Seasonal variations and sources of sedimentary organic carbon in Tokyo Bay

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ARTICLE INFO

ABSTRACT

Total organic carbon (TOC), total nitrogen (TN) contents, their stable C and N isotope ratio (δ^{13}C and δ^{15}N), and chlorophyll a ([Chl a]$_{sed}$) of surface sediments were investigated monthly to identify the seasonal variations and sources of organic matter in Tokyo Bay. The sedimentary TOC (TOC$_{sed}$) and TN (TN$_{sed}$) contents, and the sedimentary δ^{13}C and δ^{15}N (δ^{13}C$_{sed}$ and δ^{15}N$_{sed}$) values were higher in summer than other seasons. The seasonal variations were controlled by high primary production in the water column and hypoxic water in the bottom water during summer. The fraction of terrestrial and marine derived organic matter was estimated by Bayesian mixing model using stable isotope data and TOC/TN ratio. Surface sediments in Tokyo Bay are dominated by marine derived organic matter, which accounts for about $69 \pm 5\%$ of TOC$_{sed}$.

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1. Introduction

Sediments from coastal regions play an important role in global biogeochemical carbon cycle because they are the dominant reservoir for organic carbon burial in marine environments (Berner, 1989; Hedges and Keil, 1995). Sedimentary organic carbon in coastal waters can be supplied from both terrestrial and marine sources (Heip et al., 1995; Artemyev, 1996). In addition, anthropogenic input aided by sewage treatment plants and waste water treatment plants also play a significant role in the sedimentary organic matter budget in coastal waters (Pradhan et al., 2014). Despite numerous studies have been carried out, the fate of terrestrial and marine organic matter are still under debate (Krishna et al., 2013). Some studies have shown that it is primarily deposited on the coastal waters (e.g., Hedges and Parker, 1976) while the other demonstrated lateral transport over shelf to the open ocean (Keil et al., 1998; Galy et al., 2007). Therefore, knowledge of the sources of sedimentary organic carbon in coastal water and the factors controlling its distribution is essential for better understanding the global carbon cycle.

To elucidate the source and fate of organic matter in the marine environment, the elemental ratio of total organic carbon (TOC) to total nitrogen (TN) contents and stable carbon and nitrogen isotope ratios (δ^{13}C and δ^{15}N, respectively) have been widely applied (Krishna et al., 2013; Koziorowska et al., 2016). In general, terrestrial organic matter can have a wide range of TOC/TN ratios (ca. 12–400; Hedges et al., 1986), while TOC/TN ratios of marine organic matter are less variable (ca. 4–9; Meyers, 1994; Tyson, 1995; Hedges et al., 1997). Evaluation of isotope ratios indicates that terrestrial particulate organic matter

(POM) has a depleted carbon isotope ratio (δ^{13}C$_{POM}$) and nitrogen isotope ratio (δ^{15}N$_{POM}$) when compared with marine POM (Vizzini et al., 2005). Typical isotope compositions of terrestrial POM have δ^{13}C$_{POM}$ and δ^{15}N$_{POM}$ values ranging from -33 to $-25‰$ (e.g., Barth et al., 1998; Middelburg and Nieuwenhuize, 1998) and from 0 to 4‰ (Thornton and McManus, 1994), respectively. Typical δ^{13}C$_{POM}$ and δ^{15}N$_{POM}$ values of marine POM range from -22 to $-18‰$ (e.g., Peters et al., 1978; Wada et al., 1987; Middelburg and Nieuwenhuize, 1998) and 3 to 12‰ (e.g., Wada et al., 1987; Thornton and McManus, 1994), respectively. It is clear that δ^{13}C$_{POM}$ and δ^{15}N$_{POM}$ can vary seasonally (Cifuentes et al., 1988; Ogawa et al., 1994), however while eutrophication could be a factor of variation is not always a seasonal phenomenon (as could be vertical mixing). The isotope ratio of surface sediments (δ^{13}C$_{sed}$) may reflect seasonal variations in δ^{13}C$_{POM}$. Reliable estimates of sedimentary organic carbon sources probably take into account such seasonal variations; however, sedimentary organic carbon in coastal waters did not adequately account for temporal variability. In addition, sedimentary chlorophyll a ([Chl a]$_{sed}$) is also possible indicator of primary production in the water column. Coastal waters support high primary production due to the availability of inorganic nutrients. Especially, human activity has greatly accelerated the flows of nutrients to coastal waters over the past half century, causing widespread cultural eutrophication (Nixon, 1995). Excessive nutrient loads can cause higher rates of algal production, sometimes leading to exceptional algal blooms (e.g., van der Zee and Chou, 2005; Minaudo et al., 2015). Subsequently, organic matter deposition to the bottom water was increased. However, [Chl a]$_{sed}$ are affected by seagrass meadows and benthic microalgae if the basin is shallow enough for light to reach the seafloor (Paula et al., 2001).

