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# Organic manure and lime change water vapour sorption of a red soil by altering water repellency and specific surface area

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**Abstract**

Manure and lime as fertiliser and conditioner are widely used on red soils to improve soil fertility and to alleviate soil acidity. Investigating the effects of these compounds on soil interfacial properties is very important for understanding some physical, chemical, and biological processes that are often overlooked. Using a long-term field experiment (2002–2018) on a red loamy clay soil, we explored how the soil water vapour sorption isotherm, soil organic carbon (SOC), pH, cation exchange capacity (CEC), specific surface area (SSA), and water repellency (WR) interacted and were affected by low-rate pig manure (LM, 150 kg N ha$^{-1}$ year$^{-1}$), high-rate pig manure (HM, 600 kg N ha$^{-1}$ year$^{-1}$), and high-rate pig manure with lime (HML). The HML only increased soil pH relative to the HM. The SSA determined with $N_2$ ($SSA_{N2}$) showed a significant negative correlation with SOC. Both SSA determined with $H_2O$ ($SSA_{H2O}$) and contact angle (CA) were significantly positively correlated with SOC. Manure amendments increased soil water content change (WCC) in the water activity ($a_w$) range of 0.05–0.2 ($WCC_{0.05–0.2}$) by 6.3–30.2%, but decreased $WCC_{0.2–0.6}$ and $WCC_{0.6–0.93}$ by 5.1–12.5% and 2.8–7.0%, respectively. Local hysteresis became more pronounced with high manure or high manure with lime amendment in the intermediate $a_w$ range (0.45–0.75). The observed changes of water vapour sorption were attributed to the alteration of SOC affecting SSA and WR.

**HIGHLIGHTS**

- Manure effects on soil water vapour sorption depended on sorption stage and direction.
- Manure with lime treatment did not affect soil interfacial properties relative to manure treatment.
- Increasing manure application increased local hysteresis at the intermediate $a_w$ range (0.45–0.75).
- Soil water vapour sorption behaviour was linked to SOC, SSA, and WR.

**KEYWORDS**

contact angle, hysteresis, soil organic carbon, specific surface area, water vapour sorption

  

## 1 | INTRODUCTION

Agricultural soils in tropical regions are far more susceptible than soils in other parts of the globe to carbon mineralization and its knock-on impacts to a range of important soil properties. This is particularly the case for red soils, which are heavily weathered soils rich in iron oxides that have low cation exchange capacity (CEC), low pH, poor fertility, and are prone to erosion (Yang et al., 2020). These soils are dominant in tropical and subtropical regions across the globe, so their management to improve nutrient and water retention is extremely important for global food security. Organic matter management is one approach to improve soil fertility and water retention in red soils, achieved through practices such as the incorporation of manures. These inputs can: (a) increase soil organic carbon, nutrient retention, and grain yield (Liu et al., 2011; Zhou et al., 2013); (b) reduce soil acidification (Zhang et al., 2013); and (c) increase aggregate stability and alter the three-dimensional microstructure of macro-aggregates (Zhou et al., 2013). Improving these properties of red soils can increase their resilience to very large seasonal soil moisture fluctuations and high temperatures by mediating arid conditions that exacerbate plant water stress and structure destabilisation.

Under arid conditions when soils have low water content, the soil–water interaction can be quantified by the soil water vapour sorption isotherm (SWSI) (Or & Wraight, 2000). Knowledge of the SWSI is very helpful for simulations of the processes of water vapour flow and volatile organic compound transport in arid environments (Schneider & Goss, 2012). Moreover, the SWSI can improve the general understanding of mechanical processes such as swelling and shrinkage and strength-deformation (Akin & Likos, 2017; Lu, 2019). Factors affecting soil water vapour sorption behaviour include soil properties, ambient temperature, and sorption direction. Soil water vapour sorption capacity increases with increasing soil clay content, SSA, and CEC (Chen et al., 2021). Clay mineralogy can affect soil water vapour sorption process: for example, water molecules can enter the crystalline structure of montmorillonite but cannot enter the crystalline structure of kaolinite during the soil water vapour sorption process (Lu & Khorshidi, 2015). An increase of SOC may increase the amount of hydrophilic oxygen-containing functional groups in soil (e.g., carboxylic, phenolic hydroxyl, and amino groups), and further increase soil water vapour sorption capacity (Arthur et al., 2020). In addition, increased SOC may mask a portion of soil particle surfaces through aggregation, and increase soil water repellency due to greater hydrophobic functional groups (Hallett et al., 2001; Kaiser & Guggenberger, 2003) that decrease soil water vapour sorption capacity (Chen et al., 2018). Thus, the effect of SOC on soil water vapour sorption is uncertain. Schneider and Goss (2011) found an increasing temperature dependence between 5 and 40°C of the SWSIs with increasing dryness. The SWSI has hysteresis between the adsorption and desorption branches of the sorption isotherm (Prunty & Bell, 2007). The magnitude of hysteresis depends on soil clay content, clay minerals, CEC, SOC, and soil water repellency (Arthur et al., 2020; Davis et al., 2009; Zhuang et al., 2008).

