Spatial and temporal trends in total organic carbon (TOC), black carbon (BC), and total nitrogen (TN) and their relationships under different planting patterns in a restored coastal mangrove wetland: case study in Fujian, China

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\textbf{ABSTRACT}
This study aims to determine the sediment changes and the trends in TOC, BC and TN before and after restoration of the mangrove wetland in the Jinjiang Estuary and to determine the effect of the wetland restoration process on the biogeochemical cycle of carbon and nitrogen. The results suggest that the sediments were mainly silt-sized. Among different sites with different types of plants and vegetation densities, the adsorptive ability of N in the plots in plantations of Kandelia obovata, Avicennia marina and Acanthus ilicifolius was the highest. The TOC content differed (p < 0.05) with the density of the plot and significantly differed (p < 0.01) with the mangrove species at the densities of 0.5 × 1 m and 0.5 × 0.5 m. There was a positive relationship between the TOC and TN and the TOC and carbon-nitrogen ratio (C/N) (P < 0.05).

1. Introduction

Mangrove wetland is a special vegetation type located in the intertidal zone of tropical and subtropical coastal areas\cite{1,2}. These wetlands contain a special type of vegetation on silt beaches, and they are an important resource of coastal wetlands and have important ecological significance\cite{3}. Mangrove wetlands are also huge organic carbon pools on land and store large amounts of organic carbon\cite{4,5}. Research shows that mangroves average 1023 Mg carbon per hectare, and the underground carbon reserves of the global mangrove wetlands are more than 5 times that of the upper part of the ground\cite{6}. In addition to organic carbon, black carbon in the carbon pool has also attracted much attention. The main component of black carbon is highly polymerized polycyclic aromatic hydrocarbons, which are extremely difficult to degrade at ambient temperature. Because of this unique property, black carbon has a great influence on the carbon budget and the slow and insoluble carbon pool around the world. It is considered one of the inert carbon pools and is an important component of the carbon sink of the earth. Organic matter content and total nitrogen have proven to be useful variables for assessing soil conditions. They are highly valuable in the development of resources and environmental regulations. According to research, the cycling of N and C are closely related, and carbon storage depends to a large extent on the cycling of N\cite{7}.

The C/N ratio can imply a close relationship between C and N transformation in the process of soil biological decomposition. The value of C/N depends on the decomposition rates of C and N and is an important indicator that the accumulation of TN is due to the mineralization of soil nitrogen or the decomposition of organic matter\cite{8–10}. Tue et al.\cite{11} examined the patterns of sedimentation and sedimentary organic carbon content in mangrove forests along the coast of northeast Vietnam. The C/N ratios showed that sedimentary organic carbon in riverine mangrove forests mainly originated from mangrove organic matter. Currently, the degradation of mangrove wetland is serious due to human activities. Over half of the wetlands that once existed in United States have been degraded through land development\cite{12}. Southeast Asia is the global centre of mangrove development, but human activities have dramatically reduced the mangrove area in the region\cite{13}. Mangrove deforestation threatens to release large stores of carbon from soils that are vulnerable to oxidation\cite{14}. The restoration of wetlands is urgently needed, but the effects of the restoration process of degraded estuary wetlands on carbon and nitrogen in soil have rarely been reported. The Jinjiang Estuary wetland is located on the south coast of Fujian, China and is severely degraded. We examined the restoration of the Jinjiang Estuary degraded wetland in 2014. This study aims to determine the sediment changes...
and the trends in the total organic carbon (TOC), black carbon (BC), and total nitrogen (TN) before and after restoration of the mangrove wetland of the Jinjiang Estuary and to determine the effect of the wetland restoration process on the biogeochemical cycle of carbon and nitrogen. This study provides a scientific basis for determining the effect of the restoration and protection of degraded estuarine wetlands on soil carbon pools and global climate change.

2. Material and methods

2.1 Site description

This research was conducted at the Jinjiang Estuary wetland, which is one of the most important components of the Quanzhou Bay wetlands and a typical subtropical estuarine wetland in Fujian, China [15], located in the Jinjiang River Estuary, outside the south embankment of the Jinjiang River (Figure 1). The studied area was a flat muddy land covered with scattered Spartina alterniflora before reforestation. The mangrove planting area was 18.33 hectares after Spartina and other weeds were removed. The three kinds of mixed mangrove planting patterns were used to restore the wetland. (The field experiment was designed randomly and with three repetitions. Each plot was approximately 0.35 ha, and there were 27 plots in total.) The restoration pattern of KBR (planting Kandelia obovata, Bruguiera gymnorrhiza and Rhizophora stylosa) included three planting densities, referred to as KBR (1 × 1 m), KBR (1 × 0.5 m), and KBR (0.5 × 0.5 m). According to the planting mode, we named the plots KAAi (planting with Kandelia obovata, Aegiceras corniculatum and Acanthus ilicifolius) (1 × 1 m), KAAi (0.5 × 1 m), KAAi (0.5 × 0.5 m), KAAm (planting with Kandelia obovata, Aegiceras corniculatum and Avicennia marina) (1 × 1 m), KAAm (0.5 × 1 m), and KAAm (0.5 × 0.5 m).

