

Article

Dual Role of Iron Oxides in Stabilizing Particulate and Mineral-Associated Organic Carbon Under Field Management in Paddies

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Abstract

The interactions between iron oxides and organic carbon within the particulate organic matter (POM) and mineral-associated organic matter (MAOM) fractions in paddy soils remain insufficiently understood, yet they are likely crucial for unlocking the carbon sequestration potential of these systems. In this study, we investigated the distribution of soil iron oxides and organic carbon within POM and MAOM fractions following 10 years of continuous irrigation and organic amendment management. We also examined the relationship between iron oxide transformation and these two SOC (soil organic carbon) fractions. Our results demonstrated that, under both flooded irrigation and controlled irrigation regimes, straw return or manure application effectively enhanced soil carbon sequestration, as evidenced by increases in both POM-C (POM-associated organic carbon) and MAOM-C (MAOM-associated organic carbon) contents. Meanwhile, exogenous carbon inputs promoted the transformation of crystalline iron oxides into short-range ordered iron oxides and iron oxide colloids, thereby enhancing the activation and complexation degree of soil iron oxides and facilitating the formation of Fe-bound organic carbon. Further regression analysis revealed that the activation degree of iron oxides had a stronger influence on POM-C, whereas the complexation degree had a greater effect on MAOM-C. This implies that exogenous carbon inputs are effective in promoting soil carbon sequestration in both flooded and water-saving irrigated rice paddies and that iron oxide transformation plays a key role in mediating this effect.

Keywords: paddy; soil organic carbon; soil iron oxides; particulate organic matter; mineral-associated organic matter



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1. Introduction

In agroecosystems, paddy fields represent the largest anthropogenic wetland system globally, covering approximately 167 million hectares [1,2], and constitute a vital land use type for ensuring global food security [3]. Due to prolonged flooding management, paddy soils have become substantial sources of greenhouse gas emissions, particularly methane (CH₄), accounting for 12–26% of global anthropogenic CH₄ emissions [4,5]. Nevertheless, specific agricultural practices—such as tillage, irrigation regimes, fertilization strategies, and straw incorporation—can significantly improve the physicochemical properties of paddy soils and enhance their potential for soil organic carbon (SOC) sequestration [6–8].

The accumulation of SOC in paddy topsoils can, to some extent, offset CH₄ emissions and mitigate subsoil carbon losses associated with flooded cultivation [9–11]. Moreover, SOC is closely linked to soil fertility and plays a vital role in maintaining crop productivity and promoting agricultural sustainability [3,12]. Therefore, a deeper understanding of the mechanisms driving SOC sequestration in paddy fields is essential for advancing the sustainable management of rice-based agroecosystems.

The slow decomposition of rice plant residues under flooded conditions is one of the primary factors contributing to the accumulation of SOC in paddy soils [13,14]. In addition, carbon stabilization mechanisms such as the physical occlusion of SOC within soil aggregates and the formation of organo-mineral complexes also play critical roles in SOC stabilization and retention [6]. It is widely accepted that the association between soil organic carbon (SOC) and soil minerals is a key mechanism for its long-term stabilization [15], as minerals can stabilize organic matter through strong chemical bonding. The resulting microaggregates or co-precipitates further contribute to the physical protection of SOC by limiting its accessibility to extracellular enzymes and heterotrophic microorganisms, thereby enhancing its persistence in soil [16–19].

However, the periodic wet–dry cycles characteristic of paddy fields lead to pronounced fluctuations in soil redox conditions, which in turn affect the biogeochemical cycling of redox-sensitive elements, particularly iron (Fe) minerals, i.e., iron oxides [20–22]. Numerous studies have demonstrated that iron oxides form extensively under moist soil conditions with varying degrees of crystallinity. These iron oxides can retain SOC through mechanisms such as adsorption and co-precipitation, thereby playing a crucial role in regulating the stability and storage of SOC [17,23,24]. Due to their high surface reactivity, iron oxides can also act as binding agents between organic carbon and clay particles, thereby promoting the formation of organo-mineral complexes and macroaggregates [25,26]. These processes are significantly influenced by the type and crystallinity of the iron oxides involved [25,27]. In particular, reactive iron oxides (mainly short-range ordered Fe (SRO-Fe) and poorly crystalline Fe), owing to their large specific surface area, are often regarded as important “rust sinks” for SOC accumulation in soils [28]. Studies have reported that the carbon sequestration efficiency of paddy soils is 39% to 127% higher than that of adjacent upland soils, and the contribution of reactive iron oxides to SOC stabilization may be one of the key factors underlying this difference [29,30]. It is estimated that, on average, approximately 23% of SOC in agricultural soils is associated with reactive iron oxides [31].

Meanwhile, the physicochemical properties of paddy soils are significantly influenced by field management practices such as irrigation and fertilization [32], which in turn alter the forms and reactivity of iron oxides, thereby affecting the formation of iron-bound organic carbon and regulating SOC accumulation and stabilization [13,33]. In paddy fields, the two primary irrigation strategies are conventional flooding and water-saving irrigation [34,35]. Variations in soil moisture caused by these practices strongly influence soil oxygen availability, thereby affecting SOC dynamics through interactions with redox-sensitive elements such as Fe [36–38]. Under flooded conditions, the reductive dissolution of crystalline iron oxides can be triggered, promoting the formation of reactive iron oxides that bind organic carbon more effectively [39]. However, prolonged submergence may also destabilize soil aggregates due to the release of SOC during the reductive dissolution of iron oxides [40]. Compared with conventional flooding, water-saving irrigation creates a distinct soil microenvironment characterized by periodic changes in moisture content, enhanced aeration frequency, and fluctuations in redox potential [41,42]. Han et al. (2024) reported that, under water-saving irrigation, reactive iron oxides tend to transform into colloidal forms, which increases the proportion of Fe-bound organic carbon (Fe-OC) [43]. Moreover, the formation of iron–carbon associations is highly sensitive to changes in soil

pH [44]. Under long-term organic fertilization, the accumulation of organic acids can activate iron oxides, enhance their binding with organic carbon, and thereby promote SOC sequestration [28,45,46]. Excessive application of chemical nitrogen fertilizers may also lead to soil acidification, which similarly enhances the capacity of iron oxides to bind organic carbon [47]. Therefore, a comprehensive understanding of how iron oxides regulate SOC accumulation under different paddy field management practices is essential for improving the carbon sequestration potential of rice soils.

