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Spatial distribution of organic and sulfur geochemical parameters of oxic to anoxic surface sediments in Beppu Bay in southwest Japan

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Abstract

In order to elucidate the organic and sulfur geochemical processes of surface sediments associated with oxic/anoxic conditions, we have examined the relationship between the spatial distribution of sedimentary δ^{13}C, δ^{15}N, TOC, TN, TS, C/N ratio, and C/S ratio and environmental variables in Beppu Bay, Japan.

The results of the principal component analysis and redundancy analysis of these geochemical parameters revealed two dominant patterns in their variations. The first pattern is characterized by variations in δ^{13}C, δ^{15}N, and C/N, which are closely related to the distance between the river mouth and sampling sites. This pattern is attributed to the mixing of organic materials from two sources—C_3 land plants and marine phytoplankton—rather than various alternation processes such as diagenesis and eutrophication. The second pattern is characterized by variations in TOC, TN, TS, and C/S. The RDA results showed that these geochemical parameters are closely related to the water depth and DO. Meanwhile, a simple correlation analysis also showed a good correlation of TOC, TN, TS, and C/S with bottom temperature and Eh. In Beppu Bay, a significant negative correlation is observed between the depth and the dissolved oxygen concentration and Eh, indicating that the deeper bottom environments have lower oxygen availability and are more reductive. According to these observations and some findings of previous studies, the spatial variations in TOC and TN are controlled by decomposition rates. This is in contrast to those in TS and C/S, by rate of pyrite formation. Both these rates are possibly influenced by temperature or oxic/anoxic conditions.

The RDA results revealed that the two patterns in the variations of the geochemical parameters exhibit a perpendicular relation with respect to RDA axes. This indicates that the two geochemical groups are controlled only by their main factors. It is possible that TOC, TN, TS, and C/S are sensitive to temperature or oxic/anoxic conditions in Beppu Bay; in contrast, δ^{13}C, δ^{15}N, and C/N are less sensitive to these conditions.

Keywords: stable carbon and nitrogen isotope; C/N ratio; total sulfur; C/S ratio; surface sediment; anoxic; Beppu Bay; Japan

1. Introduction

Approximately 24% of the Japanese population resides in proximity to the Seto Inland Sea—the largest enclosed sea in Japan; it has some regions with oxygen-depleted bottoms (Kameda and Fujiwara, 1995, and references cited therein).

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These regions suffer from problems such as the mortality of fishes and macrobenthos (The Association for the Environmental Conservation of the Seto Inland Sea, 2001).

An increasing trend of oxygen depletion in enclosed basins and estuaries is most probably related to human-induced eutrophication (e.g., Cooper and Brush, 1991; Bratton et al., 2003); however, it might also be related to the long-term effects of natural climate variations and increased winter temperature due to global warming. Therefore, for a precise understanding of the mechanisms regarding oxygen depletion, it is essential to thoroughly investigate long-term effects of both eutrophication and climate changes on the oxic/anoxic conditions in enclosed basins and estuaries.

Recently, studies on the sedimentary records regarding oxygen depletion have been conducted in estuaries and coastal embayments; in particular, many studies have been conducted in Chesapeake Bay (e.g., Adelson et al., 2001; Zimmerman and Canuel, 2002; Bratton et al., 2003). However, these studies are still restricted to this region. Therefore, it is necessary to conduct case studies in different marine settings to develop a general understanding of the processes driving the long-term variability of anoxic coastal environments.

In order to detect changes in the marine environment and productivity and to identify the source materials, biogeochemical parameters such as stable isotopes (δ^{13}C and δ^{15}N), total organic carbon (TOC), total nitrogen (TN), and C/N ratio have been previously employed (e.g., Zimmerman and Canuel, 2002; Bratton et al., 2003). Meanwhile, total sulfur (TS) and TOC/TS (C/S) ratio was used for studying oxic/anoxic conditions in marine environments (Berner, 1984). In anoxic coastal embayments in Japan, downcore records of these geochemical parameters are scarce (e.g., Amano et al., 2004) and the lack of studies on their geochemical processes is evident.

Within the estuaries and embayments with both oxic/anoxic basins, a few studies have been conducted on the relationship between the spatial distribution of sedimentary δ^{13}C, δ^{15}N, and C/N and oxic/anoxic-related environmental variables (e.g., Bratton et al., 2003). However, there are no studies on the relationship between the distribution of these geochemical parameters and the bottom redox potential (Eh) and dissolved oxygen (DO) concentrations that are directly indicative of the oxic/anoxic condition. Furthermore, no studies have been conducted on the sensitivity of parameters such as δ^{13}C, δ^{15}N, TOC, TN, TS, C/N ratio, and C/S ratio to the oxic/anoxic conditions. The examination of the relationship between the spatial variations in these geochemical parameters and oxic/anoxic conditions could yield information on their sensitivity to the conditions and the geochemical processes caused due to oxygen-depleted conditions.

In this study, we investigated organic and sulfur geochemical parameters of the oxic/anoxic surface sediments of Beppu Bay, which has the most anoxic basin in the Seto Inland Sea. Here we examine the relationship between the spatial variations in the geochemical parameters (δ^{13}C, δ^{15}N, TOC, TN, TS, C/N ratio, and C/S ratio) and environmental variables (Eh, DO, water depth, distance between the river mouth and sampling sites, and bottom temperature) in Beppu Bay. Furthermore, we discuss the factors controlling the spatial variations in these geochemical parameters. This study can contribute to future studies conducted on the sedimentary records from Beppu Bay in order to comprehend the long-term trend in oxygen depletion and understand the mechanisms inducing oxygen depletion.

2. Regional settings

Beppu Bay is located west of the Seto Inland Sea, Japan. It has a basin with a maximum depth of 72 m in its innermost region and a 53-m-deep sill at its mouth (Fig. 1). These topographic features and the low energy of tidal mixing give rise to an anoxic bottom in the deepest and innermost regions during summer. The main rivers flowing into the bay are the Oita and the Ohno; their drainage areas are approximately 650 and 1465 km^2, respectively.

The mean annual, summer (July and August), and winter (January and February) air temperatures around the bay during the years 1900–1999 are approximately 15, 26, and 6 °C, respectively (Oita; Japan Meteorological Agency, 1999). The annual and summer (May–October) precipitations are 1750 and 1200 mm, respectively (Oita; Japan Meteorological Agency, 1999).

The thermal structure of Beppu Bay is characterized by a strong thermocline at a water depth of 50–60 m and the presence of benthic cold water below the thermocline (Kameda and Fujiwara, 1995). According to Kameda and Fujiwara (1995), this thermocline is formed after May, becomes strong from August to September, and disappears by January due to winter convection in a full water column. The DO values in the deepest regions vary with seasonal changes in the thermal structure; these values are 6 mL/L from January to March, decrease to almost zero by September, and abruptly recover from December to January (Kameda and Fujiwara, 1995).

