C/N ratios in a sediment core from Nakaumi Lagoon, southwest Japan —usefulness as an organic source indicator—

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The weight ratio of total organic carbon to total nitrogen (C/N ratio) in 20 meters of sediment core from Nakaumi Lagoon (coastal brackish lake), Japan is examined for its suitability as an organic source indicator. The C/N ratio depth profile is compared to the depth profiles of other proxies, i.e., weight ratio of total organic carbon to total organic nitrogen (C/N_{org.} ratio), stanol compositions, *n*-alkane compositions and the hydrogen-index by Rock-Eval pyrolysis.

The C/N ratios of the lagoonal sediments, which have been deposited over the last *ca.* 8,000 years, have a different profile from that of the C/N_{org.} ratio and other proxies due to the effects of a constant level of inorganic nitrogen (N_{inorg.}; *ca.* 0.04%) in the sediments. When C_{org.} content is less than 1 wt%, the presence of N_{inorg.} lowers the C/N ratio considerably, giving an inaccurate indication of organic source. C-N and C/N ratio-C_{org.} plots are useful for evaluating the effect of N_{inorg.}; if the depth profiles of the C/N ratio and C_{org.} content exhibit similar trends, this is taken as a warning that the apparent variation in the C/N ratio should be carefully examined in conjunction with the other plots and proxies. It is also found that the C/N_{org.} ratio itself also tends to increase due to the preferential decomposition of nitrogen compounds, and that in sediments containing high proportions of planktonic organic matter (OM), the sensitivity of the C/N ratio to changes in the proportions of planktonic-terrestrial OM is relatively low.

INTRODUCTION

The weight ratio of total organic carbon to total nitrogen (C/N ratio) is often used as an indicator of the source of organic matter (OM) in aquatic sediments. Although the ¹³C/¹²C ratio of OM is also an important indicator, the isotopic ratio of planktonic OM produced in estuaries and freshwater lakes is too variable to be used as an indicator in sediments originating in these environments (e.g., Fry and Sherr, 1984; Boutton, 1991; Meyers, 1994, 1997). This is because freshwater systems have a wide range inorganic $\delta^{13}\text{C}$ values (–15 to 0‰ PDB; Boutton, 1991) compared to marine systems. Other specific indicators of organic source, such as steroid compounds and

lignin phenols, are not easily analyzed due to chemical complexity. Hence, the C/N ratio, having recently become easier to obtain through the popularization of rapid elemental analysis techniques, appears to be an effective and simple indicator of organic source, particularly in lacustrine depositional environments, including estuaries.

The C/N ratio in aquatic systems is governed by the mixing of terrestrial and autochthonous OM (e.g., Müller, 1977; Rashid and Reinson, 1979; Nakai *et al.*, 1982; Ostrom and Macko, 1992; Thornton and McManus, 1994; Meyers, 1997). Proteins, which are the primary nitrogen compounds of phytoplankton and zooplankton, have C/N ratios of 5 to 6 (Bordowski, 1965a, b). Freshly-deposited OM, derived mainly from

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planktonic organisms, has a C/N ratio of 6 to 9 (Bordowskii, 1965a; Prahl *et al.*, 1980; Biggs *et al.*, 1983). In contrast, terrestrial vascular plants and their derivatives in sediments have C/N ratios of 15 or higher (Bordowskii, 1965b; Ertel and Hedges, 1984; Post *et al.*, 1985; Ertel *et al.*, 1986; Hedges *et al.*, 1986; Orem *et al.*, 1991). For example, the average C/N ratios for wood, leaf and macrophyte material in the watershed area of the Amazon River are 179, 24.1 and 39.4, respectively (Hedges *et al.*, 1986). Higher plants are the main organic producers in the terrestrial environment, and consist mainly of cellulose and lignin, which contain few nitrogen compounds.

The C/N ratio has been used as a representative proxy to reconstruct the depositional environment of coastal lagoon and freshwater lake sediments (Nakai *et al.*, 1982; Wada *et al.*, 1987; Haugen and Lichtenthaler, 1991; Mariotti *et al.*, 1991; Anderson *et al.*, 1992; Prahl *et al.*, 1994). Although the C/N ratios have been interpreted elsewhere to be nearly equal to the weight ratio of $C_{org.}$ to organic nitrogen (i.e., $C/N_{org.}$ ratio), ignoring inorganic nitrogen ($N_{inorg.}$) content, some researchers have pointed out that a relatively high $N_{inorg.}$ could affect the C/N ratio. Müller (1977) reported that C/N ratios in deep-sea sediments were anomalously low (<4), attributing this reduction to inorganic ammonia. This suggests that $N_{inorg.}$ introduces a degree of uncertainty in using C/N ratio as an indicator of organic source. In the present study, a simple method for $N_{org.}$ measurement is presented, and the effect of $N_{inorg.}$ on the C/N ratio in estuarine lagoon sediments is discussed, comparing the results with other specific indicators of organic source. The Holocene sediment core used here was taken from the Nakaumi Lagoon, southwest Japan. The indicators to which the C/N ratio is compared are stanol composition, *n*-alkane composition and the hydrogen-index (HI) by Rock-Eval pyrolysis. We also discuss the effects of the preferential decomposition of OM under oxic conditions on the C/N ratio, and evaluate the sensitivity of the C/N ratio to changes in the proportions of planktonic and terrestrial OM.