However, current research has predominantly focused on bulk soil organic carbon, without fully distinguishing the specific roles of iron oxides in different SOC fractions. In addition to promoting the accumulation of mineral-associated organic matter (MAOM) through the formation of Fe-OC complexes, iron oxides also facilitate soil aggregate formation, thereby influencing the stabilization of particulate organic matter (POM) [3]. Understanding the distinct contributions of particulate-associated and mineral-associated SOC is essential, as these two fractions differ significantly in composition, formation mechanisms, persistence, and ecological functions [48]. POM is believed to mostly consist of fragmented, incompletely decomposed plant litter, with a characteristic of faster cycling in soils [48–50]. In contrast, MAOM comprises thermolabile compounds from microbes and is stabilized via mineral interactions, resulting in residence times of years to millennia [16–19,51]. Clarifying the respective roles of iron oxides in stabilizing these SOC fractions under different irrigation and organic amendment practices will enhance our understanding of iron–carbon interactions in paddy soils.

In this study, we focused on paddy soils that had been subjected to different irrigation regimes and exogenous carbon amendments for a continuous 10-year period. We analyzed the distribution patterns of crystalline iron oxides, short-range ordered (SRO) iron oxides, and iron oxide colloids under different treatments, and evaluated their respective roles in the stabilization of organic carbon molecules. Furthermore, we investigated the relationship between iron oxide transformation and organic carbon within POM and MAOM fractions. These findings might provide mechanistic insights into iron–carbon interactions and offer practical implications for sustainable paddy field management strategies aimed at enhancing soil carbon sequestration and agricultural productivity.

2. Materials and Methods

2.1. Site Description

A long-term field experiment was conducted from 2012 to 2023 at the National Key Laboratory of Water Disaster Prevention of Hohai University, Kunshan Irrigation and Drainage Experiment Station (34°15′21″ N, 121°05′22″ E). The site is located in a northern subtropical region and has a monsoon climate, with a mean annual temperature of 16.2 °C. The annual average precipitation is 1378 mm, and the annual average water surface evaporation is 1307.2 mm. The soil is classified as Anthrosols [52], with a silty loam texture. A rice–wheat rotation is practiced in the region, with rice being planted in June to October and wheat from November and May of the next year.

2.2. Experimental Design and Soil Sampling

The field experiment was conducted in 18 plots (3 m × 7 m), with three replicates for each of six treatments. During the wheat-growing season, all plots were managed using conventional practices without treatment differentiation, whereas field treatments were implemented only during the rice season, which was the focus of this study.

The field treatments during the rice season were as follows: (i) flooded irrigation only (FI); (ii) controlled irrigation only (CI); (iii) flooded irrigation + wheat straw (FS); (iv) controlled irrigation + wheat straw (CS); (v) flooded irrigation + manure application

(FM); (vi) controlled irrigation + manure application (CM). After the wheat was harvested in May, the remaining straw was cut into pieces (5–7 cm) and then returned to the plots. The manure added was well-decomposed chicken manure. For all flooded irrigation, a 40–60 mm standing water level was maintained until the end of the milk-ripe stage. Detailed information regarding controlled irrigation and organic amendment management is shown in Tables 1 and 2, respectively. The rice transplanted in the experiment was Japonica rice named “Wuxiang 19”. Other management practices were consistent during the experiment, such as pesticide application, weeding, and harvesting.

Table 1. Soil moisture thresholds in root zone under controlled irrigation during the entire growth period of rice.

Stage	Re-Greening	Tillering			Jointing–Booting		Heading–Flowering	Milk-Ripe	Yellow-Ripe
		Early	Middle	Late	Early	Late			
Moisture thresholds	5–25 mm	$0.7\theta_{s1}-\theta_{s1}$	$0.65\theta_{s1}-\theta_{s1}$	$0.65\theta_{s1}-\theta_{s1}$	$0.7\theta_{s2}-\theta_{s2}$	$0.75\theta_{s2}-\theta_{s2}$	$0.8\theta_{s3}-\theta_{s3}$	$0.7\theta_{s3}-\theta_{s3}$	Naturally drying
Root zone depth (cm)	—	0–20	0–20	0–20	0–30	0–30	0–40	0–40	—

“5–25 mm” was the standing water depth in re-greening stage. θ_{s1} , θ_{s2} , θ_{s3} represent the saturated volumetric soil moisture for the 0–20, 0–30, and 0–40 cm soil layers, respectively.

Table 2. Organic amendment management in different treatments (flooded irrigation only (FI), controlled irrigation only (CI), flooded irrigation + wheat straw (FS), controlled irrigation + wheat straw (CS), flooded irrigation + manure application (FM), controlled irrigation + manure application (CM)) during the entire growth period of rice (kg hm^{-2}).

Fertilizer	FI and CI			FS and CS			FM and CM		
	I	II	III	I	II	III	I	II	III
Compound fertilizer	525	—	—	525	—	—	525	—	—
Urea	225	150	120	225	150	120	—	150	120
Straw	—	—	—	3000	—	—	—	—	—
Manure	—	—	—	—	—	—	7500	—	—

Compound fertilizer contained 15% N, 15% P_2O_5 , and 15% K_2O . The N portion in urea was more than 46.2%. The organic carbon in wheat straw and manure was 443 g kg^{-1} and 265 g kg^{-1} , respectively. The portion of N in wheat straw and manure was 0.58% and 1.6%, respectively. “I, II, III” represent the basal fertilizer, tillering fertilizer, and panicle fertilizer, respectively. “—” indicates no fertilizer added.

Soil samples (0–20 cm) were collected in October 2022 and 2023 during harvest, ten years after the experiment was established (Supplementary Figure S1 and Table S1 present the rainfall and temperature data recorded during the rice growing seasons of both study years). An auger was used to randomly gather five soil cores from each layer in the same plot. These cores were then thoroughly mixed to create a composite sample for each plot at each depth. Soil-removed roots and other intrusions were air-dried for further analysis.

2.3. Soil Analyses

The fractions of particulate organic matter (POM) and mineral-associated organic matter (MAOM) were separated from soil samples using ultrasonic dispersion combined with wet sieving [53]. SOC in bulk soil, POM, and MAOM fractions were determined using the wet oxidation method with $\text{K}_2\text{Cr}_2\text{O}_7$ – FeSO_4 , as described by Walkley and Black [54].