2.2 Sample collection and laboratory analysis

Each plot of soil was sampled at a depth of 1 metre with a steel tube at three randomly selected locations in April 2014 (no vegetation was planted) and April 2016 (two years after planting). We also collected 3 tubes of sediment as blank control sediments in addition to the plantation without mangrove on April 2016. In total, 140 bags of sediment were sampled and were extruded from the tube into zip-lock bags, then transferred to the lab immediately. Samples were stored in a deep-freeze chest until the experiment. After the sediments were freeze-dried and the roots and other fragments were carefully removed, they were divided into two parts. One part was directly tested for particle size fractions using a laser particle analyser (Mastersizer 2000). The rest of the sediments of each layer were ground and passed through a 2-mm sieve for testing. A few drops of hydrochloric acid were added to the 30 mg soil sample in a small porcelain boat until the sample was no longer bubbling (removal of its inorganic carbon). After washing several times, the sample was dried for 3 h at 105°C, then measured using the TOC analyser (multiN/C UV Analytik jena). We used chemo-thermal oxidation (CTO-375) for BC detection[16]. The dried samples (100 mg) were exposed to thermal oxidation (375°C, 18 h) in a muffle furnace after digestion with HCl[16]. The residual organic carbon was determined as the BC using a TOC analyser (multiN/C UV Analytik jena). The

![Figure 1. Site description.](image-url)
TN was determined using a spectrophotometer after the total content was extracted as NO\textsubscript{3} in the supernatant using the oxidation method which consisted of adding 20 ml oxidative agent (0.24 mol/L NaOH, 0.074 mol/L K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}), shaking, then oxidizing for 30 min at 135°C in high-pressure sterilizing kettle [17]. The reagents used in this study were all of analytical purity. All samples were analysed in triplicate. The relative standard deviations of the parallel samples were less than 5% for the total organic carbon and total nitrogen and less than 10% for black carbon.

2.3 Statistical analyses

Excel 2013 and Origin 8.5 were used to draw the line chart describing the vertical distribution of TOC and TN content. We calculated the Pearson’s correlation coefficients to test for relationships among parameters and identify the key indicators of recovery. Linear correlation between different parameters and one-way ANOVA was used to test for significance using SPSS 19.0. The position of the sampling point was drawn using MapInfo 9.5.

3. Results

3.1 Characteristics of surface sediment distribution of TN, TOC and BC

The surface sediment distributions of TOC, TN and BC are shown in Figure 2. Figure 2(a) reveals the total nitrogen content before and after the restoration, which were in the range of 1.1–2.56 g/kg and 1.35–2.54 g/kg, respectively. The average contents of TN before and after the restoration were 1.81 and 1.97 g/kg, respectively. There were no differences between the measured TN content before and after the wetland restoration (p > 0.05). The surface sediment TN contents were ranked in order of KAAm (1 × 1 m) > KAAm (1 × 0.5 m) > KBR (0.5 × 0.5 m) > KAAm (0.5 × 0.5 m) > KAAi (1 × 0.5 m) > KAAi (0.5 × 0.5 m) > KBR (1 × 1 m) > KAAi (1 × 1 m) > KBR (1 × 0.5 m) before the artificial recovery and were ranked in the order of KAAi (1 × 0.5 m) > KAAi (1 × 1 m) = KBR (0.5 × 0.5 m) > KAAm (0.5 × 0.5 m) > KBR (1 × 1 m) > KAAm (1 × 1 m) > KBR (1 × 0.5 m) > KAAm (1 × 0.5 m) > KAAm (0.5 × 0.5 m) two years later. The density of planting had a significant influence (p < 0.01) on the TN content in the planting patterns of KBR and KAAi. The plant species also had a significant influence (p < 0.01) on the TN content in the plots with densities of both 0.5 × 1 m and 0.5 × 0.5 m and produced only a difference (p < 0.05) in the plot with a density of 1 × 1 m.

