

Article

Parent Material, Water Regime Shifts, and Fertilization Regulate Aggregate Stability and Cadmium Adsorption in Typical Subtropical Paddy Soils

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Abstract

Cadmium (Cd) contamination in paddy soils poses health risks, yet the role of aggregate-scale Cd binding remains poorly understood under interactive agricultural management. Unlike primary textural separates that are fixed by parent material, aggregates are dynamic and manageable. This study investigates the interactive effects of parent material, water regime shifts in annual tobacco–rice rotation, and chlorine-containing fertilizers on aggregate stability, carbon/nitrogen sequestration, and cadmium (Cd) adsorption in paddy soils from subtropical paddy fields of Hunan Province, South China. Two paddy soils, Masaniutan (granite-derived sandy loam) and Shanniutan (slate/shale-derived clayey soil), were divided into four size classes. Selective removal of soil organic carbon (SOC) and free iron oxides (Fe_d), followed by Cd adsorption experiments. Shanniutan had greater aggregate stability than Masaniutan. Water regime shifts did not significantly alter aggregate structure. Chlorine fertilizers disrupted aggregates, increasing finer fractions. Cd adsorption rose as aggregate size decreased. SOC removal reduced the maximum adsorption capacity (q_m) by 36.8%, while Fe_d played a supporting role. Partial least squares structural equation modeling (PLS-SEM) revealed that parent material had a strong positive direct effect on aggregate stability (path coefficient = 2.346), while chlorine fertilization (−0.750) and water regime shifts (−0.344) had negative effects. Parent material, water regime shifts, and fertilization jointly influence aggregate stability and the distribution of cementing agents, thereby controlling Cd adsorption capacity—with SOC as the dominant factor. These findings provide a basis for sustainable paddy soil management by promoting SOC retention and avoiding excessive chloride inputs.

Keywords: soil aggregates; parent material; water regime shifts; carbon and nitrogen sequestration; cadmium adsorption



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1. Introduction

Soil aggregates are the fundamental units of soil structure and function [1]. Formed by cementation of primary mineral particles, soil organic matter, iron-(hydr) oxides, and microbial residues, aggregates represent secondary hierarchical soil structures [2]. In this respect, they differ fundamentally from textural particle-size separates (sand, silt, clay):

these textural fractions are inherited directly from parent material and remain largely unaltered under agricultural management [3]. In contrast, aggregate size distribution and stability are dynamically responsive to common field practices including crop rotation, water regime management, and fertilization [4]. These aggregate-related properties further regulate soil water movement, nutrient retention, and heavy-metal behavior, with direct consequences for crop growth, soil erosion resistance, and overall ecosystem sustainability [5]. As critical micro-reaction interfaces, aggregate fractions of varying sizes differ substantially in specific surface area, cementing components, and reactive surface sites, which together govern the retention, migration, and speciation transformation of cadmium and other heavy metals in paddy soils [6]. This makes aggregate-scale analysis a practically actionable approach for mitigating Cd risks in contaminated paddy fields. Southern China's subtropical paddy soils face significant Cd contamination, threatening rice safety and human health [7]. A nationwide survey of heavy metal contamination in Chinese soils, based on literature published from 2000 to 2019, revealed that the average Cd concentration in Chinese soils is approximately twice the soil background value, with nearly 34% of farmland soils and 45% of urban soils exceeding Cd contamination thresholds [8]. Province-level investigations further confirmed that soils in almost all Chinese provinces exhibit Cd concentrations exceeding local background values to varying degrees, with the contamination status in southern China being more severe than in northern regions [9,10]. In paddy ecosystems, the formation, stability, and turnover mechanisms of aggregates are particularly complex due to periodic flooding and drainage, frequent tillage activities, and inputs of exogenous materials such as fertilizers and straw [11]. Aggregates are not only the main reservoirs of SOC and nitrogen but also provide important physical protection for these nutrients, influencing their rapid mineralization and loss [12]. Simultaneously, aggregates serve as key interfaces for the migration, speciation transformation, and fixation of heavy metals in soils [13]. Different size classes of aggregates significantly influence the adsorption–desorption behavior and bioavailability of heavy metal elements due to variations in specific surface area, charge characteristics, and cementing components [14].

The stability of aggregates and their capacity to retain nutrients and heavy metals are influenced by multiple factors [15]. Parent material, as one of the important factors determining soil formation, directly influences the properties of primary mineral particles and the types of secondary clay minerals [16]. Previous studies have demonstrated that soils derived from contrasting parent materials, such as basalt versus alluvial deposits, develop distinct clay mineral assemblages, including kaolinite and iron oxides from basalt and illite and smectite from alluvial deposits [17]. Such differences in clay mineralogy can further impose a profound control on soil structural development and aggregation processes, such as mineral composition's cation exchange, SOC binding, and inter-particle bonding forces [18]. Water regime is another critical factor that dynamically influences the physical formation and biochemical stability of soil aggregates by altering soil moisture conditions, SOC inputs, and redox potential [19]. Periodic wetting and drying—common in many agricultural systems—can influence aggregate turnover, the release of cementing agents, and the protection of organic matter within aggregate pores [19]. Fertilization management practices directly modify soil solution chemistry and aggregate stability [20]. As major chloride-bearing fertilizer sources for croplands in China, KCl and NH_4Cl introduce massive chloride loads into agricultural soils; KCl alone contributes approximately 10 million tons of chloride per year to farmland systems [21]. The type and valence of cations play an essential role: polyvalent cations such as Ca^{2+} and Mg^{2+} promote flocculation of soil colloids and act as cation bridges binding mineral particles with organic matter, thereby enhancing aggregate stability, whereas monovalent cations like Na^+ and K^+ may cause dispersion [20]. Cl^- competes for adsorption sites, disrupts cation bridges,

and promotes iron oxide dissolution, weakening aggregate integrity [21]. Currently, most studies focus on the effects of single factors on aggregates [22]. However, there remains a lack of systematic comparative studies on parent material, water regime dynamics, inorganic fertilization practice, and their regulatory mechanisms on aggregate characteristics, nutrient sequestration, and heavy metal fixation remain unclear [23].

The adsorption and immobilization of Cd by soil aggregates represent a key aspect of their environmental function. Owing to differences in specific surface area, SOC content, and Fe_d content, aggregates of different size fractions exhibit marked differences in Cd adsorption capacity and immobilization mechanisms [24,25]. Published studies indicate that finer aggregates generally possess larger specific surface area and higher contents of SOC and Fe_d [26–28], which are expected to confer stronger Cd retention ability. However, most current studies focus on bulk soil or isolated particle-size fractions rather than a systematic aggregate-scale analysis. SOC binds Cd^{2+} via specific adsorption and nonspecific adsorption [23,24], while Fe_d retain Cd through similar mechanisms [27]. These two cementing agents vary widely in content and stability across soils from different parent materials [29], potentially leading to distinct dominant mechanisms for Cd fixation. Nevertheless, the relative contributions and dominant mechanisms of SOC versus Fe_d in Cd immobilization across different aggregate size fractions under contrasting parent materials remain poorly understood [30].

