

Analysis of historical trend of carotenoid concentrations in sediment cores from Lake Shinji, Japan

KENJI KUSUNOKI,¹ MASAHIRO SAKATA,^{2*} YUKINORI TANI,² YASUSHI SEIKE³ and KAZUYASU AYUKAWA³

¹Faculty of Education, Shizuoka University, 836 Ohya, Shizuoka 422-8529, Japan

²Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan

³Interdisciplinary Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu-cho, Matsue 690-8504, Japan

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The historical trend of the concentrations of carotenoids originating from phytoplankton in sediment cores collected at two sites in Lake Shinji, a eutrophic oligohaline lake was investigated to clarify the changes in phytoplankton community structures in the lake over the last 100 years. Eight kinds of carotenoids were detected in the sediments, i.e., astaxanthin and lutein from chlorophytes, alloxanthin from cryptophytes, canthaxanthin, echinenone and zeaxanthin from cyanobacteria, diatoxanthin from diatoms, and β -carotene from unspecified algal groups. On the basis of the stoichiometric relation between total organic carbon (TOC) and total sulfur (TS), the historical changes in the TOC concentration of sediment cores since *circa* 1970 have been attributable to the decomposition of organic matter by sulfate reduction, confirming the importance of diagenetic processes in Lake Shinji sediments. It was found that labile chlorophyll *a* is transformed diagenetically to more stable pheophytin *a* and pyropheophytin *a* within the upper 5 cm of the cores. Similarly, the concentrations ($\mu\text{g g}^{-1}$ TOC) of carotenoids, other than diatoxanthin, in the cores decreased rapidly within this zone, and in the cores lower than 5 cm below lake floor, their concentrations showed a decreasing or fixed trend with depth. This suggests that these carotenoids have been degraded in sediments depending on their stabilities. Among the diatoxanthin, lutein and zeaxanthin of which the stability is similar, the relative abundance of lutein (chlorophytes) has increased since *circa* 1970, and, conversely, the relative abundance of diatoxanthin (diatoms) has decreased. Diatoms are likely a staple food for the shellfish *Corbicula japonica* in Lake Shinji, because they are rich in lipids, which are needed for the growth and survival of *C. japonica*. Hence, the relative decrease in the number of diatoms may have some effect on the decrease in the population of *C. japonica* since the 1970s in the lake.

Keywords: eutrophic oligohaline lake, ecosystem, phytoplankton, carotenoids, sediment

INTRODUCTION

Phytoplankton is situated at the bottom of the food chain. In most estuarine environments including coastal lagoons, phytoplankton is abundant owing to a large supply of nutrients from the catchment area and plentiful solar energy, and consequently, various organisms that feed on phytoplankton live there. Thus, the estuarine environment is the most productive aquatic ecosystem (Nixon, 1988). In recent years, however, there have been increased ecological concerns associated with human activities in those productive and economically environments.

Dead phytoplankton is fed upon by other organisms and decomposed by bacteria during its settling process, and then is deposited at the bottom. Ultimately, the residue after the decomposition of dead phytoplankton is buried in the sediment. Phytoplankton has carotenoids that

are specific to major algal groups (Leavitt, 1993; Jeffrey and Vesk, 1997). The carotenoid concentrations in sediment cores from many aquatic environments, including lakes, estuaries and the ocean, have been used as indicators of productivity and major algal groups (e.g., Griffiths and Edmondson, 1975; Griffiths, 1978; Züllig, 1981; Engstrom *et al.*, 1985; Swain, 1985; Soma *et al.*, 1995; Itoh *et al.*, 2003; Rabalais *et al.*, 2004). However, it is well known that the majority of pigments are degraded in the water column and in the uppermost sediment before being incorporated into the fossil record (Furlong and Carpenter, 1988; Hurley and Armstrong, 1990; Leavitt, 1993; Bianchi *et al.*, 2000; Reuss *et al.*, 2005). Moreover, the degree of preservation of pigments differs among carotenoids and is dependent on their stabilities; hence the composition of residual carotenoids in sediment is, in general, different from that in the water column (Repeta and Gagosian, 1987; Millie *et al.*, 1993; Leavitt and Findlay, 1994; Itoh *et al.*, 2003; Hobbs *et al.*, 2010). Thus, the historical trend of carotenoid concentrations in the sediment cores should be interpreted with care on the basis

*Corresponding author (e-mail: sakatam@u-shizuoka-ken.ac.jp)

