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The Origin and Biogeochemistry of Organic Matter in Surface Sediments of Lake Shihwa and Lake Hwaong

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Abstract – To understand the origin and biogeochemistry of the organic matter in surface sediments of Lake Shihwa and Lake Hwaong, organic nitrogen, inorganic nitrogen, labile organic carbon, and residual organic carbon contents as well as stable isotope ratios for carbon and nitrogen were determined by KOBr–KOH treatment. Ratios of organic carbon to organic nitrogen (C_{org}/N_{org}) (mean = 24) were much higher than ratios of organic carbon to total nitrogen (C_{org}/N_{tot}) (mean=12), indicating the presence of significant amounts of inorganic nitrogen in the surface sediments of both lakes. Stable isotope ratios for organic nitrogen were, on average, 5.2‰ heavier than ratios of inorganic nitrogen in Lake Shihwa, but those same ratios were comparable in Lake Hwaong. This might be due to differences in the origin or the degree of degradation of sedimentary organic matter between the two lakes. In addition, stable isotope ratios for labile organic carbon were, on average, 1.4‰ heavier than those for residual organic carbon, reflecting the preferential oxidation of ^{13}C-enriched organic matter. The present study demonstrates that KOBr–KOH treatment of sedimentary organic matter can provide valuable information for understanding the origin and degradation state of organic matter in marine and brackish sediments. This also suggests that the ratio of C_{org}/N_{org} and stable isotope ratios for organic nitrogen can be used as indexes of the degree of degradation of organic matter.

Key words – nitrogen and carbon composition, stable isotope ratio, KOBr–KOH treatment, Lake Shihwa, Lake Hwaong

1. Introduction

Marine and lacustrine sediments preserve autochthonous and allochthonous substances that sink through the water column. The ratios of total nitrogen and organic carbon contents and their stable isotope compositions have been used to understand the origin of sedimentary organic matter (*e.g.* Fry and Sherr 1984), but most investigations have focused on total nitrogen (N_{tot}) rather than organic nitrogen (N_{org}). This approach is acceptable in areas where inorganic nitrogen content is negligible. However, ammonium bound to clay minerals (fixed ammonium, N_{fixed}), was shown to be a significant contributor to the inorganic nitrogen pool (Stevenson and Cheng 1972; Müller 1977; Rosenfeld 1979; Boatman and Murray 1982; Sahrawat 1995; Schubert and Calvert 2001). Additionally, higher inorganic nitrogen contents were observed in lakes that were influenced mainly by terrestrial input (Winkelmann and Knies 2005). The relative contributions of organic nitrogen and inorganic nitrogen to total sedimentary organic matter vary according to the biogeochemical environment, which includes such factors as weathering, river discharge, primary production, water depth, sedimentation rate, transportation and diagenesis (Ruttenberg and Goñi 1997). Early diagenesis affects the stable isotope ratios of organic carbon and nitrogen, even though diagenetic shifts in C/N and stable isotope ratios were assumed to be constant when studied in a paleoceanographic setting (Calvert *et al.* 1992; Francois *et al.* 1992; Altabet *et al.* 1995). Obvious changes in the isotopic composition of organic carbon relating to early diagenetic processes were observed under oxic and anoxic conditions, but such effects on the stable isotope ratio of nitrogen were large in sediments under anoxic conditions (Lehmann *et al.* 2002).

In the present study, total nitrogen and total organic carbon were fractionated by KOBr–KOH treatment. This allowed organic nitrogen, inorganic nitrogen, labile organic

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carbon and residual organic carbon, as well as their stable isotope ratios, to be determined. This paper presents a discussion of the results with the aim of understanding the origin and biogeochemical processes of organic matter in the surface sediments of brackish lakes (Lake Shihwa and Lake Hwaong).

2. Materials and Methods

Lake Shihwa and Lake Hwaong were created by dams blocking bays located on the west coast of the Korean Peninsula, as seen in Fig. 1. Lake Shihwa was completed as an artificial lake in 1994 and Lake Hwaong was constructed through reclamation in 2002. However, salinity was still high in both lakes, showing 15.0 PSU in Lake Shihwa and 29.1 PSU in Lake Hwaong. Sediment samples were taken using a grab sampler at 6 sites in Lake Shihwa on July 20, 2004 and at 10 sites in Lake Hwaong on November 27, 2003. Surface sediment samples were collected from the top 1 cm of all samples using a spatula.