Therefore, this study selected two typical paddy soils derived from granite and slate/shale in the subtropical rice-growing region of southern China. For water regime variation, we focused on the water regime shifts in the annual tobacco–rice rotation; for fertilization management, we focused on chlorine-containing fertilizers (KCl and NH_4Cl). The research focuses on elucidating how parent material properties, water regime shifts in annual tobacco–rice rotation, and fertilization practices independently and jointly influence aggregate formation and function, and further analyzes the distribution patterns of SOC and total nitrogen (TN) across different aggregate size classes as well as their intrinsic relationships with aggregate structural stability. Concurrently, by quantifying the differences in Cd adsorption capacity among various aggregate size fractions and employing selective removal experiments, the relative contributions and underlying mechanisms of SOC and Fe_d in Cd immobilization are explored in depth. The findings aim to provide a reference for optimizing soil structure, enhancing fertility, and controlling Cd pollution risks in paddy soils from the perspective of aggregate-scale management.

2. Materials and Methods

2.1. Sampling and Treatments

Typical paddy soils from agricultural regions in southern China were selected for this study. The tested soils were collected from the Beishan Town Rice Research Base in Changsha County, Hunan Province ($28^\circ 43' \text{ N}$, $113^\circ 06' \text{ E}$), and Yonghe Town in Liuyang County, Hunan Province ($28^\circ 29' \text{ N}$, $113^\circ 87' \text{ E}$). The soil types were Masaniutan and Shan-niutan, with basic physicochemical properties shown in Table 1. The two paddy soils in this study were classified according to the World Reference Base for Soil Resources as Hydragric Anthrosols [31]. The study area is characterized by a subtropical monsoonal humid climate, with pronounced seasonal variations and concurrent rain and heat. The annual mean temperature is 17.2°C , and the annual precipitation ranges from 1358.6 to 1552.5 mm.

Table 1. Basic physicochemical properties of the tested soils.

Soil Type	Parent Material	pH	OM g·kg ^{−1}	CEC cmol·kg ^{−1}	TN g·kg ^{−1}	Available Cd mg·kg ^{−1}	Total Cd mg·kg ^{−1}	Clay (<0.002 mm)	Silt (0.002– 0.02 mm)	Sand (>0.02 mm)
Masaniutan	granite-derived sandy loam	5.06	29.25	7.85	2.50	0.29	0.87	35.04%	59.31%	5.65%
Shanniutan	slate/shale- derived clayey	5.23	36.71	9.54	1.56	0.86	3.27	20.72%	32.35%	46.93%

Note: OM, organic matter; CEC, cation exchange capacity; TN, total nitrogen.

Soil pH was measured potentiometrically using a pH meter (SevenCompact S220, Mettler-Toledo AG, Greifensee, Switzerland) at a soil-to-water ratio of 1:2.5 (*m:v*) after shaking for 30 min [32]. Cation exchange capacity (CEC) was measured using the ammonium acetate exchange method at pH 7.0, where ammonium ions were desorbed by KCl and quantified via distillation-titration [33]. Fe_d were extracted by the DCB method, and the Fe concentration in the extract was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, NexION 300X, PerkinElmer Inc., Waltham, MA, USA) with a detection limit of 0.01 µg·L^{−1} [34]. SOC was analyzed using the potassium dichromate heating method, which involved external oil bath heating at 170–180 °C for 5 min, while TN was measured by the semi-micro Kjeldahl method involving digestion with H₂SO₄–H₂O₂ followed by distillation-titration [16]. Bulk soil mineral composition was characterized by X-ray diffraction (XRD, D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany). The detailed procedure is described in Supplementary Text S3. Strict quality control was performed during Cd analysis. National standard reference materials soil GBW(E)-070009 [35] and Hunan rice GBW 10045(GSB-23) [36], as well as blank tests, were used for quality assurance. The Cd recoveries were 100.7–107.7% for soil reference material and 98.7–108.1% for rice reference material. Parallel samples were prepared for each analytical batch.

The experimental field followed a typical tobacco–rice rotation system: tobacco was planted from March to July under upland conditions with drip irrigation, while late rice was transplanted in late July and harvested in October under continuous flooding (2–3 cm water layer). Five Cl[−] addition levels (0, 2, 4, 6, and 8 mmol·kg^{−1} dry soil) were established in the field using KCl and NH₄Cl as the chlorine sources. The total inputs of N, P, and K were kept constant across all treatments at 0.13 g·kg^{−1}, 0.10 g·kg^{−1}, and 0.15 g·kg^{−1}, respectively, by supplementing with K₂SO₄, (NH₄)₂SO₄, and (NH₄)₃PO₄. As a result of balancing N, P, and K, Cl[−] and SO₄^{2−} varied inversely: when Cl[−] increased from 0 to 8 mmol·kg^{−1}, SO₄^{2−} decreased from 4 to 0 mmol·kg^{−1}. The detailed anion composition of each treatment is provided in Table S1.

Soils were collected from the 0–20 cm plow layer using a five-point sampling method, air-dried at room temperature (25 ± 2 °C). Visible roots, plant residues, and hard non-breakable gravel fragment were manually removed. Soil samples from the tobacco cropping season were collected in April, while samples from the paddy late rice cropping season were collected in October. The sampling interval between the two seasons was 5–6 months, involving only short-term sampling within a single seasonal alternation cycle of tobacco–rice.

2.2. Experimental Design

2.2.1. Aggregate Fractionation

Soil aggregates were separated into four size classes by wet sieving: macroaggregate (>2 mm), mesoaggregates (2–0.25 mm), microaggregate (0.25–0.053 mm), and silt-clay fraction (<0.053 mm) [32]. Detailed sieving procedures are provided in Text S1.

Aggregate stability indices, including mean weight diameter (MWD), geometric mean diameter (GMD), and water-stable macroaggregate content ($R_{0.25}$), were calculated as follows:

$$MWD = \frac{\sum_{i=1}^n (\bar{X}_i W_i)}{\sum_{i=1}^n W_i} \quad (1)$$

$$GMD = \frac{\exp(\sum_{i=1}^n W_i \ln \bar{X}_i)}{\sum_{i=1}^n W_i} \quad (2)$$

$$R_{0.25} = \frac{M_{T>0.25}}{M_T} \quad (3)$$

where $\bar{X}_i$ is the mean diameter of the i -th aggregate size fraction (mm), and W_i is the mass proportion of the i -th aggregate size fraction (%), M_T is the total mass of water stable aggregates (g), and $M_{T>0.25}$ is the mass of water stable aggregates > 0.25 mm (g).

2.2.2. Removal of Soil Components

To elucidate the roles of SOC and Fe_d in the Cd adsorption process by soil aggregates, selective component removal methods were employed in this study. SOC was removed using the H_2O_2 oxidation [32], and Fe_d was conducted using the sodium DCB method [37]. Detailed procedures are described in Text S2. All treated samples were subsequently used for Cd adsorption experiments.

2.2.3. Cd Adsorption by Different Aggregate Size Fractions

The Cd adsorption capacity of the bulk soil and four aggregate size fractions was determined as follows: 0.1000 g of the bulk soil and each of the four aggregate size fractions were weighed into 50 mL centrifuge tubes separately. A stock Cd solution with a concentration of $1000 \text{ mg}\cdot\text{L}^{-1}$ was prepared using cadmium nitrate, and serially diluted with $0.01 \text{ mol}\cdot\text{L}^{-1}$ $NaNO_3$ to obtain Cd solutions with initial concentrations of 1, 5, 10, 20, 50, 100, 150, and $200 \text{ mg}\cdot\text{L}^{-1}$.

