Land Use and Soil Type Exert Strongly Interactive Impacts on the pH Buffering Capacity of Acidic Soils in South China

Jiayue Yang 1,2, Hui Wei 1,2,3,4, Jiaen Zhang 1,2,3,4,5,*, Zhaoji Shi 1,2, Hongru Li 1,2,3,4, Yanqiong Ye 1,2 and Ahmed Ibrahim Abdo 1,2

1 Guangdong Provincial Key Laboratory of Eco-Circular Agriculture, South China Agricultural University, Guangzhou 510642, China
2 Department of Ecology, College of Natural Resources and Environment, South China Agricultural University, Guangzhou 510642, China
3 Guangdong Engineering Technology Research Centre of Modern Eco-Agriculture and Circular Agriculture, South China Agricultural University, Guangzhou 510642, China
4 Key Laboratory of Agro-Environment in the Tropics, Ministry of Agriculture and Rural Affairs, South China Agricultural University, Guangzhou 510642, China
5 Guangdong Laboratory for Lingnan Modern Agriculture, Guangzhou 510642, China
*
Correspondence: jeanzh@scau.edu.cn; Tel.: +86-20-8528-5505

Abstract: Soil acidification is a severe environmental problem around the world. Soil pH buffering capacity (pHBC) is the intrinsic factor affecting the soil acidification rate and is intensively impacted by anthropogenic and natural conditions. However, composite assessments of the effects of land use and soil type on soil pHBC are still limited. Therefore, we collected samples of five soil types (red soil, lateritic red soil, latosol, paddy soil and acid sulphate soil) from two land use patterns of agricultural and adjacent forest fields at different depths (0–10 cm, 10–20 cm and 20–30 cm) in South China, aiming to investigate the effects of land use and soil type on soil pHBC in this region. The results show that land use, soil type and their interactions greatly influence soil pHBC and physico-chemical properties. Forest soils have a significantly higher pHBC (11.40–49.50 mmol·kg\(^{-1}\)·unit\(^{-1}\) pH), cation exchange capacity (CEC), exchangeable Al\(^{3+}\) (EAl\(^{3+}\)) and clay content than agricultural soils. Acid sulphate soil has the highest pHBC (49.27–117.83 mmol·kg\(^{-1}\)·unit\(^{-1}\) pH) values and exchangeable acid (EA) content among all investigated soil types, whereas lateritic red soil has the lowest pHBC (10.56–31.71 mmol·kg\(^{-1}\)·unit\(^{-1}\) pH). In agricultural fields, soil pHBC is positively related to CEC, soil organic carbon (SOC) and EA, indicating that agricultural soils may be in a cation exchange buffering stage. The soil pHBC of forest fields is positively correlated with SOC and EAl\(^{3+}\), implying that forest soils may be in the Al buffering stage. In conclusion, soil pHBC would vary with different land use forms and soil types, in which a series of key complex physico-chemical processes and interactions would occur to regulate soil pH buffering capacity.

Keywords: aluminum buffering; soil organic carbon; pH buffering capacity; soil acidification; soil texture

1. Introduction

With the development of modern industry and agriculture, soil acidification, resulting from acid/nitrogen deposition [1,2], land-use change [3,4] and the abuse of chemical fertilizer [5,6], has become a representative environmental problem around the world. Soil acidification causes intensive soil nutrient leaching and an increase in heavy metal activity, as well as affecting biodiversity, biogeochemical cycling of soil elements and pedogenesis and, ultimately, altering the structure and function of the terrestrial ecosystem [7–9]. Therefore, investigating the effects of environmental factors on soil acidification and controlling their mechanisms are imperative issues.

The extent of soil acidification is controlled by the coordinated regulation of environmental acid input and the intrinsic pH buffering capacity (pHBC) of soils [10,11]. However,
while numerous studies have focused on the effects of acid input, few have examined the contribution of soil pHBC to soil acidification under different environmental conditions [12]. The pHBC is a natural characteristic in soils, varying with soil physicochemical properties and mineralogy [13,14]. Previous studies have indicated that soil pHBC is greatly affected by several indicators, such as initial pH, cation exchange capacity (CEC), carbonate content and the composition or distribution of aluminum (Al)-bearing minerals [5,15,16]. Therein, soil pH seems to function as an important indicator determining soil pH buffering by controlling soil chemical composition in different pH ranges. Carbonate is largely present in soils beyond pH 7.0 and has become a pivotal component buffering the pH of alkali and near-neutral soils [17]. In soils with a pH between 4.5 and 6.0, CEC and soil organic matter (SOM) play important roles in soil pH buffering [18], whereas in acidic soils with a pH below 4.5, different forms of Al and the interactions between Al and SOM have positive contributions to the soil pH buffering process [19,20]. Ulrich [21] and Bowman et al. [22] qualitatively described the complex buffering system in soils, dividing the buffering system into five subsystems based on the pH range. At pH > 7.5, the dissolution/precipitation of carbonate controls soil pH buffering; at pH 4.5–7.0, cation exchange reactions dominate the soil pH buffering process; at pH < 4.5, different forms of Al regulate soil pH buffering; and at pH < 3.8, iron (Fe) controls the soil pH buffering system [5,21,22]. Moreover, silicate buffering also contributes to soil acid buffering at pH > 5 [5,21].

