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Natural and anthropogenic signatures on sedimentary organic matters across varying intertidal habitats in the Korean waters

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ABSTRACT

Sedimentary organic matters in the typical intertidal areas were investigated to address year-round monthly distributions and site-specific sources. Target areas included four natural tidal flats (Ganghwa, Garolim, Sinan, and Suncheon) and one artificially closed estuary (Nakdong River), South Korea (in 2018). Among the parameters monitored, mud content was a key factor controlling organic matter contents, across varying habitats, with significant positive correlations to total organic carbon (TOC, $r = 0.66$, $p < 0.001$) and total nitrogen (TN, $r = 0.44$, $p < 0.001$). The elevated TOC and TN contents and heavier carbon stable isotope ratios ($\delta^{13}C$) in sediments of Garolim and Suncheon from February to April reflected the winter microphytobenthos blooms, receiving prevailed marine sources. Whilst, the depleted $\delta^{13}C$ and $\delta^{15}N$ values in sediments of Nakdong River estuary were observed during flood season (September–October), indicating direct influence of terrestrial organic input through freshwater discharge. Overall, distributions and sources of sedimentary organic matters in the Korean coastal waters suggested variabilities in season and space, with anthropogenic alteration. The data accumulated in this study would provide baseline information for sediment organic carbon stocks in the Korean coastal waters and elsewhere.

1. Introduction

Coastal sediment has a significant ecological role on the cycling of biogeochemical organic matter locally or globally, because it serves as a large reservoir by accumulating organic carbon in marine environment (Hedges and Keil, 1995; Kubo and Kanda, 2017). Carbon dioxide (CO_2) is one of the crucial greenhouse gases for regulating climate change, and recent reports have highlighted the role that coastal ecosystems play in sequestering CO_2 from the atmosphere (Mcleod et al., 2011). Recently, the carbon captured by several coastal ecosystems such as mangrove, salt marshes, and seagrasses, namely “blue carbon”, is increasingly recognized as several studies have confirmed their roles in highly efficient CO_2 sinks (Chmura et al., 2003; Duarte et al., 2004; Bouillon et al., 2008; Lo Iacono et al., 2008; Duarte et al., 2010; Kennedy et al., 2010).

Sedimentary organic matter in coastal area is subjected to receive both terrestrial and marine origins, thus its composition would vary and change depending on the sources and fate (Graham et al., 2001; Lamb et al., 2006). Also, the supply of anthropogenic input such as industrial/municipal sewages and discharges of wastewater-treatment plant contributes to the burial of organic matter in intertidal sediments (Rumolo et al., 2011; Pradhan et al., 2014). Although many studies have been conducted on the very subject, the dynamics of sedimentary organic matters in the lotic system from rivers, estuaries, and to coastal ecosystem is still subject to debate (Krishna et al., 2013).

In particular, about half of the estuaries are artificially separated by the sea-dike in South Korea, namely called “closed estuary”, thus distributions and fate of organic matters in this closed system become

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Fig. 1. Map showing the sampling sites at (a) Ganghwa (GH1-GH3), (b) Garolim Bay (GR1-GR2), (c) Sinan (SA1-SA2), (d) Suncheon Bay (SC1-SC2), and (e) Nakdong River estuary (ND1-ND2), Korea. Surface sediments were collected monthly from January to December in 2018. All satellite images obtained from Google Map. The location of sewage treatment plant given for supplementary information in each study area, if present.

more complex (Kim et al., 2017; Noh et al., 2019). In fact, the sedimentary organic matter is likely site-specific, either accumulates in natural coastal zone (Hedges and Parker, 1976; Milliman et al., 1984) or could be transported to the open sea (Keil et al., 1998; Galy et al., 2007). Thus, it is necessary to characterize the sources of organic matter by addressing environmental factors influencing its distributions and transport, either under natural or altered environmental condition.

The carbon to nitrogen ratio (C/N) and stable isotope ratios of carbon (δ^{13}C) and nitrogen (δ^{15}N) have been widely utilized to elucidate the distribution, sources, and fate of sedimentary organic matter in aquatic environment (Meyers, 1994; Graham et al., 2001; Lamb et al., 2006; Rumolo et al., 2011; Kubo and Kanda, 2017). When determined the sources of organic matter by using such proxy, the seasonality should be carefully considered as the C/N ratios, along with δ^{13}C and δ^{15}N values, in surface sediments might temporally vary due to its association to biogeochemical components (Liu et al., 2006; Kubo and Kanda, 2017). In particular, the influence of algal primary production and/or bacterial degradation would significantly change in the nutrient enriched environments of intertidal zone, estuary, or semi-enclosed bay system (Voβ and Struck, 1997; Liu et al., 2006).

Several earlier studies have reported that the enriched δ^{13}C values were directly influenced by increasing primary production of microphytobenthos (MPBs) in Scheldt estuary (Riera et al., 2000), in Hiroshima Bay (Takai et al., 2004), and in Kwangyang Bay (Kang et al., 2006). In comparison, the δ^{15}N values of surface sediments were reported to increase with bacterial degradation (Rumolo et al., 2011; Kang et al., 2017). In addition, the δ^{13}C and δ^{15}N values revealed significant variations in response to increased discharges of water and suspended sediment from upper Nakdong River through freshwater discharge during the flood season (Liu et al., 2006; Wang et al., 2018).

In general, sediment properties such as grain size and composition are known as important environmental factors to determine the distributions and fate of organic matters in the shallow water system (Serrano et al., 2016). For example, muddy sediment mainly composed of silt and clay retains more organic matter compared to sandy fraction, due to a greater adsorption capacity of fine-grained particles by earning a larger surface area (Keil and Hedges, 1993; Burdige, 2007). Moreover, fine-grained particles enhance the preservation of organic matter through reduced redox potential and/or remineralization rates (Hedges and Keil, 1995; Dauwe et al., 2001; Burdige, 2007). Thus, the critical association of sediment properties to organic matter should be one fundamental question to address its geochemical processes.

The present study aimed to investigate how the various environmental conditions or parameters drive the spatiotemporal variations of sedimentary organic matters in the natural and altered intertidal zones. Field survey was monthly performed to identify and trace organic matters in sediment from the four typical tidal flats and one artificially closed estuary over of one year. The targeted endpoints included total organic carbon (TOC), total nitrogen (TN), water content (WC), mud content (MC), organic content (OC, by loss on ignition), benthic Chlorophyll *a* (Chl-*a*), $\delta^{13}C$, and $\delta^{15}N$ in the surface sediment. The specific objectives were to: (1) investigate regional and temporal variations of sedimentary organic matter; (2) evaluate relationship between sedimentary organic matter and geochemical properties; (3) determine effects of biological component (e.g., microalgal biomass) on sedimentary organic matter; and finally (4) elucidate sources of sedimentary organic matter, in and cross the natural and altered coastal ecosystems.

2. Materials and methods

2.1. Study area

Surface sediment samples were monthly collected from the five coastal areas in Korea for the period of one year (in 2018), encompassing 12 consecutive months. To elucidate the sources and fate of organic matter, the target study areas were selected to generally represent the typical and altered tidal flats along the west and south coasts of Korea (Fig. 1). Three areas from the west coast (Ganghwa, Garolim Bay, and Sinan) and two from the south coast (Suncheon Bay and Nakdong River estuary) would cover the typical natural intertidal systems and altered closed estuary. In specific, first, the Ganghwa tidal flat (GH1–GH3) is located at the mouth of the Han River in the mid-west of the Korean Peninsula, and lies between the Sukmo channel to the west and the Yeomha channel to the east. The huge tidal flats (~240 km^2) are developed around the Ganghwa Island, and are affected by freshwater (salinity: 23.1 psu) and tidal currents flowing from the Han River to the main waterways (Choi et al., 2011; Koh and Khim, 2014).