Fig. 1. Location of the sediment core NU9007 in Nakaumi Lagoon, southwest Japan.

MATERIALS AND METHODS

Geological and hydrological settings

Nakaumi Lagoon has an average water depth of 5.4 m, and was formed by the invasion of seawater during sea level rise and the development of the Yumigahama peninsula during the Holocene (Tokuoka *et al.*, 1990). Details of the geological setting and recent history of Nakaumi Lagoon are given by Onishi (1986) and Tokuoka *et al.* (1990). Water depth at the coring site (Fig. 1) was 6.5 m. The watershed is largely underlain by granite (Iizumi *et al.*, 1985; Kano *et al.*, 1994). At present, seawater exchange occurs through Sakai-Strait, to the northeast of the lagoon (Fig. 1). Nakaumi Lagoon receives freshwater input from the Inashi River, and low salinity water from the Ohashi River. On average, chlorinity of the lake water is 7–11 g/l in the upper layer and 14–16 g/l in the lower layer (Date *et al.*, 1989). Density stratification results in anoxic bottom water conditions during summer months (Hashitani *et al.*, 1990).

Fig. 2. (a) Sediment column description, (b) profile of median diameter of sediments (MD), (c) profile of organic carbon ($C_{\text{org.}}$) content of sediment (Sampei *et al.*, 1997b), and (d) profile of total nitrogen (N_{total}) and inorganic nitrogen ($N_{\text{inorg.}}$) contents of sediment. $N_{\text{inorg.}}$ content is the residual nitrogen in sediment after treatment with a hot 10% H_2O_2 water solution.

Sediment core collection and description

A single sediment core (NU9007) was taken during June and July, 1990 using a boring corer, which consisted of a stainless steel outer tube, and a series of aluminum inner tubes 7.4 cm in diameter and 1 m in length. Total length of the sediment core was 20.8 m. Following collection, the core was transported to Shimane University, sectioned at 2.5 cm intervals (total sample: 832) and stored at -20°C until analysis.

Sediment samples consist primarily of dark greenish-gray mud (Fig. 2(a)). Sandy silt layers occur at 16–18 m and 20 m in the core. Clear lamination was not observed at any depth, and small marine shells occur throughout the core. The Kikai-Akahoya (K-Ah) volcanic ash (6,300 yr. B.P. ^{14}C age: Arai *et al.*, 1981) was observed at 10.22 m (Hataya *et al.*, 1991). Below 20 m, sediment is dominated by fine-medium sand and gravel, which indicates shallow-water deposition prior to Holocene sea level rise (Tokuoka *et al.*, 1990).

$C_{\text{org.}}$ and N_{total} contents

$C_{\text{org.}}$ and N_{total} contents of sediments from 78 selected 2.5 cm intervals were determined by Sampei *et al.* (1997b) using a Carlo Erba 1108 elemental analyzer and YANACO CHN-corder MT-3, after treatment with 1N HCl added to the sediment weighed in cup and dried to remove the carbonate fraction. The errors (coefficient of variation) inherent in this analysis are within $\pm 3\%$. S_{total} contents of sediments from selected 42 layers were determined by HORIBA EMIA2000 elemental analyzer. The errors (coefficient of variation) inherent in this analysis are within $\pm 3\%$.

Decomposition experiments with a hot 10% H_2O_2

To determine C/ $N_{\text{org.}}$ ratio, the decomposition percentage of organic nitrogen/non-nitrogen compounds were analyzed. Preliminary experiments were carried out to test the decomposition of cellulose (tissue), casein (protein) and stearic acid (fatty acid) by a hot 10% H_2O_2 water solution treatment. 100 ml of 10% H_2O_2 water solution

were added to 0.2 g portion of cellulose (Advantec Toyo, Co., Ltd., Quantitative Ashless 5B Filter Paper), casein (Wako Pure Chemical Industries Ltd.) and stearic acid (Kanto Chemical, Co., Ltd.) at 50°C on a hot plate for periods of 1, 2, 3 and 4 days. 80 ml of supernatant were decanted, and 80 ml of fresh 10% H₂O₂ water solution added each day. After the experiments, the 10% H₂O₂ water solution was removed by decantation, and the samples were dried at 110°C for 1 hour. The weight loss during the experiment was then determined.

In addition, C/N_{org.} ratio of kerogen and humic acid from the sediment core in a hot 10% H₂O₂ water solution treatment were investigated to check decomposability of natural humic substance. The kerogen and humic acid samples were from the upper portion (1.1 m) and lower portion (16.7 m) of the sediment core. Kerogen was isolated from the sediments by acid digestion using 55% HF and 6N HCl (Durand and Nicaise, 1980). Humic acid was isolated using 0.1N NaOH + 0.1M Na₄P₂O₇ mixture (1:1). 100 ml of 10% H₂O₂ water solution were added to ca. 50 mg of kerogen and humic acid in 100 cc beakers and held at 50°C on a hot plate for 1 hour. The 10% H₂O₂ water solution was subsequently removed by decantation, and the sample dried at 110°C for 1 hour. The weight loss through the experiment was measured. The C_{org.} and N_{org.} contents of the kerogen and humic acid were determined using a Carlo Erba 1108 elemental analyzer.

