Science of the Total Environment 783 (2021) 146899

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Influence of sedimentary organic matter sources on the distribution characteristics and preservation status of organic carbon, nitrogen, phosphorus, and biogenic silica in the Daya Bay, northern South China Sea

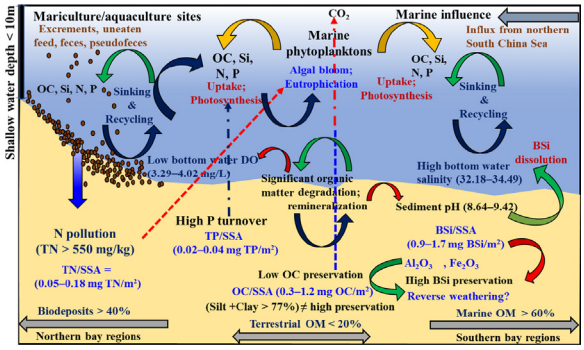
Solomon Felix Dan [a,1], Shengyong Li [b,1], Bin Yang [a,*], Dongyang Cui [c], Zhiming Ning [d], Haifang Huang [a], Jiaodi Zhou [a], Jian Yang [e]

[a] Guangxi Key Laboratory of Marine Disaster in the Beibu Gulf, Beibu Gulf University, Qinzhou 535011, China
[b] South China Sea Environmental Monitoring Center, State Oceanic Administration, Guangzhou 510300, China
[c] Key Laboratory of Urban Land Resources Monitoring and Simulation, Ministry of Natural Resources, Shenzhen 518000, China
[d] Guangxi Laboratory on the Study of Coral Reefs in the South China Sea, Guangxi University, Nanning 530004, China
[e] Research Center for Coastal Environment Engineering Technology of Shandong Province, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

HIGHLIGHTS

- Marine culture biodeposits constituted 5–55% of sedimentary OM in the Daya Bay
- Sedimentary OM influenced the distribution characteristics of biogenic elements
- N contamination in sediments was more related with fish aquaculture activities
- OC has undergone significant remineralization, and TP has a high turnover rate
- High BSi production and loadings are controlled by complex biogeochemical processes

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 December 2020
Received in revised form 28 March 2021
Accepted 29 March 2021
Available online 5 April 2021

Editor: Ashantha Goonetilleke

Keywords:
Sedimentary organic matter
Biogenic elements
Influencing factors

ABSTRACT

Surface sediment samples were collected from Daya Bay in October 2018, and analyzed for total organic carbon (OC), total nitrogen (TN) and their stable isotopes ($\delta^{13}C$ and $\delta^{15}N$), total phosphorus (TP), biogenic silica (BSi), sediment textures and specific surface area (SSA). The primary objective was to evaluate the influence of mariculture/aquaculture on the distribution characteristics of organic matter (OM), and preservation status of OC, TN, TP, and BSi in sediments. The average $\delta^{13}C$ and $\delta^{15}N$ values, and OC/TN ratios were −21.27‰, 6.74‰, and 8.90, respectively. Monte Carlo simulation results revealed that mariculture/aquaculture biodeposits accounted for >40% of the buried OM at sites where the breeding rafts and cages are located, whereas marine OM increased gradually to the open sea. Terrestrial OM was generally low accounting for 17% by average. The contents and distribution characteristics of biogenic elements were more influenced by mariculture/aquaculture and primary productivity than sediment textures. Lower OC/SSA (0.3–1.2 mg OC/m^2), TN/SSA (~0.05–0.18 mg TN/m^2), and TP/SSA (0.02–0.04 mg TP/m^2) loadings indicated that increased sequestration of labile OM in a coastal bay could contribute to significant degradation of recalcitrant OM in sediments with significant loss of P relative to

* Corresponding author.
E-mail address: binyang@bbgu.edu.cn (B. Yang).
[1] Solomon Felix Dan and Shengyong Li contributed equally to this study.

https://doi.org/10.1016/j.scitotenv.2021.146899

Preservation status
Daya Bay

OC. Nitrogen contamination in surface sediments was due to increased injection of aquaculture biodeposits, and may pose a detrimental effect on the ecological sustainability of the bay. Higher BSi/SSA loadings (0.9–1.7 mg BSi/m^2) revealed that BSi was more preserved, and that BSi-based proxy could be used for paleo-productivity studies. However, such preservation may induce adverse dissolved silicate limitation in a bay perturbed by eutrophication. Fine-grained sediments (clay and silt) accounted for >77% of the sediment texture types with higher SSA, and while controlling the contents of biogenic elements under given depositional conditions were not the main determining factors of OC, TN, TP, and BSi preservation.

1. Introduction

Global climate change due to anthropogenic carbon (C) emissions, and eutrophication of coastal waters caused by human activities, are significant environmental problems. Coastal bays play crucial roles in the cycling of C through the coupling of terrestrial, marine, and atmospheric C reservoirs. High burial and preservation of C is often associated with coastal zones characterized by high primary productivity, high sedimentation rates of fine-grained particles and organic matter (OM), weak hydrodynamics to limit re-exposure of sedimentary OM to oxygenated conditions among other factors. Nitrogen (N), phosphorus (P), and silicate (Si) are essential biogenic elements that are required for phytoplankton growth, energy transport through the food web, and for optimal functionality of coastal marine ecosystems (Dan et al., 2019a). The fluxes of these nutrients between the water column and sediments can be influenced not only by natural processes, but also by anthropogenic activities involving shellfish mariculture and fish aquaculture activities in shallow coastal bays (Sarà et al., 2004; Pan et al., 2019; Qi et al., 2019). Due to changes in the biogeochemical and physical conditions in aquatic environments, these biogenic elements could be released from surface sediments into the overlying water column in different inorganic or organic forms. Although such release may provide the necessary nutritional needs for the growth of phytoplankton and other living organisms, it may as well increase the eutrophication pressure, frequent harmful algal outbreak, which causes water quality deterioration and lower dissolved oxygen (DO) levels in coastal waters (Smith and Schindler, 2009) partly due to over-enrichment of nutrients in sediments and degradation of sedimentary OM. Thus, it is important to assess the loading and potential risks of biogenic elements in sediments, especially N and P (the limiting nutrients for algal growth) in relation to mariculture/aquaculture activities in coastal bays. Besides, the biodeposits (i.e., feces, pseudofaeces and fish feed residues) can also increase the muddy texture of bottom sediments and accumulation of sedimentary OM (Xia et al., 2019), which may enhance the burial and preservation of C. However, excessive sequestration of OM beyond the ecological balance of a bay can result in rapid microbial conversion of the buried organic carbon (OC) into carbon dioxide (CO_2). This may limit the potential of a coastal bay as an important coastal C sink. Besides, the abundance and preservation of biogenic elements in sediments in recent years could reflect past-environmental changes (especially human perturbations) partly because of the coupling with plankton productivity and/or anthropogenic inputs (Meyers, 2003). Since sedimentary OC predominantly exists in OM, and plays significant role in the biogeochemical cycling of biogenic elements in aquatic environments, therefore, it is important to assess the influence of mariculture/aquaculture activities on the distribution characteristics and preservation status of OC and other biogenic elements, especially in a eutrophic coastal bay. Such study may have important implications on the ecological status of a bay in terms of eutrophication, DO levels, and global C cycling at large.

Due to distinct C and N signatures of OM from various sources, C and N stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) have been widely applied to study the provenance of OM pools, as well as providing an understanding of the influence of anthropogenic activities on marine sedimentary OM in aquatic environments (Gao et al., 2012; Dan et al., 2019b and references therein). Generally, the $\delta^{13}C$ values are more depleted (−30‰ to −24‰, average: −27‰) in terrestrial OM than in marine OM (−22‰ to −19‰; average: −20‰) due to the differences in photosynthetic pathways between terrestrial plants and marine planktons (Ramaswamy et al., 2008; Zhao et al., 2019a). As planktons usually subsist on dissolved nitrate, the $\delta^{15}N$ of marine OM is usually elevated, and ranges from 4‰ to 10‰ (Brandes and Devol, 2002), which is usually higher than $\delta^{15}N$ values of terrestrial derived OM (average: 2‰) in most coastal marine environments (Hu et al., 2006; Zhao et al., 2019a). Besides, $\delta^{15}N$ can also be used to trace the sources of anthropogenic N pollution, and provide an understanding about the variability in the biogeochemical processing of OM in sediments. For example, the $\delta^{15}N$ values for N derived from artificial inorganic fertilizers occur in the range of −2‰ to 4‰, while the $\delta^{15}N$ values in sewage as well as in animal excreta are usually elevated, and could be as high as 10‰ to 20‰ (Cole et al., 2004). Meanwhile, $\delta^{13}C$ can also be used to trace the source of N, especially if the anthropogenic source of N and OC is similar or if total N (TN) contains significant amount of organic N (ON), which is predominantly bound to OC in the marine environment. Thus, apart from $\delta^{13}C$ and $\delta^{15}N$ values, the molar ratio of OC to TN (OC/TN) is often used to indicate the predominant sources of sedimentary OM in coastal marine environments, and mostly because of high cellulose and lignin contents, terrestrial higher plants (especially the C_3 plants) usually contain very low N, with elevated (>20) molar OC/TN ratios (Lamb et al., 2006), while the OC/TN ratio of marine OM is usually within the range of 4 to 10 (Goñi et al., 2013). Nevertheless, the $\delta^{13}C$ and $\delta^{15}N$ values of uneaten feed and faecal materials originating from fish farm and shellfish biodeposits have also been reported to occur in the range of −24‰ to −17‰ and 4.21‰ to 7.32‰, respectively, and the average OC/TN ratios of OM from aquaculture/mariculture biodepositions have been found to vary from 5 to 7 (Sarà et al., 2004; Pan et al., 2019; Xia et al., 2014, 2019 and references therein). Therefore, variability in sedimentary OM signatures can be expected in coastal mariculture/aquaculture bays due to mixed sources of sedimentary OM and other biogeochemical and physical factors that influence OM deposition and preservation in sediments (Dan et al., 2019b).

Daya Bay, a typical semi-enclosed bay, is located in Guangdong Province, southeast coast of China that has been ranked as the largest mariculture/aquaculture hub with the most developed economy in southern China. The ecological environment of the Daya Bay has been previously described by many researchers, and according to research findings, water quality of the bay was good during the early 1980s due to lower input of anthropogenic nutrients, with high productivity and biodiversity (e.g., Xu, 1989; Qing et al., 1996). The main factor impacting on the ecology, especially since the commencement of the Daya Bay Nuclear Power Station operation and mariculture over the past decades, has been anthropogenic activities (Qiu et al., 2005; Wang et al., 2008 and references therein). Nutrient limitation for phytoplankton growth had changed from N to P, and the dominant phytoplankton group has also changed from diatoms to dinoflagellates in recent decades (Wang et al., 2008). Along the South China coast, Daya Bay is one of the bays that is ecologically important for its intensive fish aquaculture and shellfish mariculture (Chen et al., 2015). Marine cage aquaculture production had increased rapidly from 142.5 tons in 1987 to 1600 tons in 2010 (Wang et al., 2014). As an anthropogenic activity, fish aquaculture alone contributes to ~39 and 206 metric tons of P and N, of which ~3% and 7% are released in dissolved phases,

respectively into the Daya Bay water annually (Qi et al., 2019). Meanwhile, study on benthic nutrient fluxes indicated that dissolved inorganic P had the highest flux at the central part of the bay and diffused from the water column to sediments, while sediment was an important source of dissolved inorganic N and Si in the bay (Zhang et al., 2019). Here, it is worth noting that the loss of biogenic elements from marine aquaculture structures to the surrounding water column do not only occur in dissolved forms (Nordvarg and Johansson, 2002), but also in particle phases (Christensen et al., 2000). Thus, increased injection of particulate nutrients through biodeposition may account for sediment contamination, especially in a semi-enclosed bay such as Daya Bay characterized by weaker hydrodynamic conditions and high culture cage density. Harmful algal bloom frequently occurs in the Daya Bay, and partly relates to increase in dissolved N pollution (Wu et al., 2017). Except for the wetlands (Zhao et al., 2019a), past studies have indicated that marine plankton is the dominant source of particulate (Ke et al., 2017) and sedimentary OM (Gao et al., 2008) in the Daya Bay. In other coastal bays, studies have shown that intensive mariculture/aquaculture can significantly change the contents and composition of marine sedimentary OM (Sarà et al., 2004; Pan et al., 2019; Xia et al., 2019; Xu et al., 2020). However, information on the influence of mariculture/aquaculture on sedimentary OM loading in the Daya Bay is scarce. Thus, better constraints are required to widen our understanding of the influence of mariculture/aquaculture activities on marine sedimentary OM pool and the distribution characteristics and preservation status of OC and other biogenic elements in the Daya Bay. This is because the constant supply of fresh and/or labile OM to surface sediments may facilitate the decomposition and/or remineralization of refractory OM, which could have a significant impact on coastal C budgets (Bianchi, 2011; Regnier et al., 2013). Moreover, increasing supply of biogenic elements from sediments during OM decomposition and/or remineralization in addition to external nutrient inputs may further worsen eutrophication pressure with detrimental consequences in the Daya Bay.

Given the ecological importance of the Daya Bay, the objectives of this study were to (1) evaluate the spatial distributions of $\delta^{13}C$ and $\delta^{15}N$, and elemental OC/TN ratios, and apply a mixing model to estimate the relative contribution of sedimentary OM from mariculture/aquaculture, marine and terrestrial sources in the Daya Bay; (2) evaluate the distribution characteristics of OC, TN, total phosphorus (TP) and biogenic silica (BSi) in surface sediments in relation to sedimentary OM sources and other environmental factors; (3) perform pollution assessments for sedimentary N and P (which are easily impacted by anthropogenic activities) by comparing the data with established sediment quality guidelines (SQGs), and assess the potential use of BSi for paleo-environmental studies (e.g., paleo-productivity); and (4) examine the loading and preservation status of OC, TN, TP, and BSi in relation to OM sources and sediment textural characteristics compared to other coastal areas. This study has important implications on the ecological health of a bay in terms of eutrophication, C burial, and preservation as well.

2. Materials and methods

2.1. Study area and sampling

Daya Bay, located within the geographical coordinates: 114.5° E–114.9° E and 22.4° N–22.9° N, is one of the largest typical subtropical semi-enclosed shallow bays (surface area, ~600 km^2) spanning through ~92 km length of the southeast coastline of China (Fig. 1). The bay is relatively shallow, and water depths in most parts are generally <30 m (average: 10 m). The study area is influenced by a typical subtropical monsoon climate with an average temperature of 29 °C during summer, and 17 °C during winter. The annual mean precipitation is 1827 mm, and ~80% of rainfall occurs between April and August (Chen et al., 2014). There are no larger rivers, except for the small Dan'ao River and other several seasonal smaller streams meandering along the coast of the bay, and the major source of water in the bay is from the South China Sea (Gao et al., 2008; Wang et al., 2008; Wei et al., 2013; Ke et al., 2017; Zhao et al., 2019a). The tidal pattern in the bay is dominated by an irregular semidiurnal tide, and the maximum tidal height is 2.57 m with an average of 1.01 m. Surface water salinity usually varies from 22.7 to 33.8 with little fluctuations, except during typhoon (Wang et al., 2008) and rainy seasons (Zhao et al., 2019a). The mean sediment deposition rate in the bay is ~0.9 cm/yr (Han, 1995). The topographic characteristics of Daya Bay has been termed complicated (Wei et al., 2013) due to the presence of more than 50 set of islands (also known as central islands)

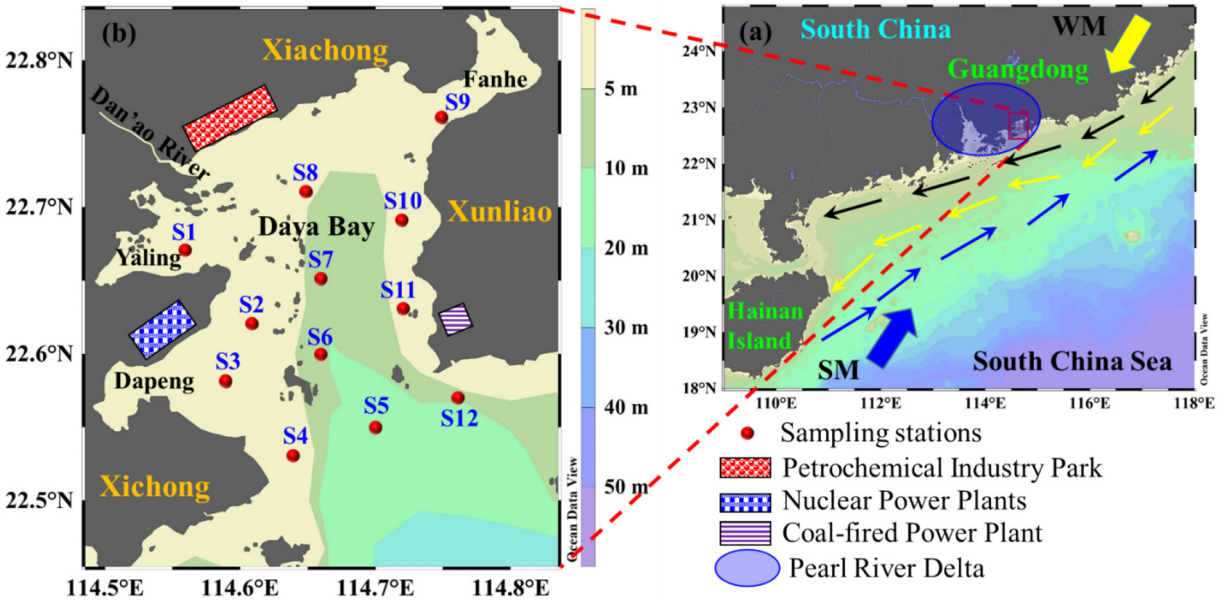


Fig. 1. Map showing (a) study area (inserted) in the northern South China Sea, and (b) surface sediment sampling stations in the Daya Bay. The study region also belongs to the Pearl River Delta (inserted blue circle; (a)), which is one of the largest economic zones with large pollutants emission in China. Sites S1, S8, and S9 are located at the marine cage culture areas, while site S3 is few kilometers away from the cage culture areas at the Dapeng cove (b). The black arrows represent longshore current, while the yellow and blue arrows show the flow direction of surface water facilitated by winter (WM) and summer (SM) monsoons (Wang et al., 1986; Liu et al., 2012a; Liu et al., 2016). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in the bay (Fig. 1b). The seawater residence time is ~90 d (Wang et al., 2008; Zhang et al., 2019). A 120-year sedimentary record retrieved in 2010 revealed that the sediment texture in the Daya Bay is predominantly composed of silt and sand accounting for 67.2% and 22.5% by average, respectively, whereas the content of clay was relatively low (average: ~10.4%) (Zhou et al., 2019). Clay mineralogy assemblage revealed that illite is the most dominant clay mineral accounting for ~40%, followed by kaolinite (39%), smectite (18%), and lastly by chlorite (4%) in the bay (Liu et al., 2012a). Two nuclear plants (i.e., the Daya Bay Nuclear Power Station and Ling'ao Nuclear Power Station, which came into operation in 1994 and 2002, respectively), are situated on the western coast of the bay (Fig. 1b). Petrochemical industry and coal-fired power plant are also located on the northern and southeastern regions of the bay, respectively. All these industrialized activities have the potential to influence the biogeochemistry of biogenic elements in the bay due to wastewater discharge. However, the bay serves as one of the main marine aquaculture areas in Guangdong Province, which is one of the most important economic zones in China.