Second, the Garolim Bay (GR1–GR2) encompassing ~90 km^2 tidal flats is a semi-enclosed bay surrounded by Seosan and Taean counties. Because there is no large river flowing into the inner bay, freshwater input is quite limited, accordingly salinity is relatively high (31.7 psu) and uniform compared to other study areas.

Third, the Sinan tidal flat (SA1–SA2) is located in southwest Korea, also covering the extended tidal flats of ~343 km^2. The Sinan tidal flat is classified as an island tidal flat, as it is surrounded by hundreds of islands and recognized as the Ramsar site because of its outstanding landscape and great marine biodiversity (Choi, 2014; Koh and Khim, 2014).

Fourth, the Suncheon Bay (SC1–SC2) is semi-closed system, on the south coast of Korea, surrounded by Yeosu Peninsula and Goheung Peninsula. The tidal flat is relatively small in size (~24 km^2), but extensive reed vegetations are developed with mud-dominated bottom, accordingly recognized as one of representative habitats for the migratory birds (Koh and Khim, 2014). Of note, facilities that discharge pollutants, e.g., sewage treatment plant, in the upstream region would be potential source for organic pollution around the bay.

Finally, the Nakdong River estuary is located on the southeastern part of the Korean peninsula (ND1–ND2), and has a well-developed delta, with ~40 km^2 of tidal flats (Joh, 2013), that is protected by sand dunes parallel to the coastline. Nakdong River is the longest river (~525 km) with the largest watersheds (~24,000 km^2) in South Korea, encompassing many cities and counties from Taeback County to Busan City. A huge estuarine barrage built in 1987 controls the discharge of freshwater through water gates, thus the estuarine delta has been significantly influenced by both anthropogenic river discharge and natural tidal forcing in morphodynamic manner (Hong et al., 2013; Williams et al., 2013).

2.2. Sampling and laboratory analyses

Surface sediments were collected from a total of 11 locations from January to December 2018, and 2–3 representative locations were selected for the monthly monitoring in each area by considering geographical and oceanographic settings. Surface sediments (0–0.5 cm) were collected in triplicate with a stainless-steel spatula. Seawater was sampled to analyze stable carbon and nitrogen isotopic compositions in particulate organic matter (POM) in water column over two seasons (March and July). All sediments and seawater samples were immediately stored at −25 °C until analysis.

For the further analyses of general sediment parameters, samples were mixed well and stored in airtight plastic bags to prevent evaporation, and were subsequently transferred to the laboratory. WC was obtained by measuring weight loss after drying sediments at 70 °C for 72 h until a constant weight was attained. MC was determined from rapid partial analysis by wet-sieving (Buchanan, 1984). Sediment textural type was classified by mud (silt + clay) content: sand (< 5% mud), sandy mud (50–75% mud), slightly sandy mud (75–95% mud), and mud (> 95% mud) (Flemming, 2000). OC was measured by burning sediments to ashes at 550 °C for 4 h (Heiri et al., 2001), to determine weight loss after combustion. Samples for measurement of benthic Chl-*a* concentration (indicating in situ MPB biomass) were collected by use of the syringe corer. The sediment samples were frozen in the field and brought to the laboratory. Benthic chlorophylls were immediately extracted with acetone (15 mL) for 24 h in the dark at 4 °C. Samples were then centrifuged at 1500 rpm for 5 min, and the supernatant aliquot was measured for Chl-*a* by the method described elsewhere (Lorenzen, 1967). The sediment samples for analyses of TOC, TN, $\delta^{13}C$, and $\delta^{15}N$ were freeze-dried, homogenized, and powdered using agate mortar. The sediment was decalcified with 10% HCl, washed twice with deionized water, and freeze-dried for TOC and $\delta^{13}C$ determination. Sediment samples for TOC, TN, $\delta^{13}C$, and $\delta^{15}N$ were measured using an Elemental Analyzer-Isotope Ratio Mass Spectrometer (EA-IRMS) (Elementar, Gmbh, Hanau, Germany). All isotopic compositions were expressed as delta notation (‰) (Eq. (1)):

$$\delta^{13}C \text{ or } \delta^{15}N\ (‰) = [R_{sample}/R_{reference} - 1] \times 1000 \tag{1}$$

where, R_{sample} and $R_{reference}$ are the composition ($^{13}C/^{12}C$ or $^{15}N/^{14}N$) of the sample and reference, respectively. Isotopic compositions were reported relative to conventional reference materials; Vienna Peedee Belemnite (VPDB) for carbon and atmospheric N_2 for nitrogen. IAEA-N-2 (International Atomic Energy Agency (IAEA), Vienna, Austria) and IAEA-CH-3, were used as working standards to calculate the analytical error of carbon and nitrogen, respectively. Measurement precision was approximately 0.04‰ for $\delta^{13}C$ and 0.2‰ for $\delta^{15}N$.

2.3. Data analysis

Pearson correlation analysis was performed to test for significant relationships among TOC and MC, TN and MC, Chl-*a* and TOC, Chl-*a* and TN, and Chl-*a* and $\delta^{13}C$. SPSS 23.0 (SPSS INC., Chicago, IL) was used to perform the statistical analysis. TOC and TN contents of sediments were analyzed to test for differences between the textural classes of sediment (mud, slightly sandy mud, sandy mud, and sand) using a *t*-test and one-way analysis of variance (ANOVA) with Bonferroni post hoc test. Before the analysis, homogeneity of variance was determined