Land use and soil type are important anthropogenic and natural factors affecting soil properties related to soil pHBC [23,24]. Previous studies reported that intensive agricultural land use could have caused severe soil acidification in Chengdu Plain in China over the last thirty years [25]. Özlu et al. [26] observed that, compared with chemical fertilizer, manure had a stronger ability to increase soil organic carbon (SOC) storage and preserve soil pH. Jiang et al. [27] found that mature forest possessed lower soil pH and higher contents of SOC, base cations and exchangeable acidic cations than a pioneer forest. Gruba and Mulder [28] suggested that tree species could significantly affect the pH dependency of Al solubility control mechanisms and the intrinsic properties of SOM in a temperate forest. These observations demonstrate the effects of land use on soil properties. However, comparative research examining the effects of different land-use types on soil pHBC has not been conducted. With regard to soil type, different types of soils established under specific geoclimatic conditions, are influenced by parent materials and the extent of soil development [29,30]. Previous studies have observed various effects of parent materials and soil type on soil pHBC and acid-neutralizing capacity. For example, Fujii et al. [31] suggested that the low acid-neutralizing capacity of granite-derived soils and the high buffering capacity of volcanic soils can be ascribed to the difference in these soils’ weatherable mineral content. Wei et al. [32] investigated the effects of simulated acid rain on three types of soil in South China and found that the pH-change responses in red soil (RS) and lateritic red soil (LRS) to acid rain were weaker than those in latosol (LTS). However, in natural conditions, soil type and human interference always exert interactive impacts on soil pHBC and physicochemical properties, and their mechanisms are still poorly understood. Investigating the interactive impacts of land use and soil type on soil pHBC and buffering mechanisms is an important topic for land development and management.

In this study, we collected soil samples from agricultural fields and adjacent forest fields under five typical soil types (RS, LRS, LTS, paddy soil and acid sulphate soil) at different soil depths (0–10 cm, 10–20 cm and 20–30 cm) in South China, aiming to investigate the effects of land use and soil type on soil chemical and physical properties and pH buffering mechanisms in South China.

2. Materials and Methods

2.1. Site Description

Soil samples were collected from Guangdong Province in Southern China (Figure 1 and Table 1), which is predominantly characterized by a typical tropical or subtropical
climate. The annual mean temperature of Guangdong Province is 19.0–24.0 °C, and the annual mean precipitation is 1300–2500 mm.

![Figure 1. Spatial distribution of sampling sites in Southern China. (a) The location of the study region in China. (b) Spatial distribution of specific sampling sites. Each icon represents a sampling plot, and each soil type is indicated by one color.](image-url)

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Land-Use Type</th>
<th>Sampling Site</th>
<th>Geographic Coordinates</th>
<th>Main Vegetation Species</th>
<th>Altitude (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS</td>
<td>Agricultural field</td>
<td>Fuxi Town, Shaoguan City, Guangdong Province, China</td>
<td>25°12′23″ N, 113°50′43″ E, 25°12′23″ N, 113°50′43″ E</td>
<td>Maize, Pinus massoniana, Triadica cochinchinensis</td>
<td>180, 200</td>
</tr>
<tr>
<td>LRS</td>
<td>Agricultural field</td>
<td>Tianhe District, Guangzhou City, Guangdong Province, China</td>
<td>23°11′34″ N, 113°22′50″ E, 23°11′34″ N, 113°22′50″ E</td>
<td>Maize, Mangifera indica, Ficus microcarpa, Schefflera arboricola</td>
<td>40, 50</td>
</tr>
<tr>
<td>LTS</td>
<td>Agricultural field</td>
<td>Nanshan Town, Zhanjiang City, Guangdong Province, China</td>
<td>20°18′33″ N, 110°10′33″ E, 20°18′33″ N, 110°10′33″ E</td>
<td>Maize, Ravenala madagascariensis</td>
<td>50, 60</td>
</tr>
<tr>
<td>PS/YLRS</td>
<td>Agricultural field</td>
<td>Luoding City, Guangdong Province, China</td>
<td>22°42′32″ N, 111°20′39″ E, 22°42′32″ N, 111°20′39″ E</td>
<td>Rice, Pinus massoniana, Cunninghamia lanceolata</td>
<td>50, 70</td>
</tr>
<tr>
<td>ASS</td>
<td>Agricultural field</td>
<td>Haiyan Town, Jiangmen City, Guangdong Province, China</td>
<td>22°9′21″ N, 112°49′28″ E</td>
<td>Rice</td>
<td>20</td>
</tr>
</tbody>
</table>

