample.

Soil water vapour sorption isotherms were measured for both adsorption and desorption for a water activity ( $a_w$ ) range from 0.03 to 0.93 at a temperature of 25°C with a vapour sorption analyser (METER Group Inc., Pullman, WA, USA). After the measurements, the reference water content of the samples was obtained by oven drying the samples at 105°C for 48 hours.

### Estimation of SA from water vapour sorption

Soil specific surface area was estimated from water sorption data based on three models; the widely used Tuller & Or (2005) model, hereafter denoted TO model, the classical Brunauer–Emmet–Teller model (BET; Brunauer *et al.* (1938)) and the Guggenheim–Anderson–Boer (GAB; van den Berg & Bruin (1981)) model.

#### The TO model

The TO model was applied to estimate SA ( $SA_{TO}$ ,  $m^2 kg^{-1}$ ) from adsorption data for the  $a_w$  range from 0.03 to 0.93, corresponding to matric potentials ranging from  $-470$  to  $-10$  MPa. In this matric potential range, capillary condensation is assumed to be negligible, only van de Waals forces on planar surfaces are considered and water exists as thin adsorbed films. Based on these assumptions, the TO model relates equilibrium soil water content,  $M$  ( $kg kg^{-1}$ ), to matric potential,  $\psi$  ( $m H_2O$ ) and SA as:

$$M = \sqrt[3]{\frac{A_{svl}}{6\pi\rho_w g\psi}} SA_{TO} \quad (1)$$

where  $A_{svl}$  (J) is the Hamaker constant for solid–vapour interactions through the intervening liquid,  $\rho_w$  is the density of water and  $g$  is acceleration due to gravity ( $m s^{-2}$ ). The value of  $A_{svl}$  was set to  $-6 \times 10^{-20}$  J as suggested in Tuller & Or (2005) and Maček *et al.* (2013).

#### The BET isotherm model

The classical BET equation (Equation (2)) was parameterized with both adsorption and desorption data for the range in  $a_w$  from 0.1 to

0.4 because the equation cannot accurately characterize isotherms for  $a_w$  values larger than 0.5 (Anderson, 1946).

$$M = \frac{M_{0B} C_B a_w}{[(1 - a_w)(1 - a_w + C_B a_w)]}, \quad (2)$$

where  $M_{0B}$  is the soil water content at monolayer coverage ( $\text{kg kg}^{-1}$ ) and  $C_B$  is the energy constant that depicts the difference in free enthalpy of the water molecules in the pure liquid state and in the monolayer.

#### The GAB isotherm model

The GAB equation was developed by Anderson (1946), de Boer (1953) and Guggenheim (1966). The equation is similar to the BET equation, but has an additional parameter ( $K$ ) to compensate for the assumption that the sorption state of the water molecules in the layers beyond the first is the same but different from that for the pure liquid state.

$$M = \frac{M_{0G} C_G K a_w}{[(1 - K a_w)(1 - K a_w + C_G K a_w)]}, \quad (3)$$

where  $M_{0G}$  ( $\text{kg kg}^{-1}$ ) and  $C_G$  are analogous to the BET equation and  $K$  represents the difference in free enthalpy of the water molecules in the pure liquid and the layers above the monolayer. When  $K$  is 1, the GAB equation reduces to the BET equation and  $M_{0B} = M_{0G}$  and  $C_B = C_G$ .

To evaluate a potential effect of the range of  $a_w$  on the model parameters, the GAB equation was parameterized with both adsorption and desorption data for two  $a_w$  ranges of 0.03 to 0.93 and 0.10 to 0.80. Subsequently,  $M_{0G}$ ,  $C_G$  and  $K$  were compared for the two ranges of water activity.

#### Model parameterization and SA estimates

All three models were parameterized with measured data by using the Levenberg–Marquardt nonlinear least squares algorithm implemented in the ‘minpack.lm’ package in R v3.3.2 (R Development Core Team, 2017). The models were fitted independently to measured adsorption and desorption data, and the accuracy of the fit was quantified with the coefficient of determination ( $R^2$ ) and the root mean squared error (RMSE).

Although the TO model provides  $SA_{TO}$  as a direct parameter estimate, the GAB and BET equations give  $M_{0B}$  and  $M_{0G}$ , respectively, which were used to calculate  $SA_{BET}$  and  $SA_{GAB}$  from Equation (4) (Newman, 1983; Quirk & Murray, 1999) for adsorption and desorption ( $SA_{BETa}$ ,  $SA_{BETd}$ ,  $SA_{GABa}$  and  $SA_{GABd}$ ):

$$SA = \frac{M_0 N A}{w_w}, \quad (4)$$

where  $M_0$  is the monolayer water content ( $\text{kg kg}^{-1}$ ) from either the GAB or BET equation,  $N$  is Avogadro’s number ( $6.02 \times 10^{23} \text{ mol}^{-1}$ ),  $A$  is the area covered by one water molecule

( $10.8 \times 10^{-20} \text{ m}^2$ ) and  $w_w$  is the molecular weight of water ( $0.018 \text{ kg mol}^{-1}$ ).

#### Relating $M_0$ values to water activity values

To determine the approximate water activity at monolayer coverage ( $a_{w0}$ ) for the soil samples based on  $M_{0G}$ , the soil samples for which quantitative or qualitative clay mineralogy was available were divided into three groups based on dominant clay mineralogy (smectite-rich samples = 60; kaolinite-rich samples = 62; illite-rich samples and samples with a mixture of clay minerals = 82). A fourth group of 15 samples that comprised primarily feldspars or illites with large contents of organic carbon (2.5 to 30.9%) and <10% clay content was also considered. For each of the groups, the  $M_{0G}$  values were compared with the measured sorption–desorption data, and  $a_w$  corresponding to that water content ( $a_{w0}$ ) was extracted for both adsorption and desorption. The identification of  $a_{w0}$  was carried out to enable the estimation of SA from a single-point water-content measurement (using Equation (4)) rather than from the entire isotherm.