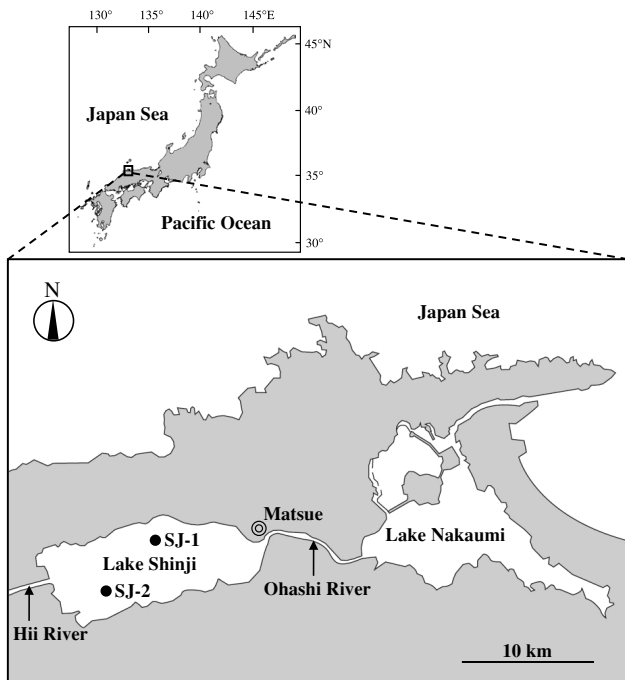


Fig. 1. Locations of sampling sites.

of the sediment conditions (e.g., redox conditions and pH in pore water; Hobbs *et al.*, 2010) at the study site.

Lake Shinji, which is located along the Japan Sea coast of western Japan (Fig. 1), has an area of 79.2 km², a volume of 3.66×10^8 m³ and a mean depth of 4.5 m (Yamamuro, 2000). Lake Shinji is a eutrophic oligohaline lake (Yamamuro and Kanai, 2005), and the value of the lake as a fishing ground has been generally recognized (Nakamura, 2000). For example, the lake has the largest catch of the shellfish *Corbicula japonica* in Japan. *C. japonica* feeds on phytoplankton and, conversely, is fed on by gobies and birds. Thus, *C. japonica* plays an important role as a secondary producer in the ecosystem of Lake Shinji. In the lake, however, the catches of *C. japonica* as well as of some fishes feeding on it have decreased since the 1970s (Shimane Agricultural Administration Office, 1953–2008). It is clear that the reduction in the catch of *C. japonica* is caused by the reduction in the population of this species (Nakamura, 1993). As a reason behind this reduction, overfishing has been suggested (Nakamura, 1993), but the catch of *C. japonica* continued to decrease even after the regulation of fishing in 1975. Moreover, the ecology of *C. japonica*, such as temperature, salinity preference, and tolerance to low oxygen concentration and sulfide, has been intensively investigated (Nakamura, 2000). However, the cause of the reduction in its population remains to be clarified. It appears that a healthy ecosystem has not been maintained in Lake Shinji for unknown reasons. The knowledge of

historical changes in phytoplankton community structures in the lake may be beneficial to elucidate the alteration of the ecosystem.

In this study, the historical trend of the concentrations of carotenoids originating from phytoplankton in sediment cores collected at two sites in Lake Shinji was investigated to clarify the changes in phytoplankton community structures in the lake over the last 100 years. The factors that control the observed historical changes in the carotenoid concentrations were also examined with the help of the historical changes in the concentrations of total organic carbon (TOC), total nitrogen (TN), total sulfur (TS) and chlorophyll *a* and its derivatives in the sediment cores.

MATERIALS AND METHODS

Sediment samples

The sediment cores were collected by a diver by inserting an acrylic plastic tube into the sediment at two sites in the lake (Fig. 1) in August 2008: Site SJ-1 (35°27' N, 132°57' E; water depth, ~4.5 m) and Site SJ-2 (35°25' N, 132°54' E; water depth, ~4.5 m). According to Kanai *et al.* (1997), the sedimentary strata at those sites are fairly undisturbed. The cores (SJ-1: 48 cm; SJ-2: 49 cm) were cut horizontally into 1 cm sections. The samples for carotenoid analysis were kept frozen at –80°C until analysis, whereas the samples for analyses of TOC, TN and TS were dried at 80°C in an oven and then ground.

Age determination of sediment cores

The ages of the sediment cores at SJ-1 and SJ-2 were obtained from the sedimentation rate, sediment water content and densities of the solid and water phases. The sedimentation rates at the study sites were assumed to correspond to those measured by Kanai *et al.* (1997) by the ²¹⁰Pb method at sites adjacent (<1 km) to our study sites (SJ-1: 0.13 g cm⁻² yr⁻¹; SJ-2: 0.20 g cm⁻² yr⁻¹), and were also extrapolated to the recent layers after 1994 when they collected the cores. This validity will be described in the Discussion section. The water content was measured from the weight loss of a wet sample upon drying at 80°C and normalized to dry-sample weight. The densities of the solid and water phases were assumed to be 2.5 and 1.0 g cm⁻³, respectively, which are used to calculate the ages of the cores from the dry mass sedimentation rates (g cm⁻² yr⁻¹).