Five soil types from agricultural lands and the adjacent forest lands, including RS, LRS, LTS, paddy soil (PS, developed from yellow lateritic red soil (YLRS)) and acid sulphate soil (ASS) were collected. For these soil types, RS, LRS, PS/YLRS and LTS belong to Oxisol [32], and ASS belongs to Histosol in US soil taxonomy [33]. The parent materials of RS, LRS, LTS, PS/YLRS and ASS are sandy shale, granite, basalt, sand mudstone and coastal mud deposit, respectively. The cultivated crop in the agricultural fields of RS, LRS and LTS was...
maize, while in the farmlands of PS and ASS was rice. Unfortunately, due to the extent of high land-development in Haiyan town, Jiangmen City of China, we did not find the appropriate forest without human interference. Thus, for ASS, there was only one land-use type of agricultural fields to be investigated in the present study. At each sampling site, five main plots (50 m × 50 m area) were randomly selected, and five sub-plots (1 m × 1 m area) were established in each main plot (one in the center and four in the corners). Soil samples were collected from each sub-plot at depths of 0–10 cm, 10–20 cm and 20–30 cm, respectively. The soil samples from the same main plot were thoroughly mixed to produce one composite sample.

2.2. Soil Analyses

After air-drying, the soil samples were ground to pass through sieves of 2, 0.25 and 0.15 mm to analyze different soil properties. The soil pHBC was determined by the method of acid/alkali titration as proposed by Nelson and Su [14]. Simply, 5 g of soil sample (passed through a 2 mm sieve) was weighed into 50 mL polyethylene centrifuge tubes and 25 mL of carbon dioxide-free water was added. Then, 0, 1, 2.5, 5 and 10 mL of either HNO$_3$ (0.1 mol·L$^{-1}$) or NaOH (0.1 mol·L$^{-1}$) were added into each tube to acidify or alkalinify the sample. Calcium chloride solution (1 mL, 0.05 mol·L$^{-1}$) and chloroform (0.2 mL) were added into each tube to inhibit ionic strength and microbial activities in the solution, respectively. The soil suspensions were intensively mixed, equilibrated on a shaker (300 r·min$^{-1}$) for 24 h at 25 $^\circ$C and then incubated for 6 days. The suspension was shaken daily for 2 min during incubation. Soil pH values were measured on the last day with a pH meter (S2 Seven2Go, Mettler Toledo, Germany).

The soil pH was measured with a soil–water ratio of 1:2.5. Soil total nitrogen (TN) and SOC were determined using an elemental analyzer (Elementar Vario III, Germany). The CEC of acidic soil was eluted with 1 mol·L$^{-1}$ ammonium acetate, then the CEC of substrates was determined by a nitrogen-fixing instrument (KN580, ALVA) [34]. Soil exchangeable acid (EA) is the sum of exchangeable H$^+$ (EH$^+$) and exchangeable Al$^{3+}$ (EAl$^{3+}$), which were determined following the KCl-extraction method [34]. Soil texture (clay, silt and sand contents) was measured with the pipette method [34].

2.3. Statistical Analysis

The acid/alkali titration curves were fitted by the sigmoid function (Equation (1)) as proposed by Nelson and Su [14], and then pHBC was calculated by Equation (2) [14]:

\[
\text{pH} = \text{pH}_{\text{min}} + \frac{a}{1 + e^{-(A-A_{\text{mid}})/b}} \quad (1)
\]

\[
\text{pHBC} = \frac{a}{(a + \text{pH}_{\text{min}} - \text{pH})(\text{pH} - \text{pH}_{\text{min}})} \quad (2)
\]

where pH$_{\text{min}}$ represents the minimum pH value of a given soil; A represents the amount of acid (−) or alkali (+) solution added to the sample; A$_{\text{mid}}$ represents the A value at the inflection point of the curve; a and b are the fitted constants.