The iron oxides were extracted by using different carbon-free extractants [55]. FeDH was extracted with sodium dithionite and HCl (DH), representing crystalline oxides in soils. FeHH was extracted with hydroxylamine acidified by HCL (HH), representing

SRO-Fe oxides (short-range ordered iron oxides) in soils. FePP was extracted with sodium pyrophosphate (PP), representing Fe oxide colloids associated with SOC. Briefly, the sample was extracted at a soil-to-extractant ratio of 1:50 with shaking at 180 rpm (revolutions per minute) for 16 h. After centrifugation and filtration, the concentrations of Fe phases (FeDH, FeHH, FePP) and their associated organic carbon (DH-OC, HH-OC, PP-OC) were determined via UV spectrophotometry and a TOC analyzer (Shimadzu, Japan), respectively. The molar ratio between extracted organic carbon and extracted iron oxides, denoted as C:Fe, reflects the binding structure between organic carbon and iron oxides within each Fe phase. The molar C:Fe ratio for each Fe phase and the activation and complexation indices of iron oxides were calculated as follows:

$$C : Fe = (OC \text{ content}/12) / (Iron \text{ oxides content}/56) \quad (1)$$

$$Fe \text{ activation degree} = FeHH \text{ content} / FeDH \text{ content} \quad (2)$$

$$Fe \text{ complexation degree} = FePP \text{ content} / FeDH \text{ content} \quad (3)$$

where 12 and 56 are the relative atomic mass of C and Fe, respectively.

2.4. Data Analyses

One-way ANOVA followed by Duncan's multiple comparison test was conducted using SPSS version 26.0 (IBM Corp., Armonk, NY, USA) to evaluate differences in SOC, iron oxides, and their bound organic carbon among different treatments. A multifactorial analysis of variance was conducted using the general linear model (GLM) procedure in SPSS. Year (Y), irrigation regimes (I), and organic amendments (C) were included as fixed factors to evaluate their main and interaction effects on SOC and iron oxide transformation indices. Additionally, regression analyses were performed using Origin Pro v.2025 (OriginLab Corp., Northampton, MA, USA) to investigate the relationships between iron oxide transformation indices and SOC, with results visually presented through graphical plots.

3. Results

3.1. Contents of SOC in Bulk Soil, POM, and MAOM Fractions

The organic carbon contents in bulk soil, particulate organic matter (POM), and mineral-associated organic matter (MAOM) after rice harvest in 2022 and 2023 are presented in Figure 1. Two-way ANOVA results (Table 3) showed that exogenous carbon input had a significant effect on SOC content in both years, whereas the effect of irrigation regime was significant only in 2022. The main effect of year (Y) was also significant ($p < 0.01$), indicating that the overall SOC level differed between 2022 and 2023 (Table S2); however, the non-significant $Y \times I$, $Y \times C$, and $Y \times I \times C$ interactions suggest that the effects of irrigation and carbon input were consistent across years and that the relative differences among treatments did not vary with year. Within the two years, the SOC content in bulk soil showed significant differences among treatments ($p < 0.01$). Compared with FI, CI exhibited a comparable SOC level. Under both irrigation regimes, either straw incorporation or manure application markedly enhanced SOC concentrations. Specifically, under flooded irrigation, SOC increased by approximately 19.71% and 30.37% in the FS and FM treatments, respectively, compared with FI; under controlled irrigation, SOC rose by about 19.38% and 36.11% in the CS and CM treatments, respectively.

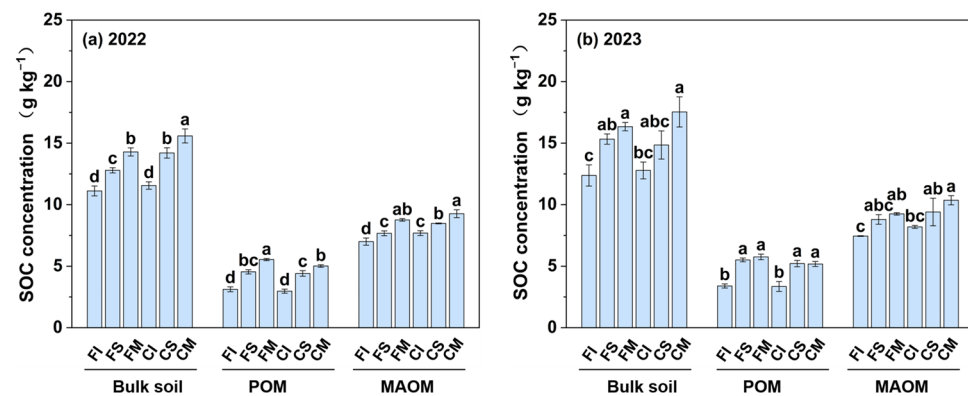


Figure 1. The SOC concentration (g kg^{-1}) in bulk soil, POM, and MAOM fractions under different irrigation and organic amendment management (mean value $\pm$ standard error). The significance is labeled by letter notation (a, b, c, d) based on the size of the mean value of the results for each treatment ($p < 0.05$).

Table 3. Two-way analysis of variance (ANOVA) of SOC in bulk soil, POM, and MAOM fractions.

ANOVA	2022			2023		
	Bulk Soil	POM	MAOM	Bulk Soil	POM	MAOM
I	**	ns	*	ns	ns	ns
C	**	**	**	**	**	**
I $\times$ C	ns	ns	ns	ns	ns	ns

ns indicates no significance; * indicates difference at $p < 0.05$ and ** indicates difference at $p < 0.01$.

For POM-associated organic carbon (POM-C), the main effect of year (Y) was significant ($p < 0.01$) (Table S2). In 2022, POM-C content ranged from 3.12 to 5.54 g kg^{-1} across treatments, accounting for approximately 25.73% to 38.77% of total SOC, with significant differences among treatments ($p < 0.01$). In 2023, the content ranged from 3.40 to 5.76 g kg^{-1} , contributing about 26.22% to 35.96% of SOC, and treatment differences remained significant ($p < 0.05$). Compared with 2022, POM-C content in 2023 increased by approximately 3.29% to 21.29% across treatments. Under the same external carbon input, POM-C contents were consistently higher under flooded irrigation than under controlled irrigation, by about 3.03% to 10.39% in 2022 and 1.35% to 11.09% in 2023.

In contrast, MAOM-associated organic carbon (MAOM-C) content ranged from 7.00 to 9.27 g kg^{-1} in 2022 and from 7.45 to 10.36 g kg^{-1} in 2023, accounting for 59.44% to 66.55% and 56.63% to 64.12% of SOC, respectively. For treatments under the same organic amendment management, MAOM-C contents were higher under controlled irrigation than under flooded irrigation, by about 5.70% to 10.46% in 2022 and 6.87% to 11.96% in 2023. As shown in Table 1, the addition of exogenous carbon consistently and significantly enhanced both POM-C and MAOM-C contents across years. Under both irrigation regimes, exogenous carbon inputs led to an increase in POM-C by approximately 45.58% to 77.43% in 2022 and 54.64% to 69.50% in 2023, and in MAOM-C by about 9.66% to 25.20% in 2022 and 14.77% to 26.40% in 2023.