The sampling array was designed to capture both the anthropogenic and marine signals in sediments within the bay as depicted in (Fig. 1b). Sites S1, S8, and S9 are in the aquaculture/mariculture areas; sites S2 and S3 are located near the nuclear power plants and few kilometers away from Dapeng mariculture/aquaculture sites. Sites S10 and S11 are located near the coal-fired plant, and may be affected by tourist activity and domestic sewage; sites S6 and S7 are located at the central bay area, while sites S4, S5, and S12 located at the bay mouth are influenced by marine input (Fig. 1b). The bottom water temperature, salinity, and DO, as well as the salinity and pH of sediment were measured using a multi-parameter probe (YSI ProDSS) after calibration with a combination of known standard solution and fresh water according to the manufacturer's protocol. Surface sediment (~5 cm) samples were collected from 12 stations using a stainless steel Van Veen grab sampler (volume: 3 L; area: 10 cm × 20 cm) on October 16, 2018. The geographical coordinates of the sampling sites were recorded using a hand-held GPS (eTrax, Garmin) for geostatistical mapping of the data. The retrieved samples were only taken from the middle of the grab to avoid any contamination from the metallic parts of the grab, and were subsampled in a N_2-filled glovebox to avoid peroxidation of organic constituents or possible contamination. In addition, the biodeposits consisting of a mixture of shellfish feces, pseudofaeces and fish feed residues from the shellfish culture and fish aquaculture sites were also collected. Samples were sealed in high-density polyethylene Ziploc bags after excluding air. All samples were transported back to the laboratory in an insulation box packed with ice. The wet sediment samples weights were taken to determine the moisture contents before freeze-drying to constant weights upon arrival at the laboratory. The freeze-dried samples were homogenized by grinding with a pre-cleaned stainless-steel pestle and mortar, and subsequently stored dry in high-density polyethylene Ziploc bags in a desiccator prior to later analyses.

2.2. Laboratory analyses

2.2.1. Sediment grain size, specific surface area, and chlorophyll-a

In order to analyze the surface sediment textures, appropriate amounts of sediment samples were treated with 30% H_2O_2 (15 mL) solution for 24 h to remove OM, and subsequently treated with 3 mol/L HCl solution (5 mL) for 24 h to remove calcareous shell particles. Surface sediment samples were fully desalinated, and later dispersed in a 0.05% $(NaPO_3)_6$ solution before measurements. Analysis was performed using a laser particle size analyzer (Mastersizer 2000 instrument (Malvern Ltd., Worcestershire, UK), which measures sediment particles in the size range of 0.02–2000 μm. Samples were measured in duplicates, and the relative error was <2% (Yang et al., 2015a). The textures of sediment were classified based on the following particle sizes (d, μm) distributions (a) sand: $d > 63$ μm, (b) silt: $4 < d < 63$ μm and (c) clay: $d < 4$ μm (Dan et al., 2019b). Sediment textural characteristics are reported in percentages (%) based on Shepard (1954) classification. Specific surface area (SSA) was determined according to the protocol reported by Waterson and Canuel (2008). Briefly, aliquot freeze-dried sediment samples were heated at 350 °C for 12 h to remove OM, and degassed for more than 2 h on the Micromeritics Flow Prep sample degas station at 250 °C to exclude water, and measured using an automatic N adsorption surface area analyzer (3H-2000BET-A, Beishide Instrument-ST Co., Ltd., China). For chlorophyll-*a* (Chl-*a*) content in surface sediments, ~0.5 g aliquot freeze-dried and homogenized sediments samples was weighed into a 25 mL centrifuge tube. Extraction was carried out in 10 mL of a 45:45:10 solvent mixture (acetone:methanol: water) in the dark at ~4 °C for 24 h. Concentrations of Chl-*a* in the investigated samples were measured using a spectrophotometric assay and standard equations (Joye et al., 1996).

2.2.2. Measurements of OC, TN, $\delta^{13}C$, and $\delta^{15}N$

Aliquot freeze-dried and homogenized sediment samples were sieved through a 200-mesh screen (~74 μm), and ~30 mg each of the surface sediments and biodeposit samples was pre-treated with 1 M HCl to eliminate inorganic carbon for the determination of OC (Yao et al., 2014; Dan et al., 2019b; Xu et al., 2020), while TN contents were determined in untreated samples (Liu et al., 2015; Xu et al., 2020). Both the contents of OC and TN in sediments and biodeposits were measured using a CHNOS Elemental Analyzer (Vario EL-II; Elementar Analysensyteme GmbH, Germany). Based on duplicate measurements, the relative error was <5% for OC, and <1.5% for TN. The $\delta^{13}C$ and $\delta^{15}N$ values of OM in the surface sediments and biodeposit samples were analyzed using an isotope ratio mass spectrometer (DELTA^{plus} XL). The isotopic ratios were reported in parts per thousand (‰), calculated as:

$$\delta(‰) = (R_{sample} - R_{standard})/R_{standard} \times 1000 \quad (1)$$

where δ (‰) denotes $\delta^{13}C$ (‰) and $\delta^{15}N$ (‰), while R_{sample} and $R_{standard}$ are the isotopic ratios of the sample and reference, respectively. The $\delta^{13}C$ values were given as ‰-deviation from the C isotope composition of the Vienna-Pee Dee Belemnite (PDB) standard, while the $\delta^{15}N$ was given as the ‰-deviation from atmospheric air standard. The reference materials analyzed together with the samples were Acetanilide (Thermo Scientific) and a certified sediment (low OC content, Elemental Micro analysis, UK). The relative error for $\delta^{13}C$ based on replicate analysis was ±0.12‰, and <0.3‰ for $\delta^{15}N$.

2.2.3. Measurements of TP, BSi, Al_2O_3 and Fe_2O_3

The abundance of TP in surface sediment samples was analyzed using the spectrophotometric phosphomolybdate blue method following a procedure involving the extraction of 0.25 g samples with 1 M HCl after ashing at 550 for 2 h (Aspila et al., 1976; Yang et al., 2019a, b; Dan et al., 2020a, b). Sediment samples were measured alongside with the standard coastal marine sediment for the Chinese seas (GBW07314). The percentage recovery of TP in our analysis was >96%, and the average relative error based on the analyses of measured and known values was generally less than ±3% ($n = 5$).

Biogenic silica (BSi) was analyzed using molybdate blue spectrophotometric method (Liu et al., 2005; Ragueneau et al., 2005) after samples extraction using a combined alkaline leaching method of DeMaster (1981) and Mortlock and Froelich (1989) modified by Liu et al. (2005) reported in details by Dan et al. (2019b). The contents of BSi are reported as weight percent as opal with assumed water content of 10% (Mortlock and Froelich, 1989; Liu et al., 2005; Dan et al., 2019b). The analytical error was generally <2% ($n = 5$) based on replicate analyzes of the same samples.

The contents of Al_2O_3 and Fe_2O_3 were analyzed to understand their influence on the stability of BSi and P in the surface sediments. Contents of Al_2O_3 and Fe_2O_3 in freeze-dried and homogenized surface sediment samples together with standard reference material (MAG-1) were analyzed using an inductively coupled plasma atomic emission

spectroscopy (ICP-AES) after a sequential pretreatment and microwave-assisted acid digestion according to Lim et al. (2013). The accuracy of the analytical protocol was checked through repeated measurement of the standard reference material together with the sediment samples, and the relative deviation between the known and measured values was generally less than ±2% ($n = 5$), with a percentage recovery of >98%.

2.3. Quantitative estimates of sedimentary OM contributions from different sources

The relative proportions of sedimentary OM from mariculture/aquaculture, biodeposition, marine and terrestrial sources in the surface sediments were estimated using Monte Carlo simulation by applying specific $\delta^{13}C$ values and OC/TN ratios as end-members (Li et al., 2012). Out of 40,000,000 random samples from the normal distribution, a total of 400,000 were taken to fulfill the equations below:

$$\delta^{13}C_{biodep} \times f_{biodep} + \delta^{13}C_{mar} \times f_{mar} + \delta^{13}C_{ter} \times f_{ter} = \delta^{13}C_{sample} \quad (2)$$

$$OC/TN_{biodep} \times f_{biodep} + OC/TN_{mar} \times f_{mar} + OC/TN_{ter} \times f_{ter} = OC/TN_{sample} \quad (3)$$

$$f_{biodep} + f_{mar} + f_{ter} = 1 \quad (4)$$

Here, f_{biodep}, f_{mar}, and f_{ter} are the fractions of mariculture/aquaculture biodeposition, marine, and terrestrial OM sources, which were calculated based on 400,000 results obtained from running the program in Enthought Python Distribution 7.2. The variability of the mean value of each end-member was generally <0.5‰ by randomly sampling each parameter value 5 times. This ensured the statistical stability of the model. The $\delta^{13}C_{mar}$ and OC/TN_{mar} values representing the marine OM end-members were taken as −20.2‰ and 5. This corresponds to the average $\delta^{13}C$ value previously reported for marine OM in the Daya Bay offshore area (Zhao et al., 2019a), and average OC/TN of marine phytoplankton (Goñi et al., 2013; Dan et al., 2019b). The $\delta^{13}C_{ter}$ and OC/TN_{ter} values representing the terrestrial OM end-members were taken as −28‰ and 22.7, and are the average values reported for terrestrial OM in the adjacent Pearl River (Yu et al., 2010) and the Daya Bay wetland (Zhao et al., 2019a). The $\delta^{13}C_{biodep}$ and OC/TN_{biodep} values representing the end-members of sediment OM derived from mariculture/aquaculture were taken as 18.5‰ and 6, respectively, and are the average values obtained by analyzing the contents of OC, TN, and $\delta^{13}C$ in biodeposits from three mariculture/aquaculture sites in this study. These end-members are also within the ranges reported for mariculture/aquaculture biodeposits, marine OM, and terrestrial OM in the literature (Sarà et al., 2004; Yokoyama et al., 2006; Ramaswamy et al., 2008; Xia et al., 2014; Dan et al., 2019b; Pan et al., 2019 and references therein). Information on the combined use of $\delta^{13}C$ and OC/TN values in the mixing model to provide relative proportions of sedimentary OM from different sources and the choice of terrestrial end-members are detailed in Section 4.1.

2.4. Contamination of status of N and P in surface sediments

The sediment quality guidelines (SQGs) by the Ministry of Environment and Energy, Ontario, Canada, were used to classify the status of N and P contamination in surface sediments of the Daya Bay. Here, surface sediments were classified as: (1) none contaminated when the content of TN is ≤550 mg/kg and TP is ≤600 mg/kg; and (2) severely contaminated when TN is >4800 mg/kg and TP is >2000 mg/kg (Persaud et al., 1993; Mudroch and Azcue, 1995; Yang et al., 2017; Dan et al., 2020a). In addition, ON index was also used to evaluate the extent of N contamination in sediments (Zhang et al., 2015). This index is obtained by multiplying the weight percentage of TN by 0.95, and classifies N contamination in sediments into: (1) uncontaminated when the index is <0.0033%; and (2) severely contaminated when the index is >0.133% (Zhang et al., 2015; Yang et al., 2017).

2.5. Statistical analysis and graphing

Pearson's correlation analysis was carried out to reveal the statistical relationships and implications among the measured parameters. The statistical significance was set at 95% ($p < 0.05$), 99% ($p < 0.01$), and 99.9% ($p < 0.001$) confidence levels. The correlation and regression plots were produced using Origin Pro 2020 software (OriginLab, USA), while the map of study area showing the sampling sites, and those showing the spatial distributions of the measured parameters were produced using Ocean Data View software (ODV Version 5.2.1) (Sclitzer, Reiner, Ocean Data View, https://odv.awi.de, 2020).

3. Results

3.1. Physicochemical parameters in bottom water and sediments, and sediment textures

The physicochemical parameters in bottom water and sediments, and sediment textural characteristics are shown in Fig. 2 and listed in Table S1. Bottom water temperature changed narrowly from 21.93 to 23.34 °C (average: 22.76 ± 0.44 °C); the highest value was found at the northwestern site S1, while the lowest value was found at the bay mouth site S5 (Fig. 2a). Bottom water salinity was considerably high ranging from 32.18 to 34.49 (average: 33.49 ± 0.72); the highest value occurred at the bay mouth site S5, while the lowest value occurred at the northwestern site S1 (Fig. 2b). Concentrations of DO in the bottom water were generally low with values ranging from 3.29 to 4.02 mg/L (average: 3.72 ± 0.25 mg/L). DO values >3.8 mg/L were found at the bay mouth sites, where the bay constantly interacts with the open sea, and at the northeastern flank of the bay, while the lowest value (3.29 mg/L) occurred at the northwestern site S1 (Fig. 2c). Surface sediment pH was slightly elevated depicting alkaline conditions with values ranging from 8.64 to 9.42 (average: 9.06 ± 0.18). The highest pH value occurred at the northern bay site S8, while the lowest value occurred at the western flank site S2 (Fig. 2d). The concentrations of Chl-*a* in surface sediments ranged from 1.68 to 8.55 μg/g (average: 4.46 ± 2.00 μg/g); the highest values (>7 μg/g) occurred at northwestern and northeastern sites S1 and S9, respectively, while the lowest value occurred at site S7 (Fig. 2e).

The textures of surface sediments in the investigated sites were mainly clayey silt as depicted in Fig. S1. In general, silt (4–63 μm) was the dominant sediment grain type, which accounted for 54.65–64.42% (average: 59.36 ± 2.94%), followed by clay (<4 μm) accounting for 19.06–39.36% (average: 30.75 ± 6.33%), while sand (>63 μm) was the least dominant grain type accounting for 0–22.28% (average: 9.88 ± 6.27%) of the total sediment texture types. The spatial distributions of sediment grain sizes are also shown in Fig. 2. Silty sediments were mostly deposited at the western flank of the bay with the highest contents at the northwestern site S1 (Fig. 2f). The deposition of clayey sediments generally decreased from the inner northern bay sites to the bay mouth areas, with the highest content occurring at the northeast site S9 (Fig. 2g). As would be expected, the contents of sandy sediments increased gradually from the inner bay to the bay mouth regions, with the highest content at site S5, while the lowest content was found at site S1 (Fig. 2g). The values for SSA ranged from 7.71 to 17.14 $m^2\ g^{-1}$ (average: 11.93 ± 3.54 $m^2\ g^{-1}$), the highest value was found at site S8, while the lowest value at site S1 (Fig. 2h).