N_{inorg.} and N_{org.} contents

N_{inorg.} and N_{org.} contents of the sediments were determined by preferential leaching of 30 selected core segments. 10 ml of 1N HCl were added to 500 mg of dry sediment and left for 10 minutes, followed by three washings with distilled water at room temperature to remove salts. Samples were centrifuged at 3000 r.p.m. for 20 minutes, and then oven-dried at 70°C for 24 hours. The C_{org.} and N_{total} contents were analyzed using 30 mg of the dry sample. 50 ml of 1N KCl were added to the residue, which was then put in an ultrasonic tank for 30 minutes for extraction of exchangeable

NH₄⁺ (N_{exchange}; Itihara, 1983b). Following repeated washing with distilled water at room temperature and drying at 70°C for 24 hours, half of the sample was analyzed for N_{exchange} by difference. Then, 100 ml of 10% H₂O₂ water solution were added to the other half of the sample, and left for two weeks at 50°C on a hot plate in order to oxidize the OM. It took at least a week for the percentage decomposed to become nearly constant. To ensure the decomposition, 80 ml of supernatant were decanted, and 80 ml of fresh 10% H₂O₂ water solution added every two days. After decomposition, the sample was washed five times with distilled water at room temperature, centrifuged at 3000 r.p.m. for 20 minutes, and dried at 70°C for 24 hours, then analyzed for residual C_{org.} and residual nitrogen (N_{resid.}) contents using a Carlo Erba 1108 elemental analyzer and YANACO CHN-corder MT-3. Decomposed OM was calculated from the difference between the C_{org.} contents before and after the treatment. The N_{org.} contents were calculated from the difference between N_{total} and N_{inorg.} (i.e., N_{resid.} + N_{exchange}). For determination of low nitrogen contents, blank values were measured several times using the elemental analyzer. The average value of the blank was subtracted from the sample values. The error (coefficient of variation) inherent in the N_{inorg.} content measurement was determined by analysis of five replicate samples, producing results within ±5%.

Grain size

A wet 1 g split of each sample was treated with 10% H₂O₂ water solution and left for several days at room temperature for decomposition of OM and pyrite. The median diameter of sediment grains (MD) was then measured using a laser size analyzer (Seishin Kigyo Laser PRO-7000S).

Stanol composition

Stanol composition analysis was performed on 31 selected sediment layers. The analytical procedure was derived from those of Nishimura and Koyama (1977), Kondo and Ishiwatari (1992), Kondo *et al.* (1992) and Shimizu *et al.* (1992).

Each wet sediment sample was dried at 50°C for 24 hours and powdered to less than #200 mesh size sieve in agateware. Extractable organic matter (EOM) was extracted from each sample (*ca.* 15 g) in a Soxhlet apparatus by benzene and methanol (9:1 v/v) for 24 hours. In the course of the extraction, elemental sulfur was removed by activated copper. The EOM thus recovered was dried at room temperature. The EOM was subjected to thin layer chromatography (TLC), which was performed on a 80–100 mesh silica gel (Kieselgel 60 PF₂₅₄, Merck) plate with *n*-hexane. Fractions for hydrocarbon and polyaromatic hydrocarbon were removed. The polar compound fraction was then extracted sequentially with KOH/ethanol (30 ml of 0.5 N KOH in ethanol/10 g dry sample) by refluxing for 2 hours. *n*-Hexane and diethylether mixture (1:1 v/v) was added to the fraction, and sterol compounds were extracted.

Sterol compounds were identified by gas chromatography (GC: Shimadzu GC 14A) coupled with a mass spectrometer (MS: Shimadzu GC/MS QP2000A system). GC/MS analysis of the sterol fractions was performed following derivatization to trimethylsilyl (TMS) ethers at 60°C for 1 hour with N-trimethylsilylimidazole (TMSI, GL Sciences Co., Inc.). The GC is equipped with a programmable temperature injection system and a fused silica capillary column (30 m × 0.25 mm I.D.) coated with (5%-Phenyl)Methylpolysiloxane (DB-5: J&W Co.). The temperature was programmed from 40°C to 300°C at the rate of 4°C/min. Helium was used as a carrier gas at a flow rate of 3 ml/min. The MS was scanned every 0.5 second over *m/z* 50 to 550, and the spectral data obtained were stored in the computer system. All spectra were recorded at an electron energy of 70 eV. Cholesterol standard (Nacalai Tesque, Inc.) was used for checking retention time. Structural identification of the stanols was based on the GC/MS analysis, in comparison with authentic stanols, and also by comparison of the detailed mass spectral fragmentation patterns with those of authentic stanol TMS ethers (Brooks *et al.*, 1973; Kondo *et al.*, 1993). Relative composition of C₂₇-, C₂₈-

and C₂₉-stanol was obtained by the *m/z* 215 ion intensity (Nishimura, 1982; Shimizu *et al.*, 1992).