3.2. Contents of Fe-OC in MAOM

The content of total iron-oxide-bound organic carbon (Fe-OC) in the MAOM fraction is presented in Figure 2. Significant differences in Fe-OC content were observed among treatments in both years ($p < 0.01$). In 2022, Fe-OC content ranged from 3.68 to 4.38 g kg^{-1} , accounting for approximately 47.30% to 52.85% of MAOM-C. In 2023, it ranged from 3.83 to 5.18 g kg^{-1} , contributing about 50.11% to 55.60% of MAOM-C. In 2022, the CI

treatment exhibited significantly higher Fe-OC content than the FI treatment, whereas no significant difference was observed between the two in 2023. Compared with FI, the FS and FM treatments increased Fe-OC contents by approximately 9.79% and 17.79% in 2022, and by about 27.36% and 24.90% in 2023, respectively. Similarly, compared with CI, Fe-OC contents in the CS and CM treatments increased by approximately 5.07% and 7.80% in 2022 and by 24.21% and 26.46% in 2023, respectively.

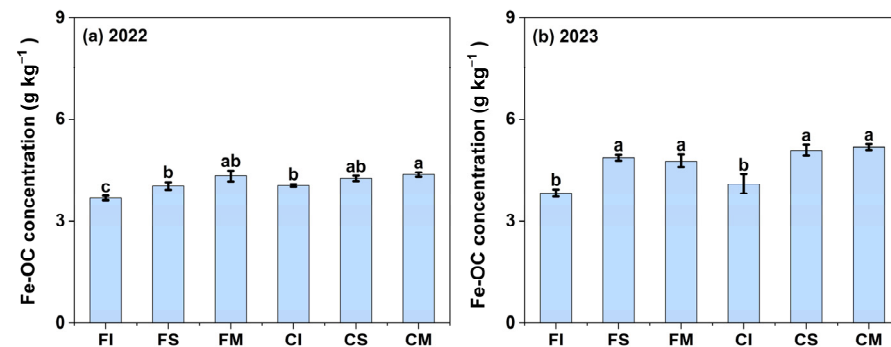


Figure 2. The Fe-OC concentration in MAOM fractions (g kg^{-1}) under different irrigation and organic amendment management (mean value $\pm$ standard error). The significance is labeled by letter notation (a, b, c) based on the size of the mean value of the results for each treatment ($p < 0.05$).

The distribution of organic carbon bound to the three forms of iron oxides was consistent across treatments and years, in the following order: PP-OC > HH-OC > DH-OC (Figure 3). In 2022, PP-OC accounted for 46.54% to 51.23% of total Fe-OC, HH-OC for 30.70% to 34.89%, and DH-OC for 16.60% to 19.67%. In 2023, the corresponding proportions were 46.89% to 52.14% for PP-OC, 30.20% to 34.94% for HH-OC, and 15.83% to 20.04% for DH-OC. In 2022, the contents of DH-OC and HH-OC varied significantly among treatments ($p < 0.01$), with treatment rankings as follows: DH-OC, FI < CS < CI < FS < FM < CM; HH-OC, FI < CI < CS < FS < FM < CM. In 2023, significant differences were observed for HH-OC and PP-OC ($p < 0.05$), with the treatment rankings being: HH-OC, FI < CI < FS < FM < CS < CM; PP-OC, FI < CI < FM < CM < FS < CS.

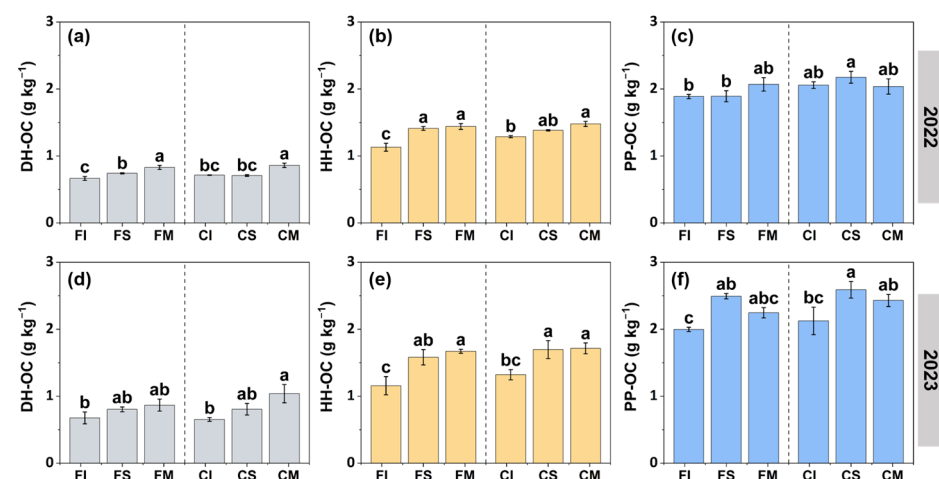


Figure 3. Fe-OC contents (g kg^{-1}) under different irrigation and organic amendment treatments. Panels (a–c) show the contents of FeDH-, FeHH-, and FePP-associated organic carbon (denoted as DH-OC, HH-OC, and PP-OC, respectively) in 2022; panels (d–f) show the corresponding values in 2023 (mean $\pm$ standard error). The significance is labeled by letter notation (a, b, c) based on the size of the mean value of the results for each treatment ($p < 0.05$).