Subsequently, 10 mL of the Cd solution with different concentrations was added to each soil sample. The centrifuge tubes were placed in a constant-temperature shaker and oscillated at 25°C and $200 \text{ r}\cdot\text{min}^{-1}$ for 24 h. After oscillation, the tubes were centrifuged at $3000 \text{ r}\cdot\text{min}^{-1}$ for 5 min. The supernatant was filtered through qualitative filter paper, diluted to a constant volume, and the Cd concentration was determined using a flame atomic absorption spectrophotometer (PerkinElmer Inc., Waltham, MA, USA).

The Cd adsorption capacity of the soil was calculated using the following formula [38]:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (4)$$

where q_e is the equilibrium adsorption capacity [$\text{mg}\cdot\text{g}^{-1}$]; C_0 is the initial Cd concentration [$\text{mg}\cdot\text{L}^{-1}$]; C_e is the equilibrium Cd concentration in the supernatant [$\text{mg}\cdot\text{L}^{-1}$]; V is the volume of the Cd solution [L]; and m is the mass of the soil sample [g].

In the study of soil adsorption characteristics, Langmuir and Freundlich isotherm adsorption models are two commonly used models at present.

The Langmuir model is expressed by the following equation:

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e} \quad (5)$$

where q_e is the Cd adsorption capacity at equilibrium [$\text{mg}\cdot\text{g}^{-1}$]; q_m is the monolayer saturated adsorption capacity [$\text{mg}\cdot\text{g}^{-1}$]; C_e is the Cd concentration at equilibrium [$\text{mg}\cdot\text{L}^{-1}$]; and K_l is the Langmuir model parameter [$\text{L}\cdot\text{mg}^{-1}$].

The Freundlich model is expressed by the following equation:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (6)$$

where q_e is the Cd adsorption capacity at equilibrium [$\text{mg} \cdot \text{g}^{-1}$]; C_e is the Cd concentration at equilibrium [$\text{mg} \cdot \text{L}^{-1}$]; K_f is the Freundlich model parameter [$\text{L} \cdot \text{mg}^{-1}$]; and n is the Freundlich model parameter [dimensionless]. Generally, adsorption is favorable when $0.1 < 1/n < 0.5$.

2.3. Statistical Analysis

All data were expressed as mean $\pm$ standard deviation ($n = 3$). One-way analysis of variance (ANOVA) followed by Duncan's multiple comparison test ($p < 0.05$) were used to detect significant differences between treatments. Normality and homogeneity of variances were verified using Shapiro–Wilk and Levene's tests prior to ANOVA. Cd adsorption isotherms were fitted using nonlinear least squares in Origin 2023. Spearman correlation analysis was used to explore relationships between maximum adsorption capacity (q_m) and soil physicochemical properties.

Partial least squares structural equation modeling (PLS-SEM) was performed using SmartPLS 4.0 to evaluate the direct effects of parent material, water regime shifts, and Cl^- addition on aggregate stability, with aggregate stability as a latent variable indicated by MWD, GMD, and $R_{0.25}$. Path coefficients and their significance were determined by bootstrapping (5000 resamples). The coefficient of determination (R^2) was used to assess the model's explanatory power. Mantel test (999 permutations, R version 4.2.1, vegan package) was conducted to assess the overall correlation between the environmental factor matrix (parent material, seasonal alternation, Cl^- level) and the aggregate stability matrix (MWD, GMD, $R_{0.25}$).

3. Results

3.1. Effects of Soil Parent Material, Water Regime Shifts, and Fertilization Management on Aggregate Stability and Distribution

3.1.1. Aggregate Stability and Distribution in Soils Derived from Different Parent Materials

Macroaggregates dominated both soils, but their abundance differed significantly by parent material: Shanniutan contained 76% macroaggregates, markedly higher than Masaniutan ($p < 0.05$). Conversely, the silt-clay fraction in Masaniutan accounted for only 3%, and the mesoaggregate proportion and was 1.92 fold higher in Masaniutan than in Shanniutan (Figure 1).

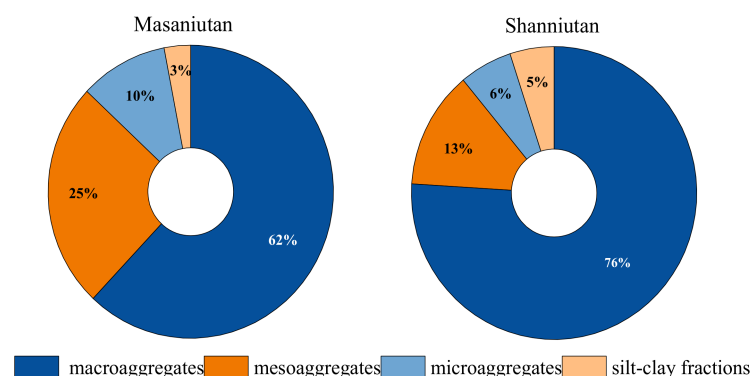


Figure 1. Characteristics of aggregate size distribution in paddy soils derived from different parent materials.

Aggregate stability indices (Table 2) showed that MWD and GMD of Shanniutan were significantly higher than those of Masaniutan ($p < 0.05$), by 8.93% and 11.94%, respectively. $R_{0.25}$ did not differ significantly between soils (Table 2).

Table 2. Soil aggregate stability index of Masaniutan and Shanniutan.

Soil Type	Aggregate Stability Index		
	MWD (mm)	GMD (mm)	$R_{0.25}$ (%)
Masaniutan	1.85 ± 0.04 b	1.35 ± 0.03 b	87 ± 5 a
Shanniutan	2.07 ± 0.03 a	1.52 ± 0.06 a	89 ± 6 a

Data are presented as mean $\pm$ standard deviation, $n = 3$; different lowercase letters in the same column indicate significant differences between soil types at $p < 0.05$.

The distribution characteristics of soil SOC and Fe_d in different aggregate size classes of the two soils are shown in Figure 2. Mean SOC content in Shanniutan was $16.93 \text{ g} \cdot \text{kg}^{-1}$, approximately 6% higher than that in Masaniutan at $16.01 \text{ g} \cdot \text{kg}^{-1}$. However, the magnitude of this difference varied substantially by aggregate size. In the bulk soil, Shanniutan had a 27% higher SOC content than Masaniutan, with values of $21.29 \pm 1.84 \text{ g} \cdot \text{kg}^{-1}$ and $16.97 \pm 1.46 \text{ g} \cdot \text{kg}^{-1}$ ($p < 0.05$). In the silt-clay fraction, Masaniutan exhibited a 13% higher SOC content than Shanniutan, at $27.13 \pm 2.34 \text{ g} \cdot \text{kg}^{-1}$ versus $22.40 \pm 1.93 \text{ g} \cdot \text{kg}^{-1}$ ($p < 0.05$). With decreasing aggregate size, the SOC content increased significantly—for Masaniutan, the SOC content in the silt-clay fraction was 3.30 times that in macroaggregates ($p < 0.05$), while for Shanniutan it was 2.43 times ($p < 0.05$).