Sediment samples were freeze-dried and homogenized after grinding. Total nitrogen content (N_{tot}) was determined in untreated bulk homogenized sediment samples. Total organic carbon (TOC) was measured in acidified (2 N HCl) subsamples, which did not contain any carbonates. Two different forms of inorganic nitrogen, *i.e.* exchangeable ammonium ($NH_4^+{}_{exch}$) and ammonium fixed to the lattices of clay minerals (N_{fixed}), were determined by the following

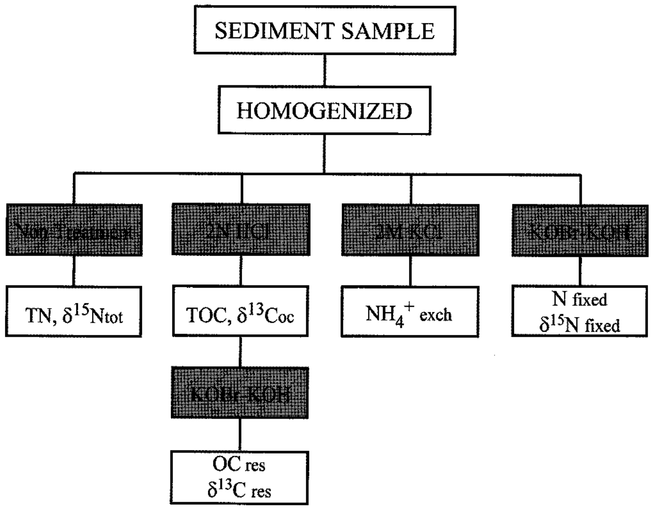

Fig. 2. Flow chart of analytical methods.

analytical methods (Fig. 2). Exchangeable ammonium ($NH_4^+{}_{exch}$) was extracted using 2 M KCl (Keeney and Nelson 1982) and measured using a spectrophotometer. In the present study, $NH_4^+{}_{exch}$ accounted for only 2.5% of inorganic nitrogen (31.8 μg N/g) in Lake Shihwa and 2.0% of inorganic nitrogen (7.9 μg N/g) in Lake Hwaong (Fig. 4). The $NH_4^+{}_{exch}$ contents in both lakes were comparable with those reported by some other researchers; *e.g.* 150 μg N/g in Pettaquamscutt sediment, 35 μg N/g in Long Island Sound sediment, 8 μg N/g in Florida Bay (Rosenfeld 1979) and 46.2–72.8 μg N/g in a core sample from Saanich Inlet, British Columbia (Boatman and Murray 1982).