A new Vapour Sorption Analyser (VSA) (METER Group, Inc., Pullman, USA) can quickly and automatically obtain highly detailed SWSIs, and provide great potential to understand interfacial processes governing water transport and retention (Arthur et al., 2014). Using the VSA on a temperate sandy loam soil, Arthur et al. (2015) investigated the effects of manure on SWSI. As this study was limited to 2 years of amendment and one field replicate, it was difficult to clarify the effects of long-term manure application on soil water vapour sorption. Zhou et al. (2020) reported that 33 years application of pig or cow manure did not significantly increase soil water vapour sorption at $a_w < 0.75$ in an expansive soil (Vertisol). As the mineralogy of red soil is dominated by weakly swelling clay minerals, applied manure may have different effects on water vapour sorption behaviour. Additionally, the SWSIs can be divided into the three stages representing different sorption mechanisms: monolayer sorption, multilayer sorption, and capillary condensation (Chen et al., 2018). Due to the difference in soil–water interaction mechanisms, the input of manure may produce different effects on soil water vapour sorption at different stages. Lime as a soil acidity conditioner is also often applied to tropical red soils together with manure, which may also affect soil water vapour sorption by aggregating particles and decreasing the SSA (Haynes & Naidu, 1998). However, to our knowledge, the effects of long-term manure or manure with lime application on water vapour sorption of soils are unclear, with red soils having mineralogical properties that produce different SWSI behaviour than temperate soils. Such soils dominate in tropical regions, where SOC dynamics and impacts to soil water dynamics are the most important to understand due to poor structural stability and drought stress occurrence (Li et al., 2020; Zhou et al., 2013).

In this study, we hypothesised that manure or manure with lime amendments alter the properties of a red soil such as SOC, CEC, SSA, and water repellency (WR), which will impact its water vapour sorption behaviour at different stages. Thus, the objectives of this work are (a) to investigate the changes of water vapour sorption behaviour for a red soil after receiving long-term manure or manure with amendments, and (b) to identify the factors affecting its water vapour sorption behaviour.

## 2 | MATERIALS AND METHODS

### 2.1 | Experimental site, design, and sampling

A field experiment explored manure and lime amendments to a red soil at the Yingtan National Agroecosystem Field Experiment Station, Chinese Academy of Sciences, Yujiang Country, Jiangxi Province, China (28°15′20″N, 116°55′30″E). The experiment site has a typical subtropical climate, with a mean annual temperature of 17.6°C and precipitation of 1795 mm. The soil is classified as an Udic Ferralsols in the Chinese Soil Taxonomy and a Ferric Acrisol according to the FAO classification system. The soil is loamy clay with 36.3% clay, 42.5% silt, and 21.2% sand. The dominant clay minerals are kaolinite, hydromica, vermiculite, Fe/Al oxide, and chlorite, which accounted for 26%, 21%, 17%, 16%, and 14%, respectively.

The field experiment commenced in 2002 and had four treatments: (a) no amendment (Control); (b) low-rate pig manure (150 kg N $ha^{-1}$ $year^{-1}$, LM); (c) high-rate pig manure (600 kg N $ha^{-1}$ $year^{-1}$, HM); and (5) high-rate pig manure (600 kg N $ha^{-1}$ $year^{-1}$) and lime applied once every 3 years at 3000 kg $Ca(OH)_2$ $ha^{-1}$ (HML). Plots of 2 m × 2 m had the same slope, and were set up in a completely randomised design with three replicates. Since all the plots were laid out on flat ground, the influence between different plots was assumed to be negligible. The field was ploughed annually and planted with a maize monoculture (cultivar No. 11 from Denghai) from April to July, and left fallow for the remaining time. All aboveground and most belowground residues were removed after harvest each year. Sampling of the topsoil (0–15 cm) was done in July 2017 after the harvest of maize. Five soil cores were randomly collected with an auger in each plot and then pooled together to form a bulk sample. The bulk samples were air-dried, passed through a 2 mm sieve and stored for further analysis.

### 2.2 | Laboratory measurements and analysis

Basic soil properties were measured using approaches described by Lu (2000). Soil organic carbon (SOC) was determined by oxidation with potassium dichromate in a heated oil bath. Soil pH was determined using a glass electrode with a 1:2.5 soil:water ratio. The cation exchange capacity (CEC) was measured by the ammonium acetate method.

Soil–water contact angle (CA) was determined with a Sigma 700 Process Tensiometer (One Attension) using the capillary rise method (Ramírez-Flores et al., 2008). Five grams of air-dried soil samples were packed into a 15.2 mm diameter and 60 mm height stainless steel capillary tube fitted with a spring plunger that provided a consistent stress. Filter paper was placed at the porous base of the tube that came into contact with the wetting liquid when the stage was lifted on the process tensiometer. The contact angle was determined using the Washburn equation, using water and ethanol as the wetting liquids.

The SWSIs were determined with a fully automated AquaLab Vapour Sorption Analyser (METER Group, Inc., Pullman, USA). The instrument settings were: Dynamic Dewpoint Isotherm (DDI) mode, adsorption followed by desorption, $a_w$ range of 0.05–0.93, resolution of 0.02, air-flow rate of 100 mL $min^{-1}$, and temperature of 25°C. Approximately 3.0 g of air-dried sample was used in each measurement. After the isotherm measurements, samples were oven-dried at 105°C for 48 h to determine soil water contents. Soil specific surface area based on water vapour ($SSA_{H2O}$) was determined from the water vapour adsorption isotherm in water activity ($a_w$) range between 0.1 and 0.3 using the Brunauer–Emmett–Teller (BET) method. SSA was also measured using nitrogen ($SSA_{N2}$) with a specific surface area analyser (V-Sorb 2800P, Gold App Instruments, China). Air-dried soil samples were degassed at 150°C in $N_2$ flowing tubes prior to analysis. The $SSA_{N2}$ is directly calculated with the BET equation.

