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 m² g⁻¹), 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 (m² g⁻¹), 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 m² g⁻¹ in sandy soil to more than 200 m² g⁻¹ in smectitic soil. The SA of soil often comprises ‘external’ and ‘internal’ surfaces depending on the dominant clay mineral.
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) (Yuksel & 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 N₂ or CO₂ (Kim et al., 2016) or polar molecules such as water (Cerato & Lutenegger, 2002), ethylene glycol, methylene blue (Hang & Brindley, 1970) or ethylene glycol monoethyl ether (EGME) (Cerato & Lutenegger, 2002). Large non-polar molecules such as N₂ 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 (SAEGME). 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 m² g⁻¹ to about 200 m² g⁻¹. (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 N₂ adsorption, is one approach for estimating SA from water sorption (Quirk, 1955). In general, the SA from BET modelling (SA_BET) of water sorption data is similar to SAEGME for non-swelling soil (e.g. Akin & Likos, 2014). For swelling soil, however, SA_BET is smaller than SAEGME 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 m² g⁻¹. 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) 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
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).

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, m² 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, 𝜈 (m H₂O) and SA as:

\[ M = \sqrt[6]{\frac{A_{svl}}{6\pi\rho_w g \gamma \psi}} \cdot SA_{TO}, \]  

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

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

\[
M = \frac{M_{\text{GG}} C_B a_w}{\left(1 - a_w \right) \left(1 - a_w + C_B a_w\right)},
\]

where \( M_{\text{GG}} \) is the soil water content at monolayer coverage (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.

\[
M = \frac{M_{\text{GG}} C_G K a_w}{\left(1 - K a_w \right) \left(1 - K a_w + C_G K a_w\right)},
\]

where \( M_{\text{GG}} \) (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 \( K = 1 \), the GAB equation reduces to the BET equation and \( M_{\text{GG}} = M_{\text{GG}} \) 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, \( M_{\text{GG}} \), \( C_G \) 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 \( S_{\text{TO}} \) as a direct parameter estimate, the GAB and BET equations give \( M_{\text{GG}} \) and \( M_{\text{GG}} \), respectively, which were used to calculate \( S_{\text{BET}} \) and \( S_{\text{GAB}} \) from Equation (4) (Newman, 1983; Quirk & Murray, 1999) for adsorption and desorption (\( S_{\text{BETa}}, S_{\text{BETd}}, S_{\text{GABa}} \) and \( S_{\text{GABd}} \)):

\[
S_{A} = \frac{M_{\text{GG}}}{w_a},
\]

where \( M_0 \) is the monolayer water content (kg kg\(^{-1}\)) from either the GAB or BET equation, \( N \) is Avogadro’s number (\( 6.02 \times 10^{23} \) mol\(^{-1}\)), \( A \) is the area covered by one water molecule \((10.8 \times 10^{-20} \text{ m}^2)\) and \( w_a \) is the molecular weight of water (0.018 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 \( M_{\text{GG}} \), 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 \( M_{\text{GG}} \) 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 (\( S_{\text{TO}}, S_{\text{BET}} \) and \( S_{\text{GAB}} \)) with \( S_{\text{EGME}}, \) two indices were used (root-mean squared error (RMSE) and the mean error or bias (ME)).

\[
\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left(S_{\text{X}} - S_{\text{EGME}}\right)^2},
\]

\[
\text{ME} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left(S_{\text{X}} - S_{\text{EGME}}\right)},
\]

where \( S_{\text{X}} \) 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 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 m\(^2\) g\(^{-1}\) for matric potential ranges from -10 to -200 MPa and -10 to -470 MPa, respectively. The GAB and BET equations fitted the measured data well, with average RMSE and \( R^2 \) values of 0.0005 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
Cinthemultilayerresultsinanmuchlargerentropiccontentofmobilityofwatermoleculesinthebulkliquidcomparedwiththattheotherhand,thegreatlyincreasednumberofconfigurationsand
Ksuggests.Ingeneral,thoseinthemultilayer,whichiscontrarytowhattheBETequation
moleculeswithinsubsequentmultilayersischangesthenumberofconfigurationssothatthe
liquidbecomennegligible.

