# Organic carbon accumulation on soil mineral surfaces in paddy soils derived from tidal wetlands

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## ARTICLE INFO

## ABSTRACT

We studied organic carbon (OC) accumulation in organo-mineral associations during soil development on calcareous parent material. Two chronosequences in the Zhejiang Province, PR China, were investigated; one under paddy cultivation with a maximum soil age of 2000 years, and the other under upland crops where the oldest soil was 700 years old. Bulk soils and soil fractions of the uppermost A horizons were analyzed for OC concentrations, radiocarbon ($^{14}$C) contents, total pedogenic iron oxide concentration and oxalate extractable proportions of iron (Fe$_{OX}$) oxides. The specific surface area of soil minerals was measured with the Brunauer–Emmett–Teller (BET-N$_2$) method on four conditions: untreated, after organic matter removal, after iron oxide removal and after removal of both. Initial soil formation on calcareous marine sediments includes soil decalcification and OC accumulation. Paddy soils are characterized by an accelerated decalcification, higher contents of OC and Fe$_{OX}$ oxides, and a pronounced accumulation of modern OC. The mineral constitution of the soil material indicated already a certain degree of weathering since the earliest stages of pedogenesis and remained unchanged in paddy and non-paddy soils. The study provides no evidence of formation of new clay-sized minerals during soil development, which could supply new surfaces for OC accumulation. However, the study revealed higher OC coverage on mineral surfaces in decalcified paddy soils. Therefore, we assume the specific surface area and the specific affinity of Fe$_{OX}$ oxides for OC storage to play an important role for OC accumulation in organo-mineral associations. In contrast, the surface area of minerals in non-paddy soils, in which decalcification and the proportion of Fe$_{OX}$ oxides were much lower, showed significantly lower OC coverage. Selective removal of SOM or iron oxides clearly showed that iron oxides and SOM protect each other in organo-mineral associations primarily in paddy fine clay-sized fraction. Thus, we explained the higher OC coverage on mineral surfaces by complex association between clay minerals, iron oxides and SOM in paddy soils.

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## 1. Introduction

The accumulation of organic matter is an important soil-forming process. It is considered that the structural organization of organic matter and mineral constitutions in organo-mineral associations are the major mechanism of soil organic matter (SOM) stabilization (Balabane and Plante, 2004; Eusterhues et al., 2005). A positive correlation of the SOM content and mineral constitutions is known from the literature (Bosatta and Agren, 1997; Dümig et al., 2012; Jenkinson and Rayner, 1977; Jenkinson et al., 1987; Kaiser and Guggenberger, 2000; Kiem and Kögel-Knabner, 2002). This is explained by the large mineral surface area of soil minerals and the possibility of SOM adsorption on

their surface (Balabane and Plante, 2004; Tipping, 1981; Wagai and Mayer, 2007) or by their ability to interconnect particles to aggregates (Eusterhues et al., 2005). Organo-mineral associations are more resistant to biodegradation (Chenu and Plante, 2006), resulting in a slow turnover time of the clay-bound organic matter (Balesdent et al., 1987). However, the understanding of the degree and mechanisms of organic coverage on soil mineral surfaces is still incomplete (von Lützow et al., 2006; Wagai et al., 2009). The abundance of the mineral surface areas and the adsorption of organic matter on these mineral surfaces seem to be an important process in SOM stabilization (Kaiser and Guggenberger, 2003). In this context, clay-sized minerals, in particularly expandable phyllosilicates and sesquioxides are known to be providers of highest mineral surface areas for adsorption of organic matter (Bartoli et al., 2007; Cornell and Schwertmann, 2003; Ransom et al., 1998; Theng, 1979). Clay-sized minerals, such as smectites and vermiculites, provide a high surface area up to 800 m$^2$ g$^{-1}$ (Carter et al., 1986; Robert and Chenu, 1992) and in general stabilize more SOM than sand-