As the mineralogy of the red soil is dominated by weakly swelling clay minerals, interlayer sorption is unlikely to be the main mechanism for water vapour sorption. Here, we divided the measured water vapour sorption data into three $a_w$ ranges (0.05–0.2, 0.2–0.6, and 0.6–0.93), and calculated water content changes within each $a_w$ range ($WCC_{0.05–0.2}$, $WCC_{0.2–0.6}$, and $WCC_{0.6–0.93}$). Then, the WCCs during the adsorption and desorption process were used to evaluate the effects of manure and manure with lime amendments on soil water vapour sorption.

The local hysteresis of SWSIs at a given $a_w$ ($H_s$) could be quantified as the difference between the water content at the desorption ($M_d$) and adsorption ($M_a$) branches (Zhuang et al., 2008).

$$H_s = (M_d - M_a) \times 100 \quad (1)$$

In some cases, the measured data points on the desorption branch and the adsorption branch under a specific $a_w$ might not exist for the same $a_w$, so the $H_s$ was calculated at the selected water activity interval (0.05) based on local interpolation.

### 2.3 | Statistical analysis

To compare the differences in soil properties among different treatments, a one-way ANOVA analysis was conducted using IBM SPSS Statistics 25. Fisher's least significant difference (LSD) method was used for the multiple comparisons of means. A linear correlation analysis was performed between soil properties and selected variables. A significance level of 0.05 was used throughout the study unless stated otherwise. All data were normally distributed and did not require transformations.

## 3 | RESULTS

### 3.1 | SOC, pH, and CEC

Amending the red soil with manure and lime had an impact on a range of soil properties (Table 1). Compared with the Control, the LM treatment increased SOC by 72%, and the HM and HML treatments increased SOC by 116–128%. The LM treatment had no effect on soil pH. However, both HM and HML treatments increased soil pH relative to the Control, and the HML treatment had a more significant effect on increasing soil pH compared with the HM treatment due to the addition of lime. The HM and HML treatments significantly increased CEC relative to the Control (Table 1), but LM showed no impact.

### 3.2 | Water vapour sorption and hysteresis

Manure amendment, but not lime, had a large impact on water vapour sorption (Figure 1). During water vapour adsorption and desorption processes, $WCC_{0.05–0.2}$ increased by 6.3–30.2%, but $WCC_{0.2–0.6}$ and $WCC_{0.6–0.93}$ decreased by 5.1–12.5% and 2.8–7.0%, respectively, for all manure treatments relative to the Control. Generally, no differences in the WCC were found among all manure treatments. These results suggest that manure amendments increased monolayer sorption, but decreased multilayer sorption and capillary condensation.

Figure 2 presents the $H_s$ of SWSIs at different water activity levels. Treatments HM and HML had no significant effect on the $H_s$ at $a_w < \sim 0.45$ and $a_w > \sim 0.75$. In the $a_w$ range between ~0.45 and ~0.75, the LM treatment had no significant effect on $H_s$, but the HM and HML treatments significantly increased $H_s$. The largest difference of $H_s$ between the two high manure amendments (HM and HML) and the Control was ~0.12, and appeared at $a_w = \sim 0.65$.

### 3.3 | Specific surface area

The SSAs determined by nitrogen ($SSA_{N2}$) and water vapour ($SSA_{H2O}$) are shown in Figure 3. Generally, manure amendments decreased $SSA_{N2}$ but increased $SSA_{H2O}$. Specifically, the LM, HM, and HML treatments decreased $SSA_{N2}$ by 5.8–13.5%, and increased $SSA_{H2O}$ by 12.4–18.2% relative to the Control. The $SSA_{H2O}$ values were always larger than $SSA_{N2}$ values regardless of manure or manure with lime treatment. The difference between $SSA_{H2O}$ and $SSA_{N2}$ was smallest (22.0%) for the Control, and the differences between $SSA_{H2O}$ and $SSA_{N2}$ ranged from 45.5% to 66.8% for the LM, HM, and HML treatments.

### 3.4 | Contact angle

Soil–water CA values for the four different treatments varied between 59.8° and 81.2°. Manure amendments significantly increased CA by 26.8–35.8% compared with the Control (Table 1), with no differences found among LM, HM, and HML.

**TABLE 1** Soil organic carbon (SOC), pH, cation exchange capacity (CEC), soil–water contact angle (CA) for no amendment (control), 150 kg N $ha^{-1}$ $year^{-1}$ pig manure (LM); (3) 600 kg N $ha^{-1}$ $year^{-1}$ pig manure (HM), 600 kg N $ha^{-1}$ $year^{-1}$ pig manure and lime applied once every 3 years at 3000 kg $Ca(OH)_2$ $ha^{-1}$ (HML)

| Treatment | SOC (g $kg^{-1}$) | pH | CEC (cmol $kg^{-1}$) | CA (degree) |
|---|---|---|---|---|
| Control | 4.3 ± 0.5c | 4.8 ± 0.1c | 14.5 ± 0.6b | 59.8 ± 5.3b |
| LM | 7.4 ± 0.4b | 4.8 ± 0.0c | 15.0 ± 0.2b | 75.8 ± 4.7a |
| HM | 9.8 ± 0.6a | 5.8 ± 0.1b | 16.9 ± 0.4a | 81.2 ± 3.1a |
| HML | 9.3 ± 0.6a | 6.6 ± 0.0a | 16.5 ± 1.0a | 80.5 ± 3.3a |

*Note*: Different letters following values in the same column indicate significant difference at the $p < 0.05$ level (LSD).