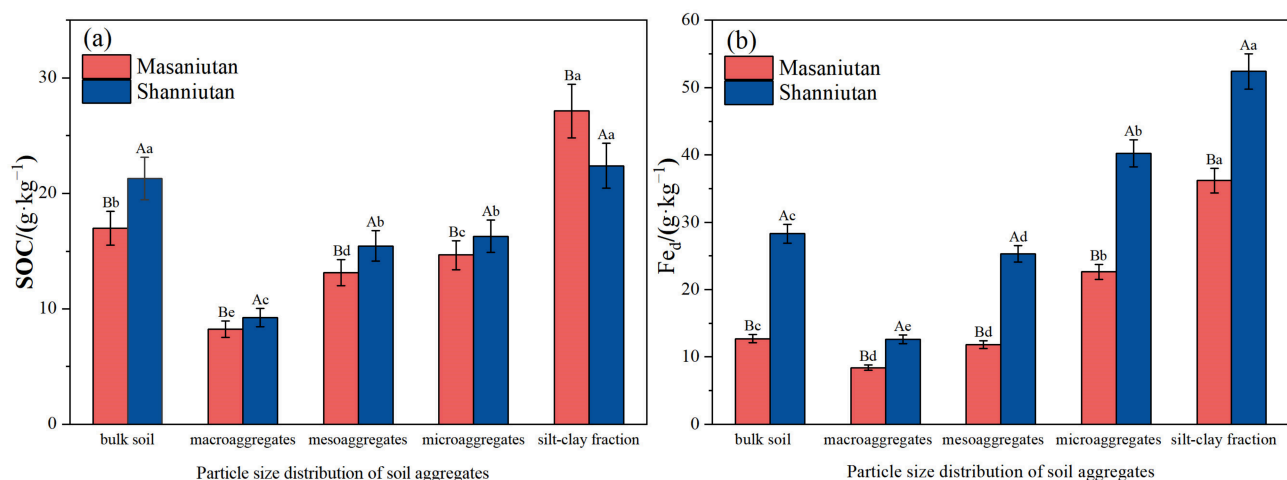


Figure 2. Distribution of SOC (a) and Fe_d (b) in different aggregate size fractions of Masaniutan and Shanniutan paddy soils. Different uppercase letters indicate significant differences between the two soils for the same aggregate size fraction at $p < 0.05$, and different lowercase letters indicate significant differences among aggregate size fractions for the same soil at $p < 0.05$ ($n = 3$).

As shown in Figure 2b, the overall mean Fe_d content across all aggregate size classes in Shanniutan was $31.76 \text{ g} \cdot \text{kg}^{-1}$, approximately 1.73 times that in Masaniutan at $18.34 \text{ g} \cdot \text{kg}^{-1}$, with substantial variation by aggregate size. Specifically, in the bulk soil, Shanniutan had a 2.23 times higher Fe_d content than Masaniutan, with values of $28.3 \pm 1.42 \text{ g} \cdot \text{kg}^{-1}$ and $12.7 \pm 0.64 \text{ g} \cdot \text{kg}^{-1}$, respectively ($p < 0.05$), and this pattern held across all aggregate size classes. The Fe_d content increased with decreasing aggregate size—especially in the silt-clay fraction, where it was notably higher than in macroaggregates: 4.16 times higher in Shanniutan and 4.31 times higher in Masaniutan ($p < 0.05$ for both).

3.1.2. Aggregate Stability During Different Cropping Seasons Under Water Regime Shifts in the Tobacco–Rice Rotation

Figure 3 presents the aggregate size distribution in the tobacco–rice rotation system. Statistical analysis indicated that water regime shifts in annual tobacco–rice rotation did not exert a significant effect on any aggregate stability indicator (MWD, GMD, or $R_{0.25}$; $p > 0.05$, Table 3). Macroaggregates were the predominant fraction in both cropping seasons, accounting for $57.33\% \pm 2.15\%$ and $63.18\% \pm 2.42\%$ of the total aggregates in the tobacco and rice cropping seasons. Within each cropping season, the proportion of macroaggregates was significantly higher than that of all smaller-sized aggregate fractions ($p < 0.05$). Mesoaggregates were numerically more abundant in the tobacco cropping season, with a proportion of $30.63\% \pm 3.82\%$, compared to $22.72\% \pm 4.60\%$ in the rice cropping season. Microaggregates also showed a higher numerical proportion in the tobacco cropping season at $5.91\% \pm 1.29\%$ relative to $3.60\% \pm 2.58\%$ in the rice cropping season, while the silt-clay fraction exhibited the opposite trend, with a greater numerical proportion in the rice season of $10.50\% \pm 3.35\%$ versus $5.98\% \pm 1.32\%$ in the tobacco season. No statistically significant differences were observed in the key stability indices of soil aggregates between the tobacco cropping season and the rice cropping season ($p > 0.05$), indicating that short-term shifts in water regime exerted a limited impact on the overall stability of aggregates.

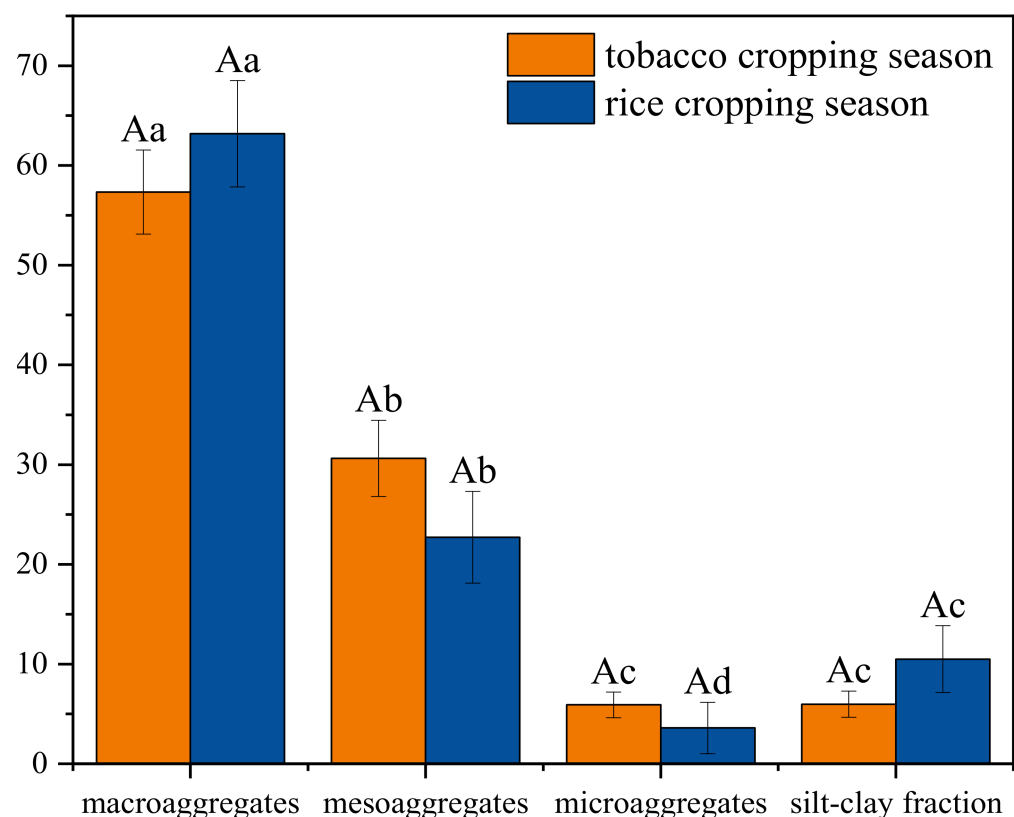


Figure 3. Size distribution of soil aggregates in different cropping seasons under tobacco–rice seasonal alternation. Data are presented as mean $\pm$ standard deviation ($n = 3$). Different uppercase letters indicate significant differences between seasons for the same aggregate size class at $p < 0.05$, and different lowercase letters indicate significant differences among aggregate size classes within the same season at $p < 0.05$.