#### Comparison of SA estimates

To compare the various estimates of SA ( $SA_{TO}$ ,  $SA_{BET}$  and  $SA_{GAB}$ ) with  $SA_{EGME}$ , two indices were used (root-mean squared error (RMSE) and the mean error or bias (ME)).

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (SA_X - SA_{EGME})^2}, \quad (5)$$

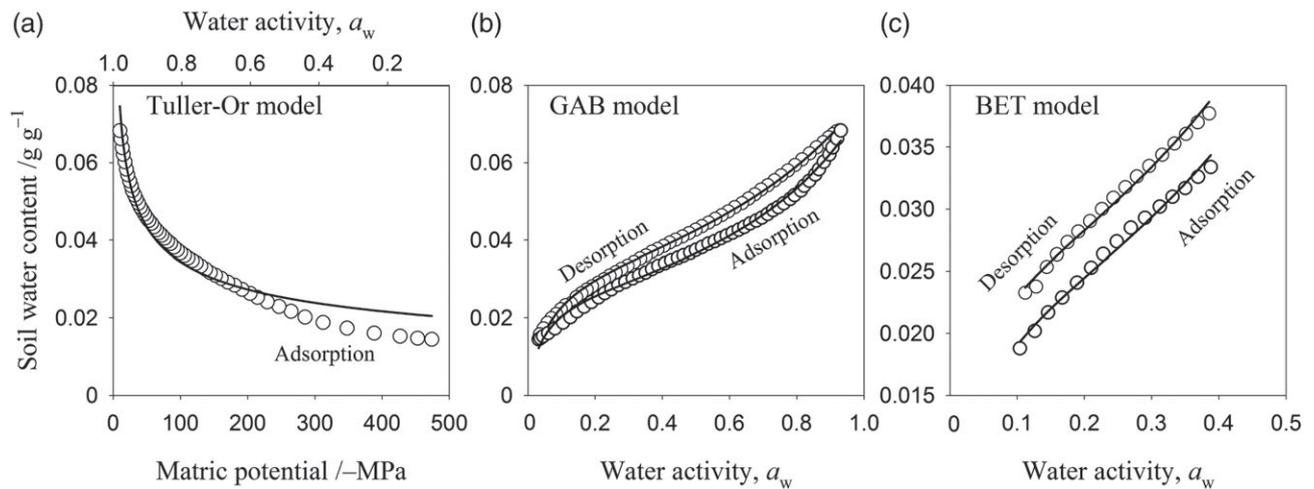
$$ME = \sqrt{\frac{1}{n} \sum_{i=1}^n (SA_X - SA_{EGME})}, \quad (6)$$

where  $SA_X$  denotes a measure of SA derived from water vapour sorption and  $n$  is the number of samples.

## Results and discussion

#### Modelling of water vapour sorption isotherms

Typical water vapour sorption isotherms and an example for parameterization of each of the TO, GAB and BET models for a silty clay loam soil are presented in Figure 2. The TO model generally over-predicts soil water content for matric potentials below  $-200 \text{ MPa}$ , but this trend has minimal effect on the accuracy of prediction of SA (Arthur *et al.*, 2013). For example, the SA derived with the TO model for the sample presented in Figure 2 was  $109.9$  and  $108.7 \text{ m}^2 \text{ g}^{-1}$  for matric potential ranges from  $-10$  to  $-200 \text{ MPa}$  and  $-10$  to  $-470 \text{ MPa}$ , respectively. The GAB and BET equations fitted the measured data well, with average RMSE and  $R^2$  values of  $0.0005 \text{ g g}^{-1}$  and  $0.99$ , respectively. However, for a few soil samples with large amounts of kaolinite clay and exhibiting Type III isotherms (Brunauer *et al.*, 1940), the GAB and BET equations fitted to measured data returned unrealistically large



**Figure 2** Model fit of (a) Tuller–Or model to the adsorption isotherm, and (b) Guggenheim–Anderson–Boer (GAB) and (c) Brunauer–Emmet–Teller (BET) model to the adsorption–desorption isotherms of a silty clay loam soil. The matric potential range for the Tuller–Or model in (a) corresponds to a water activity range of 0.03 to 0.93.

$C$  parameters ( $C > 200$ ). Nevertheless, the  $M_0$  and  $K$  values for these samples were as expected;  $M_0$  for these soils corresponded to water contents between  $a_w$  of 0.10 and 0.40, and  $K < 1.0$ . This suggests that estimation of SA is not affected markedly by large  $C$  values.

