Vertical distribution and influencing factors of deep soil organic carbon in a typical subtropical agricultural watershed

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Abstract

Soil organic carbon is one of the most commonly used indicators of soil health, as it plays a vital role in maintaining fertility and combating global warming. Understanding the vertical distribution and controlling factors of organic carbon in the entire regolith, rather than just the routinely defined upper 1 m portion of the soil, is crucial for assessing soil health in a holistic perspective. In this study, 21 boreholes in four different land uses were drilled from the land surface down to the bedrock in a typical subtropical agricultural watershed. The total organic carbon stock in the regolith ranged from 77.8 Mg C ha^{-1} to 311.8 Mg C ha^{-1} and the organic carbon content showed a progressive decline from land surface to bedrock. However, on average, only 19.0 % of total organic carbon was stored at the depth 0-30 cm and 17.7% between 30 and 100 cm, whereas 63.3 % was stored below 100 cm. Total organic carbon stock was significantly higher under paddy fields than under cropland, orchard or woodland in the upper 100 cm ($p < 0.05$) possibly due to straw incorporation, flooding of the paddy soils and their position on the lower slopes where eroded soil was deposited. However, there was no significant difference in total organic carbon stock below 200 cm ($p > 0.05$). According to the boosted regression tree analysis, soil texture outperformed the other edaphic factors and was the primary edaphic factor controlling TOC content of the different soils. The results show that there is a large carbon reservoir in the deep regolith. Land use strongly affects the distribution of carbon in the top 100 cm soil layers but has little effect on deep soil organic carbon. Deep TOC were closely linked to soil texture. This study highlights the importance of deep soil organic carbon for soil health and understanding the factors controlling its content for improved estimates of soil carbon storage.

Key words: deep soil organic carbon; vertical distribution; edaphic factor; land use;

Earth's critical zone

1. Introduction

Soil is the largest pool of carbon in terrestrial ecosystems and holds twice as much carbon (C) as the atmosphere (Schlesinger and Bernhardt, 2013). Even a small percentage change in soil C may introduce significant change in atmospheric CO_2 concentrations (Lal, 2003). Deep soil organic C (SOC) may comprise a large terrestrial C pool, but is arguably the least investigated component of the terrestrial C pool (Wade et al., 2019). Deep SOC is generally unsaturated with low C concentrations (Wang et al., 2015). Therefore, it has been suggested that more SOC could be sequestered through enhanced C input into deep soil by root penetration and vertical transport of dissolved organic C (Lorenz and Lal, 2005), which may have the potential to counterbalance the current increase in atmospheric CO_2 (Minasny et al., 2017). To this end, the vertical distribution and stock of deep SOC are important in assessing the potential for soil C sequestration and for informing related management policies.

Deep SOC is mainly sourced from dissolved organic matter, plant roots and root exudates, bioturbation, and translocation of particulate organic matter and clay-bound organic matter (Rumpel and Kögel-Knabner, 2011). A key feature of deep SOC is its slow turnover times at centennial or millennial timescales; the underlying mechanisms for this slow turnover remain unclear (Jackson et al., 2017; Trumbore, 2009). This characteristic has been used to support the assumption that deep SOC sequestration is negligible or resistant to surface environment change (Chabbi et al., 2009; Li et al., 2021). However, this assumption is likely to overlook the potential of deep soil horizons in storing high proportions of SOC stocks at depth (Richter and Babbar, 1991). Moreover, deep SOC may have a significantly different response to global change than surface soil layers (Bernal et al., 2016). Therefore, quantifying the magnitude and distribution characteristics of deep SOC can provide additional understanding of C cycling in the whole regolith profile, which will help to improve terrestrial C assessment and combat global warming.

Studies on soil C have historically focussed on shallow soil layers, which limits our understanding of soil dynamics deep in the soil profile (Harrison et al., 2011). These studies have explored the stock and distribution of SOC in the topsoil at global (Arrouays et al., 2014; Hengl et al., 2017), continental (Grunwald et al., 2011; Orgiazzi et al., 2017), national (Luo et al., 2010), regional (Song et al., 2016) or local scales (Liu et al., 2016). They have provided a significant contribution to the assessment of the SOC inventory in the top layers of the soil. However, much less attention has been given to the stock and spatial distribution of C stored deeper than 20 cm, especially deeper than 100 cm, which is important for understanding the biogeochemical cycling of C over longer timescales (Gross and Harrison, 2019; Rumpel and Kögel-Knabner, 2011). It is estimated that these deep SOC reserves are very large. Batjes (1996) predicted that estimates of global SOC stocks could increase substantially from 1462–1548 Pg C in the upper 100 cm to 2376–2456 Pg C if the 100 to 200 cm soil layer was included in the estimates. Jobbágy and Jackson (2000) further reported that global SOC storage in the top 300 cm of soil was 56% more than that in the top 100 cm (i.e. 2344 Pg C to 300 cm compared to only 1502 Pg C to 100 cm). Other estimates have emphasized the importance of SOC at different depths or multiple scales (Davidson et al., 2011; Harper and Tibbett, 2013; Tarnocai et al., 2009). In China’s Loess Plateau with a semi-arid and arid climate, previous studies have showed that deep SOC contributes significantly to the total soil C budget (Gao et al., 2017; Jia et al., 2020; Li et al., 2021; Yang et al., 2020a; Yu et al., 2019a). These studies highlighted that an accurate SOC inventory should include deep soil layers, but data on deep SOC remains scarce, mainly due to the challenges of deep soil sampling, especially in subtropical humid regions. In these regions, soil organic matter is more rapidly decomposed due to warmer and wetter environment (Bellè et al., 2022; Don et al., 2011; Yao et al., 2019), so the deep SOC stock is assumed to be negligible, but with little supporting evidence. Investigations into the vertical distribution of deep SOC in subtropical regions are, therefore, urgently needed to fill this knowledge gap.

Edaphic properties, such as soil texture and pH, are the innate factors that regulate SOC stabilization and stocks (Dungait et al., 2012). Physical protection of occluded particulate SOC is an important stabilisation mechanism (Six et al., 2000), but how this mechanism functions along the depth gradient is elusive because the processes of aggregate formation in shallow and deeper soil layers may be quite different (Rumpel and Kögel-Knabner, 2011). In addition, the variation with depth in soil physicochemical properties that control the availability of water, nutrients, oxygen and other resources that are important for the operation of C cycling (Lehmann and Kleber, 2015; Schmidt et al., 2011), needs further investigation. By dividing the regolith (from land surface to soil-bedrock interface) into shallow (< 100 cm) and deep (> 100 cm) soil layers, the effects of edaphic properties can be explicitly identified.

Unlike the edaphic properties, land use could affect the SOC stock through altered land cover and management practices (Wang et al., 2015). Although extensive studies have investigated the impacts of land use (Conforti et al., 2016; Yu et al., 2020b), knowledge gaps regarding its effect on deep soil layers still exist. Most studies have focussed only on the upper 100 cm of the soil, which cannot adequately reflect the impacts of land use on the stock and distribution of SOC in deeper soil layers (Schwanghart and Jarmer, 2011; Singh et al., 2018). The depth of potential land use influence on SOC remains poorly defined. By explicitly comparing the stocks of SOC in different land uses at deeper depth, we aim to gain insight into the effect of land use on the vertical distribution of SOC.

