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# Labile and recalcitrant sediment organic carbon pools in the Pearl River Estuary, southern China

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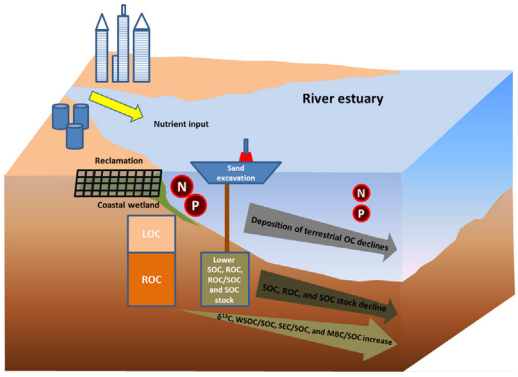
## HIGHLIGHTS

- Labile and recalcitrant sediment organic carbon (SOC) were studied in estuary.
- Larger recalcitrant organic carbon (ROC) and SOC stock was found in inner estuary.
- Higher ratio of labile organic carbon fraction to SOC was found in outer estuary.
- Sand excavation reduced SOC, ROC, ROC/SOC, and SOC stock.
- The estimated SOC stock in the Pearl River Estuary was 34.0 Mg C $ha^{-1}$.

## GRAPHICAL ABSTRACT

Schematic picture of labile and recalcitrant sediment organic carbon pools and their change trends in the river estuary ecosystem.

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## ABSTRACT

Little is known about the labile and recalcitrant sediment organic carbon (SOC) in estuarine ecosystem, and the effects of human activities on SOC sequestration also remain poorly understood. In this study, sediment cores in the Pearl River Estuary (PRE) and adjacent coastal areas in the South China Sea were collected to analyse variations in the sources of SOC and its labile and recalcitrant pools. Concentrations of SOC, microbial biomass carbon (MBC), and recalcitrant organic carbon (ROC) ranged from 4.37 to 10.4 g/kg, 0.522 to 1.53 g/kg, and 1.59 to 5.42 g/kg, respectively, with their corresponding mean values as 7.20 ± 1.43 g/kg, 0.896 ± 0.228 g/kg, and 3.71 ± 1.01 g/kg, respectively. ROC was the chief fraction of SOC, and SOC, MBC and ROC has a similar source. Higher SOC and MBC were observed in the upper sediments, which might be attributable to the enhancement of seawater nutrient and particulate organic carbon concentrations in recent decades. Higher concentrations of SOC, ROC, and SOC stock were found in the inner estuary relative to the outer estuary due to a higher terrigenous organic carbon contribution, while the ratio of water-soluble organic carbon, salt-extractable carbon, and MBC to SOC exhibited a contrasting trend caused by a higher autochthonous contribution. Sand excavation reduced SOC, ROC, ROC/SOC, and SOC stock. The estimated SOC stock of the top 75 cm of sediment in the PRE was 34.0 Mg C

*Abbreviations:* SOC, sediment organic carbon; PRE, Pearl River Estuary; LOC, labile organic carbon; WSOC, water-soluble organic carbon; SEC, salt-extractable carbon; MBC, microbial biomass carbon; ROC, recalcitrant organic carbon; OC, organic carbon; DIN, dissolved inorganic nitrogen; DIP, dissolved inorganic phosphate; BD, bulk density.

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$ha^{-1}$, and the reduction of SOC stock in the PRE due to sea reclamation from 1973 to 2015 was 1,171,159.6 Mg C. Therefore, measures should be taken to control sea reclamation and sand excavation activities in the PRE to enhance carbon sequestration capacity.



## 1. Introduction

The accumulation of organic carbon (OC) in estuarine and coastal sediments plays a critical role in global carbon sequestration as >80% of the carbon buried in the oceans occurs in these shallow marine systems (Berner, 1982; Hedges and Keil, 1995; Hu et al., 2016). In estuarine areas, sediment receives OC mainly from a combination of autochthonous sources (e.g. phytoplankton) and allochthonous sources (e.g. river input) (Dubois et al., 2012; Volkman et al., 2008; Zhang et al., 2009b). OC from different sources have varied burial efficiencies, and influence the lability and preservation of sediment organic carbon (SOC) (Liu et al., 2016; Watanabe and Kuwae, 2015). Water-soluble OC (WSOC) and salt-extractable carbon (SEC) are the direct reservoirs of OC that is readily available for sediment microbial metabolism (Liu et al., 2016; Rochette and Gregorich, 1998; Yang et al., 2013), while microbial biomass carbon (MBC) represents the microbial biomass in sediments (Fang et al., 2005; Liu et al., 2016). Recalcitrant organic carbon (ROC), the SOC remaining after acid hydrolysis, represents the relatively stable SOC pool (Cheng et al., 2007), which is resistant to microbial decomposition. Currently, most research into the SOC in estuaries has focused on the total SOC and its source rather than on SOC sub-pools (Dubois et al., 2012; He et al., 2010; Hu et al., 2006a; Zhang et al., 2009b). To better understand the processes responsible for SOC preservation in estuarine and shallow coastal systems, it is necessary to also study the labile organic carbon (LOC) and ROC pools.

The Pearl River is the largest river in southern China, and empties into the South China Sea through eight outlets (Zhang et al., 2009b). A large volume of terrigenous organic matter exported from the Pearl River may be transported to the Pearl River Estuary (PRE) and adjacent ocean areas (Dai et al., 2007; Zhang et al., 2009b), with about 80% of particles deposited within the PRE (Wai et al., 2004). The previous study has revealed that the terrestrial OC is mainly deposited to the west of the PRE (Chen et al., 2008; He et al., 2010; Hu et al., 2006a; Zhang et al., 2009b). However, the SOC sequestration capacity in the PRE itself remains poorly understood. The PRE is one of the core regions of economic growth in China. Owing to rapid economic development in recent decades, the PRE has received high loadings of anthropogenic nutrients and pollutants (He et al., 2010; Zhang et al., 2009b). It is also under constant threat from sea reclamation including agricultural and industrial development and practices, aquaculture, town construction, harbor, and wharf reclamation (Zhang et al., 2016). These activities are capable of destroying wetlands, altering hydrodynamic conditions, and enhancing water pollution. Statistical analyses have indicated that the area of sea reclamation in the PRE increased by 27,286.68 ha from 1973 to 2015 (Zhang et al., 2016). This has undoubtedly induced loss of coastal wetland areas as carbon sinks in the PRE. Additionally, sand excavations have also been conducted in the PRE. For example, the area of sand excavations was ~1926 ha between 2005 and 2009 due to the need for rapid industrialization (South China Sea Institute of Oceanology, Chinese Academy of Sciences, 2009). Do these human activities influence the source of SOC and its labile and recalcitrant pools, thereby affect SOC sequestration capacity in the estuarine ecosystem? Little information is currently available.