3.3. Characteristics of Iron Oxide Distribution in MAOM Under Different Management

3.3.1. Contents of Iron Oxides

The distribution patterns of the three forms of iron oxides were consistent across all treatments, in the following order: FeDH > FeHH > FePP (Table 4). In 2022, FeDH contents ranged from 11.07 to 12.21 g kg⁻¹ and from 10.77 to 12.05 g kg⁻¹ in 2023, with no significant differences observed among treatments in either year ($p > 0.05$). In contrast, FeHH contents showed significant treatment effects in both years ($p < 0.01$), with ranges of 2.05 to 2.61 g kg⁻¹ in 2022 and 2.03 to 2.52 g kg⁻¹ in 2023. FeHH contents under FI and CI treatments remained relatively stable across the two years, while both straw return and manure application significantly increased FeHH concentrations under both irrigation regimes. Compared with FI, FeHH contents in FS and FM increased by approximately 20.05% and 27.63% in 2022 and by 17.12% and 20.20% in 2023, respectively. Compared with CI, FeHH contents in CS and CM increased by about 9.25% and 12.19% in 2022 and by 20.27% and 22.74% in 2023, respectively. However, except for a significant difference between FM and CM in 2022, FeHH contents were generally similar between the two irrigation regimes under the same carbon input. FePP contents ranged from 0.63 to 0.75 g kg⁻¹ in 2022 and from 0.62 to 0.85 g kg⁻¹ in 2023, with significant differences among treatments ($p < 0.05$). Similar to FeHH, FePP contents were higher under treatments with external carbon inputs. Specifically, compared with FI, FePP contents in FS and FM increased by approximately 7.97% and 9.24% in 2022 and by 17.41% and 12.18% in 2023, respectively. Compared with CI, CS and CM treatments showed increases of about 16.92% and 10.85% in 2022 and 30.27% and 24.03% in 2023, respectively.

Table 4. Concentrations of iron oxides in MAOM (g kg⁻¹) under different irrigation and organic amendment management (mean value $\pm$ standard error).

Year	Iron Oxides	FI	FS	FM	CI	CS	CM
2022	FeDH	12.18 $\pm$ 0.30 a	11.30 $\pm$ 0.35 a	12.01 $\pm$ 0.24 a	12.21 $\pm$ 0.38 a	11.19 $\pm$ 0.73 a	11.06 $\pm$ 0.12 a
	FeHH	2.04 $\pm$ 0.03 c	2.45 $\pm$ 0.03 ab	2.61 $\pm$ 0.08 a	2.09 $\pm$ 0.05 c	2.29 $\pm$ 0.05 b	2.35 $\pm$ 0.02 b
	FePP	0.62 $\pm$ 0.00 c	0.67 $\pm$ 0.01 bc	0.68 $\pm$ 0.02 abc	0.64 $\pm$ 0.02 c	0.74 $\pm$ 0.02 a	0.71 $\pm$ 0.02 ab
2023	FeDH	12.04 $\pm$ 0.69 a	11.02 $\pm$ 0.18 a	11.17 $\pm$ 0.32 a	11.93 $\pm$ 0.62 a	11.26 $\pm$ 0.53 a	10.76 $\pm$ 0.27 a
	FeHH	2.02 $\pm$ 0.00 b	2.37 $\pm$ 0.02 a	2.43 $\pm$ 0.05 a	2.05 $\pm$ 0.10 b	2.47 $\pm$ 0.04 a	2.52 $\pm$ 0.07 a
	FePP	0.62 $\pm$ 0.03 c	0.72 $\pm$ 0.06 abc	0.69 $\pm$ 0.03 bc	0.65 $\pm$ 0.02 c	0.85 $\pm$ 0.05 a	0.81 $\pm$ 0.01 ab

Different lowercase letters indicate significant differences among different treatments ($p < 0.05$).

3.3.2. Transformation Indices of Iron Oxides

Given the interrelated nature of transformations among different iron oxide forms, the assessment of iron oxides should not be limited to the content of a single type. Therefore, iron oxide transformation indices were calculated (Figure 4) to further evaluate the effects of different water and carbon management practices on soil iron oxides in paddy fields.

The activation degree of iron oxides ranged from 0.17 to 0.22 in 2022 and from 0.17 to 0.23 in 2023, with significant differences among treatments ($p < 0.01$). Two-way ANOVA results (Table 5) indicated that, compared with irrigation regime, external carbon input had a more pronounced effect on iron oxide activation across both years ($p < 0.01$). The activation degrees under FI and CI treatments were similar, whereas both straw return and manure application significantly increased the activation degree under both irrigation regimes. Specifically, compared with FI, FS and FM treatments increased the activation degree by 29.62% and 29.42% in 2022 and by 27.29% and 29.18% in 2023, respectively. Compared with CI, CS and CM treatments increased the activation degree by 19.69% and 23.58% in 2022 and by 26.50% and 29.18% in 2023, respectively. However, no significant differences were observed between irrigation regimes under the same organic amendment.

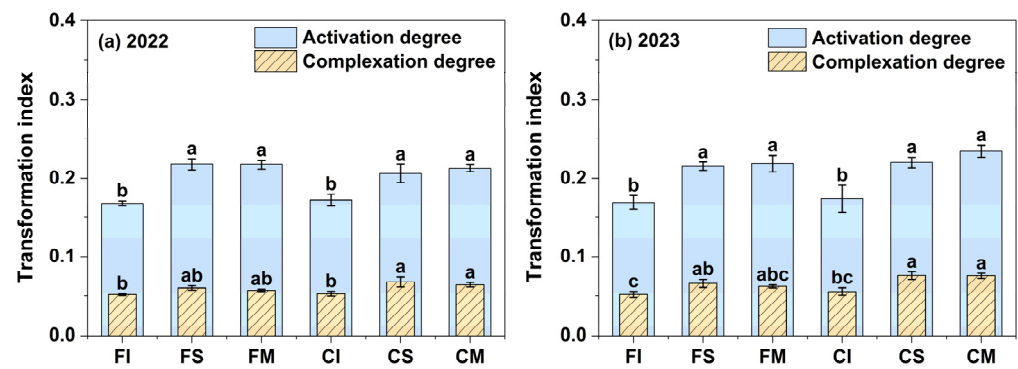


Figure 4. The transformation indices (activation degree and complexation degree) of iron oxides under different irrigation and organic amendment management (mean value $\pm$ standard error). The significance was labeled by letter notation (a, b, c) based on the size of the mean value of the results for each treatment ($p < 0.05$).

Table 5. Two-way analysis of variance (ANOVA) of activation degree and complexation degree of iron oxides.

ANOVA	2022		2023	
	Activation Degree	Complexation Degree	Activation Degree	Complexation Degree
I	ns	ns	ns	*
C	**	*	**	**
I $\times$ C	ns	ns	ns	ns

ns indicates no significance; * indicates difference at $p < 0.05$ and ** indicates difference at $p < 0.01$.