Red soils are generally acidic and highly weathered soils, that are widely distributed in tropical and subtropical regions around the world (Eswaran et al., 2012). They are approximately equivalent to Acrisols, Alisols and Ferralsols (IUSS Working Group WRB, 2015) or Ultisols and Oxisols (Soil Survey Staff, 2014). In China, they cover an area of more than 2×10^6 km^2 (Liu et al., 2017) and are the most important soil resources of southern China. Because of some unfavourable properties (e.g., low pH and SOC content) and long-term inappropriate management, red soils are often subject to severe degradation (Wilson et al., 2004). Many studies have suggested that the quality of degraded red soils could be greatly enhanced by increasing the SOC content (Gong et al., 2013; Huang et al., 2010; Zhang and Xu, 2005).

The SOC content of red soils has been investigated with respect to its spatial variation (Jiang and Guo, 2019; Zhang et al., 2010), contribution to soil aggregation (Peng et al., 2015) and to provide estimates of the C pools (Qian et al., 2013). However, most of these studies have focused only on the upper 100 cm of the soil. As a result, studies on the spatial distribution and storage of SOC in the deep soil layers are limited, and the impact of changes in land use on deep SOC also remains poorly understood. The critical zone approach aims to study the whole regolith, and so provides an opportunity to investigate C processes in both shallow and deeper soil layers (Yang et al., 2020c). Determining the vertical distribution and influencing factors of SOC stocks in a red soil critical zone will allow the potential for C sequestration and maintenance of the quality and security of soil resources to be more fully assessed (Zhang et al., 2019).

In this study, we assessed the profile distribution of total organic C (TOC) across the entire regolith of a representative subtropical red soil critical zone in a typical subtropical agricultural watershed. The specific objectives are to (1) evaluate the vertical distribution of TOC from the land surface to the surface of the bedrock (up to 1950 cm), (2) estimate the TOC storage in the entire regolith, and (3) examine the effects of edaphic factors and land use on the vertical distribution of TOC.

2. Materials and methods

2.1 Study area

The study area (116°53′–116°55′N, 28°13′–28°14′E) is near to the well-established Sunjia Red Soil Critical Zone Observatory (RSCZO), Yingtan, China (Yang et al., 2020c). It has an area of 2 × 2 km^2 with an altitude that varies from 38 to 74 m above sea level (Fig. 1), and a mean slope of 2.4°. This area has a subtropical monsoon climate with a mean annual precipitation of 1795 mm and a mean annual temperature of 17.8 ℃. The land uses were mainly paddy field (area proportion = 28%), cropland (23%), orchards (9%), woodland (19%), and the other (21%, including ponds, roads, ditches and buildings). Land management was distinct among the four land uses (Yang et al., 2020b). The main crops in croplands were peanuts (*Arachis hypogaea*), sweet potatoes (*Ipomoea batatas*), cassava (*Manihot esculenta*), oilseed rape (*Brassica napus*), turnips (*Brassica rapa*) and watermelons (*Citrullus lanatus*). The main trees in woodlands were camphor (*Cinnamomum camphora*) and masson pine (*Pinus massoniana*). Mandarin citrus (*Citrus reticulata Blanco*) and chestnut (*Castanea mollissima BI.*) were the main orchard trees. The regoliths were developed from the underlying sandstone and Quaternary red clay as parent materials.

(**Fig.1** is about here)

2.2 Sample collection and analysis

In March 2018, 21 sampling sites were selected for borehole drilling based on a careful field investigation (Fig. 1). Among them, 8, 7, 3 and 3 sites were from paddy field, cropland, orchard and woodland, respectively. The selected sites well represented the major land management practices, and landscape positions in the catchment (Yang et al., 2020c). A cylinder with an internal diameter of 13 cm was used to obtain a continuous core from land surface to fresh bedrock at each site. Soil samples in the upper 100 cm, 100-500 cm and below 500 cm were collected at 10 cm, 20 cm and 50 cm depth intervals, respectively. For bulk density (BD) measurements, a 100 cm^3 standard stainless-steel cutting ring was used to collect undisturbed samples from the centre of each core. Pictures representing the sampling campaign can be seen in Fig. 2.

(**Fig.2** is about here)

Regolith samples were air-dried, ground in an agate mortar with a pestle and sieved through a nylon mesh before being used for the analysis of TOC (g kg^{-1}), particle-size distribution (sand, silt and clay content; % by volume) and pH (H_2O). BD is a weighted average of the densities of its material components in which TOC is an important part. pH indicates the soil acid-base environment which is vital for microbe to process SOC. Water content (WC) is related to hydrological processes which determine the erosion and deposition of particles. Particle-size distribution may impact the accumulation of SOC in minerals (Six et al., 2002). For the above reasons, we selected them as potential influencing factors for analysis in the present study.

TOC was measured by the $K_2Cr_2O_7$-H_2SO_4 wet oxidation method of the Walkley-Black procedure (Nelson and Sommers, 1982). Particle-size distribution was measured using a Beckman Coulter LS230 laser diffraction particle size analyser (Zhang and Gong, 2012). pH was measured using a digital pH meter in a 1:2.5 soil: water solution. BD (g cm^{-3}) was measured by drying the sample to a constant weight at 105 °C. WC was determined by drying the field-moist samples at 105 °C to a constant weight for about 12 hours. Descriptive statistics of the above properties are presented in Figs. S1-3. Further physicochemical properties for each individual borehole can be found in previous studies (Yang et al., 2020b, c).

Cumulative TOC stock was calculated using the following equation (Jia et al., 2020):

$$S_h = \sum_{i=1}^{n} \frac{BD_i \times TOC_i \times T_i \times (1-\theta_i)}{10} \quad (1)$$

where S_h represents the cumulative TOC stock (Mg C ha^{-1}) within a certain depth interval h (cm) which consist of n layers in total; BD_i, TOC_i and T_i are respectively the BD (g cm^{-3}), TOC (g kg^{-1}) and thickness (cm) of the i^{th} layer; and θ_i is the volume percentage of gravel (> 2 mm) of the ith layer (%). As described above, samples were collected at 10, 20 and 50 cm depth intervals and the regolith thickness varied among boreholes, so T_i is 10, 20 and 50 cm at depth 0-100 cm, 100-500 cm and below 500 cm, respectively.

2.3 Statistical analysis

Pearson correlation analysis was used to determine the relationship between TOC and regolith physicochemical properties. A one-way analysis of variance followed by a least significant difference test ($p < 0.05$) was conducted by using the *agricolae* package (Mendiburu, 2019). The *ggplot2* package (Wickham, 2016) was used to produce statistical plots.

In order to quantify the relative importance of regolith properties in explaining the vertical variability of TOC, we applied the boosted regression tree (BRT) model using data from depths 0-100 cm and 100 cm - bedrock respectively. BRT is a commonly used machine learning algorithm developed by Friedman et al. (2000), which combines two powerful statistical algorithms: boosting and regression trees. The boosting algorithm develops a final model by iterating and progressively adding trees to the model. Regression trees were used to analyze the relationship between response variable and explanatory variables, in which a binary split was applied to fit a simple model to each resulting section (Wang et al., 2017). Compared with other machine learning algorithms, BRT model has been evidenced to have a high predictive accuracy and good interpretability of the relationship between variables (Müller et al., 2013). The BRT model was conducted with the *dismo* (Hijmans et al., 2017) and *gbm* (Elith et al., 2008) packages.

