

Carbon, nitrogen, and sulfur isotope changes and hydro-geological processes in a saline lake chain

Hideyuki Doi^{1,*}, Eisuke Kikuchi², Chitoshi Mizota³, Nobuya Satoh³, Shuichi Shikano², Natalia Yurlova⁴, Elena Yadrenkina⁴ & Elena Zuykova⁴

¹Graduate School of Life Sciences, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

²Center for Northeast Asian Studies, Tohoku University, Kawauchi, Aoba-ku, Sendai 980-8576, Japan

³Faculty of Agriculture, Iwate University, 3-18-8, Ueda, Morioka 020-8550, Japan

⁴Institute of Animal Systematics and Ecology, Siberian Branch of Russian Academy Sciences, Frunze Str., 11, Novosibirsk, 630091, Russia

(*Author for correspondence: Tel.: +81-22-217-7561, Fax: +81-22-217-7560, E-mail: h-doi@cneas.tohoku.ac.jp)

Received 26 November 2003; in revised form 25 March 2004; accepted 19 April 2004

Key words: stable isotopes, Lake Chany, particulate organic matter, Chironomidae, sediment, sulfate reduction, denitrification

Abstract

The ionic concentrations, conductivity and pH of water in the Lake Chany complex in West Siberian Russia change from the mouth to the interior of the lake. This difference is indicative of marked evaporation of lake water from the closed water body system in the dry climate of Western Siberia. The carbon isotope composition of particulate organic matter (POM, composed mainly of phytoplankton) clearly changes, along with the pH of the water, reflecting the concentration of dissolved CO₂. Carbon and nitrogen isotope signatures of *Chironomus plumosus* larvae, a benthic invertebrate that may feed on bulk lake sediment, systematically increase, along with those of POM and sediment organic matter (SOM), through the lake chain. Both sulfate-sulfur and nitrogen isotope compositions of the POM and SOM increase with distance from the estuary into the Lake Chany complex. Heavier sulfur and nitrogen isotope recycling from the sediment, caused by microbial sulfate reduction and denitrification, respectively, may have led to the increased sulfate-sulfur and nitrogen isotope compositions of the POM and SOM.

Introduction

Spatial variation within a lake and/or among lakes plays an important role in the structuring of lake ecosystems, at a variety of scales (Soranno et al., 1999). Limnologists have revealed vertical variation in environmental conditions and material flow, such as thermoclines and nutrient cycling (e.g., Wetzel, 2001). Soranno et al. (1999) hypothesized that lake chains, i.e., series of lakes connected through surface or groundwater flow, influence lake material processes, such as primary production and nutrient cycling, across a wide range of spatial scales. They showed that general

spatial gradients exist in some solute concentrations, especially in nonreactive components, along a lake chain. Lake chain patterns can influence lake material cycling processes, as well as material quantities. Moreover, lake hydro-geological processes have been shown to differ along lake chain gradients (Webster et al., 2000).

Soranno et al. (1999) found fewer patterns in reactive constituents such as dissolved nutrients along a lake chain, probably because of different local conditions that affected internal processing rates. The nonreactive variables, such as alkalinity, conductivity, and Ca concentration, however, tended to show spatial gradients down the lake chain.

Stable isotope ratios of nutrients have been widely used as natural tracers for the analysis of food web structure and material flow in lakes. Stable isotope ratios of materials can show spatial gradients along lake chains in the form of concentrations of non-reactive variables, as isotope ratio itself is not a quantitative factor, but a qualitative factor. In lake ecosystems, suspended and sediment organic matters have been shown to constitute dominant forms of organic matter, and to adequately reveal variations in nutrient contents (e.g., Zohary et al., 1994; Doi et al., 2003a,b). Moreover, Covich et al. (1999) suggested that benthic invertebrates play an important role in linking sediment organic matter to benthic and pelagic food webs. Food sources for benthic invertebrates, however, have not been adequately described for lake chains with gradients of sediment organic material. Recently, carbon isotope ratios, in combination with nitrogen, have been used to elucidate the importance of suspended and sediment organic material in aquatic ecosystems (e.g., Mayers, 1994; Doi et al., 2003a), and for consumer food source analysis (e.g., Bootsma et al., 1996; Vander Zanden & Vadeboncoeur, 2002; Vadeboncoeur et al., 2003). Moreover, sulfur isotope signatures can be used to study sulfur flows in saline aquatic ecosystems where sulfate-reducing bacteria are often involved (Krouse & Grinenko, 1991). In this study spatial gradients of carbon,

nitrogen, and sulfur stable isotope ratios along the inland saline lake chain are described and their causes discussed.

Materials and methods

Study area

Lake Chany is located in the Barabinskaya lowlands of Western Siberia, in the Novosibirsk region between the Ob and Irtysh Rivers ($54^{\circ} 30' - 55^{\circ} 09' \text{ N}$, $76^{\circ} 48' - 78^{\circ} 12' \text{ E}$), at an altitude of 106 m above sea level (Figs 1 and 2). The average water depth is 2.2 m and the maximum depth is 8.5 m. Lake Chany consists of three associated lakes, moderately saline lakes, Lakes Bolshye Chany (large) Chany, Malye (small) Chany, and Yarkul, which are connected by narrow channels (Fig. 1), and is an enclosed water body with no outflowing river. Lake Bolshye Chany consists of three pools, Chiyaikhiskii, Tagano-Kazantsevskii, and Yarkov. Lake Malye Chany together with pools from Lake Bolshye Chany form a lake chain. The salinity of the chain increases from the point where the river flows into Lake Malye Chany to the innermost part of the lake complex, the Yarkov Pool of Lake Bolshye Chany. The chosen study sites were: the estuarine part of the Kargat River,