The mixed-effects model was used to test the significances of the main and interaction effects among land use, soil type, soil depth. A one-way analysis of variance (ANOVA) was used to test the significance levels of soil properties within the soil type and depth, while a paired-samples t-test was used to detect the significance levels in different land-use types. The Duncan method was used for post hoc multiple comparisons when the data met the assumption of homogeneity of variances; otherwise, the Tamhane’s T2 method was used. The relationship between soil pHBC and soil properties was analyzed by the mixed-effects model. Due to the deficiency of data from ASS in the forest fields, only the data from four types of soils (including RS, LRS, LTS and PS/YLRS) were tested in the mixed-effects models.
The statistical analyses of the mixed-effects model were implemented using IBM SPSS Statistics 17.0 (IBM Corp., Armonk, NY, USA) and R statistical software (R 4.0.2). The fittings of the sigmoid function were conducted in SigmaPlot 14.0 (Systat Software Inc., San Jose, CA, USA), and the significance level of all data was set at \( p < 0.05 \). The figures were drawn by Origin 9.0, SigmaPlot 14.0, Adobe Photoshop CC 2019 and Adobe Illustrator CC 2019.

### 3. Results

#### 3.1. Variations in Soil pHBC and Physicochemical Properties

The mixed-effects model showed that soil pHBC was significantly affected by land use (\( p < 0.001 \)), soil type (\( p < 0.001 \)), soil depth (\( p < 0.001 \)) and their interactions (\( p < 0.05 \) for all, Table 2). The significant variations between land-use types mainly originated from LRS at the 10–20 cm depth and PS/YLRS at all depths (Figure 2). For agricultural soils, ASS had the highest pHBC values (49.27–117.83 mmol H\(^+\)·kg\(^{-1}\)·soil unit\(^{-1}\) pH), while the pHBC values of RS, LRS, LTS and PS ranged between 10.56–33.55 mmol H\(^+\)·kg\(^{-1}\)·soil unit\(^{-1}\) pH (Figure 2). For forest soils, LRS had the lowest pHBC values (11.40–30.55 mmol H\(^+\)·kg\(^{-1}\)·soil unit\(^{-1}\) pH), while YLRS had relatively high pHBC values (27.50–39.52 mmol H\(^+\)·kg\(^{-1}\)·soil unit\(^{-1}\) pH, Figure 2). Under different soil types, the pHBC values in forest soils of LRS (at 10–20 cm depth) and PS/YLRS (at all depths) were significantly higher than those of agricultural soils (Figure 2). The pHBC values in forest soils of RS (at all depths) and LTS (at 0–10 cm and 20–30 cm depths) were higher than those of agricultural soils, but the variations were not significant (Figure 2). At different soil depths, the significant decline in soil pHBC with an increasing depth only occurred in the RS and LRS of agricultural soils, while the pHBC in forest soils did not differ in the soil depths (Figure 2).

#### Table 2. Mixed-effect models for the effects of land use, soil type, soil depth and their interactions in soil pHBC and physicochemical properties. *: \( p < 0.05 \), **: \( p < 0.01 \), ***: \( p < 0.001 \), NS: nonsignificant. The digits represent \( F \) values.

<table>
<thead>
<tr>
<th>Land Use</th>
<th>Soil Type</th>
<th>Soil Depth</th>
<th>Land Use × Soil Type</th>
<th>Land Use × Soil Depth</th>
<th>Soil Type × Soil Depth</th>
<th>Land Use × Soil Type × Soil Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>pHBC</td>
<td>22.80 ***</td>
<td>7.17 ***</td>
<td>11.62 ***</td>
<td>5.72 **</td>
<td>5.58 **</td>
<td>4.11 **</td>
</tr>
<tr>
<td>pH</td>
<td>39.03 ***</td>
<td>19.36 ***</td>
<td>8.14 ***</td>
<td>50.21 ***</td>
<td>6.93 **</td>
<td>0.94 NS</td>
</tr>
<tr>
<td>CEC</td>
<td>53.77 ***</td>
<td>34.59 ***</td>
<td>21.12 ***</td>
<td>10.65 ***</td>
<td>1.53 NS</td>
<td>8.94 ***</td>
</tr>
<tr>
<td>SOC</td>
<td>7.30 *</td>
<td>1.53 NS</td>
<td>80.18 ***</td>
<td>6.68 **</td>
<td>6.04 **</td>
<td>5.37 ***</td>
</tr>
<tr>
<td>C:N ratio</td>
<td>0.93 NS</td>
<td>15.06 ***</td>
<td>47.77 ***</td>
<td>7.15 ***</td>
<td>4.04 *</td>
<td>1.7 NS</td>
</tr>
<tr>
<td>TN</td>
<td>8.22 **</td>
<td>7.22 ***</td>
<td>36.03 ***</td>
<td>3.71 *</td>
<td>2.01 NS</td>
<td>2.68 *</td>
</tr>
<tr>
<td>EA</td>
<td>166.00 ***</td>
<td>41.53 ***</td>
<td>2.24 NS</td>
<td>34.81 ***</td>
<td>33.60 ***</td>
<td>4.83 ***</td>
</tr>
<tr>
<td>EH(^+)</td>
<td>1.36 NS</td>
<td>13.64 ***</td>
<td>20.18 ***</td>
<td>7.89 ***</td>
<td>16.80 ***</td>
<td>2.26 *</td>
</tr>
<tr>
<td>EAI(^3+)</td>
<td>183.68 ***</td>
<td>41.74 ***</td>
<td>3.90 *</td>
<td>36.73 ***</td>
<td>27.81 ***</td>
<td>6.28 ***</td>
</tr>
<tr>
<td>clay</td>
<td>7.65 ***</td>
<td>770.53 ***</td>
<td>7.59 ***</td>
<td>10.99 ***</td>
<td>0.89 NS</td>
<td>8.78 ***</td>
</tr>
<tr>
<td>silt</td>
<td>227.59 ***</td>
<td>110.22 ***</td>
<td>0.87 NS</td>
<td>105.88 ***</td>
<td>2.26 NS</td>
<td>1.58 NS</td>
</tr>
<tr>
<td>sand</td>
<td>0.04 NS</td>
<td>503.59 ***</td>
<td>16.34 ***</td>
<td>13.47 ***</td>
<td>0.41 NS</td>
<td>7.82 ***</td>
</tr>
</tbody>
</table>