All the above analyses were conducted with R language (R Core Team, 2021).

3. Results

3.1 Vertical distribution of total organic carbon

Vertical patterns of TOC contents from the land surface to the soil-bedrock interface for the boreholes are shown in Fig. 3. The TOC contents decreased with increasing depth, especially rapidly in the first 50 cm soil layer. Below that depth, TOC showed a slower decline. The highest TOC content (29.6 g kg^{-1}) was observed at depth 0–10 cm of paddy field regolith (P1), whereas the lowest TOC (3.8 g kg^{-1}) at the same depth was observed in the orchard (O3). The mean TOC at depth 0–10 cm was 12.5 g kg^{-1}. Generally, the TOC contents in deep soils were almost constant and at a low level, and our results showed that the mean TOC content below 100 cm was only 1.2 g kg^{-1}, while the corresponding values for the first 30 cm and 100 cm were 7.5 g kg^{-1} and 4.1

g kg^{-1}, respectively.

(**Fig.3** is about here)

The means and standard deviations of TOC stocks at different depth intervals (0-30 cm, 30-100 cm, 0-100 cm, and 100 cm - bedrock) are shown in Table 1. The cumulative TOC stocks at depth 0-30 cm were 44.2 ± 9.0 Mg C ha^{-1}, 21.4 ± 4.2 Mg C ha^{-1}, 23.9 ± 7.1 Mg C ha^{-1} and 17.9 ± 5.1 Mg C ha^{-1} for paddy field, cropland, woodland and orchard, respectively. The cumulative TOC stocks at depth 0-100 cm were significantly higher in paddy fields than in other land uses; 79.5 ± 16.0 Mg C ha^{-1} for paddy fields, 47.3 ± 6.6 Mg C ha^{-1} for orchards, 45.4 ± 9.2 Mg C ha^{-1} for woodland and 41.2 ± 5.3 Mg C ha^{-1} for cropland.

(**Table 1** is about here)

The cumulative distribution and proportion of TOC stock for the boreholes are shown in Fig. 4. The cumulative TOC stock throughout the regolith ranged from 77.8 Mg C ha^{-1} in cropland regolith 1 (C1) to 311.8 Mg C ha^{-1} in paddy field regolith 7 (P7). The ratio of TOC stored below 100 cm to the TOC in the top 100 cm ranged from 0.7 in paddy field regolith 4 (P4) to 6.7 in woodland regolith 3 (W3). The percentage of TOC in the whole regolith that was stored at depth 0-30 cm ranged from 7.1% in orchard regolith 3 (O3) to 30.9 % in paddy regolith 8 (P8), with a mean of 19.0 %. On average, only 36.7 % of TOC was stored in the upper 100 cm, of which 19.0% was stored within depth 0-30 cm (tillage layer). Detailed information on the cumulative TOC stock for each individual depth increment can be found in Fig. S4.

(**Fig.4** is about here)

3.2 Relative importance of edaphic factors

Fig. 5 shows the Pearson correlation between TOC and selected edaphic factors for the depths of 0-100 cm and 100 cm-bedrock, respectively. Fig. 6 shows the results of BRT analysis on data at depths 0-100 cm and 100 cm-bedrock, respectively. For the 0-100 cm section, WC was identified as an important influencing factor (relative importance = 34.15%), followed by BD (24.05%), sand (14.59%), clay (12.14%), silt (7.71%) and pH (7.37%). Soil texture (represented by sand, clay and silt) explained 34.44% of the variability in total, and was determined as the most important influencing factor for this section. For the 100 cm-bedrock section, pH was an important factor (25.27%), followed by BD (23.67%), clay (22.12%), sand (12.45%), WC (9.07%) and silt (7.43%). Similar to the 0-100 cm section, soil texture has a relatively high importance (42%). Overall, soil texture was the primary controlling factor for both 0-100 cm (34.44%) and 100 cm-bedrock (42%).

(**Fig.5** is about here)

(**Fig.6** is about here)

3.3 Total organic carbon at different regolith depths among different land use types

The vertical distribution of TOC in paddy field, cropland, orchard and woodland are shown in Fig. 7. In general, they all showed a depletion pattern with increasing depth from land surface to 500 cm. The TOC content for each land use was significantly greater in the upper layers (0-20 cm) than that in the lower layers (> 20 cm). However, differences both between land uses and with depth can still be identified. The TOC content range across the entire profile was 0.9-21.4 g kg^{-1} for paddy fields, 1.0-7.3 g kg^{-1} for cropland, 1.0-5.8 g kg^{-1} for orchards and 0.7-7.7 g kg^{-1} for woodland. Significant differences among the four land uses were observed only in the upper 90 cm. The paddy fields had higher TOC contents than the other land uses in almost all layers in the upper 90 cm. By contrast, cropland had the lowest TOC contents in almost all layers.

(**Fig.7** is about here)

We compared the statistically significant difference in TOC stock among land uses at different depths (Fig. 8). The TOC stock was significantly higher under paddy field than under other land uses at depths 0-30 and 0-100 cm. Below depth 100 cm, there was no significant difference in TOC stock among the four land uses despite the TOC stock under paddy field having a higher variation. In the vertical direction, a similar pattern was observed among the different land uses with peak stock at depth 0-100 cm. Under cropland, orchard and woodland, there was no significant difference in TOC stock at depths 0-30 cm, 100-200 cm or 200-300 cm. However, this was not the case in the paddy fields. For paddy fields, the TOC stored at 0-30 cm was significantly greater than that stored at 200-300 cm.

(**Fig.8** is about here)

4. Discussion

4.1 Importance of deep total organic carbon pool in the critical zone

Our results showed that the mean TOC concentration within the top 100 cm of the soil was 3.4 times greater than the concentration below 100 cm (Fig. 3; 4.1 vs. 1.2 g kg^{-1}). The lower concentration of TOC below 100 cm is as expected, due to the lower biomass inputs (Hu et al., 2014). However, because of the large depth of the regolith, which was observed to have a mean depth of 770 cm (Yang et al., 2020b), the TOC stock below 100 cm was 2.1 times greater than that stored in the top 100 cm (Fig. S4). On average, 63.3 % of TOC was stored below 100 cm (Fig. 4). Jia et al. (2020) also reported that the storage of SOC mainly depended on soil depth. This finding strongly supports our hypothesis that the largest proportion of the TOC is stored below 100 cm. It is also in agreement with the assertion of previous studies (Borchard et al., 2019; Harper and Tibbett, 2013; Hobley and Wilson, 2016; Jobbágy and Jackson, 2000; Wade et al., 2019) that TOC in deep layers should not be ignored when estimating the inventory of TOC in terrestrial ecosystems. Therefore, TOC stored in deep regoliths should be taken into account to avoid the systematic underestimation of TOC stocks. Moreover, these deep TOC stocks may respond differently to the global warming compared with TOC in the surface soils (Harper and Tibbett, 2013; Harrison et al., 2011; Rumpel and Kögel-Knabner, 2011). This finding may also be applied to the other tropical and subtropical regions around the world that have similarly thick regoliths. To date, no study has estimated TOC in the entire critical zone at a global, continental or even national level, so we do not know the true size of the terrestrial C pool. Future critical zone studies should attempt to fill this knowledge gap.