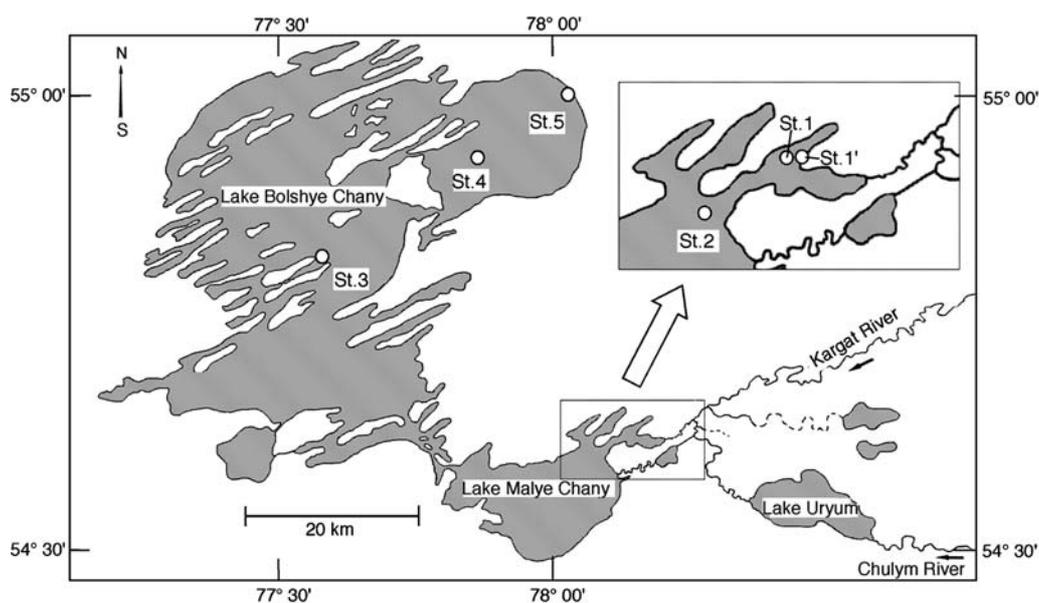


Figure 1. Approximate locations of the sample sites in the Lake Chany complex.

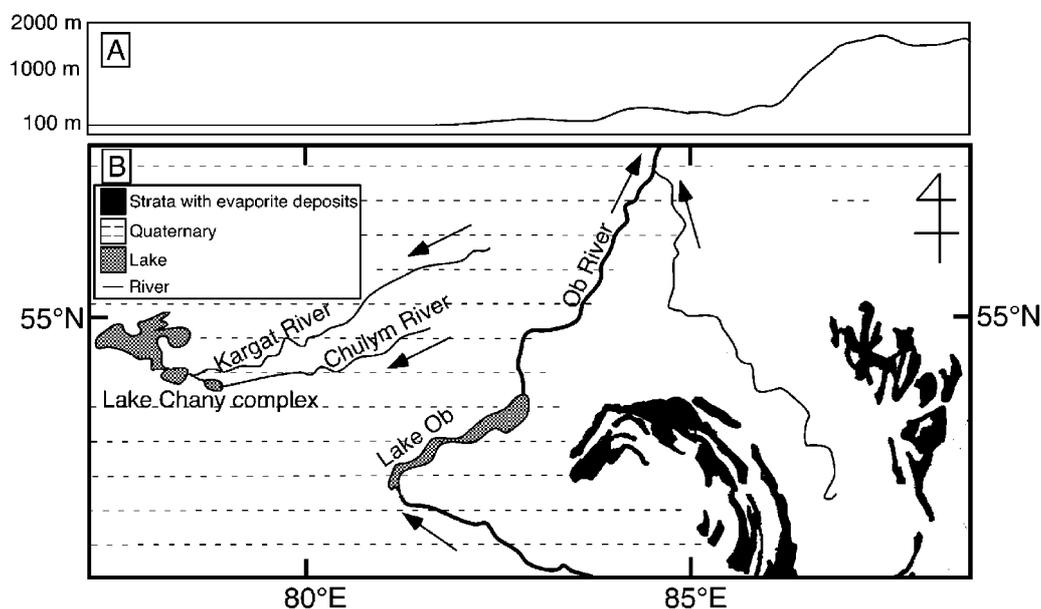


Figure 2. Schematic illustration of the topography (A) and simplified geology (B) around Lake Chany and its catchment area. The surface geology is cited from the Academy of Geological Science of China, Peking (1975), with modifications. Blank areas indicate rock types unrelated to this study. Solid arrows indicate the direction of mass flow of surface water.

Stations 1 and 1', at the center and the shore of the Kargat River, respectively; Lake Malye Chany, Station 2; Tagano-Kazantsevskii Pool, at the central part of Lake Bolshye Chany, Station 3; the deeper part of Yarkov Pool, Station 4; and the innermost part of Yarkov Pool, Station 5 (Fig. 1).

Site geology and geomorphology

Lake Chany is located inland, more than 2000 km from the present coastline; therefore solute composition in the lakes is not likely to be influenced by airborne sea spray. The lake is situated on mid Quaternary lowlands (Fig. 2), consisting of gravel and sand river deposits carried from the hills and mountains east of Lake Chany. The basement of the hills and mountains is composed of pre-Quaternary formations, Precambrian to Neogene. Of these formations, both Cambrian and Silurian strata are characterized by a distinct occurrence of evaporitic deposits (Fig. 2; cited from Academy of Geological Science of China 1975). Evaporites are relics of former oceans, or non-marine water bodies, which usually contain abundant anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and a variety of other minerals, including halite (NaCl) (Pilot 1991). The solute composition of Lake Chany water is

highly influenced by the dissolution of these fossil salts from the basement rocks, as described below.

Analysis of water samples

The water temperature, pH, dissolved oxygen, and conductivity of the surface water were measured using multiple *in situ* water quality meters (U-22, Horiba Co.). Water samples were collected from Stations 1, 2, 3, and 4 on 20–23 August 2001. Chlorophyll-*a* was measured with an Aquaflow chlorophyll-*a* meter (Turner Designs Co.). Concentrations of dissolved anion and cation species in the lake water were measured by ion chromatography (DX-120, Dionex Co.).

Sample collection and preparation for isotope analysis

Sampling for carbon and nitrogen isotope measurements was carried out at Stations 1, 2, 3, and 4 on 20–23 August 2001. POM was collected by filtering water samples with a Whatman glass fiber filter (GF/F), which had been precombusted at 500 °C for 2 h. SOM and *C. plumosus* larvae samples were collected at each sampling station using a Petersen grab. Samples for POM and SOM analysis were treated with 1 mol L⁻¹ HCl to remove possible

carbonate contamination. The larvae were sorted using a binocular stereo microscope and left in water for more than 12 h to allow time for their guts to empty. *Phragmites australis* L., the dominant marsh plant species surrounding Lake Chany, was collected near Station 1. These samples were oven dried at 60 °C and stored frozen until isotope analysis.