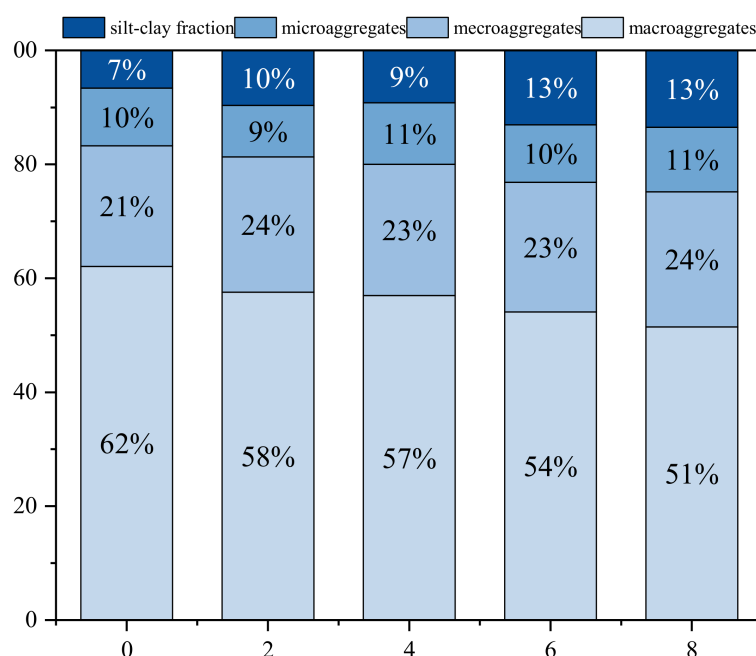
Table 3. Indicators of soil aggregate stability in different types of tobacco–rice fields.

Cropping Season	MWD (mm)	GMD (mm)	R _{0.25} (%)
Tobacco	1.79 ± 0.13 a	1.26 ± 0.16 a	87 ± 2 a
Rice	1.84 ± 0.18 a	1.12 ± 0.39 a	83 ± 8 a

Data are presented as mean ± standard deviation, $n = 3$; different lowercase letters in the same column indicate significant differences between cropping seasons at $p < 0.05$.

3.1.3. Aggregate Stability and Distribution Under Varying Rates Chlorine-Containing Fertilizers

Figure 4 illustrates the changes in the proportional distribution of soil aggregates across different particle sizes under varying Cl^- addition levels from 0 to 8 $\text{mmol}\cdot\text{L}^{-1}$. With increasing Cl^- concentration, the proportions of macroaggregates and mesoaggregates gradually decreased, while the proportions of microaggregates and silt-clay fractions increased significantly ($p < 0.05$). At 8 $\text{mmol}\cdot\text{L}^{-1}$, macroaggregates decreased by 14.52% and mesoaggregates by 20.83% relative to the control; microaggregates increased by 37.66% and the silt clay fraction by 40.88%.

**Figure 4.** Distribution of soil aggregate size fractions under different chloride addition level.

Aggregate stability indices under Cl^- treatments are presented in Table 4. Compared with the control at 0 $\text{mmol}\cdot\text{L}^{-1}$, which had MWD of 1.81 ± 0.02 mm, GMD of 1.18 ± 0.03 mm, and $R_{0.25}$ of 83.27%, higher Cl^- levels progressively reduced MWD, GMD, and $R_{0.25}$. At 8 $\text{mmol}\cdot\text{L}^{-1}$, MWD decreased to 1.57 ± 0.01 mm, GMD to 0.82 ± 0.01 mm, and $R_{0.25}$ to 75.18%. Duncan's multiple range test indicated that MWD, GMD and $R_{0.25}$ under Cl^- addition were significantly lower than the control ($p < 0.05$). No significant differences were observed between the 2 and 4 $\text{mmol}\cdot\text{L}^{-1}$ treatments, whereas further increases in Cl^- to 6 and 8 $\text{mmol}\cdot\text{L}^{-1}$ caused additional significant reductions in aggregate-stability indices. These results confirm that Cl^- promotes aggregate dispersion and reduces stability, potentially undermining C/N sequestration and heavy metal immobilization.

Table 4. Indicators of soil aggregate stability under different chlorine-containing fertilization rates.

Cl [−]	MWD (mm)	GMD (mm)	R _{0.25} (%)
0	1.81 ± 0.02 a	1.18 ± 0.03 a	83 ± 4 a
2	1.72 ± 0.01 b	1.03 ± 0.01 b	82 ± 2 b
4	1.70 ± 0.01 b	1.01 ± 0.02 b	80 ± 4 b
6	1.63 ± 0.01 c	0.87 ± 0.01 c	77 ± 4 c
8	1.57 ± 0.01 d	0.82 ± 0.01 d	75 ± 3 d

Data are presented as mean ± standard deviation, $n = 3$. Different lowercase letters in the same column indicate significant differences at $p < 0.05$.

3.2. Distribution Characteristics of SOC and TN in Different Aggregate Size Fractions Under Water Regime Shifts in the Tobacco–Rice Rotation

In the tobacco–rice water regime shifts system, the distribution of TN and SOC among different aggregate size fractions showed numerical trends across aggregate size fractions and between cropping seasons (Figure 5).

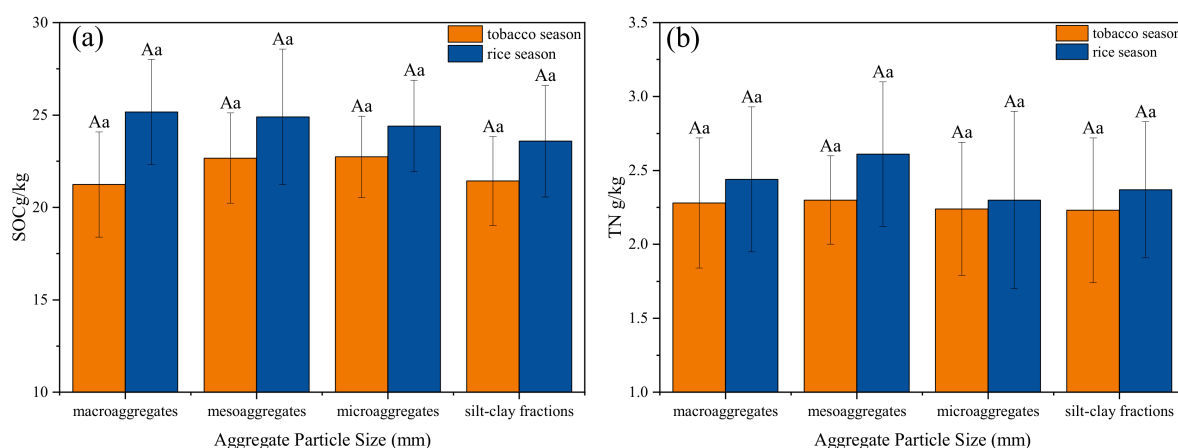


Figure 5. Distribution characteristics of SOC and TN in aggregates of different sizes under tobacco–rice seasonal alternation. (a) SOC distribution in different aggregate-size fractions; (b) TN distribution in different aggregate-size fractions. Data are presented as mean ± standard deviation ($n = 3$). Different uppercase letters indicate significant differences between growing seasons for the same aggregate size class at $p < 0.05$, and different lowercase letters indicate significant differences among different aggregate size classes within the same season at $p < 0.05$.