Land use, soil type, soil depth and their interactions significantly affected pH, CEC, C:N ratio, EA, EAI\(^3+\), clay and silt, while the dominant factors affecting SOC were land use and soil depth (Table 2). On the other hand, the soil TN, EH\(^+\) and sand were substantially influenced by soil type and depth (Table 2). In agricultural soils, ASS had the lowest pH values (pH 3.05–3.88), while the pH values of RS, LRS, LTS and PS ranged between 3.55–5.95 (Figure 3a). The soil pH of RS was lower than that of LRS, LTS and PS in agricultural fields (Figure 3a). In forest soils, LRS had the lowest pH values (pH 3.66–4.70), while LTS had the highest pH values (pH 4.88–5.86, Figure 3a). For most of the soil types, the pH in agricultural soils was significantly higher than that in forest soils (Figure 3a).
All data presented are the means of five replicates (R<sub>p</sub> = 0.05). There were significant variations in silt content between land-use types in RS, LRS, LTS (LRS), latosol (LTS), paddy soil (PS)/yellow lateritic red soil (YLRS) and acid sulphate soil (ASS). The effects of the soil texture on soil pH<sub>B</sub>C were not recorded in either SOC (R<sub>p</sub> < 0.001) and EAl<sup>3+</sup> (R<sub>p</sub> = 0.008), Figure 4). In forest soils, soil pH<sub>B</sub>C was positively correlated with SOC (R<sup>2</sup> = 0.211, p = 0.001), C:N ratio (R<sup>2</sup> = 0.581, p < 0.001), TN (R<sup>2</sup> = 0.190, p = 0.008, Figure 4). In forest soils, soil pH<sub>B</sub>C was positively correlated with SOC (R<sup>2</sup> = 0.444, p = 0.020), TN (R<sup>2</sup> = 0.059, p = 0.004), C:N ratio (R<sup>2</sup> = 0.119, p = 0.017) and EAI<sup>3+</sup> (R<sup>2</sup> = 0.113, p = 0.018), while it was not related to pH and CEC (Figure 4). The effects of the soil texture on soil pH<sub>B</sub>C were not recorded in either agricultural or forest fields (Figure 4).

Figure 2. pH<sub>B</sub>C values of different land-use and soil types, including red soil (RS), lateritic red soil (LRS), latosol (LTS), paddy soil (PS)/yellow lateritic red soil (YLRS) and acid sulphate soil (ASS). The fittings of mixed-effects model showed that the pH<sub>B</sub>C of agricultural soil was positively correlated with CEC (R<sup>2</sup> = 0.581, p < 0.001), SOC (R<sup>2</sup> = 0.161, p < 0.001), TN (R<sup>2</sup> = 0.122, p = 0.001), C:N ratio (R<sup>2</sup> = 0.172, p < 0.001), EA (R<sup>2</sup> = 0.267, p < 0.001), EAI<sup>3+</sup> (R<sup>2</sup> = 0.211, p = 0.001), while it was negatively related with soil pH (R<sup>2</sup> = 0.190, p = 0.008, Figure 4). In forest soils, soil pH<sub>B</sub>C was positively correlated with SOC (R<sup>2</sup> = 0.044, p = 0.020), TN (R<sup>2</sup> = 0.059, p = 0.004), C:N ratio (R<sup>2</sup> = 0.049, p = 0.028), EA (R<sup>2</sup> = 0.119, p = 0.017) and EAI<sup>3+</sup> (R<sup>2</sup> = 0.113, p = 0.018), while it was not related to pH and CEC (Figure 4). The effects of the soil texture on soil pH<sub>B</sub>C were not recorded in either agricultural or forest fields (Figure 4).