3.2. $\delta^{13}C$ and $\delta^{15}N$, bulk OC, TN, TP, BSi, Al_2O_3 and Fe_2O_3

The $\delta^{13}C$ and $\delta^{15}N$ values, and the abundance of OC, TN, TP, BSi, Al_2O_3 and Fe_2O_3 are presented in Table S1, and their spatial distributions are depicted in Fig. 3. The $\delta^{13}C$ values ranged from −21.75‰ to −20.59‰ (average: −21.27 ± 0.38‰), while $\delta^{15}N$ values ranged from 6.12‰ to 7.12‰ (average: 6.74 ± 0.29‰). The spatial distribution of $\delta^{13}C$ showed a progressive decrease from the inner bay to the bay mouth (Fig. 3a),

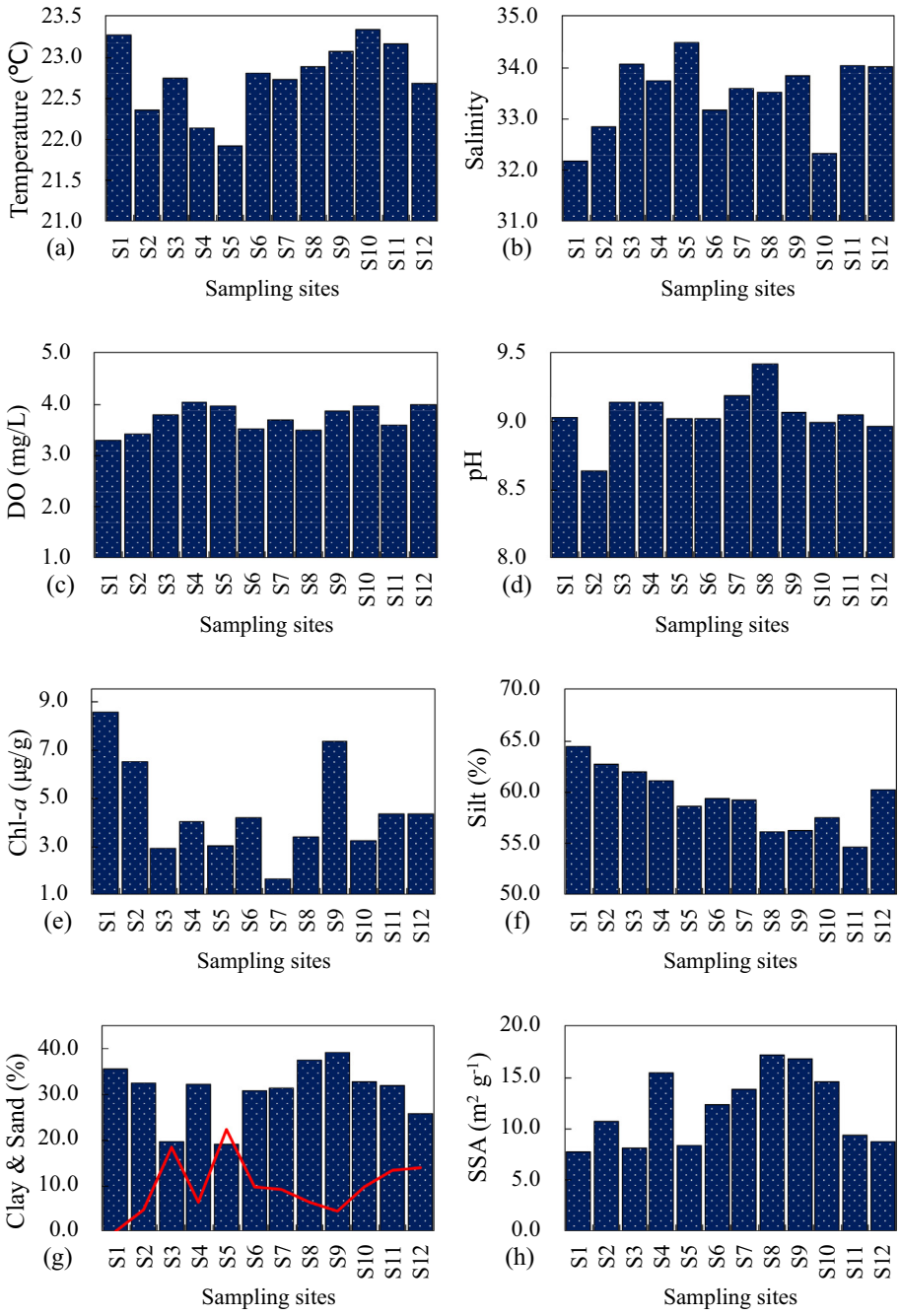


Fig. 2. Spatial distributions of physicochemical parameters in bottom water (temperature, salinity, and dissolved oxygen) and sediment (pH and chlorophyll-*a*), and sediment textural properties (silt, clay, sand, and specific surface area) in the Daya Bay. The red line in Fig. g represents percentage of clay contents. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

while $\delta^{15}N$ generally decreased from the eastern flank to the western flank of the bay (Fig. 3b). OC ranged from 0.28% to 1.18% (average: 0.80 ± 0.26%), while TN ranged from 0.07% to 0.17% (average: 0.11 ± 0.03%). The contents of OC (Fig. 3g) and TN (Fig. 3h) were more elevated at the northern bay regions, and generally decreased seaward to the mouth of the bay, respectively. The molar OC/TN ratio ranged from 3.65 to 12.30 (average: 8.90 ± 2.62), and generally increased from the inner bay to the bay mouth. Relatively lower OC/TN ratios (<6) appeared at the eastern flank sites 10 and 11 where OC values were generally low (<0.5%) as shown in Fig. 3c. Concentrations of TP ranged from 9.47 to 11.44 μmol/g (average: 10.55 ± 0.67 μmol/g), higher abundance was found in the north central and southeast regions of the bay mouth (Fig. 3i). BSi ranged from 0.94 to 1.76% (average: 1.42 ± 0.23%), the highest abundance was found at the northeastern site S9, corresponding to the site with the highest OC abundance, and decreased gradually from the inner bay with a slight increase at the bay mouth (Fig. 3j). The contents of Al_2O_3 and Fe_2O_3 ranged from 12.08 to 18.70% (average: 14.95 ± 2.14%) and 3.98–5.78% (average: 4.93 ± 0.64%), respectively, and their spatial distributions were like that of clayey sediment and SSA (Fig. 3k–l).

TN pollution index was ~1 to 3-fold higher when compared to the lowest N pollution threshold of 550 mg/kg in sediments, but ~3–7 fold lower when compared to severe N contamination threshold of 4800 mg/kg in the sediments (Table S2). ON pollution index ranged from 0.07 to 0.16, and was generally higher than the lowest ON pollution threshold of 0.0033% and severe ON contamination threshold of

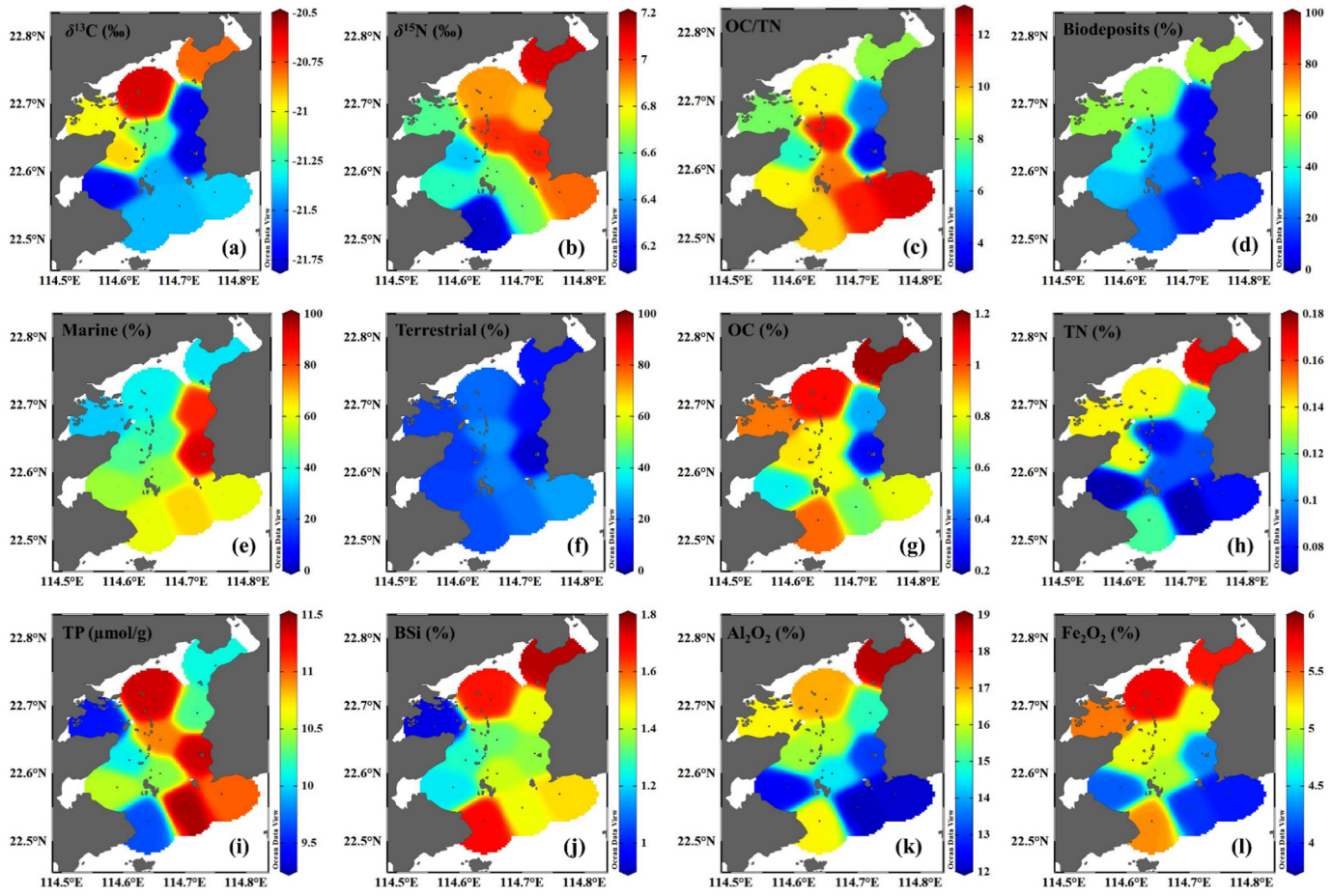


Fig. 3. Spatial distributions of (a) $\delta^{13}C$, (b) $\delta^{15}N$, (c) OC/TN ratio, (d) biodeposits OM (%), (e) marine OM (%), (f) terrestrial OM (%), (g) OC (%), (h) TN (%), TP (μmol/g) (i), (j) BSi (%), (k) Al_2O_3 (%), and (l) Fe_2O_3 (%) in surface sediments of the Daya Bay.

0.133% at sites S1, S2, S8, and S9 (Table S2). TP pollution index in the surface sediments varied narrowly, and was ~1.7–2 fold lower when compared to the lowest P pollution threshold of 600 mg/kg, and ~6–7 fold lower when compared to the severe P pollution threshold of 2000 mg/kg (Table S2).

3.3. Proportions of sedimentary OM from mariculture/aquaculture biodeposits, terrestrial and marine sources

The proportional estimate of sedimentary OM from mariculture/aquaculture biodeposits ranged from 5 to 55% with an average of 28% (Table S2), and generally decreased from the northern and western regions of the bay to the eastern and southern regions of the bay (Fig. 3d). Marine OM accounted for 32–93% with an average of 55% (Table S2), and generally increased from the inner bay to the bay mouth (Fig. 3e), while terrestrial OM was generally low accounting for 2–28% with an average of 17% (Table S2), and was mainly deposited at the central and southeastern regions of the bay (Fig. 3f).

3.4. Pearson correlation results

Pearson correlation results are shown in Fig. 4a. The relationship between OC and TN was statistically significant ($p < 0.05$) (Fig. 4a–b). Moreover, OC had positive (but not significant) correlations with silt, clay, and SSA ($p > 0.05$). TN exhibited significant positive correlations with clay ($p < 0.001$) and Chl-*a* ($p < 0.01$), with no significant relationship (although positive) with silt ($p > 0.05$). Both OC and TN exhibited significant negative correlations with sand ($p < 0.001$), while TP had a significant positive correlation with sand ($p < 0.05$), and negative relationship with silt, clay and SSA ($p < 0.05$). BSi had a significant positive correlation with SSA ($p < 0.01$), no significant positive correlations with clay and sand ($p > 0.05$), and significant negative relationship with silt ($p < 0.05$). BSi exhibited positive relationships (although not statistically significant) with Al_2O_3 and Fe_2O_3, and the correlations between TP and Al_2O_3, and Fe_2O_3 were negative and not statistically significant. The correlation between $\delta^{13}C$ and $\delta^{15}N$ was positive with no statistical significance ($p > 0.05$), and the regression plots showed scattered points ($r^2 = 0.01$) (Fig. 4c). The relationship between the $\delta^{13}C$ and OC/TN was also positive, and the regression plot (Fig. 4d) showed scattered points ($r^2 = 0.04$) with no significant correlation ($p > 0.05$). The relationship between $\delta^{15}N$ and OC/TN was negative and not significant ($p > 0.05$) with scattered plotted points ($r^2 = 0.02$) as depicted in Fig. 4e. The correlation between OC/TN and OC was positive, while that of OC/TN versus TN was negative, and these correlations were not statistically significant ($p > 0.05$). However, there was a significant relationship between $\delta^{13}C$ and OC ($p < 0.001$), and TN ($p < 0.01$), but no relationship existed between $\delta^{15}N$ and TN (Fig. 4a). The regression plot between the estimated OM from mariculture/aquaculture biodeposits exhibited a significant relationship with OC ($r^2 = 0.62$), and with TN ($r^2 = 0.60$) (Fig. 4f).

4. Discussion

4.1. Isotopic constraints, OC/TN ratios, and distribution characteristics of sedimentary OM

The $\delta^{13}C$ and $\delta^{15}N$ values, and OC/TN ratios of OM can be reliably used to probe the sources, quantify the relative proportions, and provide an understanding of the factors influencing the distribution characteristics and

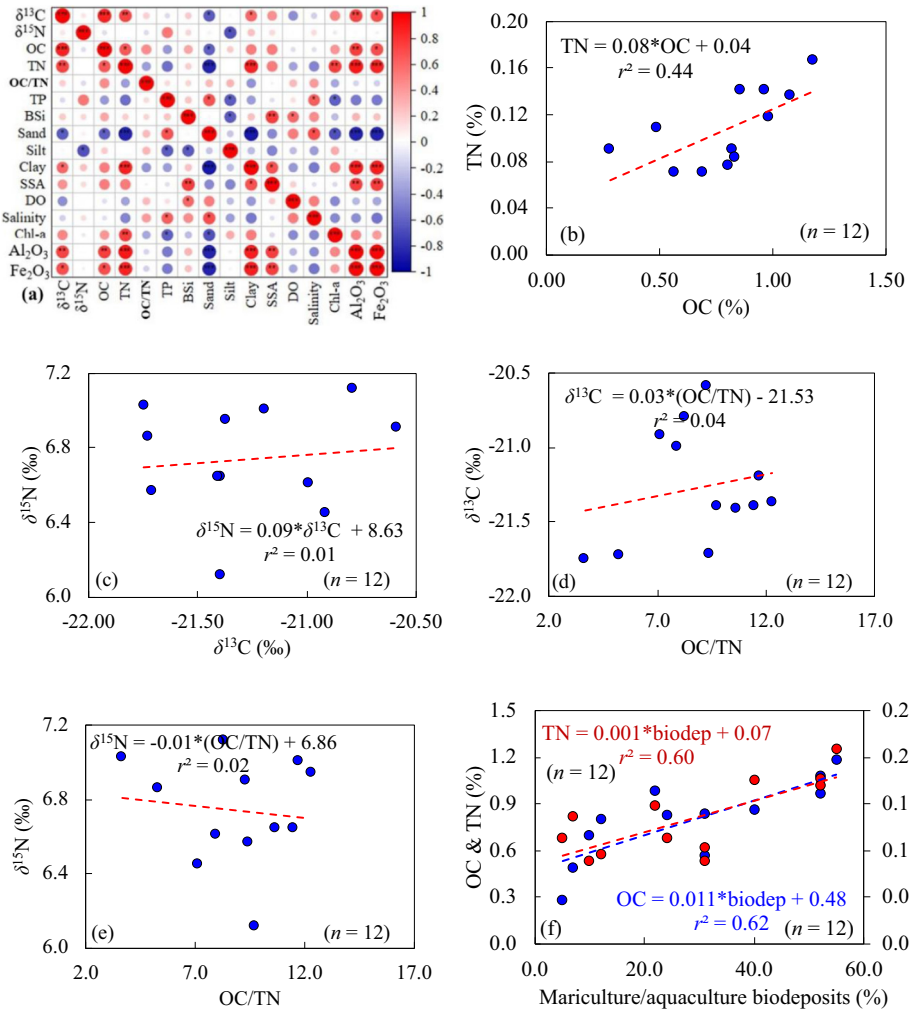


Fig. 4. (a) Pearson correlation matrix showing the relationships among the studied parameters; the red and blue colored circles signify positive and negative correlations, respectively, and the black asterisk denotes the degree of significance (i.e., $^{*}p \le 0.05$; $^{**}p \le 0.01$; $^{***}p \le 0.001$), which increases as both the colour intensity and circle size increases. Relationship between (b) TN and OC, (c) $\delta^{15}N$ and $\delta^{13}C$, (d) $\delta^{13}C$ and OC/TN, (e) $\delta^{15}N$ and OC/TN, and (f) Mariculture/aquaculture biodeposits vs. OC, TN in surface sediments of the Daya Bay. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