For sulfur isotope analysis of the lake water dissolved sulfates, water samples were collected at Stations 1, 1', 2, 3, 4, and 5 on 9–15 August 2002. The water samples were filtered with a Millipore filter (pore size 0.25 μm) and acidified with a few drops of 1 mol L⁻¹ HCl to remove dissolved bicarbonates. Lake sediments were also collected from near Stations 1, 2, and 5 in 9–15 August 2002 using a Petersen grab. Excess sulfates from the sediment samples were removed by repeated centrifugal washings with SO₄-free water and then freeze-dried. A fraction of the dry sediments was treated with warm H₂O₂ solution to oxidize sulfides. The resulting sulfates were recovered by centrifugal washing with water acidified with dilute HCl. All solutions containing sulfates were brought to a boil. Sulfates were recovered, in the form of BaSO₄, by adding warm 10% BaCl₂ solution, and subsequently dried for isotope analysis.

Isotope analysis

The carbon and nitrogen isotope ratios of the sample materials were measured with a mass spectrometer (DELTA plus, Finnigan MAT) directly connected to an elemental analyzer (NA-2500, CE Instruments). Normally, three replications were run for carbon and nitrogen isotope analysis. Dry BaSO₄ was used for sulfur isotope

analysis, following a procedure described by Yanagisawa & Sakai (1983). Analysis was carried out at the Institute for Study of the Earth's Interior, Okayama University, using a VG Isogas SIRA 10 mass spectrometer. Isotope results are reported by common notation, as follows:

$$\delta^{13}\text{C} \text{ or } \delta^{15}\text{N} \text{ or } \delta^{34}\text{S} = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000 (\text{‰})$$

where R is ¹³C/¹²C, ¹⁵N/¹⁴N, and ³⁴S/³²S ratios for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$, respectively. Pee Dee Belemnite (PDB) for $\delta^{13}\text{C}$, air N₂ for $\delta^{15}\text{N}$, and Canyon Diablo Troilite (CDT) for $\delta^{34}\text{S}$ were used as references. The analytical errors were within $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, and within $\pm 0.1\text{‰}$ for $\delta^{34}\text{S}$.

Results

Physical and chemical composition of waters from Lake Chany

The physical and chemical properties of surface water collected from the sampling sites are shown in Table 1. Water temperature and dissolved oxygen did not vary much among stations. The pH of the lake water was slightly lower at Station 1 (8.4) than at Stations 2–4 (8.8–8.9). Conductivity was higher at Stations 3 and 4 (1.03–1.12 S m⁻¹) than at Stations 1 and 2 (0.178–0.191 S m⁻¹). The highest salinity was observed at Station 4 (1.12 S m⁻¹). The trend of increasing conductivity toward the lake shore was probably due to evaporation in the arid to semi-arid climate of the study area. Concentrations of chlorophyll-*a* in the lake water gradually decreased from Stations 1 to 4, suggesting that production of phytoplankton may have been low in Lake Bolshye Chany (Stations 3 and 4).

Table 1. Physical and chemical composition of surface waters from Lake Chany sampling sites in August 2001

	Water temperature (°C)	Water depth (m)	Conductivity (S m ⁻¹)	Chlorophyll- <i>a</i> ($\mu\text{g L}^{-1}$)	Dissolved oxygen (mg L ⁻¹)	pH	Ionic composition (g L ⁻¹)					
							Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻
Station 1	19.9	1.0	0.191	69.4	9.2	8.4	0.65	0.04	0.11	0.15	0.38	0.27
Station 2	18.9	2.2	0.178	28.8	8.6	8.8	0.25	0.01	0.09	0.06	0.28	0.16
Station 3	18.8	2.0	1.03	5.7	10.2	8.9	1.59	0.03	0.40	0.05	1.79	0.79
Station 4	19.0	5.5	1.12	5.7	9.6	8.8	2.56	0.04	0.63	0.04	3.04	1.09
Seawater*							11.0	0.4	1.3	0.4	18.9	2.65

* Fearon (1946).

The ionic composition of the lake water was fairly similar at all stations, although all ion concentrations increased from Stations 1 to 4, along with the conductivity increase, except for Ca^{2+} concentrations. The cation and anion concentrations of lake waters around the world have been shown to be greatest for Ca^{2+} , followed by Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , and Cl^- , in that order (Wetzel, 2001). The ionic composition of Lake Chany waters, however, did not follow this trend. Concentrations of Na^+ and Mg^{2+} in Lake Chany were higher than Ca^{2+} , and Cl^- concentrations were higher than SO_4^{2-} . These ionic compositions more closely resemble seawater (Table 1) than normal lake water.

Isotope composition of POM and marsh plants

As shown in Figure 3, the isotope composition of POM varied among sites. $\delta^{13}\text{C}$ values of POM ranged from -26.6‰ to -21.3‰ , and significantly increased from Stations 1 to 4 (multiple comparison

Holm test, $p < 0.05$, $n = 3$). $\delta^{15}\text{N}$ values of POM, $+3.0$ to $+9.6\text{‰}$, significantly increased from Stations 1 and 2 to Station 4 (Holm test, $p < 0.05$, $n = 3$). At Stations 1 and 2, the $\delta^{15}\text{N}$ values of POM were nearly identical, $+3.0$ and $+3.1\text{‰}$, respectively. POM at Station 4 had the highest $\delta^{13}\text{C}$ value, $-21.3 \pm 0.3\text{‰}$ (mean \pm 1 SD, $n = 3$), and $\delta^{15}\text{N}$ value, $+9.6 \pm 0.4\text{‰}$, of all stations. Thus, both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ concentrations in POM tended to increase from the riverine site, Station 1, to the innermost part of Lake Chany, the Yarkov Pool, Station 4. The $\delta^{13}\text{C}$ value of *P. australis* was $-25.8 \pm 0.2\text{‰}$, which is close to the upper limits of -30 to -26‰ for terrestrial C_3 plants (France, 1995).