#### The $C_B$ , $C_G$ and $K$ parameters

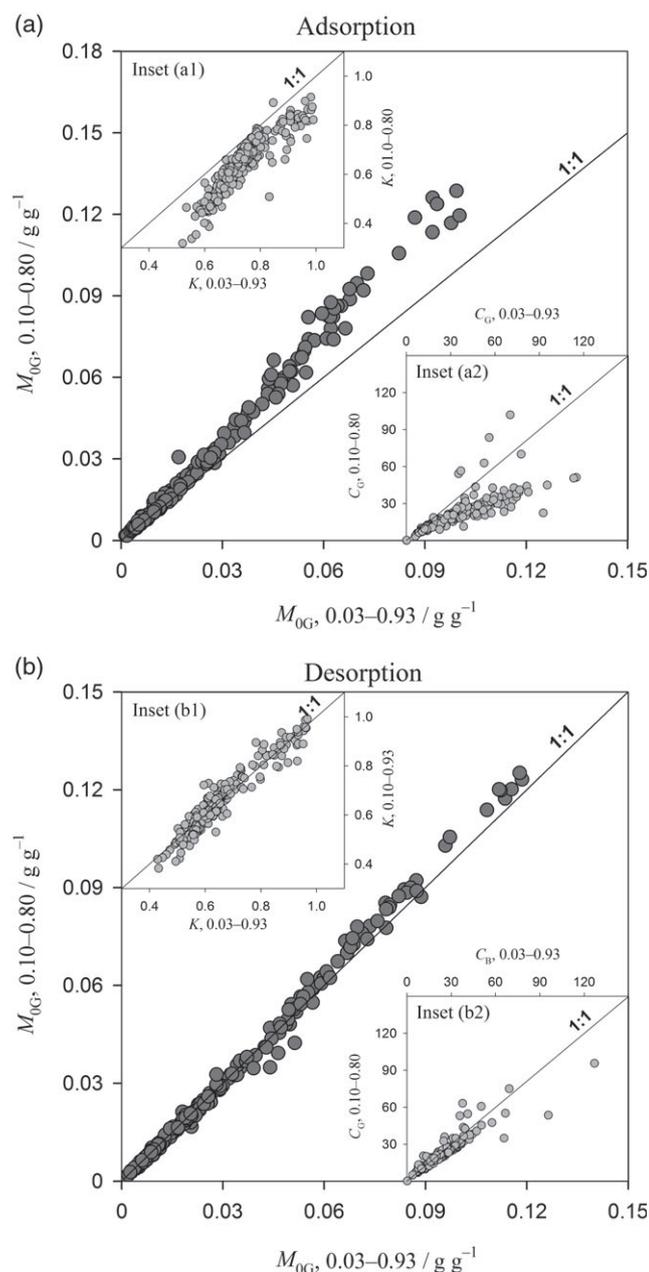
The  $C_G$  and  $C_B$  parameters are both energy constants related to the difference between free enthalpy of the water molecules in the pure liquid state and in the monolayer (or first sorbed layer). Thus, they represent the binding strength of water to the primary binding surfaces such as exchangeable cations and mineral surfaces (Prost *et al.*, 1998; Sabard *et al.*, 2012). Large  $C$  values indicate that water is more strongly bound in the monolayer, and the difference in enthalpy between the monolayer molecules and the subsequent layers is larger. For the samples investigated, the values of  $C_B$  were larger than  $C_G$  and for desorption  $C_B \approx 1.5 \times C_G$  for  $C_B$  values  $\leq 100$ . This observation, as noted by Akin & Likos (2017), is due to the inclusion of the parameter  $K$  in the GAB equation, which compensates for the fact that the sorption energy beyond the monolayer is smaller than that of liquefaction. The smaller interaction enthalpy of the multilayer molecules with the sorbent suggests that  $K$  has a smaller enthalpic contribution than  $C_G$ . On the other hand, the greatly increased number of configurations and mobility of water molecules in the bulk liquid compared with that in the multilayer results in a much larger entropic content of  $K$  than  $C$  (Quirijns *et al.*, 2005). The value of  $K$  reduces as more molecules are grouped together in a multilayer, and is closer to unity as the difference between the molecules in the monolayer and the bulk liquid becomes negligible.

For all samples examined  $K$  was  $< 1$ , indicating that the water molecules within the monolayer were more strongly bound than those in the multilayer, which is contrary to what the BET equation suggests. In general,  $K$  increases with increasing strength of

interaction between the sorbent and sorbate. The  $K$  values were larger (0.52 to 0.99) for adsorption than for desorption (0.43 to 0.97), and reflected the prevailing clay mineralogy in the soil samples. For example, the  $K$  values obtained from desorption averaged ( $\pm$ SE)  $0.56 \pm 0.005$ ,  $0.62 \pm 0.005$  and  $0.84 \pm 0.015$  for samples dominated by smectite, illite and mixed clays, and kaolinites, respectively. For different kaolinite–bentonite mixtures, Akin & Likos (2017) reported  $K$  values of  $\sim 0.88$  for 100% kaolinite, which decreased to  $\sim 0.52$  when 20–100% bentonite was added. A similar trend was observed for a part of this dataset in Arthur *et al.* (2016), where larger  $K$  values for kaolinite-dominated soils were attributed to their smaller surface areas compared with smectite clays and, consequently, stronger interactions between sorption sites and water molecules. Moreover, the large  $K$  values (as large as 0.99) for kaolinitic soils suggest that the assumptions made in the BET model are applicable to a certain extent for soils dominated by kaolinite clays.