burial of sedimentary OM in coastal marine systems. Generally, rivers are the major channels by which terrestrial OM with associated biogenic elements are shuttled to the coastal marine environments (e.g., Liu et al., 2009; Dan et al., 2019a), and both anthropogenic point and non-point sources contribute to OM load in rivers and marine environments (Savage, 2005; Ke et al., 2017). The lack of major rivers directly discharging into the Daya Bay would limit the transport and burial of terrestrial OM in the surface sediments. For example, past study had indicated that terrestrial OM was an important component accounting for 35–78% of sedimentary OM pool in the Daya Bay wetland sediments, and the $\delta^{13}C$ values as low as −28‰ were reported (Zhao et al., 2019a). Thus, if the small streams flowing into the Daya Bay, especially at the northern regions of the bay play important roles in transporting terrestrial OM into the bay, then the measured $\delta^{13}C$ and $\delta^{15}N$ values in the surface sediments deposited especially at sites S1, S8 and S9 during this study would have been low (at least <−24‰ for $\delta^{13}C$ for and 4‰ for $\delta^{15}N$). In contrast, the $\delta^{13}C$ and $\delta^{15}N$ values at these sites were higher ranging from −20.99‰ to −20.59‰ and 6.67‰ to 7.12‰, respectively. This clearly shows that: firstly, the input of terrestrial OM from these small rivers into the bay is generally limited. Secondly, it is possible that other sources of sedimentary OM may prevail thus diluting terrestrial OM in the bay. Adjacent to the Daya Bay is the Pearl River (Fig. 1a), which is the second largest river in China that has been ranked thirteenth among the largest rivers in the world in terms of water discharge and suspended sediment load (Zhang et al., 1999). The Pearl River does not flow directly into the Daya Bay, but rather flows directly into the northern South China Sea. However, terrigenous material is a noticeable component in the Pearl River and its nearby coastal sediments, but the amount of sedimentary OM from terrestrial source declines from >50% in the inner estuary region to ~10% in the outer estuarine sediments and across the shelf (Yu et al., 2010). Previous studies have reported that fluvial transports from the Pearl River and Taiwan Island are important sources of terrestrial OM in the northern South China Sea (Wang et al., 1986; Pelejero, 2003; Luo et al., 2014; Liu et al., 2016). As shown in Fig. 1a, the direction of coastal current together with the surface circulation, facilitated by monsoons, depicts a general water movement from the Taiwan Strait in the northeastern region to the northwestern region of the sea during winter season. During summer season, the surface circulation changes its direction and flow from the northwestern to the northeastern region of the sea. Recent study on clay mineral assemblage in the northern South China Sea indicated that kaolinite (46%) and illite (35%) are the dominant clay minerals in the Pearl River, while illite (56%) and chlorite (36%) are the dominant clay minerals transported from Taiwan into the northern South China Sea (Liu et al., 2016). However, previous study had reported comparable average amount of illite (40%) and kaolinite (39%) in surface sediments of the Daya Bay (Liu et al., 2012a). Thus, it is expected that small amount

of terrestrial OM from the Pearl River or Taiwan Island, or that which is drained from the northern South China Sea coast may be transported by the coastal currents into the Daya Bay either in winter or summer. Although most of the terrestrial OM from the Pearl River is transported westward (Yu et al., 2010; Liu et al., 2012b), it is expected the terrestrial materials from the Pearl River would influence the Daya Bay more than materials transported from the Taiwan Island considering the proximity and distance for fluvial drift, even though illite is the dominant clay mineral transported from the Taiwan Island.

Higher $\delta^{13}C$ values were previously reported in the suspended particulate matter in the Daya Bay during summer (average: −17.4‰) and winter (average: −22.1‰) (Ke et al., 2017) compared to the lower $\delta^{13}C$ values (average: −24.57‰), which were reported in the nearby Pearl River Estuary (Liu et al., 2012b). Moreover, the lower OC/TN ratios together with the higher $\delta^{13}C$ values indicated lower contribution of ^{13}C-depleted terrigenous OM in the suspended particulate matter in the Daya Bay (Ke et al., 2017). In this study, the measured $\delta^{13}C$ and $\delta^{15}N$ values were higher that could be dominantly attributed to sedimentary OM input from terrestrial C_3 plants, and the $\delta^{15}N$ values were lower than ranges reported for anthropogenic sewage (10–20‰), and higher than an average value of 0.2‰ for agricultural fertilizer waste (Savage, 2005; Ramaswamy et al., 2008; Goñi et al., 2013; Dan et al., 2019b). Moreover, the $\delta^{15}N$ values in surface sediments of the Daya Bay during this study are higher than −10.6‰ to −6.5‰ previously reported in suspended particulate matter in the Dan'ao River (Ke et al., 2017). The authors had attributed the significantly lower $\delta^{15}N$ values to hypereutrophic nature of this river due to sewage input. However, the $\delta^{15}N$ values in this study indicate that sewage input might be restricted to this river or rapidly decomposed in the bay water column without being incorporated into the sediments. Gao et al. (2008) had previously studied the composition and sources of OM and its solvent extractable components in surface sediments, and suggested that marine autogenic input could be the major source of sedimentary OM in the Daya Bay. The highest OC/TN ratio (12) was reported at the northern inner bay site by Gao et al. (2008), and together with the presence of *n*-alkan-2-ones provided evidence of trace amount of terrigenous input. The highest OC/TN ratio of 12.3 in this study is consistent with previous report by Gao et al. (2008), but occurred at the bay mouth site S12. The OC/TN ratio of 12.3 as found in this study generally indicated there is an intermixture of sedimentary OM, more contributions from marine source than terrestrial source. Moreover, variation in the study sites where the highest OC/TN ratio was found in this study compared with previous study by Gao et al. (2008) may be related to seasonal changes in the depositional patterns of sedimentary OM in the Daya Bay. Therefore, the findings in this study are consistent with the earlier reports by Gao et al. (2008) and Ke et al. (2017) in the surface sediments and suspended particulate matter, respectively, with conclusion that marine photosynthetic organisms rather than terrestrial OM, could contribute more to the particulate and sedimentary OM in the Daya Bay.

Daya Bay is a typical mariculture/aquaculture bay in the Guangdong Province of China, where its mariculture/aquaculture nodes are distributed at the northern and western regions of the bay. Therefore, providing a quantitative estimate and evaluating the distribution characteristics of sedimentary OM derived from mariculture/aquaculture biodeposits is important for the fact that it will contribute to the understanding of the factors influencing the cycling and burial of biogenic elements including C in sediments, not just in the Daya Bay but also in other worldwide coastal marine systems used for mariculture/aquaculture activities. It is also essential because sedimentary OM could act as an internal source of nutrients and energy, which may have important implications on the ecological sustainability of coastal marine ecosystems and eutrophication. The measured $\delta^{13}C$ and $\delta^{15}N$ values, and the OC/TN ratios in surface sediments of the Daya Bay during this study were mostly within the ranges reported for sedimentary OM from mariculture/aquaculture and marine sources as reported for other coastal marine environments (Sarà et al., 2004; Gao et al., 2008; Pan et al., 2019; Xia et al., 2019), with lower signals of terrestrial plants OM, sewage effluents and agricultural fertilizer input. Therefore, mariculture/aquaculture as an anthropogenic activity and marine productivity are considered as significant sources of sedimentary OM in the Daya Bay. Nevertheless, several factors could influence the $\delta^{15}N$ values and OC/TN ratios in sediments. For example, the $\delta^{15}N$ values could be easily changed by a series of complex biogeochemical processes over time as dynamic cycling of N is typically subject to kinetic isotopic fractionation, especially during transformation and recycling of particulate and dissolved N compounds. Heterotrophic microorganisms, which are active in deamination were reported to alter N isotopic composition of OM and increased the $\delta^{15}N$ of terrigenous particulates from ~4‰ to 9‰ (i.e., replace by their own biomass) making it quite different from the original source of OM (Caraco et al., 1998). Although the $\delta^{15}N$ values reported in this study occurred in a very narrow range (~6.12‰ to 7.12‰), it is undoubted that through decomposition, the cycling of N could create isotopically higher ^{15}N values in OM deposited in surface sediments of the Daya Bay. The OC/TN ratios could be influenced by hydrodynamic sorting of sediment particles. This is because lower OC/TN ratios are frequently found in fine-grained sediments than in coarse sandy sediments, partly because of the larger proportions of clay minerals, which have negative surface charges and large SSA capable of adsorbing considerable amount of N. As shown in Fig. 4a, the OC/TN ratio showed no significant correlation with sandy, silty, and clayey sediment particles, and SSA. This indicated that there is no influence of sediment textural properties on OC/TN ratios. Thus, the scattered and no significant correlation (Fig. 4e) between $\delta^{15}N$ and OC/TN ratios could be partly attributed to other processes such as the decomposition and microbial mineralization of sedimentary OM. Increase in microbial mineralization may reduce the total amount of N present in sedimentary OM with preferential loss of ^{14}N from the organic substrate, which becomes enriched in ^{15}N. As a result, decomposed OM will contain little amount of N with enriched ^{15}N. Thus, the OC/TN ratios might increase or decrease during the decomposition of sedimentary OM from various sources.

Generally, the combination of $\delta^{13}C$ and $\delta^{15}N$ values, and/or with OC/TN ratios can be applied to provide quantitative estimates of OM from various sources in coastal marine sediments. To provide a reliable estimate of the source proportions of sedimentary OM, the correlation between the measured $\delta^{13}C$ and $\delta^{15}N$ values in the investigated sediment samples should be positive and significant, or the relationship among the $\delta^{13}C$ and $\delta^{15}N$ values, and OC/TN ratios should be negative and significant too, otherwise, the estimates may be strongly biased. In this study, the scattered points, poor relationship, and lack of evidence for anthropogenic sewage pollution in surface sediments of the Daya Bay limits the combined use of $\delta^{13}C$ vs $\delta^{15}N$ (Fig. 4c) and $\delta^{15}N$ vs OC/TN (Fig. 4e) for estimating the proportions of sedimentary OM from different sources. The positive relationship (although not significant) between $\delta^{13}C$ and OC/TN (Fig. 4d) (rather than being negative as would be expected in large river dominated coastal ecosystems), and the highest OC/TN ratio of 12.3 at the bay mouth site indicated that the dominant source of water in the Daya Bay comes from South China Sea. It also implied that relatively small amount of terrestrial OM from the Pearl River (which is the dominant source of terrestrial OM in the nearby coastal region) could have been transported and deposited into the bay. The strong relationship between $\delta^{13}C$ and OC and between $\delta^{13}C$ and TN (Fig. 4a) and the relationship between OC and TN (Fig. 4a–b) not only suggested considerable amount of TN in surface sediments of the Daya Bay may be composed of ON, it as well indicated that the $\delta^{13}C$ and OC/TN-based mixing model, rather than the combined use of $\delta^{15}N$ vs OC/TN or $\delta^{13}C$ vs $\delta^{15}N$, can be reliably applied to provide quantitative estimates of the proportions of sedimentary OM from marine, terrestrial and mariculture/aquaculture sources in the Daya Bay.

According to Monte Carlo simulation results, marine plankton was the dominant source of sedimentary OM in the Daya Bay, and its relative abundance generally increased from the inner bay regions to the bay mouth, with more abundance at the western region of the bay (Fig. 3e). Mariculture/aquaculture biodeposits was the second highest source of sedimentary OM, and its abundance decreased rapidly from the shallow inner bay regions (where mariculture/aquaculture cages and/or rafts are located) to the bay mouth (Fig. 3d). Similar findings were also reported in other study areas where intensive mariculture/aquaculture are practiced such as in Italy (Sarà et al., 2004), Australia (Ye et al., 1991), and China (Xia et al., 2019; Pan et al., 2019; Xu et al., 2020). The proportion of sedimentary OM from terrestrial source was the least with more depositions at the central and southwest regions of the bay (Fig. 3f). The relatively high amount of sedimentary OM (>40%) from mariculture/aquaculture biodeposits at the marine culture areas may be related to rapid deposition of faecal and pseudofaecel materials and fish feed residue due to shallow water depths. Because of the labile nature of marine culture biodeposits, it is possible that considerable amount of the nutrients from uneaten fish feeds must have been re-dissolved into the water column, and together with nutrients supplied from the South China Sea and other sources contributes to high productivity in surface water of the Daya Bay (Zhang et al., 2008; Zhao et al., 2019a; Zhang et al., 2019). This eventually resulted in the relatively higher contributions of sedimentary OM from marine source even at the mariculture/aquaculture sites. In overall, the lower terrestrial OM proportions may have been a direct result of the possible presence of priming effect under lower DO conditions in bottom water of the Daya Bay (Fig. 2c; Table S1), which may have occurred due to enhanced nutrients (N and P) efflux from sediments (van Oevelen et al., 2009). Enhanced nutrients efflux has a strong link with increased phytoplankton production in the water column (Conley et al., 2009), and may have resulted in enhanced degradation of recalcitrant terrestrial OM (Bianchi, 2011) due to injection of labile OM from marine plankton and/or mariculture/aquaculture biodeposition in the Daya Bay. In summary, the estimated proportions of sedimentary OM in the Daya Bay during this study may not measure up to the exact quantity derived from different sources of input incorporated into the sediments, but rather represent integrated results of both natural and anthropogenic processes that influence the biogeochemical cycling of biogenic elements, primary production in the overlying water, preservation of OC, and other biogenic elements in sediments. Thus, the spatial distributions of sedimentary OM from either mariculture/aquaculture biodeposits, marine plankton and/or terrestrial sources may have important implications for the content and distribution characteristics of biogenic elements in the Daya Bay as discussed in the subsequent sections below. Nevertheless, as the biogeochemical processes and distributional pattern of sedimentary OM and biogenic elements may as well vary in different seasons (Restrepo et al., 2017), the findings in this study may not be exclusively indicative of the prevailing conditions in the bay at all seasons.

4.2. Distribution characteristics of biogenic elements in surface sediments

4.2.1. OC and TN

The abundance of OC and TN are determined by their origins and/or delivery routes, including depositional processes and degree of OM preservation, and may be used as a primary proxy for describing the abundance of sedimentary OM. Sedimentary OC to some extent represents the bulk fraction of OM that escapes remineralization during deposition because only ~1% of OM produced within the upper water column could be deposited in the bottom sediments (Middelburg and Meysman, 2007). However, OC sedimentation rate can be very high, especially in shallow coastal marine environments (Cai et al., 2006). The comparison between OC and TN in surface sediments of the Daya Bay and other coastal marine ecosystems are presented in Table 1. The levels of OC and TN in the Daya Bay are within the ranges reported for other coastal ecosystems dominated by mariculture/aquaculture activities such as the Maowei Sea (Xu et al., 2020) and Sangou Bay (Xia et al., 2019) in China, lower than that of Chesapeake Bay (USA) (Zimmerman and Canuel, 2000), and ~2 to 4-fold lower than the range reported by Dan et al. (2019b) for the Cross River Estuary and adjacent shelf (a typical mangrove dominated coastal ecosystem) in West Africa. Increase in marine productivity could obscure the signatures of terrestrial OC and TN. The relatively higher abundance of marine OM in the surface sediments during this study suggested that its degradation and/or consumption rates are probably lower than that of OM derived from mariculture/aquaculture. This might be possible as OC or TN dispersed from the mariculture/aquaculture areas are usually composed of highly labile compounds (Pearson and Black, 2000). Terrestrial OM is usually more refractory and resistant to rapid degradation than sedimentary OM from marine source. In coastal marine systems with

Table 1
Range of biogenic elements in surface sediments of the Daya Bay and other coastal marine system.