4.2 Effect of edaphic factors on total organic carbon storage

Past studies have evidenced that edaphic factors govern the stability and decomposition of TOC (Hemingway et al., 2019; Lehmann and Kleber, 2015; Schmidt et al., 2011; Xu et al., 2016), and thereby affect the vertical distribution of TOC (Cao et al., 2021). Our results showed that soil texture was the most important edaphic factor affecting TOC variation in the whole regolith (Fig. 6). For the 0-100 cm section, sand (14.59%), clay (12.14%) and silt (7.71%) jointly explained 34.44% of the variability in TOC; for the 100 cm – bedrock section, clay (22.12%), silt (12.45%) and sand (7.43%) combined accounted for 42% of the relative importance (Fig. 6). Of the three texture variables, clay content showed the greatest effect on TOC. This is likely to be due to significant impacts of soil clay on the formation and transformation of soil aggregates which regulate access of micro-organisms and nutrients to the TOC (Luo et al., 2021; Sun et al., 2020). Decomposition of TOC can be reduced if it is occluded within soil aggregates and/or adsorbed onto mineral surfaces (Six et al., 2000). Previous studies have found that clay minerals play an important role in stabilizing subsoil TOC (Dick et al., 2005; Rumpel and Kögel-Knabner, 2011; Six et al., 2002; Wade et al., 2019). Soil clay can greatly increase C accumulation and stabilization due to its effect on mineral surface area and the formation of soil aggregates (Fernandez et al., 2019). Therefore, the capacity for TOC sequestration is enhanced as the soil clay content increases (Mathieu et al., 2015).

Soil WC contributed greatly to the variation in TOC (Yu et al., 2019a). Our study showed that WC has a significant effect on the TOC stocks at depths of 0-100 cm (Fig. 6). The WC explained 34.15% and 9.07% of the variability in TOC concentration for the 0-100 cm section and the 100 cm-bedrock section, respectively. This is consistent with other reports that WC can affect the decomposition, mineralization and transformation of TOC (Davidson et al., 2000; Yu et al., 2019a). While losses of TOC by decomposition increase with WC up to field capacity in the shallow soils, but plant growth also increases the C inputs to the soil (Mayer et al., 2019; Yang et al., 2020a). Therefore, with sufficient water-availability, organic matter can accumulate and be transported down into the soil profile. By contrast, WC in deep soils tends to stay at a relatively stable level (Fig. S2), so its effect on TOC accumulation in deep soils decreases with increasing depth compared to that in the shallow soil.

In this study, BD had an important influence on TOC stocks (Fig. 6). Soil BD is the weighted average of the densities of its components including soil minerals, TOC, and air- or water-filled pores (Yang et al., 2014). It is closely related to soil porosity, water infiltration and solute transport in the whole soil profile (Kojima et al., 2018; Lu et al., 2019). Soil porosity has been found to strongly influence dissolved organic C leaching in both surface and subsurface soils (Liu et al., 2019; McGlynn and McDonnell, 2003; Niu et al., 2021; Rizinjirabake et al., 2019). Soil BD can also impact the oxygen available for microbial decomposition of organic matter (Six et al., 2002). In our study, BD increased from 1.3 to 1.5 g cm^{-3} from 0-10 cm to 180-200 cm (Fig. S2), which may affect the transport of dissolved organic C (Kojima et al., 2018). Furthermore, because of the increase of soil BD and therefore the decrease of soil porosity with increasing depth, the transport of dissolved oxygen will be inhibited, so that the microbial decomposition of organic matter will be limited. Thus, BD strongly influences the variation in TOC throughout the whole soil profile.

The results showed that pH strongly influenced TOC (Fig. 5 and 6). This is supported by past studies that have suggested that soil pH can mediate the decomposition of TOC (Hagedorn et al., 2012; Tonon et al., 2010). Decomposition of soil organic matter is mainly conducted by microbial processes, so changes in the microbial community and enzymes produced influence the decomposition rate (Zhang et al., 2020). Our previous studies have shown that substantial bacterial communities relating to acidification exist even at the bottom of a 6.2 m red soil profile (Wu et al., 2019b; Zhao et al., 2019). It has been reported that a lower pH will significantly depress microbial activities during soil organic matter decomposition and therefore decrease microbial-derived C accumulation but also result in slower decomposition and so increased TOC (Kemmitt et al., 2006; Liu et al., 2014). Low soil pH can also facilitate the chemical and physical protection of TOC. The decrease in soil pH can increase the positive charges of variable charge minerals, which has been observed to increase organic matter adsorption (McBride, 1994; Spielvogel et al., 2008). The decrease in soil pH would also depress the ionization of organic acids, so weakening the repulsion between negatively-charged clays and organic matter in aggregates (Sparks, 2003; Zhang et al., 2020). This explains the observed importance of soil pH in controlling the variation in TOC.

4.3 Effect of land use on total organic carbon storage

The TOC in the four land-use types considered all showed similar exponential patterns of decline down the soil profile (Fig. 7). Land use only markedly impacted TOC to a depth of 200 cm, with significant differences between the four land-use types only being observed in the upper 100 cm (Fig. 7). Below 200 cm, no significant effect of land use was observed in the TOC stocks (Fig. 8). This is in contrast to observations in the Loess Plateau, where a number of authors have reported significant differences at depths below 200 cm (Jia et al., 2017; Wang et al., 2016; Yu et al., 2019b). This could be due to buried soil layers in the Loess Plateau, which may contain a large amount of C (Jia et al., 2020), but could also be due to the dry climate under which deep rooting systems develop and fine roots increase the TOC in the deep soil layers (Niu et al., 2021). Some of the woodlands included in this study were only converted from the other land uses in the year 2000 (Yang et al., 2020b), so any changes in TOC due to land use would not have had sufficient time to move down the regolith.

The mean TOC stocks in the top 100 cm under the paddy fields (79.5 Mg C ha^{-1}) were significantly higher than those under the other three land uses (47.3 Mg C ha^{-1} for orchard, 45.4 Mg C ha^{-1} for woodland and 41.2 Mg C ha^{-1} for cropland) (Fig. 8). Woodland is considered to have a large C input from above ground biomass (Lal, 2004), but its effect in this study was not significant. The greater TOC stocks in the paddy fields relative to other land uses can partially be explained by higher TOC inputs due to the straw being ploughed into the soil rather than being burned or removed (Li et al., 2010; Zhu et al., 2010). This is now a typical practice for most paddy fields in China. In a study conducted at national scale, Zhao et al. (2018) reported the average SOC stock in the topsoil of cropland had increased from 28.6 Mg C ha^{-1} in 1980 to 32.9 Mg C ha^{-1} in 2011, and this was largely attributed to crop residue inputs. In our study area, it is common practice to incorporate straw in paddy fields, while no similar practice is used in the other land uses. The long-term cultivation history of paddy fields may also strengthen the impact of repeated inputs of straw to the soil. Wu et al. (2019a) reported that the old paddy fields in our study area had been cultivated for over 100 years, so would be expected to be in steady state with respect to the inputs, while the main tree species in the woodland were just older than 30 years.