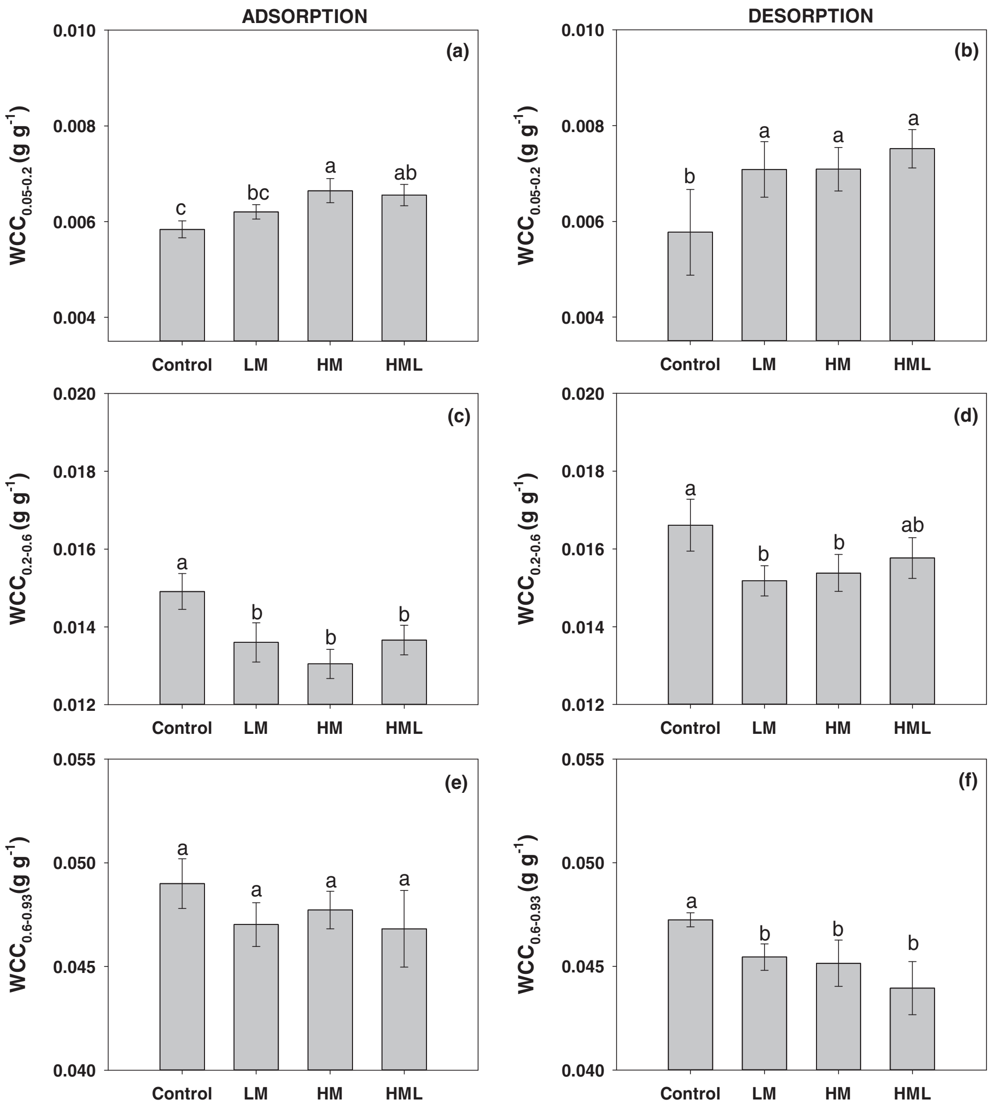


**FIGURE 1** Effects of manure amendments on water content changes ($WCC_{0.05–0.2}$, $WCC_{0.2–0.6}$, and $WCC_{0.6–0.93}$) at three different water activity ranges (0.05–0.2, 0.2–0.6, and 0.6–0.93) during adsorption and desorption process. Vertical bars denote the standard errors for means of each treatment (n = 3). Different letters above the bars indicate significant differences at $p < 0.05$. Control, no amendment; LM, 150 kg N $ha^{-1}$ $year^{-1}$ pig manure; HM, 600 kg N $ha^{-1}$ $year^{-1}$ pig manure; HML, 600 kg N $ha^{-1}$ $year^{-1}$ pig manure and lime applied once every 3 years at 3000 kg $Ca(OH)_2$ $ha^{-1}$