#### Range of water activity and GAB parameters

The effect of the range in  $a_w$  of measured sorption isotherms on the magnitude of the GAB parameters for both adsorption and desorption is presented in Figure 3. For both sorption directions,  $M_{0G}$  was larger for the 0.10 to 0.80 range in  $a_w$  than for the 0.03 to 0.93 range, with a larger difference observed for adsorption than for desorption. In addition, the  $C_G$  and  $K$  parameters for adsorption were larger for the 0.03 to 0.93 range in  $a_w$  than for the 0.10 to 0.80 range. For desorption,  $C_G$  and  $K$  did not differ markedly for the two ranges of  $a_w$ . These observations suggest that for adsorption, the measurement range of  $a_w$  might have a considerable effect on the magnitude of the GAB parameters obtained, whereas this is not the case for desorption. For some soils and clay materials, the adsorption isotherm is not always reproducible because of sensitivity to initial water content, presence of hydrophobic substances and the fact



**Figure 3** Comparison of the Guggenheim–Anderson–Boer (GAB) model parameters ( $M_{OG}$ ,  $C_G$  and  $K$ ) for adsorption and desorption isotherms measured in the water activity range from 0.03 to 0.93 and 0.10 to 0.8.

that the adsorption process is challenged by stronger intermolecular forces than desorption (Johansen & Dunning, 1957; Lu & Khorshidi, 2015). These factors might explain the observed discrepancy between the two sorption directions (adsorption and desorption).

#### The BET and GAB monolayer parameters

The  $M_{OB}$  and  $M_{OG}$  parameters represent the approximate monolayer water content ( $w_m$ ). For the desorption isotherms (0.03–0.93  $a_w$ ) of the soil samples investigated  $M_{OB} = 0.73 \times M_{OG}$ . The  $M_{OB}$  values

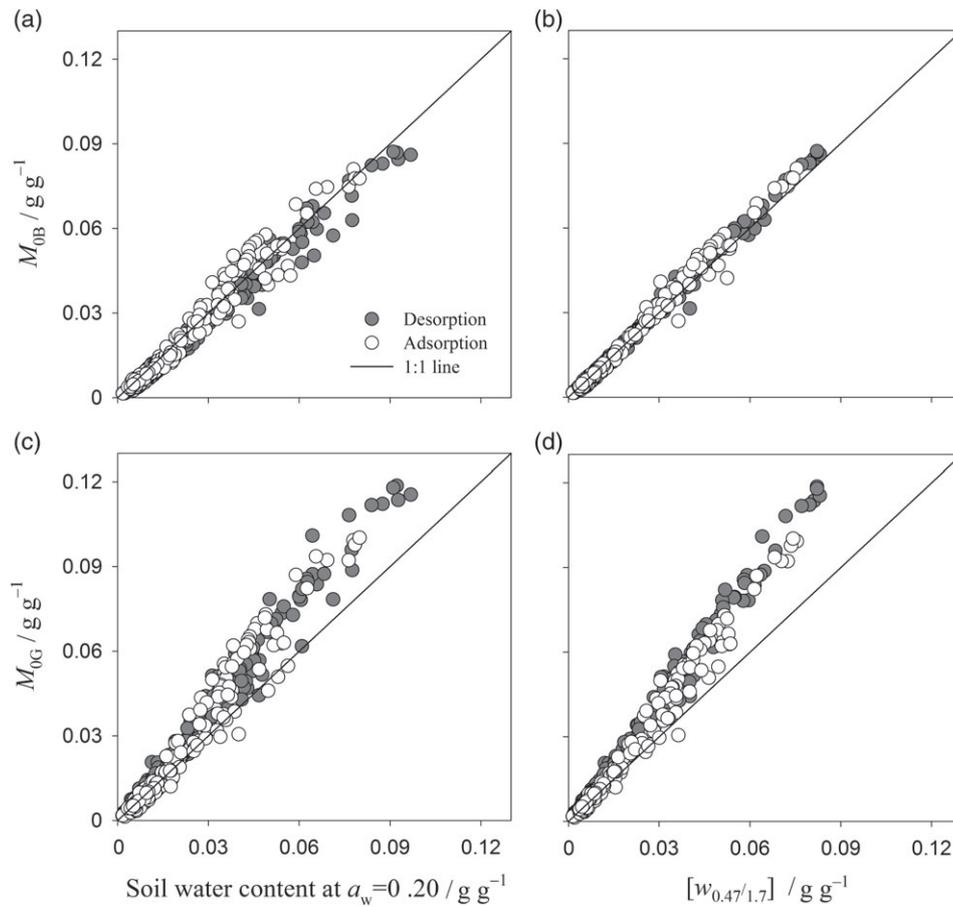
**Table 2** Relations between Brunauer–Emmet–Teller (BET) and Guggenheim–Anderson–Boer (GAB) monolayer parameters ( $M_{OB}$  and  $M_{OG}$ ) and soil water contents at water activity,  $a_w$ , of 0.20 ( $w_{0.20}$ ),  $a_w$  of 0.47 ( $w_{0.47}$ ) and soil water content at  $a_w = 0.47$  divided by 1.7 ( $w_{0.47/1.7}$ ) for adsorption and desorption.

	$w_{0.20}$ (x)	$w_{0.47/1.7}$ (x)	$w_{0.47}$ (x)
Adsorption			
$M_{OB}$	0.99x; $r = 0.98$	1.05x; $r = 0.99$	0.62x; $r = 0.99$
$M_{OG}$	1.20x; $r = 0.97$	1.27x; $r = 0.99$	0.75x; $r = 0.99$
Desorption			
$M_{OB}$	0.92x; $r = 0.99$	1.03x; $r = 0.99$	0.61x; $r = 0.99$
$M_{OG}$	1.26x; $r = 0.99$	1.40x; $r = 0.99$	0.82x; $r = 0.99$