On the basis of our survey conducted on August 2, 2005, the temperatures of the upper layer (0–40 m), uppermost thermocline (40–50 m), and benthic cold water (60–72 m) were 19–27, 19–20, and 11 °C, respectively. The bottom surface below the uppermost thermocline (<40 m) was hypoxic (<2 mg/L), partially suboxic (<0.3 mg/L) or anoxic (<0.2 mg/L). Due to the 28-mm precipitation that occurred during the four days before the survey, the water salinity at the surface between a depth of 0 and 5 m in the southern region of Beppu Bay was in the range of 29–31. In this region, the salinity below 5 m is between 32 and 33.5. The salinity from the surface to the bottom of the northern and central region of the bay ranges between 31 and 33.5. This observation indicates that a river plume existed in the southern part of Beppu Bay during the survey.

3. Methods

3.1. Samples and geochemical analysis

Surface sediments (the uppermost 1 cm) were collected in August 2006 from Beppu Bay at depths of 21–72 m (Fig. 1; Table 1) using a Smith–McIntyre grab sampler. We confirmed

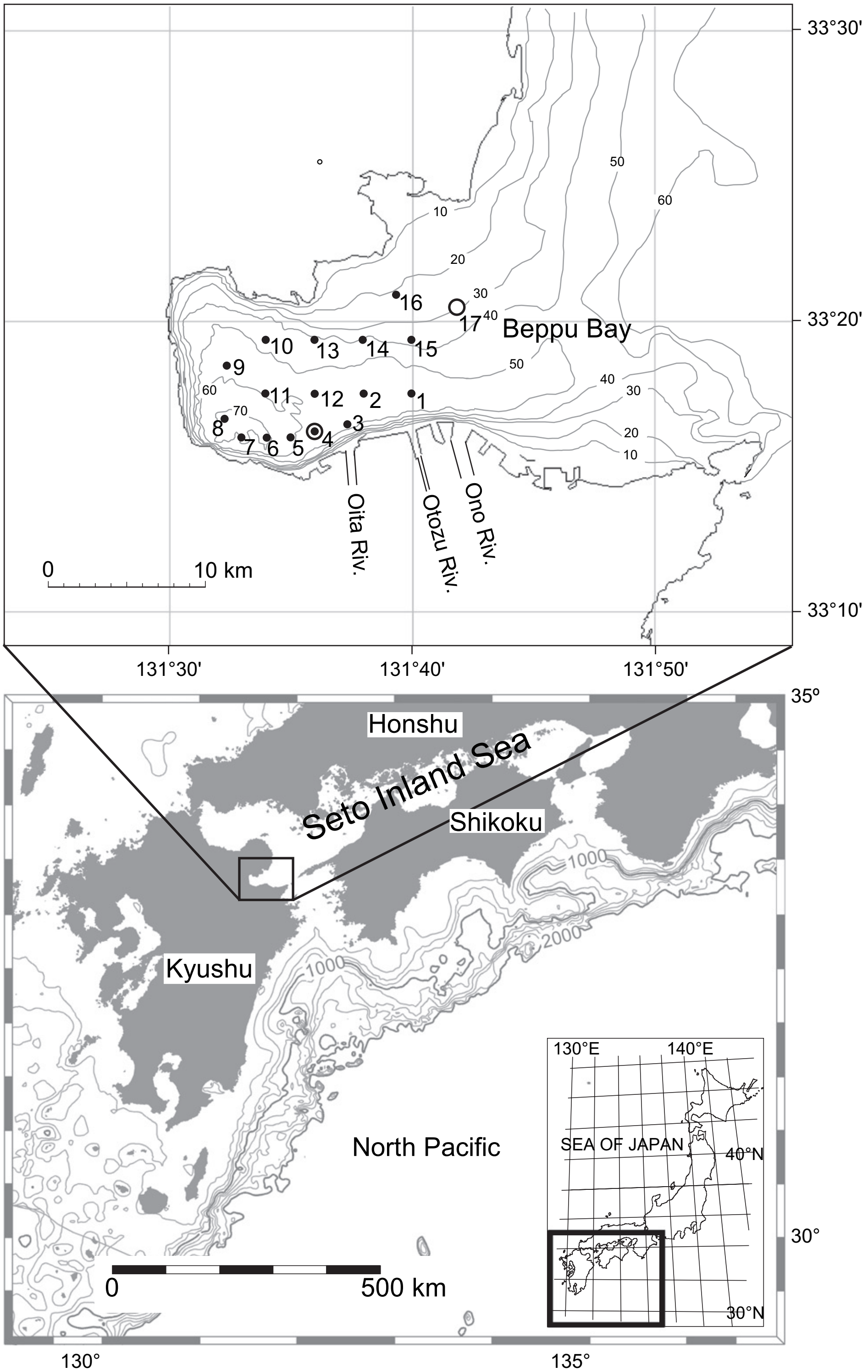

Fig. 1. Study area in Beppu Bay located in southwest Japan. Solid circles denote the sampling sites for surface sediments; open circles, the sampling sites for POM.

that all the samples were collected without disturbing the sediment–water interface. In all the samples, mostly clay-silt grains were observed. At the same sites, we measured the DO concentration in the bottom water and the Eh value in the uppermost surface sediment. These measurements were conducted using the undisturbed samples collected by a gravity corer; a DO/Eh meter (D-55, HORIBA, Ltd., Japan) was employed. Further, we measured the depths, temperatures, and salinities at each site using Chlorotec (ACL200-DK, ALEC Electronics Co., Ltd.). All the samples were immediately frozen at −20 °C until the analysis was performed. The samples were dried at 60 °C and ground to a fine powder.

In the analyses of stable isotopes, TOC, and TN, the subsamples were acidified with a 1 M HCl solution for a day to eliminate any carbonates; the acidified subsamples were again dried and then homogenized.

In order to examine the isotopic values and C/N ratios of the source organisms (phytoplankton) of sedimentary organic materials, particulate organic matter (POM with size fractions of 0.7–100 μm) was collected at water depths of 2 or 10 m from Beppu Bay (Fig. 1). The sampling sites were selected by spatial distribution of the surface salinity, and the samples at the sites that did not influence fresh water were employed. The POM fractions mainly comprised algal-derived organic matter because the chlorophyll concentration (fluorescence intensity of Chlorotec) at the sampling depth was high in the water column; further, there was no effect of the river plume as the salinity was high. The POMs were filtered by precombusted GF/F filters after being sieved by a 100-μm mesh sieve. The samples were frozen at −20 °C until the analysis was performed. The samples were dried at 60 °C and ground to a fine powder; lipids were removed with a chloroform/methanol (2:1) solution. The samples were exposed to concentrated 12 M HCl vapors for a day to eliminate any carbonates and then dried.

The stable isotope ratios of carbon (δ^{13}C) or nitrogen (δ^{15}N), TOC, and TN in the surface sediment samples and POMs were measured using a mass spectrometer (ANCA-SL, PDZ Europa, Ltd.) at the Center for Marine Environmental Studies, Ehime University, Japan. Further, δ^{13}C and δ^{15}N were expressed in per mil deviations from the standard value by the following equation:

$$\delta^{13}\mathrm{C},\ \delta^{15}\mathrm{N} = \left(R_{\mathrm{sample}}/R_{\mathrm{standard}} - 1\right)1000$$

where $R = {}^{13}\mathrm{C}/{}^{12}\mathrm{C}$ or ${}^{15}\mathrm{N}/{}^{14}\mathrm{N}$. Pee Dee Belemnite (PDB) limestone carbonate and atmospheric nitrogen (N_2) were used as standards for the carbon and nitrogen isotopic ratios, respectively. The analytical error was ±0.01‰ and ±0.19‰ for δ^{13}C and δ^{15}N, respectively. L-Histidine ($\delta^{15}\mathrm{N} = -7.81$‰) was used as reference material.