From Figure 2(b), we can see that the content of TOC was in the range of 12.02–16.60 g/kg before the restoration and ranged from 9.24–16.27 g/kg two years after restoration. The average contents were 14.36 g/kg and 12.02 g/kg, respectively. There was a difference between the content of TOC (p < 0.05), which showed a decreasing tendency before and after the restoration, and there was also a difference among the TOC of different sites (p < 0.05). The surface TOC content was ranked in the order of KBR (1 × 0.5 m) > KBR (0.5 × 0.5 m) > KBR (1 × 1 m) > KAAi (1 × 0.5 m) > KAAi (1 × 1 m) > KAAm (0.5 × 0.5 m) > KAAm (1 × 1 m) > KAAi (0.5 × 0.5 m) before mangrove planting and was ranked...
Vertical distribution characteristics of BC under different planting patterns

The vertical distribution of TOC can be seen in Figure 6–8. The average BC contents of KBR (1 × 1 m), KAAi (1 × 1 m) and KAAm (1 × 1 m) before restoration were 1.96 g/kg, 1.80 g/kg and 1.51 g/kg, respectively, and after the restoration, the contents were 1.25 g/kg, 2.49 g/kg, and 1.97 g/kg, respectively. Before restoration, the contents of KBR (1 × 0.5 m), KAAi (1 × 0.5 m) and KAAm (1 × 0.5 m) were 1.80 g/kg, 1.97 g/kg, and 1.31 g/kg, respectively, and the values changed to 2.497 g/kg, 2.477 g/kg and 1.607 g/kg, respectively, after restoration. For the patterns of KBR (0.5 × 0.5 m), KAAi (0.5 × 0.5 m) and KAAm (0.5 × 0.5 m) before restoration, the contents were 2.13 g/kg, 2.73 g/kg, and 2.97 g/kg, respectively, and after the restoration, the content changed to 1.33 g/kg, 1.74 g/kg, and 1.54 g/kg, respectively. The vertical distribution of BC under different planting patterns can be seen in the figures below. From Figure 6–8 and the data, we can see that except for the planting mode of KBR (1 × 1 m), two years after restoration, the content of BC in the sediment increased following the pattern of KBR (1 × 1 m) and KAAm (1 × 1 m). The increasing tendency also appeared for all three kinds of patterns with the density of 1 × 0.5 m. Under the planting modes of KBR (0.5 × 0.5 m), KAAi (0.5 × 0.5 m) and KAAm (0.5 × 0.5 m), the BC content of all three decreased two years after restoration. After restoration, the BC tended to decrease from surface to the depth of 40–80 cm and had a small increase from 80–100 cm, of which the tendency was similar to that of the TOC vertical distribution in some of the planting patterns. Two years after restoration, the average BC content was slightly decreased, but the BC content after afforestation didn’t show a significant difference with the content before (P > 0.05). According to one-way ANOVA analysis, the BC content showed a significant difference with the density in the pattern of KBR (P < 0.01) and showed a difference with the density in the patterns of KAAi and KAAm (P < 0.05). With the plants used in KBR, the planting pattern of KBR (1 × 0.5 m) had the highest value among the three. On the plot with KAAi, the pattern of KAAi (1 × 1 m) had the highest content of BC, and for the plants of KAAm, the largest value of BC in the sediment also existed in the pattern of KAAm (1 × 1 m).

Vertical distribution characteristics of TN and C:N under different planting patterns

Figure 9–11 shows the vertical distribution of TN under different planting patterns. Using SPSS to perform one-way ANOVA analysis of the differences, we obtained the result that the TN content showed a
difference \( (p < 0.05) \) with the density of the plot. On the KBR plot, the difference was significant \( (p < 0.01) \). The sediment could produce the most TN (2.37 g/kg) with mangrove planted under the density of
0.5 × 0.5 m and KBR (1 × 1 m), with average of 1.79 g/kg, and KBR (1 × 0.5 m), with an average of 1.27 g/kg. In the KAAi plot, the TN content was ranked KAAi (1 × 0.5 m) (2.58 g/kg)>KAAi (1 × 1 m) (2.25 g/kg)

Figure 6. Vertical distribution of BC for the planting patterns of (a) KBR (1 × 1 m), (b) KBR (1 × 0.5 m) and (c) KBR (0.5 × 0.5 m).

Figure 7. Vertical distribution of BC for the planting patterns of (a) KAAi (1 × 1 m), (b) KAAi (1 × 0.5 m) and (c) KAAi (0.5 × 0.5 m).