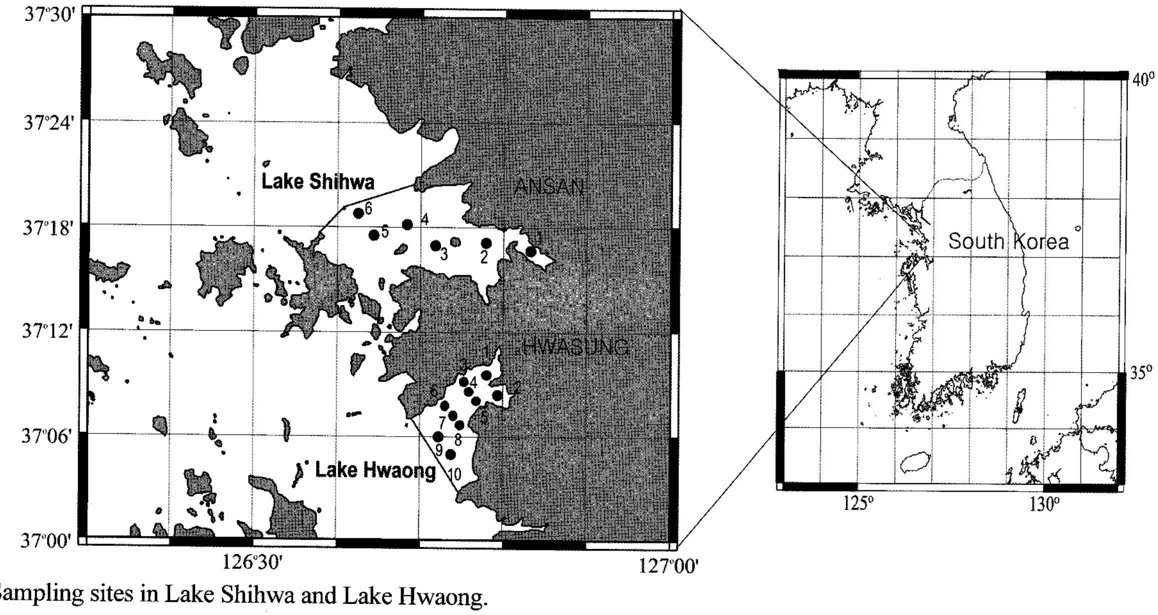

Fig. 1. Sampling sites in Lake Shihwa and Lake Hwaong.

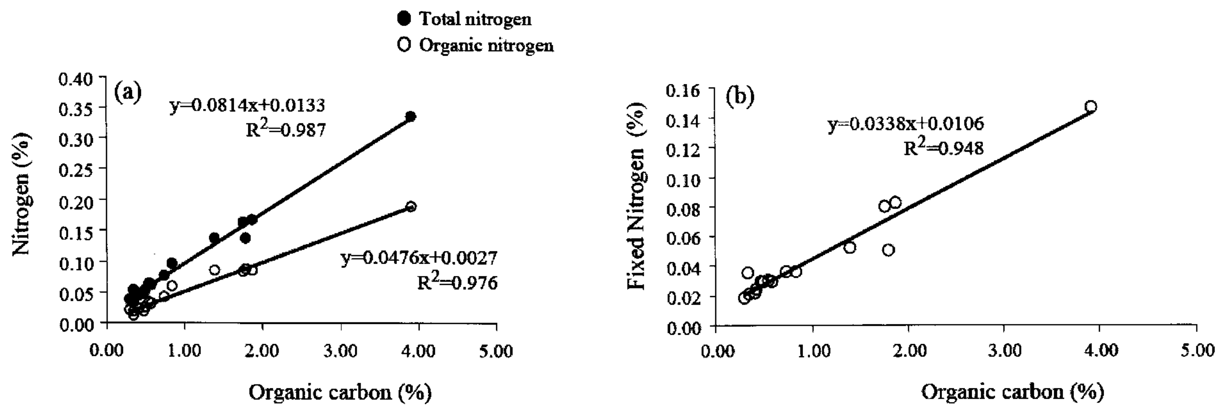

Fig. 3. Correlation between (a) total organic carbon (TOC) and total nitrogen (N_{tot}) and (b) TOC and organic nitrogen (N_{org}) in the surface sediments of Lake Shihwa and Lake Hwaong.

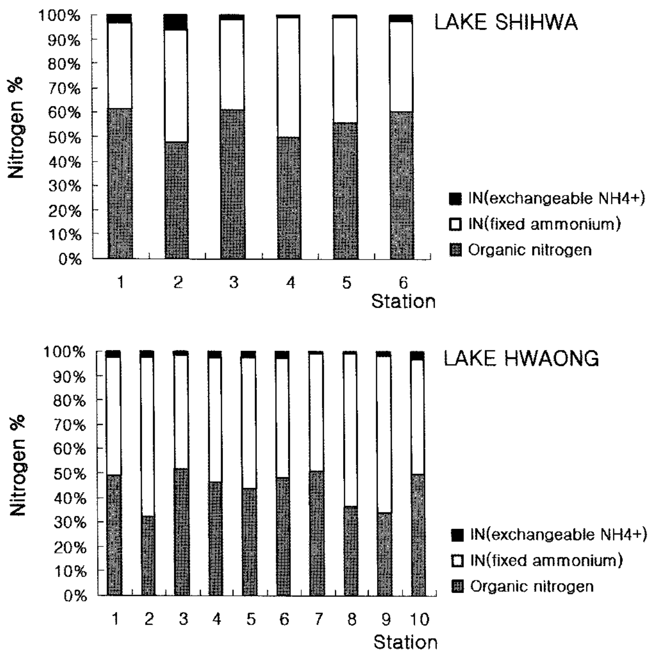

Fig. 4. Nitrogen composition of surface sediments in Lake Shihwa and Lake Hwaong.