Soil texture was significantly influenced by land use, soil type, soil depth and their interactions (Table 2 and Figure 3). The LTS had the highest clay content, while RS and LRS had relatively low clay contents under each land-use type (Figure 3i). In the agricultural soils, ASS had the highest silt content, while LRS had the lowest silt content at all soil depths (Figure 3j). In forest soils, RS had the highest silt content at all soil depths (Figure 3). There were significant variations in silt content between land-use types in RS, LRS, LTS and PS/YLRS, especially at 0–10 cm soil depth (Figure 3). Under land-use types, LTS had the lowest sand content (1.18–5.69%), ASS had a relatively low sand content (9.19–44.43%), and PS/YLRS, especially at 0–10 cm depth (Figure 3j). Under land-use types, LTS had the lowest silt content, while LRS had the lowest silt content at all soil depths (Figure 3j). In forest soils, soil pH<sub>B</sub>C was positively correlated with SOC (R<sup>2</sup> = 0.113, p = 0.018), while it was not related to pH and CEC (Figure 4). The effects of the soil texture on soil pH<sub>B</sub>C were not recorded in either agricultural or forest fields (Figure 4).
Figure 3. Soil physicochemical properties under two land-use types and five soil types (n = 5). All data presented are the means of five replicates ± standard deviations. The abbreviations of RS, LRS, LTS, PS/YLRS and ASS represent red soil, lateritic red soil, latosol, paddy soil/yellow lateritic red soil and acid sulphate soil, respectively. The abbreviations of CEC, SOC, TN, EA, EH⁺ and EAl³⁺ represent cation exchangeable capacity, soil organic carbon, total nitrogen, exchangeable acid, exchangeable H⁺ ion and exchangeable Al³⁺ ion, respectively. The uppercase letters indicate significant differences between soil types in the same land-use type and depth (p < 0.05). The lowercase letters indicate significant differences between depths in the same land-use type and soil type (p < 0.05). The symbol “*” indicates the significant differences between agricultural fields and forest fields in the same soil type and depth (p < 0.05).
Figure 4. The relationship between soil pHBC and physicochemical properties in agricultural (n = 60) and forest (n = 60) fields. The abbreviations of CEC, SOC, TN, EA, EH$^+$ and EAl$^{3+}$ represent cation exchangeable capacity, soil organic carbon, total nitrogen, exchangeable acid, exchangeable H$^+$ ion and exchangeable Al$^{3+}$ ion, respectively.

The results showed that the CEC was positively correlated with the SOC in both agricultural ($R^2 = 0.043, p < 0.001$) and forest fields ($R^2 = 0.235, p < 0.001$), while clay was not significantly related to CEC in either of the two land-use types (Figure 5). The soil pH was negatively correlated with SOC in forest fields ($R^2 = 0.019, p = 0.036$), while a clear relationship between pH and SOC was not observed in agricultural fields (Figure 5c). Soil pH had no relation with clay content in either agricultural or forest fields (Figure 5d).

Figure 5. The relationships between four pairs of soil physicochemical properties (i.e., (a) CEC and SOC, (b) CEC and clay, (c) pH and SOC, and (d) pH and clay) under different land-use types (n = 60). The abbreviations of CEC and SOC represent cation exchangeable capacity and soil organic carbon.
4. Discussion

4.1. Responses of Soil pH Buffering Capacity and Physicochemical Properties to Land Use and Soil Type

In this study, we observed that forest soils had significantly lower pH values, higher pHBC, CEC, EA and EA\(^{3+}\) than agricultural soils (Figures 2 and 3). This phenomenon is partly in accordance with previous studies. Jiang et al. [35] observed that natural forest soils in subtropics had low soil pH and high content of Al compounds. Alvarez et al. [3] also suggested that tree could decrease soil pH, increase EA and soil total acidity in the Argentine Pampas. This was ascribed to the decomposition of plant litter, the dissociation of H\(^+\) ions from the functional groups of SOM and the release of the secretions in rhizosphere [28,35,36]. Meanwhile, soil acidification may facilitate the retention of SOC via inhibiting microbial activities [37]. The negative relationship between the pH and SOC of forest soils has demonstrated their interactions to some extent (Figure 5c). However, the retention and properties of SOM was highly dependent on vegetation type and the extent of human interference. In present study, we observed that although the SOC contents in the two land-use types were at a similar level, the CEC in forest soils was significantly higher than that in agricultural soils (Figure 3b). This indicated that the SOM in forest soils could provide more CEC than that in agricultural soils, which was rarely proposed by previous studies. Luo et al. [17] suggested that the contribution of SOC to soil pHBC might be affected by the charge properties of SOC. Wang et al. [38] observed that land use could significantly alter the chemical composition of SOM, via the complex interactions among SOC, soil texture and pH. Thus, the different cation exchange properties of SOM in the two land-use types may be ascribed to the complex interactive factors by land-use type, and the SOM in forest soils may have more carboxyl and hydroxyl than agricultural soils.