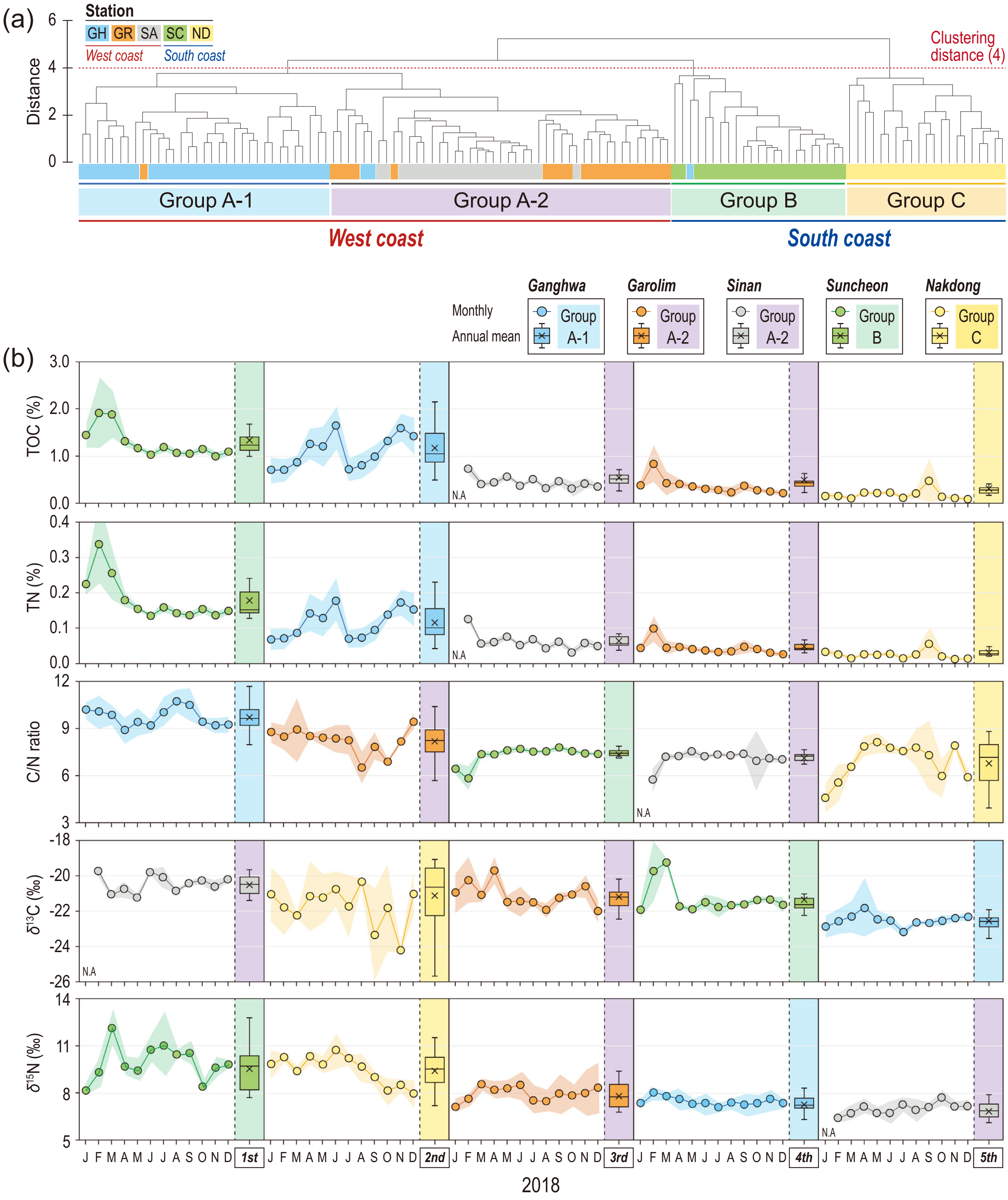

Fig. 2. (a) Cluster analysis and (b) monthly variations of TOC (%), TN (%), C/N ratio, δ^{13}C (‰), and δ^{15}N (‰) in surface sediments of five intertidal flats, Korea. Blue, orange, grey, green, and yellow lines denote at Ganghwa, Garolim, Sinan, Suncheon, and Nakdong River estuary, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Data statistics on the physicochemical parameters of sediment properties, collected from Ganghwa, Garolim, Sinan, Suncheon, and Nakdong River estuary, during the period of 12 months, from January to December in 2018.

	Ganghwa			Garolim			Sinan[a]			Suncheon			Nakdong River estuary		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
WC (%)	12.2	58.5	30.1 (± 13.0)	30.2	85.9	44.6 (± 13.7)	33.2	43.4	39.4 (± 2.6)	40.6	82.3	57.9 (± 7.2)	17.8	40.9	27.5 (± 4.1)
MC (%)	59.0	99.8	87.7 (± 13.4)	62.5	99.1	87.2 (± 11.4)	91.2	99.6	98.0 (± 1.9)	84.9	99.8	96.5 (± 4.0)	1.5	36.5	5.8 (± 7.3)
OC (%)	3.3	9.7	5.8 (± 1.4)	2.4	6.4	4.1 (± 0.8)	3.5	10.1	6.2 (± 1.7)	7.1	16.9	9.6 (± 2.5)	1.3	4.1	2.4 (± 0.8)
Chl-*a* (mg m^{-2})	6.7	84.0	31.7 (± 21.5)	13.1	107.8	37.7 (± 22.5)	4.9	47.9	15.7 (± 10.1)	4.2	496.0	43.2 (± 100.7)	8.7	119.3	49.2 (± 30.3)
TOC (%)	0.39	2.09	1.09 (± 0.42)	0.15	1.11	0.36 (± 0.19)	0.18	0.82	0.44 (± 0.14)	0.93	2.42	1.27 (± 0.37)	0.07	0.80	0.19 (± 0.15)
TN (%)	0.04	0.23	0.11 (± 0.05)	0.02	0.12	0.04 (± 0.02)	0.03	0.13	0.06 (± 0.02)	0.13	0.46	0.18 (± 0.07)	0.01	0.09	0.03 (± 0.02)
C/N	7.9	11.7	9.7 (± 0.8)	5.7	10.4	8.2 (± 1.0)	5.1	8.3	7.1 (± 0.7)	5.2	7.9	7.3 (± 0.6)	3.9	8.8	6.8 (± 1.4)
δ^{13}C (‰)	−23.5	−19.9	−22.5 (± 0.6)	−22.4	−19.2	−21.1 (± 0.8)	−21.4	−19.6	−20.5 (± 0.5)	−22.2	−18.6	−21.3 (± 0.9)	−25.7	−19.0	−21.1 (± 1.8)
δ^{15}N (‰)	6.3	8.3	7.3 (± 0.5)	6.7	9.4	7.9 (± 0.8)	6.1	7.9	6.9 (± 0.5)	7.7	12.9	9.6 (± 1.3)	7.2	11.5	9.5 (± 1.0)

WC, water contents; MC, mud contents; OC, organic contents; Chl-*a*, chlorophyll *a*; TOC, total organic carbon; TN, total nitrogen; C/N, carbon to nitrogen ratio; δ^{13}C and δ^{15}N, carbon and nitrogen stable isotope ratios.

[a] Samples were collected from Sinan over 11 months (February–December) of 2018.

between groups by Levene's homogeneity test, meeting the assumption of homogeneity of variance ($p > 0.05$). The same statistical method was used to test differences in δ^{13}C and δ^{15}N of the Nakdong River estuary sediments (ND1 and ND2) in aspect of natural and altered responses. To characterize surface sediment groups in the sampling areas, cluster analysis was performed with PRIMER 6 statistical software (PRIMER-E Ltd., Plymouth, UK). Euclidean distance was calculated, and data were subjected to group average sorting. Principle component analysis (PCA) was performed to explore overall correlations across sedimentary organic matter and environmental parameters.

3. Results and discussion

3.1. Spatiotemporal distributions of sedimentary organic matter

The data of sedimentary TOC, TN, C/N ratio, δ^{13}C, and δ^{15}N in the five coastal areas generally indicated their varied distributions spatially and temporally (Fig. 2). First, by grouping in cluster analysis, stations were well-grouped according to locality (i.e., Group A (A1 & A2), B, and C at 4 of distance). In particular, geographical difference was playing as a key criterion in a subgrouping among stations such as Group A1 and A2 in west coast and Group B and C in south coast of Korea. Further, by locality, the SC had the greatest TOC (1.27 ± 0.37%) and TN (0.18 ± 0.07%), followed by GH (TOC: 1.09 ± 0.42%; TN: 0.11 ± 0.05%), SA (TOC: 0.44 ± 0.14%; TN: 0.06 ± 0.02%), GR (TOC: 0.36 ± 0.19%; TN: 0.04 ± 0.02%), and ND (TOC: 0.19 ± 0.15%; TN: 0.03 ± 0.02%) (Fig. 2a, b). Second, the TOC and TN contents of the surface sediment generally showed high monthly fluctuations, particularly at GH, reflecting combined influences of freshwater input from the Han River and tidal circulation (Choi et al., 2011). Of note, certain tidal flats showed distinct seasonal variations, i.e., elevated TOC and TN were characteristic at muddy bottom dominated bays of GR and SC during the winter to early spring. This phenomenon could occur as the large amounts of organic matter generated by MPB production might have increased the flux of organic matter to the sediments (Kubo and Kanda, 2017). Whilst, the sand-dominant sediments of ND showed the smallest TOC and TN with weakened seasonal and monthly variabilities, among the five coastal areas.