Inorganic nitrogen (N_{fixed}), which is the ammonium bound to clay minerals (Schachtschabel 1961; Stevenson and Cheng 1972; Müller 1977; Schubert and Calvert 2001), was determined by treating bulk samples with a KOBr–KOH solution to eliminate the organic nitrogen fraction (Silva and Bremner 1966; Schubert and Calvert 2001). Detailed analytical procedures were as follows. A 20 ml volume of the KOBr–KOH solution was added to finely ground sediment. The solution was mixed gently and allowed to stand for 2 hours. Then, 60 ml of distilled water was added, and the mixture was boiled vigorously for 20 minutes on a hot plate. After the mixture cooled overnight, the sample was washed with 0.5 M KCl to remove the released ammonium.

In the present study, the oxidation efficiency of KOBr–KOH treatment was examined using seagrass, an *echidonarus* salt marsh plant and microalgae. The average efficiency of the oxidation treatment of organic nitrogen was > 99% for *Zostera marina* (seagrass), > 99% for *Echinodorus amazonicus* (salt marsh plant) and > 98% for blue green algae (microalgae), showing the almost complete removal of organic nitrogen by this method. In a previous study, the efficiency of oxidation of the organic nitrogen fraction (hydrolyzable and nonhydrolyzable organic nitrogen) was also greater than 98% using the same method (Silva and Bremner 1966).

The stable isotope ratios of total organic carbon, residual organic carbon, total nitrogen and inorganic nitrogen were measured using an elemental analyzer combined with a mass spectrometer (Delta plus, Finnigan MAT). Sediment samples were treated with 2 N HCl for decarbonation and with KOBr–KOH for organic matter oxidation. The analytical precision of the carbon determinations in the treated samples was ± 0.09% for carbon contents and ± 0.25‰ for carbon isotope ratios in Lake Shihwa, while precision was ± 0.01% for carbon contents and ± 0.53‰ for carbon isotope ratios in Lake Hwaong. The precision of the nitrogen determinations in the samples treated with KOBr was ± 0.009% for nitrogen contents and ± 0.20‰ for its isotope ratios in Lake Shihwa, and ± 0.003% for nitrogen contents and ± 0.32‰ for its isotope ratios in Lake Hwaong. Atmospheric nitrogen and PDB (Pee Dee Belimnite) were used as standards for the determination of $\delta^{15}N$ (‰) and $\delta^{13}C$ (‰) values. Organic nitrogen (N_{org}) content was estimated as the difference between total nitrogen (N_{tot}) and inorganic nitrogen (N_{fixed}). Labile organic carbon content was calculated as the difference between total organic carbon (C_{org}) and residual organic carbon (C_{resi}) after KOBr–KOH treatment. The values of $\delta^{15}N_{org}$ and $\delta^{13}C_{labile}$ were calculated by the following isotope–mass balance equations.

$$(\delta^{15}N_{org} \times \text{fraction } N_{org}) + (\delta^{15}N_{fixed} \times \text{fraction } N_{fixed}) = \delta^{15}N_{tot} \times 100$$
$$\rightarrow \delta^{15}N_{org} = (\delta^{15}N_{tot} \times 100 - \delta^{15}N_{fixed} \times \text{fraction } N_{fixed})/\text{fraction } N_{org} \quad (1)$$

$$(\delta^{13}C_{resi} \times \text{fraction } C_{resi}) + (\delta^{13}C_{labile} \times \text{fraction } C_{labile}) = \delta^{13}C_{org} \times 100$$
$$\rightarrow \delta^{13}C_{labile} = (\delta^{13}C_{org} \times 100 - \delta^{13}C_{resi} \times \text{fraction } C_{resi})/\text{fraction } C_{labile} \quad (2)$$

In addition, in order to understand the clay mineral composition of the surface sediment samples, X-ray powder diffraction data for quantitative analysis were obtained with a High Resolution X-ray Diffractometer (SIMENS D5005) operated at 40 kV and 25 mA. A graphite monochromatized CuKα (λ=1.5406) was used. The collected data were analyzed using SIROQUANT v.3 program. Clay contents were estimated as the sum of the illite, kaolinite and chlorite contents. Illite contribution to the total clay content was also calculated.