Study area	OC (%)	TN (%)	TP (μmol/g)	BSi (%)	Reference
Daya Bay, China	0.28–1.18	0.07–0.17	9.47–11.44	0.94–1.76	This study
Daya Bay, China	0.86–1.60	~0.1–0.21			Gao et al. (2008)
Maowei Sea	0.10–1.19	0.01–0.10	10.16–33.33	0.25–0.9	Xu et al. (2020); Yang et al. (2019a)
Chesapeake Bay, USA	0.75–3.46	0.33–0.47		~2.8	Zimmerman and Canuel (2000)
Jiaozhou Bay, China	0.07–0.45	0.16–0.48		0.94–2.00	Dai et al. (2007)
Pearl River Estuary, China	0.88–1.15	0.03–0.05	11–18.7	1.04–2.16	Qi et al. (2010); Wang et al. (2015); Yue et al. (2007)
Zhelin Bay, China	0.15–0.75	0.02–0.15		1.83–2.98	Feng et al. (2011); Zhou et al. (2018)
Ailian Bay, China	0.58–1.21	0.06–0.17			Pan et al. (2019)
Sangou Bay, China	0.2–1.08	0.018–0.14			Xia et al. (2019)
East China Sea, China	0.46–1.23	0.08–0.2		0.2–0.9	Gu et al. (2017); Wang et al. (2014)
Yellow River estuary and adjacent shelf, China	0.08–0.91	0.01–0.11		0.1–1.1	Liu et al. (2015)
Cross River estuary system and adjacent shelf, Nigeria	0.47–5.28	0.08–0.33	9.21–18.20	0.09–0.74	Dan et al. (2019b, 2020a)
Gulf of Trieste, Adriatic Sea	0.5–1.3	0.1–0.17			Ogrinc et al. (2005)
Beppu Bay, Japan	1.8–2.9	0.21–0.37			Kuwae et al. (2007)
Bohai Bay, Bohai Sea	0.85–7.24	0.03–0.47	10–20		Gao et al. (2012); Liu et al. (2004)
Yellow Sea			7.5–18		Liu et al. (2004)
Continental Shelf of the Northern South China Sea	0.10–1.30		5.10–18.79		Yang et al. (2018)
Mondego estuary, Portugal			15.0–55.0		Coelho et al. (2004)
Gulf of Gdańsk (southern Baltic Sea)			1.75–975.17		Łukawska-Matuszewska and Bolałek (2008)
Admiralty Bay (Antarctica)			23.04–42.73		Berbel and Braga (2014)
Southeastern Arabian Sea shelf			~6.74–34.87		Sudheesh et al. (2017)
Northern Beibu Gulf			1.15–15.42		Dan et al. (2020b)
Sundarbans, India	0.64–2.28			~0.01–0.85	Dhame et al. (2016)
Izmir Bay, Turkey				0.26–1.35	Ozkan et al. (2014)

less influence of anthropogenic nutrients to limit unusual algal bloom, the contents of natural terrestrial OC and TN in sediments are expected to be higher (e.g., Dan et al., 2019a, b). In overall, differences in the levels of sedimentary OC and TN between the Daya Bay and other coastal areas may be attributed to the dominant sources of input of sedimentary OM, and factors affecting OC and TN distributions, burial, and preservation in sediments (Zimmerman and Canuel, 2000; Qi et al., 2010; Yu et al., 2010).

The N derived from marine aquaculture feedstuff and the excrement of cultured organisms was important in the Daya Bay, especially in the northern and western regions of the bay (Peng et al., 2001). The annual release of N from fish cage cultures in the Daya Bay has reached 205.6 metric tons, with 7.0% contributions to dissolved N in the water column (Qi et al., 2019). It is inevitable that N loss from cage cultures to the surrounding water does not only occur in dissolved forms (Nordvarg and Johansson, 2002), but also in particle forms (Christensen et al., 2000). About 50% and 11% of sedimentary OC and TN were reported to be derived from aquaculture, respectively, in the Mediterranean (Gulf of Castellammare, Sicily) (Sarà et al., 2004). As observed in this study, the contents of OC and TN were higher in surface sediments deposited at the inner bay regions (Fig. 3g and Fig. 3h) dominated by mariculture/aquaculture biodepositions (Fig. 3d). In agreement with the mixing model results (discussed in Section 4.1), this indicated that the biodeposit excrements generated from mariculture/aquaculture (Fig. 3d) as well marine OM (Fig. 3e) may play differential roles in the contents and distribution characteristics of OC and TN (Fig. 3g–h) in surface sediments of the Daya Bay. The higher contents of Chl-*a* in the northern inner regions (Fig. 2e) also reflect higher primary productivity. The significant relationship between TN and Chl-*a* (Fig. 4a) suggested the released N from sediments contributes to higher primary productivity and algal bloom frequently reported in the Daya Bay (Wang et al., 2008; Wu et al., 2017). Increase in dissolved N load has caused series of shifts in phytoplankton community from diatoms to dinoflagellates in recent years (Zhang et al., 2008). Higher abundance of dinoflagellate cysts was also found at the northern inner bay sediments, especially at the mariculture/aquaculture sites, due to increase in N availability, under favorable environmental factors (Li et al., 2019). As shown in Fig. 2a, the bottom water temperature was generally high at the inner bay sites, and lower at the bay mouth sites, while the opposite trend was observed for bottom water salinity (Fig. 2b). Such changes in bottom physicochemical conditions support the growth of dinoflagellates in the Daya Bay (Li et al., 2019). Although the relationship between OC and TN was statistically significant (Fig. 4a), the intercept from the linear relationship (Fig. 4b) suggested inorganic N could averagely account for ~36% of TN in surface sediments of the Daya Bay.

Interestingly, the levels of OC and TN in the surface sediments during this study are relatively lower than that previously reported by Gao et al. (2008). Although such differences may also relate to changes in primary productivity, changes in surface runoff or hydrodynamics and biogeochemical conditions in different seasons, significant degradation and/or remineralization may have been an important factor that controls OM content in recent years. Thus, the lower OC/TN ratios (<6) in sediments, especially at the eastern flank of the bay (Fig. 3c) may have partly resulted from N incorporation in sediments during OM degradation (e.g., Goñi et al., 2003), and may not exclusively imply enhanced algal contributions due to lower OC abundance (<0.5%) (Fig. 3g) even though high deposition of marine OM was found at this region according to Monte Carlo simulation results (Fig. 3e). Thus, suspended sediments enriched with inorganic N could also lower the OC/TN ratio of suspended particulate matter in the surface water. This consensus may support the lower OC/TN ratios in sediments and suspended particulate matter previously reported in the Daya Bay by Gao et al. (2008) and Ke et al. (2017), respectively. Generally, the contamination level of N in surface sediments of the Daya Bay can be considered as moderate based on the SQGs and ON index (Persaud et al., 1993; Mudroch and Azcue, 1995; Zhang et al., 2015; Yang et al., 2017) although the severity had increased at the mariculture/aquaculture sites (Table S2), and could be attributed to marine culture activities (Christensen et al., 2000; Nordvarg and Johansson, 2002; Qi et al., 2019). This was supported by the significant relationship between TN ($r^2 = 0.60$), OC ($r^2 = 0.62$) and the estimated proportions of sedimentary OM derived mariculture/aquaculture biodeposits (Fig. 4f). These correlations imply that the biodeposit excrements from marine culture activities can influence not only the distribution characteristics of OC and/or composition of sedimentary OM, but can also lead to N contamination in sediments. This finding has important implications for eutrophication and frequency of harmful algal outbreak in coastal mariculture/aquaculture bays, due to internal release potential of nutrients from surface sediments.

4.2.2. Phosphorus

As an important macronutrient, P is essentially required for primary production and energy transport through the food web. The cycling and bioavailability of P can be influenced by the biogeochemistry of C, and many reported cases of aquatic degradation and alteration of global biogeochemical cycles in recent years have been linked to anthropogenic P load (Jickells et al., 2014). The enrichment of TP in sediments can be used to evaluate the extent of anthropogenic P pollution in aquatic environments (Persaud et al., 1993; Mudroch and Azcue, 1995; Zhang et al., 2016; Yang et al., 2017). Generally, when TP load exceeds 600 mg/kg in coastal sediments, it would pose ecological risk in aquatic environment due to its efflux potential from sediment into the overlying water under reducing conditions (Mudroch and Azcue, 1995; Berbel et al., 2015; Dan et al., 2020a, b). The narrow range and pollution index values of ~1.7 to 2-fold lower than the lowest P pollution threshold of 600 mg/kg, and ~6 to 7-fold lower when compared to the severe P pollution threshold of 2000 mg/kg (Table S2) as observed in this study generally indicated that surface sediments in the Daya Bay are unpolluted by P. The range of sedimentary TP in this study is also lower when compared to the levels reported for other coastal marine environments with or without mariculture/aquaculture such as the Cross River Estuary and adjacent shelf (Dan et al., 2020a), Pearl River Estuary (Yue et al., 2007), Mondego estuary in Portugal (Coelho et al., 2004), and southeastern Arabian Sea shelf (Sudheesh et al., 2017) among others (Table 1). Except for the Cross River estuary and adjacent shelf (Dan et al., 2020a), sources and enrichment of P in many other cited coastal marine systems have been linked to increasing anthropogenic activities involving agriculture fertilizer application and sewage discharge (Table 1). Moreover, other factors such as the biogeochemical complexation of P with Fe and Al oxides under oxidative conditions usually result in the enrichment of P in sediments (Yang et al., 2018, 2019a, b; Dan et al., 2020a). Thus, differences in the levels of sedimentary TP between the Daya Bay and other coastal marine systems may be dependent on factors such as anthropogenic P emissions, sources of P and biogeochemical/physical processes affecting P cycling, availability, and enrichment in sediments.

Recent report has shown that the concentrations of dissolved P in surface water of the Daya Bay have remarkably decreased in recent years, and was partly attributed to the implementation of phosphate detergent ban in Shenzhen in October 1999, and although the dissolved P trend has been decreasing in recent decades, its concentrations in surface water of the Daya Bay is generally higher than the threshold value for phytoplankton growth (Wu et al., 2017). Earlier study had reported changes in nutrient structure from N-limitation to P-limitation, which resulted in the proportional changes and diversity of dinoflagellates in phytoplankton assemblage since 1990s (Zhang et al., 2008). All these findings partly imply that there is a strong P coupling cycling between surface water and benthic sediment in the Daya Bay. The ban of phosphate detergent may have slightly contributed to the reduced P content in the water column. The P released from fish cages in the dissolved phase together with an efficient regeneration and/or release of different P forms from sediments to maintain the surface water

productivity may have also contributed to lower TP content in the surface sediments. The significant positive correlation between TP and sand (Fig. 4a) suggested that portions of sedimentary TP, especially at the central and southeast regions of the bay (Fig. 3i) may be dominantly bound to detrital apatite. This is because apatite P is usually found in close association with minerals such as quartz and feldspar that are the major components of coarse sandy sediments with larger particle sizes, small SSA and lower OC contents (Meng et al., 2014). However, the lower abundance of sandy sediments (<10% by average of the sediment texture types), suggested that detrital apatite P may be a relatively minor component of sedimentary TP in the Daya Bay. Previous study indicated that dissolved inorganic P had the highest flux at the central regions of the bay and diffused from the water column to the sediment (Zhang et al., 2019). This may partly account for higher abundance of P at the central part of the bay through simple adsorption on sediment (Fig. 3h). As previously mentioned, P can be released and then transported to the overlying water to enhance production cycle, especially when the DO content of bottom water or porewater is low, or under anoxic or suboxic conditions during sedimentary OM degradation. As shown in Fig. 4a, negative relationships were found among TP, Fe_2O_3, and Al_2O_3, and together with the lower DO levels in bottom water implies that Fe and Al oxides are less likely to accumulate P in surface sediments of the Daya Bay. Thus, the lower TP contents, especially at the northeastern and western regions may have resulted from significant loss of P relative to OC in sediments during OM degradation and/or reductive release from metallic oxides. However, more studies are suggested to clarify the underlying mechanisms influencing the speciation of both inorganic and organic P in the Daya Bay. Moreover, further reduction of anthropogenic P load is important to curb the potential increase in eutrophication and frequency of harmful algal outbreak in the Daya Bay due to efficient recycling potential of P in surface sediments.

4.2.3. Biogenic silica

Silica is widely assimilated by diatoms, and later being transformed into particulate amorphous silicon referred to as BSi (Sospedra et al., 2018). According to Zhao et al. (2019b), concentrations of particulate BSi in the Daya Bay are significantly higher than values reported in the South China Sea (Cao et al., 2012; Yang et al., 2015b), and the highest abundance usually occurs during summer season when diatom population is highest in the Daya Bay. In this study, the contents of BSi in almost all the investigated sited were >1%, with the least abundance (0.94%) occurring at the mariculture site S1 (Table S1, Fig. 3j). As presented in Table 1, the range of BSi in surface sediments of the Daya Bay is higher than reported values for several coastal marine systems (e.g., Ozkan et al., 2014; Wang et al., 2014; Liu et al., 2015; Dhame et al., 2016; Gu et al., 2017; Dan et al., 2019b). Moreover, it is also higher than reported values for the Maowei Sea (Xu et al., 2020), which is one of the most intensive mariculture bays in China, but lower than reported values for the Chesapeake Bay (Zimmerman and Canuel, 2000) and the Pearl River Estuary (Wang et al., 2015). Normally, cultured shellfish do not require external feed but only depend on nutrients, phytoplankton and zooplanktons for growth and reproduction, but farmed fish requires external feed, which contains vital nutrients. Selective feeding on plankton such as diatoms by the cultured shellfishes may reduce the proportion of marine-diatoms based OM, especially in coastal areas where mariculture/aquaculture is intensely practiced. Algal bloom frequently occurs in most of these bays including the Daya Bay (e.g., Gu et al., 2017; Wu et al., 2017; Li et al., 2019), and after the bloom, the silicifiers may sink faster than other algae, and slow dissolution may limit the diffusion of Si back to the water column, which would eventually result in the net accumulation of BSi in sediments. This may become a problem in bays where other nutrients such as N and P are efficiently recycled. For example, laboratory simulation studies by Zheng et al. (2001) indicated that rapid degradation of ON causes efficient recycling of N in the Daya Bay. Moreover, efficient N remineralization was suggested to be the key factors for high diatom production in the Daya Bay (Zhao et al., 2019b). Previous study also indicated that eutrophication enhances the bio-transformation of dissolved Si to BSi (Pastuszak et al., 2003). Thus, more sinking of BSi to the sediment can occur due to efficient recycling of other nutrients, and sustained eutrophication as well. This can also result in more BSi production and longer accumulation of BSi than N and P. Higher fluxes of BSi in the Daya Bay than in the open South China Sea (Zhao et al., 2019b) clearly indicated that BSi is efficiently buried in the Daya Bay, partly resulting in elevated contents in the surface sediments during this study compared to other coastal marine systems (Table 1).

The sinking of diatoms debris due to its ballast effect increases the deposition of particulate OC from the water column, and this represent an important factor for evaluating the efficiency of marine biological pumps (Nelson et al., 1995; Guinder et al., 2015), and also enhances the strong coupling between OC and BSi as observed in sediments (Wang et al., 2014 and references therein). The higher abundance of BSi in sediments deposited in the north central and northeastern regions of the bay (Fig. 4j) may have partly resulted from increased BSi production due to the abundance of nutrients in the surface water (Zhao et al., 2019b and references therein). The similarity of the site with the highest abundance of BSi and OC as observed in this study (Table S1, Fig. 3g and j) would suggest a strong coupling between BSi production and OC cycling. However, the relationship between BSi and OC was not statistically significant (Fig. 4a) as also reported in other study areas (e.g., Dhame et al., 2016). The lack of statistically significant relationship between BSi and OC may probably have resulted from additional source of BSi, or loss of OC relative to BSi in the surface sediments among several other factors. The positive relationship between BSi and bottom water salinity (Fig. 4a), suggested that lithogenic BSi may have been transported from the northern South China Sea into the bay. This may have also partly accounted for the slightly elevated abundance of BSi (>1.4%) in the southern region compared to the northwestern and western regions of the bay (Fig. 3j). Phytoliths are produced by higher plants, and together with diatoms are important sources of BSi in surface sediments (Ran et al., 2016; Dan et al., 2019b). Previous studies have indicated that materials from phytoliths are less sensitive to dissolution than those from diatoms (Saccone et al., 2006; Meunier et al., 2014). Thus, higher BSi values at the bay mouth sites can be partly attributed to the supply of phytoliths from higher plants during the transport and deposition of terrestrial OM into the Daya Bay. In addition, the coupling between BSi and OC may have been influenced by contributions of sedimentary OM from other plankton species such as dinoflagellates or cyanobacteria due to possible changes in N/P and Si/N ratios in the water column. The molar BSi/OC ratio in surface sediments of the Daya Bay during this study ranged from 0.42 to 2.08 with an average of 0.87 ± 0.43, and are generally higher than the Redfield ratio (Si/C ratio), while BSi/TN ratio ranged from 3.3 to 10.29 with an average of 7.12 ± 2.08. These ratios do not only implied that BSi is relatively abundant, with indication that marine/photosynthetic organisms contribute more to sedimentary OM, but also suggested that both OC and TN may be rapidly decomposed and remineralized compared to BSi in surface sediments of the Daya Bay. In general, the differences between BSi contents and spatial distributions in sediments of the Daya Bay compared to other coastal marine systems with or without mariculture/aquaculture may be dependent on the feeding selectivity of shellfish on diatoms, the level of primary productivity in relation to nutrient bioavailability, sinking efficiency of BSi from the water column to the sediment, external sources of BSi, and differences in the biogeochemical factors enhancing BSi accumulation, preservation and/or dissolution rates in the surface sediments (more details in Section 4.3 below).