Isotope composition of SOM

The isotope composition of SOM followed a similar trend to POM (Fig. 3). The $\delta^{13}\text{C}$ values of SOM ranged from -25.8 to -21.8‰ , and tended to increase from Stations 1 to 4. In addition, the $\delta^{15}\text{N}$

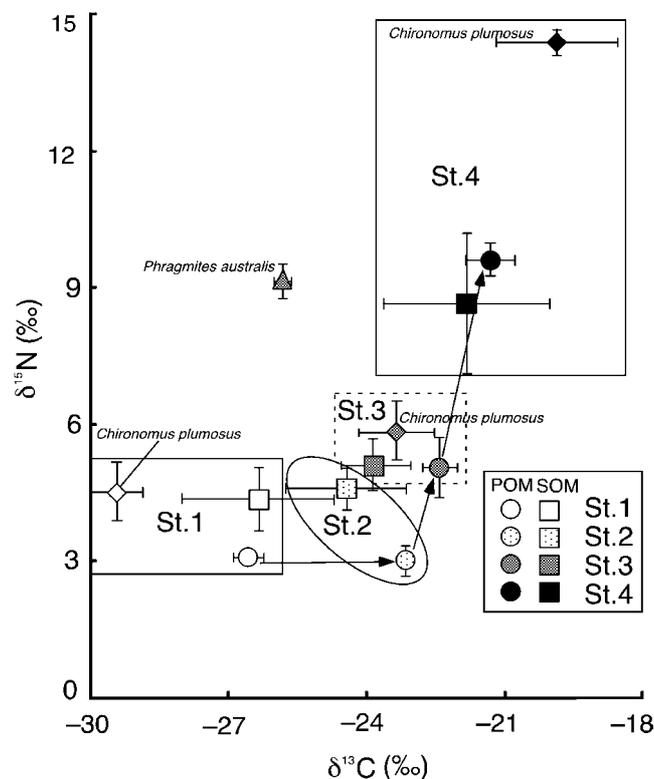


Figure 3. The relationship between carbon and nitrogen isotope ratios of biological and prey materials collected from Lake Chany. Each symbol and error bar indicates the mean value and standard deviation (sample number = 3), respectively. POM – particulate organic matter, SOM – sediment organic matter. St. 1 to St. 4 = Station 1 to Station 4 (see Fig. 1).

values of SOM ranged from +4.3 to +8.6‰, tending to increase from Stations 1 to 4. $\delta^{15}\text{N}$ values of SOM at Station 4, $+8.6 \pm 1.5\text{‰}$, were significantly higher than those at Stations 1–3 (Holm test, $p < 0.01$, $n = 3$). Thus, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of SOM tended to increase from the riverine site to the Yarkov Pool. Standard deviations of the isotope concentrations examined for SOM were higher than those for POM, indicating heterogeneity of organic sources.

Isotope composition of Chironomus plumosus larvae

Chironomus plumosus larva (Diptera, Chironomidae) was a common, predominant benthic macro-invertebrate species in all parts of Lake Chany. Samples of *C. plumosus* larvae were collected from all sampling sites, except Station 2 (Fig. 3). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of *C. plumosus* larvae at Station 1, $-29.4 \pm 0.6\text{‰}$ and $4.5 \pm 0.6\text{‰}$, were significantly lower than those of the larvae at Station 3 ($-23.0 \pm 0.6\text{‰}$ and $+5.8 \pm 1.0\text{‰}$) (Holm test, $p < 0.01$, $n = 3$). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of larvae at Station 4, $-19.8 \pm 1.3\text{‰}$ and $+14.4 \pm 0.3\text{‰}$, were higher than those of Stations 1 and 3 (Holm test, $p < 0.01$, $n = 3$).

Sulfur isotope compositions of dissolved sulfates and associated sediment sulfides

$\delta^{34}\text{S}$ values of sulfates in the lake water ranged from +27.3 to +32.2‰, and tended to slightly increase from Stations 1 to 5 (Table 2). $\delta^{34}\text{S}$ values of sulfates from the riverine Stations 1 and 1' and from Lake Malye Chany, Station 2, were lower

than those from Lake Bolshye Chany, Stations 3–5. $\delta^{34}\text{S}$ values of sulfides in lake sediment varied inconsistently among sites, from +6.0 to +21.0‰. The highest $\delta^{34}\text{S}$ value among the stations was observed for sediment sulfides from Station 5.

Discussion

Isotope compositions of phytoplankton

The isotope values of POM, which is composed mainly of phytoplankton, have been shown to vary in lake ecosystems (Yoshioka et al., 1989; Takahashi et al., 1990; Zohary et al., 1994). In Lake Chany, $\delta^{13}\text{C}$ values of POM varied among sites and significantly increased from Stations 1 to 2 (Fig. 3). In addition, the pH of the lake water increased from Station 1 (8.4) to Stations 2–4 (8.8–8.9) (Table 1). In this pH range of 8–9, dissolved CO_2 proportions in water have been shown to decrease from 2.5% (at pH 8) to 0.3% (at pH 9), while bicarbonate concentrations increase (Wetzel, 2001). Fry (1996) suggested that diatoms adapt to low CO_2 (high pH) conditions by increased use of carbonic anhydrase (CA) to keep CO_2 levels in their cells in a normal range, or adapt by rapidly using CO_2 as it dissociates from bicarbonate, before enough time for isotope equilibrium has elapsed. Moreover, algal use of bicarbonate as a carbon substrate has been shown to result in enriched $\delta^{13}\text{C}$ values, because the $\delta^{13}\text{C}$ value of bicarbonate is isotopically heavier than that of CO_2 , and isotope fractionation in CA is negative (Yoshioka, 1997). Thus, under conditions of high CO_2 concentrations (low pH), $\delta^{13}\text{C}$ values of POM become low, since phytoplankton consume mainly

Table 2. Sulfur isotope composition of the sulfate and associated sulfides from sediments in Lake Chany, collected in August 2002

Station	Sulfate		Sulfide		Fractionation (sulfate-sulfide)
	g L^{-1}	$\delta^{34}\text{S}$ (‰)	g kg^{-1}	$\delta^{34}\text{S}$ (‰)	
1	0.2	+27.3	7.0	+12.2	+15.1
1'	0.3	+28.7	7.7	+6.0	+22.7
2	0.3	+28.1	7.4	+10.0	+18.1
3	0.8	+31.8	ND	ND	ND
4	1.1	+32.2	ND	ND	ND
5	1.1	+32.2	15.1	+21.0	+11.2

ND – not determined.