The second reason for the high C content in the top 100 cm in the paddy fields may be due to the slower decomposition rate of SOC due to the saturated condition of the soil (Li et al., 2010; Zhang and He, 2004). Unlike the other land uses, paddy fields are flooded with an approximately 5 cm deep layer of water for most of the growing season, which creates a water saturation zone. Mayer et al. (2019) reported that water saturation in agricultural soil slows decomposition of SOC, resulting in high subsoil

(30–100 cm) SOC content.

However, perhaps the most important reason for the higher TOC content in the top 100 cm of the paddy fields could be their landscape location, which is usually on the lower slopes, where soil is likely to be deposited following erosion from the upper slopes (Boix-Fayos et al., 2009). Therefore, paddy fields are likely to accumulate nutrients and fine soil particles, resulting in an inherently higher TOC content of the paddy soils due to topography (Singh et al., 2018).

4.4 Limitations and future studies

By expanding from subsurface 0-100 cm soil layers to the profile of the entire regolith, this study has provided an important investigation into the vertical distribution of TOC in a typical red soil critical zone. However, there remain some limitations associated with the study design that should be noted.

The study cannot directly compare the relative importance of land use and edaphic factors on the TOC distribution. This is because land use was not included in the BRT analysis alongside the edaphic factors. Land use is a categorical variable while edaphic factors can be treated as numerical. Although the BRT model can deal with categorical and numerical variables at the same time, this complicates explanation of the model results, so was not done. The study also did not account for any potential changes in edaphic factors over time. This is a reasonable assumption for stable characteristics, such as soil texture, but may introduce uncertainty for factors, such as soil moisture, which are highly dynamic. However, the moisture content of deep soil layers is more stable, so this is not likely to be a problem at depth (Yang et al., 2012). Because the study did not account for the impact of topography on the TOC content, this may have affected the findings with respect to some land uses, such as paddy soils. Topographic factors distribute organic matter down a slope by erosion-deposition processes (Yu et al., 2020a). Future studies could provide explicit assessment of the impact of topographical features of TOC distribution.

All 21 boreholes showed a similar exponential-depletion pattern of TOC content down the profile, independent of land use, while significant differences existed in TOC stock between different land uses in the top 100 cm soil layers. This suggests that land use had little impact on the TOC in the deeper part of the regolith. Therefore, it may be possible to provide regional estimates of deep TOC stocks simply by fitting a depth function (Bishop et al., 1999; Liu et al., 2016). Based on this assumption, Song et al. (2019) mapped the three-dimensional distribution of deep organic matter in the RSCZO. However, the degree of decline in the upper soil layers varied among different land uses; paddy fields showed a more rapid decrease in TOC than other land uses, so the effect of land use should be taken into account when developing depth functions to estimate TOC stocks (Liu et al., 2016). Furthermore, the time since land use change can have a significant effect on the distribution and amount of TOC deep in the regolith (Zhou et al., 2019), so further research is needed to explicitly investigate the impact of time since land use change on TOC deep in the regolith profile.

5. Conclusions

The TOC content and stock generally showed exponential depletion patterns from the land surface to the surface of the bedrock. On average, 63.3 % of TOC was stored below 100 cm, which confirmed the importance of deep soil when estimating SOC inventory in tropical and subtropical regions. Land use significantly affect the vertical distribution of TOC in the upper 100 cm, but did not markedly affect it below 200 cm. Soil texture was identified as the primary edaphic factor controlling TOC content of the different soils. This study provides important evidence to better understand deep soil C cycling and to provide better estimates of terrestrial C storage.

Acknowledgement

This study was financially supported by the National Key Research and Development Plan of China (2018YFE0107000), the National Natural Science Foundation of China (42107334), the Second Tibetan Plateau Scientific Expedition and Research Program (2019QZKK0306), and the China Postdoctoral Science Foundation (2021TQ0337, 2021M703305). Special thanks go to our colleagues of Soils in Time and Space team for their help during field survey and laboratory analysis.

Appendix A. Supplementary data

The following are the Supplementary data to this article:

Supplementary data 1.

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Table and Figure Captions

Table 1. Means and standard deviations (in brackets) of total organic carbon stocks (Mg C ha^{-1}) at different depth intervals.

Figure 1 Global distribution of red soil (referenced as Oxisols and Ultisols) (a) derived from Eswaran et al. (2012). Location of the study area in China (b). Spatial distribution of the 21 boreholes with an aerial base map (c). Numbers affiliated are drilling order during the field investigation.

Figure 2 Vertical distribution of TOC content from land surface to bedrock for the 21 drilling boreholes. The data for W3 between 1050 and 1950 cm was not shown for clarity.

Figure 3 Vertical distribution of cumulative TOC stock and proportion from land surface to bedrock for the 21 drilling boreholes. The data for W3 between 1050 and 1950 cm was not shown for clarity.

Figure 4 Relative importance of regolith properties (pH, silt, clay, sand, BD and WC) of the BRT models. Data are from depths 0 cm – bedrock, 0-100 cm and 100 cm - bedrock respectively. TOC, total organic carbon stock; BD, bulk density; WC, water content. The black line represents the cumulative TOC stock with increasing depth, while the blue line indicates the cumulative proportion of TOC with increasing depth.

Figure 5 Vertical distribution of TOC under different land use types at different depth intervals. Different lowercase letters (a and b) indicate that values were significantly different in the same land use ($p < 0.05$).

Figure 6 The distribution of mean TOC stock for different land uses at four depths.

Different lowercase letters (a, b and c) indicate that values were significantly different in the same land use ($p < 0.05$). Different uppercase letters (A, B and C) indicate that values were significantly different at the same depth ($p < 0.05$). The error bars indicate the standard error. n is the number of sample sites.

Figure 7 The distribution of mean TOC stock for different land uses at four depths. Different lowercase letters (a, b and c) indicate that values were significantly different in the same land use ($p < 0.05$). Different uppercase letters (A, B and C) indicate that values were significantly different at the same depth ($p < 0.05$). The error bars indicate the standard error. n is the number of sample sites.

Table 1. Means and standard deviations (in brackets) of TOC stocks (Mg C ha^{-1}) at different depth intervals.

Depth (cm)	Paddy field (n=8)	Cropland (n=7)	Woodland (n=3)	Orchard (n=3)	Total (n=21)
0-30 cm	44.2 (9.0)	21.4 (4.2)	23.9 (7.1)	17.9 (5.1)	23.0 (13.3)
30-100 cm	35.3 (8.4)	19.9 (3.1)	21.5 (2.2)	29.4 (9.7)	27.3 (9.4)
0-100 cm	79.5 (16.0)	41.2 (5.3)	45.4 (9.2)	47.3 (6.6)	57.3 (20.9)
100 cm-bedrock	111.5 (53.2)	113.2 (55.0)	125.2 (73.3)	90.8 (44.3)	111.1 (52.2)