Sediment cores in the PRE were collected to analyse the $\delta^{13}C$ of SOC to determine the relative contribution of terrigenous OC. Additionally, LOC (e.g. MBC, SEC, and WSOC) and ROC pools were also analysed along with the SOC sequestration capacity. $^{210}Pb$ was measured to determine the sediment chronology, reflecting the changing trend in the above parameters, while nutrients in the sediment and seawater were also measured to assess their influence on SOC pools. The results of this study may improve the understanding of the sources of SOC and its sequestration capacity in the PRE, as well as the role of SOC sub-pools in the C sequestration of subtropical fluvial and estuarine ecosystems.

## 2. Materials and methods

### 2.1. Sample collection

Sediment cores were collected at four sites in July of 2013 using a multi-corer (Fig. 1). Sites 1, 2, and 3 (e.g. S1, S2, and S3) were chiefly affected by the nutrient input from the river, while Site 4 (S4) was located in the adjacent coastal area beyond the PRE, with less nutrient input and anthropogenic effects (Ma et al., 2009; Zhang et al., 2009a). Furthermore, S1 was also influenced by the activity of sand excavations. S2 and S3 were within the wetland area. Reclamation was mainly performed in the wetland area, and may affect S2 and S3 indirectly by changing the local hydrological conditions and sediment transport dynamics. The water depths in S1, S2, S3, and S4 were 11.0 m, 5.0 m, 5.8 m, and 29.0 m, respectively. The mean water velocity was 0.44 ± 0.13 m/s, and it was higher in S1 relative to the other three sites. The length of the sediment cores in S1, S2, S3, and S4 were 75 cm, 100 cm, 110 cm, and 75 cm, respectively. Sediment cores were sliced at 5-cm intervals, and divided into two sub-samples. The two sub-samples were stored at 4 °C and −20 °C, respectively, before analysis. The overlying seawater was also sampled simultaneously. Each water sample was immediately filtered through Whatman GF/F filters (0.7 μm pore size) for measuring dissolved inorganic nitrogen (DIN = nitrate + nitrite + ammonium) and dissolved inorganic phosphate (DIP). The DIN and DIP were measured by standard colorimetric techniques using a CANY 722s spectrophotometer.

### 2.2. Laboratory analyses

Seawater nitrate, nitrite, ammonium, and DIP were determined using zinc-cadmium reduction, hydrochloride naphthodiamide, hypobromite oxidation, and phosphorus molybdenum blue spectrophotometry, respectively (General Administration of Quality Supervision, 2008).

The sediment samples that stored at 4 °C were used for analysis of bulk density (BD), WSOC, SEC, MBC, and ROC. BD was determined after drying at 105 °C for 24 h. WSOC and SEC were both extracted from 10 g moist sediment samples with additions of 30 mL deionized water (Bijay-Singh and Whitchead, 1988) and 30 mL of 0.5 M $K_2SO_4$ (Fang et al., 2005; Liu et al., 2016), respectively. After shaking for 30 min, the mixtures were centrifuged for 10 min and then filtered through GF/F filters (Whatman, 450 °C, 3 h) into a pre-combusted Apragaz bottle (450 °C, 3 h) for analysis of total OC. MBC was determined using the chloroform fumigation–extraction method (Liu et al., 2017; Vance et al., 1987; Yang et al., 2013). This method involved fumigation of 10 g of moist sediment in a chloroform atmosphere for 24 h, and then rapid extraction with 0.5 M $K_2SO_4$ as the SEC extraction method. Sediment MBC was calculated according to the equation: MBC = Ec/0.38, where Ec is the OC content difference between the fumigation-treated and untreated sediments (Yang et al., 2013). The untreated sediment filtrate was the SEC. A Shimadzu TOC analyser ($TOC\text{-}V_{CPH}$) for OC analysis was utilized for all of the filtrates. Potassium hydrogen phthalate was used as the reference, and the precision of analysis was <2%. Additionally, the ROC was measured by acid hydrolysis