The C/N ratio, a discriminating proxy of terrestrial and marine origin (Rumolo et al., 2011), varied slightly cross the study areas with total mean of 8.0 (3.9–11.7). The monthly variation in C/N ratio was the greatest at ND (3.9–8.8), followed by GR (5.7–10.4), GH (7.9–11.7), SA (5.1–8.3), and SC (5.2–7.9). Considering the mean C/N ratio, only GH sediments (9.7) were found to be dominated by terrestrial organic sources (Hedges et al., 1986). Whilst, all the other coastal areas might have received primarily marine-derived organic matter, considering its reported C/N ratios of 4–9 (Meyers, 1994; Hedges et al., 1997; Kubo and Kanda, 2017). Typical δ^{13}C and δ^{15}N values of marine organic matters were reported to range from −22 to −18‰ (Peters et al., 1978; Wada et al., 1987; Middelburg and Nieuwenhuize, 1998) and 3 to 12‰ (Wada et al., 1987; Thornton and McManus, 1994; Lamb et al., 2006), reflecting marine phytoplankton (Yamaguchi et al., 2003). Particularly in Korea, δ^{13}C of marine organic matters was reported to range from −20.5 to −17.7‰ (mean: −19.0‰) in west coast (Kang et al., 2003; Suh and Shin, 2013; Lee et al., 2017; Park et al., 2019) and −22.9 to −18.20 (mean: −20.3‰) in south coast (Kang et al., 2003; Kang et al., 2007; Park et al., 2015; Park et al., 2019). Whilst, the typical isotope compositions of terrestrial organic matter showed that δ^{13}C and δ^{15}N values ranged from −33 to −25‰ (Barth et al., 1998; Middelburg and Nieuwenhuize, 1998) and from 0 to 4‰ (Thornton and McManus, 1994), of which isotopic signatures are indicative of C3 plants. (Maksymowska et al., 2000). Moreover, terrestrial plants that use the C3 photosynthetic pathway constitute about 90% of all plants, and these plants preferentially take up ^{12}C by diffusion resulting in depletion of ^{13}C organic matter compared to marine organic matters (Lamb et al., 2006).

Similar to the results of C/N signatures, the four target areas (GR, SA, SC, and ND; except for ND2) reflected marine dominated signatures, with mean δ^{13}C values of −20.81‰ (Table 1 and Fig. S2). In contrast, GH sediments exhibited terrestrial origin, with lighter δ^{13}C values (mean: −22.54‰). In the meantime, the δ^{15}N values also reflected the site-specific variations of coastal organic matter. For example, GH, GR, and SA showed lesser monthly variations in δ^{15}N, whereas elevated peak of δ^{15}N at SC was observed in the early spring (February–March) (Fig. 2b). Meantime, the C/N ratio, δ^{13}C and δ^{15}N signatures in ND clearly indicated the impact of increased freshwater discharge during the flood season (September–October) (Fig. S2). The signature of seasonality in δ^{13}C and δ^{15}N was consistent to the seasonal pattern in river discharge, with maximum discharge coinciding in the summer monsoon period (Hong et al., 2013). Of note, the western water gate of Nakdong estuarine barrage is only operated during the flood season, whilst the main watergate is opened daily during the ebb tide (The Korea Ministry of Environment, 2015). Thus, a large amount of suspended particles and organics inside the main Nakdong water gates flow out and affect the distributions of mud and organic matter contents in estuarine sediments (Williams et al., 2013). In summary, our results demonstrated that spatiotemporal distributions of sediment organic matter at tidal flats and estuary generally reflected the geographical settings with anthropogenic impacts embedded.

3.2. *Effects of the mud contents on sedimentary TOC and TN*

In general, the coastal sediments collected from the target study areas represented mud dominated bottom fraction, with average of > 85% mud content, except for ND. SA had the greatest MC (mean ± SD, 98.0 ± 1.9%), followed by SC (96.5 ± 4.0%), GH (87.7 ± 13.4%), GR (87.2 ± 11.4%), and ND (5.8 ± 7.3%) (Table 1). Meantime, not surprisingly, the MC did not show certain seasonal patterns throughout the year, except for flood season at ND. TOC and TN were generally greater in mud-dominant sediments (0.83 ± 0.50% and 0.10 ± 0.07%, respectively) compared to those in sand-dominant ones (0.19 ± 0.15% and 0.03 ± 0.02%). Thus, the relationships between sedimentary organic matter (TOC and TN) and MC (% of particles < 63 µm) in different regions were scrutinized (Fig. 3). The analysis revealed that the MC showed significant positive correlations to TOC ($r = 0.66$, $p < 0.001$) and TN ($r = 0.44$, $p < 0.001$), respectively. There was no significant difference in the TOC and TN cross various sediment facies (mud, slightly sandy mud, sandy mud, sand); however, there was a significant difference in TOC ($n = 18$, $F = 20.07$, $p < 0.01$) and TN ($n = 18$, $F = 9.99$, $p < 0.01$) between sand and non-sand fractions (mud, slightly sandy mud, and sandy mud). MC can be used to predict sediment TOC and TN in bare intertidal sediments, and is used as a cost-effective proxy or indicator of organic matter (Serrano et al., 2016).

The positive relationship between mud and organic matter found in the present study was consistent to the several previous reports (Keil and Hedges, 1993; Bergamaschi et al., 1997; Flemming and Delafontaine, 2000), generally supporting greater adsorption capacity of fine particles to organics (Mayer, 1994; Burdige, 2007). Because fine-grained sediments (e.g., mud) provide more binding sites for organic matter flocculation by providing larger surface areas than coarse-grained sediments (e.g., sand), cohesive sediments contain greater organic matter in surface sediments (Keil and Hedges, 1993; Mayer, 1994; Burdige, 2007). Meantime, it should be noted that TOC and TN in mud-dominant sediments (> 85%) slightly varied (Fig. 3), possibly indicating prevailing allochthonous sources at some locations (Kennedy et al., 2010; Serrano et al., 2016). In fact, many other factors could control adsorption, affinity, and residence time of particle fractions to organic matter, thus additional aspects such as chemical stabilization (Percival et al., 2000; Galy et al., 2007) and some biological interactions (Sherr, 1982; Danovaro et al., 1994) should also be taken into consideration.

3.3. *Effects of benthic microalgae on sedimentary TOC and TN*

As mentioned earlier, the elevated TOC and TN contents at some tidal flats, particularly in GR and SC, were observed during the periods of MPB winter bloom. Thus, a special caution was given to address the effect of benthic microalgal biomass and distributions on sedimentary TOC and TN. The sediment Chl-*a*, measured as proxy of benthic microalgal biomass, generally indicated high productive intertidal zone across the five study areas (Park et al., 2014). The ND showed the greatest concentrations of Chl-*a* (49.2 ± 30.3 mg Chl-*a* m^{-2}), on average, followed by SC (43.2 ± 101 mg Chl-*a* m^{-2}), GR (37.7 ± 22.5 mg Chl-*a* m^{-2}), GH (31.7 ± 21.5 mg Chl-*a* m^{-2}), and SA (15.7 ± 10.1 mg Chl-*a* m^{-2}) (Table 1 and Fig. 4). It should be noted that some fraction of high concentrations of benthic Chl-*a* in ND included not only MPB but also freshwater-derived microalgae such as cyanobacteria etc. In general, the benthic Chl-*a* in surface sediments found in the present study were comparable to the previously reported