3. Results and Discussion

Fractionation of total nitrogen and organic carbon

Total nitrogen (N_{tot}), inorganic nitrogen (N_{fixed}) and organic nitrogen (N_{org}), as well as total organic carbon (TOC), residual organic carbon (OC_{resi}) and labile organic carbon (OC_{labile}), were determined in surface sediments collected from Lake Shihwa and Lake Hwaong (Table 1). Total nitrogen contents, including inorganic and organic nitrogen, were 3 times higher in Lake Shihwa than in Lake Hwaong. Total organic carbon contents, composed of residual organic carbon (OC_{resi}) and labile organic carbon (OC_{labile}), were also 4 times higher in Lake Shihwa than in Lake Hwaong.

The proportion of total organic carbon present as labile organic carbon was slightly higher in Lake Shihwa than in Lake Hwaong. The average percentage of total nitrogen present as organic nitrogen was 57% in Lake Shihwa and 45% in Lake Hwaong. Ratios of organic carbon to organic nitrogen (C_{org}/N_{org}; mean = 23 in Lake Shihwa and mean = 25 in Lake Hwaong), obtained by removing inorganic

Table 1. Measurements of carbon and nitrogen fractions in sediment samples from Lake Shihwa and Lake Hwaong [a]

	station	N_{tot}%	N_{fixed}%	N_{org}%	%N_{org}	TOC (%)	OC_{resi}(%)	OC_{labile}(%)	% C_{labile}	C_{org}/N_{tot} (molar)	C_{org}/N_{org} (molar)	Clay (%)	Illite (%)
Lake Shihwa	1	0.14	0.050	0.086	63	1.80	0.78	1.02	57	15	24	39	80
	2	0.16	0.080	0.083	51	1.76	0.64	1.12	64	13	25	53	68
	3	0.10	0.035	0.059	62	0.84	0.23	0.61	73	10	17	24	95
	4	0.17	0.082	0.084	51	1.88	0.81	1.07	57	13	26	42	58
	5	0.33	0.146	0.188	56	3.92	1.63	2.29	59	14	24	40	87
	6	0.14	0.052	0.084	62	1.40	0.51	0.89	63	12	19	33	90
	Average	0.17	0.07	0.10	57	1.93	0.77	1.17	62	13	23	39	80
Lake Hwaong	1	0.037	0.018	0.019	50	0.30	0.15	0.15	50	12	19	30	94
	2	0.052	0.035	0.017	33	0.34	0.20	0.15	43	11	23	27	91
	3	0.076	0.036	0.040	53	0.74	0.21	0.53	72	10	22	39	93
	4	0.046	0.024	0.022	47	0.42	0.17	0.26	61	11	23	37	91
	5	0.053	0.029	0.024	45	0.50	0.18	0.32	64	11	25	34	69
	6	0.044	0.022	0.022	50	0.41	0.15	0.27	64	11	22	31	89
	7	0.063	0.030	0.032	52	0.55	0.26	0.30	53	10	20	32	89
	8	0.046	0.029	0.017	37	0.48	0.23	0.26	53	11	34	30	83
	9	0.031	0.021	0.011	34	0.35	0.18	0.18	50	11	38	35	94
	10	0.060	0.029	0.031	51	0.58	0.21	0.35	64	10	22	28	85
	Average	0.051	0.027	0.023	45	0.47	0.19	0.28	57	11	25	32	88

[a]Total nitrogen content (N_{tot}), inorganic nitrogen content (N_{fixed}), organic nitrogen contents (N_{org}), percentage of organic nitrogen content to total nitrogen content (%N_{org}), total organic carbon (TOC), residual organic carbon (OC_{resi}), labile organic carbon (OC_{labile}), percentage of labile organic carbon content to total organic carbon content (%OC_{labile}) and total organic carbon/total nitrogen ratio (C_{org}/N_{tot}), total organic carbon/organic nitrogen (C_{org}/N_{org}).