The decline in soil pH could cause the dissolution of Al from the soil solid phase, which promoted free Al\(^{3+}\) to occupy cation-binding sites and form EAl\(^{3+}\) [28,36]. The increase in EAl\(^{3+}\) content implied the rise in Al-compound content in the soil solution. Therefore, forest soils might possess more Al compounds than agricultural soils. Forest soils in the present study may have already been in the Al buffering stage. In addition, in terms of the pH values of each soil type, the ASS in the present study had an extremely low pH, high EAl\(^{3+}\) content and high soil pHBC, which may imply that the buffering capacity of the Al buffering system was stronger than that of the cation exchange or silicate buffering systems.

Soil type was another important factor affecting soil properties. In this study, ASS had the lowest soil pH, the highest TN, EA (including EH\(^+\) and EAl\(^{3+}\)) and silt contents and relatively high CEC and SOC contents (Figure 3). This might be because ASS originated from long-term waterlogged environments, which caused sulfate to reduce into sulfide, while Fe was reduced from Fe\(^{3+}\) to Fe\(^{2+}\), and finally facilitated the formation of iron sulfide or metastable iron sulfide [39,40]. Iron sulfide’s exposure to the air facilitates the production of sulfuric acid, which causes severe soil acidification (pH < 4) [41]. The extremely low soil pH enhances heavy metal availability, inhibits microbial activities and further influences SOC mineralization. In addition, the chemical properties of ASS may cause the sand to transform into silt.

In our study, the LTS was derived from basalt with a relatively high pH, low EA and EAl\(^{3+}\) content, and had the highest clay content and lowest sand content among the investigated soil types (Figure 3), which was partly in accordance with the previous studies [42–44]. This might be because LTS was the most highly weathered soil among the investigated soil types, which was located in tropical regions and formed Fe/Al oxides in soil minerals. Negatively charged clay minerals overlap with positively charged Fe/Al oxides in LTS, which causes the decline in the net charge, further decreases EA on the surface of clay minerals and improves soil pH [45,46]. In addition, previous studies have suggested that high SOC storage was an important feature in basalt-derived soils, because of the close binding between SOC and minerals [47]. However, we did not observe a distinct positive correlation between SOC and clay content in LTS. This might be because the basalt-derived soils mentioned in the previous studies were located in temperate...
regions and contained a 2:1 mineral type with plenty of permanent charges, leading to the strong binding with SOC and inhibiting SOC mineralization [18]. On the contrary, the clay minerals of highly weathered soils in the (sub)tropics are dominated by a 1:1 mineral type, presenting poor binding with SOC [18]. Moreover, a (sub)tropical monsoon climate might facilitate SOC mineralization, which resulted in the relatively low SOC content of LTS in the current study.

Previous investigations have reported that granite-derived soils always present a low acid-neutralization capacity, high sand content and poor SOC storage [48,49]. In the present study, the lowest soil pHBC and highest sand content were observed in granite-derived LRS (Figures 2 and 3), which is partly in accordance with previous studies. The low pHBC of LRS might be due to the low content of weathered minerals [49]. The low SOC content in agricultural LRS and relatively high SOC content in forest soils implied the effects of land use on SOC storage in granite-derived LRS (Figure 3c).

The RS and PS/YLRS were both derived from sandy shale in the present study; however, they had different responses of pH values to land-use types (Figure 3a). We supposed that, in RS, the lower soil pH of agricultural soils may be caused by the fertilization during cultivated practice, resulting in soil acidification [6], while the higher soil pH in the PS/YLRS of agricultural soils resulted from the changes in soil oxidation-reduction potential under the continual change in flood–dry conditions [50].