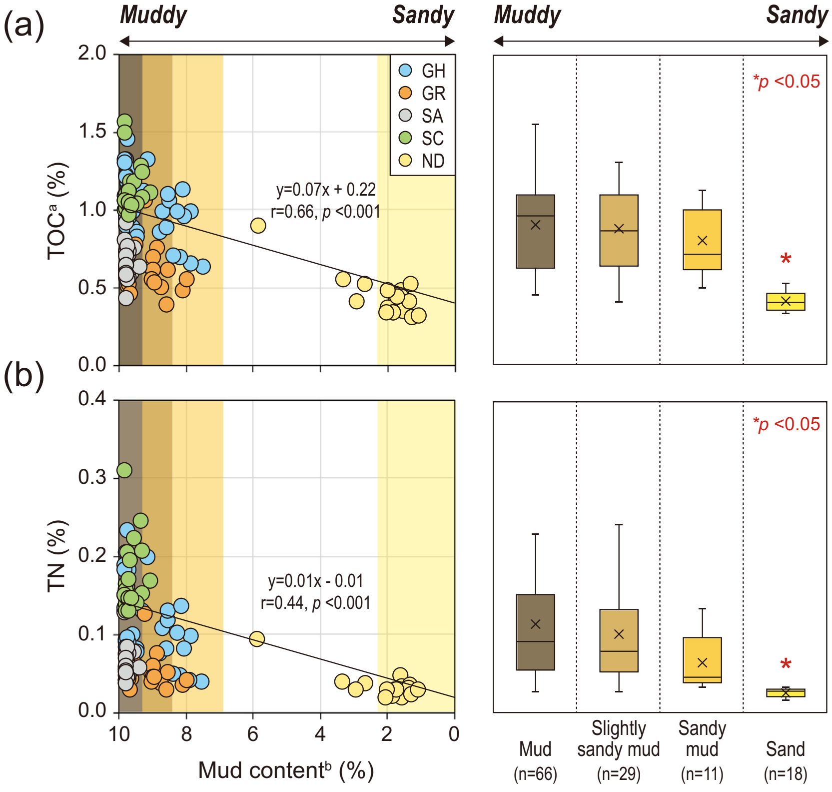

Fig. 3. Relationships between mud contents and (a) TOC and (b) TN in surface sediments of five intertidal flats, Korea. [a] TOC and [b] mud contents in the surface sediments were square root transformed for normality. Sediment textural types were classified based on mud (silt + clay) contents: sand (< 5% mud), sandy mud (50–75% mud), slightly sandy mud (75–95% mud), and mud (> 95% mud) (Flemming, 2000).

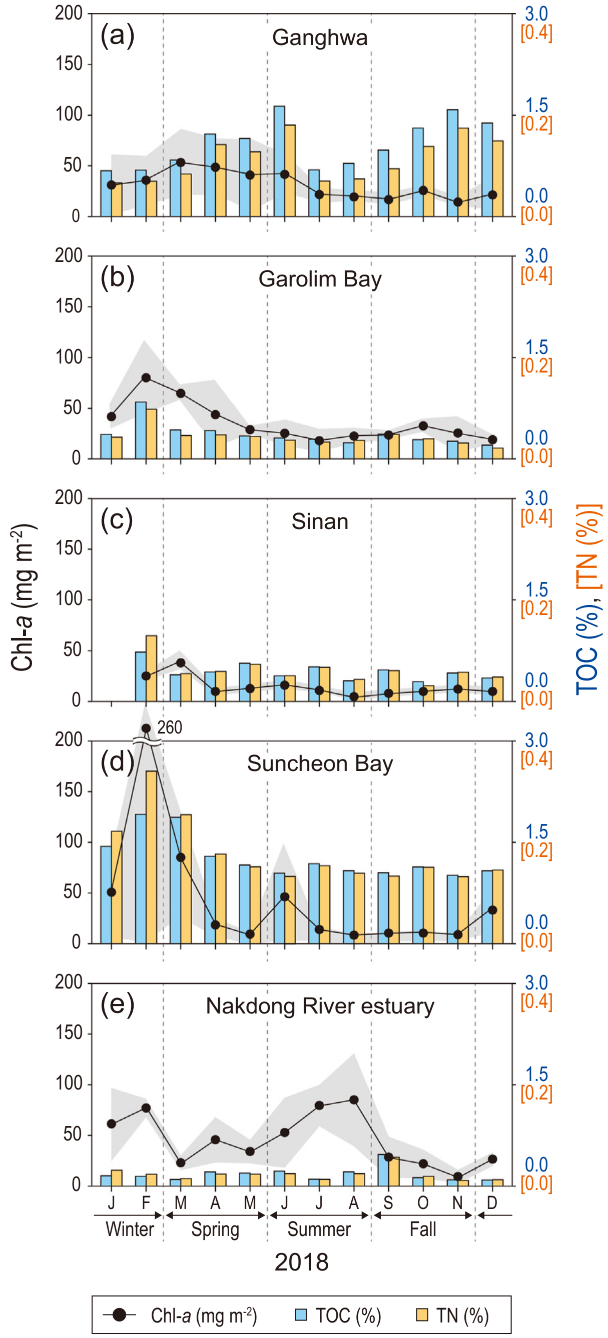

Fig. 4. Monthly variations of Chl-*a* (mg m^{-2}) (black lines), TOC (%) (blue bars), and TN (%) (orange bars) in the surface sediments from (a) Ganghwa, (b) Garolim, (c) Sinan, (d) Suncheon, and (e) Nakdong River estuary, Korea. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

values in the Asian tidal flats (Magni and Montani, 1997; Park et al., 2014).

In aspect of seasonal variability of benthic microalgal biomass, the patterns are characterized into three-case groups; 1) distinct seasonal variations with winter algal bloom (GR and SC); 2) relatively constant algal biomass with weak sign of spring bloom (GH and SA); and finally 3) irregular temporal fluctuation with elevated algal biomass during summer flooding time (ND). Thus, relatively great TOC and TN found in the four tidal flat sediments were apparently influenced by the MPB blooms during the corresponding periods; say pattern 1 and 2 above. Of note, the small TOC and TN from ND did not reflect the elevated microalgal biomass, thus large proportion of microalgae did not seem to contribute as sources of organic matter, particularly in sand dominated bottom (Liu et al., 2016).

The relationship between benthic Chl-*a* and the amount of organic matter in each area further explain the direct association between algal biomass and sedimentary organic parameters in site-specific manner. For example, Chl-*a* concentrations were significantly correlated with TOC ($r = 0.54$, $p < 0.05$ and $r = 0.78$, $p < 0.01$, respectively), TN ($r = 0.55$, $p < 0.05$ and $r = 0.89$, $p < 0.01$), and δ^{13}C ($r = 0.55$, $p < 0.05$ and $r = 0.74$, $p < 0.01$) in GR and SC (Fig. S1). This result apparently suggested that benthic primary producers significantly contribute to sedimentary organic matter in these natural tidal flats. In contrast, the relationships between benthic Chl-*a* and organic matter parameters were not statistically significant for GH, SA, and ND, which were categorized as pattern 2 and 3 groups above (Fig. S1). It should be noted that, however, the GH became to show significant association of MPB to organic matters when excluded certain periods; viz., January–March. Altogether, the results of present study generally supported that the greater production in response to winter and/or spring microalgal blooms would have influenced the enriched benthic condition cross the typical soft bottom tidal flats of Korea (Kwon et al., 2018; Montani et al., 2003). Of note, surface sediments from all the natural tidal flats were primarily composed of marine-derived organic matter, suggesting important ecological role of MPB in the given system (Koh and Khim, 2014). Considering the significant CO_2 sink by the microalgal biofilm on surface sediments of the tidal flats (Chen et al., 2019), its ecological role should also be addressed in a holistic view.