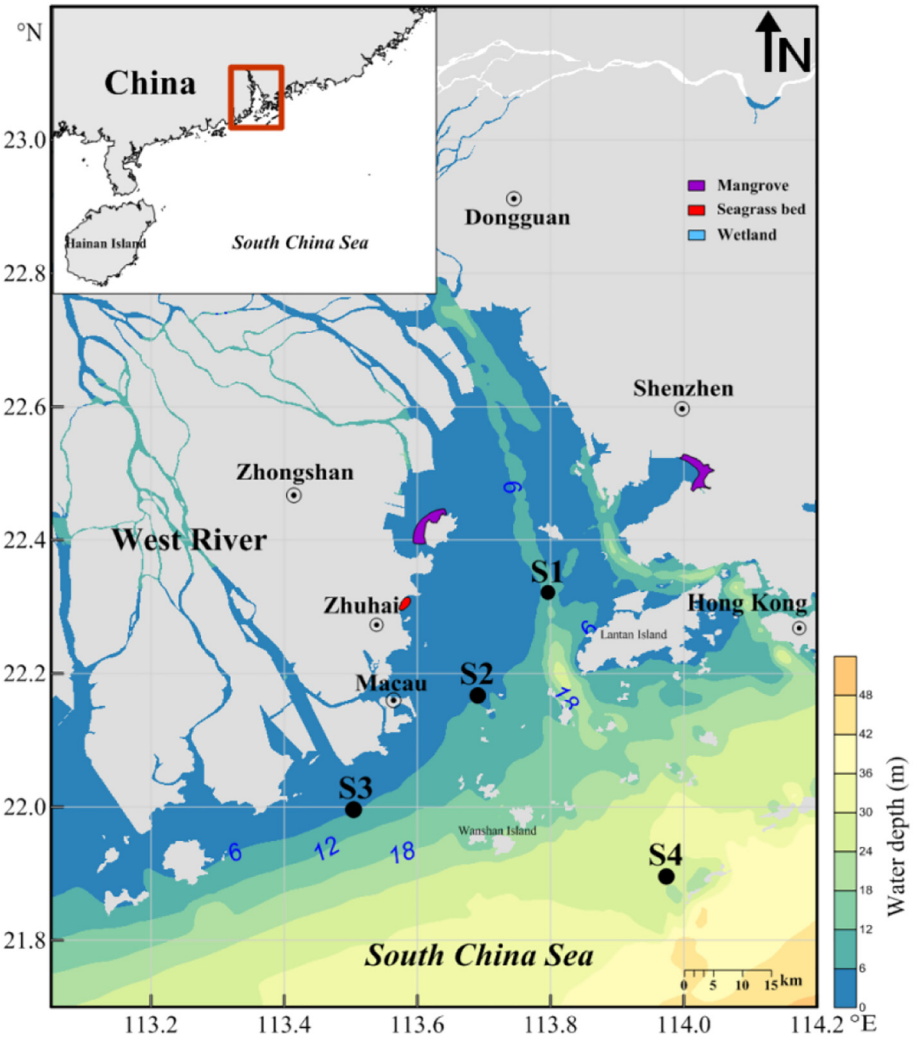


**Fig. 1.** Sampling sites of sediment cores in the Pearl River Estuary and the adjacent coastal area.

(Cheng et al., 2007; Collins et al., 2000; Dodla et al., 2012). Sediment samples with 6 mol/L HCl (1:10) were added to digestion tubes and incubated for 16 h. After cooling to room temperature, samples were centrifuged and then the overlying solution was discarded. The residual samples, taken as the recalcitrant pool, were then washed with deionized water and oven-dried at 40 °C. After drying, the residual samples were weighed and analysed for OC analysis by a Vario EL-III CHN analyser. Certified Reference Material of GBW07301a stream sediment was used as the reference, and the precision of analysis was <0.2%.

Frozen sediment samples were used for analysis of $\delta^{13}C$ and SOC. The subsamples were freeze-dried, and then ground and homogenized with a mortar and pestle. The sediment samples were acidified with 1 mol/L HCl overnight at room temperature to remove carbonate, and this was followed by washing with distilled water and drying at 40 °C in an oven. SOC was determined using an elemental analyser (Vario EL-III CHN analyser). $\delta^{13}C$ was analysed via an isotope ratio mass spectrometer (Thermo Scientific MAT 253). All isotopic data were expressed in the conventional delta notation ($\delta^{13}C$) relative to Peedee Belemnite. The precision of duplicate analyses was <0.2‰.

A sample of 0.1 g was weighed and placed in a 50 mL colorimetric tube. A 25 mL potassium persulfate-sodium hydroxide mixture solution (NaOH: $K_2S_2O_8$ = 0.15 mol/L: 0.15 mol/L) was added to the tube. The tube was then autoclaved at 124 °C for 1 h. After natural cooling, during which sediment particles settled down, the supernatant was determined for total nitrogen (TN) through sulfanilamide naphthylethylenediamine spectrophotometry and for total phosphorus (TP) through phosphorus molybdate blue spectrophotometry (Li et al., 2007).

Sediment age based on the $^{210}Pb_{ex}$ dating techniques was only derived from the core sediment sample in S4, which was less influenced by human disturbance. The sedimentation rate was calculated using excess $^{210}Pb$, which was determined by alpha-spectrometry (via $^{210}Po$ as well as the added tracer of $^{209}Po$) at the Radioactivity Monitoring Laboratory of South China Sea Environment Monitoring Center, State Oceanic Administration. Radiometric dates were calculated using the constant initial $^{210}Pb$ concentration model (Godoy et al., 1998; Goldberg, 1963).

The stock of SOC, WSOC, SEC, MBC, and ROC of the sediment cores were estimated following the calculation of Howard et al. (2014) (Table 1).

### 2.3. Statistical analyses

In this study, a two end-member mixing model was used to calculate the relative contributions of SOC sources with consideration of terrestrial organic matter and aquatic organic matter (Zhang et al., 2009b).

$$\delta^{13}C_{SOC} = f_1 * \delta^{13}C_T + f_2 * \delta^{13}C_a.$$

$\delta^{13}C_{SOC}$, $\delta^{13}C_T$, and $\delta^{13}C_a$ represent the carbon isotopic compositions of the SOC, terrestrial, and aquatic OC, respectively. The proportion of terrestrial OC was $f_1$ and that of aquatic OC was $f_2$, where $f_1 + f_2 = 1$.

**Table 1**
Process of calculating the stock of sediment organic carbon (SOC), water-soluble organic carbon (WSOC), salt-extractable carbon (SEC), microbial biomass carbon (MBC), and recalcitrant organic carbon (ROC).

| SOC/WSOC/SEC/MBC/ROC (%) | Dry bulk density ($g/cm^3$) | Thickness interval of core section (cm) | Sediment carbon density ($g/cm^3$) | Amount carbon in core section ($g/cm^2$) | Core carbon content ($g/cm^2$) | Total core carbon (Mg C $ha^{-1}$) |
|---|---|---|---|---|---|---|
| A | B | C | D = A/100 * B | E = D * C | F = E1 + E2 + E3… | G = F * (1 Mg/1,000,000 g) * (100,000,000 $cm^2$/1 ha) |

The previous study has shown that the $\delta^{13}C$ of the terrestrial organic matter imported by the Pearl River was −25‰ (Yu et al., 2010), and that the $\delta^{13}C$ of the autochthonous sources (e.g. phytoplankton) was −20.9‰ (Chen et al., 2008). The relative contribution of terrigenous OC to SOC in this study was calculated according to the $\delta^{13}C$ value of the two potential SOC sources (Chen et al., 2008; Yu et al., 2010). Pearson's correlation was used to assess the correlations among SOC, WSOC, SEC, MBC, ROC, WSOC/SOC, SEC/SOC, MBC/SOC, ROC/SOC, $\delta^{13}C$, BD, TN, and TP.

## 3. Results

### 3.1. Seawater nutrients

Nitrate was the main form of DIN in S1, S2, and S3, while ammonium was the main form in S4. The concentrations of ammonium, nitrite, nitrate, DIN, and DIP in S1, S2, and S3 were all higher than in S4 (Table 2). In particular, nitrate concentration in S1, S2, and S3 were about 42.9, 92.6, and 55.1 times that in S4, respectively, while ammonium concentration in S1, S2, and S3 were about 1.7, 3.4, and 2.6 times that in S4, respectively. DIN concentration in S1, S2, and S3 were about 10.8, 22.1, and 13.2 times that in S4, respectively.

### 3.2. Sediment physiochemical parameters

Sand composition in S4 was significantly lower than in S1, S2, and S3 (Table 3). Furthermore, the combined composition of sand and silt exhibited the trend: S1 > S2 > S4 > S3. No obvious trend was observed for the sediment water content. The ratio of C/N in S1 was significantly higher than in the other three sites.

The depth profile of $^{210}Pb$ activity in the sediment core of S4 was shown in Fig. 2. The In($^{210}Pb_{ex}$) activity depths can be fit reasonably to simple linear equations with a slope of −0.0359 ($r^2 = 0.9157$), corresponding to sedimentation rates of about 1.149 cm/year. The $^{210}Pb$-derived sedimentation rates indicated that the sediment core covered approximately 52 years of sediment deposition.