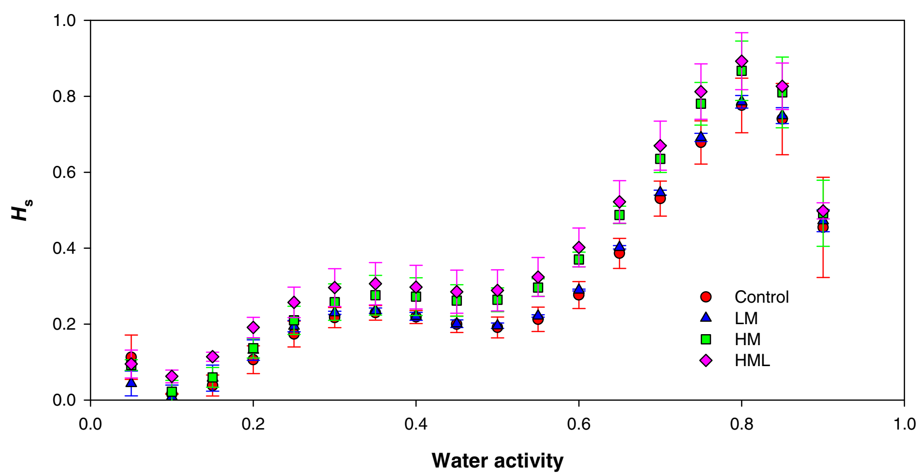


**FIGURE 2** The local hysteresis ($H_s$) values of soil water vapour sorption isotherms at 0.05 water activity interval for four different treatments. Control, no amendment; LM, 150 kg N $ha^{-1}$ $year^{-1}$ pig manure; HM, 600 kg N $ha^{-1}$ $year^{-1}$ pig manure; HML, 600 kg N $ha^{-1}$ $year^{-1}$ pig manure and lime applied once every 3 years at 3000 kg $Ca(OH)_2$ $ha^{-1}$. Bars denote the standard errors for means of each treatment ($n = 3$)

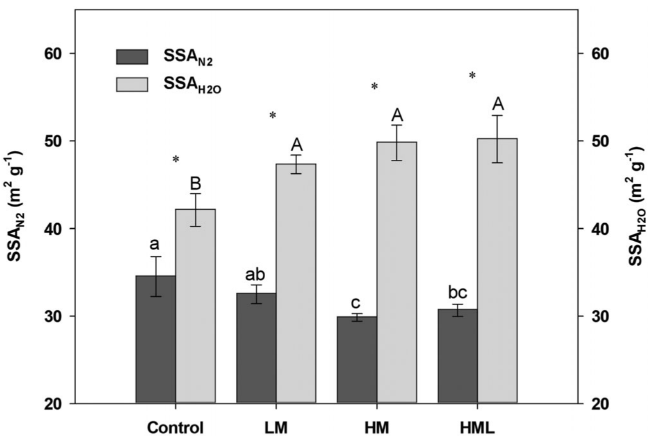


FIGURE 3 Effects of manure amendments on soil specific surface areas determined by nitrogen ($SSA_{N2}$) and water vapour ($SSA_{H2O}$). Vertical bars denote the standard errors for means of each treatment ($n = 3$). Different letters above the bars indicate significant differences at $p < 0.05$. Asterisks indicate a significant difference between $SSA_{H2O}$ and $SSA_{N2}$ for the same treatment at $p < 0.05$. Control, no amendment; LM, 150 kg N $ha^{-1}$ $year^{-1}$ pig manure; HM, 600 kg N $ha^{-1}$ $year^{-1}$ pig manure; HML, 600 kg N $ha^{-1}$ $year^{-1}$ pig manure and lime applied once every 3 years at 3000 kg $Ca(OH)_2$ $ha^{-1}$

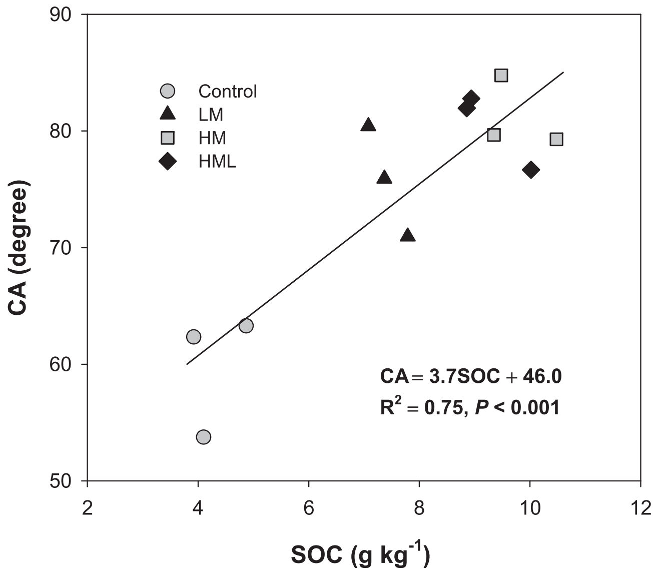


FIGURE 4 Relationship between contact angle (CA) and soil organic carbon (SOC) content