The TS values of the core samples were measured using a CHNS elemental analyzer (Flash EA1112, Thermo Finnigan) at the Center for Advanced Marine Core Research at Kochi University, Japan. The analytical error was ±0.04% for TS. The C/S ratios were determined using TS and TOC values, which were measured by a mass spectrometer.

3.2. Data analysis

In order to identify the primary factors influencing the variations in the geochemical parameters (δ^{13}C, δ^{15}N, TOC, TN, TS, C/N ratio, and C/S ratio), we performed a principal component analysis (PCA) of these data ($n = 16$). Redundancy analysis (RDA) (ter Braak and Smilauer, 2002) and a simple correlation analysis were used to examine the relationships between the geochemical parameters and six environmental variables shown in Table 1 (except surface salinity). The ordination technique, RDA, was used not only in many studies on ecological issues but also in paleolimnological studies on different units of geochemical data (e.g., Björck et al., 1993; Koinig et al., 2003). PCA and RDA computations were performed on centered and standardized data using CANOCO for Windows 4.5 (ter Braak and Smilauer, 2002). In the RDA computation, the correlation matrix option was selected since the variables are expressed using different units, and the scaling was conducted on a correlation biplot. Samples that did not yield relevant environmental data were eliminated from the analysis ($n = 11$). The significance of each environmental variable was tested by 499 unrestricted Monte Carlo permutations.

4. Results

Table 1 lists the values of geochemical data (δ^{13}C, δ^{15}N, C/N ratio, TOC, TN, TS, and C/S ratio) and environmental variables (water depth, Eh, DO, bottom temperature, bottom salinity, and distance from the Oita river mouth). The δ^{13}C and δ^{15}N values varied from −24.7 to −21.2‰ and from 3.6 to 6.4‰, respectively; low values were observed in the region near the Oita river mouth (St. 1–5). The C/N ratio varied within 9.2–13.8; high values were observed in the region near the river mouth (10.4–13.8). The TOC, TN, and TS values varied within 1.8–2.9%, within 0.21–0.37%, and within 0.51–1.36%, respectively. These observed values were high in the deepest and innermost regions of the bay (St. 6–9). The C/S ratios varied within 2.1–4.4; low values were observed in the deepest and innermost regions of the bay (St. 6–9). The δ^{13}C and δ^{15}N values of POM ranged from −22.2 to −21.9‰ and from 5.9 to 6.2‰, respectively—almost similar to those of the sedimentary δ^{13}C and δ^{15}N values, except the region near the river mouth (St. 1–5). In contrast, the observed C/N ratios of POM were 8.6–8.7, which are lower than those of the surface sediments.

4.1. Principal component analysis of geochemical parameters

The results of the PCA revealed two main axes that explain most of the variation in all the geochemical parameters (Fig. 2; Table 2). The first principal component (PC1) accounted for 67% of the variation; together with the second principal component (PC2), this value increased to 93% (Table 2). The loadings of δ^{13}C, δ^{15}N, C/N, TN, TS, and C/S on PC1 are high (−0.84, −0.89, −0.95, −0.80, and 0.92, respectively); however, the loading of TOC is low (−0.51). In contrast, the loading of TOC on PC2 is high (−0.81), whereas the other parameters exhibited low values. On the basis of the distribution of sample PC scores on the PC1 and PC2 axes, five sectors were identified (Fig. 2). Sector A is characterized by high PC1 and low PC2 values; in contrast, Sector B is characterized by low PC1 and low PC2 values (Fig. 2). In Beppu Bay, the spatial distribution of these sectors revealed that Sector A is located near the river mouths in the southern region of the bay. In contrast, Sector B is located in the deepest and innermost regions of the bay (Fig. 3). Sector C is characterized by

Table 1
Sample locations, environmental parameters, and measured geochemical parameters employed in this study. POM is the particulate organic matter in the water. ND denotes no data. C/N and C/S are atomic ratios of total organic carbon concentrations against total nitrogen and total sulfur concentrations, respectively

St.	Location	Sample	Water depth (m)	Eh (mV)	DO (mg/L)	Bottom temperature (°C)	Bottom salinity	Surface salinity	Distance from the Oita river mouth (km)	δ^{13}C (‰)	δ^{15}N (‰)	C/N	TOC (%)	TN (%)	TS (%)	C/S
1	33°17.50°N, 131°40.08°E	Surface sediment	53.1	−156	ND	17.6	33.5	29.0	5.3	−22.7	5.4	10.4	2.6	0.29	0.68	3.8
2	33°17.38°N, 131°37.99°E	Surface sediment	55.9	−53	0.21	13.5	33.2	31.2	3.7	−22.5	5.3	10.9	2.6	0.28	0.76	3.4
3	33°16.45°N, 131°37.34°E	Surface sediment	50.7	−160	0.81	17.8	33.3	30.7	1.7	−24.7	3.6	13.8	2.5	0.21	0.62	4.0
4	33°16.20°N, 131°35.98°E	Surface sediment	56.8	−120	ND	15.5	32.8	30.9	2.6	−23.4	4.9	11.8	2.5	0.25	0.64	3.9
5	33°16.01°N, 131°35.03°E	Surface sediment	59.9	−111	0.29	ND	ND	30.8	3.9	−24.5	4.1	12.9	2.4	0.21	0.54	4.4
6	33°16.02°N, 131°34.35°E	Surface sediment	67.2	−195	0.20	11.5	33.1	30.8	5.4	−22.1	5.9	9.9	2.8	0.33	1.33	2.1
7	33°16.02°N, 131°32.97°E	Surface sediment	69.7	−321	0.56	11.4	33.1	30.2	7.0	−21.8	6.1	9.6	2.9	0.36	1.36	2.2
8	33°16.48°N, 131°32.32°E	Surface sediment	72.3	−363	0.24	11.4	33.1	30.8	8.3	−21.7	6.3	9.3	2.9	0.37	1.25	2.3
9	33°18.48°N, 131°32.37°E	Surface sediment	57.0	−341	0.50	13.9	33.0	31.3	9.5	−21.2	6.4	9.2	2.7	0.34	0.97	2.8
10	33°19.33°N, 131°33.97°E	Surface sediment	45.9	ND	0.90	ND	ND	31.0	8.9	−21.3	6.1	9.4	2.3	0.29	0.68	3.4
11	33°17.48°N, 131°34.04°E	Surface sediment	57.6	−301	0.50	12.7	32.6	31.7	6.5	−21.4	6.4	9.4	2.6	0.32	0.90	2.9
12	33°17.51°N, 131°35.99°E	Surface sediment	54.0	−58	1.52	13.3	33.0	ND	4.3	−21.7	6.0	9.7	2.7	0.32	0.84	3.2
13	33°19.32°N, 131°36.07°E	Surface sediment	34.8	−100	1.40	25.1	ND	ND	7.4	−21.5	6.1	9.2	2.2	0.28	0.70	3.2
14	33°19.33°N, 131°38.03°E	Surface sediment	44.6	−264	3.23	20.0	33.5	ND	7.1	−21.5	6.1	9.2	2.4	0.31	0.68	3.6
15	33°19.33°N, 131°39.97°E	Surface sediment	39.0	90	4.15	20.6	ND	32.2	8.0	−21.8	5.7	9.4	2.3	0.29	0.66	3.5
16	33°20.89°N, 131°39.35°E	Surface sediment	21.0	77	2.63	21.5	33.4	32.3	10.3	−21.7	6.0	9.6	1.8	0.22	0.51	3.6
17	33°21.98°N, 131°41.70°E	POM	0.5							−21.9	6.2	8.6				
4	33°16.20°N, 131°35.98°E	POM	10							−22.2	5.9	8.7				