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sized minerals, which can be attributed to higher adsorption to mineral surfaces (Balabane and Plante, 2004). Most of the previously mentioned studies were done on relatively acid forest and agricultural soils or sandy subsoils. Investigations on the importance of clay-sized minerals and iron oxides for organic carbon (OC) accumulation are not available for paddy soil development starting from calcareous parent material with successive decalcification. At Hangzhou Bay, PR China, new agricultural land has been created by consecutive land reclamation with protective dikes over the past 2000 years, and it has been used for cultivation of flooded rice or non-inundated upland crops. The parent material is a calcareous marine sediment, which is influenced by suspended Yangtze River load. The management of the paddy soils (e.g., flooding and drainage) produces special soil properties. Flooding and discharge lead to a gradual carbonate loss and subsequent pH decrease during rice cultivation (Wissing et al., 2011). Thus, the pedogenesis of paddy soils differs remarkably from that of corresponding non-inundated croplands (Li et al., 2005) where decalcification is much slower. Faster decalcification caused by the paddy management accelerates other pedogenic processes. Paddy soil development favors OC accumulation due to high inputs of OC (Gong and Xu, 1990; Tanji et al., 2003) and/or retards the OC decomposition because of the periodic anoxic conditions that lead to enhanced SOM accumulation (Lal, 2002; Neue et al., 1997; Sahrawat, 2004; Wissing et al., 2011; Wu, 2011; Zhang and He, 2004). This is also confirmed by a higher radiocarbon ($^{14}$C)-documented replacement of "old" carbon by "modern" carbon over time than in non-inundated non-paddy soils due to plow pan development (Bräuer et al., 2012). The accumulation of SOM by association with oxalate-extractable iron ($Fe_{OX}$) has already been identified as a relevant feature in paddy soils (Pan et al., 2003a, 2003b). Wissing et al. (2013) found higher $Fe_{OX}$ contents in paddy soils than in non-inundated upland soils. The authors pointed out that the higher proportion of $Fe_{OX}$ seems to be responsible for a large proportion of mineral-associated SOM in paddy soils. Thus, the ability to stabilize OC is more pronounced in paddy soils compared to corresponding upland soils (Wissing et al., 2013).

In the present study, a chronosequence approach was applied to investigate soil development from calcareous parent material in order to assess the organic coverage on mineral surfaces. Our major research interest was to elucidate the evolution of organo-mineral associations during initial soil formation and if the OC coverage on mineral surface area is different in paddy agricultural systems with periodical submergence and drainage compared to soils under dryland cropping. A paddy and a non-paddy soil chronosequence in Zhejiang Province, PR China were used, to compare soil development and OC accumulation, starting from calcareous parent material with successive decalcification. Therefore, we addressed the following three research questions:

(i) Does decalcification control organic matter accumulation and accelerate the formation of clay minerals and iron oxides in paddy soils?
(ii) Is the OC coverage on soil minerals (clay mineral and iron oxide) higher in paddy soils, and does the OC coverage increase with soil development?
(iii) Which soil component accumulates more OC per gram fraction-clay minerals or iron (hydr)oxides?

For this approach, samples were taken from differently aged paddy (50–2000 years) and non-paddy soils (50–700 years). A particle size fractionation of the Ap horizon was applied to the soils in order to isolate the clay-sized fractions, and their iron oxides were extracted by using the dithionite–citrate–bicarbonate (DCB) method. The specific surface area (SSA) of the <20 μm fraction was measured by the Brunauer–Emmett–Teller (BET-$N_2$) method (Brunauer et al., 1938). To investigate the accessibility of those mineral surfaces for OC coverage during pedogenesis, we used selective removal of organic matter and iron oxides by combining hydrogen peroxide ($H_2O_2$) and DCB treatments.

## 2. Materials and methods

### 2.1. Study area and soil description

The study area was located in the eastern part of the PR China, near the city of Cixi (30°10′N, 121°14′E), Zhejiang Province. The investigation region is affected by river runoff and tide and the parent material consists of estuarine sediment, which originated from the Yangtze (Changjiang) River. With a sediment load of ca. 480 million tons per year (Milliman

**Table 1**
Basic soil parameters of mudflat (0 years), 30-year-old marshland, and paddy (P) and non-paddy (NP) bulk soils (uppermost A horizons): Depths, horizon denominations, pH values, concentrations of inorganic carbon (IC) and organic carbon (OC), dithionite- and oxalate-extractable iron oxides ($Fe_{DCB}$ and $Fe_{OX}$, respectively) and base saturation (BS). All numbers give the arithmetic mean ($n = 3$) with standard errors. The effect of the soil age was tested and significant differences ($p \leq 0.05$) within the paddy and non-paddy chronosequence are indicated by italic letters. The clay content from soil texture analysis was determined in a single measurement. The effect of the soil management was tested by comparing mean values of all age classes of paddy and non-paddy soils over 700 and 2000 years pedogenesis. * represents significant differences ($p \leq 0.05$) between paddy and non-paddy soils.