Stanols are major derivatives from steroid compounds, which are known as indicators of planktonic and terrestrial OM (Shimizu *et al.*, 1992; Meyers and Ishiwatari, 1993). C₂₉-steroid compounds, in general, are major sterols in higher plants. In contrast, plankton contains dominant C₂₇-steroid compounds (e.g., Nishimura, 1977; Nishimura and Koyama, 1977; Huang and Meinschein, 1979; Killops and Killops, 1993). Stanols survive unaltered at anoxic sediment surface, in contrast with stenols, and are also sometimes more abundant than stenols in sediments below about 10 cm depth (Nishimura and Koyama, 1977; Gaskell and Eglinton, 1976). In the Nakaumi Lagoon sediments, reducing conditions in the sediments are sufficiently strong enough to produce sedimentary pyrite (Sampei *et al.*, 1992).

n-Alkanes

Normal alkane composition analysis was performed on 31 selected sediment layers: same sample with stanol analysis. The *n*-alkane fraction on the TLC plate was then extracted with *n*-hexane. *n*-Alkanes were determined by gas chromatography (GC: Shimadzu GC 14A). The column and temperature condition is same with that for stanol analysis. *n*-C₃₂ alkane standard (Kishida, Inc.) was used as an external standard.

The source of *n*-alkanes has been often discussed by many researchers. Long-chain *n*-alkanes, particularly C₂₇, C₂₉ and C₃₁ (vascular plants origin), are well known as a source indicator of terrestrial OM, and short chain *n*-alkanes less than C₂₀ are from planktonic OM (e.g., Colombo *et al.*, 1996; Meyers, 1997; Tenzer *et al.*, 1999).

Rock-Eval

Dry sediments (100 mg) from 22 selected depth of the core were placed in the small cup of Rock-Eval plus TOC system and analyzed for the peak area "S₂" of hydrocarbons produced by heating the sample from 300°C to 550°C. The HI is given by S₂/C_{org.} (mg hydrocarbons/g organic carbon).

Rock-Eval method is a technique for the anhydrous pyrolysis of petroleum source rocks developed by the Institute Francais du Petrole (IFP). This analyzer enables the chemical composition of kerogen and its organic type to be determined (Tissot and Welte, 1984; Killops and Killops, 1993). Recently, this method is used as an organic source indicator for recent sediments (e.g., Smith, 1990; Schubert and Stein, 1996; Meyers, 1997).

RESULTS

Decomposition experiments with a hot 10% H₂O₂

The proportions of decomposed cellulose, casein and stearic acid after the decomposition using a hot 10% H₂O₂ water solution are shown in Table 1. Casein, which is a nitrogen-containing compound, is more decomposable than cellulose and stearic acid, which have no nitrogen. Changes in the C/N ratio of the kerogen and humic acid at two depths in the sediment core are shown in Ta-

Table 1. Proportion of the decomposed casein, cellulose and stearic acid after experimental decomposition using a hot 10% H₂O₂ water solution

Time (hour)	Proportion decomposed (%)		
	Casein	Cellulose	Stearic acid
0	0	0	0
24	61	26	6
46	85	55	7
68	97	65	8
92	99	62	8

ble 2. After decomposition, the C/N ratios of the residual kerogen and humic acid become greater than the initial values.

C_{org.}, N_{total} and N_{inorg.} contents of sediment core

The C_{org.} profile of the sediment core is shown in Fig. 2(c) (Sampei *et al.*, 1997b), ranging between 0.11 to 3.0 wt%. The distribution has a broad peak at around 4 m (3.0 wt%), gradually decreasing down the core to the minimum at 20 m (0.11 wt%). There is some variability at 16–18 m, corresponding to silt layers in the core.

The profile of N_{total} (Fig. 2(d)) is similar to that for C_{org.}, with lower values in the range 0.029 to 0.25 wt%. The N_{inorg.} content is uniform down the core, with values of the order of 0.04 wt% (Fig. 2(d) and Table 3). N_{exchange} was not detected in any of the samples.

Grain size

The median diameter (MD) of the sediment grains ranged from 2.9 to 24.5 μ m in diameter (Fig. 2(b)). The grain size is consistent at approximately 4 μ m except for between 16–18 m and again at 18–19.5 m where the grain size increase into the 23–24.5 μ m range, corresponding to layers of silt and sand, respectively.

Profile of C/N and C/N_{org.} ratio

The C/N ratios throughout the sediment core are slightly lower than the C/N_{org.} ratios, and have a somewhat different distribution (Figs. 3(a) and (b): Meyers, 1997). Two maxima occur in the C/N ratio profile; the first is a broad peak with a C/N ratio of >10 at 0–12 m, with a maximum of

Table 2. Proportion and C/N ratio of the decomposed kerogen and humic acid isolated from 1.1 m and 16.7 m depth of the sediment core after experimental decomposition using a hot 10% H₂O₂ water solution

Time (hour)	Proportion decomposed (%)				C/N ratio (wt) of residual matter			
	Kerogen		Humic acid		Kerogen		Humic acid	
	1.1 m	16.7 m	1.1 m	16.7 m	1.1 m	16.7 m	1.1 m	16.7 m
0	0	0	0	0	18.9	19.6	12.3	20.2
1	82	84	34	62	20.2	26.4	13.1	23.5

Fig. 3. Profiles of (a) weight ratio of C_{org} , content of sediment to N_{total} content of sediment (C/N ratio), (b) weight ratio of C_{org} , content of sediment to organic nitrogen content of sediment (C/N_{org} ratio; personally communicated with P. A. Meyers, 1997), (c) proportion of C_{29} -stanol to $C_{27}+C_{28}+C_{29}$ -stanol, (d) proportion of n - $C_{27}+C_{29}+C_{31}$ alkane to $<n$ - C_{20} alkane and (e) hydrogen-index (HI) by Rock Eval pyrolysis.