The difference between the molecules in the monolayer and the bulk
aregroupedtogetherinamultilayer,andequationiscloseruntounityasthe
valuesofCB,GandKparametersarelargerforadsorptionthandesorption.(Prost
1998; Sabard et al., 2012).LargeCvaluesindicatethatwaterismoresignificantly
inentalphaboundintheominolayer,andthedifferenceinentalphabound
betweenthemonomoleculesandthesubsequent
islarger. Forsamplesinvestigated,thecvaluesofCB
werelessthanCGetfordesorptionCB∼1.5×CGforCB
values≤100. Thisobservation,asnotedbyAkin&Likos(2017),
isduetotheinclusionoftheparameterKintheGABequation,
whichcompensatesforthefactthatthesorptionenergybeyond
themonomlayerissmallerthanthatofliquefaction.Thesmaller
interactionentalphabythemultilayermoleculeswiththesorbent
suggeststhatKhasasmallerenthalpichowthanCGetfordesorption
values.C(Quirijns et al., 2005). ThevalueofKreducesasmolecules
aregroupedtogetherinatemultilayer,andequaleasunityasthe
differencebetweenthemoleculesintheominolayerandthebulk
becomesnegligible.

ForallsamplesexaminedK<1,indicatingthatthewater
moleculeswithintheominolayerweremorestronglybound
thanthoseintheultilayer,whichiscontrarytowhattheBETequation
suggests.Ingeneral,Kincreaseswithincreasingstrengthof
interactionbetweenthesorbentandsorbate. TheKvalues
larger(0.52to0.99)foradsorptionthanfordesorption(0.43to
0.97),andreflectedtheprevalingclaymineralogyinthesoil
samples. Forexample, theKvaluesobtainedfromdesorption
averaged(±SE)0.56±0.005,0.62±0.005and0.84±0.015
samplesdominatedbysmectite,illiteandmixedclays,andaluminos
ites,respectively. Fordifferentkaolinite-bentonitemixtures,Akin
&Likos(2017)reportedKvaluesof∼0.88for100%kaolinite,
whichdecreasedto∼0.52when20–100%bentonitewasadded.
A similar trend was observed for a part of this dataset in Arthur
(2016), where larger K values for kaolinite-dominated soils were
attributedtotheirsmallersurfaceareascomparedwithsmectite
claysand, consequently, stronger interactions between sorption
sitesandwatermolecules.Moreover, thelargeKvalues(ashigh
0.99)forkaolinics saltsuggeststhattheassumptionsmadeinthe
BETmodelareapplicabletoacertainextentforsolidsdominated
bykaoliniteclays.

Range of water activity and GAB parameters
The effect of therangeinawofmeasuredsorptionisothermson
themagnitudeoftheGABparametersforbothadsorptionanddesorption
ispresentedinFigure3.Forbothsorptiondirections,M0G
largerforthe0.10to0.80rangeinawthanforthe0.03to0.93range,
withalargerdifferenceobservedforadsorptionthandesorption.
Inaddition, theCGandKparametersforadsorptionwerelargerfor
the0.03to0.93rangeinawthanforthe0.10to0.80range. For
desorption, CG and Kdid not differ markedly for the tworanges
ofaw. These observations suggestthat for adsorption, themeasurement
rangeofawmighthaveconsiderableeffectonthemagnitude
oftheGABparametersobtained,whereasthisisnotthecase
for desorption. For somesoilsoflyclay materials, theadsorption
isothermisanotalwaysreproduciblebecausesensitivitytoini
watercontent,presenceofhydrophobicsubstancesandthefact
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 \(M_{0B}\) and \(M_{0G}\) parameters represent the approximate monolayer water content \(w_m\). For the desorption isotherms \((0.03–0.93, a_w)\) of the soil samples investigated \(M_{0B} = 0.73 \times M_{0G}\). The \(M_{0B}\) values ranged from 0.0014 to 0.0810 g g\(^{-1}\) and from 0.0016 to 0.0872 g g\(^{-1}\) for adsorption and desorption, respectively. For \(M_{0G}\), the range was from 0.0014 to 0.1002 and 0.0021 to 0.1186 g g\(^{-1}\) for adsorption and desorption, respectively (Figure 4). The larger values of \(M_{0G}\) compared with \(M_{0B}\), 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 \(M_{0G}\) 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 \(a_w = 0.47\) (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, \(M_{0B}\) and \(M_{0G}\) 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 \(M_{0B}\) 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 \(M_{0B}\), regardless of sorption direction (Figure 4b). Previous studies (Akin & Likos, 2014; Khorshidi et al., 2017) have shown that for soils with swelling clay minerals, \(M_{0B}\) 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 \(M_{0B}\) represented \(w_{0.47}/1.7\) accurately regardless of clay mineralogy. Conversely, \(M_{0G}\) 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 \(M_{0G}\) values less than 0.03 g g\(^{-1}\).