### 3.3. Sediment organic carbon and its fraction

Vertical profiles of SOC and its fraction were depicted in Fig. 3. SOC, WSOC, SEC, MBC, and ROC concentrations ranged from 4.37 to 10.4 g/kg, 0.569 to 1.39 g/kg, 0.608 to 1.86 g/kg, 0.522 to 1.53 g/kg, and 1.59 to 5.42 g/kg, respectively, with their corresponding mean values as 7.20 ± 1.43 g/kg, 0.893 ± 0.180 g/kg, 1.11 ± 0.264 g/kg, 0.896 ± 0.228 g/kg, and 3.71 ± 1.01 g/kg, respectively. SOC in S2 and S3 were all higher than that in the same sediment layer in S1 and S4. SOC in S2 and S4 exhibited a decreasing trend from the surface layer, while it fluctuated more in S1. The minimum SOC concentration was observed in S1. Similarly, ROC concentration in S2 and S3 were also all higher than that in the same sediment layer in S1 and S4. ROC remained relatively stable in S2, S3, and S4, but it was more volatile in the upper portion of the sediment core in S1. No apparent trend was observed for WSOC and SEC in these sites. MBC concentration was higher in S3 and S4 than in S1 and S2. It exhibited a decreasing trend in the upper portions of the sediment core and remained relatively stable in the lower portions of the sediment core.

WSOC/SOC, SEC/SOC, MBC/SOC, and ROC/SOC ranged from 7.4% to 20.3%, 6.6% to 28.1%, 7.7% to 20.5%, and 30.8 to 65.3%, respectively, with the corresponding average value as 13.0% ± 3.2%, 16.1% ± 4.9%, 12.6% ± 3.1%, and 51.2% ± 9.1%, respectively (Fig. 4). MBC/SOC decreased sharply in the upper 20 cm of sediment, and then remained relatively stable in the deeper sediment layers, while ROC/SOC exhibited an increasing trend with depth. Higher WSOC/SOC, SEC/SOC, and MBC/SOC were observed within the same sediment layers in S4 compared to the other three sediment cores, while lower ROC/SOC was observed in S1.

### 3.4. $\delta^{13}C$ of sediment organic carbon and its source

The $\delta^{13}C$ of sediment ranged from −24.1‰ to −20.9‰, averaging −22.3‰ ± 0.9‰ (Fig.5a), while the relative contribution of terrigenous source ranged between 0.4% and 78.0%, with the mean value as 33.9% ± 23.0% (Fig.5b). The vertical profile of sediment $\delta^{13}C$ revealed an increasing trend with depth, and it fluctuated the most in S1. A similar trend was observed for the vertical distribution of the relative contribution of terrigenous source. The sediment $\delta^{13}C$ was all higher in S4 than in the other stations within the same layer, while it exhibited a contrasting trend for the relative contribution of terrigenous source.

### 3.5. Relationships between parameters

Relationships between parameters were also analysed (Table 4). A significant positive relationship was observed between SOC and WSOC, MBC and ROC, while the opposite was found between SOC and WSOC/SOC, SEC/SOC and MBC/SEC. There was a significant positive relationship between SEC and MBC, SEC/SOC, and MBC/SOC. $\delta^{13}C$ exhibited a markedly positive relationship with WSOC/SOC and SEC/SOC, while showing a significant negative relationship with SOC, MBC, and ROC. A significant negative relationship was also found between BD and SEC, MBC, SEC/SOC and MBC/SOC. WSOC and SEC were positively correlated with MBC. TN had a significant positive relationship with SOC, WSOC, MBC, ROC, and ROC/SOC, while had a negative relationship with WSOC/SOC, SEC/SOC, and $\delta^{13}C$. A significant positive correlation

**Table 2**
Seawater nutrients in the Pearl River Estuary.

| Parameters | Ammonium (mg/L) | Nitrite (mg/L) | Nitrate (mg/L) | DIN (mg/L) | DIP (mg/L) |
|---|---|---|---|---|---|
| S1 | 0.038 | 0.060 | 0.300 | 0.398 | 0.017 |
| S2 | 0.075 | 0.095 | 0.648 | 0.818 | 0.028 |
| S3 | 0.058 | 0.046 | 0.386 | 0.489 | 0.015 |
| S4 | 0.022 | 0.008 | 0.007 | 0.037 | 0.013 |

**Table 3**
Sediment grain size, water content and C/N.

| Sites | S1 | S2 | S3 | S4 |
|---|---|---|---|---|
| Sand (%) | 28.7 ± 3.9 | 34.5 ± 7.7 | 14.1 ± 5.6 | 9.7 ± 5.0 |
| Silt (%) | 67.8 ± 2.5 | 61.7 ± 6.3 | 75.8 ± 4.7 | 81.9 ± 5.7 |
| Clay (%) | 3.5 ± 3.6 | 3.9 ± 2.0 | 10.2 ± 3.2 | 8.5 ± 4.3 |
| Water content (%) | 0.43 ± 0.02 | 0.40 ± 0.02 | 0.44 ± 0.03 | 0.47 ± 0.03 |
| C/N | 27.37 ± 6.80 | 17.76 ± 1.69 | 14.37 ± 1.50 | 17.20 ± 2.29 |