For the complexation degree of iron oxides, values ranged from 0.05 to 0.07 in 2022 ($p < 0.05$) and from 0.05 to 0.08 in 2023 ($p < 0.01$), with significant differences among treatments in both years. Two-way ANOVA showed that external carbon input significantly affected the complexation degree across both years, while the irrigation regime had a significant effect only in 2023. Compared with FI, FS and FM treatments increased the complexation degree by 16.56% and 10.72% in 2022 and by 27.50% and 20.28% in 2023, respectively. Compared with CI, CS and CM treatments increased the complexation degree by 28.67% and 22.00% in 2022 and by 37.08% and 36.47% in 2023, respectively. Under the same external carbon input, the complexation degrees were comparable between flooded and controlled irrigation treatments in 2022, whereas in 2023, the complexation degree under controlled irrigation was approximately 7.17% to 21.59% higher than that under flooded irrigation.

3.3.3. C:Fe Molar Ratio

The molar ratios of carbon to iron (C:Fe) associated with different types of iron oxides were calculated to elucidate their binding characteristics with organic carbon in soil (Table 6). The molar ratios of Fe-bound organic carbon to FeDH ranged from 0.25 to 0.36 in 2022 and from 0.26 to 0.45 in 2023, with significant differences among treatments ($p < 0.01$). Compared with the FI treatment, the molar ratios in FS and FM treatments were approximately 20.40% and 26.73% higher in 2022 and 30.69% and 38.71% higher in 2023, respectively. Similarly, compared with the CI treatment, the molar ratios in CS and CM treatments were approximately 8.61% and 32.69% higher in 2022 and 29.98% and 75.01% higher in 2023, respectively. For FeHH, the molar ratios of Fe-bound organic carbon ranged from 2.57 to 2.93 in 2022 and from 2.66 to 3.21 in 2023, while the ratios for FePP ranged from 13.03 to 14.98 in 2022 and from 13.94 to 16.19 in 2023. However, no significant differences were found among treatments in either year for FeHH and FePP.

Table 6. C:Fe molar ratios of extractable iron oxides and their associated organic carbon.

Year	C:Fe	FI	FS	FM	CI	CS	CM
2022	DH	0.25 ± 0.00 d	0.30 ± 0.00 bc	0.32 ± 0.01 b	0.27 ± 0.00 cd	0.29 ± 0.01 bc	0.36 ± 0.01 a
	HH	2.57 ± 0.09 b	2.68 ± 0.07 ab	2.58 ± 0.16 b	2.86 ± 0.09 ab	2.81 ± 0.04 ab	2.93 ± 0.10 a
	PP	14.02 ± 0.28 a	13.02 ± 0.68 a	14.13 ± 1.08 a	14.98 ± 0.24 a	13.53 ± 0.32 a	13.37 ± 0.60 a
2023	DH	0.26 ± 0.02 c	0.33 ± 0.00 bc	0.36 ± 0.02 b	0.25 ± 0.00 c	0.33 ± 0.02 bc	0.44 ± 0.04 a
	HH	2.66 ± 0.32 a	3.11 ± 0.23 a	3.21 ± 0.12 a	3.03 ± 0.30 a	3.20 ± 0.21 a	3.18 ± 0.23 a
	PP	15.15 ± 1.13 a	16.18 ± 1.32 a	15.09 ± 0.56 a	15.31 ± 2.24 a	14.18 ± 0.56 a	13.94 ± 0.47 a

DH, samples extracted by dithionite-HCl, HH, samples extracted by acidified hydroxylamine, PP, samples extracted by sodium pyrophosphate. Values are means ± SEM. The significance was labeled by letter notation (a, b, c, d) based on the size of the mean value of the results for each treatment ($p < 0.05$).

3.4. Relationship Between Soil Iron Oxides and Soil Organic Carbon

Correlation analyses were conducted between the transformation indices of soil iron oxides and the organic carbon in both POM and MAOM fractions (Figure 5). The results showed that both the activation degree and complexation degree of iron oxides were significantly positively correlated with the organic carbon contents in these two fractions. Specifically, the activation degree exhibited a stronger correlation with POM-C ($R^2 = 0.55$, $p < 0.01$) than with MAOM-C ($R^2 = 0.35$, $p < 0.01$), whereas the complexation degree was more strongly correlated with MAOM-C ($R^2 = 0.40$, $p < 0.01$).

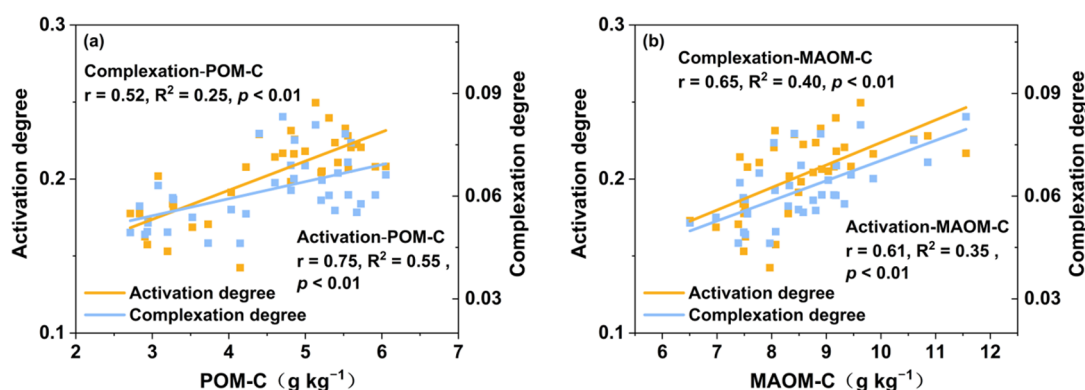


Figure 5. Relationship between the transformation indices of iron oxides and POM-C (a) and MAOM-C (b), respectively.

4. Discussion

4.1. Effects of Irrigation and Organic Amendment Management on Soil Organic Carbon

Enhancing the accumulation of soil organic carbon in agricultural soils is not only critical for maintaining and improving soil fertility but also represents a key strategy for mitigating climate change [56]. In this study, both continuous straw return and manure application over multiple years significantly increased SOC content under both flooded and controlled irrigation regimes, consistent with findings reported in previous studies [57–59]. After the incorporation of crop straw and manure into the soil, low-molecular-weight carbon compounds are preferentially utilized by microorganisms, while high-molecular-weight compounds are either gradually decomposed or stabilized in the form of humic substances [60,61]. Moreover, the nutrients contained in exogenous organic inputs can stimulate microbial growth and metabolism as well as crop development, providing positive feedback that promotes the accumulation of both microbial- and plant-derived carbon in the soil. The accelerated accumulation of SOM through large carbon inputs from plant residues and organic fertilizers has become a characteristic of paddy soils [6,62,63].