| Site | Depth (cm) | Horizon[a] (FAO) | pH[b] (KCl) | IC[c] (mg g$^1$) | OC[c] (mg g$^{-1}$) | $Fe_{DCB}$[c] (mg g$^{-1}$) | $Fe_{OX}$[c] (mg g$^{-1}$) | BS[d] (% of CECpot) | Clay content <2.0 μm[e] (g kg$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| Mudflat (0 years)[f] | 0–30 | – | 8.2 ± – | 5.0 ± – | 5.1 ± – | 5.3 ± – | 4.1 ± – | >100 | – |
| Marsh (30 years)[f] | 0–13 | – | 7.8 ± – | 4.0 ± – | 10.9 ± – | 6.2 ± – | 2.4 ± – | >100 | – |
| P 50 | 0–7 | Alp | 7.4 ± 0.0 a | 1.4 ± 0.3 a | 17.8 ± 0.5 b | 7.0 ± 0.1 a | 2.6 ± 0.6 a | >100 | 290 |
| P 100 | 0–9 | Alp1 | 5.0 ± 0.2 bc | b.d.l ± – b | 17.6 ± 1.0 bc | 6.8 ± 0.4 a | 3.0 ± 0.3 a | 72 | 279 |
| P 300 | 0–18 | Alp | 5.8 ± 0.3 b | b.d.l ± – b | 22.6 ± 2.0 bc[b] | 6.6 ± 0.1 a | 2.2 ± 0.3 a | 71 | 245 |
| P 700 | 0–10 | Alp1 | 6.7 ± 0.1 a | b.d.l ± – b | 22.3 ± 2.2 b | 6.8 ± 0.2 a | 3.3 ± 0.7 a | 82 | 286 |
| P 1000 | 0–10 | Alp | 5.2 ± 0.3 bc | b.d.l ± – b | 14.0 ± 0.8 c | 7.3 ± 0.2 a | 3.0 ± 0.4 a | 69 | 277 |
| P 2000 | 0–15 | Alp | 5.1 ± 0.1 c | b.d.l ± – b | 30.0 ± 0.9 a[b] | 4.4 ± 0.1 b | 2.8 ± 0.2 a | 58 | 242 |
| Mean (50–700 years) | | | 6.2 | | 20.1* | 6.8 | 2.8* | | 275 |
| Mean (50–2000 years) | | | 5.9 | | 20.7* | 6.5 | 2.8* | | 270* |
| NP 50 | 0–9 | Ap | 7.3 ± 0.1 a | 1.6 ± 0.1 a | 10.6 ± 0.0 a | 6.3 ± 0.2 a | 1.5 ± 0.3 a | >100 | 208 |
| NP 100 | 0–14 | Ap1 | 7.3 ± 0.1 a | 0.7 ± 0.1 ab | 10.8 ± 0.0 a | 7.0 ± 0.3 a | 1.3 ± 0.2 a | >100 | 272 |
| NP 300 | 0–11 | Ap | 7.0 ± 0.2 a | 0.1 ± 0.2 b | 10.5 ± 0.0 a | 6.3 ± 0.1 a | 0.7 ± 0.2 a | 95 | 237 |
| NP 700 | 0–11 | Ap1 | 5.9 ± 0.3 b | b.d.l ± – | 11.0 ± 0.3 a | 5.0 ± 0.9 a | 1.5 ± 0.6 a | 74 | 190 |
| Mean (50–700 yrs) | | | 6.9 | | 10.7 | 6.2 | 1.3 | | 227 |

[a] Guidelines for soil profile description (FAO, 2006).
[b] pH values, determined by the laboratory of the Institute for Agricultural and Nutritional Sciences at the Martin-Luther University in Halle-Wittenberg, were already published in Wissing et al. (2013).
[c] Carbon data, $Fe_{DCB}$ and $Fe_{OX}$ were published in Wissing et al. (2011, 2013).
[d] BS of the paddy and non-paddy soils was already published in Kölbl et al. (2014–in this issue). BS only meaningful for carbonate free horizons and BS saturation >100% due to carbonates.
[e] Clay content from soil texture analysis was published in Wissing et al. (2013). Statistics of pH values, OC, $Fe_{DCB}$ and $Fe_{OX}$ were published in Wissing et al. (2011, 2013). b.d.l. = below the detection limit. The effect of the soil management on the bulk soil parameter IC was not assignable due to less than two IC values of paddy soils.
[f] pH values, carbon data and base saturation (BS) of mudflat and marshland from Kalbitz et al. (2013).