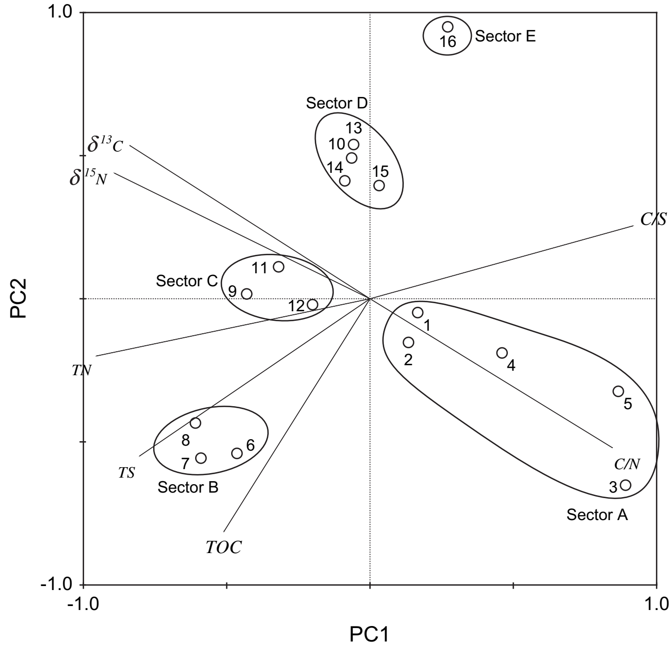

Fig. 2. Principal component analysis (PCA) biplot of the geochemical parameters measured from the surface sediments in Beppu Bay. Open circles with numbers denote the sample PC scores of each site. Sectors A, B, C, D, and E show the groups categorized according to particular PC scores.

low PC1 and low PC2 values; Sectors D and E are characterized by high PC2 values. The distribution pattern of Sectors B, C, D, and E on the PC axes exhibits a linear but stepwise increase in PC1 and PC2 values (Fig. 2). According to the spatial pattern of these sectors in Beppu Bay, Sector B is located in the deepest region; in contrast, Sector E is located in the shallowest region and Sectors C and D are located in an intermediate-depth region (Fig. 3). As shown in Fig. 2, the linear trend of Sectors B, C, D, and E is parallel to the direction of TOC, indicating that the distribution pattern of Sectors B, C, D, and E is closely related to the TOC variation. In addition, a simple correlation analysis revealed that the TOC values were very closely correlated with the water depth ($r = 0.93$) and bottom temperature ($r = 0.85$) (Table 3). The TN, TS, and C/S values were also correlated with the water depth and bottom temperature. Furthermore, the TOC, TN, TS, and C/S values showed a significant correlation with the Eh values. The TOC and TS values also revealed significant correlations with the DO values.

Table 2
Statistics of the PCA results of organic and sulfur geochemical parameters. In the text, Axis 1 and Axis 2 are represented by PC1 and PC2, respectively

	Axis 1	Axis 2	Axis 3	Axis 4
Eigenvalues	0.70	0.26	0.04	0.00
δ^{13}C	−0.84	0.54	−0.05	−0.07
δ^{15}N	−0.89	0.44	−0.03	−0.05
C/N	0.85	−0.52	0.05	−0.09
TOC	−0.51	−0.81	−0.27	−0.05
TN	−0.95	−0.20	−0.21	0.06
TS	−0.80	−0.55	0.22	0.05
C/S	0.92	0.25	−0.30	0.04

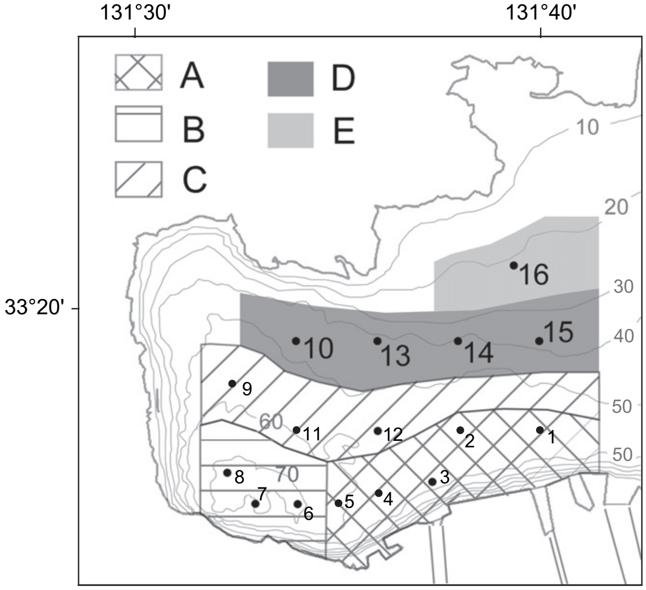

Fig. 3. Distribution map of sectors identified by PCA in Beppu Bay.

The PCA biplots reveal that the sample score variation associated with Sectors A and C is closely related to the δ^{13}C, δ^{15}N, and C/N values (Fig. 2). The results of a simple correlation analysis revealed that the δ^{13}C, δ^{15}N, and C/N values were very closely correlated with the distance from the Oita river mouth.

4.2. Redundancy analysis of geochemical parameters and environmental variables

The eigenvalues of the first two RDA axes were high (RDA Axis 1 (RD1): 0.64 and RDA Axis 2 (RD2): 0.27) when compared with the subsequent axes and accounted for 90.8% of the variance in the geochemical data (Table 4). The correlations between the geochemical data and environmental variables for RD1 and RD2 were high (0.99 and 0.97, respectively). Both the axes accounted for 97.1% of the variance in the relation between the geochemical parameters and six environment variables. The results of the permutation tests revealed the statistical significance of the effects of three environmental variables: water depth ($P = 0.004$), distance from the Oita river mouth ($P = 0.002$), and DO ($P = 0.020$). On the other hand, the results revealed the nonsignificant values of the effects of Eh, bottom temperature, and bottom salinity. The distance from the Oita river mouth was significantly correlated with RD1 because the absolute *t*-value of a regression coefficient is greater than two (ter Braak and Smilauer, 2002) (Table 5). In addition, the depth and DO were significantly correlated with RD2 (Table 5).