Compared to the direct carbon input from organic amendments, the effect of irrigation regimes on SOC content was relatively minor (Table 3). Further analysis of soil carbon pools revealed that exogenous carbon inputs significantly increased both POM-C and MAOM-C

under both irrigation regimes. Specifically, POM-C levels tended to be higher under flooded irrigation, while MAOM-C was slightly greater under controlled irrigation. However, neither trend was statistically significant and thus they require further validation. Generally, the POM fraction serves as the primary carrier of newly added carbon, consisting largely of incompletely decomposed plant debris and coarse organic particles. Theoretically, with continuous additions of carbon from straw and manure, the POM fraction can accumulate carbon without a strict upper limit [64,65]. Previous studies have shown that paddy soils possess high carbon sequestration potential due to the reduced degradation rate of SOC under anaerobic conditions, which mainly applies to conventionally flooding irrigated paddy systems [66]. Under flooded irrigation, organic inputs such as straw and manure are subjected to slower microbial turnover due to oxygen limitation, allowing particulate organic matter to persist in the soil POM fraction [60,61,66].

In contrast, under controlled irrigation, the presence of aerobic conditions enhances microbial activity, accelerating the decomposition of SOC with the increased production of microbial metabolites and necromass [67,68]. During this process, POM-C can serve as a precursor to MAOM-C, undergoing microbial transformation into more stable organo-mineral complexes [64,69,70]. In addition to exogenous inputs, the primary source of organic carbon in soils is derived from plant inputs, which is subsequently stabilized through complex biotic and abiotic processes [70,71]. Compared with flooded irrigation, rice plants under controlled irrigation tend to develop more extensive root systems, potentially enhancing the input of plant-derived carbon into the soil. These low-molecular-weight root exudates can be readily adsorbed onto mineral surfaces or metabolized by microbes to become part of the MAOM fraction [64].

Therefore, different irrigation regimes may influence SOC accumulation through distinct mechanisms. However, compared to organic amendments, such effects are generally more indirect. Notably, in the presence of exogenous carbon inputs, regardless of whether irrigation affects SOC retention via the POM or MAOM pathway, organic amendments remain the primary driving force for SOC accumulation in paddy soils.

4.2. Effects of Irrigation and Organic Amendment Management on Iron Oxides

Compared to irrigation regimes, straw return and manure application had a more pronounced effect on the transformation of soil iron oxides (Table 5). Under exogenous carbon inputs, both the activation and complexation degree of iron oxides increased, indicating a shift in iron oxide composition from crystalline iron oxides (FeDH) to more reactive forms (FeHH) and Fe-organic complexes (FePP) (Figure 4). This shift can be attributed, on the one hand, to enhanced microbial activity stimulated by external carbon sources. Microbial metabolism produces low-molecular-weight organic acids, which lower soil pH and promote mineral dissolution by disrupting iron oxide crystallinity [72,73]. On the other hand, the availability of more labile substrates under organic amendments increases the microbial demand for electron acceptors during carbon mineralization [74]. As one of the dominant electron acceptors in soil, iron oxides are consequently subjected to accelerated transformation [6,74].

Different types of iron oxides bind with organic carbon via distinct mechanisms, meaning that shifts in iron oxide forms can affect their capacity to stabilize organic carbon. Generally, adsorption and co-precipitation are the primary modes through which iron oxides protect SOC. A ratio of 1.0 means the maximal sorption capacity for organic carbon of iron oxides, whereas a higher ratio (>1) means the formation of co-precipitation (6~10) or chelate with organic ligands (>10) [23,75,76].

In this study, FeDH exhibited C:Fe ratios below 1 across all treatments, suggesting that its carbon stabilization function was dominated by adsorption (Table 6). FeHH showed

C:Fe ratios ranging from 2.62 to 3.06, implying the involvement of both adsorption and co-precipitation. FePP had C:Fe ratios exceeding 10, indicating that, in addition to co-precipitation, complexation through chelation played a key role in SOC stabilization. Among the three iron oxide types, FeHH and FePP exhibited higher C:Fe ratios than FeDH, suggesting greater carbon-binding capacities. Therefore, regardless of the irrigation regime, the enhanced activation and complexation of iron oxides induced by exogenous carbon additions increased the potential for SOC association with FeHH and FePP, thereby promoting the formation of HH-OC or PP-OC and ultimately elevating Fe-OC levels in the soil (Figures 2 and 3).

4.3. Relationship Between Iron Oxides and Soil Organic Carbon Accumulation

As a dominant soil mineral, iron oxides are expected to influence the organic carbon content in the MAOM pool due to their ability to bind with organic matter. As previously discussed, irrigation and organic amendment management can alter the activation and complexation degree of iron oxides, thereby influencing Fe-OC formation and subsequently affecting MAOM-C accumulation (Figure 5). The corresponding correlation coefficients ($r = 0.61$ and 0.65) indicate a moderate and meaningful association between iron oxide activation/complexation and MAOM-C. However, the relatively modest R^2 values (0.35 and 0.40) show that, although Fe-OC accounts for a substantial portion of MAOM-C (approximately 48.70% to 54.19%) under different treatments, it is not the sole determinant of MAOM-C accumulation. Other soil components—such as aluminum oxides and clay minerals—may compete with iron oxides for organic carbon binding, thus playing significant roles in MAOM-C formation [77,78]. Furthermore, the selective nature of mineral–organic associations implies that increased activation or complexation of iron oxides does not necessarily lead to unlimited accumulation of MAOM-C [6,79,80].

Interestingly, iron oxide transformation also showed a significant positive correlation with POM-C, particularly the activation degree, which had a higher R^2 (0.55) than that with MAOM-C. This suggests that the transformation from FeDH to FeHH is closely linked to the stabilization and accumulation of POM-C. Given the relatively weaker correlation with MAOM-C, the influence of iron oxides on POM-C may not primarily stem from their bond with organic matter. Instead, this effect is likely mediated by other mechanisms, such as their role in promoting soil aggregation. Previous studies have identified iron oxides as key inorganic binding agents that facilitate the formation and stabilization of macroaggregates in soils [25,26,81]. In particular, short-range ordered Fe (FeHH) exhibits a greater specific surface area and surface reactivity than crystalline forms, enabling stronger interactions with organic matter to form stable organo-mineral complexes [82,83]. These complexes also help prevent recrystallization of iron oxides, thereby preserving their binding capacity and promoting macroaggregate formation and stability [84,85]. Meanwhile, macroaggregates serve as key reservoirs for newly incorporated carbon in soils. Over time, carbon that has undergone microbial decomposition gradually transitions into microaggregates [86,87]. Therefore, as a critical inorganic binding agent in aggregate formation, FeHH might exert a significant influence on POM-C accumulation.