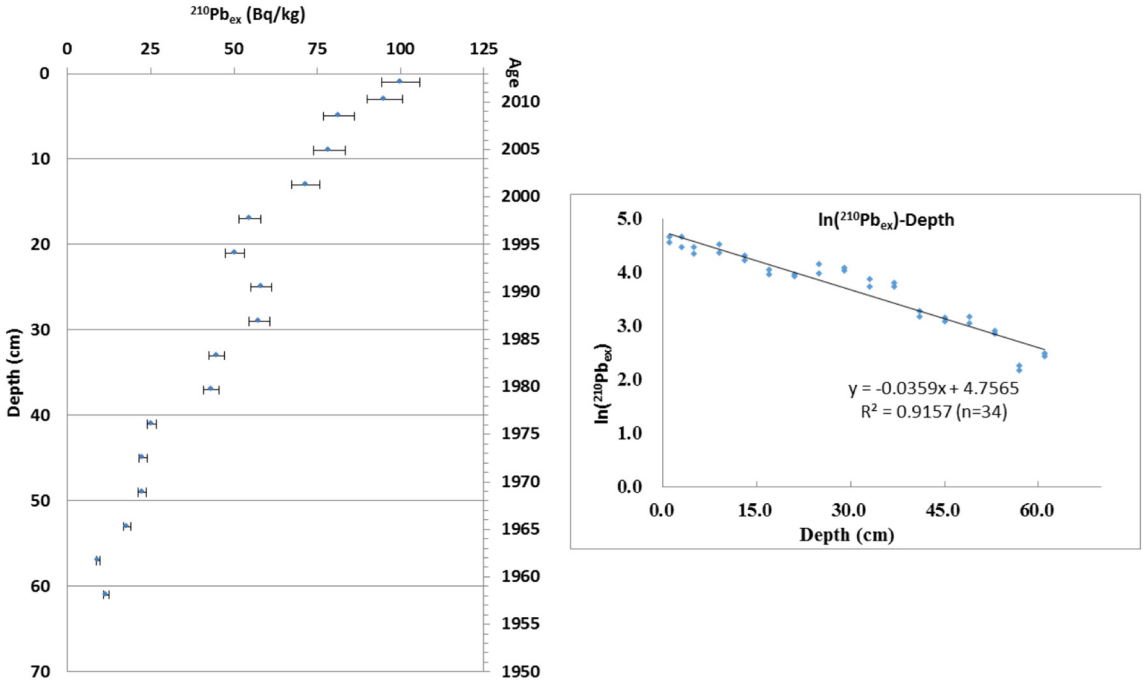


**Fig. 2.** Depth profiles of $^{210}$Pb activity in the sediment core of S4.

was found between TP and SOC, ROC, ROC/SOC, while the converse was observed between TP and WSOC/SOC, SEC/SOC, MBC/SOC.

### 3.6. Sediment organic carbon stock

Vertical profiles of amount carbon in each core section (5 cm) were shown in Fig. 6. The amount carbon in each core section ranged from 1.1 to 5.2 Mg C ha$^{-1}$, averaging 2.4 ± 0.9 Mg C ha$^{-1}$. It was lower in S4 than in other stations within the same core section. The stock of WSOC, SEC, MBC, ROC, and SOC of the 75-cm sediment core ranged from 3.09 to 4.84 Mg C ha$^{-1}$, 3.98 to 6.26 Mg C ha$^{-1}$, 3.38 to 5.37 Mg C ha$^{-1}$, 10.01 to 23.38 Mg C ha$^{-1}$, and 19.60 to 44.33 Mg C ha$^{-1}$, respectively, with the mean value of 4.09 ± 0.77 Mg C ha$^{-1}$, 5.38 ± 0.98 Mg C ha$^{-1}$, 4.04 ± 0.90 Mg C ha$^{-1}$, 16.98 ± 7.31 Mg C ha$^{-1}$, and 34.03 ± 11.28 Mg C ha$^{-1}$, respectively. SOC stock exhibited a trend in the order: S2 > S3 > S1 > S4 (Fig. 7).

## 4. Discussion

The results presented here indicated that the sediment dating using $^{210}$Pb allowed an analysis of the urbanization and industrialization in the PRE in recent decades (since 1961), and the sedimentation rate was also similar to the ranges observed in the previous study (Ye et al., 2012). With the rapid urbanization and industrial development of the PRE in the past decades, human activities have induced larger nutrient inputs, wetland habitat loss, hydrological change and so on. For example, seawater nutrient concentrations in the PRE exhibited a continuous increasing trend, with mean values of about 0.7 mg/L (Huang et al., 2003), 1.06 mg/L (Ma et al., 2009) and 1.33 mg/L (this study) for 1998, 2006, and 2013, respectively. Particulate organic carbon (POC) exhibited a similar trend as well. The POC concentration was 245 mg/L (Chen et al., 1987), 541.9 mg/L (Liu et al., 2012), and 676 mg/L (Guo et al., 2016) in 1987, 2010, and 2013, respectively. Higher SOC, $\delta^{13}$C, and the calculated relative contribution of terrigenous organic matter in the upper layers of sediment cores also indicated more terrestrial OC had been delivered to the PRE in recent decades (Fig. S1 in supporting material) (Jia and Peng, 2003; Zhang et al., 2009b).

### 4.1. Source and fraction of sediment organic carbon

The present study revealed that higher sediment $\delta^{13}$C in the outer estuary indicated a higher contribution of marine organic matter. Zhang et al. (2010) also found that organic matter in the PRE was mainly derived from mixed sources of terrestrial and aquatic origins, whereas the organic matter in the adjacent shelves was predominantly algal-derived. Furthermore, higher concentration of SOC was observed in the northwestern part of the estuary, which may result from greater deposition of terrestrial OC in this region induced by the Coriolis effect in the PRE (He et al., 2010; Zhang et al., 2009b). Interestingly, the lowest SOC content was found in S1 with more fluctuation in the trend of vertical distribution. This was dominantly associated with sand excavation. Since the middle of the 1980s, a large-scale of sand excavation in the PRE has led to a great alteration of fluvial process and the hydrological conditions (Han et al., 2005; Tang et al., 2011). During sand excavation, larger materials descend to the seabed more rapidly than finer grained material (Phua, 2002), and coarse sediments can induce lower OC concentration (Ricart et al., 2017). Furthermore, sand excavation also enhances the contact of the sediment and water with high dissolved oxygen (DO), thereby increasing the instability and degradation of sediment organic matter.

SOC is primarily divided into LOC (e.g. WSOC, SEC, and MBC) and ROC, and it affects the carbon transformation and biogeochemical cycle (Cheng et al., 2007; Dodla et al., 2012; Fang et al., 2005; Hicks, 2007; Liu et al., 2016; Yang et al., 2013). The SEC content in our study (0.608–1.86 g/kg) was relatively lower than in the coastal wetland soils of the Mississippi River (0.900–2.80 g/kg) (Dodla et al., 2012), but was higher than in seagrass beds (0.212–0.292 g/kg) (Liu et al., 2016). The concentration of MBC (0.522–1.53 g/kg) in our study was also significantly higher than in seagrass bed (0.0573–0.694 g/kg) (Liu et al., 2016) and in the coastal wetland of eastern China (Yang et al., 2013). Significant positive relationships between SOC and WSOC, MBC, and ROC were observed, suggesting they have similar sources. A positive correlation between SOC and LOC fraction was also observed in the coastal wetland soils of the Mississippi River deltaic plain (Dodla et al., 2012) and forest soils (Wang and Wang, 2007). LOC fraction increased with increasing amounts of SOC, and WSOC and MBC could be used for assessing the lability of wetland SOC (Dodla et al.,