In this study, seasonal variations in TOC$_{sed}$, TN$_{sed}$, δ^{13}C$_{sed}$, δ^{15}N$_{sed}$, and [Chl a]$_{sed}$ in the surface sediments of Tokyo Bay were observed. In

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addition, suspended POM in freshwater and seawater were measured to determine isotope values of terrestrial and marine POM throughout the year. These data were then used to assess the sedimentary organic carbon sources based on Bayesian mixing models.

2. Materials and methods

2.1. Study area

Tokyo Bay is a semi-enclosed embayment with an area of approximately 920 km^2 and a mean water depth of 19 m. The bay is bounded by highly urbanized areas. The bay has suffered from severe cultural eutrophication since the late 1950s, along with rapid development in catchment areas including the Tokyo metropolis. Nutrient concentrations in the bay decreased from 1990s to present due to reduced load of nutrients and yet phytoplankton blooms persist throughout the year (Kanda et al., 2008). Moreover, anoxic bottom waters consistently appear during summer in northwest part of the bay. About 80% of the freshwater flowing into the bay occurred from the northwest part of the bay. Therefore, higher concentrations of anthropogenic substances (e.g., alkylbenzenens (Ambe, 1973); coprostanol (Ogura and Ichikawa, 1983)) were observed at the northwest part of the bay sediment. In contrast, anthropogenic substance concentrations at other parts of the bay were lower than that of northwest part of the bay and homogeneous distributions (Ambe, 1973). Then, we selected two sampling stations at the northwestern part of the bay and the central bay (Fig. 1). Although the benthic fauna in the bay is mainly composed of Polychaeta, the development of hypoxia from June to October led to mass mortality of macrobenthos with complete defaunation (Kodama et al., 2012). Seagrass meadows also occupy <2% of the total area of the bay (Central Environmental Council, 2010). There are no benthic microalgae in the bay sediment because the light did not reach the sediment

Fig. 1. Sampling locations in Tokyo Bay.

throughout the year (Shinpo, 2007). Accordingly, we can reasonably assume that observed sedimentary organic carbon and nitrogen represent terrestrial and marine origin and that Chl *a* of surface sediment mainly represent water column production.

2.2. Sample collection

Surface sediment and surface seawater samples of Tokyo Bay were collected monthly from May 2012 to April 2013 on the research vessel Seiyo-maru of Tokyo University of Marine Science and Technology. Surface sediment samples were collected using a multiple-corer (Rigo Co., Ltd., Tokyo, Japan) at station F3 and a gravity core sampler (HR type core sampler; Rigo Co., Ltd., Tokyo, Japan) at station F6 (Fig. 1). The sediment core samples were collected triplicate, cut into 0–1 cm sections, put into polyethylene bags, and stored at −25 °C until analysis. Surface seawater samples were collected at stations F3 and F6 in Teflon-coated 8 L Niskin bottles mounted on a conductivity–temperature–depth (CTD) rosette (Falmouth Scientific Inc., Bourne, MA, USA) with a chlorophyll fluorometer (SCF; Seapoint Sensors Inc., Exeter, NH, USA) and a dissolved oxygen (DO) sensor (RINKO-3 ARO-CAV; JFE Advantech Co., Ltd., Hyogo, Japan). Freshwater samples were collected monthly from the lower Arakawa River station and effluent of the Shibaura sewage treatment plant (STP) between May 2012 and April 2013 (Fig. 1). Both seawater and freshwater samples were transferred into HCl acid-washed 1-L polyethylene bottles and kept in the dark until being processed in the laboratory. Samples for suspended POM measurement were filtered through precombusted (450 °C, 3 h) GF/F filters, after which the filters were stored at −80 °C until analysis. Water samples for chlorophyll *a* (Chl *a*) measurement were filtered through precombusted (450 °C, 3 h) GF/F filters. After filtration, chlorophyllous pigments were extracted using *N,N*-dimethylformamide (Suzuki and Ishimaru, 1990) and stored at −25 °C until analysis.