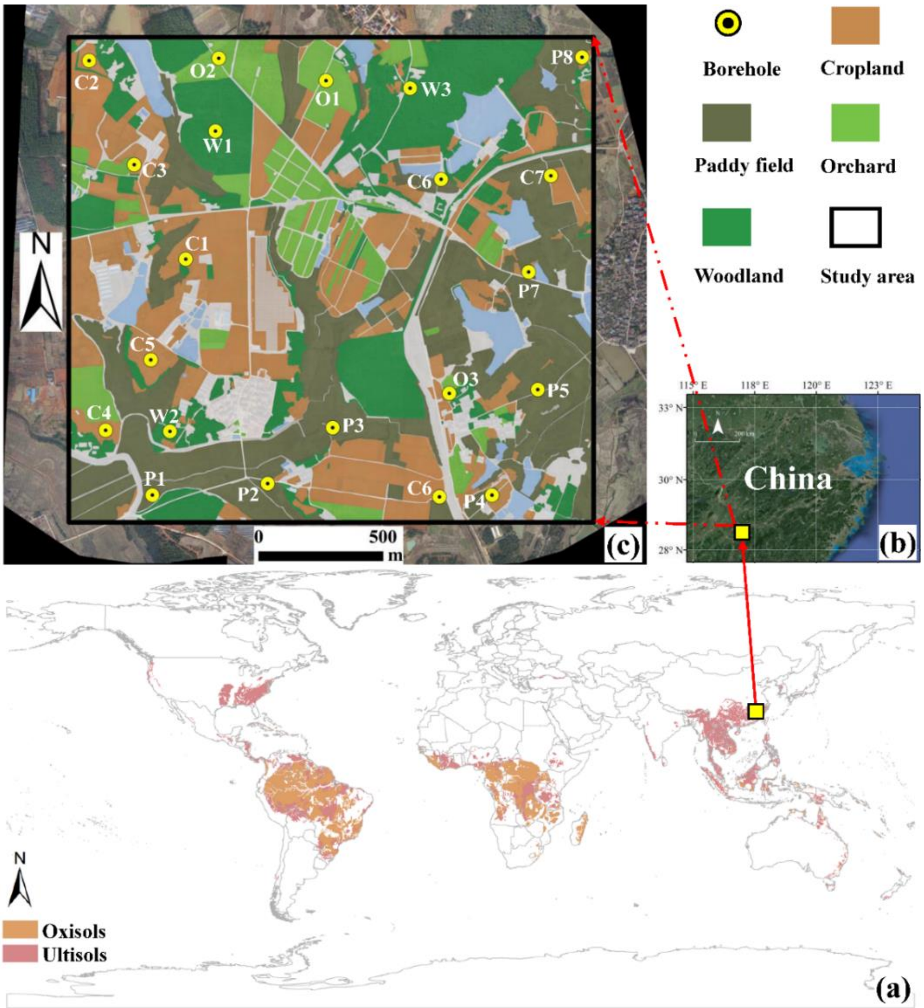


Figure 1 Global distribution of red soil (referenced as Oxisols and Ultisols) (a) derived from Eswaran et al. (2012). Location of the study area in China (b). Spatial distribution of the 21 boreholes with an aerial base map (c). Numbers affiliated are drilling order during the field investigation.

Figure 2 Borehole drilling in the field (a). Regolith core obtained by the drill (b). Observation and measurement of regolith core (c). Soil adhering to the inner wall of cylinder was cut and discarded to avoid potential contamination (d). Regolith core used to sample (e). Sampling strategy at different depth intervals (f).

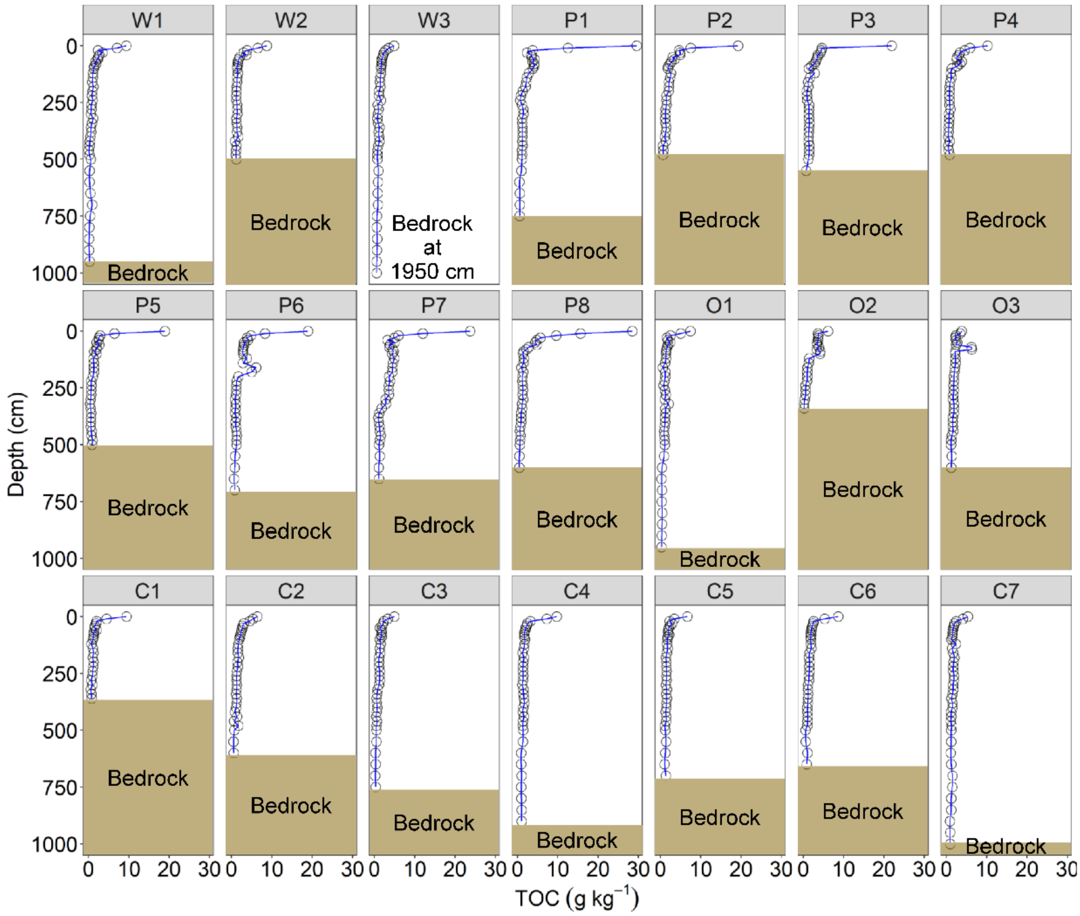


Figure 3 Vertical distribution of TOC content from land surface to bedrock for the 21 drilling boreholes. The data for W3 between 1050 and 1950 cm was not shown for clarity.