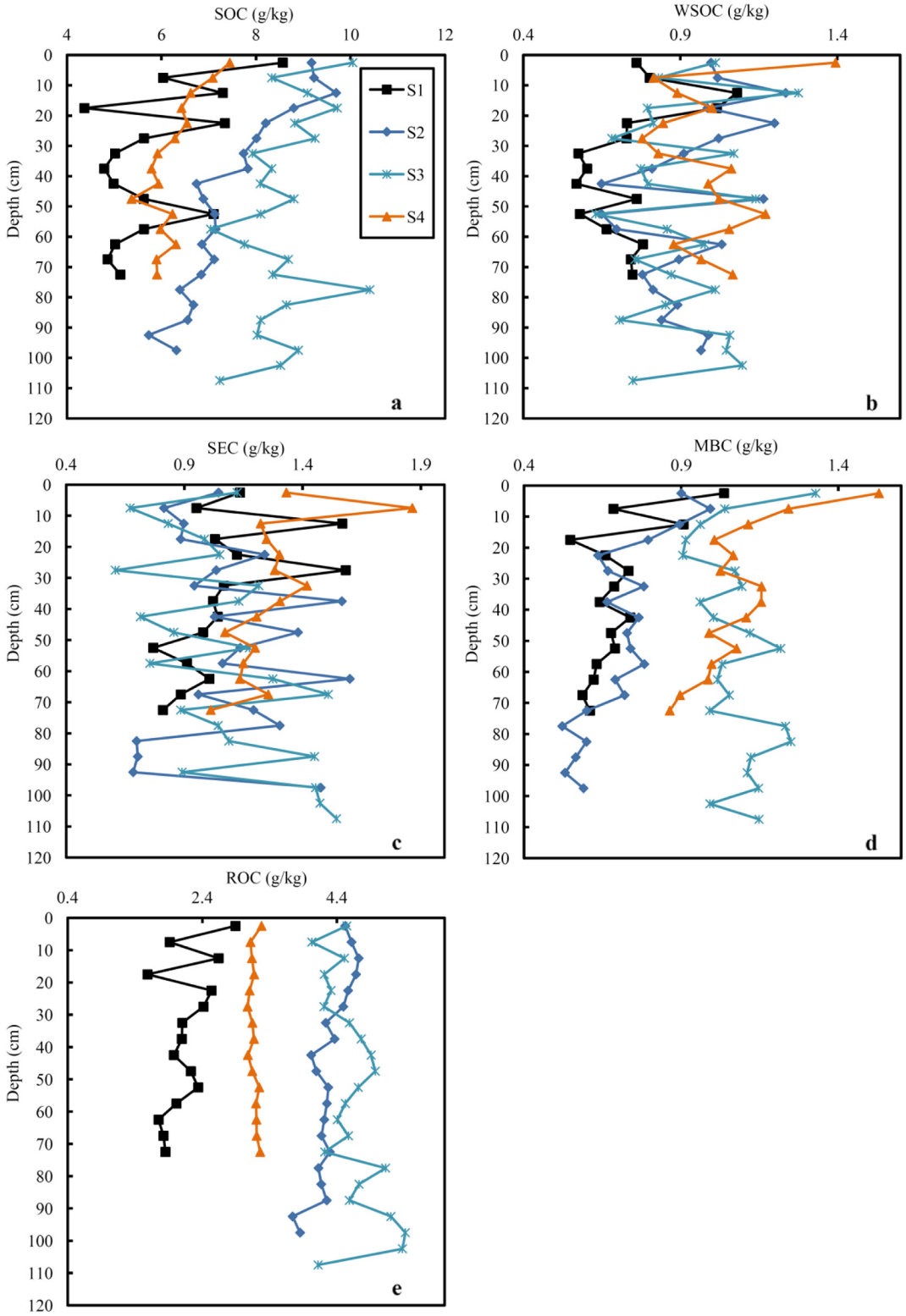


**Fig. 3.** Vertical profiles of SOC (a), WSOC (b), SEC (c), MBC (d), and ROC content (e) in the Pearl River Estuary and the adjacent coastal area.

2012). The positive relationship observed between WSOC and MBC suggested WSOC was the most important substrate for sediment microbes, microbial metabolites (e.g. polysaccharide mucilage) in turn contribute substantially to sediment WSOC concentration (Yang et al., 2013). Higher SEC, MBC, and their proportion to SOC in lower BD sediments was associated with the depression of C mineralization in compacted soils (Neve and Hofman, 2000; Wang et al., 2009). A significant negative relationship between $\delta^{13}C$ and SOC, MBC, and ROC indicated that they were influenced by the input of terrestrial organic matter and hydrodynamic conditions. Similarly, a significant positive correlation between sediment nutrients (TN and TP) and ROC, ROC/SOC, further suggested that terrestrial plants rich in lignin and cellulose contributed to ROC in the PRE. The mean ratios of WSOC, SEC, MBC, and ROC to SOC were 13.0%, 16.1%, 12.6%, and 51.2%, respectively, indicating that the majority