4.3. Loading and preservation status of OC, TN, TP, and BSi

The primary driving mechanism of C transition from the active surficial C cycle to the slower geologic C cycle is the preservation in coastal

marine sediments (Keil, 2017). The abundance of OC may influence the levels TN and TP contents since OM can control the sorption/release of nutrients in sediments. The association or loading of OC on sediments surface (OC/SSA) can be used to characterize its preservation status in coastal marine environments (Blair and Aller, 2012). This is because OC to some extent can stabilize against decay within aggregates of fine-grained sediments (Mead and Goñi, 2008) due to limited exposure to exoenzymes. Generally, the OC/SSA loadings occur in the range of 0.4–1.0 mg OC/m^2 in sediments deposited in rivers and coastal environments (Blair and Aller, 2012). High OC/SSA loadings (>1 mg OC/m^2) are often found in sediments deposited in less turbulent coastal marine system, characterized by high productivity, eutrophication, and lower DO levels in bottom water (Bianchi et al., 2018). This is because weak hydrodynamic conditions tend to protect aggregates, while lower DO in the bottom water limits animal gut passage and/or bioturbation particles, which eventually lead to the preservation of aggregates (Zimmerman and Canuel, 2000). Lower OC/SSA loadings (<0.4 mg OC/m^2) have been reported in coastal marine systems with either high or low sedimentation rate, and where the surface sediments are frequently remobilized and reoxygenated (Aller and Blair, 2006; Yao et al., 2014). In general, OC/SSA loadings >1 mg OC/m^2 indicated less mineralization and high preservation efficiency, while lower OC/SSA loadings <0.4 mg OC/m^2 indicated significant remineralization and low preservation efficiency of OC in sediments (Blair and Aller, 2012). Thus, this general paradigm, which defines the adsorption or aggregation is used to discuss the loading characteristics and preservation status of bulk biogenic elements (OC, TN, TP, and BSi) in surface sediments of the Daya Bay.

Generally, the hydrodynamic condition in the Daya Bay is relatively weak with high deposition of fine-grain sediments (78–100%) (Gao et al., 2008), and the sedimentation rate is relatively high (~0.9 cm^2/yr on average) (Han, 1995; Gao et al., 2008). The level of DO in bottom water was generally low (<4 mg/L) as found in this study (Section 3.1; Fig. 2c). Thus, it is expected that these environmental conditions in addition to other factors previously mentioned in preceding paragraphs perhaps would increase the loading and preservation of OC and other biogenic elements in sediments of the Daya Bay. The loadings of biogenic elements in the surface sediments are presented in Table S2. The OC/SSA loadings ranged from 0.3 to 1.25 mg OC/m^2 (average: ~0.7 mg OC/m^2), and were generally <1 mg OC/m^2 in many of the investigated sites (Fig. 5a), and decreased exponentially with increasing SSA (Fig. S2a). The highest loading occurred at the northern bay site S1, which situates in one of the intensive mariculture/aquaculture areas of the bay that often experience eutrophication (Fig. 5a and Fig. 6a). The lowest concentration of DO in bottom water was also recorded at this site, and both silt and clay were the only sediment type in site S1. (Table S1; Fig. 2c), which appeared to favour the preservation and lower mineralization of OC at site S1 compared to other studied sites. In general, the OC/SSA loadings in the Daya Bay were higher than those reported for the Changjiang Estuary and adjacent shelf (Yao et al., 2014), and Amazon shelf (Aller and Blair, 2006), but were in a medium range compared to the loadings reported from the Papua New Guinea margin (Goñi et al., 2008) (Fig. 6a). This suggests that sedimentary OC in the Daya Bay has undergone intermediate to efficient remineralization, which varies across the bay compared with efficient remineralization reported for the mobile mud deposits that are frequently remobilized and reoxygenated irrespective of high sedimentation rates (Aller and Blair, 2006). This is clearly depicted by the relationship between $\delta^{13}C^{*}$OC/SSA and OC/SSA (Fig. 6b). There is a significant loss of OC with decreasing of OC/SSA, and the isotopic composition of OC lost through remineralization is −20.8‰ (geometric mean slope) compared to −19.4‰ reported for the Changjiang Estuary and adjacent shelf, and −18.4‰ and −28.5‰ reported for French Guiana mudbank deposits and Amazon shelf, respectively (Fig. 6b). The isotopic signature of net OC loss (i.e., δ^{13}C of −20.8‰) from surface sediments of the Daya Bay is within the range reported for both mariculture/

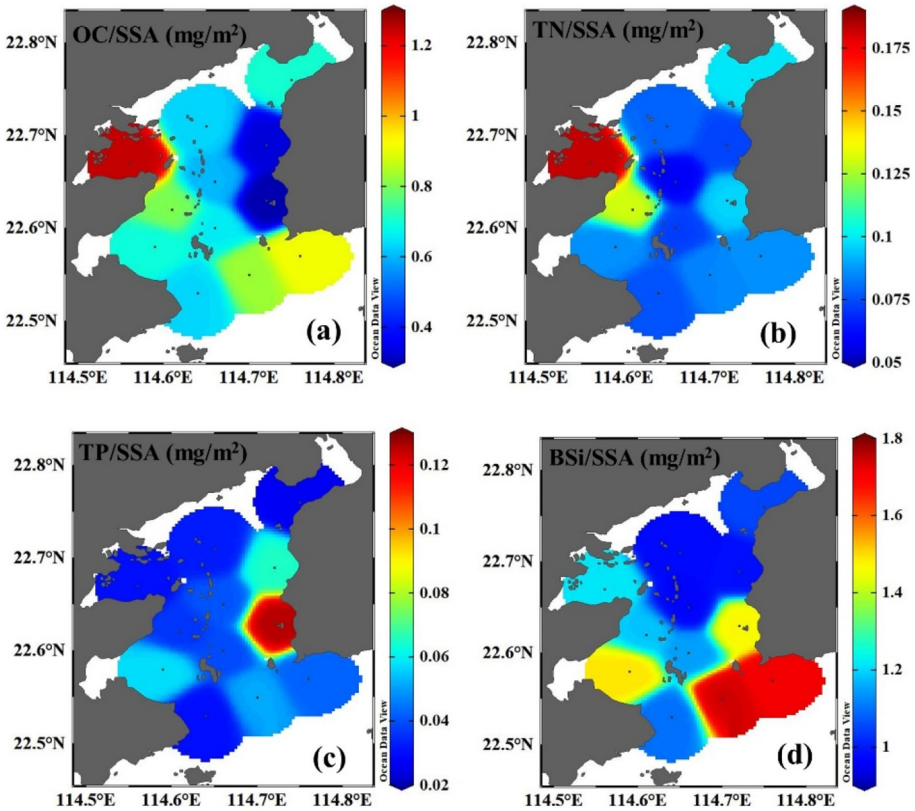


Fig. 5. Spatial distributions of OC, TN, TP, and BSi loadings in surface sediments of the Daya Bay.

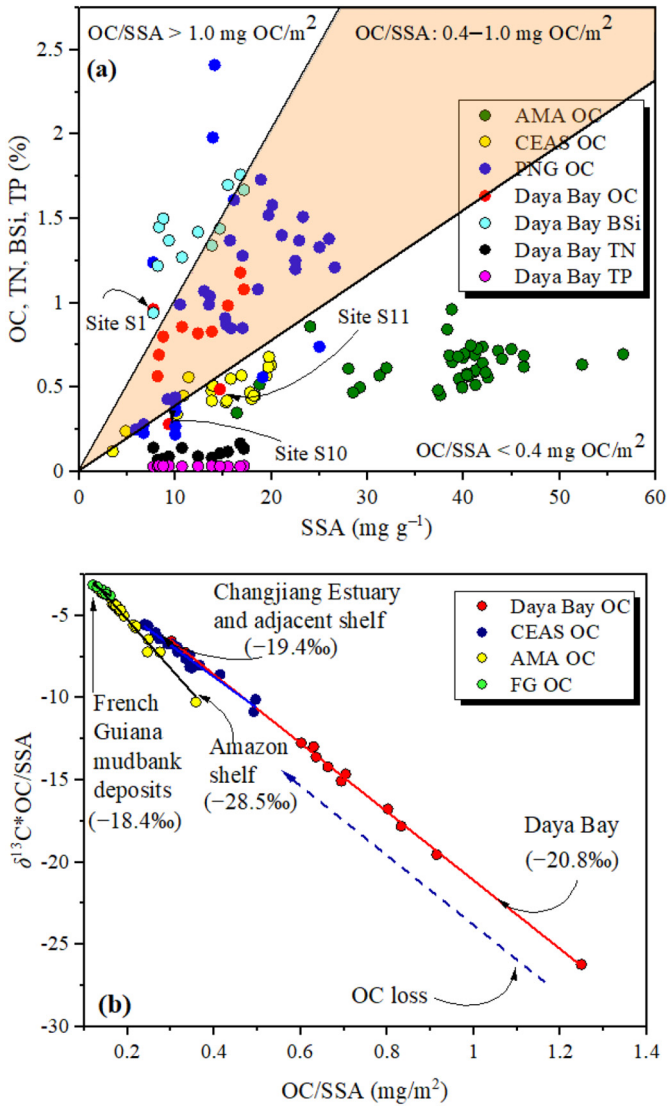


Fig. 6. (a) Relationship of OC versus SSA in surface sediments of the Daya Bay compared with the Changjiang Estuary and adjacent shelf (CEAS) (Yao et al., 2014), Amazon shelf (AMA) (Aller and Blair, 2006), and Papua New Guinea (PNG) margin (Goñi et al., 2008), and preservation status of BSi, TN, and TP in Daya Bay. (b) The reference sites (S1, S10, and S11) are only applicable to OC loadings in the Daya Bay. (b) Relationship between $\delta^{13}C^{*}OC/SSA$ and OCSSA in surface sediments of the Daya Bay depicting the net loss of OC compared to Changjiang Estuary and adjacent shelf (Yao et al., 2014), Amazon shelf and French Guiana mudbank deposits (Aller and Blair, 2006).

aquaculture biodeposition and marine OM, and together with the fractional estimates (discussed in Section 4.1) and sedimentation rate, it is suggested that the burial efficiency of OC from these sources will probably be <20%, respectively in the Daya Bay. This is because the increase in the intensity of aquaculture farming and density may not necessarily favour the preservation efficiency as the sequestration of OC via mariculture/aquaculture and high productivity beyond the ecological balance may cause a proliferation of bacteria, which could efficiently convert fixed OC into CO_2. High bacterial growth may lead to more lower DO levels, which could eventually lead to other environmental problems such as hypoxia and death of aquatic organisms.

The loading ratio (~0.06–0.18 mg TN/m^2) of TN although slightly elevated than the ON/SSA (<0.02–0.1 mg ON/m^2) reported by Aller and Blair (2006) for the Amazon shelf, suggested that there is a highly efficient net decomposition and/or remineralization of different species or forms of N (inorganic and organic) in the Daya Bay sediments (Fig. 6a). Just like OC, the TN/SSA loadings decreased exponentially with increasing SSA (Fig. S2b). The highest N loading of ~0.18 mg TN/m^2, which is far less than that of OC (1.25 mg OC/m^2) also occurred at site S1 (Fig. 5b), implying that N has a high turnover rate than OC in the Daya Bay. In fact, it is possible that during decomposition and remineralization of OM, the released N from the sediments would increase the eutrophication and algal bloom, which is frequently reported in surface water of the Daya Bay (Zhang et al., 2008; Li et al., 2019). The TP loadings ranged from ~0.02 to 0.04 mg TP/m^2, much lower than TN and OC loadings (Fig. 5c), and also decreased exponentially with increasing SSA (Fig. S2c). Efficient remineralization of sedimentary OM usually results in lower OC abundance (<1.0%) and thus account for lower OC/SSA loadings in sediments (Aller and Blair, 2006). Moreover, preferential loss of labile P fractions relative to OC during OM decomposition has been reported in many coastal marine systems (Meng et al., 2014; Dan et al., 2020a, b, and references therein). The OC levels in sediments of the Daya Bay were generally <1% during this study, and slightly lower than previously reported (Gao et al., 2008) (Table 1). Therefore, despite relatively high sedimentation rate, the lower OC levels (<1%), low OC/SSA loadings (<1.0 mg OC/m^2 at almost all the studied sites) and lower TP/SSA loadings than OC/SSA and TN/SSA (Fig. 6a) indicated significant loss of P during OC degradation, remineralization and/or remobilization (Blair and Aller, 2012).

The loadings of BSi were relatively high (0.9–1.7 mg BSi/m^2), and exceeded 1.0 mg BSi/m^2 in most of the studied sites except for the northern mariculture sites (Fig. 5d and Fig. 6a). The slightly lower loadings of BSi in the northern regions of the bay (irrespective of the finer sediment accumulation) may have been influenced by selective feeding of diatoms by the cultured species or dissolution of diatoms cells in sediments relative to OC. Just like OC, TN, and TP, the BSi/SSA loadings decreased exponentially with increase in SSA (Fig. S2d). The high BSi loadings and higher BSi/OC, BSi/TN, BSi/TP ratios as observed in this study indicated that C, N and P are rapidly recycled, while BSi is well preserved in sediments of the Daya Bay (Fig. 6a). The content of BSi in sediments has been found to have a close link with biosiliceous productivity of the overlying water. The growth of diatoms is also controlled by P supply as the enrichment of P in surface water increases BSi production, provided dissolved Si in the water column is not limiting (Schelske et al., 1986). P is often the limiting nutrient for phytoplankton growth in many coastal marine systems (e.g., Dan et al., 2019a), and because large sedimentary reserves and concomitant internal source of P from sediments may become a common problem in eutrophic bays, any mechanism that accelerates the release of P from sediments into the overlying water may contribute to eutrophication pressure in coastal waters. On the other hand, if the cycling of Si is relatively stable (i.e., if the input of Si balances the outflow and/or by the burial of BSi in sediments), the increased loading of other macronutrients (N and P) required by phytoplankton, may directly favour the outbreak of other phytoplankton groups at the expense of diatoms. Under eutrophication and when dissolved Si is limiting, silicate may increase the competitive desorption of P from Al–Fe oxides at the sediment-water interface through ion-exchange mechanisms (Tallberg, 2000). This is because the surfaces of BSi particles in sediments are commonly coated and enriched quickly with Al and Fe oxides (e.g., Rickert et al., 2002 and references therein). The rapid recycling of P as shown by the low TP/SSA loadings, and higher BSi/TP ratios more than the Redfield ratio partly supports more BSi production and accumulation as observed in this study. The BSi loadings in this study suggested the debris from diatoms are well preserved in the Daya Bay, and that BSi-based proxies could be used for paleo-productivity reconstruction in the study area. However, high accumulation of BSi in sediments could induce adverse dissolved Si limitation perturbed by eutrophication in the bay. Studies have shown that BSi is usually involved in the formation of aluminosilicate phases by reverse-weathering reactions during early diagenesis in sediments (Michalopoulos and Aller, 2004; Wang et al., 2015). In this study, both the Al and Fe oxides were higher in the regions dominated by fine-grained sediments (Fig. 3j–k), and had significant positive correlations with clay ($p < 0.001$) and SSA ($p < 0.01$), and positive correlation

(although not statistically significant) with BSi (Fig. 4a). Strong relationship between BSi and the Al and Fe oxides would significantly lower silica solubility or dissolution rates (van Cappellen et al., 2002). The positive correlations among BSi, Al_2O_3, and Fe_2O_3 (Fig. 4a) suggested reverse-weathering reactions mechanisms during early diagenesis may contribute to BSi preservation in sediments of the Daya Bay. The pH range of 7.2–8.5 in the marine environment decreases the surface density of silanol groups (van Cappellen et al., 2002), which can result in a slower dissolution kinetics, and decreases the capacity of BSi surfaces to build up surface charge for attachment of metal ligands at the sediment-water interface. Salinity can also influence BSi dissolution rates due to the presence of cations that have catalytic effects on the hydrolysis of siloxane bonds on Si surface (Loucaides et al., 2008). Thus, salinity fluctuation can have an indirect influence on BSi dissolution by influencing the microbial respiration rates (Cunha et al., 2000). Alkaline pH and higher salinity have been found to increases BSi dissolution rates by a factor of 5 from freshwater to saltwater (Loucaides et al., 2008), and this enables more BSi recycling. As mentioned earlier in this study, the bottom water of Daya Bay is highly saline (salinity: 32.18–34.49) and the surface sediments are alkaline (pH: 8.64–9.42). Thus, these factors provide suitable conditions for BSi recycling. However, the higher BSi loadings, especially in sediments with relatively higher amount of sandy textures, lower SSA (Fig. 2g–h and Fig. 5d) and poor correlations with silt and clay (Fig. 4a), suggested the accumulation, preservation, and distributional characteristics of BSi in surface sediments are controlled by complex processes in the Daya Bay. Therefore, further studies on the biogeochemical cycling of BSi are required to clarify the underlying mechanisms behind its enrichment and loading in surface sediments of the Daya Bay.