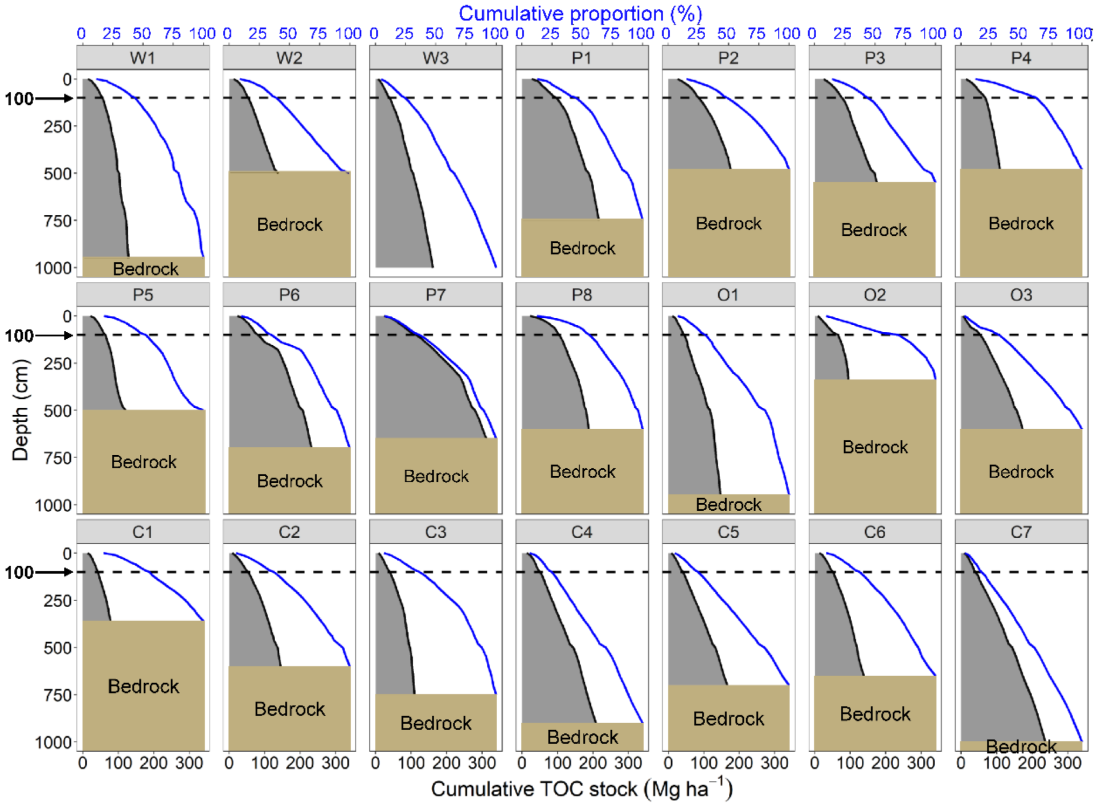


Figure 4 Vertical distribution of cumulative TOC stock and proportion from land surface to bedrock for the 21 drilling boreholes. The data for W3 between 1050 and 1950 cm was not shown for clarity. The black line represents the cumulative TOC stock with increasing depth, while the blue line indicates the cumulative proportion of TOC with increasing depth.

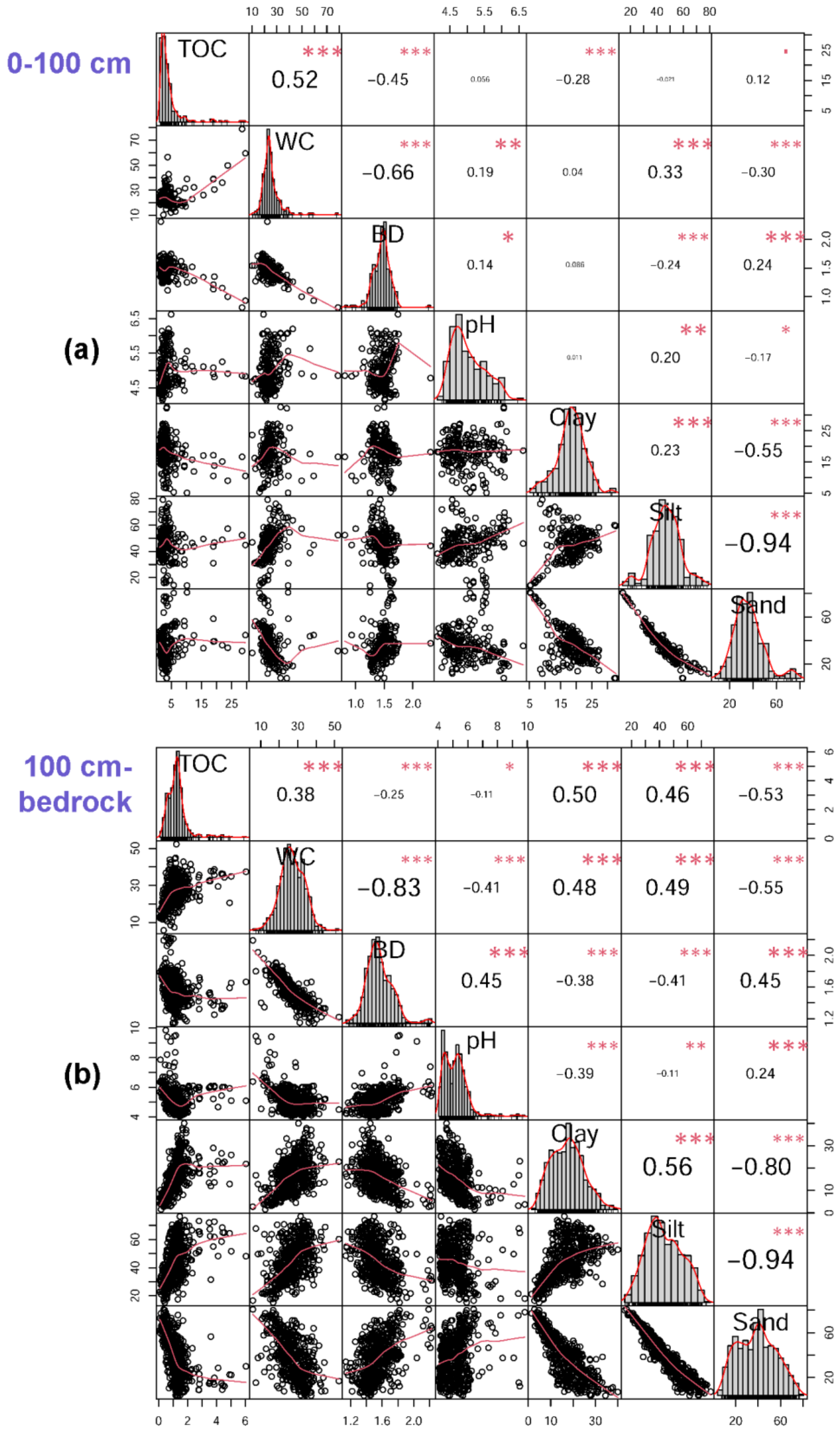


Figure 5 Pearson correlation between total organic carbon (TOC) and selected edaphic factors for the depths of 0-100 cm and 100 cm-bedrock, respectively. *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$.