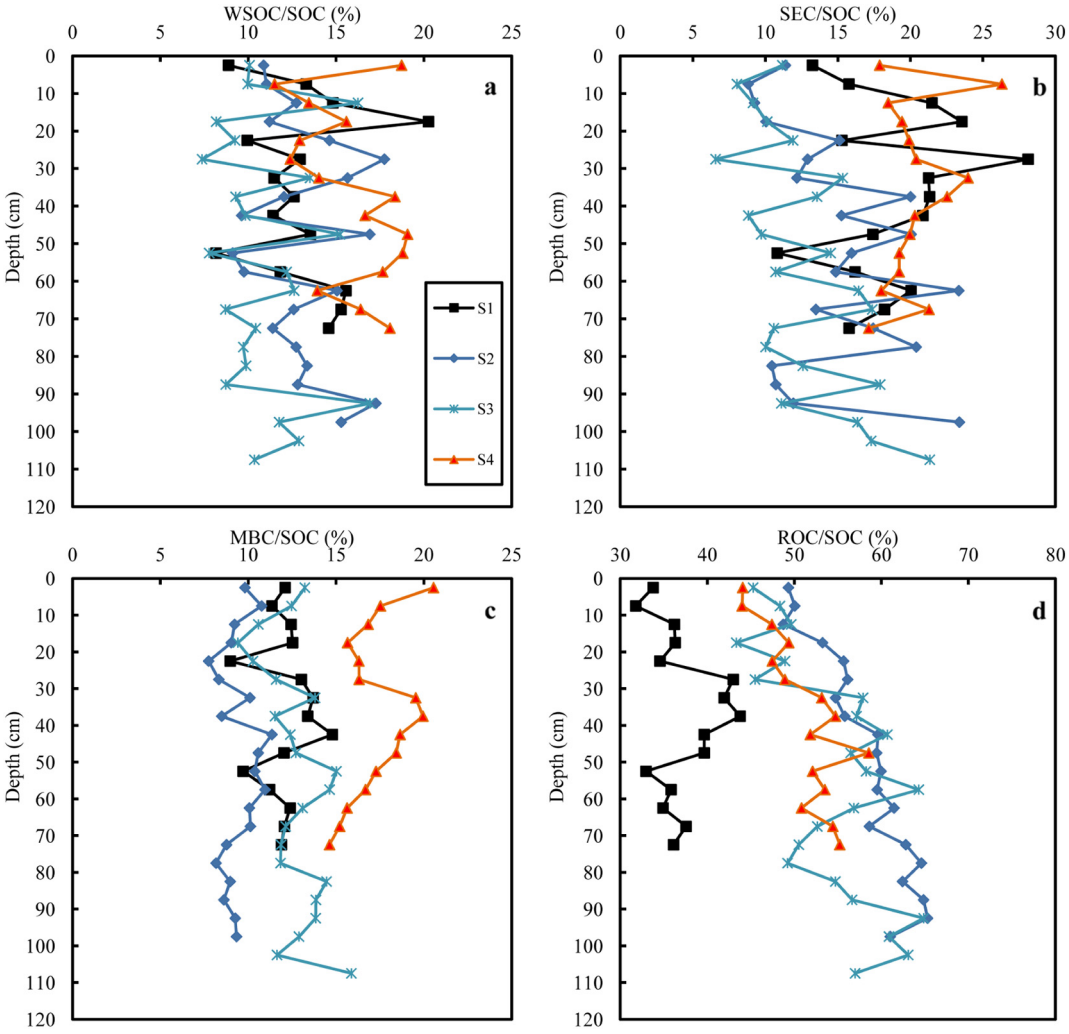


**Fig. 4.** Vertical profiles of the WSOC/SOC (a), SEC/SOC (b), MBC/SOC (c), and ROC/SOC (d) in the Pearl River Estuary and the adjacent coastal area.

of SOC in the PRE was relatively recalcitrant. The ROC content tended to be more stable in the whole core sediment than the other labile carbon pool. Hu et al. (2006b) suggested that microbes within the sediments dominantly utilized a labile pool of organic matter derived from algae for their growth in the PRE. This might explain why there was a seaward increasing trend in MBC content. MBC and MBC/SOC both exhibited a declining trend in the upper layers of sediment core and remained relatively stable in the lower layers. Similarly, the MBC/SOC value was

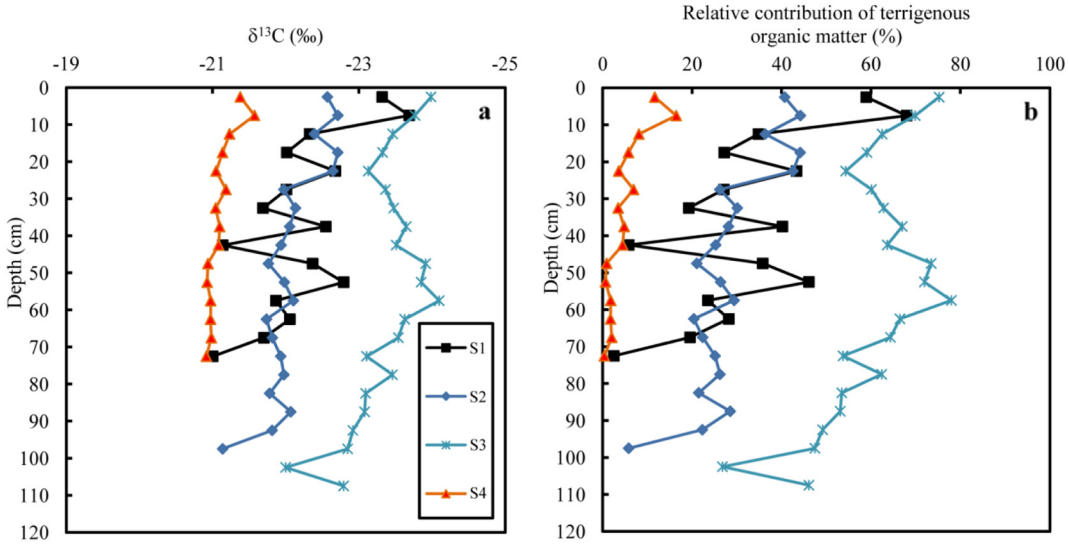


**Fig. 5.** Vertical profiles of the $\delta^{13}C$ (a) in the sediment and the relative contribution of terrigenous organic matter (b) in the Pearl River Estuary and the adjacent coastal area.

**Table 4**
The Pearson's correlation coefficients between parameters (n = 72).

| parameters | SOC | WSOC | SEC | MBC | ROC | WSOC/SOC | SEC/SOC | MBC/SOC | ROC/SOC | $\delta^{13}C$ | BD | TN | TP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SOC | 1.00 | 0.25* | −0.07 | 0.48** | 0.80** | −0.49** | −0.68** | −0.31** | 0.20 | −0.50** | 0.15 | 0.83** | 0.61** |
| WSOC | 0.25* | 1.00 | −0.05 | 0.28* | 0.31** | 0.70** | −0.19 | 0.10 | 0.23* | 0.09 | −0.12 | 0.30* | 0.16 |
| SEC | −0.07 | −0.05 | 1.00 | 0.25* | −0.00 | −0.01 | 0.76** | 0.32** | 0.08 | 0.12 | −0.30** | −0.04 | −0.20 |
| MBC | 0.48** | 0.28* | 0.25* | 1.00 | 0.36** | −0.08 | −0.10 | 0.68** | 0.08 | −0.39** | −0.51** | 0.57** | −0.04 |
| ROC | 0.80** | 0.31** | −0.00 | 0.36** | 1.00 | −0.31** | −0.53** | −0.28* | 0.75** | −0.26* | 0.21 | 0.81** | 0.67** |
| WSOC/SOC | −0.49** | 0.70** | −0.01 | −0.08 | −0.31** | 1.00 | 0.33** | 0.34** | 0.03 | 0.42** | −0.23 | −0.32** | −0.31** |
| SEC/SOC | −0.68** | −0.19 | 0.76** | −0.10 | −0.53** | 0.33** | 1.00 | 0.45** | −0.13 | 0.40** | −0.32** | −0.55** | −0.53** |
| MBC/SOC | −0.31** | 0.10 | 0.32** | 0.68** | −0.28* | 0.34** | 0.45** | 1.00 | −0.09 | 0.04 | −0.69** | −0.08 | −0.53** |
| ROC/SOC | 0.20 | 0.23* | 0.08 | 0.08 | 0.75** | 0.03 | −0.13 | −0.09 | 1.00 | 0.19 | 0.14 | 0.38** | 0.42** |
| $\delta^{13}C$ | −0.50** | 0.09 | 0.12 | −0.39** | −0.26* | 0.42** | 0.40** | 0.04 | 0.17 | 1.00 | −0.03 | −0.46** | −0.00 |
| BD | 0.15 | −0.12 | −0.30** | −0.51** | 0.21 | −0.23 | −0.32** | −0.69** | 0.14 | −0.03 | 1.00 | −0.00 | 0.47** |
| TN | 0.83** | 0.30* | −0.04 | 0.57** | 0.81** | −0.32** | −0.55** | −0.08 | 0.38** | −0.46** | −0.00 | 1.00 | 0.58** |
| TP | 0.61** | 0.16 | −0.20 | −0.04 | 0.67** | −0.31** | −0.53** | −0.53** | 0.42** | −0.00 | 0.47** | 0.58** | 1.00 |