CO₂ gas, not bicarbonate, by using CA. Under conditions of low CO₂ concentrations (high pH), however, $\delta^{13}\text{C}$ values of POM are high, since phytoplankton consume mainly bicarbonate. Consequently, the variable $\delta^{13}\text{C}$ values of POM are influenced by the DIC species changes in the water.

The $\delta^{15}\text{N}$ value of POM significantly increased from Stations 2 to 4. The high values of POM $\delta^{15}\text{N}$ in the inner part of Lake Chany could be caused by denitrification in the sediment and evaporation of ammonium in the alkaline waters (pH 8.4–8.9) of Lake Chany. Nitrogen isotope changing of POM may be dependant on the chemical concentration process of ammonium and nitrate, since the concentrations of ammonium and nitrate were affected the nitrogen isotope values of POM by photosynthesis and denitrification. Although nitrate and ammonium concentrations could not be clearly measured in the lake water, due to high concentrations of humic acid, nitrate is known to be the common form of inorganic nitrogen in freshwater lakes (Wetzel, 2001). The denitrification of dissolved nitrates by microorganisms in oxygen-depleted waters and in sediments selectively releases ¹⁴N₂, leaving the remaining nitrate enriched in ¹⁵N (Cline & Kaplan, 1975). Measured enrichment factors associated with denitrification have ranged from 28 to 33‰ (Robinson, 2001). Moreover, the evaporation of ammonium in alkaline waters would indicate high nitrogen isotope fractionation, e.g., 40–60‰ for NH₃ volatilization (Robinson, 2001). Moreover, the degassing of ammonium may occur in high pH water (Emerson et al., 1975). In Lake Chany, pH of water was increased though the water flow. At pH of 8.4 (Station 1), NH₄ (lipid):NH₃ (gas) calculated by Emerson et al. (1975) was 10.4:1, while was 3.2:1 at pH of 8.9 (Station 4). The nitrogen isotope fractionation from NH₄ (lipid) to NH₃ (gas) is 1–7‰, and not influenced by the pH and temperature of water (Norlin et al., 2002). Thus, the isotope fractionation for degassing of ammonium is lower than those for NH₃ volatilization. The degassing of ammonium at high pH would also cause the increase in the $\delta^{15}\text{N}$ value of POM through the water flow, although the isotope fractionation is lower.

Consequently, the nitrate and ammonium remaining after denitrification, degassing and evaporation would have high $\delta^{15}\text{N}$ values. These

effects of nitrogen transformation and $\delta^{15}\text{N}$ enrichment would gradually accumulate in the Yarkov Pool, Station 5, at the end of the Lake Chany complex. Therefore, the $\delta^{15}\text{N}$ values of POM should increase from Lake Malye Chany to the Yarkov Pool.

Isotope values of SOM

SOM is generally derived from several sources, including many species of benthic and planktonic microalgae, as well as aquatic and terrestrial plants (e.g., Meyers, 1994). Carbon isotope signatures have been used as reliable tracers to determine origins of SOM, as $\delta^{13}\text{C}$ compositions of organic detritus have been reported to be conservative, even following extensive and prolonged microbial decomposition (Haines, 1976; Schwinghamer et al., 1983; Gearing et al., 1984; Fenton & Ritz, 1988; Doi et al., 2003a). In Lake Chany, $\delta^{13}\text{C}$ values of SOM were similar to those of POM and tended to increase from Stations 1 to 4, like the POM values, indicating that SOM was derived mainly from POM, and therefore mainly phytoplankton in origin. Moreover, $\delta^{13}\text{C}$ values of SOM had higher standard deviations than those of POM. This may be due to the segregation processes in the sediments acting on a well mixed POM pool, since Lake Chany complex is very shallow (mean water depth; 2.2 m).

$\delta^{15}\text{N}$ has also been used to determine sources of SOM, although it is less reliable as a provenance indicator because it records not only the organic matter origin but also the degree of diagenetic alteration (Thornton & McMamus, 1994). The $\delta^{15}\text{N}$ values of SOM at Stations 1–3 tended to be higher than those of POM. This may indicate the accumulation in the sediment of refractory, decomposed phytoplankton detritus that had been enriched with ¹⁵N. Because labile organic matter such as proteins are easily decomposed by heterotrophic microbes (Findlay & Tenore, 1982), more refractory substances, which are enriched with ¹⁵N during decomposition, would tend to accumulate in sediment (Wada, 1980; Owen, 1985). Marsh plants (*Phragmites australis*, $\delta^{13}\text{C}$: $-25.8 \pm 0.2\text{‰}$, $\delta^{15}\text{N}$: $+9.0 \pm 0.1\text{‰}$) surrounding the lake had very different $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ values, as compared to those of SOM, suggesting that the contribution of marsh plants to SOM was

negligible. In Lake Chany $\delta^{15}\text{N}$ values of SOM, as with $\delta^{13}\text{C}$ values, tended to increase from Stations 1 to 4, along with values for POM, and were even higher than the values for POM, due to microbial decomposition in the sediment.

Isotope values of Chironomus plumosus larvae

The analysis of trophic relationships using stable isotope ratios has generally been based on the premise that the enrichment of $\delta^{13}\text{C}$ during trophic transfer is slight ($+0.8 \pm 1.1\%$, mean ± 1 SD, range from -0.6% to $+2.7\%$), while that of $\delta^{15}\text{N}$ is fairly large ($+3.4 \pm 1.1\%$, range from 1.3 to 5.3%) (DeNiro & Epstein, 1978; Minagawa & Wada, 1984). *Chironomus plumosus* larvae have been described as surface deposit feeders (McLachlan, 1977) that feed on organic matter in surface sediments or fresh deposits. The $\delta^{13}\text{C}$ values of *C. plumosus* larvae at Station 1 were much lower than the values of SOM and POM. Further studies are needed to determine the food source of the chironomids, at least at Station 1. Kiyashko et al. (2001) suggested that *Stictochironomus* sp. (Diptera; Chironimidae), with $\delta^{13}\text{C}$ values from -64.0 to -34.3% , selectively ingest methanotrophic bacteria that are extremely ^{13}C -depleted, and they suspected that the trophic association of some Chironimidae species with methanotrophic bacteria could be a widespread phenomenon. Such relationships with chemoautotrophic producers may exist in the chironomids in Lake Chany.