The RDA results (Fig. 4) demonstrated a similar pattern to the PCA results (Fig. 2). The five sectors in the RDA axes were distributed at similar locations in the PCA axes; further, the directions of the geochemical parameters—δ^{13}C, δ^{15}N,

Table 3
Statistics of simple correlation analysis between the geochemical parameters and environmental variables. The correlation coefficient values are given (in parenthesis, P values). Nonsignificant data are not listed

Variables	δ^{13}C	δ^{15}N	C/N	TOC	TN	TS	C/S
Water depth				0.93 (<0.01)	0.54 (0.03)	0.73 (<0.01)	−0.63 (<0.01)
Bottom temperature				0.85 (<0.01)	−0.61 (0.02)	−0.76 (<0.01)	0.62 (0.02)
DO				−0.70 (<0.01)		−0.56 (0.04)	
Eh				−0.72 (<0.01)	−0.64 (0.01)	−0.66 (<0.01)	0.55 (0.03)
Distance from the Oita river mouth	0.79 (<0.01)	0.77 (<0.01)	−0.81 (<0.01)				

TOC, TN, TS, C/N, and C/S—along the RDA axes were also similar to those along the PCA axes. This implies that the distribution pattern of variations in the geochemical parameters, as revealed in the RDA axes, is reliable.

The RDA results revealed the two close relationships between the geochemical parameters and environmental variables. (1) Relationship between the δ^{13}C, δ^{15}N, and C/N values and the distance from the river mouth. (2) Relationship between the TOC, TN, TS, and C/S values and the water depth and DO. The direction of the distribution pattern of the sample scores associated with Sectors A and C is similar to that of the arrows in relation (1). Therefore, the sample score variations associated with these sectors are mainly attributed to the variations in the distance from the river mouth. In contrast, the distribution pattern of the sample scores associated with Sectors B, C, D, and E is parallel to the arrow directions in relation (2). This indicates that the sample score variations associated with these sectors are mainly attributed to the variations in water depth and DO.

5. Discussion

The PCA and RDA results revealed two dominant patterns in the variations in the geochemical parameters of surface sediments in Beppu Bay. Pattern (1) is characterized by variations in the δ^{13}C, δ^{15}N, and C/N values, which are closely correlated with the distance from the river mouth to sampling sites. Pattern (2) is characterized by variations in the TOC, TN, TS, and C/S values, which are closely correlated with the water depth and DO. With respect to the PCA and RDA axes, the directions of these two patterns are almost perpendicular to each other. This indicates that both these patterns are mainly influenced by their respective main factors. In the following sections, we discuss the factors influencing these two patterns of variations in the geochemical parameters.

Table 4
Summary of the results of RDA of geochemical parameters, which is constrained to six environmental variables. In the text, Axis 1 and Axis 2 are represented by RD1 and RD2, respectively

Statistics	Axis 1	Axis 2	Axis 3	Axis 4
Eigenvalues	0.64	0.27	0.02	0.01
Geochemical data−environment correlations	0.99	0.97	0.64	0.75
Cumulative percentage variance of geochemical data	63.5	90.8	92.4	93.5
Cumulative percentage variance of geochemical data−environment relation	67.9	97.1	98.8	99.9

5.1. Factors controlling the spatial variations in δ^{13}C, δ^{15}N, and C/N

Based on the difference in the values among the sources, δ^{13}C, δ^{15}N, and C/N have been widely used to elucidate the source and fate of organic matter in a marine environment (Hedges and Parker, 1976; Fry and Sherr, 1984; Wada et al., 1987; Thornton and McManus, 1994; Tyson, 1995; Ogawa and Ogura, 1997; Andrews et al., 1998; Middelburg and Nieuwenhuize, 1998; Naidu et al., 2000; Cloern et al., 2002; Gordon and Goñi, 2003; Goñi et al., 2003; Owen and Lee, 2004; Usui et al., 2006). The close relationship between the variation in the δ^{13}C, δ^{15}N, and C/N values and the distance from the river mouth suggests that the spatial variations in these parameters of surface sedimentary organic matter may be explained by the mixing of sources such as terrestrial organic matter

Table 5
Inter-set correlations of the environmental variables with the axes (A) and t-values of regression coefficients (B). Data are assumed to be statistically significant when the absolute t-value is higher than two (ter Braak and Smilauer, 2002). Variables such as water depth, distance from the Oita river mouth, and DO were significant, as tested by 499 unrestricted Monte Carlo permutation tests ($P = 0.004$, $P = 0.002$, and $P = 0.020$, respectively)

	Axis 1	Axis 2	Axis 3	Axis 4
(A) Inter-set correlations				
Depth	−0.64	−0.72	0.01	−0.11
Eh	0.57	0.40	0.00	0.22
DO	0.31	0.66	0.34	0.30
Distance from the Oita river mouth	−0.45	0.69	−0.17	0.25
Bottom temperature	0.67	0.57	0.14	0.26
Bottom salinity	0.38	0.21	0.21	0.59
(B) t-Values of regression coefficients				
Depth	0.97	−2.01	−0.07	0.88
Eh	1.69	−1.18	−0.42	0.92
DO	−5.18	2.60	1.26	−0.74
Distance from the Oita river mouth	−3.53	0.91	−0.76	1.15
Bottom temperature	3.77	−1.66	−0.24	0.71
Bottom salinity	−1.49	0.11	0.05	0.19

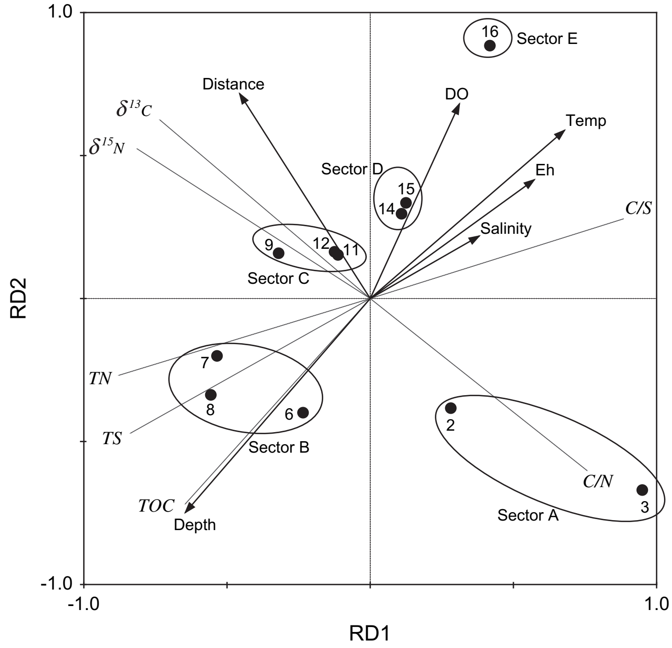

Fig. 4. Redundancy analysis (RDA) biplot of the geochemical parameters, sample scores, and environmental variables. Open circles with numbers denote sample RD scores of each site. Distance denotes the distance from the Oita river mouth to the sampling site; Temp, the bottom temperature; Depth, the water depth; DO, the dissolved oxygen concentration; Eh, the redox potential; and Salinity, the bottom water salinity. The arrow directions serve as an approximation of the correlation coefficient by the calculation of the cosine of the angle between two arrows.

from rivers and marine-derived organic matter. This interpretation is consistent with those of many previous studies (e.g., Andrews et al., 1998; Owen and Lee, 2004; Usui et al., 2006). The δ^{13}C and δ^{15}N values of surface sediments, except those in front of the river mouth (Sector A, Fig. 3), are in the range from −22.1 to −21.3‰ and from 5.7 to 6.4‰, respectively (Table 1). These values are almost consistent with those of POM (ranging from −22.2 to −21.9‰ and from 5.9 to 6.2‰, respectively, mainly derived from phytoplankton; see the descriptions in Section 3.1) in Beppu Bay. Therefore, the sedimented organic matters of Sector B, C, D, and E samples are possibly mainly composed of phytoplankton. In contrast, the values in front of the river mouth (Sector A) were lower (from −24.7 to −22.5‰ and from 3.6 to 5.4‰, respectively) than those in the other sites and those of POM. In general, C_3 plant-derived organic matter shows a δ^{13}C value ranging from −35 to −25‰ (Meyers, 1994; Cloern et al., 2002) and δ^{15}N value in the range 0–4‰ (Wada, 1986; Peterson and Howarth, 1987). According to these values and those of POM in Beppu Bay, the values of Sector A samples possibly represent mixing of C_3 plant-derived and phytoplankton-derived organic matter. The δ^{13}C values in Sector A samples cannot be explained by C_4 plant materials because the δ^{13}C values are much higher (−18 to −10‰, Meyers, 1994; Cloern et al., 2002) than the observed values in Sector A samples. This observation indicates that the C_4 plant contribution to the sedimented organic matter can be neglected in this study.