5. Conclusion

Long-term preservation of OC in coastal marine environments is one of the reasons for research on marine C cycle to understand the role and feedback between climate change and the global C cycle. This study showed that sedimentary OM derived from mariculture/aquaculture biodeposits and influencing factors on the distribution characteristics and preservation of OM could be studied using the $\delta^{13}C$ and $\delta^{15}N$, and OC/TN ratios in a coastal bay predominated by marine sedimentary OM. The percentage proportions of sedimentary OM from mariculture biodeposit excrements were higher at the northern bay region dominated by the mariculture/aquaculture cages and/or rafts, while the distribution of sedimentary OM originating from marine photosynthetic organisms showed an increasing trend toward the open South China Sea. The abundance of terrestrial OM was the least in the Daya Bay. The estimated proportions of sedimentary OM were the integrated results of both natural and anthropogenic processes that influence the biogeochemical cycling of biogenic elements, primary production of the overlying water and preservation of OC, and other biogenic elements in sediments. The contents and distribution characteristics of OC, TN, TP, and BSi in surface sediments were directly and/or indirectly influenced by mariculture/aquaculture activities, marine productivity, and other environmental factors. The presence of mariculture/aquaculture structures, high primary productivity, lack of major rivers draining into the bay, weaker hydrodynamics condition, and the presence of small island structures, all favoured the deposition of fine-grained sediments (>77%), which should at least provide an ideal condition for the preservation of OC. However, the overall lower OC/SSA, TN/SSA, and TP/SSA loadings, and decrease in the loadings of biogenic element with increasing SSA indicated that sedimentary OM has undergone significant degradation and remineralization of OC, as well as significant loss of P relative to OC. The contamination level of N in sediments varied between moderate to severe, indicating that increased injection of marine aquaculture excrements, especially in bays with weak hydrodynamic conditions could lead to deterioration and eutrophication of the water body due to the potential of surface sediment as an internal source of biogenic elements in coastal marine systems. The higher BSi/SSA loadings indicated that the preservation of BSi is somewhat related to reverse weathering reaction mechanisms, and that BSi-based proxies could be used for paleo-productivity reconstruction in the Daya Bay. High preservation of BSi may also induce adverse dissolved Si limitation in the surface water perturbed by eutrophication. Environmental conditions such as high accumulation of fine-grained sediments with higher SSA, lower DO levels in the bottom water, relatively high sedimentation rates, weaker hydrodynamics could control the contents of biogenic elements but do not generally translate to high burial and preservation of OC and other biogenic elements as shown in this study compared to other coastal ecosystems. However, biogeochemical processes endemic to each of the biogenic elements may exert a first order control on the preservation, which further illustrated that the conditional degradation character is different for sedimentary OM from various sources, and in different coastal marine systems. This study has important environmental significance for the ecological status of coastal eutrophic bays, especially those used for mariculture/aquaculture, and global C cycling and budgets at large.

CRediT authorship contribution statement

Solomon Felix Dan: Conceptualization, Writing – original draft, Writing – review & editing. **Shengyong Li:** Writing – original draft, Writing – review & editing. **Bin Yang:** Methodology, Writing – review & editing. **Dongyang Cui:** Methodology, Investigation. **Zhiming Ning:** Investigation. **Haifang Huang:** Formal analysis. **Jiaodi Zhou:** Formal analysis. **Jian Yang:** Methodology, Investigation.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Acknowledgement

We sincerely thank our colleagues from the marine biogeochemistry laboratory for their help in field sampling. This work was supported by grants from the National Natural Science Foundation of China (Nos. 41706083 and 41606099), the Guangxi Natural Science Foundation, Chinas (No. 2018GXNSFDA28102), the Scientific Research Startup Fund of Beibu Gulf University (No. 2020KYQD01), and the Open Fund of Key Laboratory of Urban Land Resources Monitoring and Simulation, Ministry of Natural Resources (No. KF-2019-04-002).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.146899.

References

Aller, R.C., Blair, N.E., 2006. Carbon remineralization in the Amazon-Guianas tropical mobile mudbelt: a sedimentary incinerator. Cont. Shelf Res. 26, 2241–2259.
Aspila, K.I., Agemian, H., Chau, A.S.Y., 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst 101, 187–197.
Berbel, G.B.B., Braga, E.S., 2014. Phosphorus in Antarctic surface marine sediments chemical speciation in Admiralty Bay. Antarct. Sci. 26, 281–289.
Berbel, G.B.B., Favaro, D.I.T., Braga, E.S., 2015. Impact of harbour, industry and sewage on the phosphorus geochemistry of a subtropical estuary in Brazil. Mar. Pollut. Bull. 93, 44–52.
Bianchi, T.S., 2011. The role of terrestrially derived organic carbon in the coastal ocean: a changing paradigm and the priming effect. Proc. Natl. Acad. Sci. 108, 19473–19481.
Bianchi, T.S., Cui, X., Blair, N.E., Burdige, D.J., Eglinton, T.I., Galy, V., 2018. Centers of organic carbon burial and oxidation at the land-ocean interface. Org. Geochem. 115, 138–155.
Blair, N.E., Aller, R.C., 2012. The fate of terrestrial organic carbon in the marine environment. Annu. Rev. Mar. Sci. 4, 401–423.
Brandes, J.A., Devol, A.H., 2002. A global marine-fixed nitrogen isotopic budget: implications for Holocene nitrogen cycling. Glob. Biogeochem. Cycles 16, 1–14.

Cai, J.G., Xu, J.L., Yang, S.Y., Bao, Y.J., Lu, L.F., 2006. The fractionation of an argillaceous sediment and difference in organic matter enrichment in different fractions. Geol. J. China Univ. 12, 234–241.

Cao, Z., Frank, M., Dai, M., Grasse, P., Ehlert, C., 2012. Silicon isotope constraints on sources and utilization of silicic acid in the northern South China Sea. Geochim. Cosmochim. Acta 97, 88–104.

van Cappellen, P., Dixit, S., van Beusekom, J., 2002. Biogenic silica dissolution in the oceans: reconciling experimental and field-based dissolution rates. Glob. Biogeochem. Cycles 16, 10–23.

Caraco, N.F., Lampman, G., Cole, J.J., Limburg, K.E., Pace, M.L., Fisher, D., 1998. Microbial assimilation of DIN in a nitrogen rich estuary: implications for food quality and isotope studies. Mar. Ecol. Prog. Ser. 167, 59–71.

Chen, J., Liu, S., Deng, J., Chen, Z., Lu, P., Li, L., 2014. Variation characteristics of wet deposition of nitrogen in Daya Bay, Huizhou. J. South China Norm. Univ. 2, 479–482 (in Chinese with English abstract).

Chen, Z., Xu, S., Qiu, Y., 2015. Using a food-web model to assess the trophic structure and energy flows in Daya Bay, China. Cont. Shelf Res. 111, 316–326.

Christensen, P.B., Rysgaard, S., Sloth, N.P., Dalsgaard, T., Schwaerter, S., 2000. Sediment mineralization, nutrient fluxes, denitrification and dissimilatory nitrate reduction to ammonium in an estuarine fjord with sea cage trout farms. Aquat. Microb. Ecol. 21, 73–84.

Coelho, J.P., Flindt, M.R., Jensen, H.S., Lillebø, A.I., Pardal, M.A., 2004. Phosphorus speciation and availability in intertidal sediments of a temperate estuary: relation to eutrophication and annual P-fluxes. Estuar. Coast. Shelf Sci. 61, 583–590.

Cole, M.L., Valiela, I., Kroeger, K.D., Tomasky, G.L., Cebrian, J., Wigand, C., Carvalho da Silva, M.H., 2004. Assessment of a $\delta^{15}N$ isotopic method to indicate anthropogenic eutrophication in aquatic ecosystems. J. Environ. Qual. 33, 124–132.

Conley, D.J., Carstensen, J., Vaquer-Sunyer, R., Duarte, C.M., 2009. Ecosystem thresholds with hypoxia. Hydrobiologia 629, 21–29.

Cunha, M.A., Almeida, M.A., Alcantara, F., 2000. Patterns of ectoenzymatic and heterotrophic bacterial activities along a salinity gradient in a shallow tidal estuary. Mar. Ecol. Prog. Ser. 204, 1–12.

Dai, J., Song, J., Li, X., Yuan, H., Li, N., Zheng, G., 2007. Environmental changes reflected by sedimentary geochemistry in recent hundred years of Jiaozhou Bay, North China. Environ. Pollut. 145, 656–667.

Dan, S.F., Liu, S.M., Udoh, E.C., Ding, S., 2019a. Nutrient biogeochemistry in the Cross River estuary system and adjacent Gulf of Guinea, south East Nigeria (West Africa). Cont. Shelf Res. 179, 1–17.

Dan, S.F., Liu, S.M., Yang, B., Udoh, E.C., Umoh, U., Ewa-Oboho, I., 2019b. Geochemical discrimination of bulk organic matter in surface sediments of the Cross River estuary system and adjacent shelf, South East Nigeria (West Africa). Sci. Total Environ. 678, 351–368.

Dan, S.F., Liu, S.M., Yang, B., 2020a. Geochemical fractionation, potential bioavailability and ecological risk of phosphorus in surface sediments of the Cross River estuary system and adjacent shelf, South East Nigeria (West Africa). J. Mar. Syst. 201, 103244.

Dan, S.F., Lan, W., Yang, B., Han, L., Xu, C., Lu, D., Kang, Z., Huang, H., Ning, Z., 2020b. Bulk sedimentary phosphorus in relation to organic carbon, sediment textural properties and hydrodynamics in the northern Beibu Gulf, South China Sea. Mar. Pollut. Bull. 155, 111176.

DeMaster, D.J., 1981. The supply and accumulation of silica in the marine environment. Geochim. Cosmochim. Acta 45, 1715–1732.

Dhame, S., Kumar, A., Ramanathan, A., Chaudhari, P., 2016. Elemental composition, distribution and control of biogenic silica in the anthropogenically disturbed and pristine zone inter-tidal sediments of Indian Sundarbans mangrove-estuarine complex. Mar. Pollut. Bull. 111, 68–85.

Feng, J., Wang, Z.H., Gu, Y.G., Zhang, K., 2011. The distribution of biogenic elements in surface sediments from aquacultural areas of Zhelin Bay. J. Jinan Univ. 32, 69–73 (in Chinese).

Gao, X.L., Chen, S.Y., Long, A., 2008. Composition and sources of organic matter and its solvent extractable components in surface sediments of a bay under serious anthropogenic influences: Daya Bay, China. Mar. Pollut. Bull. 56, 1066–1075.

Gao, X.L., Yang, Y., Wang, C., 2012. Geochemistry of organic carbon and nitrogen in surface sediments of coastal Bohai Bay inferred from their ratios and stable isotopic signatures. Mar. Pollut. Bull. 64, 1148–1155.

Goñi, M.A., Teixeira, M.J., Perkey, D.W., 2003. Sources and distribution of organic matter in a river-dominated estuary (Winyah Bay, SC, USA). Estuar. Coast. Shelf Sci. 57, 1023–1048.

Goñi, M.A., Monacci, N., Gisewhite, R., Crockett, J., Nittrouer, C., Ogston, A., Alin, S.R., Aalto, R., 2008. Terrigenous organic matter in sediments from the Fly River delta-clinoform system (Papua New Guinea). J. Geophys. Res. Earth Surf. 113, F01S10.

Goñi, M.A., O'Connor, A.E., Kuzyk, Z.Z., Yunker, M.B., Gobeil, C., Macdonald, R.W., 2013. Distribution and sources of organic matter in surface marine sediments across the north American Arctic margin. J. Geophys. Res. Oceans 118, 4017–4035.

Gu, Y.G., Ouyang, J., Ning, J.J., Wang, Z.H., 2017. Distribution and sources of organic carbon, nitrogen and their isotopes in surface sediments from the largest mariculture zone of the eastern Guangdong coast, South China. Mar. Pollut. Bull. 120, 286–291.

Guinder, V.A., López-Abbate, M.C., Berasategui, A.A., Negrin, V.L., Zapperi, G., Pratolongo, P.D., Severini, M.D.F., Popovich, C.A., 2015. Influence of the winter phytoplankton bloom on the settled material in a temperate shallow estuary. Oceanologia 57, 50–60.

Han, W.Y., 1995. Chemistry in Daya Bay. In: Han, W.Y. (Ed.), Marine Chemistry of the Nansha Islands and South China Sea. China Ocean Press, Beijing, China, pp. 60–103.

Hu, J.F., Peng, P.A., Jia, G.D., Mai, B.X., Zhang, G., 2006. Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China. Mar. Chem. 98, 274–285.

Jickells, T.T., Andrews, J.E., Parkes, D.J., Suratman, S., Aziz, A.A., Hee, Y.Y., 2014. Nutrient transport through estuaries: the importance of the estuarine geography. Estuar. Coast. Shelve Sci. 150, 215–229.

Joye, S.B., Mazzotta, M.L., Hollibaugh, J.T., 1996. Community metabolism in microbial mats: the occurrence of biologically-mediated iron and manganese reduction. Estuar. Coast. Shelf Sci. 43, 747–766.

Ke, Z., Tan, Y., Huang, L., Zhao, C., Jiang, X., 2017. Spatial distributions of $\delta^{13}C$, $\delta^{15}N$ and C/N ratios in suspended particulate organic matter of a bay under serious anthropogenic influences: Daya Bay, China. Mar. Pollut. Bull. 114, 183–191.

Keil, R., 2017. Anthropogenic forcing of organic carbon and calcium carbonate preservation in marine sediments. Annu. Rev. Mar. Sci. 9, 151–172.

Kuwae, M., Yamaguchi, H., Tsugeki, N.K., Miyasaka, H., Fukumori, K., Ikehara, M., Genkai-Kato, M., Omori, K., Sugimoto, T., Ishida, S., Takeoka, H., 2007. Spatial distribution of organic and sulfur geochemical parameters of oxic to anoxic surface sediments in Beppu Bay in southwest Japan. Estuar. Coast. Shelf Sci. 72, 348–358.

Lamb, A.L., Wilson, G.P., Leng, M.J., 2006. A review of coastal palaeoclimate and relative sea-level reconstructions using $\delta^{13}C$ and C/N ratios in organic material. Earth Sci. Rev. 75, 29–57.

Li, X., Bianchi, T.S., Allison, M.A., Chapman, P., Mitra, S., Zhang, Z., Yang, G., Yu, Z., 2012. Composition, abundance and age of total organic carbon in surface sediments from the inner shelf of the East China Sea. Mar. Chem. 145–147, 37–52.

Li, Y., Tang, Y.N., Shen, P.P., Li, G., Tan, Y.H., 2019. Distribution of harmful dinoflagellate cysts in the surface sediments of Daya Bay of the South China Sea and their relationship to environmental factors. Int. Biodeterior. Biodegrad. 139, 44–53.

Lim, D.I., Choi, J.Y., Shin, H.H., Rho, K.C., Jung, H.S., 2013. Multielement geochemistry of offshore sediments in the southeastern Yellow Sea and implications for sediment origin and dispersal. Quat. Int. 298, 196–206.

Liu, D., Li, X., Emeis, K.C., Wang, Y., Richard, P., 2015. Distribution and sources of organic matter in surface sediments of Bohai Sea near the Yellow River Estuary, China. Estuar. Coast. Shelf Sci. 165, 128–136.

Liu, J., Yan, W., Lu, Z.C.J., 2012a. Sediment sources and their contribution along northern coast of the South China Sea: evidence from clay minerals of surface sediments. Cont. Shelf Res. 47, 156–164.

Liu, Q.X., Huang, X.P., Zhang, X., Zhang, L., Ye, F., 2012b. Distribution and sources of particulate organic carbon in the Pearl River estuary in summer 2010. Acta Ecol. Sin. 32, 4403–4412 (in Chinese).

Liu, S.M., Zhang, J., Li, D.J., 2004. Phosphorus cycling in sediments of the Bohai and Yellow Seas. Estuar. Coast. Shelf Sci. 59, 209–218.

Liu, S.M., Zhang, J., Li, R.X., 2005. Ecological significance of biogenic silica in the East China Sea. Mar. Ecol. Progr. Ser. 290, 15–26.

Liu, S.M., Hong, G.H., Zhang, J., Ye, X.W., Jiang, X.L., 2009. Nutrient budgets for large Chinese estuaries. Biogeosciences 6, 2245–2263.

Liu, Z., Zhao, Y., Colin, C., Stattegger, K., Wiesner, M.G., Huh, C.-A., Zhang, Y., Li, X., Sompongchaiyakul, P., You, C.-F., Huang, C.-Y., et al., 2016. Source-to-sink transport processes of fluvial sediments in the South China Sea. Earth Sci. Rev. 153, 238–273.

Loucaides, S., Van Cappellen, P., Behrends, T., 2008. Dissolution of biogenic silica from land to ocean: role of salinity and pH. Limnol. Oceanogr. 53, 1614–1621.

Łukawska-Matuszewska, K., Bolałek, J., 2008. Spatial distribution of phosphorus forms in sediments in the Gulf of Gdańsk (southern Baltic Sea). Cont. Shelf Res. 28, 977–990.

Luo, C., Chen, M., Xiang, R., Liu, J., Zhang, L., Lu, J., Yang, M., 2014. Modern pollen distribution in marine sediments from the northern part of the South China Sea. Mar. Micropaleontol. 108, 41–56.

Mead, R.N., Goñi, M.A., 2008. Matrix protected OM in a river dominated margin: a possible mechanism to sequester terrestrial OM? Geochim. Cosmochim. Acta 72, 2673–2686.

Meng, J., Yao, P., Yu, Z.G., Bianchi, T.S., Zhao, B., Pan, H.H., Li, D., 2014. Speciation, bioavailability and preservation of phosphorus in surface sediments of the Changjiang Estuary and adjacent East China Sea inner shelf. Estuar. Coast. Shelf Sci. 144, 27–38.