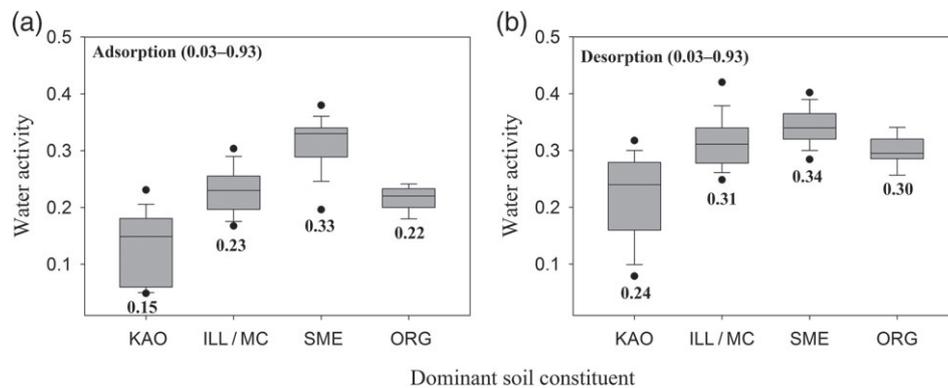
x, water content at selected  $a_w$  values; r, correlation coefficient.

ranged from 0.0014 to 0.0810  $\text{g g}^{-1}$  and from 0.0016 to 0.0872  $\text{g g}^{-1}$  for adsorption and desorption, respectively. For  $M_{OG}$ , the range was from 0.0014 to 0.1002 and 0.0021 to 0.1186  $\text{g g}^{-1}$  for adsorption and desorption, respectively (Figure 4). The larger values of  $M_{OG}$  compared with  $M_{OB}$ , in particular for soils with swelling clay minerals (where  $K < 0.65$ ), results from the ability of the respective models to fit the isotherms of such types of soil. As the fraction of swelling clay minerals in the samples increases, the BET equation fails to characterize the isotherms, whereas the GAB equation has no such limitation. The values of  $a_w$  that correspond to the estimated values of  $M_{OG}$  were obtained and compared for various soil groups. Hereafter, this  $a_w$  value is denoted  $a_{w0}$ . The identification of  $a_{w0}$  is important because it is the basis for estimating SA from a single water content measurement. Previous studies have suggested different values of  $a_{w0}$ . For example, for soil composed of non-swelling clay minerals such as kaolinite and illite,  $a_{w0}$  has been reported as being between 0.19 and 0.21 (Quirk, 1955; Quirk & Murray, 1999). Based on the close relation between ethylene glycol and water retention at  $a_w = 0.47$ , monolayer coverage for soils with swelling clay minerals like smectite is reported to occur at around  $a_w$  of 0.47 (Newman, 1983). For illitic or kaolinitic soils,  $w_m$  can also be approximated as the water content at  $a_w = 0.47$  divided by a factor of 1.7 ( $w_{0.47/1.7}$ ).

In Figure 4 and Table 2,  $M_{OB}$  and  $M_{OG}$  values for all soil samples considered, regardless of clay mineralogy, are compared with the soil water content at 0.20 ( $w_{0.20}$ ) and also with  $w_{0.47/1.7}$ . Although  $M_{OB}$  seems to be approximated fairly well with  $w_{0.20}$  in Figure 4(a), it is clear that  $w_{0.47/1.7}$  accords better with  $M_{OB}$ , regardless of sorption direction (Figure 4b). Previous studies (Akin & Likos, 2014; Khorshidi *et al.*, 2017) have shown that for soils with swelling clay minerals,  $M_{OB}$  is a poor approximation of  $w_m$  because the BET model is only applicable for  $a_w < 0.40$ . Thus, it does not resolve the region of the isotherms where the effect of clay mineralogy is prominent. Despite this, it is interesting to note that for all soil samples investigated  $M_{OB}$  represented  $w_{0.47/1.7}$  accurately regardless of clay mineralogy. Conversely,  $M_{OG}$  was larger (25–40%) than both  $w_{0.20}$  and  $w_{0.47/1.7}$  for all samples, except for those with small surface areas corresponding to  $M_{OG}$  values less than 0.03  $\text{g g}^{-1}$ .