Table 2 Relations between Brunauer–Emmet–Teller (BET) and Guggenheim–Anderson–Boer (GAB) monolayer parameters \((M_{0B}\) and \(M_{0G}\)) 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.

<table>
<thead>
<tr>
<th></th>
<th>(w_{0.20}) (x)</th>
<th>(w_{0.47}/1.7) (x)</th>
<th>(w_{0.47}) (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(M_{0B})</td>
<td>0.99x; r = 0.98</td>
<td>1.05x; r = 0.99</td>
<td>0.62x; r = 0.99</td>
</tr>
<tr>
<td>(M_{0G})</td>
<td>1.20x; r = 0.97</td>
<td>1.27x; r = 0.99</td>
<td>0.75x; r = 0.99</td>
</tr>
<tr>
<td>Desorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(M_{0B})</td>
<td>0.92x; r = 0.99</td>
<td>1.03x; r = 0.99</td>
<td>0.61x; r = 0.99</td>
</tr>
<tr>
<td>(M_{0G})</td>
<td>1.26x; r = 0.99</td>
<td>1.40x; r = 0.99</td>
<td>0.82x; r = 0.99</td>
</tr>
</tbody>
</table>

\(x\), water content at selected \(a_w\) values; \(r\), correlation coefficient.
Soil specific surface area derived from GAB model

Figure 4 The Brunauer–Emmet–Teller (BET) and Guggenheim–Anderson–Boer (GAB) monolayer parameters \( \left( M_{0B} \right. \) 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 \( \left( w_{0.47} / 1.7 \right) \). 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 (GABₐ) and desorption (GABₖ); BET, Brunauer–Emmet–Teller estimate from adsorption (BETₐ) and desorption (BETₖ). Values in the legend indicate RMSE, root mean squared error (m² g⁻¹), and ME, mean error or bias (m² g⁻¹), respectively.

**Effect of sorption direction and soil constituents on GAB-based \( aw₀ \)**

The soil clay mineral composition affects \( aw₀ \), and the trends shown in Figure 4(b) and Table 2 suggest that for the majority of samples, \( M_{6G} \) is larger than \( w_{0.20} \), but smaller than \( w_{0.47} \). To evaluate further the approximate \( aw₀ \) for the soil samples based on \( M_{6G} \), boxplots depicting the \( aw₀ \) 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, \( aw₀ \) ranges from 0.15 to 0.34. As expected, kaolinite-rich samples had the smallest median \( aw₀ \) (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 \( aw₀ \) 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 \( aw₀ \) 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 \( aw₀ \) remained the same. More detail on \( aw₀ \) values for the four soil groups for the two \( aw₀ \) ranges discussed above is provided in Figure S1 (Supporting Information).
for the same mineral was 0.18 g g$^{-1}$.

Based on this, Newman (1983) showed that a water sorption-based approximation of monolayer cover for kaolinitic samples as suggested previously, and (ii) the GAB model evaluates a $w_0$ 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 g g$^{-1}$ and the assumption that a molecule of water covers 10.8 $\times$ 10$^{-20}$ m$^2$. Based on this, Newman (1983) showed that a water sorption-based calculation of SA of 798 m$^2$ g$^{-1}$ for the clay mineral was in accord with the SA (780 to 800 m$^2$ 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 g g$^{-1}$, similar to that reported by Mooney et al. (1952). However, the $M_{ad}$ obtained for the same mineral was 0.18 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 $N_2$ or $CO_2$ 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$_{GAB}$ 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$_{TO}$, SA$_{GABA}$, SA$_{GABd}$, SA$_{BETa}$ and SA$_{BETd}$) 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$_{GAB}$. For kaolinite-rich samples, SA$_{TO}$ consistently overestimated SA$_{GAB}$ (Figure 6a). The SA$_{GAB}$ estimates were better than SA$_{TO}$, but also showed some differences from the measured data (Figure 6b). The SA estimates based on BET were generally in accord with SA$_{GAB}$, although 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$_{BET}$ corresponds to SA$_{GAB}$ to a considerable degree.