Table 3. Proportion of the decomposed organic carbon, and the undecomposable residual nitrogen content of sediments from selected portions of the core, after treatment with a hot 10% H₂O₂ water solution

Sample depth (m)	Decomposed organic matter (%)	Residual N content (%) of sediments
0.025	77.4	0.039
0.225	91.7	0.041
1.225	89.3	0.078
1.625	88.0	0.024
1.825	90.2	0.038
2.625	93.3	0.040
3.625	91.5	0.046
4.025	95.4	0.060
5.025	94.0	0.034
6.025	93.8	0.046
7.025	96.2	0.047
8.025	89.3	0.064
9.225	88.1	0.043
11.025	91.1	0.038
12.225	91.3	0.034
13.225	84.5	0.047
13.425	75.2	0.020
13.825	77.6	0.023
14.025	82.3	0.033
14.825	88.4	0.035
16.025	90.7	0.030
17.025	81.6	0.015
17.425	82.5	0.025
17.825	85.0	0.038
18.025	87.5	0.021
18.625	85.8	0.021
18.825	88.2	0.030
19.825	47.3	0.033
20.025	29.3	0.029
20.350	25.5	0.017
overall		
Avg.=82.4		Avg.=0.036
$\sigma = 17.5$		$\sigma = 0.014$
n = 30		n = 30

12.4 at 4 m, and the second clear peak occurs at 16–18 m, with a maximum of 16.9 at 17.8 m.

The C/N_{org} ratios of the fine sediments (MD = 3–4 μ m) in the upper and middle sections of the core (0–12 m) are in the range 10.8–16.7 (Fig. 3(b)), increasing in the lower sections from 20.7 at 13 m to about 50 at 20 m, except for an abrupt peak of 108 at 19.8 m.

Stanol and n-alkanes

Figure 3(c) shows the profile of relative abundance of C₂₉ to C₂₇+C₂₈+C₂₉-stanol. Stenol is not shown in the figure as it degrades more rapidly than stanol under oxidative conditions (Nishimura, 1978), and in this case stenol fluctuated signifi-

cantly without yielding any useful observations (Table 4).

Although the ratio shows some scatter, the values decrease from a high near the core bottom, to a low at around 4 m. At the bottom of the core, stanol was not detected. The relative abundance of C₂₉-stanol in the core indicates that there is a small percentage of terrestrial OM preserved at around 4 m, and a high percentage near the core bottom. The profile of relative abundance of C₂₉-stanol composition is in better agreement with that of the C/N_{org} ratio than with the C/N ratio, as discussed below, except for around 4 m and the uppermost section of the core.

The C₂₇ + C₂₉ + C₃₁/C_{<20} n-alkane ratio (higher plant marker) decreases between 2 m and 7 m, with a minimum at 4 m (Fig. 3(d)). The plot is extended only down to 12 m, as below this the CPI (C₂₄–C₃₄ odd-even Carbon Preference Index: Tissot and Welte, 1984) was low (near 1) and there was abundant UCM (unresolved complex mixture), indicating that this lower section of the core may have been contaminated by machine oil from drilling.

Rock-Eval

Figure 3(e) shows the depth profile of HI (plankton marker). The lowest value of 20 mg/gC occurs at a depth of 19 m, and the highest of 240 mg/gC occurs between 0.5 m and 6 m.

DISCUSSION

N_{inorg.} content

As shown in Table 3, OM in the sediments was not completely decomposed by a hot 10% H₂O₂ water solution. The residual nitrogen after decomposition, however, mostly consisted of inorganic components. Figure 4 shows the proportion of residual nitrogen, which is notably higher than that of residual organic carbon. From Table 1, the decomposition rate of nitrogen compounds (casein) is higher than that of non-nitrogen compounds (cellulose or stearic acid), suggesting that less organic nitrogen remained after a hot 10% H₂O₂ water solution treatment than organic carbon. Table 2 shows that the C/N ratios of the

Table 4. Stanol and stenol compositions from selected portions of the sediment core

Depth (m)	Stanol composition			Stenol composition		
	C ₂₇ (%)	C ₂₈ (%)	C ₂₉ (%)	C ₂₇ (%)	C ₂₈ (%)	C ₂₉ (%)
0.025	29.7	19.8	50.5	52.4	10.5	37.1
0.225	39.5	15.7	44.8	49.9	13.7	36.5
1.425	39.9	16.7	43.4	44.5	14.5	40.9
1.625	46.3	19.9	33.8	40.4	16.6	43.0
2.025	34.9	15.3	49.8	40.6	13.6	45.8
2.625	40.4	19.1	40.5	61.0	8.4	30.6
2.825	39.6	14.6	45.9	45.4	15.8	38.8
3.225	37.7	15.0	47.3	42.0	14.5	43.5
3.825	51.7	14.0	34.2	37.8	14.7	47.4
4.025	44.7	16.1	39.2	38.0	9.9	52.0
4.225	54.4	12.7	32.8	54.5	14.6	30.8
5.225	47.6	9.1	43.3	52.1	15.3	32.6
5.425	38.7	11.3	50.0	41.9	8.9	49.2
5.625	44.5	13.3	42.2	37.6	22.4	40.0
6.225	38.3	10.9	50.8	48.8	8.2	43.1
6.825	36.0	11.1	52.9	29.9	11.0	59.1
7.225	36.0	10.7	53.3	38.4	12.0	49.6
8.225	45.4	10.0	44.6	50.6	12.4	37.0
8.425	36.3	11.4	52.3	46.5	11.5	42.0
9.425	41.1	11.8	47.1	47.2	13.8	39.0
10.225	37.0	14.1	49.0	52.3	11.9	35.8
11.825	39.8	12.7	47.5	49.1	14.1	36.8
12.425	37.1	15.0	47.9	44.1	16.6	39.3
13.225	40.9	10.1	49.0	60.6	12.2	27.3
13.825	39.5	10.6	49.9	60.6	10.3	29.1
14.825	37.2	4.6	58.2	33.8	4.5	61.7
15.625	39.8	11.8	48.4	56.5	11.3	32.2
17.625	20.3	13.4	66.3	33.6	12.1	54.3
18.425	26.1	10.7	63.2	38.2	12.1	49.7
18.825	17.1	24.9	58.0	50.8	10.7	38.5
19.825	42.8	12.6	44.6	79.7	5.8	14.5