The δ^{13}C and δ^{15}N values of POM can be changed by postproduction processes such as the preferential removal of organic compounds with different isotope ratios from bulk POM, ^{13}C and ^{15}N enrichments in the residual POM during degradation, transformations through the food chain, and/or the immobilization of ambient N from the POM with different δ^{15}N (Benner et al., 1987, 1991; Michener and Schell, 1994; Lehmann et al., 2002). These processes might result in changes in the sedimentary δ^{13}C and δ^{15}N values. However, the δ^{13}C and δ^{15}N values in the surface sediments in Beppu Bay were close to those of suspended POM (Table 1). Therefore, the changes in the δ^{13}C and δ^{15}N values of POM during settling and diagenesis were probably limited in Beppu Bay.

Isotopic alternation due to eutrophication might also cause changes in sedimentary carbon and nitrogen isotope ratios. HCO_3 assimilation by phytoplankton, resulting from dissolved CO_2 limitation under high-productivity conditions, leads to increased algal δ^{13}C values in a water column (Fogel et al., 1992). Photosynthetic assimilation of heavy residual NO_3^- or NH_4^+ generated through denitrification, which produces considerable positive fractionation (up to +40‰), influences the POM δ^{15}N values (Montoya, 1994). In fact, this effect on the sedimentary δ^{15}N was reported in Chesapeake Bay (Bratton et al., 2003). However, δ^{13}C values as high as those of POM in the water column (−17‰) reported by Fogel et al. (1992) and δ^{15}N values as high as 9–10‰ of the uppermost core samples reported by Bratton et al. (2003) are not observed in our samples from Beppu Bay. Hence, the effects due to eutrophication appear to be minor. It is, therefore, concluded that the spatial variations in δ^{13}C and δ^{15}N of the surface sedimentary organic matter may be controlled by the mixing of sources of C_3 plant-derived organic matter from rivers and marine phytoplankton-derived organic matter.

The C/N ratio of the Beppu Bay sediments exhibits high values in Sector A (10.4–13.8; Table 1), suggesting that Sector A samples are abundant in terrestrial-derived organic matter with high C/N ratios (12–70 (mode: 16–20); combined data from Meyers, 1994; Cloern et al., 2002). In contrast, the C/N ratios in sectors other than Sector A show lower values (9.2–9.9) as compared to those of Sector A. However, these values are higher than those of POM (8.6–8.7; Table 1), whereas the δ^{13}C and δ^{15}N values are almost the same as those of the POM. This discrepancy between the sedimentary C/N ratios and those of the POM suggests the effect of diagenesis on sedimentary C/N. Organic N is generally remineralized faster than organic C, which serves to increase the C/N ratios (Tyson, 1995). This effect can increase the C/N ratios during the decomposition of nitrogenous planktonic organic matter (Lehmann et al., 2002). Even if this effect is exerted on the sedimentary C/N ratios, the close relationship between the C/N ratio and the distance from the river mouth suggests that the spatial variations in the sedimentary C/N ratios as well as the sedimentary δ^{13}C and δ^{15}N values in Beppu Bay are controlled by the mixing of terrestrial-derived and algal-derived organic matter.

5.2. Factors influencing the spatial variations in the TOC, TN, TS, and C/S values

Pattern (2) is characterized by variations in the TOC, TN, TS, and C/S values, which are closely related to the water depth and DO. The spatial variations in the TOC and TN values with the water depth and DO are probably related to the following two factors. (a) The spatial difference in the primary production in Beppu Bay, which is related to the thickness of the production layer depending on the water depth. (b) The spatial difference in the decomposition rates in the sediment–water interface, which is dependent on the water depth and DO. If factor (a) is significant, algal biomass should be more abundant in the deeper sites. However, this is inconsistent with the following observations. Both the annual-mean and monthly-mean transparencies in Beppu Bay from 1973 to 2002 (Tamura, 2004) reveal high values in the deeper sites corresponding to Sector B (depth: 60–70 m), indicating low algal biomass concentration in the deeper sites. Therefore, factor (a) is not the cause of the spatial variations in the TOC and TN values.

If factor (b) is the main cause of the variations in the sedimentary TOC and TN values, the following factors are related to the spatial difference in the decomposition rates: temperature (Jørgensen, 1983; Westrich and Berner, 1988) and oxic/anoxic conditions (Henrichs, 1992). In fact, these factors are closely related with the water depth (for bottom temperature, $r^2 = 0.8$ ($P < 0.01$); for DO, $r^2 = 0.5$ ($P < 0.01$); and for Eh, $r^2 = 0.5$ ($P < 0.01$)). The latter factor can significantly affect the decomposition rates when it is accompanied by bioturbation or other activities of higher organisms that may enhance the rates of organic matter oxidation to a greater extent than that by oxygen alone (Kristensen and Blackburn, 1987; Andersen and Kristensen, 1988).

The results of the simple correlation analysis revealed that the TOC and TN values are strongly correlated with the bottom temperature, indicating the importance of temperature on the decomposition rates. However, the results of the permutation tests in the RDA revealed the statistical significance of the effect of DO but nonsignificant values of the effect of bottom temperature. This result suggests that oxic/anoxic conditions may also be important in this process. As described above, the DO and Eh values showed a close correlation with the water depth, indicating that the deeper regions have a lower oxygen availability and are more reductive. Such environments should constrain the activity of benthos and decrease the decomposition rates. At this stage, we cannot determine whether temperature or oxic/anoxic condition is the important factor because the seasonal relationship between the TOC and TN values and these environmental factors is still unknown. However, the RDA results in this study suggest the importance of DO as a factor influencing the spatial variations in the TOC and TN values (Fig. 4).