The distribution of TN was relatively uniform. During both the tobacco and rice cropping seasons, TN content showed a slight increasing trend with increasing aggregate size, but the differences among the various size fractions were not statistically significant ($p > 0.05$). TN contents in all aggregate fractions were generally slightly higher in the rice cropping season than in the tobacco cropping season. TN content in macroaggregates increased from $2.28 \text{ g} \cdot \text{kg}^{-1}$ in the tobacco season to $2.44 \text{ g} \cdot \text{kg}^{-1}$ in the rice season, suggesting a possible positive effect.

The SOC distribution exhibited distinct numerical patterns between seasons, despite the lack of statistical significance. During the tobacco cropping season, SOC displayed a subtle unimodal pattern, with microaggregates having the highest content at $22.74 \pm 2.20 \text{ g} \cdot \text{kg}^{-1}$, followed by mesoaggregates at $22.67 \pm 2.44 \text{ g} \cdot \text{kg}^{-1}$, silt-clay fractions at $21.43 \pm 2.41 \text{ g} \cdot \text{kg}^{-1}$, and macroaggregates at $21.24 \pm 2.85 \text{ g} \cdot \text{kg}^{-1}$. In contrast, the rice cropping season showed a gradual numerical decline in SOC with decreasing aggregate size: macroaggregates had the highest value at $25.16 \pm 2.84 \text{ g} \cdot \text{kg}^{-1}$, followed by mesoaggregates at $24.90 \pm 3.67 \text{ g} \cdot \text{kg}^{-1}$, microaggregates at $24.40 \pm 2.48 \text{ g} \cdot \text{kg}^{-1}$, and silt-clay fractions

at $23.58 \pm 3.02 \text{ g} \cdot \text{kg}^{-1}$. The 18.4% increase in macroaggregate SOC under flooding was not statistically significant.

3.3. Adsorption of Cd by Soil Aggregates of Different Particle Sizes

The removal efficiencies of SOC and Fe_d by the selective extraction methods are shown in Figure 6, which served as the basis for the subsequent Cd adsorption experiments on the treated aggregates (Figure 7). Cd adsorption isotherms (Figure 7a,b) exhibited a clear particle size dependence: silt-clay fraction > microaggregates > mesoaggregates > bulk soil > macroaggregates. The silt-clay fraction exhibited the highest adsorption capacity (q_e), with values of $6.990 \text{ mg} \cdot \text{g}^{-1}$ for Masaniutan and $8.070 \text{ mg} \cdot \text{g}^{-1}$ for Shanniutan, while macroaggregates showed the lowest q_e at $5.777 \text{ mg} \cdot \text{g}^{-1}$ and $7.201 \text{ mg} \cdot \text{g}^{-1}$. Across all particle sizes, Shanniutan aggregates exhibited a Cd adsorption capacity that was 1.21 to 1.35 times higher than that of Masaniutan, associated with its higher clay mineral and Fe_d contents.

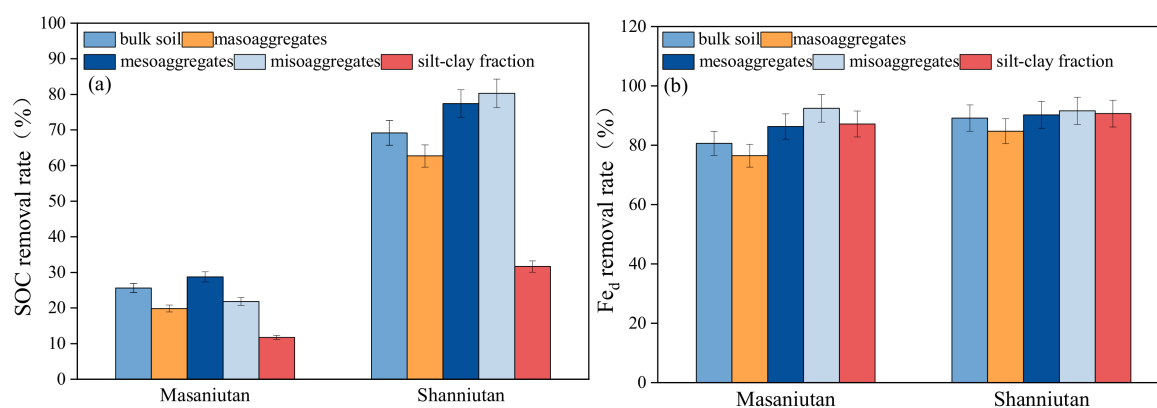


Figure 6. Removal efficiencies of SOC (a) and Fe_d (b) in different aggregate size classes of Masaniutan and Shanniutan soils after selective component removal.

The Langmuir and Freundlich models were employed to quantify the adsorption mechanism (Table S1), with the Langmuir model, which describes monolayer chemisorption, providing significantly better fits than the Freundlich model, representing multilayer physical adsorption, for all aggregates. The Freundlich model parameter $1/n$ fell within 0.1–0.5 for both soils, indicating favorable Cd adsorption, and the maximum adsorption capacity (q_m) derived from the Langmuir model followed the same particle-size trend as q_e , further validating the particle-size dependence of Cd adsorption—consistent with the trend observed for Fe_d distribution. Spearman correlation analysis revealed that q_m was significantly positively correlated with Fe_d content in the untreated aggregate fractions ($r = 0.830$, $p < 0.01$), while no significant correlation was observed between q_m and SOC ($r = 0.479$, $p > 0.05$). However, correlation analysis only reflects the variation in component content across aggregate fractions, whereas the functional contributions of SOC and Fe_d to Cd adsorption were directly evaluated through selective removal experiments.

Selective component removal experiments were conducted to clarify their regulatory roles in Cd adsorption. SOC was removed by H_2O_2 oxidation, with distinct removal efficiencies between the two soils (Figure 6a): Shanniutan exhibited SOC removal rates ranging from 31.64% in the silt-clay fraction to 80.29% in microaggregates, with a removal rate of 69.19% in bulk soil. In contrast, Masaniutan SOC was more stable, with removal rates between 11.73% and 28.72%, indicating higher chemical stability of SOC in its silt-clay fraction. After SOC removal, Cd adsorption isotherms retained the particle-size-dependent trend but showed reduced q_e , especially at high C_e exceeding $100 \text{ mg} \cdot \text{L}^{-1}$, as shown in Figure 7c,d. In the Masaniutan soil, q_m decreased by an average of 36.80%

(Table S2). Notably, the microaggregates showed the most substantial decline of 41.48%, from $6.654 \text{ mg}\cdot\text{g}^{-1}$ to $4.703 \text{ mg}\cdot\text{g}^{-1}$, indicating that this fraction relies most heavily on SOC for Cd adsorption. In contrast, Shanniutan soil exhibited a lower average q_m reduction of 16.98%, which was significantly less than that in Masaniutan soil. It is noteworthy that the removal of SOC did not alter the fundamental particle size-dependent gradient of Cd adsorption—the silt-clay fraction continued to exhibit the highest adsorption capacity in both soils.