* $p < 0.05$.
** $p < 0.01$.

found to decrease in the soil profile with the depth (Lavahum et al., 1996; Susyan et al., 2009). The increased seawater nutrients and POC in the PRE in recent decades might enhanced OC available for microbial use, thereby induced higher MBC in the upper sediment layers. Furthermore, ROC/SOC increased with depth. The portion of humified, less easily available soil organic matter also increased as a function of depth (Lavahum et al., 1996). ROC in S2 and S3 were both higher than in S4, which was associated with the higher exportation of terrestrial plants rich in lignin and cellulose to S2 and S3 (Zhang et al., 2010). However, the lowest ROC and ROC/SOC were both observed in S1. This was also chiefly due to sand excavation. Furthermore, a higher proportion of LOC (e.g. WSOC/SOC, SEC/SOC, and MBC/SOC) was observed in the outer estuary than in the inner estuary, indicating a higher SOC turnover rate in the outer estuary (Liu et al., 2016). Higher available C and microbial biomass were supported in per unit SOC in the outer estuary (Yang et al., 2013). This was consistent with a higher autochthonous contribution (e.g. phytoplankton), as phytoplankton was rich in labile compositions like carbohydrates, amino acids, sugars, and low-molecular-weight organic acids (Hardison et al., 2013).

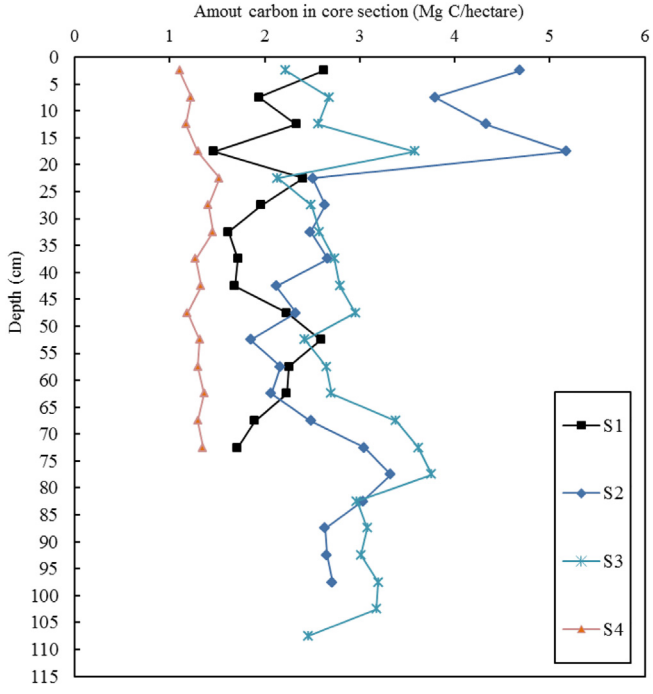


**Fig. 6.** Vertical profile of amount carbon in core section in the Pearl River Estuary.

### 4.2. Sediment organic carbon sequestration

The estimated mean SOC stock of the top 75 cm of sediment core in the PRE was 34.0 Mg C $ha^{-1}$. If this value is multiplied two times (equaling to the top 1.5 m), it was still remarkably less than in river deltas of Moreton Bay, Australia (175–504 Mg C $ha^{-1}$, the top 1.5 m) (Hayes et al., 2017) and the riverine wetlands within La Encrucijada Biosphere Reserve, Mexico (e.g. mangrove: 505.9 ± 72.6 Mg C $ha^{-1}$; Marsh: 298.3 ± 39.0 Mg C $ha^{-1}$; peat seamp forest: 614.6 ± 85.7 Mg C $ha^{-1}$) (Adame et al., 2015). Higher SOC stock was observed in the inner estuary, which was associated with greater C sequestration rates in the upper compared to the lower estuary (Adame et al., 2015). Similarly, sites in river deltas exhibited larger SOC stock than those in non-riverine settings, because of higher sediment accretion and nutrients influx to these systems from riverine sources (Hayes et al., 2017). Furthermore, sand excavation in S1 might weaken carbon sequestration. Therefore, sand excavation activity in the PRE should be reduced or prohibited to maintain the carbon sequestration capacity in estuarine ecosystem. From the increased sea reclamation area (27,286.68 ha) between 1973 and 2015 (Zhang et al., 2016) and the mean SOC stock of S2 and S3 in the wetland area (42.92 Mg C $ha^{-1}$), the overall reduction of SOC stock (the upper 75 cm sediment) of the PRE due to sea reclamation was 1,171,159.6 Mg C. It is critical for the local government to adjust economic development plans to minimize sea reclamation activities to preserve the carbon sinks in the PRE.

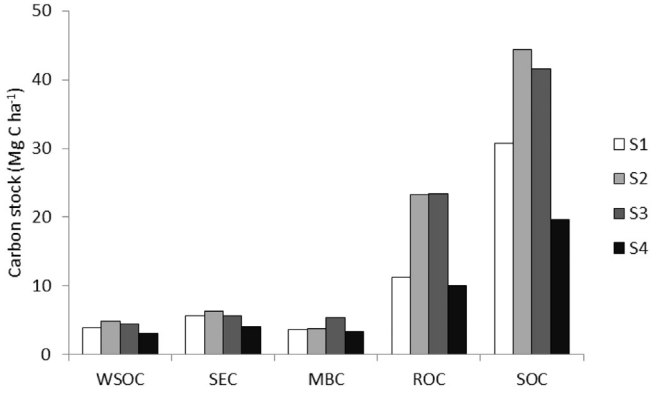


**Fig. 7.** The stock of WSOC, SEC, MBC, ROC, and SOC of the 75-cm sediment core in the Pearl River Estuary.

## 5. Conclusion

In summary, ROC was the main fraction of SOC. The increased seawater nutrients and POC in recent decades might cause higher concentrations of SOC and MBC in the upper sediments of the PRE. Larger terrigenous organic carbon contribution in the inner estuary enhanced SOC, ROC, and SOC stock, while higher autochthonous contribution in the outer estuary stimulated the $\delta^{13}C$ and the proportion of LOC fraction to SOC (e.g. WSOC/SOC, SEC/SOC, and MBC/SOC). Sand excavation might decrease SOC, ROC, ROC/SOC, and SOC stock. Considering the importance of the estuarine ecosystem, additional investigations of LOC and ROC pools in the estuary along global coastlines should be conducted to determine the overall carbon sequestration capacity.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.05.389.

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