3.4. Site-specific variabilities in sources of sedimentary organic matters

GR, SA, SC, and ND1 represented a typical signature of marine-derived organic matters, with δ^{13}C values ranging from −22.44 to −18.5‰ (mean: −20.81‰) (Fig. 5). In comparison, GH and ND2 sediments were of terrestrial origin, with δ^{13}C values of −25.71 to −19.57‰ (mean: −22.47‰). The result indicated that the corresponding sediments were directly affected by freshwater discharges from the Han River and Nakdong River, respectively, through waterways. Meantime, the surface sediments and seawater of ND1 and ND2 contained apparently different organic sources. For example, the δ^{13}C values measured in ND1 sediment ranged between −20.38 and

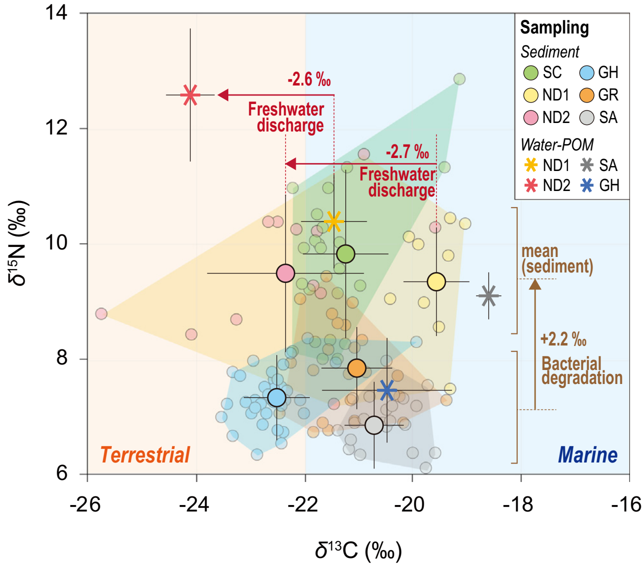

Fig. 5. Scatter plots of stable carbon and nitrogen isotopic composition (δ^{13}C and δ^{15}N) of the surface sediments and particulate organic matter (POM) collected from five intertidal flats, Korea. Mean values of sediment and water samples are presented as total mean with standard deviation (black line).

−19.03‰ (mean: −19.61‰), seawater ranged between −22.37 and −20.64‰ (mean: −21.50‰), indicating signature of marine-derived organic matter (Fig. 5). This can be simply explained by the limited freshwater discharge from western Nakdong River to estuary via Noksan water gate. Of note, since the construction of Noksan water gate in 1934, the very gate has been operating only for controlling the water level in the freshwater reservoir, accordingly terrestrial influence to the western Nakdong estuary would be negligible. In contrast, the surface sediments and seawater of ND2 indicated a terrestrial source, with δ^{13}C values ranging from −25.71 to −19.57‰ (mean: −22.28‰) in sediments, −24.12 to −24.00‰ (mean: −24.06‰) in seawater, due to freshwater discharge through the two main Nakdong water gates (Fig. 1). Altogether, the multiple features of sedimentary organic matter in ND are resulted from the simultaneous operations of Noksan and Nakdong water gates, providing complex dynamics under altered environment of closed Nakdong River estuary.

The potential sources of organic matter in coastal sediments would vary from terrestrial detritus, marine phytoplankton, MPB, and to sewage (Liu et al., 2006). In particular, the δ^{15}N signature could be potentially useful to determine the sources in respect to pollution, for example, isotopically lighter δ^{15}N (mean: 3‰) is characteristic for non-treated freshwater input to the coast (Van Dover et al., 1992). Moreover, low δ^{15}N signatures of organic matters in sediment and POM were reported near the industrial complexes of Sihwa coastal area, in which region was severely contaminated by several classes of persistent toxic substances (PTSs) including PAHs, SOs, and APs (Lee et al., 2017; Hong et al., 2019). The slighted enriched values of δ^{15}N in SC and ND supported the fact that sewage treated freshwater are discharged into the lower reaches for both areas. SC has a sewage treatment plant to purify wastewater from the barn and upstream agricultural area and the ND has a sewage treatment plant to purify wastewater from the surrounding industrial and municipal facilities (Fig. 1). Of note, anthropogenic nitrogen sources after the sewage treatment are typically more ^{15}N-enriched up to 19‰ (Voss et al., 2000; Bohlin et al., 2006), subsequently sediment δ^{15}N becomes heavier with average of 10‰ (Heaton, 1986; Savage et al., 2004). In addition, the significant difference ($p < 0.01$) between the group of locations near the sewage treatment plants (ND1, ND2, and SC) and the other group of locations (SA, GH, and GR) supported the site-specific distributions of sedimentary organic matter (Fig. 5). The δ^{15}N of the other regions (GH, GR, and SA) was of marine origin, ranging from 6.08 to 9.41‰.

3.5. Factors affecting complex dynamics of sedimentary organic matter

Table 2 shows the result of the Pearson correlations between sedimentary organic matter and general sediment properties. The result showed that TOC and TN were significantly, positively correlated with WC, MC, OC, and Chl-*a* ($p < 0.05$). A significant positive relationship was found for Chl-*a* with TOC and TN ($p < 0.05$) in GR and SC (Fig. S1). The relationships of TOC and TN with selected sediment parameters at these sampling locations are summarized in a PCA biplot for the sampling period (Fig. 6). The first two axes of the PCA explained a high proportion of variance (i.e., 39.2% and 21.4% for axes 1 and 2, respectively). The results revealed the relationship between the sampling sites, which were clustered into four groups on the PCA diagram. Group A1 had δ^{13}C and C/N ratios of terrestrial origin, and mostly included muddy tidal flat of GH, which showed prevailed input of terrestrial organic matter from the Han River. Group A2 was located in GR and SA, and had mud-dominant samples, representing marine derived δ^{13}C and δ^{15}N. Group B identified samples with the greatest TOC, TN, and MC, and was localized in SC. The δ^{13}C of sediments was of marine origin, whilst the sediments had greater δ^{15}N, due to a sewage treatment plant located in the upstream region. Finally, Group C locations showed the smallest TOC and TN values in the dataset, which were characterized by sand-dominant intertidal flats in ND. The area was also characteristic with relatively great δ^{15}N signature, due to sewage treatment plant, industrial, and municipal facilities. In summary, the

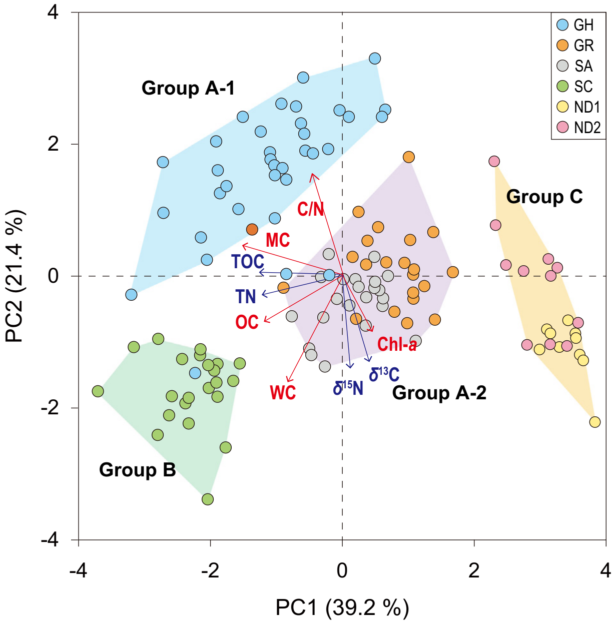

Fig. 6. Principal component analysis (PCA) ordination showing the first and second axes, indicating the relationship between sedimentary organic matters and sediment properties. Partial correlations of the significant environmental variables are superimposed on the ordination as vectors; blue arrows represent sedimentary organic matter and red arrows refer to the influencing factors. The length and direction of sediment property vectors indicate the strength and direction of the relationship to sedimentary organic matter. Cluster analysis was overlaid on the PCA plot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Pearson correlation analysis of the sedimentary organic matter and sediment environmental parameters. Values in bold indicate that the correlation was significant at $p < 0.01$ (matched with ++).