2.3. Sample analysis

The sediment samples for TOC$_{sed}$, TN$_{sed}$, δ^{13}C$_{sed}$, and δ^{15}N$_{sed}$ analyses were freeze-dried, homogenized, and powdered using a mortar and pestle. The analyses were preceded by treatment of samples with 1 mol L^{-1} HCl to remove carbonates. The water samples for suspended POC and δ^{13}C$_{POM}$ analyses were dried at 60 °C, then acidified with vapor at 12 mol L^{-1} HCl to remove carbonate before analysis. Sediment samples for TOC$_{sed}$, TN$_{sed}$, δ^{13}C$_{sed}$, δ^{15}N$_{sed}$, and water samples for suspended POC and δ^{13}C$_{POM}$ were measured using a Hydra 20–20 isotope ratio mass spectrometer coupled to an ANCA-GSL elemental analyzer (SerCon Ltd., Crewe, UK). Analytical precision for δ^{13}C and δ^{15}N were 0.08‰ and 0.22‰, respectively. The sediment samples were measured in triplicate. To prepare sediment samples for [Chl *a*]$_{sed}$ analysis, about 0.2 g of freeze-dried homogenized sediments were sonicated with 8 mL of *N,N*-dimethylformamide (Suzuki and Ishimaru, 1990) and pigments were extracted for 24 h at −25 °C in the dark until analysis. Sediment samples for [Chl *a*]$_{sed}$ and water samples for Chl *a* was then measured using a fluorometer (TD-700, Turner Designs, Sunnyvale, CA, USA).

2.4. Data analysis

The Bayesian mixing model, Stable Isotope Analysis in R (SIAR) developed by Parnell et al. (2010), was used to assess the relative contributions of sedimentary organic carbon sources (river, sewage treatment plant, and marine organic carbon) based on the δ^{13}C, δ^{15}N, and TN/TOC signatures. We choose TN/TOC rather than TOC/TN ratios in the model because TN/TOC ratios were statistically more robust; the higher TOC concentration is the denominator and behaves linearly in end-member mixtures (Goñi et al., 2003; Perdue and Koprivnjak, 2007). For each source, we report the mean value and the 95% confidence interval of the estimate of the proportional contr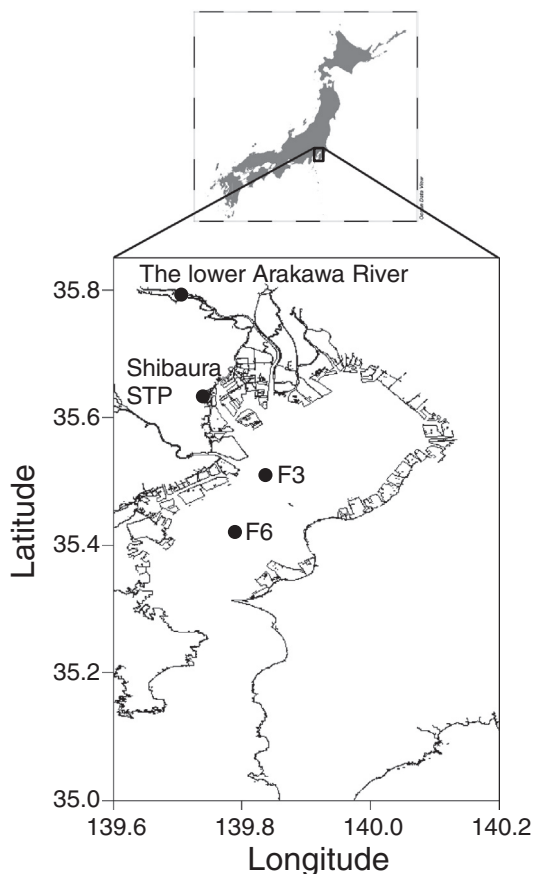ibution of each source to the observed value.