Furthermore, from the perspective of both POM-C and MAOM-C accumulation, the ability of iron oxides to facilitate the retention of carbon derived from exogenous inputs plays a critical role in soil carbon stabilization (Figure 6). Remarkably, under varying irrigation regimes and organic amendments, the contribution of iron oxide activation to POM-C stabilization exceeded their influence on MAOM-C formation. This finding underscores the multifaceted importance of iron oxides in the accumulation and stabilization of SOC in paddy soils.

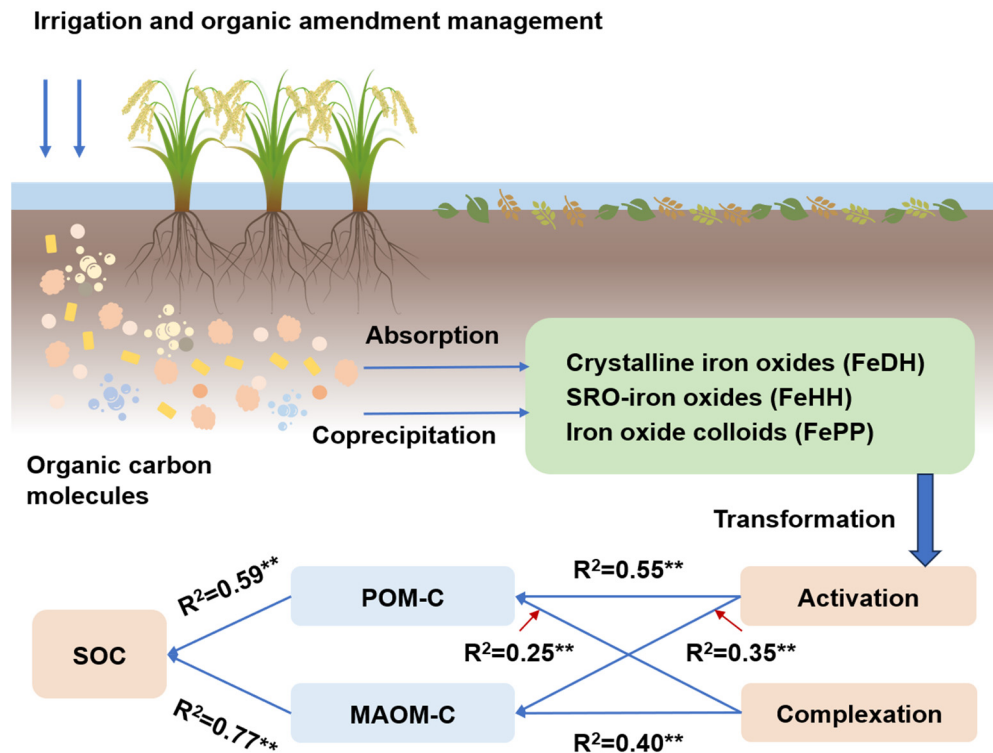


Figure 6. Pathways by which the transformation of iron oxides influences SOC in bulk soil via POM-C and MAOM-C under different irrigation and organic amendment practices. R^2 values indicate the proportion of variance in the target variable explained by the source variable of each arrow. ** Indicates significance at $p \leq 0.01$.

4.4. Implications

It should be noted that, although this study demonstrates that irrigation regimes and organic amendments can influence the accumulation of organic carbon in the soil—either as POM-C or MAOM-C—by altering iron oxide transformations, the responses of these variables to irrigation were not completely consistent in 2022 and 2023. For example, in 2022 the irrigation regime had significant effects on SOC (bulk soil), POM-C, and MAOM-C, whereas in 2023 these effects were no longer significant. This discrepancy is likely related to the differences in rainfall between the two rice-growing seasons. Because the primary goal of the water-saving (controlled) irrigation regime is to reduce irrigation water while maintaining yield, it necessarily relies on the effective use of rainfall. As shown in Figure S1 and Table S1, total rainfall during the 2023 rice season was about 517.37 mm, whereas in 2022 it was only 338.64 mm. In the controlled-irrigation plots, the greater rainfall slowed the decline in soil water from saturation to the irrigation threshold and even allowed the water table to rise quickly back to saturation or near-saturation after rain, markedly reducing the soil moisture gradient between the two irrigation regimes. This, in turn, diminished the detectable differences in the accumulation of SOC and its fractions attributable to irrigation. A similar pattern was observed for the degree of iron oxide complexation: in 2023 the combination of controlled irrigation and exogenous carbon addition enhanced the complexation degree much more markedly than in 2022. Compared with 2022, the comparatively wetter conditions in 2023 created a mildly oxic environment that both promoted the transformation of part of the FeDH fraction and preserved the newly formed FePP from reductive dissolution that would otherwise occur under continuous flooding, thereby favoring a higher complexation degree. Taken together, these results indicate that the influence of irrigation regime on iron-mediated pathways of organic carbon accumulation varies from year to year and is likely modulated by weather

conditions. At the same time, they underscore the high sensitivity of iron–organic matter interactions to soil moisture conditions. Therefore, future research should continue to explore the coupling between soil moisture dynamics and iron-mediated organic carbon accumulation pathways.

5. Conclusions

After a long-term field experiment with continuous irrigation and organic amendment management since 2012, we collected soil samples after rice harvest in the 10th year (2022) and the 11th year (2023). The results revealed significant differences emerged in the distribution of iron oxides and organic carbon in paddy soils across different treatments. Under both irrigation regimes, straw return and manure application enhanced the activation and complexation degree of iron oxides, thereby increasing Fe-OC content, with similar levels observed between the two irrigation modes. Moreover, both straw return and manure application increased the contents of POM-C and MAOM-C. Notably, POM-C was more abundant under flooded irrigation, whereas MAOM-C levels were higher under controlled irrigation. The transformation of iron oxides was significantly positively correlated with both POM-C and MAOM-C contents. Specifically, the activation degree of iron oxides had a stronger influence on POM-C, while their complexation degree played a more critical role in MAOM-C accumulation. Overall, these results indicate that exogenous carbon inputs effectively promote soil carbon sequestration under both flooding and water-saving irrigation regimes, with iron oxide transformations playing a pivotal role in mediating this effect. Given the distinct functions of POM-C and MAOM-C within the soil organic carbon pool, these findings underscore the dual role of iron oxides in mediating organic carbon stabilization in paddy soils.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agriculture15131385/s1>.

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