	TOC	TN	C/N	δ^{13}C	δ^{15}N	WC	MC	OC	Chl-*a*
TOC		++	++	+		++	++	++	++
TN	0.953					++	++	++	++
C/N	**0.243**	0.016		++	++	+	++		
δ^{13}C	−0.225	−0.049	**−0.556**			++			++
δ^{15}N	0.060	0.129	**−0.260**	0.161		++	++		
WC	**0.307**	**0.434**	−0.220	**0.270**	**0.240**		++	++	+
MC	**0.508**	**0.469**	**0.261**	−0.106	**−0.353**	**0.422**		++	
OC	**0.637**	**0.695**	−0.007	0.017	0.073	**0.540**	**0.636**		
Chl-*a*	**0.255**	**0.413**	−0.162	0.294	0.144	0.207	−0.103	0.153	

++ Significantly correlated at $p < 0.01$ level (2-tailed).

+ Significantly correlated at $p < 0.05$ level (2-tailed).

clusters of clearly identified groups cross varying locality and habitats successfully demonstrated the complex (in)direct association between sediment properties and isotopic signatures of organic matter.

4. Conclusions

Overall, the present study clearly demonstrated the spatiotemporal distributions and sources of sedimentary organic matters in the typical coastal waters of Korea. The set of results indicated that great variations in time and space with varying sources and origin across natural and altered coastal environments. In general, the terrestrial input considerably influenced the sediment dynamics in Ganghwa and Nakdong River estuary, with direct strong impact from freshwater discharges. The other three tidal flats reflected prevailing marine-derived origin as for the sources of sedimentary organic matters. Regardless of the locality, MC was a key environmental factor regulating the dynamics of sedimentary organic matter in coastal environment, supported by its positive correlations to TOC, TN, and δ^{15}N. Meantime, the elevated sedimentary organic matters found in the typical tidal flats, such as Garolim and Suncheon, in specific season generally well reflected winter to spring MPB blooms. It was also noteworthy that the combined impacts of terrestrial and marine-derived forcing on sediment dynamics were evidenced in the altered environment of the closed Nakdong River estuary. In conclusion, the origin and sources of sedimentary organic matter in the coastal environment significantly varied in time and space, and the factors affecting its spatiotemporal variations included MC, algal biomass, and WC. The data provided in the present study will serve as baseline information relating to the sediment sequestration in the tidal flats of South Korea or elsewhere in a global "blue carbon" regime.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.105166.

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<Appendix A Supplementary Material>

Natural and anthropogenic signatures on sedimentary organic matters across varying intertidal habitats in the Korean waters

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Table of Contents

Supplementary Tables

Supplementary Figures

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Table S1. Data on total organic carbon and total nitrogen in surface sediments by sediment textual types.

Sediment textual type[a]	n	Mud contents (%)	Total organic carbon (%)	Total nitrogen (%)
Mud	66	95 <	0.87 ± 0.53	0.11 ± 0.08
Slightly sandy mud	29	75 ~ 95	0.82 ± 0.45	0.10 ± 0.06
Sandy mud	11	50 ~ 75	0.60 ± 0.36	0.06 ± 0.04
Muddy sand	1	25 ~ 50	0.80 ± 0.25	0.09 ± 0.03
Slightly muddy sand	3	5 ~ 25	0.25 ± 0.07	0.03 ± 0.01
Sand	18	< 5	0.15 ± 0.06	0.02 ± 0.01

[a] Sediment textural types were classified by mud (silt + clay) contents: sand (< 5 % mud), slightly muddy sand (5-25 % mud), muddy sand (25-50 % mud), sandy mud (50-75 % mud), slightly sandy mud (75-95 % mud), and mud (> 95 % mud) (Flemming, 2000).

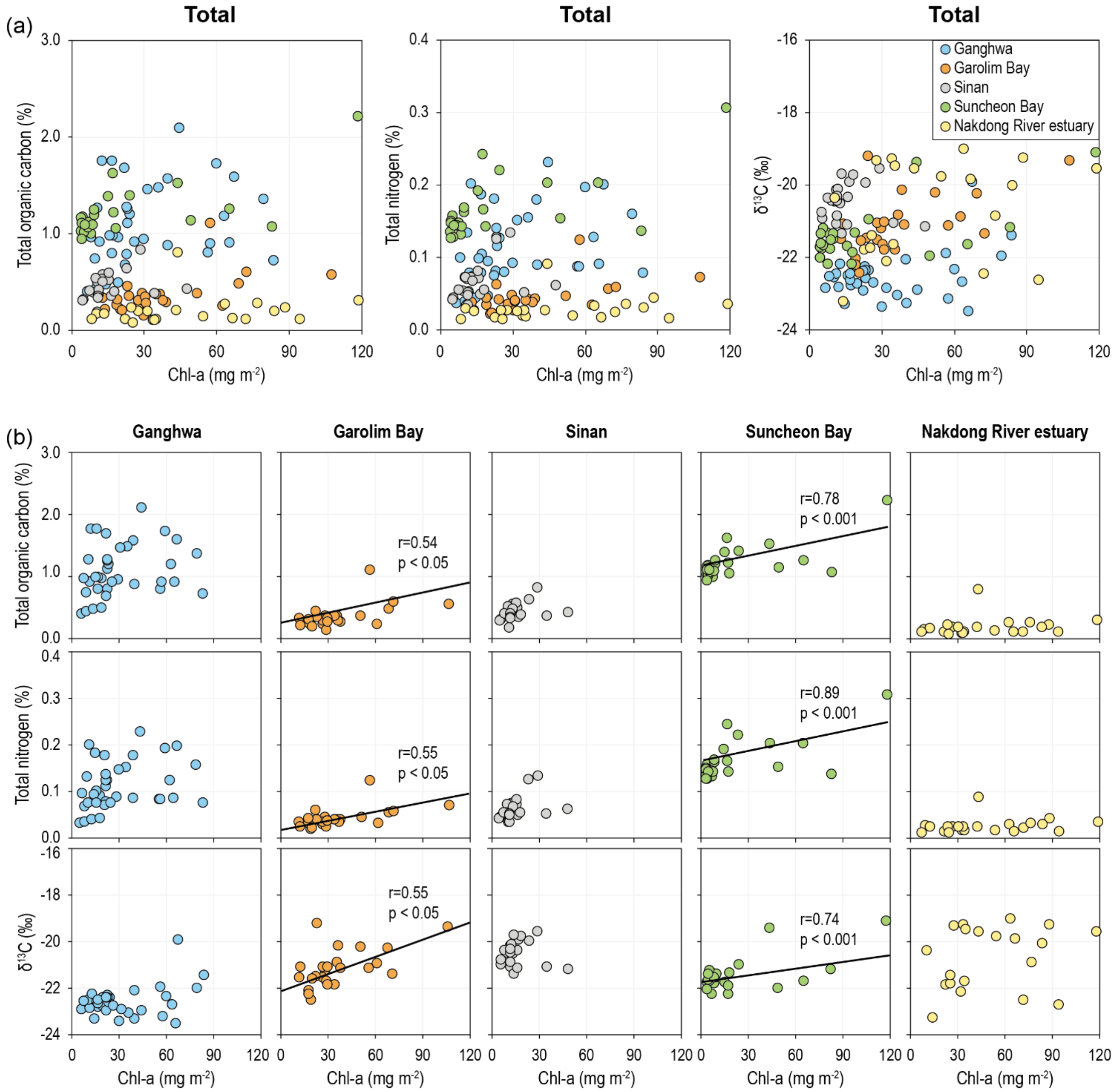

Figure. S1. Relationship between Chlorophyll a (Chl-*a*) and Total organic carbon (TOC), Total nitrogen (TN), Carbon stable isotopic ratio ($\delta^{13}C$) at (a) Total, (b) Ganghwa, Garolim Bay, Sinan, Suncheon Bay and Nakdong River estuary