## 4 | DISCUSSION

### 4.1 | Effects of manure amendments on SOC, CEC, and pH

In red soil, the application of pig manure at the rate of 150 kg N $ha^{-1}$ $year^{-1}$ increased SOC and CA, and at a high dose of 600 kg N $ha^{-1}$ $year^{-1}$ increased SOC, pH, CEC, and CA. Various studies on organic matter incorporation to red soils also reported that SOC increased markedly, as did CEC and pH (Cheng et al., 2021; Li et al., 2020; Liu et al., 2020; Zhou et al., 2013). In this study, low-rate manure application had no significant effect on CEC and pH, likely because, unlike HM and HML, it was insufficient to overcome inherent properties of the soil. A simulated acidification experiment for soils amended by long-term manure application suggested that the release of exchangeable base cations and the protonation of organic anions are the reasons why long-term manure application increased soil pH (Shi et al., 2019). Additionally, the pH of pig manure used in this field experiment was in the range of 7.1–8.5, so the direct application of manure could neutralise soil acidity and increase soil pH. Extensive studies in both temperate and tropical regions have shown lime application to increase SOC, CEC, and pH (Haynes & Naidu, 1998), but we only observed a pH increase. It is possible that the addition of a high-dose pig manure masked the impact of lime on other soil properties. Ideally, a lime only treatment would have allowed for lime impacts to be investigated on their own. Our primary aim in selecting this field experiment, however, was access to multiple years of manure application on a red soil.

### 4.2 | Effects of manure amendments on contact angle and specific surface area

Soil water repellency reduces the affinity of soils to water, significantly affecting the retention and movement of water and solute in soils, soil structure, carbon sequestration, seed emergence and plant growth (Doerr et al., 2007). Manure amendments significantly increased soil water repellency as indicated by the CA (Table 1). The correlation analysis showed that CA had a significantly positive correlation with SOC (Figure 4), suggesting that the change of soil water repellency was caused by manure amendment increasing SOC. Previous studies also found that WR can be related to SOC (Hallett et al., 2001; Mataix-Solera & Doerr, 2004; McKissock et al., 1998). Sometimes CA and SOC can be poorly correlated (Hallett et al., 2001), but our high correlation might be because the dominant form of amended SOC was the same across treatments.

The SSA plays an important role in many soil processes, including carbon sequestration, contaminant adsorption, ion exchange reactions, microbial attachment, water imbibition and drainage, and soil aggregation (Lu & Zhang, 2020; Pennell, 2002). The correlation analysis showed that $SSA_{N2}$ was negatively correlated with SOC (Figure 5a), as found by other studies (Kaiser & Guggenberger, 2003; Mayer & Xing, 2001; Pennell et al., 1995). It is possible that the organic matter coated the surface of clay minerals that had a greater surface area accessible to $N_2$ than the organic coating (Burford et al., 1964). Moreover, SOC may bind clay particles together to reduce their effective surface area (Feller et al., 1992). In contrast to $SSA_{N2}$, $SSA_{H2O}$ was positively correlated with SOC (Figure 5b). This disagreed with the increased WR measured for soils amended with manure. One reason might be that the SOC itself could adsorb water due to the presence of hydrophilic groups (Kirschbaum et al., 2020; Wang et al., 2011). When a polar molecule (e.g. ethylene glycol) was used to determine SSA, SOC also increased SSA due to the retention of polar molecules by SOC (Pennell et al., 1995). The $SSA_{H2O}$ was determined based on the monolayer water vapour sorption data, and cation hydration is an important mechanism for monolayer sorption (Chen et al., 2021). The correlation analysis showed that the CEC had a positive correlation with SOC ($r = 0.85$, $p < 0.01$). Thus, the increased CEC might be another reason for the positive correlation between $SSA_{H2O}$ and SOC.