4.2. Effects of Land-Use Type on Soil pH Buffering Patterns

Our results show that agricultural and forest soils seem to be in different buffering stages. In agricultural soils, soil pHBC was positively correlated with CEC and SOC (Figure 4), implying that agricultural soils were in a cation exchange buffering stage [17,51]. The positive correlation between pHBC and EA implied the low base saturation of soils, which was the feature of highly weathered acidic soils [52]. The positive relationship between pHBC and EH+ implied that H+ ions still have advantages in the competition with Al3+ for binding sites, and play an important role in regulating soil pH [16]. In forest soils, soil pHBC was positively correlated with SOC and EA[Al], but was not related to CEC (Figure 4), although the contribution of SOC to CEC was demonstrated (Figure 5a). This might be because the buffering of SOM to soil pH was not only dependent on providing CEC, but also on the interactions with Al. Skyllberg [53] suggested that SOM and Al3+ could form Al–SOM complexes under acidic conditions. The complexation/decomplexation of Al–SOM compounds was an important mechanism in the soil pH buffering system during Al buffering stage of acidic soils [32,54]. Therefore, we inferred that forest soils in the present study might be in the Al buffering stage.

Based on the results of this study, we considered that land-use type impacted soil pHBC via affecting SOC turnover, soil pH, Al activities and the interactions of Al–SOM–pH. Soil texture was affected by land-use type to some extent; however, the dominant factor of soil texture is soil type, which is intensively affected by parent materials. Land use, soil type and their interactions greatly impact soil properties, further affecting soil pHBC.

5. Conclusions

This study showed that land use and soil type could significantly affect soil pHBC and physico-chemical properties. Forest soils had higher pHBC (11.40–49.50 mmol·kg⁻¹·unit⁻¹ pH), CEC, EA[Al] and clay contents than agricultural soils, while the pH values of forest soils (on average: 4.84) were significantly lower than those of agricultural soils (on average: 5.28). Acid sulphate soil had the highest pHBC (49.27–117.83 mmol·kg⁻¹·unit⁻¹ pH), EA content and the lowest soil pH, whereas latosol had the highest clay content among all the investigated soil types. Moreover, land-use type considerably changed soil pH buffering patterns. Agricultural soils might be in the cation exchange buffering stage, while forest soils might be in the Al buffering stage. In addition, this study also indicated that the forest soils had a higher pHBC which is helpful to stabilize soil
pH and a greater capacity to keep soil CEC and nutrients than the agricultural soils in South China.

**Author Contributions:** Conceptualization, J.Z., J.Y. and H.W.; methodology, J.Y., Z.S. and H.L.; formal analysis, J.Y. and Z.S.; writing—original draft preparation, J.Y.; writing—review and editing, J.Y., J.Z., H.W. and A.I.A.; visualization, J.Y., Z.S. and Y.Y.; supervision, J.Z.; project administration, J.Z. and H.W.; funding acquisition, J.Z. and H.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China (grant numbers U1701236, 32071641), the Joint Team Project of Guangdong Laboratory for Lingnan Modern Agriculture (grant number NT2021010) and Guangdong Science and Technology Project (grant number 2019B030301007 and 2021A1515012507).

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data for the analysis in this study are available upon request from the corresponding author.

**Acknowledgments:** Huimin Xiang, Xiaoran Shan, Jiawen Zhong and Saifei Li are appreciated for their helps on soil collections.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


8. Datta, A.; Mandal, B. Production (via N-fertilization) and correction (by liming) of acidity in soils contribute a huge efflux of CO$_2$ to atmosphere: Real or arbitrary. *Global Chang. Biol.* 2018, 24, 3280–3281. [CrossRef]


20. Gruba, P.; Mulder, J.; Brozek, S. Modelling the pH dependency of dissolved calcium and aluminium in O, A and B horizons of acid forest soils. Geoderma 2013, 206, 85–91. [CrossRef]
23. Tang, X.; Hu, J.; Lu, Y.; Qiu, J.; Dong, Y.; Li, B. Soil C, N, P stocks and stoichiometry as related to land use types and erosion conditions in lateritic red soil region, south China. Catena 2022, 210, 105888. [CrossRef]
28. Gruba, P.; Mulder, J. Tree species affect cation exchange capacity (CEC) and cation binding properties of organic matter in acid forest soils. Sci. Total Environ. 2015, 511, 655–662. [CrossRef]
30. Pichler, V.; Gomórová, E.; Leuschner, C.; Homolák, M.; Abrudan, I.V.; Pichlerová, M.; Střelcová, K.; Filippo, A.D.; Sitko, R. Parent material effect on soil organic carbon concentration under primeval European beech forests at a regional scale. Forests 2021, 12, 405. [CrossRef]
32. Wei, H.; Liu, Y.; Xiang, H.; Zhang, J.; Li, S.; Yang, J. Soil pH responses to simulated acid rain leaching in three agricultural soils. Sustainability 2020, 12, 280. [CrossRef]
35. Jiang, J.; Wang, Y.-P.; Yu, M.; Cao, N.; Yan, J. Soil organic matter is important for acid buffering and reducing aluminum leaching from acidic forest soils. Chem. Geol. 2018, 501, 86–94. [CrossRef]