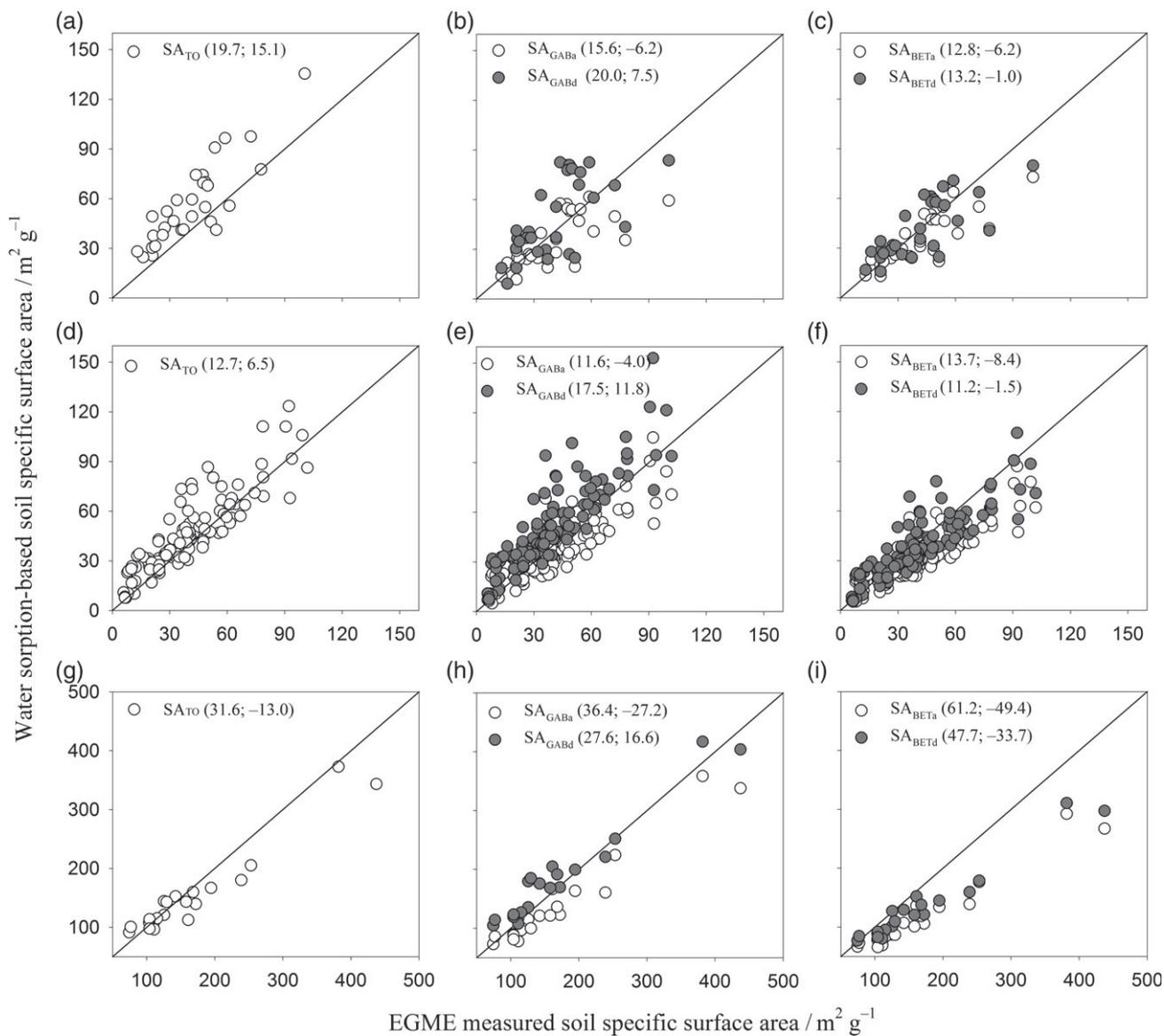
**Figure 4** The Brunauer–Emmet–Teller (BET) and Guggenheim–Anderson–Boer (GAB) monolayer parameters ( $M_{0B}$  and  $M_{0G}$ ) obtained from adsorption and desorption isotherms compared with (a, c) soil water contents at water activity,  $a_w$ , of 0.20 and (b, d) soil water content at  $a_w = 0.47$  divided by 1.7 ( $w_{0.47/1.7}$ ). For further details see Table 2.



**Figure 5** Boxplots depicting water activity values at which the Guggenheim–Anderson–Boer (GAB) model evaluates the monolayer parameter for four groups of soil samples (KAO, kaolinite-rich samples; ILL/MC, illite-rich or mixed clay samples; SME, smectite-rich samples; ORG, samples rich in organic carbon from 3 to 31%). Values below boxes represent median water activity values for each soil group.

On the other hand,  $w_{0.47}$  was larger than both  $M_{0B}$  and  $M_{0G}$  for adsorption and desorption. The similarity between  $M_{0G}$  and  $w_{0.47/1.7}$  for samples with small surface areas is because the majority of those samples contained kaolinites and their sorption mechanisms are similar to those described by the classical multimolecular BET

theory. For samples with large surface areas (with correspondingly larger  $M_{0G}$  values), the similarities cease because the BET theory no longer applies. More detail on the relations between  $M_{0B}$  and  $M_{0G}$  and  $w_{0.20}$  and  $w_{0.47/1.7}$  for adsorption and desorption are provided in detail in Table 2.



**Figure 6** Scatterplots of EGME soil specific surface area (SA) compared with water sorption-based SA estimates for soil samples dominated by (a,b,c) kaolinite, (d,e,f) illite and mixed clays, and (g,h,i) smectites. Legend subscripts: TO, estimate from Tuller–Or model; GAB, Guggenheim–Andersen–Boer (GAB) estimate from adsorption (GAB<sub>a</sub>) and desorption (GAB<sub>d</sub>); BET, Brunauer–Emmet–Teller estimate from adsorption (BET<sub>a</sub>) and desorption (BET<sub>d</sub>). Values in the legend indicate RMSE, root mean squared error ( $\text{m}^2 \text{g}^{-1}$ ), and ME, mean error or bias ( $\text{m}^2 \text{g}^{-1}$ ), respectively.

#### Effect of sorption direction and soil constituents on GAB-based $a_{w0}$

The soil clay mineral composition affects  $a_{w0}$ , and the trends shown in Figure 4(b) and Table 2 suggest that for the majority of samples,  $M_{0G}$  is larger than  $w_{0.20}$ , but smaller than  $w_{0.47}$ . To evaluate further the approximate  $a_{w0}$  for the soil samples based on  $M_{0G}$ , boxplots depicting the  $a_{w0}$  of the four soil groups (smectite-rich, kaolinite-rich, illite-rich or mixed-clay and organic-rich samples) for adsorption and desorption are presented in Figure 5. For all four groups, combining adsorption and desorption,  $a_{w0}$  ranges from 0.15 to 0.34. As expected, kaolinite-rich samples had the smallest

median  $a_{w0}$  (0.15 for adsorption and 0.24 for desorption) and that for smectite-rich soils was the largest (0.31 for adsorption and 0.34 for desorption). Soils composed of illites or relatively even proportions of different clay minerals had median  $a_{w0}$  values of 0.23 and 0.31 for adsorption and desorption, respectively. The presence of organic carbon in the samples (up to 31%) had no effect on  $a_{w0}$  values because the values were similar to that obtained for illitic soil, which was the dominant clay mineral. For illite-rich samples, organic carbon increased the equilibrium water content at monolayer coverage, whereas  $a_{w0}$  remained the same. More detail on  $a_{w0}$  values for the four soil groups for the two  $a_w$  ranges discussed above is provided in Figure S1 (Supporting Information).