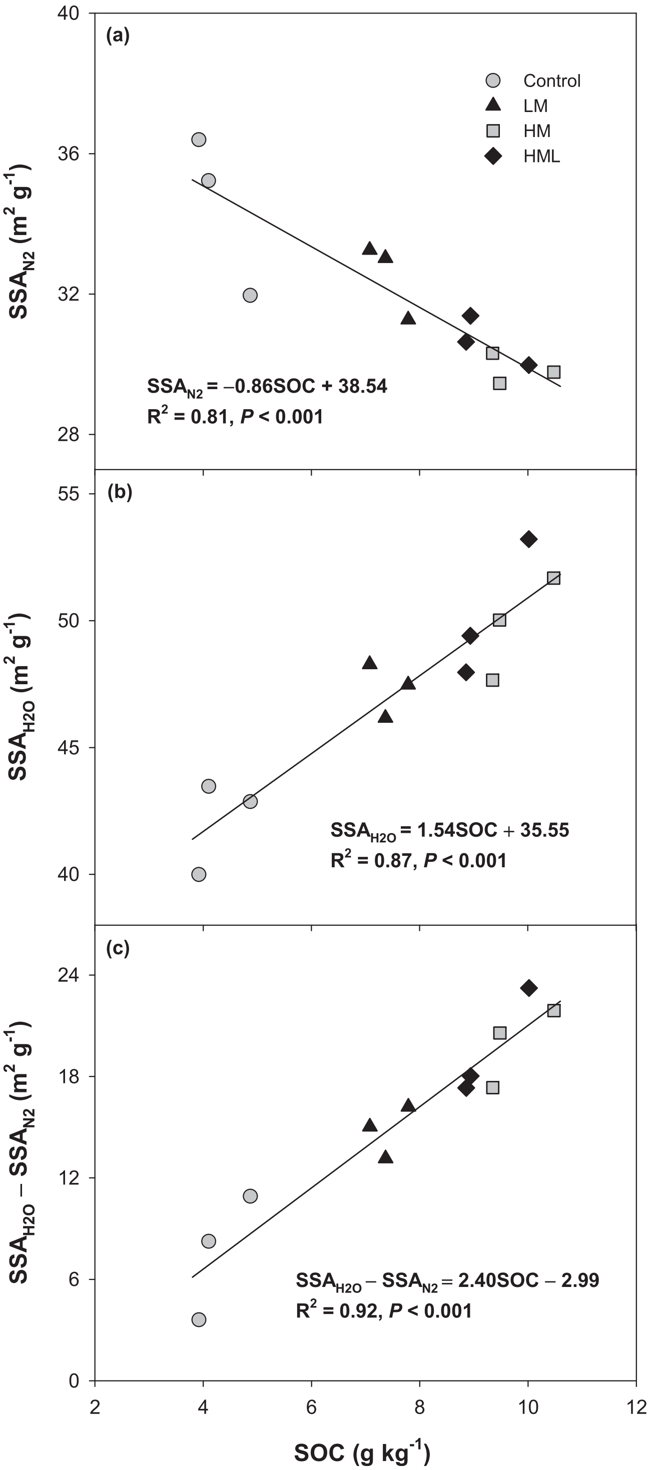


FIGURE 5 Relationships between soil organic carbon (SOC) content and specific surface areas determined by the $N_2$–BET method ($SSA_{N2}$) (a), or the $H_2O$–BET method ($SSA_{H2O}$) (b), or the difference between $SSA_{H2O}$ and $SSA_{N2}$ (c)

We found $SSA_{H2O}$ to be higher than $SSA_{N2}$, agreeing with previous studies (Arthur et al., 2013; Jong, 1999; Zhou et al., 2020). The retention of water molecules by SOC might be one reason for the higher $SSA_{H2O}$ values. Compared with $N_2$, water molecules are smaller and could diffuse into the interlayer surfaces and micropores of clay minerals (Arthur et al., 2013). As the red soils dominated by kaolinite/hydromica had poor swelling characteristics, the higher $SSA_{H2O}$ values might also be caused by the diffusion of water molecules into micropores.

The difference between $SSA_{H2O}$ and $SSA_{N2}$ was greater for manure treatments relative to the Control (Figure 2), and showed a positive correlation with SOC (Figure 5c). The retention of water by SOC and the decrease of mineral surface area might be the main reason for the larger difference between $SSA_{H2O}$ and $SSA_{N2}$ at high manure amendment. The difference between $SSA_{H2O}$ and $SSA_{N2}$ reflected the contribution of SOC to SSA, as $SSA_{N2}$ was affected mostly by the mineral surfaces, whereas $SSA_{H2O}$ was also likely affected by SOC. CA was correlated with SOC, the difference between $SSA_{H2O}$ and $SSA_{N2}$ ($r = 0.79$), and $SSA_{N2}$ ($r = -0.74$), suggesting interfacial properties at mineral surfaces driven by SOC controls WR. Zhou et al. (2020) reported that long-term pig or cow manure application decreased the $SSA_{H2O}$ in an expansive soil (Vertisol), and the difference between $SSA_{H2O}$ and $SSA_{N2}$ did not show a significant correlation with SOC. These results were inconsistent with the result of this study, but likely due to the type of clay minerals.

## 4.3 | Effects of manure amendments on water vapour sorption and hysteresis

Understanding the effects of manure amendments on soil water vapour sorption and its hysteresis are crucial for

TABLE 2 Correlation coefficients between water content changes (WCC) in three different $a_w$ ranges ($0.05 < a_w < 0.2$, $0.2 < a_w < 0.6$, and $0.6 < a_w < 0.93$) against each of soil organic carbon (SOC), cation exchange capacity (CEC), soil–water contact angle (CA), specific surface areas determined by the $N_2$–BET method ($SSA_{N2}$) or the $H_2O$–BET method ($SSA_{H2O}$), and the difference between $SSA_{H2O}$ and $SSA_{N2}$

| Direction | WCC | SOC | CEC | CA | $SSAN_2$ | $SSAH_2O$ | $SSAH_2O$-$SSAN_2$ |
|---|---|---|---|---|---|---|---|
| Adsorption | $WCC_{0.05–0.2}$ | 0.89** | 0.86** | 0.71** | −0.75** | 0.88** | 0.87** |
| | $WCC_{0.2–0.6}$ | −0.82** | −0.74** | −0.71** | 0.81** | −0.74** | −0.80** |
| | $WCC_{0.6–0.93}$ | −0.48 | −0.37 | −0.44 | 0.42 | −0.65* | −0.59* |
| Desorption | $WCC_{0.05–0.2}$ | 0.64* | 0.44 | 0.75** | −0.71** | 0.63* | 0.69* |
| | $WCC_{0.2–0.6}$ | −0.69* | −0.39 | −0.66* | 0.66* | −0.74** | −0.74** |
| | $WCC_{0.6–0.93}$ | −0.79** | −0.66* | −0.76** | 0.65* | −0.85** | −0.81** |

*Significant correlation at the 0.05 probability level.
**Significant correlation at the 0.01 probability level.