Meunier, J.D., Keller, C., Guntzer, F., Riotte, J., Braun, J.J., Anupama, K., 2014. Assessment of the 1% Na_2CO_3 technique to quantify the phytolith pool. Geoderma 216, 30–35.

Meyers, P.A., 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. Org. Geochem. 34, 261–289.

Michalopoulos, Panagiotis, Aller, Robert C., 2004. Early diagenesis of biogenic silica in the Amazon delta: alteration, authigenic clay formation, and storage. Geochim. Cosmochim. Acta 68, 1061–1085.

Middelburg, J.J., Meysman, F.J., 2007. Burial at sea. Science 316, 1294–1295.

Mortlock, R.A., Froelich, P.N., 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. Deep Sea Res. Pt. A 36, 1415–1426.

Mudroch, A., Azcue, J.M., 1995. Manual of Aquatic Sediment Sampling. Lewis Publishers, pp. 194–200.

Nelson, D.M., Tréguer, P., Brzezinski, M.A., Leynaert, A., Quéguiner, B., 1995. Production and dissolution of biogenic silica in the ocean: revised global estimates, comparison with regional data and relationship to biogenic sedimentation. Glob. Biogeochem. Cycles 9 (3), 359–372.

Nordvarg, L., Johansson, T., 2002. The effects of fish farm effluents on the water quality in the Aland archipelago, Baltic Sea. Aquac. Eng. 25, 253–279.

van Oevelen, D., Duineveld, G., Lavaleye, M., Mienis, F., Soetaert, K., Heip, C.H., 2009. The cold-water coral community as a hot spot for carbon cycling on continental margins: a food-web analysis from Rockall Bank (northeast Atlantic). Limnol. Oceanogr. 54, 1829.

Ogrinc, N., Fontolan, G., Faganeli, J., Covelli, S., 2005. Carbon and nitrogen isotope compositions of OM in coastal marine sediments (the Gulf of Trieste, N Adriatic Sea): indicators of sources and preservation. Mar. Chem. 95, 163–181.

Ozkan, E.Yesim, Baha Buyukisik, H., Kontas, Aynur, 2014. Biogeochemical behavior and distribution of biogenic silica in marine sediments from Izmir Bay, Aegean Sea (Turkey). Mar. Chem. 164, 1–8.
Pan, Z., Gao, Q.F., Dong, S.L., Wang, F., Li, H.D., Zhao, K., Jiang, X.Y., 2019. Effects of abalone (*Haliotis discus hannai Ino*) and kelp (*Saccharina japonica*) mariculture on sources, distribution, and preservation of sedimentary organic carbon in Ailian Bay, China: identified by coupling stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) with C/N ratio analyses. Mar. Pollut. Bull. 141, 387–397.
Pastuszak, M., Nagel, K., Grelowski, A., Mohrholz, V., Zalewski, M., 2003. Nutrient dynamics in the Pomeranian Bay (Southern Baltic): impact of the Oder River outflow. Estuaries 26 (5), 1238–1254.
Pearson, T.H., Black, K.D., 2000. The environmental impacts of marine fish cage culture. In: Black, K.D. (Ed.), Environmental Impacts of Aquaculture. Sheffield Academic Press, Sheffield, pp. 1–31.
Pelejero, C., 2003. Terrigenous n-alkane input in the South China Sea: high-resolution records and surface sediments. Chem. Geol. 200, 89–103.
Peng, Y.H., Wang, Z.D., Gao, H.L., Chen, H.R., Pan, M.X., Huang, H.H., 2001. Biogeochemistry of inorganic nitrogen in the water of aquacultural boxes at Dapeng'Ao Daya Bay. Mar. Sci. Bull. 20, 16–24.
Persaud, D., Jaagumagi, R., Hayton, A., 1993. Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario. Water Resources Branch. Ontario Ministry of the Environment, Toronto.
Qi, S., Leipe, T., Rueckert, P., Di, Z., Harff, J., 2010. Geochemical sources, deposition and enrichment of heavy metals in short sediment cores from the Pearl River Estuary, Southern China. J. Mar. Syst. 82, S28–S42.
Qi, Z., Shi, R., Yu, Z., Han, T., Li, C., Xu, S., Xu, S., Liang, Q., Yu, W., Lin, H., et al., 2019. Nutrient release from fish cage aquaculture and mitigation strategies in Daya Bay, southern China. Mar. Pollut. Bull. 146, 399–407.
Qing, N., Lin, Y., Guo, C., Jin, Q., 1996. A preliminary study on energy flow of cultivating shellfishes in Dapeng'ao, Daya bay. In: Zou, R. (Ed.), Sustainable Use of Marine Bioresources in Daya Bay. Science Press, Beijing, China, pp. 15–20.
Qiu, Y.W., Wang, Z.D., Zhu, L.S., 2005. Variation trend of nutrient and chlorophyll contents and their effects on ecological environment in Daya Bay. J. Oceanogr. Taiwan Strait 24, 131–139.
Ragueneau, O., Tréguer, P., Leynaert, A., Anderson, R.F., Brzezinski, M.A., DeMaster, D.J., Dugdale, R.C., Dymond, J., Fischer, G., François, R., Heinze, C., Maier-Reimer, E., Martin-Jézéquel, V., Nelson, D.M., Quéguiner, B., 2005. A review of the Si cycle in the modern ocean: a recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy. Glob. Planet. Chang. 26, 317–365.
Ramaswamy, V., Gaye, B., Shirodkar, P.V., Rao, P.S., Chivas, A.R., Wheeler, D., Thwin, S., 2008. Distribution and sources of organic carbon, nitrogen and their isotopic signatures in sediments from the Ayeyarwady (Irrawaddy) continental shelf, northern Andaman Sea. Mar. Chem. 111, 137–150.
Ran, X., Liu, S., Liu, J., Zang, J., Che, H., Ma, Y., Wang, Y., 2016. Composition and variability in the export of biogenic silica in the Changjiang River and the effect of Three Gorges Reservoir. Sci. Total Environ. 571, 1191–1199.
Regnier, P., Friedlingstein, P., Ciais, P., et al., 2013. Anthropogenic perturbation of the carbon fluxes from land to ocean. Nat. Geosci. 6, 597–607.
Restrepo, J.C., Escobar, J., Otero, L., Franco, D., Pierini, J., Correa, I., 2017. Factors influencing the distribution and characteristics of surface sediment in the Bay of Cartagena, Colombia. J. Coast. Res. 33 (1), 135–148.
Rickert, D., Schlüter, M., Wallmann, K., 2002. Dissolution kinetics of biogenic silica from the water column to the sediments. Geochim. Cosmochim. Acta 66, 439–455.
Saccone, L., Conley, D.J., Sauer, D., 2006. Methodologies for amorphous silica analysis. J. Geochem. Explor. 88, 235–238.
Sarà, G., Scilipoti, D., Mazzola, A., Modica, A., 2004. Effect of fish farming wastes on sedimentary and particulate OM origin in a Southern Mediterranean area (Gulf of Castellammare, Sicily): a multiple stable isotope study. Aquaculture 234, 199–213.
Savage, C., 2005. Tracing the influence of sewage nitrogen in a coastal ecosystem using stable nitrogen isotopes. AMBIO J. Human Environ. 34, 145–150.
Schelske, C.L., Stoermer, E.F., Fahnenstiel, G.L., Haibach, M., 1986. Phosphorus enrichment silica utilization and biogeochemical silica depletion in the Great Lakes USA Canada. Can. J. Fish. Aquat. Sci. 43, 407–415.
Shepard, F.P., 1954. Nomenclature based on sand–silt–clay ratios. J. Sediment. Petrol. 24, 151–158.
Smith, V.H., Schindler, D.W., 2009. Eutrophication science: where do we go from here? Trends Ecol. Evol. 24, 201–207.
Sospedra, J., Niencheski, F.H., Falco, S., Andrade, C.F.F., Attisano, K.K., Rodilla, M., 2018. Identifying the main sources of silicate in coastal waters of the Southern Gulf of Valencia (Western Mediterranean Sea). Oceanologia 60, 52–64.
Sudheesh, V., Movitha, M., Hatha, A.A.M., Renjith, K.R., Resmi, P., Rahiman, M., Nair, S.M., 2017. Effects of seasonal anoxia on the distribution of phosphorus fractions in the surface sediments of southeastern Arabian Sea shelf. Cont. Shelf Res. 150, 57–64.
Tallberg, P., 2000. Silicon and Its Impacts on Phosphorus in Eutrophic Freshwater Lakes. University of Helsinki.
Wang, L., Fan, D., Li, W., Liao, Y., Zhang, X., Liu, M., Yang, Z., 2014. Grain-size effect of biogenic silica in the surface sediments of the East China Sea. Cont. Shelf Res. 81, 29–37.
Wang, Y., Ren, M., Zhu, D., 1986. Sediment supply to the continental shelf by the major rivers of China. J. Geol. Soc. Lond. 143, 935–944.
Wang, Y., Lou, Z., Sun, C., Sun, S., 2008. Ecological environment changes in Daya Bay, China, from 1982 to 2004. Mar. Pollut. Bull. 56, 1871–1879.
Wang, Z.H., Feng, J., Nie, X.P., 2015. Recent environmental changes reflected by metals and biogenic elements in sediments from the Guishan Island, the Pearl River Estuary, China. Estuar. Coast. Shelf Sci. 164, 493–505.
Waterson, E.J., Canuel, E.A., 2008. Sources of sedimentary organic matter in the Mississippi River and adjacent Gulf of Mexico as revealed by lipid biomarker and $\delta^{13}C$ TOC analyses. Org. Geochem. 39, 422–439.
Wei, X., Ni, P., Zhan, H., 2013. Monitoring cooling water discharge using Lagrangian coherent structures: a case study in Daya Bay, China. Mar. Pollut. Bull. 75, 105–113.
Wu, M.L., Wang, Y.S., Wang, Y.T., Yin, J.P., Dong, J.D., Jiang, Z.Y., Sun, F.L., 2017. Scenarios of nutrient alterations and responses of phytoplankton in changing Daya Bay, South China Sea. J. Mar. Syst. 165, 1–12.
Xia, B., Cui, Y., Chen, B., Cui, Z., Qu, K., Ma, F., 2014. Carbon and nitrogen isotopes analysis and sources of organic matter in surface sediments from the Sanggou Bay and its adjacent areas, China. Acta Oceanol. Sin. 33, 48–57.
Xia, B., Han, Q., Chen, B., Sui, Q., Jiang, T., Sun, X.M., Zhu, L., Chai, C., Qu, K.M., 2019. Influence of shellfish biodeposition on coastal sedimentary organic matter: a case study from Sanggou Bay, China. Cont. Shelf Res. 172, 12–21.
Xu, C., Yang, B., Dan, S.F., Zhang, D., Liao, R., Lu, D., Li, R., Ning, Z., Peng, S., 2020. Spatiotemporal variations of biogenic elements and sources of sedimentary organic matter in the largest oyster mariculture bay (Maowei Sea), Southwest China. Sci. Total Environ. 730, 139056.
Xu, G.Z., 1989. Environment and Resource in Daya Bay. Anhui Science and Technology Press, Hefei, China (in Chinese).
Yang, B., Cao, L., Liu, S.M., Zhang, G.S., 2015a. Biogeochemistry of bulk organic matter and biogenic elements in surface sediments of the Yangtze River Estuary and adjacent sea. Mar. Pollut. Bull. 96, 471–484.
Yang, B., Liu, S.M., Zhang, G.L., 2018. Geochemical forms and characteristics of phosphorus in surface sediments from the northern South China Sea. Mar. Chem. 198, 44–55.
Yang, B., Lan, R.Z., Lu, D.L., Dan, S.F., Kang, Z.J., Jiang, Q.C., Lan, W.L., Zhong, Q.P., 2019a. Phosphorus biogeochemical cycling in intertidal surface sediments from the Maowei Sea in the northern Beibu Gulf. Reg. Stud. Mar. Sci. 28, 100624.
Yang, B., Zhou, J.B., Lu, D.L., Dan, S.F., Zhang, D., Lan, W.L., Kang, Z.J., Ning, Z.M., Cui, D.Y., 2019b. Phosphorus chemical speciation and seasonal variations in surface sediments of the Maowei Sea, northern Beibu Gulf. Mar. Pollut. Bull. 141, 61–69.
Yang, W., Chen, M., Zheng, M., He, Z., Zhang, X., Qiu, Y., Xu, W., Ma, L., Lin, Z., Hu, W., Zeng, J., 2015b. Influence of a decaying cyclonic eddy on biogenic silica and particulate organic carbon in the tropical South China Sea based on ^{234}Th-^{238}U disequilibrium. PLoS One 10, e0136948.
Yang, Y., Gao, B., Hao, H., Zhou, H., Lu, J., 2017. Nitrogen and phosphorus in sediments in China: a national-scale assessment and review. Sci. Total Environ. 576, 840–849.
Yao, P., Zhao, B., Bianchi, T.S., Guo, Z., Zhao, M., Li, D., Pan, H., Wang, J., Zhang, T., Yu, Z., 2014. Remineralization of sedimentary organic carbon in mud deposits of the Changjiang Estuary and adjacent shelf: implications for carbon preservation and authigenic mineral formation. Cont. Shelf Res. 91, 1–11.
Ye, L.X., Ritz, D.A., Fenton, G.E., Lewis, M.E., 1991. Tracing the influence on sediments of organic waste from a salmonid farm using stable isotope analysis. J. Exp. Mar. Biol. Ecol. 145, 161–174.
Yokoyama, H., Abo, K., Ishihi, Y., 2006. Quantifying aquaculture-derived OM in the sediment in and around a coastal fish farm using stable carbon and nitrogen isotope ratios. Aquaculture 254, 411–425.
Yu, F., Zong, Y., Lloyd, J.M., Huang, G., Leng, M.J., Kendrick, C., Lamb, A., Yim, W.W., 2010. Bulk organic $\delta^{13}C$ and C/N as indicators for sediment sources in the Pearl River delta and estuary, southern China. Estuar. Coast. Shelf Sci. 87, 618–630.
Yue, W.Z., Huang, X.P., Sun, C.C., 2007. Distribution and pollution of nitrogen and phosphorus in surface sediments from the Pearl River estuary. Oceanol. Limnol. Sin. 38, 111–117.
Zhang, J., Yu, Z.G., Wang, J.T., Ren, J.L., Chen, H.T., Xiong, H., Dong, L.X., Xu, W.Y., 1999. The subtropical Zhujiang (Pearl River) estuary: nutrient, trace species and their relationship to photosynthesis. Estuar. Coast. Shelf Sci. 49, 385–400.
Zhang, L., Xiong, L., Zhang, J., Jiang, Z., Zhao, C., Wu, Y., Liu, S., Huang, X., 2019. The benthic fluxes of nutrients and the potential influences of sediment on the eutrophication in Daya Bay, South China. Mar. Pollut. Bull. 149, 110540.
Zhang, Y., Lu, S., Qi, Y., 2008. Changes on community structure and population by phytoplankton in aquacultural area of Daya Bay 2003–2004. Mar. Environ. Sci. 27, 131–134.
Zhang, Y., Gao, X., Wang, C., Chen, C.-T.A., Zhou, F., Yang, Y., 2016. Geochemistry of phosphorus in sediment cores from Sishili Bay, China. Mar. Pollut. Bull. 113, 552–558.
Zhang, Z., Lv, Y., Zhang, W., Zhang, Y., Sun, C., Marhaba, T., 2015. Phosphorus, organic matter and nitrogen distribution characteristics of the surface sediments in Nansi Lake, China. Environ. Earth Sci. 73, 5669–5675.
Zhao, C., Jiang, Z., Wu, Y., Liu, S., Cui, L., Zhang, J., Huang, X., 2019a. Origins of sediment OM and their contributions at three contrasting wetlands in a coastal semi enclosed ecosystem. Mar. Pollut. Bull. 139, 32–39.
Zhao, X., Yang, W., Ma, H., Li, J., Chen, M., Fang, Z., Zhang, X., Zeng, J., Qiu, Y., Zheng, M., 2019b. Seasonal variations in the abundance and sinking flux of biogenic silica in Daya Bay, northern South China Sea. Oceanologia 61, 239–251.
Zheng, A., Shen, H., Liu, J., Li, W., Chen, Q., 2001. The mechanism of low nutrients high productivity in Daya Bay. Mar. Sci. 25 (11), 48–52 (in Chinese with English Abstract).
Zhou, F.X., Gao, X.L., Yuan, H.M., Song, J.M., Chen, F., 2018. The distribution and seasonal variations of sedimentary organic matter in the East China Sea shelf. Mar. Pollut. Bull. 129, 163–171.
Zhou, P., Li, D., Zhao, L., Li, H., Ni, Z., Zhao, F., Yu, H., Li, X., 2019. A 120-year sedimentary record and its environmental implications, in a T dated marine sediment core from Daya Bay in the northeastern South China Sea. Mar. Pollut. Bull. 145, 248–253.
Zimmerman, A.R., Canuel, E.A., 2000. A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: anthropogenic influence on organic matter composition. Mar. Chem. 69, 117–137.