**Table 3** Comparison of soil specific surface area (SA) measured with the ethyl glycol monoethyl ether (EGME) method and water vapour sorption determined with the Tuller–Or (TO), Guggenheim–Anderson–Boer (GAB) and the Brunauer–Emmet–Teller (BET) models for adsorption and desorption isotherms

SA estimate (y)	Indicator	SA <sub>EGME</sub> (x)	SA <sub>TO</sub> (x)
SA <sub>TO</sub>	RMSE	17.72	
	ME	5.60	
	LR Equation	$y = 0.82x + 15.5; R^2 = 0.93$	
SA <sub>GABa</sub>	RMSE	17.58	22.10
	ME	-7.40	-15.57
	LR Equation	$y = 0.80x + 3.71; R^2 = 0.94$	$y = 0.95x - 11.6; R^2 = 0.95$
SA <sub>GABd</sub>	RMSE	19.53	22.37
	ME	11.60	8.02
	LR Equation	$y = 0.99x + 12.4; R^2 = 0.93$	$y = 1.18x - 7.32; R^2 = 0.97$
SA <sub>BETa</sub>	RMSE	25.41	34.23
	ME	-13.32	-26.32
	LR Equation	$y = 0.66x + 6.10; R^2 = 0.95$	$y = 0.76x - 5.52; R^2 = 0.96$
SA <sub>BETd</sub>	RMSE	20.51	21.55
	ME	-5.60	-16.23
	LR Equation	$y = 0.72x + 10.4; R^2 = 0.93$	$y = 0.86x - 3.59; R^2 = 0.98$

SA subscripts: TO, estimate from Tuller–Or model; GAB, Guggenheim–Anderson–Boer (GAB) estimate from adsorption (GAB<sub>a</sub>) and desorption (GAB<sub>d</sub>); BET, Brunauer–Emmet–Teller estimate from adsorption (BET<sub>a</sub>) and desorption (BET<sub>d</sub>). RMSE, root mean squared error ( $\text{m}^2 \text{g}^{-1}$ ); ME, mean error or bias ( $\text{m}^2 \text{g}^{-1}$ ); LR, linear regression.

Two observations from Figure 5 are: (i)  $a_{w0}$  of 0.20 is a reasonable approximation of monolayer cover for kaolinitic samples as suggested previously, and (ii) the GAB model evaluates  $M_{0G}$  at much smaller  $a_{w0}$  values than the 0.47 reported in the literature (Newman, 1983). Figure 5 shows that all the smectitic samples have an  $a_{w0} < 0.42$ . The  $a_{w0}$  value of 0.47 for swelling soil originated from Mooney *et al.* (1952), who reported that the weight of water sorbed at  $a_{w0} = 0.47$  for Wyoming Ca montmorillonite was  $0.221 \text{ g g}^{-1}$  and the assumption that a molecule of water covers  $10.8 \times 10^{-20} \text{ m}^2$ . Based on this, Newman (1983) showed that a water sorption-based calculation of SA of  $798 \text{ m}^2 \text{ g}^{-1}$  for the clay mineral was in accord with the SA (780 to  $800 \text{ m}^2 \text{ g}^{-1}$ ) estimated from unit cell dimensions and particle size. In the present study, we also measured the desorption isotherm for a similar Wyoming Ca montmorillonite and found that the water sorbed at  $a_{w0} = 0.47$  was  $0.21 \text{ g g}^{-1}$ , similar to that reported by Mooney *et al.* (1952). However, the  $M_{0G}$  obtained for the same mineral was  $0.18 \text{ g g}^{-1}$ , corresponding to an  $a_{w0}$  value of 0.33. This might explain the discrepancy between the work of Newman (1983) and the data presented here.

#### Comparison of SA estimates for different soil groups and different methods

Soil specific surface area has been determined previously by either adsorption of EGME (Cerato & Lutenegger, 2002), a combination of  $\text{N}_2$  or  $\text{CO}_2$  with the BET model (de Jonge *et al.*, 2000), or with various water vapour sorption approaches such as the application of scaling relationships between adsorbed water film thickness and SA (Tuller & Or, 2005), single-point measurements (Newman, 1983), BET modelling (Akin & Likos, 2017) or by consideration of the hydration processes of swelling soils (Khorshidi *et al.*, 2017). All

the approaches listed have their advantages and limitations, some of which are discussed in Heister (2014). For this study, we considered SA<sub>EGME</sub> as the reference for comparison, not because it presents the best estimate of SA, but because it is still the most widely applied method and provides a reasonable estimate of the total surface area.