simulations of the processes of water vapour flow and volatile organic compound transport in arid environments (Schneider & Goss, 2012). Manure amendments increased monolayer sorption but decreased multilayer sorption and capillary condensation. The factors affecting monolayer water vapour sorption were the same as those of the $SSA_{H2O}$, so we do not discuss them here. The correlation analysis suggested that the $WCC_{0.2–0.6}$ and $WCC_{0.6–0.93}$ had negative correlations with SOC, CA, $SSA_{H2O}$, and $SSA_{H2O}$-$SSA_{N2}$ and a positive correlation with $SSA_{N2}$ (Table 2). This result implies that the decrease in the WCC at multilayer sorption and capillary condensation might be due to the increase in soil water repellency caused by manure amendments. For gas adsorption by porous materials, the mesopores (2–50 nm) play a very important role in the stages of multilayer adsorption and capillary condensation (Thommes, 2010). The coating of clay mineral surfaces with organic matter can reduce mineral SSA and clog soil pores (Kaiser & Guggenberger, 2003; Pennell et al., 1995). Thus, the lower WCC for soils with higher SOC content at multilayer sorption and capillary condensation stages could also arise from the interaction between organic matter and pores.

Previous studies reported water vapour sorption for soils with low clay content increased with increasing SOC content, but water vapour sorption for soils with high clay content had no significant relationship with SOC content (Arthur et al., 2015; Chen et al., 2014). However, we found that the increase of SOC produced different effects on soil water vapour sorption at different $a_w$ ranges in a red loamy clay soil. There are a couple possible reasons: (a) previous studies only considered the total amount of water adsorbed by soils at different $a_w$ conditions; or (b) our samples had different clay content and mineral types from studies in the literature that are dominated by soils from temperate climates.

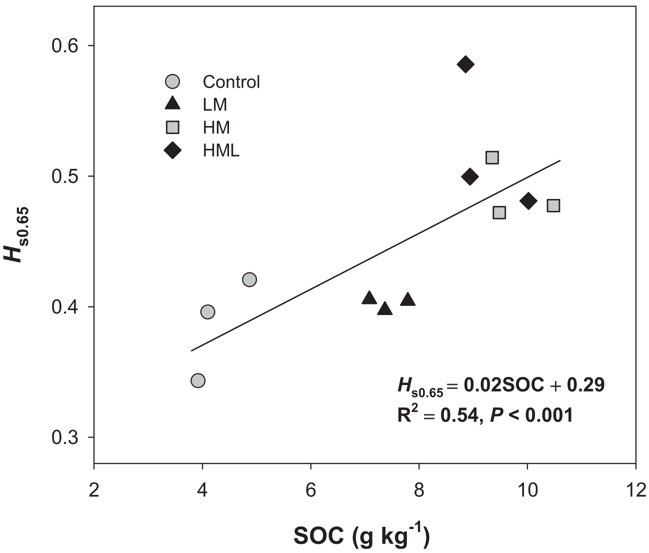


FIGURE 6 Relationship between local hysteresis of soil water vapour sorption isotherms at $a_w = 0.65$ ($H_{s0.65}$) and soil organic carbon (SOC) content

The hysteresis mechanism of SWSIs was due to the difference between the energy required for the desorption (heat of evaporation) and adsorption (heat of liquefaction) of water (Lu & Khorshidi, 2015). At low and high $a_w$ ranges, the high ratio of clay content to SOC (37–85) may have masked the effect of manure amendments on the differences between the heat of evaporation and the heat of liquefaction. Thus, the $H_s$ values did not differ greatly due to manure amendment rate or manure with lime. A significant positive correlation between $H_{s0.65}$ ($H_s$ value at $a_w = 0.65$) and SOC suggested that the change in $H_s$ at the intermediate $a_w$ range was due to the increase in SOC caused by manure amendments ($0.45 < a_w < 0.75$) (Figure 6). Previous research also reported that increased SOC leads to greater soil water vapour hysteresis (Zhuang et al., 2008). Arthur et al. (2020) speculated that this phenomenon might be due to the conformational changes in the structure of organic matter during the sorption process.

Thus, we confirmed that long-term manure applied to red soils affected soil water vapour sorption by altering SOC, SSA, and CA. What is less certain from our investigation was the impact of long-term manure on the soil pore size distribution, the difference between $SSA_{H2O}$ and $SSA_{N2}$, and correlation to CA suggests this is important. For red soils, amorphous Fe/Al oxides create nanopores (<50 nm) (Meng, 2014) that increase SSA (Zinn et al., 2017). Therefore, the aggregation and content of Fe/Al oxides and changes to smaller pores for manure amended red soils may also affect soil water vapour sorption. As the pore size distribution and the content of amorphous Fe/Al oxides were not measured in this study, further studies are needed to clarify their role in water vapour sorption for red soils after receiving long-term manure application.

## 5 | CONCLUSIONS

Long-term manure but not lime amendments affected water vapour sorption and associated soil properties in a red loamy clay soil. Lime only increased soil pH. Manure amendments increased monolayer sorption but decreased multilayer sorption and condensation. The HM and HML treatments significantly increased $H_s$ in the intermediate $a_w$ range (0.45–0.75). The changes in water vapour sorption behaviours were because manure amendments increased SOC, leading to increased WR and $SSA_{H2O}$, and decreased $SSA_{N2}$. The results of this study are very helpful for understanding the effects of long-term manure or manure with lime amendments on some processes in red soils, such as carbon sequestration, the retention and movement of water and solute, and soil structure change.

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## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available on request from the corresponding author.

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