kerogen and humic acid residue after decomposition are higher than the initial ratios. These results indicate that the residual nitrogen after treatment can be regarded as nearly equivalent to N_{inorg} , and the residual organic carbon could be from resistant OM such as cellulose from vascular plants with little nitrogen (Table 1; Rosenfield, 1981; Haugen and Lichtentaler, 1991). The undecomposable OM is abundant in the lower part of the core (Fig. 4), and is consistent with the sedimentary facies of the lower sections (16–20 m), where there is a rapid supply of coarser terrestrial sediment (Fig. 2(b)) with entrained vascular plant debris.

The N_{inorg} discussed above is thought to be primarily fixed in minerals. The N_{inorg} may be present in the form of NH_4^+ in clay minerals (Stevenson, 1962; Itihara and Honma, 1979; Itihara, 1983a, b), and is not easily exchangeable for K^+ in light of the present results of the KCl extraction experiment. Müller (1977) reported that ammonium ions are fixed mainly in the interlayers of alumina silicates with high-layer charges, such as illites and vermiculites. Itihara and Honma (1979) also showed that NH_4^+ occurs in biotite from granitic and metamorphic rocks. Late Mesozoic to early Tertiary granitic rocks are widely distributed in the watershed region of

Fig. 4. Proportion of the residual nitrogen after treatment with a hot 10% H_2O_2 water solution vs. proportion of residual organic carbon after the same treatment. The sediments from bottom of the core (19.8–20.4 m) contain rather undecomposable organic matter.

Nakaumi Lagoon (Iizumi *et al.*, 1985; Kano *et al.*, 1994), and clay mica group minerals in the mud may thus be the major constituents hosting inorganic nitrogen.

Apparent variation in C/N ratio

Relatively high and constant $N_{\text{inorg.}}$ concentrations affect the accuracy of conventional interpretations of the C/N profile (N_{total}) of sediment core. The slight peak in the C/N ratio at 0–12 m (Fig. 3(a)) can be attributed to the variation in $N_{\text{org.}}$, as the profiles of both $C_{\text{org.}}$ and N_{total} for the same depth interval (Figs. 2(c) and (d)) are virtually identical, while the $N_{\text{inorg.}}$ varies slightly (Fig. 2(d), Table 3: Avg. = 0.045%, σ = 0.013%; n = 15). The C-N plot in Fig. 5 illustrates this point more clearly. $C_{\text{org.}}$ correlates well with N_{total} in the 0–12 m interval, and the C/N and $C/N_{\text{org.}}$ ratios can be expressed as $L/(H_1 + H_2)$ and L/H_1 , respectively (from the figure), where L is $C_{\text{org.}}$ content, H_1 is $N_{\text{org.}}$ content and H_2 is $N_{\text{inorg.}}$ content. C/N decreases with decreasing $C_{\text{org.}}$ and $N_{\text{org.}}$ contents due to the constancy of $N_{\text{inorg.}}$. This relationship is expressed in terms of C/N ratio against $C_{\text{org.}}$ in Fig. 6. Thus, the broad peak of the C/N ratio of the sediment between 0 m and 12 m could have arisen

Fig. 5. Plots of $C_{\text{org.}}$ content of sediment vs. N_{total} content of sediment (L : $C_{\text{org.}}$ content, H_1 : $N_{\text{org.}}$ content, H_2 : $N_{\text{inorg.}}$ content). The $C_{\text{org.}}$ is better correlated with N_{total} from 0–12 m (Eq. (1): $C_{\text{org.}} = 15.1 \times N_{\text{total}} - 0.679$, r (correlation coefficient) = 0.939, n (sample number) = 46) than from 12–20 m (Eq. (2): $C_{\text{org.}} = 21.2 \times N_{\text{total}} - 0.675$, r = 0.726, n = 32).

from the constant $N_{\text{inorg.}}$ content. The effect of $N_{\text{inorg.}}$ on the C/N ratio is pronounced when the $C_{\text{org.}}$ content is under 1 wt% (Fig. 6). The abnormally low C/N ratios of 3.2–4.1 at the bottom of the core were developed in this way with rather low $C_{\text{org.}}$ and $N_{\text{org.}}$ content.