The various estimates of SA (SA<sub>TO</sub>, SA<sub>GABa</sub>, SA<sub>GABd</sub>, SA<sub>BETa</sub> and SA<sub>BETd</sub>) of 168 samples are presented in Figure 6 based on their predominant clay mineralogy to illustrate how the water sorption-based estimates of SA compare with SA<sub>EGME</sub>. For kaolinite-rich samples, SA<sub>TO</sub> consistently overestimated SA<sub>EGME</sub> (Figure 6a). The SA<sub>GAB</sub> estimates were better than SA<sub>TO</sub>, but also showed some differences from the measured data (Figure 6b). The SA estimates based on BET were generally in accord with SA<sub>EGME</sub>, albeit they were underestimated for some samples (Figure 6c). This trend confirms that for samples with the majority or all of their surface areas originating from external surfaces, the BET equation can be applied to estimate SA accurately (Akin & Likos, 2014). Earlier, we mentioned that the GAB  $K$  value depended on the dominant clay mineralogy; for kaolinitic soils,  $K$  is closer to 1 than for soils with illites and smectites. As  $K$  approaches 1, there is little difference between the molecules in the multilayer and liquid molecules, and the BET theory is sufficiently appropriate. This explains why for kaolinite-rich soils, SA<sub>BET</sub> corresponds to SA<sub>EGME</sub> to a considerable degree.

For samples where the clay mineral was illite or a mixture of minerals, SA<sub>TO</sub> was similar to SA<sub>EGME</sub> (Figure 6d). The majority of the studies that have applied the TO model ( $A_{svl} = -6 \times 10^{-20} \text{ J}$ ) to derive SA are based on samples composed of illites or a mixture of clay minerals. The results showed good estimates of SA when compared with the EGME estimates, although the model overestimated

the thickness of the water film at very small matric potentials (e.g. Resurreccion *et al.*, 2011; Arthur *et al.*, 2013; Maček *et al.*, 2013). Estimates of SA from the GAB model were also similar to those of  $SA_{EGME}$ ; there was some under- and over-estimation for  $SA_{GABa}$  and  $SA_{GABd}$ , respectively (Figure 6e). In general,  $SA_{BET}$  underestimated  $SA_{EGME}$  for the illite and mixed clay soils, especially as the SA of the sample gets larger (Figure 6f). For samples with appreciable amounts of swelling clay minerals such as smectite,  $SA_{GABd}$  provided the best estimate of  $SA_{EGME}$  compared with  $SA_{BET}$ , which underestimated  $SA_{EGME}$ . The underestimation of SA by the BET equation for swelling clay samples was expected because the equation is only applicable for the  $a_{w0}$  range from 0.1 to 0.4, a range that does not resolve the effect of clay mineralogy on the shape of the isotherm (Khorshidi *et al.*, 2017). Further comparisons of  $SA_{TO}$  on the one hand and  $SA_{GABa}$ ,  $SA_{GABd}$ ,  $SA_{BETA}$  and  $SA_{BETd}$  on the other were carried out for the whole dataset together and are presented in Table 3 and in Figure S2 (Supporting information). Both GAB estimates were in accord with  $SA_{TO}$ , whereas the BET estimates were generally smaller than  $SA_{TO}$ .

## Conclusions and perspectives

In this study we evaluated the potential applicability of the Guggenheim–Anderson–de Boer (GAB) equation monolayer parameter ( $M_{0G}$ ) for estimation of soil specific surface area (SA) from soil water vapour sorption and compared the findings with previously applied methods based on either EGME or water sorption. Parameters of the GAB model were affected by the range of measured data used for the analyses, especially for the adsorption isotherm. Regardless of sorption direction or the range of measured data, the GAB monolayer and energy parameters were different from those obtained with the BET equation. Based on the GAB model and for desorption data,  $M_{0G}$  corresponded to water activity or relative humidity of 0.24 for kaolinite-rich soil, 0.31 for illite-rich or mixed clay soils, 0.34 for smectitic soil and 0.30 for organic matter-rich soil. For smectite-rich soil, the value of 0.34 differed markedly from the value of 0.47 suggested previously. Considering all samples investigated, the GAB model provided reasonable estimates of SA when compared with SA obtained with the EGME method. However, for kaolinitic soil, the BET equation still provides the best measure of SA among all the methods evaluated. Based on the above, we conclude that to estimate the SA of natural soil samples, the GAB model provides a good alternative to the TO model (which is applicable to adsorption data only) or the BET model (which fails as the fraction of swelling clay minerals in soil increases). The average  $a_w$  values obtained for  $M_{0G}$  will facilitate easier and more accurate estimation of SA from the one-point method based on the dominant clay mineralogy. Another consideration is that this study opted for the EGME method as the standard measure of SA and these conclusions are based on that. However, several studies have reiterated the challenges and limitations of the EGME method and present a strong case for moving towards the use of water as the probe molecule for SA measurements of soil and pure clay samples.

## Supporting Information

The following supporting information is available in the online version of this article:

**Table S1.** Particle size distribution and organic carbon content of soil samples.

**Figure S1.** Boxplots of water activity values at which the GAB model evaluates the monolayer parameter for four groups of soils (kaolinite-rich, illite-rich and mixed clay, smectite-rich soils, and soils rich in organic carbon from 3 to 30.9%) for adsorption (A) and desorption (D) data. [A0.93 and D0.93] and [A0.80 and D0.80] represent adsorption and desorption based on a water activity range of 0.03–0.93 and 0.10–0.80, respectively. Values on top of boxes represent median water activity values for each soil group.

**Figure S2.** Scatter plots showing comparison of specific surface area (SA) estimated from Tuller–Or model with the Guggenheim–Anderson–Boer (GAB) estimate from adsorption ( $GAB_a$ ) and desorption ( $GAB_d$ ) and the BET, Brunauer–Emmett–Teller, estimate from adsorption ( $BET_a$ ) and desorption ( $BET_d$ ).

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