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of *C. plumosus* larvae at Stations 1–4 also tended to change along with those of SOM and POM. At Stations 3 and 4, the food sources of *C. plumosus* larvae could be explained as POM deposited on the surface of sediments, and/or SOM, since differences in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ between the chironomids and potential food sources (POM and SOM) were within, or not very different from, the range of change expected during a trophic transfer.

Sulfur isotope variations of sulfates and sulfides

The $\delta^{34}\text{S}$ values of sulfates in continental river water represent a crustal average of the sulfur reservoir in whole rocks from catchment areas. The $\delta^{34}\text{S}$ value of sulfates in the discharge-weight-

ted average in Russia is estimated to be $+8\%$ (Nriagu, 1991). Nevertheless, the $\delta^{34}\text{S}$ value of river water sulfates collected from Station 1 ($+27.8\%$) was much higher than this common value and present seawater sulfate levels ($+21.0\%$; Rees et al., 1978). Such a high $\delta^{34}\text{S}$ value is indicative of a very local origin for the sulfates. From the unique solute composition chemistry of the Lake Chany waters (Table 1), together with geological evidence, a plausible origin for the sulfates is the dissolution of marine evaporitic deposits occurring in the hills and mountains to the east of the lake complex (Fig. 2). Evaporite is a distinct mineral constituent of both the Cambrian and Silurian formations in southern Russia (Fig. 2; Academy of Geological Science of China, 1975).

It has been well documented that the $\delta^{34}\text{S}$ values of marine sulfates have changed over geological time, reflecting global events. Higher $\delta^{34}\text{S}$ values have been reported from the late pre-Cambrian period (around $+28\%$), and values have gradually decreased to present-day levels ($+21\%$) (Claypool et al., 1980). Various $\delta^{34}\text{S}$ values for Cambrian sulfate formations from the Irkutsk Basin in the Siberian platform, which are stratigraphically equivalent to the formations east of Lake Chany, are known (Pisarchik & Golubchina, 1975; Claypool et al., 1980). The $\delta^{34}\text{S}$ values of these sulfates range from $+22.0$ to $+33.3\%$ ($n = 26$, Pisarchik & Golubchina, 1975) and $+30.3 \pm 2.4\%$ ($n = 59$, Claypool et al., 1980). Sulfate $\delta^{34}\text{S}$ values from the overlying Silurian formation are reportedly $+28.2\%$ ($n = 1$; Claypool et al., 1980). These reported $\delta^{34}\text{S}$ values are nearly comparable to those obtained from the inflowing river sulfates in the Lake Chany complex ($\delta^{34}\text{S} = +27.3$ to $+28.7\%$; Table 2). The geological and geomorphological interpretations of the data reinforce a fossil evaporite origin for the relevant solutes in the Lake Chany waters, as previously observed for one sulfate sample dissolved in the Lena River ($\delta^{34}\text{S} = +32.0\%$; Rabinovich & Grinenko, 1979).

Sulfate-reducing bacteria produce sulfides that are depleted in ^{34}S during the dissimilatory reduction (Jones & Starkey, 1957; Harrison & Thode, 1958; Kaplan & Rittenberg, 1964). The isotope composition of sulfides in sediments provides an indication of the activity of sulfate-

reducing bacteria during the microbial sulfide formation. In Lake Chany, the $\delta^{34}\text{S}$ values of sulfates at Stations 3–5 were higher than those of sulfates collected at Stations 1 and 2, and apparent sulfur isotope fractionation (the difference between $\delta^{34}\text{S}$ values of sulfate and associated sulfide) varied from +11.2 to +22.7‰ (Table 2). Such a difference is indicative of a microbial origin for the sediment sulfides. Sulfur isotope fractionation in a range from 30‰ to 40‰ has been observed when the natural population of sulfate-reducing bacteria in sediment metabolizes with natural organic substrates at environmental temperatures (Canfield, 2001). The sulfur isotope fractionation of sulfur reducing bacteria is determined by sulfate concentration, transfer of sulfate and chemoautotrophic activity of them (Harrison & Thode, 1958; Kaplan & Rittenberg, 1964; Canfield, 2001). The sulfur isotope fractionation observed for Lake Chany sediments was lower than those known for marine and estuarine ecosystems.

While the degree of sulfur isotope fractionation during microbial sulfate reduction has been debated (Krouse & Grinenko, 1991), the isotope composition of sedimentary sulfides provides some indication of the process of sulfide formation. The following mechanisms are plausible for the lower sulfur isotope fractionation observed in Lake Chany. First, isotope fractionation by sulfate-reducing bacteria is lower under low sulfate concentrations than under high sulfate concentrations (Harrison & Thode, 1958; Canfield, 2001). In Lake Chany, dissolved sulfate concentrations in the water were markedly lower than in common seawater (Table 1). Due to this sulfate limitation, the sulfate-reducing bacteria in Lake Chany tend to form heavier sulfide-sulfur ^{34}S from sulfates than do bacteria in marine or estuarine systems. Second, the texture of the substrate (system open vs. closed) could influence by the sulfur isotope fractionation due to the changing of mass transfer for sulfate (Thode, 1991), such that fractionation would be higher in sandy sediments than in clay sediments. The Lake Chany sediments are uniformly sandy in texture, which could open sulfate ion. The lower observed sulfur isotope fractionation would not be expected to be responsible for the semi-closed system during the microbial reduction.

Thirdly, the microbial sulfide formation is a function of the rate of sulfate reduction. Canfield (2001) showed that lower isotopic fractionations often associates with lower temperatures during the growth. From these reasons, we interpret that the lower isotopic fractionation between dissolved sulfate and associated sulfides in the sediments from Lake Chany is probably due to the combined effects of low sulfate concentration associated with lower activity of the sulfate-reducing bacteria under lower ambient temperature (estimated annual air temperature: $<8^\circ\text{C}$).

Carbon, nitrogen, and sulfur isotopes along hydro-geological gradients

Soranno et al. (1999) analyzed long-term chemical and biological data from lake chains and suggested that nonreactive lake constituents show increasing concentrations down the lake chain. In Lake Chany, the accumulation of nonreactive ions, including sodium and chloride ions, might be accelerated by the lake's particular landscape characteristics, i.e., the shallow, wide, and closed water body located in an arid region, and result in increasing conductivity and salts along a gradient from the inflowing river to the interior.