Figure 8. Vertical distribution of BC for the planting patterns of (a) KAAm (1 × 1 m), (b) KAAm (1 × 0.5 m) and (c) KAAm (0.5 × 0.5 m).
KAAi (0.5 × 0.5 m) (2.06 g/kg) and in the KAAm plot, it was ranked KAAm (1 × 1 m) (1.49 g/kg) > KAAm (1 × 0.5 m) (1.37 g/kg) > KAAm (0.5 × 0.5 m) (1.24 g/kg). The TN content also showed a significant difference (p < 0.01) with the species of the planted mangrove. At the sites with densities of 1 × 1 m, 0.5 × 1 m and 0.5 × 0.5 m, the TN content was ranked KAAi (1 × 1 m) > KBR (1 × 1 m) > KAAm (1 × 1 m), KAAi (1 × 0.5 m) > KAAm (1 × 0.5 m) > KBR (1 × 0.5 m) and KBR (0.5 × 0.5 m) > KAAi (0.5 × 0.5 m) > KAAm (0.5 × 0.5 m). Except for plots KBR (1 × 1 m) and KBR (0.5 × 0.5 m), the TN content for the other planting patterns observed before restoration was higher than the content observed after restoration.

Although we obtained results from the experiments, changes in total C and N occur slowly and can be difficult to detect because of large background levels of C and N in the soil[19].

4. Discussion

We can see that TOC content was reduced following cultivation. The maximum amount appeared in the upper part of the sediment between 10 cm-40 cm, a lesser amount appeared at a depth of 60 cm, and the minimum amount could have followed a different pattern. Ha et al [20], studied the TOC in the soil of a mangrove forest in northern Vietnam. They found that there was a depth-related distribution of organic carbon in the soil, with the highest concentrations measured between 20 and 60 cm depth. It was generally thought that the TOC content had a close relationship with the depth and decreased exponentially[21,22]. However, descriptions such as this cannot reflect the real vertical changes in restored wetlands according to our results. The TOC content possibly decreased due to high decay.

Figure 9. Vertical distribution of TN for the planting patterns of (a) KBR (1 × 1 m), (b) KBR (1 × 0.5 m) and (c) KBR (0.5 × 0.5 m).

Figure 10. Vertical distribution of TN for the planting patterns of (a) KAAi (1 × 1 m), (b) KAAi (1 × 0.5 m) and (c) KAAi (0.5 × 0.5 m).
rates that likely offset the increases in litter inputs to the soil [23]. The processes that mainly control soil C storage following reforestation are determined by a balance between litter input and soil C decomposition [24,25]. There was an interannual variability for the artificial mangrove wetland. This factor was also reported in many studies of constructed wetlands [20,26]. The organic matter in the soil of Santiago Bay wetland did not show an upward trend after restoration [27]. Most of the assessed attributes failed to show that the organic carbon content did not increase in the short term near Puget Sound [28]. The soil organic matter failed to follow an increasing trajectory in San Diego Bay. Scientists predict that constructed marsh soil will not match that of natural wetlands in the long term [27].

Before restoration, the percentage of BC in the TOC was 14.7%, and after restoration, the percentage of BC jumped to 16.03%. Preliminary data has demonstrated that [29] BC is removed from faster cycling carbon of pools and accumulates in soils, which is based on the high resistance of BC against oxidation [30,31].

Mangrove leaves form a large pool of nitrogen that is a major driver of element cycles and detrital food webs inside mangrove forests. It is inferred that the amount of labile nitrogenous organic matter plays a major role in determining the rate of decomposition of leaf litter in mangroves [32]. Mangroves can absorb nitrogen from sediment and water, and their residues containing the absorbed nitrogen will be deposited into the soil over time. We concluded from the contents observed that the effect of denitrogenation under the planting pattern of plot KAAm was more obvious than that in the others. The trends in distribution showed differences at different sites. However, the overall tendency was a decrease with soil depth. Most of the contents were accumulated on the surface (0–50 cm), and depths of 0–20 cm contained the most nitrogen (Figure 5, Figure 6, Figure 7). This result demonstrated that the plant recovery project presented a regular pattern of nitrogen accumulation through upper-level enrichment. The TN densities increased gradually with the mangrove restoration [26], and the TN values and C:N decreased compared with the beginning sediment characteristics. The reason was the increased plant N use and increased leaching of labile N from the SOM (soil organic matter) with reforestation [33]. This effect was probably because the increased litter input was offset by a fast C loss rate in the first few years due to the high decay rates that likely offset increases in litter inputs to the soil [23]. Nair et al. [34] reported that the C:N values in natural wetlands in central and northern Florida ranged from 15–25 and decreased with time in restored wetlands. Soil C:N ratios in natural sites ranged from 8–12, indicating ample N for plant uptake [12]. The reduction also suggests that cultivation enhanced the processing of C and, subsequently, N mineralization by increasing microbial activity [35].