nitrogen, were much higher than ratios of organic carbon to total nitrogen (C_{org}/N_{tot}; mean = 13 in Lake Shihwa and mean = 11 in Lake Hwaong) (Table 1). High C_{org}/N_{org} ratios may reflect not only large contributions of terrestrial organic matter in both lakes but also the degradation of organic matter. Typical C_{org}/N_{org} ratios range from 5 to 7 for marine organic matter (Redfield *et al.* 1963) and are typically > 20 for terrestrial organic matter (Scheffer and Schachtschnabel 1984). These ratios are due to the large abundance of cellulose compared with the relatively small nitrogen content of terrestrial vascular plants (Philip 1997). However, C_{org}/N_{org} in sedimentary organic matter can be enhanced by the degradation of organic nitrogen through a rapid deamination process before and after sedimentation (Hartman *et al.* 1973; Butcher *et al.* 1992).

The contributions of inorganic nitrogen to total nitrogen (43% in Lake Shihwa and 55% in Lake Hwaong) were greater than the 14% measured in surface sediments of the eastern subtropical Atlantic (Freudenthal *et al.* 2001). On the other hand, they were close to the average 43% (ranging from 28% to 63% at 17 sampling sites) found in surface sediments of the Arctic Ocean (Schuberts and Calvert 2001). Kang *et al.* (2007) reported that inorganic nitrogen made up around 58% and 56% of the total nitrogen contents in 2 sediment cores from the Holocene period (St. 25 and St. 35) collected in the Kara Sea.

Additionally, by drawing a plot of total N (TN) or organic N (ON) contents versus TOC contents at all stations in both lakes (Fig. 3), the intercepts on the y-axis can be defined as the proportion of nitrogen that is not related to TOC. For this study these were 0.0133 for TN and 0.0027 for ON. The y-intercept for TN implies an excess of N that is not bound to organic matter. The excess N makes up 40% of the average N_{fixed} content (ranging from 9.1% to 73% at all stations in both lakes), indicating the presence of significant amounts of inorganic nitrogen. However, these excess N contributions did not correspond to the actual N_{fixed} content at every station, measured after KOBr–KOH treatment. In a previous study, Schubert and Calvert (2001) also reported a range in the proportion of excess N in the N_{fixed} contents (53–130%, average 76%) of surface sediments from the Arctic Ocean. These large variations in the contribution of excess N to the N_{fixed} content might be due to various factors in the sedimentary environment, such as clay mineral composition and ammonium content associated with the lattice structure of clay minerals (Winkelmann and Knies 2005). In the present study, exchangeable ammonium as a fraction of inorganic nitrogen accounted for only 2.3%, on average, of the total nitrogen (2.5% in Lake Shihwa and 2.0% in Lake Hwaong in Fig. 4). These low contents of exchangeable ammonium demonstrate the predominance of soil-derived ammonium in both lakes, suggesting that the higher inorganic nitrogen contents are caused by higher clay contents in the surface sediments (Table 1).

Illite contributes on average 80% to the clay mineral content in Lake Shihwa sediments and 88% in Lake Hwaong sediments (Table 1). Illite may be a major source of inorganic nitrogen (N_{fixed}) because ammonium (NH_4^+) substitutes for K^+ in the interlayer exchange sites of illite (Scheffer and Schachtschnabel 1984). The NH_4^+ incorporated into the inner part of the illite lattice is released only in the presence of extremely low concentrations of NH_4^+ and K^+. Therefore, the isotopic composition of inorganic nitrogen in coastal sediments can be represented by the isotopic ratio of nitrogen (NH_4^+) fixed in the illite crystal in terrestrial samples, considering the high K^+ concentration of seawater.