In the present study, carbon and nitrogen isotope signatures of POM and SOM clearly increased from the input river to the interior of Lake Chany. The accumulation of nonreactive ions (conductivity) resulted in an increase of pH from 8.4 to 8.9. The gradient of pH along the length of the Lake Chany complex resulted in a parallel gradient in carbon isotope ratios, through DIC species, which used by phytoplankton, changed.

The mechanism for changes in the nitrogen isotope signature could differ from that for carbon. The increase in the nitrogen isotope signature may be explained by the recycling of heavier nitrogen from the sediment owing to denitrification by microorganisms in the sediment. The present results also show that the sulfur isotope signature of sulfate increases along the gradient from the river to the interior of Lake Chany. The $\delta^{34}\text{S}$ values of sulfate increased with the increases of sulfate concentrations in the water from Stations 1 to 5. The increases in $\delta^{34}\text{S}$ values of sulfate may be due to recycling of ^{34}S -enriched sulfate from the sediment, as with the increase in the

nitrogen isotope signature, by sulfate-reducing bacterial activity, which was increased by the high sulfate concentrations. In addition, at Station 5, high contents of sulfide in the sediment may indicate high sulfate-reducing bacterial activity. Thus, the effect of recycling from the sediment increases with distance into the lake complex, in the form of increased sulfur and nitrogen isotope signatures.

The isotope signature of the benthic invertebrate *C. plumosus* larvae changed longitudinally, along with the values of SOM, from the river to the interior of the Lake Chany complex. These results suggest that *C. plumosus* larvae are linked to the carbon and nitrogen isotope changes along the lake chain.

Thus, the present isotope results show that the effects of nitrogen and sulfur material flow in the bottom sediment accumulate, as seen by the increase in their isotope signatures in some water components ($\delta^{15}\text{N}$ of POM and $\delta^{34}\text{S}$ of sulfate) in the lake chain. This would suggest that the isotope ratios of some nutrients behave like nonreactive components in the lake chain. This study constitutes a first step toward revealing nitrogen and sulfur material flow between bottom sediments and surface water, and material pathways from nutrients to consumers in lake chain ecosystems.

Acknowledgements

We thank Dr K. Itoh, Department of Agriculture, Tohoku University, for her permission to use the stable isotope analytical facilities in her laboratory. We thank Dr K. Hirabayashi, Department of Applied Biology, Faculty of Textile Science and Technology, Shinshu University, for his helping us to identify the chironomid larvae. We thank Prof. Dr M. Moshkin, Institute of Animal Systematics and Ecology, SBRAS (Siberian Branch of Russian Academy Sciences), for his inviting us to this study. We thank Dr A. Yurlov, Institute of Animal Systematics and Ecology, SBRAS and Dr A. V. Yadrenkin, Institute of Oil and Gas Geology, SBRAS for his helping our sampling. This study was supported partly by Grant-in-Aid for Scientific Research (B) from Japan Society for the Promotion of Science (No. 13575004, 16405005).

References

- Academy of Geological Science of China, Peking, 1975. The geological map of Asia. Cartographic Publishing House, Peking Joint Publishing Co., Hong Kong Branch, Hong Kong, China.
- Bootsma, H. A., R. E. Hecky, R. H. Hesslein & G. F. Turner, 1996. Food partitioning among lake Malawi nearshore fishes as revealed by stable isotope analysis. *Ecology* 77: 1286–1290.
- Canfield, D. E., 2001. Isotope fractionation by natural populations of sulfate-reducing bacteria. *Geochimica et Cosmochimica Acta* 65: 1117–1124.
- Claypool, G. E., W.T. Holser, I. R. Kaplan, H. Sakai & I. Zak, 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology* 28: 199–260.
- Cline, J. D. & I. R. Kaplan, 1975. Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean. *Marine Chemistry* 38: 453–477.
- Covich, A. P., M. A. Palmer & T. A. Cowl, 1999. The role of benthic invertebrate species in freshwater ecosystems. *BioScience* 49: 119–127.
- DeNiro, M. J. & S. Epstein, 1978. Influence of diet on the distribution of carbon isotopes in animals. *Geochimica et Cosmochimica Acta* 48: 1135–1140.
- Doi, H., E. Kikuchi, S. Hino, T. Itoh, S. Takagi & S. Shikano, 2003a. Isotopic ($\delta^{13}\text{C}$) evidence for autochthonous origin of sediment organic matter in small, acidic Lake Katanuma, Japan. *Marine and Freshwater Research* 54: 253–257.
- Doi, H., E. Kikuchi, S. Hino, T. Itoh, S. Takagi & S. Shikano, 2003b. Seasonal dynamics of carbon stable isotope ratios of particulate organic matter and benthic diatoms in strongly acidic Lake Katanuma. *Aquatic Microbial Ecology* 33: 87–94.
- Emerson, K., R. C. Russo, R. E. Lund & R. V. Thurston, 1995. Aqueous ammonia equilibrium calculations: Effect of pH and temperature. *Journal of the Fisheries Research Board of Canada* 32: 2379–2383.
- Fenton, G. E. & D. A. Ritz, 1988. Changes in carbon and hydrogen stable isotope ratios of macroalgae and seagrass during decomposition. *Estuarine, Coastal and Shelf Sciences* 26: 429–436.
- Findlay, W. & K. R. Tenore, 1982. Nitrogen source for the detritivore polychaete, *Capitella capitata*: detritus substrate or microbes? *Science* 218: 371–372.
- Fearon, W. R., 1946. *An Introduction to Biochemistry*. Heinemann, London.
- France, R. L., 1995. Critical examination of stable isotope analysis as a means for tracing carbon pathways in stream ecosystems. *Canadian Journal of Fisheries and Aquatic Sciences* 52: 651–656.
- Fry, B., 1996. $^{13}\text{C}/^{12}\text{C}$ fractionation by marine diatoms. *Marine Ecology Progress Series* 134: 283–294.
- Gearing, J. N., R. J. Gearing, D. T. Rudrick, A. G. Requejo & M. J. Hutchins, 1984. Isotope variability of organic carbon in a phytoplankton based temperate estuary. *Geochimica et Cosmochimica Acta* 48: 1089–1098.
- Harrison, A. G. & H. G. Thode, 1958. Mechanisms of the bacterial reduction of sulfate from isotope fractionation studies. *Transactions of the Faraday Society* 53: 84–92.