The C/N values of the studied area varied from 4.74–11.78 (Table 1), with an average of 6.89. Vertically, the ratio at 20–60 cm was higher than those of the other layers. This result may have been related to the root system distribution. Plot KAAm, with the highest C/N values, was influenced mostly by the marine life. There was a positive relationship between the TOC and TN and the TOC and C/N (Table 2, P < 0.05). Hossain et al. investigated the total organic carbon contents together with the total nitrogen of the surface sediments of the Sundarbans mangrove forest in Bangladesh. The TOC and TN also showed strong positive correlations between them [36]. The C/N depends on the input and decomposition of C/N. C/N showed a difference with the TOC content showing that mangroves had a certain effect on the TOC.
Table 1. The C/N variation in soil after restoration.

| Pattern                  | Depth (cm) | 0–20 | 20–40 | 40–60 | 60–80 | 80–100 | ave |
|--------------------------|------------|------|-------|-------|-------|--------|-----|
| KBR (1 × 1 m)            |            | 6.04 | 6.28  | 7.75  | 6.73  | 6.07   | 6.57|
| KBR (1 × 0.5 m)          |            | 11.27| 11.96 | 10.98 | 8.57  | 11.78  | 10.91|
| KBR (0.5 × 0.5 m)        |            | 4.78 | 6.25  | 5.57  | 4.89  | 5.11   | 5.32|
| KAA (1 × 1 m)            |            | 4.74 | 5.77  | 5.60  | 5.31  | 5.14   | 5.31|
| KAA (1 × 0.5 m)          |            | 5.41 | 4.71  | 4.82  | 6.99  | 4.66   | 5.32|
| KAA (0.5 × 0.5 m)        |            | 6.44 | 4.96  | 5.81  | 7.50  | 5.95   | 6.13|
| KaAm (1 × 1 m)           |            | 6.46 | 7.73  | 6.32  | 7.07  | 7.10   | 6.93|
| KaAm (1 × 0.5 m)         |            | 6.73 | 8.14  | 7.01  | 7.19  | 7.22   | 7.26|
| KAAm (0.5 × 0.5 m)       |            | 7.80 | 7.92  | 9.09  | 8.17  | 8.74   | 8.34|
| Blank                    |            | 5.91 | 6.19  | 6.40  | 8.02  | 7.42   | 6.79|
| ave                      |            | 6.56 | 6.99  | 6.93  | 7.04  | 6.92   | 6.89|

Table 2. Pearson correlations of two periods between different layers.

|          | TOC  | BC   | TN   | C/N  |
|----------|------|------|------|------|
| TOC      | 1    |      |      |      |
| BC       | 0.29 | 1    |      |      |
| TN       | 0.757* | 0.606 | 1    |      |
| C/N      | 0.700* | –0.232 | 0.064 | 1    |

It is generally known that the carbon-nitrogen ratio is a vital sign of whether soil nitrogen mineralization and the decomposition of organic matter are restricted by TN[8,37]. Carbon-nitrogen ratios lower than 25 indicate that there are higher soil humic amounts and that soil organic matter decomposition is not restricted by the lack of nitrogen. From the table, we can see that the ratio was far lower than 25 and that nitrogen mineralization became weak at 20–60 cm and recovered with depth.

5. Conclusion

We found that the TOC and TN and BC contents were reduced following cultivation. The TOC content ranking 2 years after restoration were nearly as same as the former ranking, except in three plots. The TOC showed a difference with the density and plantation. The average BC content slightly decreased, but the BC content after afforestation showed a significant difference with the density of the restoration. The plot with *Kandelia obovata*, *Bruguiera gymnorrhiza* and *Rhizophora stylosa* (KBR) at a density of 1 × 0.5 m showed the highest value. The maximum amount appeared in the upper layer between 10 cm-40 cm, a lesser amount appeared at a depth of 60 cm, and the minimum amount could have followed a different trend. These results may have been due to the high decay rates that likely offset increases in litter inputs to the soil, and there was an interannual variability for the artificial mangrove wetland. There was a positive relationship between the TOC and TN and the TOC and C/N but no significant relationship between the TN and TOC. The plant recovery project presented a regular pattern of nitrogen accumulation in terms of upper layer enrichment. Constructed marsh soil may match that of natural wetlands in the long term, so long-term observations should be carried out in further studies.

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Disclosure statement

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