The C-N diagram is also useful for the approximate determination of average $N_{\text{inorg.}}$ as predicted by Martens *et al.* (1992). The intercept on the N_{total} axis of Eq. (1) in Fig. 5 is 0.045 wt%, which is identical to the measured average $N_{\text{inorg.}}$ content of 0.045 wt% from 0–12 m (Table 3). It is noteworthy that the error in the estimation of $N_{\text{inorg.}}$ content by this method increases when the minimum N_{total} content in the data set is high. These methods are applicable when the $C_{\text{org.}}$ content of sediment is consistent with the N_{total} content. This is often the case, with high correlation coefficients for $C_{\text{org.}}$ and N_{total} ($r > 0.9$) reported in the literature (e.g., Hedges *et al.*, 1986, 1988; Martens *et al.*, 1992).

Fig. 6. Plots of C/N ratio of sediment vs. $C_{org.}$ content of sediment. Equations (1)' and (2)' are modified from Eqs. (1) and (2) in Fig. 5, respectively. The C/N ratio decreases with decreasing in $C_{org.}$ content because of constant $N_{inorg.}$.

Apparent variations in the C/N ratio should be checked when the ratio decreases with decreasing $C_{org.}$ content as seen in the sediment core in the 0–12 m interval (Figs. 2(c) and 3(a)). A model for apparent changes in the C/N ratio of sediment core is shown in Fig. 7. Case I in Figs. 7(a) and (d) is the model for a constant $C/N_{org.}$ ratio, however, the C/N ratio (Fig. 7(e)) changes contrary to conventional interpretation with varying $C_{org.}$ (Fig. 7(b)) due to the constant $N_{inorg.}$ (Fig. 7(a)). If such variations in $C_{org.}$ and C/N ratio profiles are observed in sediment core, the apparent changes in the C/N ratio should be carefully verified. A case for a true increase in planktonic OM over terrestrial OM (case II), and a case for a true increase in terrestrial OM over planktonic OM (case III) are shown for reference (Figs. 7(a) and (c)). These cases reveal that intrinsic successive changes in the C/N ratio gives a curved line on a C-N cross plot diagram (Fig. 7(a)).

Fig. 7. (a) Model plots of $C_{org.}$ content of sediment vs. N_{total} content of sediment including 0.04% $N_{inorg.}$, (b) model profile of $C_{org.}$ content, (c) model profile of proportion for planktonic organic matter (POM: expressed by proportion of carbon in the figure), (d) true change in $C/N_{org.}$ ratio of the model sediment based on (a), (b) and (c), and (e) apparent change in C/N ratio of the model sediment based on (a), (b) and (c). The C/N ratios of POM and TOM (terrestrial organic matter) were assumed 6 and 50, respectively. Changes in proportion of POM were simulated at rates of 1%/0.1% $C_{org.}$ (case II), -1%/0.1% $C_{org.}$ (case III) and 0%/0.1% $C_{org.}$ (case I) upward the model sediment core from the bottom with starting POM/TOM ratio of 1.

Fig. 8. C/S ratio profile of the sediment core: bottom oxic/anoxic indicator for brackish/marine water environment.

C/N_{org.} ratio change by preferential decomposition

Interpretation is aided by taking the $C/N_{org.}$ ratio, which compensates to a certain degree for this anomalous variation in C/N. However, a small but clear difference between the profiles of the $C/N_{org.}$ ratio and the other proxies still remains. The difference occurs at around 4 m down the sediment core; the $C/N_{org.}$ ratio is nearly constant whereas the other proxies clearly tend toward the plankton-rich zone. This is thought to be due to the fact that the planktonic OM at around 4 m was rather oxidized and decomposed at the time of deposition. A preferential loss of nitrogen relative to carbon during the decomposition of planktonic OM as it sank through the water column and settled down in the sediment results in an increase in the C/N (Gordon, 1971; Müller, 1977; Rosenfield, 1981; Saino and Hattori, 1987). As an example, at ocean depths of around 1000 m, C/N ratios have been found to be higher than 10, increasing to

around 15 at greater depth (Müller, 1977). Figure 8 shows the changes in oxic/anoxic lake-bottom conditions in the Nakaumi Lagoon in the last 8,000 years by means of C/S ratios. The C/S ratio is one useful indicator of oxic/anoxic bottom conditions in marine-brackish lake environments (Berner, 1989; Sampei *et al.*, 1997a). The C/S ratios at around 4 m down the sediment core show that oxic conditions were dominant at the lake bottom. The age of the sediment at this depth in the core is around 2.5 ka, corresponding to a cool period with low primary productivity in the paleo-Nakaumi Lagoon (Sampei *et al.*, 1997b). During a warm period (called the Climatic Optimum) that occurred around 6.0 ka (around 10 m down the sediment core), higher rainfall increased the input of nutrients to the lake, causing higher primary productivity and resulting in anoxic bottom conditions (Sampei *et al.*, 1997b). According to Sampei *et al.* (1997b), in warm climatic conditions there is a high rate of accumulation of planktonic organic carbon accompanied by low $C_{org.}$ content in the sediments due to dilution by inorganic clays.

Sensitivity of C/N ratio to proportional changes in planktonic/terrestrial OM

A further reason why the $C/N_{org.}$ ratio profile differs from the profiles of other proxies at around 4 m down the sediment core is that there appears to be a non-linear sensitivity in C/N ratio to changes in the proportion of planktonic and terrestrial OM; when planktonic OM is predominant, the sensitivity of the C/N ratio to the change is low. This relationship is explained in Fig. 9 based on the following equation:

$$C/N \text{ ratio} = (1 + k)PT/(T + kP),$$

where $C_t/C_p = k$, $C_p/N_p = P$, $C_t/N_t = T$, C_p : planktonic carbon weight, C_t : terrestrial carbon weight, N_p : planktonic nitrogen weight, and N_t : terrestrial nitrogen weight.