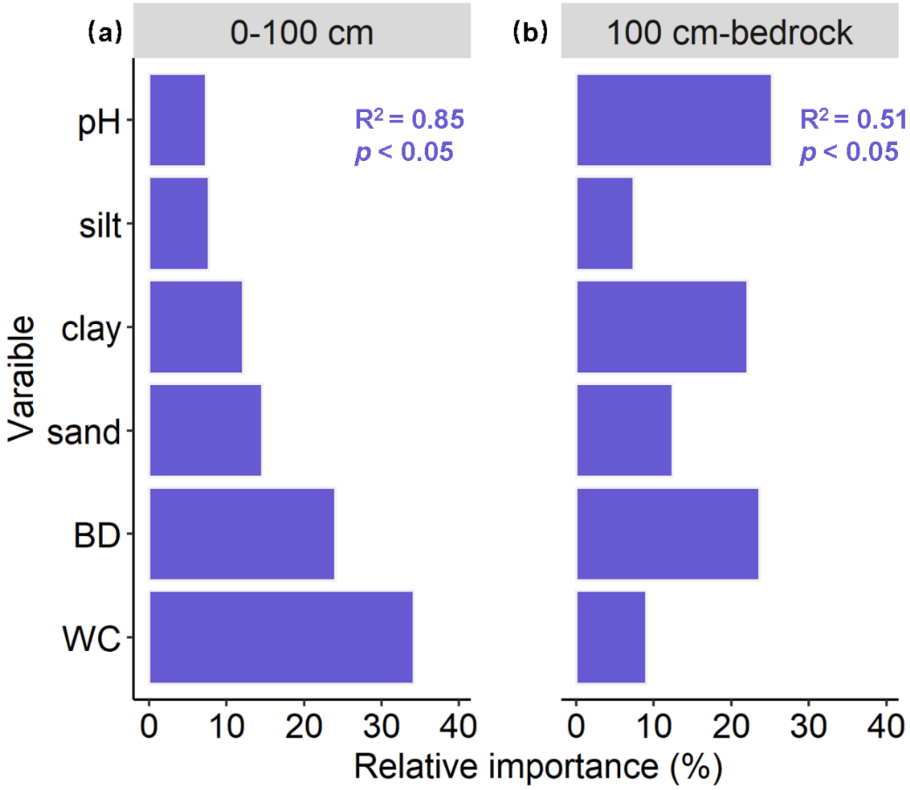
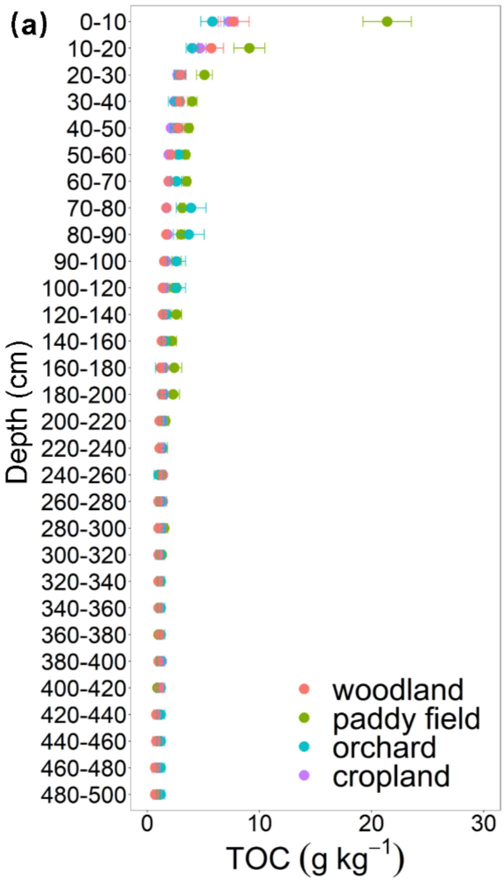


Figure 6 Relative importance of regolith properties (pH, silt, clay, sand, BD and WC) of the BRT models. Data are from depths 0-100 cm and 100 cm - bedrock respectively. TOC, total organic carbon stock; BD, bulk density; WC, water content.



(b)

Depth (cm)	W	P	O	C
0–10	b	a	b	b
10–20	ab	a	b	b
20–30	b	a	b	b
30–40	ab	a	b	b
40–50	ab	a	b	b
50–60	b	a	ab	b
60–70	b	a	b	b
70–80	b	a	a	b
80–90	b	a	a	b
90–100	a	a	a	a
100–120	a	a	a	a
120–140	a	a	a	a
140–160	a	a	a	a
160–180	a	a	a	a
180–200	a	a	a	a
200–220	a	a	a	a
220–240	a	a	a	a
240–260	a	a	a	a
260–280	a	a	a	a
280–300	a	a	a	a
300–320	a	a	a	a
320–340	a	a	a	a
340–360	a	a	a	a
360–380	a	a	a	a
380–400	a	a	a	a
400–420	a	a	a	a
420–440	a	a	a	a
440–460	a	a	a	a
460–480	a	a	a	a
480-500	a	a	a	a

Figure 7 Vertical distribution of TOC under different land use types at different depth intervals. Different lowercase letters (a and b) indicate that values were significantly different in the same land use ($p < 0.05$).

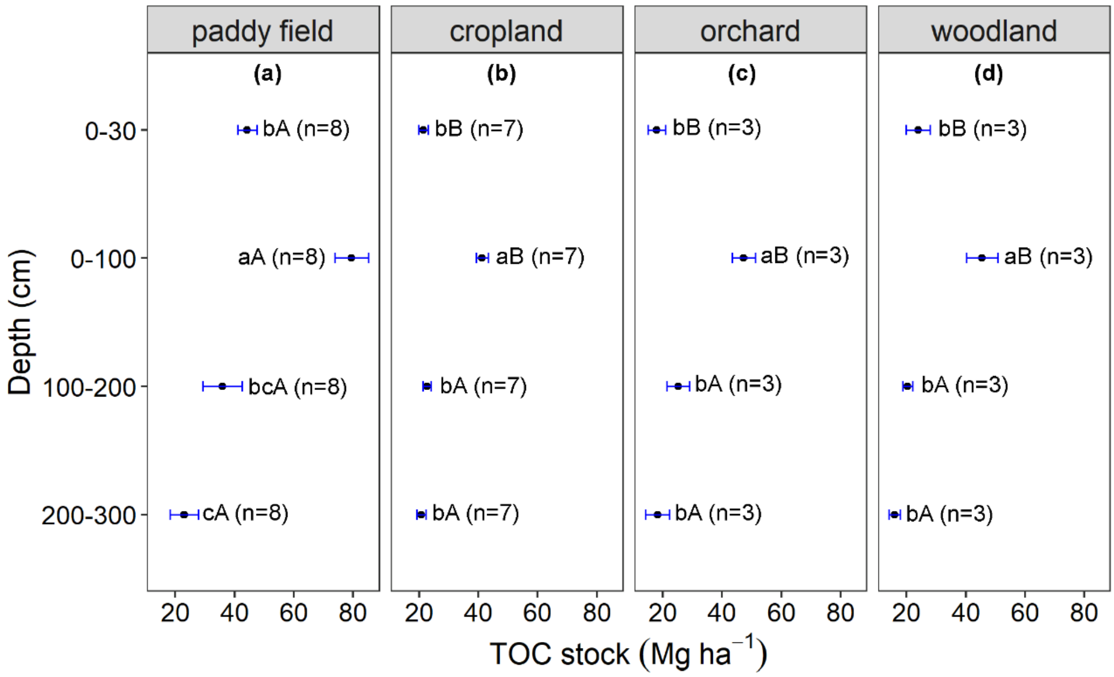


Figure 8 The distribution of mean TOC stock for different land uses at four depths. Different lowercase letters (a, b and c) indicate that values were significantly different in the same land use ($p < 0.05$). Different uppercase letters (A, B and C) indicate that values were significantly different at the same depth ($p < 0.05$). The error bars indicate the standard error. n is the number of sample sites.