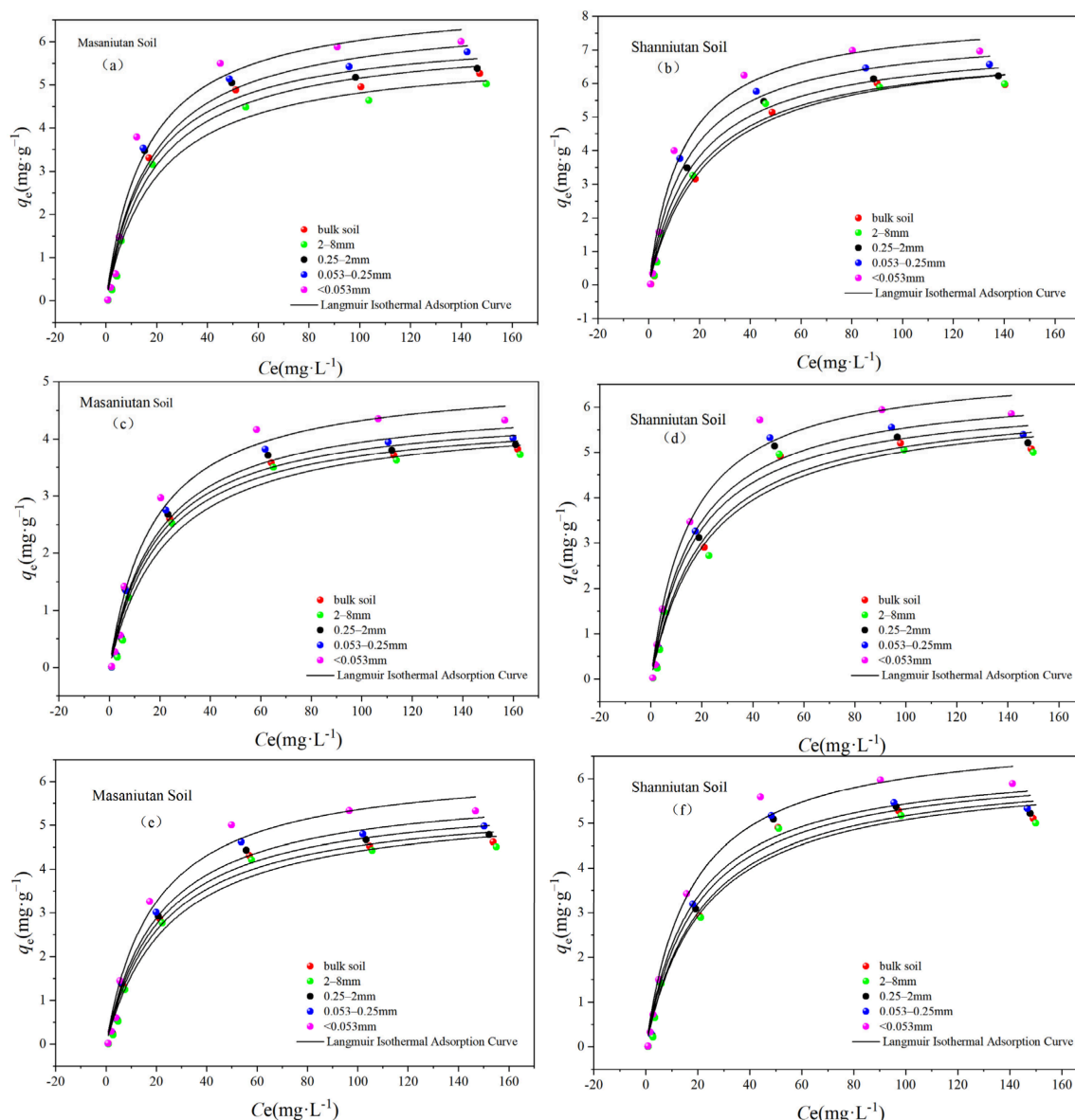


Figure 7. Cd adsorption isotherms for different aggregate size fractions of Masaniutan and Shanniutan soils under various treatments: (a,b) bulk soils; (c,d) after removal of SOC; (e,f) after removal of Fe_d .

Fe_d were removed using the DCB method, with distinct but high removal efficiencies across both soils and all aggregates (Figure 6b): Masaniutan showed Fe_d removal rates ranging from 76.47% in macroaggregates to 92.46% in the silt-clay fraction, with a removal rate of 80.65% in bulk soil, while Shanniutan exhibited slightly higher Fe_d removal rates, ranging from 84.72% in macroaggregates to 91.62% in the silt-clay fraction, and 89.16% in bulk soil. Residual Fe_d contents were negligibly low after DCB treatment, such that their influence on Cd adsorption–desorption could be ignored. Similar to SOC removal, Fe_d removal primarily reduced q_e at high C_e while retaining the particle-size-dependent trend

(Figure 7e,f). However, the reduction in q_m was less pronounced than that caused by SOC removal: Masaniutan exhibited an average q_m decline of 9.33%, with the largest decrease of 13.5% observed in mesoaggregates. Shanniutan soil showed a 15.83% decrease in saturated adsorption capacity, with the mesoaggregates experiencing the greatest decline of 18.41%.

4. Discussion

4.1. Influence of Parent Material, Water Regime Shifts, and Fertilization Management on Aggregate Stability and Distribution

Parent material type is one of the key factors determining the distribution and structural stability of soil aggregates [39]. The greater MWD and GMD of Shanniutan (Table 2) can be attributed to its higher contents of secondary clay minerals and Fe oxides, as revealed by XRD analysis (Figure S1), which promote interparticle cohesion through cation bridging and oxide cementation [40]. In contrast, Masaniutan is dominated by primary minerals including quartz and feldspar, and exhibits slower weathering rates, resulting in aggregates that rely more heavily on SOC for stability. This SOC-dependent bonding is generally more susceptible to changes in microbial activity and organic inputs, leading to lower inherent structural strength compared to the oxide-bonded aggregates in Shanniutan [41].

The water regime shift system dynamically influences aggregates composition and stability through seasonal alternating wet dry cycles [42]. Viewed from Figure 3, the proportion of macroaggregates increased numerically during the flooded rice cropping season, reaching $63.18\% \pm 2.42\%$, compared to $57.33\% \pm 2.15\%$ in the upland tobacco cropping season, accompanied by elevated SOC and TN contents under flooding. These changes suggest coupled physical and biochemical processes [43]. Flooding reduces tillage disturbance, suppresses aerobic microbial decomposition, and straw return adds exogenous organic inputs, jointly promoting C and N accumulation within macroaggregates [44]. However, the lack of significant changes in key stability indices (MWD, GMD, $R_{0.25}$) between the tobacco and rice seasons (Table 3) suggests that a single cycle of upland paddy alternation is insufficient to alter the inherent soil structure [45].

Chlorine fertilization, in contrast, produced clear and concentration-dependent aggregate disruption. These results indicate that Cl^- introduction promotes aggregate dispersion and structural refinement [46]. The underlying mechanisms are primarily attributed to the disruption of cation bridges by Cl^- . Cl^- can form soluble ion pairs (e.g., CaCl^+ , MgCl^+) with polyvalent cations such as Ca^{2+} and Mg^{2+} in soil solution, thereby weakening the bridging role of these cations between clay minerals and organic matter, and reducing the stability of macroaggregates [47]. Additionally, Cl^- may form soluble complexes with Fe^{3+} and Al^{3+} under acidic conditions, promoting the dissolution of iron and aluminum oxides that serve as important inorganic cementing agents, thus dismantling the cementation framework of aggregates. The salinity effect caused by high Cl^- concentrations may also compress the electrical double layer, altering inter-particle forces and contributing to aggregate dispersion. Furthermore, monovalent cations such as Na^+ , when present in irrigation water or associated with fertilizers, can displace Ca^{2+} through cation exchange, further exacerbating aggregate dispersion and structural degradation.