For samples where the clay mineral was illite or a mixture of minerals, SA$_{TO}$ was similar to SA$_{GAB}$ (Figure 6d). The majority of the studies that have applied the TO model ($A_{ad} = -6$ $\times$ 10$^{-20}$ 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

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**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.

<table>
<thead>
<tr>
<th>SA estimate ($y$)</th>
<th>Indicator</th>
<th>SA$_{EGME}$ ($x$)</th>
<th>SA$_{TO}$ ($x$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA$_{TO}$</td>
<td>RMSE</td>
<td>17.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ME</td>
<td>5.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LR Equation</td>
<td>$y = 0.82x + 15.5$; $R^2 = 0.93$</td>
<td></td>
</tr>
<tr>
<td>SA$_{GABA}$</td>
<td>RMSE</td>
<td>17.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ME</td>
<td>-7.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LR Equation</td>
<td>$y = 0.80x + 3.71$; $R^2 = 0.94$</td>
<td>$y = 0.95x - 11.6$; $R^2 = 0.95$</td>
</tr>
<tr>
<td>SA$_{GABd}$</td>
<td>RMSE</td>
<td>19.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ME</td>
<td>11.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LR Equation</td>
<td>$y = 0.99x + 12.4$; $R^2 = 0.93$</td>
<td>$y = 1.18x - 7.32$; $R^2 = 0.97$</td>
</tr>
<tr>
<td>SA$_{BETa}$</td>
<td>RMSE</td>
<td>25.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ME</td>
<td>-13.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LR Equation</td>
<td>$y = 0.66x + 6.10$; $R^2 = 0.95$</td>
<td>$y = 0.76x - 5.52$; $R^2 = 0.96$</td>
</tr>
<tr>
<td>SA$_{BETd}$</td>
<td>RMSE</td>
<td>20.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ME</td>
<td>-5.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LR Equation</td>
<td>$y = 0.72x + 10.4$; $R^2 = 0.93$</td>
<td>$y = 0.86x - 3.59$; $R^2 = 0.98$</td>
</tr>
</tbody>
</table>

SA subscripts: TO, estimate from Tuller–Or model; GAB, Guggenheim–Anderson–Boer (GAB) estimate from adsorption (GABA) and desorption (GABd); BET, Brunauer–Emmet–Teller estimate from adsorption (BETa) and desorption (BETd). RMSE, root mean squared error (m$^2$ g$^{-1}$); ME, mean error or bias (m$^2$ g$^{-1}$); LR, linear regression.
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 SAEGME; there was some under- and over-estimation for SAGABa and SAGABd, respectively (Figure 6e). In general, SABET underestimated SAEGME 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, SAGAB provided the best estimate of SAEGME compared with SABET, which underestimated SAEGME. The underestimation of SA by the BET equation for swelling clay samples was expected because the equation is only applicable for the BET equation for swelling clay samples was expected because the equation is only applicable for the shape of the isotherm (Khorshidi et al., 2017). Further comparisons of SATO on the one hand and SAGABA, SAGABD, SABETa and SABETd on the other were carried out for the whole dataset together and are presented in Table 3 and in Figure S2. Both GAB estimates were in accord with SATO, whereas the BET estimates were generally smaller than SATO.

Conclusions and perspectives

In this study we evaluated the potential applicability of the Guggenheim–Anderson–de Boer (GAB) equation monolayer parameter \(M_{\infty} \) 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, \(M_{\infty}\) 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 \(M_{\infty}\) 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 Fuller–Or model with the Guggenheim–Anderson–Boer (GAB) estimate from adsorption \(GABa\) and desorption \(GABd\) and the BET, Brunauer–Emmet–Teller, estimate \(BETa\) and desorption \(BETd\).

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References