The variation in the TS and C/S values is related to the formation of pyrite, which is influenced mainly by the supply rates of organic matter or hydrogen sulfide (H_2S) (Berner, 1984). Although the TOC value is the highest in the deepest region corresponding to Sector B, this high TOC value cannot be explained by the supply rate of organic matter. This is because the high transparency in the deepest region (Tamura, 2004) indicates a low organic matter flux into the bottom of this region. Therefore, it is more probable that pyrite formation is influenced by the supply rates of H_2S. Previous studies on sedimentary pyrite formation showed that the supply rate of H_2S is influenced by temperature (Westrich and Berner, 1988) and oxic/anoxic condition (Berner, 1984). In general, the TS (sulfide sulfur) concentration is higher in euxinic reductive marine sediments, which are abundantly supplied with H_2S, than in oxic marine sediments. Therefore, in more reductive conditions, the TS value is higher and C/S ratio is low (Berner, 1984). Our observations were consistent with the previous results; the samples in the deepest region (Sector B) with reductive condition showed high TS values and low C/S ratio (Table 1). Furthermore, the TS and C/S values showed a good correlation with Eh value (Table 3). However, these values are also correlated with temperature (Table 3). These results suggest that temperature and/or oxic/anoxic condition influence the spatial variations in these parameters. It is still unknown whether temperature or oxic/anoxic condition is the important factor influencing the variations in these parameters because seasonal changes in the relationship of TS and C/S values with temperature and Eh are not considered in this study. Nevertheless, good correlations between Eh values and TS and C/S values in the simple correlation analysis and between DO and TS and C/S values in the RDA suggest that the TS and C/S values are closely related to the processes of oxic/anoxic conditions.

Sedimentation rates might be an alternative factor that influences the variations in the TOC, TN, TS, and C/S values (Toth and Lerman, 1977; Berner, 1984). In both oxic/anoxic marine sediments, rapid sedimentation can lead to rapid burial of reactive organic compounds (Toth and Lerman, 1977; Berner, 1984); this results in a high production of H_2S and enhancing the pyrite formation (Berner, 1984). According to these observations, spatial variations of sedimentation rate would result in spatial variations in the TOC, TN, TS, and C/S values. It is necessary to conduct further studies on the relationship between sedimentation rates and spatial variations in these geochemical parameters.

5.3. Geochemical parameters sensitive to oxic/anoxic conditions

We have observed that there are two dominant patterns in the spatial variations in the organic and sulfur geochemical parameters. The first pattern is characterized by $\delta^{13}C$, $\delta^{15}N$, and C/N, which are related to the mixing of source materials; the second, by TOC, TN, TS, and C/S, which are related to the spatial difference in the temperature and oxic/anoxic conditions. The two patterns are perpendicular with respect to the PCA and RDA axes, implying that the two geochemical groups are influenced only by their main factors. In other words, it implies that the $\delta^{13}C$, $\delta^{15}N$, and C/N values are not sensitive to oxic/anoxic conditions. Bratton et al. (2003)

reported an increasing trend in the sedimentary $\delta^{15}N$ values associated with oxygen depletion in Chesapeake Bay. They concluded that the trend observed in the core samples is due to changes in the $\delta^{15}N$ values of nutrient and phytoplankton over time, which is influenced by the isotopic fractionation effect of denitrification under oxygen-depletion conditions. This study highlighted the importance of $\delta^{15}N$ as an indicator for inferring the trend of eutrophication and oxic/anoxic conditions. However, in Beppu Bay the RDA results revealed that the effect of oxygen depletion has no or marginal influence on the sedimentary $\delta^{15}N$ value. This might be due to the minor effect of denitrification on algal $\delta^{15}N$ and resulting sedimentary $\delta^{15}N$. In our results, the TOC, TN, TS, and C/S values are probably sensitive to oxic/anoxic conditions in Beppu Bay as compared to $\delta^{15}N$.

6. Conclusion

In order to elucidate the organic and sulfur geochemical processes of surface sediments associated with oxic/anoxic conditions, we have examined the relationship between the spatial variations in the values of sedimentary $\delta^{13}C$, $\delta^{15}N$, TOC, TN, TS, C/N ratio, and C/S ratio and those of environmental variables in Beppu Bay, Japan.

The PCA of these geochemical parameters revealed the first two axes which account for 96% of the total variance. In addition, RDA of these parameters, which was constrained to environmental variables, accounted for 91% of the total variance. The results of the PCA and RDA revealed two dominant patterns in the variations in the values of geochemical parameters. The first pattern is characterized by variations in the $\delta^{13}C$, $\delta^{15}N$, and C/N values, which are closely related to the distance between the river mouth and sampling sites. This pattern is attributed to the mixing of two source organic materials—C_3 land plants and marine phytoplankton—rather than various alternation processes such as diagenesis and eutrophication.

The second pattern is characterized by variations in the TOC, TN, TS, and C/S values. The RDA results revealed that these geochemical parameters are closely related to the water depth and DO. In contrast, the simple correlation analysis also showed a good correlation of TOC, TN, TS, and C/S with bottom temperature. In Beppu Bay, a significant negative correlation is observed between depth and DO and depth and Eh value, indicating that deeper bottom environments have lower oxygen availability and are more reductive. According to these observations and some findings of previous studies, spatial variations in the TOC and TN are influenced by the decomposition rates; in contrast, spatial variations in the TS and C/S, by rates of pyrite formation. Both decomposition and pyrite formation rates are possibly influenced by temperature or oxic/anoxic conditions. The sedimentation rate might be an alternative factor influencing the variations in the TOC, TN, TS, and C/S values. However, it is necessary to conduct further studies on the relationship between the sedimentation rates and spatial variations of these geochemical parameters. Nevertheless, the good correlation of these geochemical parameters with DO in the RDA and with Eh in the simple correlation analysis suggests that these parameters are related to oxic/anoxic conditions in the bottom environments of Beppu Bay.

The RDA results revealed that the spatial variations in the organic and sulfur geochemical parameters can be explained by the two dominant patterns as described above. The two patterns exhibit a perpendicular relation with respect to the PCA and RDA axes, implying that the two geochemical groups are controlled only by their main factors. Parameters such as TOC, TN, TS, and C/S are probably sensitive to the temperature or oxic/anoxic conditions in Beppu Bay; in contrast, $\delta^{13}C$, $\delta^{15}N$, and C/N are less sensitive to these conditions.

Our study suggested the possibility of inferring long-term records of marine oxygen depletion in Beppu Bay using the indicators of these organic and sulfur geochemical parameters. In the future, it is expected to be capable of elucidating a trend in oxygen depletion in Beppu Bay.

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References

Adelson, J.M., Helz, G.R., Miller, C.V., 2001. Reconstructing the rise of recent coastal anoxia: molybdenum in Chesapeake Bay sediments. Geochimica et Cosmochimica Acta 65, 237–252.

Amano, A., Inoue, T., Iwamoto, N., Shioya, F., Inouchi, Y., 2004. Bottom environmental changes during the past 100 years in Kitanada Bay, Ehime Prefecture, Southwest Japan. The Journal of Geological Society of Japan 110, 518–527.

Andrews, J.E., Greenaway, A.M., Dennis, P.F., 1998. Combined carbon isotope and C/N ratios as indicators of source and fate of organic matter in a poorly flushed, tropical estuary: Hunts Bay, Kingston Harbour, Jamaica. Estuarine, Coastal and Shelf Science 46, 743–756.

Andersen, F.Ø., Kristensen, E., 1988. The influence of macrofauna on estuarine benthic community metabolism: a microcosm study. Marine Biology 99, 591–603.

Benner, R., Fogel, M.L., Sprague, E.K., Hodson, R.E., 1987. Depletion of ^{13}C in lignin and its implications for stable carbon isotope studies. Nature 329, 708–710.