PLS-SEM (Figure S2) results showed that the model had strong explanatory power with a coefficient of determination (R^2) of 0.962, indicating that the three factors collectively explained 96.2% of the variation in aggregate stability. Path analysis revealed that parent material exerted a significant positive direct effect on aggregate stability (path coefficient = 2.346), acting as the dominant factor determining the inherent stability of soil aggregates. Chlorine-containing fertilization significantly reduced aggregate stability (path coefficient = -0.750), indicating that high chlorine input aggravated the breakdown of macroaggregates. Short-term tobacco–rice seasonal alternation had a weak effect on

aggregate stability, consistent with the non-significant difference in seasonal treatments observed in one-way ANOVA. In the measurement model, the outer loadings of MWD, GMD, and $R_{0.25}$ were 0.977, 0.968, and 0.974, respectively, all exceeding 0.90, indicating good reliability and convergent validity of the latent variable for aggregate stability.

To further verify the overall correlation between the environmental factor matrix and aggregate stability variation, Mantel test was performed. The results showed that the environmental factor matrix composed of parent material, seasonal alternation, and chlorine-containing fertilization was significantly positively correlated with the aggregate stability matrix (Mantel's $r = 0.6215$, $p = 0.005$, permutations = 999), indicating that the overall variation in environmental factors was highly consistent with the change in aggregate stability, providing supplementary verification for the path analysis results of the PLS-SEM model.

4.2. Distribution Characteristics of SOC and TN in Different Aggregate Sizes Under Tobacco–Rice Rotation

In this study, the distribution of SOC and TN across aggregate size classes showed numerical trends that varied with particle size and cropping season, although none of these differences reached statistical significance ($p > 0.05$, Figure 5). This numerical enrichment likely reflects flooding-induced suppression of aerobic decomposition and enhanced physical protection within macroaggregate pores [44,48], but the absence of significance confirms that a single seasonal cycle is insufficient to produce measurable carbon accrual. The relatively uniform TN distribution across fractions suggests that nitrogen is more evenly retained at the aggregate scale through clay mineral adsorption and organo-mineral associations [49,50].

4.3. Cd Adsorption Affected by Soil Aggregates of Different Size Fractions

Soil aggregates serve as critical micro-interfaces for the migration and transformation of heavy metals in soils, and their capacity to immobilize Cd is a central process regulating Cd's environmental behavior and bioavailability [51]. This pattern is primarily attributed to differences in specific surface area and key adsorption components (SOC and Fe_d). Smaller aggregates possess larger specific surface areas, offering more potential adsorption sites, and are generally enriched with higher contents of SOC and Fe_d [52]. This observation is consistent with the findings of Liu et al. (2023), who reported that the $<2\ \mu\text{m}$ aggregate fraction served as the dominant sink for Cd adsorption in a Pb–Cd competitive system [53]. While their study focused on competitive adsorption between Pb and Cd, our work examined Cd adsorption under single-metal conditions across aggregates derived from contrasting parent materials, providing complementary insights into the role of aggregate size in Cd retention [53]. The Langmuir model provided a better fit than the Freundlich model, and the Langmuir-derived q_m was used as a comparative index for Cd adsorption capacity across aggregate fractions [54]. The Freundlich model parameter $1/n$ fell within 0.1–0.5 for both soils, confirming favorable Cd adsorption.

The substantial reduction in q_m after SOC removal (Table S2) indicates that SOC plays a dominant role in Cd adsorption in these aggregates [55]. This indicates that SOC plays a dominant role in Cd adsorption in these aggregates, as its removal caused the most pronounced reduction in q_m among the two removed components [55]. Rich in oxygen-containing functional groups such as carboxyl, phenolic hydroxyl, and carbonyl groups, SOC can strongly bind Cd^{2+} through surface complexation and cation exchange. In contrast, Shanniutan exhibited a relatively smaller decrease after SOC removal, attributed to its higher content of secondary clay minerals such as montmorillonite and kaolinite, which possess significant permanent and variable charge surfaces and partly compensate for the

loss of adsorption capacity [56], also revealing differences in the emphasis of Cd fixation mechanisms due to variations in soil parent material [57].

Fe_d play a non-negligible auxiliary role in Cd adsorption, consistent with previous findings that iron oxides can contribute to Cd adsorption through surface complexation and coprecipitation [27,58,59]. Their surfaces are rich in hydroxyl functional groups that form inner-sphere complexes with Cd^{2+} through specific adsorption and can induce Cd-Fe coprecipitates under alternating redox conditions in paddy soils, thereby enhancing Cd immobilization within aggregates [52,56]. This mechanism is particularly pronounced in finer aggregate fractions, where Fe_d content is substantially higher [30]. Following DCB treatment, the reduction in q_m was less pronounced than that caused by SOC removal, confirming Fe_d as a synergistic rather than dominant factor [27,55].

Notably, even after the removal of SOC or Fe_d , the fundamental trend of increasing adsorption capacity with decreasing particle size remained unchanged, indicating that the inherent mineral composition and large specific surface area of fine-sized aggregates enable them to maintain relatively high adsorption potential even in the absence of key cementing components [55]. Furthermore, Shanniutan exhibited stronger Cd fixation ability and greater resistance to component-removal disturbances compared to Masaniutan, which is attributed to its higher content of secondary clay minerals and Fe_d . This suggests that parent material indirectly influences the Cd fixation potential and stability of aggregates by regulating the composition of secondary minerals and the distribution of cementing agents [60].

5. Conclusions

In summary, this study suggests that the structure and function of paddy soil aggregates may be influenced by parent material, water regime shifts, and chlorine-containing fertilization. Slate/shale derived Shanniutan formed more stable aggregates dominated by inorganic Fe/clay cementation, whereas granite-derived Masaniutan relied more on organic binding. The rice cropping season within the tobacco–rice rotation enhanced physical protection and boosted carbon/nitrogen sequestration in macroaggregates. In contrast, chlorine-containing fertilizers disrupted aggregate integrity. Cd adsorption capacity increased with decreasing aggregate size, with SOC providing substantial contributions and Fe_d playing secondary supporting roles. These findings, though constrained by the limited number of soil types and sampling events, cautiously advocate for integrated management that leverages flooded phases for C/N accrual, and promotes organic amendments to concurrently improve soil structure, fertility, and heavy metal immobilization capacity. Combined with existing literature regarding chloride-related Cd mobilization risk, our aggregate-stability results further imply need for prudent management of chlorine-containing fertilizer inputs in Cd-contaminated paddy soils. Future studies with more soil types and long-term observations are needed to confirm these trends.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/agronomy16181761/s1>, Table S1: Anion composition of the five chlorine-containing fertilizer treatments ($\text{mmol}\cdot\text{kg}^{-1}$ dry soil); Table S2: Isothermal adsorption model parameters for Cd in different aggregate size fractions of Masaniutan and Shanniutan paddy soils; Table S3: Isothermal adsorption model parameters for Cd in different aggregate size fractions of Masaniutan and Shanniutan paddy soils after OM removal; Table S4: Isothermal adsorption model parameters for Cd in different aggregate size fractions of Masaniutan and Shanniutan paddy soils after Fe_d removal; Figure S1: X-ray diffraction of soils from Masaniutan and Shanniutan. Figure S2: PLS-SEM model showing the direct effects of parent material, water regime shifts in annual tobacco–rice rotation, and chlorine-containing fertilization on soil aggregate stability. Numbers on arrows are standardized path coefficients; numbers below indicators are outer loadings. $R^2 = 0.962$; Text S1: De-

tailed Wet Sieving Procedure; Text S2: Detailed Procedures for Selective Removal of Soil Components; Text S3: X-ray diffraction (XRD) analysis.

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