- Haines, E. B. & C. L. Montague, 1979. Food sources of estuarine invertebrates analyzed using $^{13}\text{C}/^{12}\text{C}$ ratios. *Ecology* 60: 48–56.
- Jones, G. E. & R. J. Starkey, 1957. Fractionation of stable isotopes of sulfur by micro-organisms and their role in deposition of native sulfur. *Journal of Applied Microbiology* 5: 111–115.
- Kaplan, I. R. & S. C. Rittenberg, 1964. Microbiological fractionation of sulfur isotopes. *Journal of General Microbiology* 15: 96–101.
- Krouse, R. H. & V. A. Grinenko, 1991. *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment*. SCOPE 43, John Wiley & Sons Ltd.: 440.
- McLachlan, A. J., 1977. Some Effects of Tube shape on the feeding of *Chironomus plumosus* L. (Diptera: Chironomidae). *Journal of Animal Ecology* 46: 139–146.
- Meyers, P. A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology* 144, 289–302.
- Minagawa, M. & E. Wada., 1984. Stepwise enrichment of ^{15}N along food chains: Further evidence and the relation between $\delta^{15}\text{N}$ and animal age. *Geochimica et Cosmochimica Acta* 48: 1135–1140.
- Norlin, E., K. Irgum & K. E. A. Ohlsson, 2002. Determination of the $^{15}\text{N}/^{14}\text{N}$ ratio of ammonium and ammonia in aqueous solutions by equilibrium headspace-gas chromatography-combustion-isotope ratio mass spectrometry. *The Analyst* 127: 735–740.
- Nriagu, J. R., 1991. Rivers, In Krouse, H. R. & V. A. Grinenko (eds), *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment*. SCOPE 43 John Wiley & Sons Ltd.: 225–229.
- Owens, N. J. P., 1985. Variations in the natural abundance of $\delta^{15}\text{N}$ in estuarine suspended particulate organic matter: a specific indicator of biological processing. *Estuarine, Coastal and Shelf Science* 20: 505–510.
- Pilot, J., 1991. Sulphur and oxygen isotope composition of marine evaporite and barite strata. In Krouse, H. R. & V. A. Grinenko (eds), *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment*. SCOPE 43, John Wiley & Sons Ltd.: 68–87.
- Pisarchik, Y. K. & M. N. Golubchina, 1975. Sulfur isotope compositions for Cambrian calcium sulfates from the Siberian platform. *Geochemistry International* 12: 227–230.
- Rabinovich, A. L. & V. A. Grinenko, 1979. Sulfate sulfur isotope ratios for USSR river water. *Geochemistry International* 16: 68–79.
- Rees, C. E., W. J. Jenkins & J. Monster, 1978. The sulphur isotopic composition of ocean water sulphate. *Geochimica et Cosmochimica Acta* 42: 377–381.
- Robison, D., 2001. $\delta^{15}\text{N}$ as an integrator of the nitrogen cycle. *Trends in Ecology and Evolution* 16: 153–162.
- Schwingamer, P., F. C. Tan & D. C. Gordon, 1983. Stable carbon isotope studies of Pecks Cove mudflat ecosystem in the Cumberland Basin, Bay of Fundy. *Canadian Journal of Fisheries and Aquatic Sciences* 40: 262–272.
- Soranno, P. A., K. E. Webster, J. L. Riera, T. K. Kratz, J. S. Baron, P. A. Bukaveckas, G. W. Kling, D. S. White, N. Caine, R. C. Lathrop & P. R. Leavitt, 1999. Spatial variation among lakes within landscapes: ecological organization along lake chains. *Ecosystems* 2: 375–410.
- Takahashi, T., T. Yoshioka, E. Wada & M. Sakamoto, 1990. Carbon isotope discrimination by phytoplankton and photosynthetic bacteria in monomictic Lake Fukami-ike. *Archiv für Hydrobiologie* 120: 197–210.
- Thode, H. G., 1991. Sulphur isotopes in nature and the environment: an overview. In Krouse, H. R. & V. A. Grinenko (eds), *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment*. SCOPE 43, John Wiley & Sons Ltd.: 1–26.
- Thornton, S. E. & J. McManus, 1994. Application of organic carbon and nitrogen stable isotope ratios 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.
- Yanagisawa, F. & H. Sakai, 1983. Thermal decomposition of barium sulfate-vanadium pentoxide-silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratios measurements. *Analytical Chemistry* 55: 985–987.
- Yoshioka, T., 1997. Phytoplanktonic carbon isotope fractionation: equations accounting for CO_2 -concentrating mechanisms. *Journal of Plankton Research* 19: 1455–1476.
- Yoshioka, T., H. Hayashi & E. Wada, 1989. Seasonal variations of carbon and nitrogen isotope ratios of plankton and sinking particles in Lake Kizaki. *Japanese Journal of Limnology* 50: 313–320.
- Vadeboncoeur, Y., E. Jeppesen, M. J. Vander Zanden, H. Schierup, K. Christoffersen & D. M. Lodge, 2003. From Greenland to green lakes: Cultural eutrophication and the loss of benthic pathways in lakes. *Limnology and Oceanography* 48: 1408–1418.
- Vander Zanden, M. J. & Y. Vadeboncoeur, 2002. Fishes as integrators of benthic and pelagic food webs in lakes. *Ecology* 83: 2152–2161.
- Wada, E., 1980. Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments. In Goldberg, E. D., Y. Horibe & K. Saruhashi (eds), *Isotope Marine Chemistry*, Uchida Rokakuho, Tokyo, Japan: 375–398.
- Webster, K.E., P. A. Soranno, S.B. Baines, T. K. Kratz, C. J. Bowser, P. J. Dillon, P. Campbell, E. J. Fee & R. E. Hecky, 2000. Structuring features of lake districts: landscape controls on lake chemical responses to drought. *Freshwater Biology* 43: 499–515.
- Wetzel, R. G. 2001. *Limnology Lake and River Ecosystems*, 3rd edn. Academic Press, San Diego: 169–173; 236.
- Zohary, T., J. Erez, M. Gophen, I. Berman-Frank, M. Stiller, 1994. Seasonality of stable carbon isotopes within the pelagic food web of Lake Kinneret. *Limnology and Oceanography* 39: 1030–1043.