The change in the C/N ratio for a given increase in planktonic OM% is significantly larger at small proportions of planktonic OM than at greater proportions (Fig. 9(a)). The relationship is clarified

Fig. 9. (a) C/N ratio vs. proportional changes in POM (expressed by proportion of carbon in the figure) and (b) sensitivity (deviation) of C/N ratio to 10% increase in POM. The C/N ratio of POM was supposed to change from 6 to 15 by oxidation for (a), and fixed to be 6 for (b). The C/N ratio of TOM was assumed 50 for (a) and (b). Arrows in (a) indicate different proportion of POM to the same C/N ratio due to changing degree of oxidation.

in Fig. 9(b); increasing the proportion of planktonic OM from 80% to 90% causes a mere 1.2 change in the C/N ratio, whereas from 10% to 20%, the change in the C/N ratio is 8.

At 4 m down the sediment core, the proportion of planktonic OM has been estimated at about 75% (Sampei *et al.*, 1997b). Consequently, the sensitivity of the C/N ratio at around this depth is low. Only a small variation in the C/N ratio can be expected in this region, even with a large variation in the proportion of planktonic OM.

Reconstruction of depositional environment using C/N_{org} ratio and other proxies

The profiles of the C/N_{org} ratio, stanol composition, *n*-alkane composition and HI, which differ in trend from the profile of the C/N ratio (Fig. 3), permit more accurate reconstruction of major depositional condition changes in the study area after the Holocene sea level rise to be made. The C/N_{org} ratio was ignored in the upper 8 m of the sediment core for the purpose of this discussion

due to the inaccuracy of the results in this region for this indicator, as shown above. Based on the profiles and the MD of the sediment core, the depositional environment for the core site can be reconstructed as follows:

In the 16 m to 20 m interbedded silt-sand interval of the sediment core, the profiles indicate that terrestrial OM is predominant. The coarser grain size of this interval (Fig. 2(b)) is consistent with this inference, suggesting that terrestrial OM was transported rapidly from the watershed via the Inashi River and/or the Ou River (Fig. 1). This interpretation is consistent with the results of pollen, diatom and echo-sounding analyses (Onishi, 1986; Tokuoka *et al.*, 1990), and adds further detail to the reconstruction. With rising sea level, the river mouth regressed away from the core site. The origin of the coarse sediments at 16–18 m is thought to be directly due to the Inashi and Ou Rivers and shore sand and silt trapped by wave action. It is probable that a fine sand bar migrated to the delta area over the core site, because sand

bars are generally created during abrupt sea level rises, and move toward the shore line (Heron *et al.*, 1984). A protected back marsh may have existed between the sand bar and the shore line during the period corresponding to 18–19.5 m. With increasing water depth, the depositional environment is thought to have become stable and less energetic, as indicated by the fineness of the sediments ($MD = 3\text{--}4\ \mu\text{m}$) between 0 m and 15 m, suggesting that the site was located a significant distance from the river mouth (e.g., Orton and Reading, 1993). Between 4 m and 15 m, terrestrial OM gradually decreases upward in the core, with the lowest value at about 4–5 m, indicating a reduced terrestrial OM supply. Between 0 m and 4 m, the proxies show some scatter and a slight increase in terrestrial OM. This reconstruction of the chronological variation in organic source is consistent with the reconstruction made from profiles based on the mass accumulation rates of terrestrial and planktonic organic carbon by Sampei *et al.* (1997b).

CONCLUSIONS

On the basis of our analyses of the sediment core from Nakaumi Lagoon, southwest Japan, the following conclusions are drawn:

(1) Two broad peaks are observed in the C/N ratio profile of the 20 m sediment core, however the C/N ratio as an organic source indicator offers a different (partially reverse) interpretation from that of other proxies, identified as attributable to the presence of approximately constant $N_{\text{inorg.}}$ content (*ca.* 0.04%) and a wide range of N_{total} content (0.029–0.25%). The presence of $N_{\text{inorg.}}$ lowers the C/N ratio such that it decreases with decreasing N_{total} and $C_{\text{org.}}$ content. This tendency is pronounced when the $C_{\text{org.}}$ content is less than 1 wt%, at which the accuracy of the C/N ratio as an organic source indicator becomes suspect. Our results suggest that the apparent variation in the C/N ratio should be carefully checked when the C/N ratio and $C_{\text{org.}}$ content have similar profiles. The apparent variation can be evaluated using C-N and C/N ratio- $C_{\text{org.}}$ diagrams.

(2) A simple and practical decomposition method for OM by the addition of a hot 10% H_2O_2 water solution allows the $C/N_{\text{org.}}$ ratio to be determined easily.

(3) The $C/N_{\text{org.}}$ ratio also exhibited a small contradiction of the results indicated by other proxies, attributable to the preferential decomposition of nitrogen compound during cool climatic conditions around 2.5 ka, corresponding to oxalic lake-bottom conditions in Nakaumi Lagoon.

(4) If the sediment contains a large proportion of planktonic OM, the sensitivity of the C/N ratio to small changes in planktonic-terrestrial OM composition is low.

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