Benner, R., Fogel, M.L., Sprague, E.K., 1991. Diagenesis of below ground biomass of *Spartina alterniflora* in salt-marsh sediments. Limnology and Oceanography 36, 1358–1374.

Berner, R., 1984. Sedimentary pyrite formation: an update. Geochimica et Cosmochimica Acta 48, 605–615.

Björck, S., Håkansson, H., Olsson, S., Barnekow, L., Janssens, J., 1993. Palaeoclimatic studies in South Shetland Islands, Antarctica, based on numerous stratigraphic variables in lake sediments. Journal of Paleolimnology 8, 233–272.

Bratton, J.F., Colman, S.M., Seal II, R.R., 2003. Eutrophication and carbon sources in Chesapeake Bay over the last 2700 yr: human impacts in context. Geochimica et Cosmochimica Acta 67, 3385–3402.

ter Braak, C.J.F., Smilauer, P., 2002. CANOCO Reference Manual and CanoDraw for Windows User's Guide: Software for Canonical Community Ordination (Version 4.5). Microcomputer Power, Ithaca, NY, USA, 500 pp.

Cloern, J.E., Canuel, E.A., Harris, D., 2002. Stable carbon and nitrogen isotopic composition of aquatic and terrestrial plants of the San Francisco Bay estuarine system. Limnology and Oceanography 47, 713–729.

Cooper, S.R., Brush, G.S., 1991. Long-term history of Chesapeake Bay anoxia. Science 254, 992–996.

Fogel, M.L., Cifuentes, L.A., Velinsky, D.J., Sharp, J.H., 1992. Relationship of carbon availability in estuarine phytoplankton to isotopic composition. Marine Ecology Progress Series 82, 291–300.

Fry, B., Sherr, E.B., 1984. δ^{13}C measurements as indicators of carbon flow in marine and freshwater ecosystems. Contributions in Marine Science 27, 13–47.

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). Estuarine, Coastal and Shelf Science 57, 1023–1048.

Gordon, E.S., Goñi, M.A., 2003. Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico. Geochimica et Cosmochimica Acta 67, 2359–2375.

Hedges, J.I., Parker, P.L., 1976. Land-derived organic matter in surface sediments from the Gulf of Mexico. Geochimica et Cosmochimica Acta 40, 1019–1029.

Henrichs, S.M., 1992. Early diagenesis of organic matter in marine sediments: progress and perplexity. Marine Chemistry 39, 119–149.

Japan Meteorological Agency, 1999. Annual Report. Japan Meteorological Agency, CD-ROM.

Jørgensen, B.B., 1983. Processes at the sediment–water interface. In: Bolin, B., Cook, R. (Eds.), The Major Biogeochemical Cycles and Their Interactions, SCOPE 21. Wiley, New York, pp. 477–509.

Kameda, T., Fujiwara, T., 1995. Ventilation time and anoxia of the benthic cold water in Beppu Bay. Bulletin of Coastal Oceanography 33, 59–68 (in Japanese).

Koinig, K.A., Shotyk, W., Lotter, A.F., Ohlendorf, C., Sturm, M., 2003. 9000 years of geochemical evolution of lithogenic major and trace elements in the sediment of an alpine lake—the role of climate, vegetation, and land use history. Journal of Paleolimnology 30, 307–320.

Kristensen, E., Blackburn, T.H., 1987. The fate of organic carbon and nitrogen in experimental marine sediment systems: influence of bioturbation and anoxia. Journal of Marine Research 45, 231–257.

Lehmann, M.F., Bernasconi, S.M., Barbieri, A., McKenzie, J.A., 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochimica et Cosmochimica Acta 66, 3573–3584.

Meyers, P.A., 1994. Preservation of source identification of sedimentary organic matter during and after deposition. Chemical Geology 144, 289–302.

Michener, R.H., Schell, D.M., 1994. Stable isotope ratios as tracers in marine aquatic food webs. In: Lajtha, K., Michener, R.H. (Eds.), Stable Isotopes in Ecology and Environmental Science. Blackwell Scientific Publications, pp. 138–157.

Middelburg, J.J., Nieuwenhuize, J., 1998. Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary. Marine Chemistry 60, 217–225.

Montoya, J.P., 1994. Nitrogen isotope fractionation in the modern ocean: implications for the sedimentary record. In: Zahn, R., Pedersen, T.F., Kaminski, M.A., Labeyrie, L. (Eds.), Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change. Springer-Verlag, Berlin, Germany, pp. 259–279.

Naidu, A.S., Cooper, L.W., Finney, B.P., Macdonald, R.W., Alexander, C., Semiletov, I.P., 2000. Organic carbon isotope ratios (δ^{13}C) of Arctic Amerasian Continental shelf sediments. International Journal of Earth Sciences 89, 522–532.

Ogawa, N., Ogura, N., 1997. Dynamics of particulate organic matter in the Tamagawa Estuary and Inner Tokyo Bay. Estuarine, Coastal and Shelf Science 44, 263–273.

Owen, R.B., Lee, R., 2004. Human impacts on organic matter sedimentation in a proximal sheld setting, Hong Kong. Continental Shelf Research 24, 583–602.

Peterson, B.J., Howarth, R.W., 1987. Sulfur, carbon, and nitrogen isotopes used to trace organic matter flow in the salt-marsh estuaries of Sapelo Island, Georgia. Limnology and Oceanography 32, 1195–1213.

Tamura, Y., 2004. Studies of the transparency in waters of Iyo-nada and Beppu Bay—horizontal distribution and seasonal changes. Annual Report on Oita Prefectural Fisheries Research Center 5, 11–18 (in Japanese).

The Association for the Environmental Conservation of the Seto Inland Sea, 2001. The Environmental Conservation of the Seto Inland Sea. The Association for the Environmental Conservation of the Seto Inland Sea, Kobe, Japan, 102 pp.

Thornton, S.F., McManus, J., 1994. Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary, Scotland. Estuarine, Coastal and Shelf Science 38, 219–233.

Toth, D.J., Lerman, A., 1977. Organic matter reactivity and sedimentation rates in the ocean. American Journal of Science 277, 465–485.

Tyson, R.V., 1995. Sedimentary Organic Matter. Chapman and Hall, London.

Usui, T., Nagao, S., Yamamoto, M., Suzuki, K., Kudo, I., Montani, S., Noda, A., Minagaw, M., 2006. Distribution and sources of organic matter in surficial sediments on the shelf and slope off Tokachi, western North Pacific, inferred from C and N stable isotopes and C/N ratios. Marine Chemistry 98, 241–259.

Wada, E., 1986. Isotope effects in the biological processes—variation of ^{13}C and ^{15}N abundances in biosphere. Radioisotopes 35, 136–146 (in Japanese).

Wada, E., Minagawa, M., Mizutani, H., Tsuji, T., Imaizumi, R., Karasawa, K., 1987. Biogeochemical studies on the transport of organic matter along the Otsuchi River watershed, Japan. Estuarine, Coastal and Shelf Science 25, 321–336.

Westrich, J.T., Berner, R.A., 1988. The effect of temperature on rates of sulfate reduction in marine sediments. Geomicrobiology Journal 6, 99–117.

Zimmerman, A.R., Canuel, E.A., 2002. Sediment geochemical records of eutrophication in the mesohaline Chesapeake Bay. Limnology and Oceanography 47, 1084–1093.