Stable isotope ratios of nitrogen and organic carbon fractions

Stable isotope ratios for organic nitrogen were heavier in Lake Shihwa than in Lake Hwaong (Table 2). Fig. 5 shows the apparently enriched ^{15}N values of organic nitrogen compared with those of total and inorganic nitrogen in Lake Shihwa. However, stable isotope ratios of organic nitrogen were similar to those of other nitrogen fractions in Lake Hwaong. These results may be due to differences between the lakes in the origin and state of decomposition of sedimentary organic matter. The preferential decomposition of labile organic compounds occurs through diagenetic processes such as deamination and decarboxylation, resulting in heavier stable isotope ratios in residual organic matter. In addition, relatively lighter stable isotope ratios of N_{fixed} may result from the presence of ammonium fixed to the lattices of clay minerals such as illite and kaolinite. Therefore, the various $\delta^{15}N_{fixed}$ values were due to different origins of nitrogen and different environmental conditions. In addition, there was a notable difference in the $\delta^{15}N_{org}$ values among sites in Lake Shihwa. The lighter $\delta^{15}N_{org}$ values observed in the surface sediment of the upper stream area (St. 1) in Lake Shihwa may reflect a greater influence of terrestrial organic matter, corresponding to the lighter $\delta^{13}C$ values at the same site in Fig. 6.

On the other hand, the stable isotope ratios of residual

Table 2. Stable isotope ratios in sediment samples of Lake Shihwa and Lake Hwaong[a]

	Station	$\delta^{15}N_{tot}$	$\delta^{15}N_{fixed}$	$\delta^{15}N_{org}$	$\delta^{13}C_{TOC}$	$\delta^{13}C_{labile}$	$\delta^{13}C_{resi}$
Lake Shihwa	1	2.69	0.99	3.68	-24.5	-24.2	-25.0
	2	3.93	2.86	4.97	-22.7	-22.2	-23.5
	3	6.43	0.36	10.11	-20.0	-19.6	-21.2
	4	5.69	3.16	8.17	-21.4	-21.0	-22.0
	5	6.91	5.18	8.25	-21.8	-20.8	-23.1
	6	7.51	2.06	10.87	-20.9	-20.9	-20.9
	Average	5.53	2.44	7.68	-21.9	-21.4	-22.6
Lake Hwaong	1	4.00	3.70	4.30	-22.7	-22.3	-23.2
	2	4.92	4.82	5.11	-21.5	-19.6	-22.9
	3	3.98	4.14	3.83	-22.4	-22.1	-23.2
	4	3.88	3.61	4.17	-22.2	-22.0	-22.5
	5	3.73	4.52	2.76	-21.9	-21.3	-22.9
	6	4.18	4.23	4.13	-21.6	-20.8	-23.2
	7	4.69	4.67	4.70	-22.2	-21.6	-22.8
	8	3.38	3.78	2.69	-22.2	-21.7	-22.9
	9	3.02	3.24	2.61	-22.2	-21.5	-22.8
	10	5.44	5.36	5.51	-22.1	-21.8	-22.6
	Average	4.12	4.21	3.98	-22.1	-21.5	-22.9

[a] $\delta^{15}N$ measured on the total nitrogen fraction ($\delta^{15}N_{tot}$), inorganic nitrogen ($\delta^{15}N_{fixed}$) and organic nitrogen ($\delta^{15}N_{org}$) (‰versus air). $\delta^{13}C$ measured on the total organic carbon fraction ($\delta^{13}C_{TOC}$), organic labile ($\delta^{13}C_{labile}$) and residual carbon fraction ($\delta^{13}C_{resi}$) (‰ versus PDB).