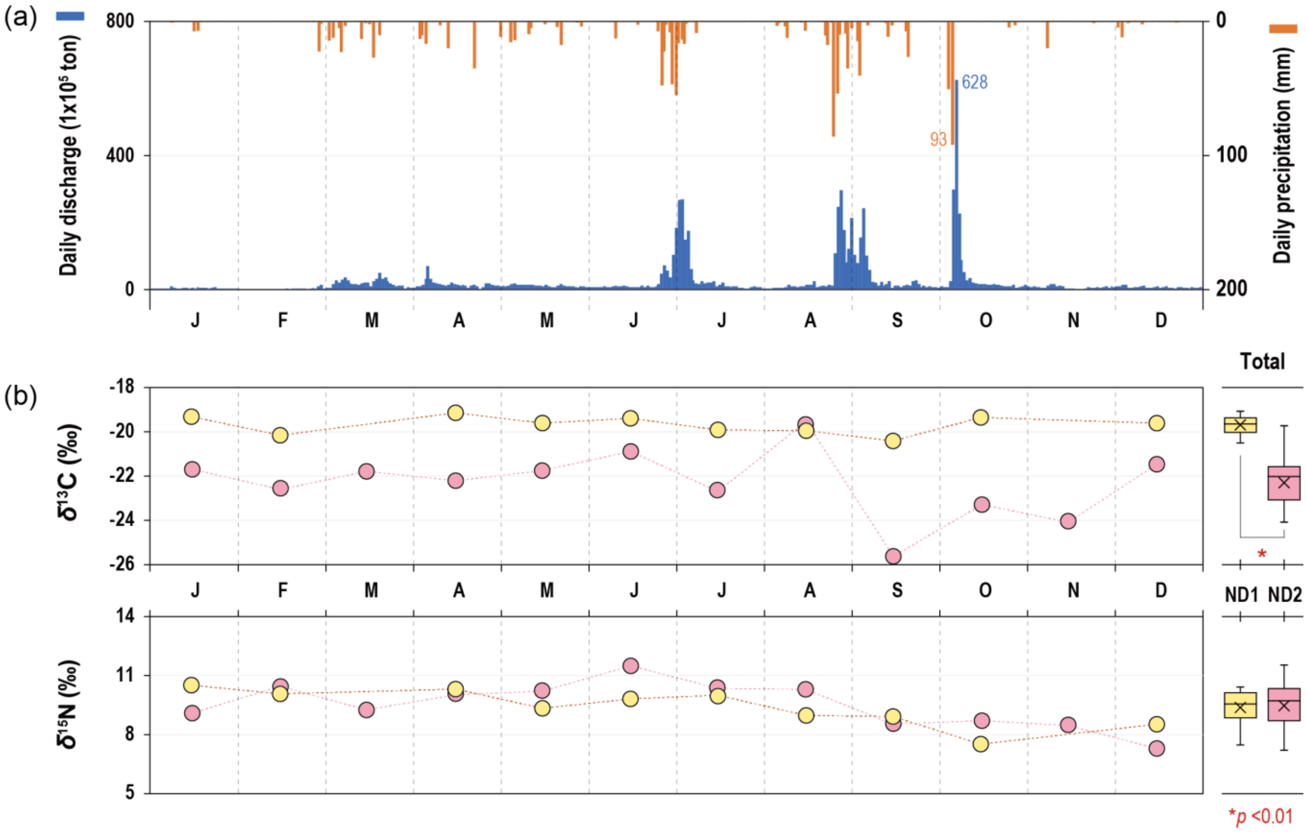

Figure. S2. (a) Daily discharge in water mass (1x10^5 ton, blue bar) and daily precipitation rate (mm, orange bar) in Nakdong River estuary from January to December in 2018. (b) Stable carbon and nitrogen isotopic ratios ($\delta^{13}C$ and $\delta^{15}N$) of surface sediments in Nakdong River estuary. Surface sediments were collected from two sites including Nakdong River estuary 1 (ND1) and Nakdong River estuary 2 (ND2).

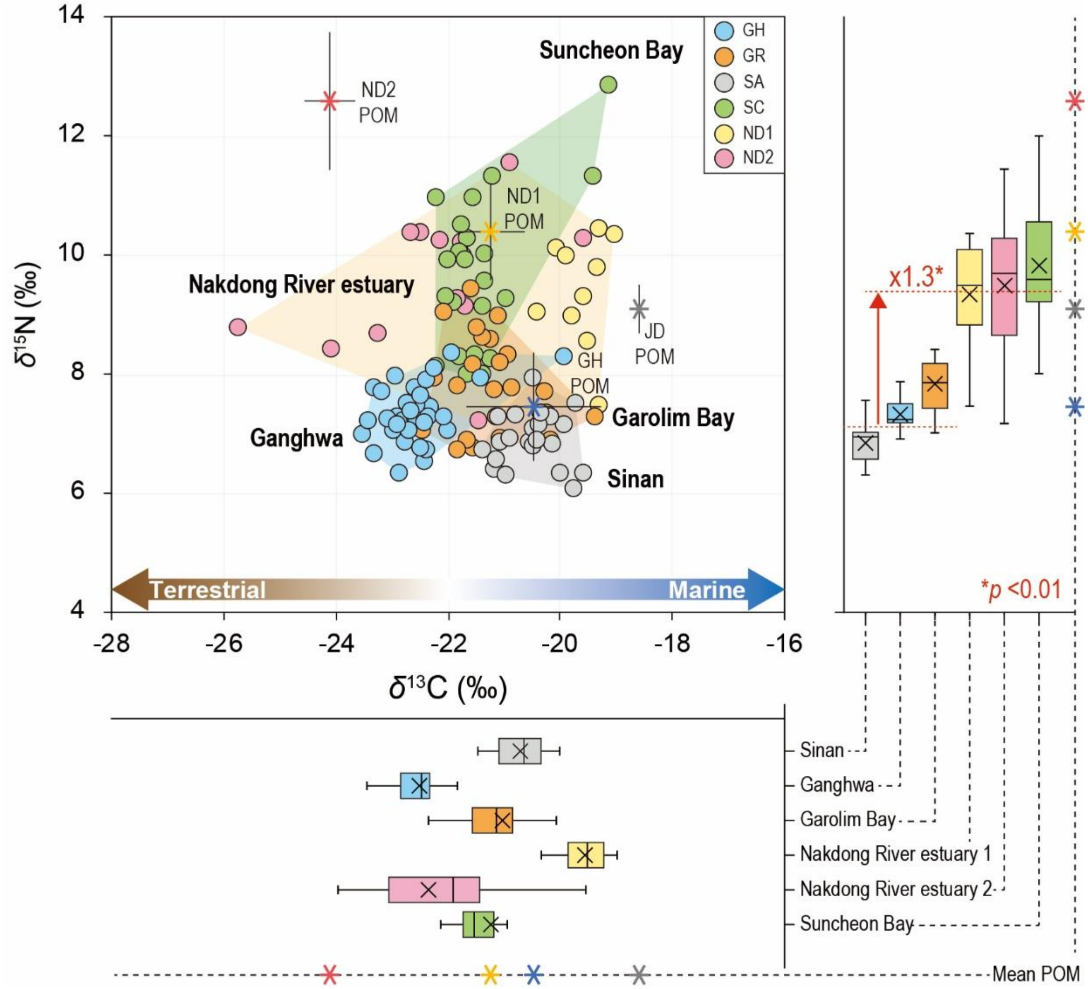

Figure. S3. Scatter plots of stable carbon and nitrogen isotopic composition ($\delta^{13}C$ and $\delta^{15}N$) of the surface sediments and particulate organic matter (POM). POM is presented as total mean with standard deviation (black line).