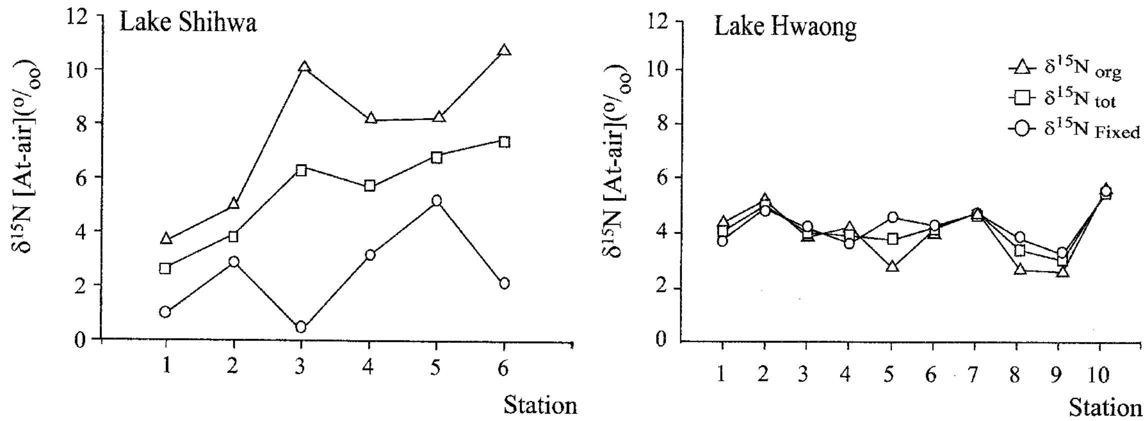

Fig. 5. Stable isotope ratios for nitrogen fractions of surface sediments from Lake Shihwa and Lake Hwaong.

organic carbon showed lighter values than labile organic carbon at all stations in both lakes (Fig. 6). The average stable isotope ratios of labile organic carbon and residual organic carbon were –21.4‰ and –22.6‰ in Lake Shihwa, and –21.5‰ and –22.9‰ in Lake Hwaong (Table 2). In a previous study, Freudental *et al.* (2001) reported that the isotope ratio of C_{resi} was lighter (–24‰ to –22‰) than $\delta^{13}C_{labile}$ (around –19‰) in subtropical zones of the Atlantic Ocean. Degradation of organic compounds causes a depletion in the stable isotope ratios of carbon in residual organic matter, due to the preferential degradation of ^{13}C-enriched organic matter (McArthur *et al.* 1992; Prahl *et al.* 1997; Lehmann *et al.* 2002). Furthermore, considering the typical stable isotope ratios (about –27‰) of terrestrial organic matter (Peterson and Howarth 1987; Tyson 1995; Meyers 1997), the origin of sedimentary organic matter in both lakes seemed to be mainly algal rather than terrestrial. These isotopic ratios provide grounds for rejecting the possibility that there was a large contribution of terrestrial organic matter to these lakes; this is especially based on the

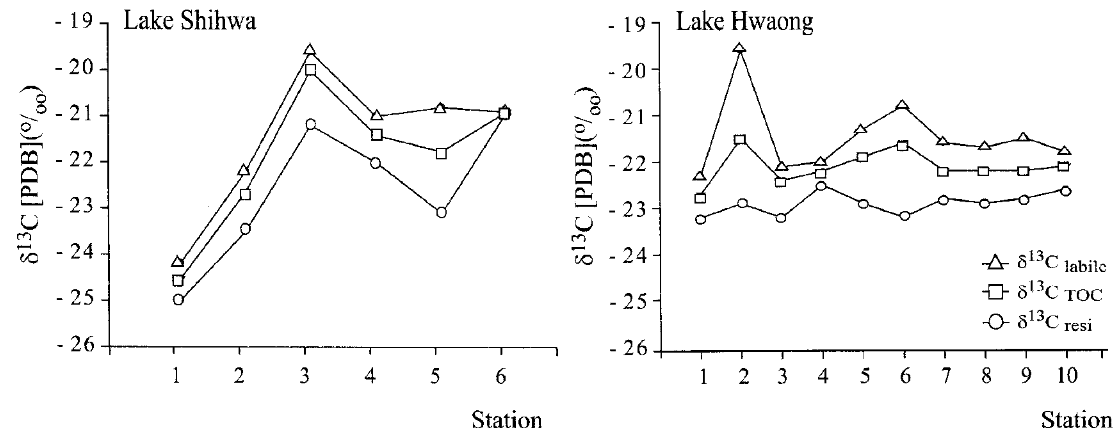

Fig. 6. Stable isotope ratios for organic carbon fractions of surface sediments from Lake Shihwa and Lake Hwaong.

high C_{org}/N_{org} ratios shown in Table 1. Therefore, the C_{org}/N_{org} ratio was more likely influenced by the degree of degradation of the sedimentary organic matter rather than by the origin of the organic matter.

In conclusion, the C_{org}/N_{org} ratio and the stable isotope ratio for organic nitrogen are potential indexes of the degradation degree of organic matter. The present study suggests that KOBr–KOH treatment of sedimentary organic matter could provide valuable information for understanding the origin and degradation state of organic matter in marine and brackish sediments.

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