Chemical analyses

For the determination of the concentrations of carotenoids and chlorophyll *a* and its derivatives, i.e., pheophytin *a* and pyropheophytin *a*, in the sediments, the thawed wet samples were dehydrated by centrifugation at 3,000 rpm for 5 min and then subjected to extraction

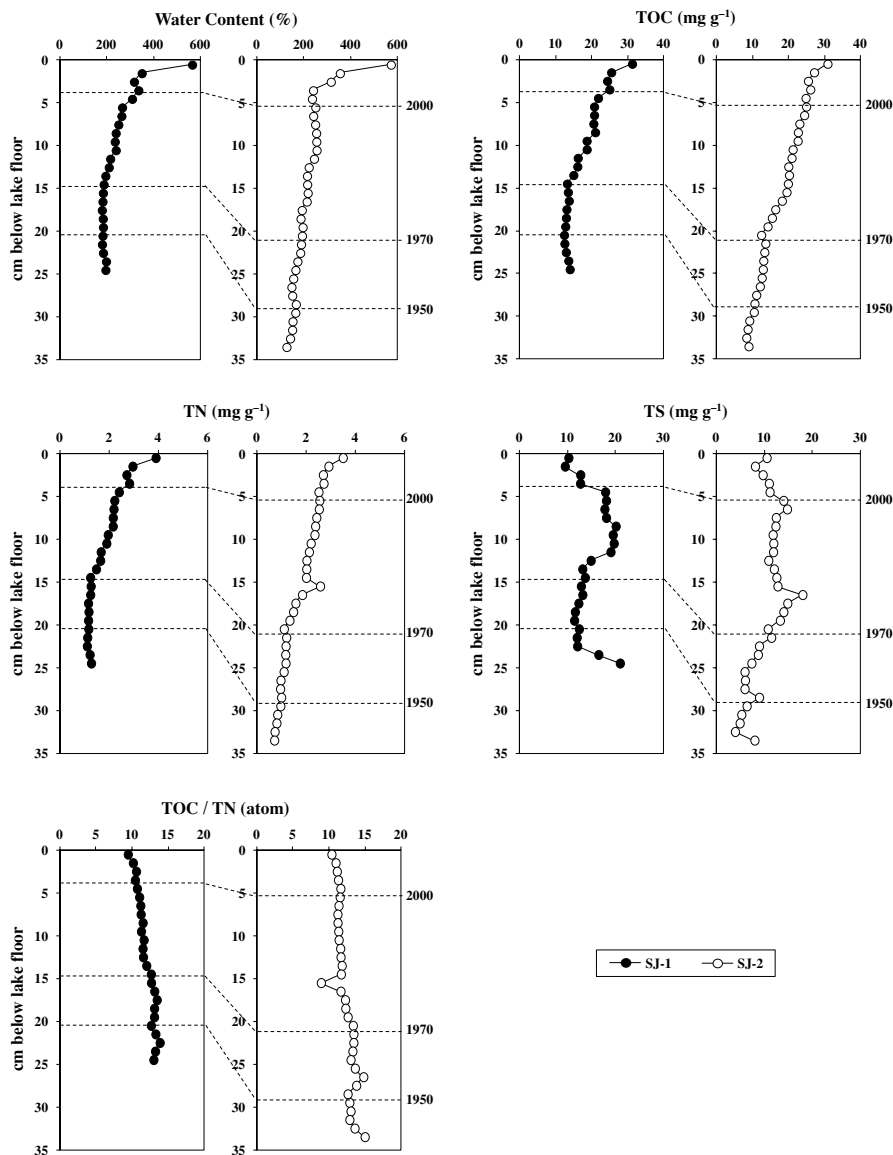


Fig. 2. Vertical profiles of water content (%), concentrations (mg g^{-1} , dry basis) of total organic carbon (TOC), total nitrogen (TN) and total sulfur (TS) and TOC/TN atomic ratio in sediment cores. The depth in the cores corresponding to 1950, 1970 and 2000, which were estimated on the basis of ^{210}Pb dating by Kanai *et al.* (1997), is indicated in the figures (also shown in Figs. 3 and 4).

three times using 3 ml of acetone as the extracting solvent under ultrasonic irradiation at 0°C for 15 min. An internal standard, mesoporphyrin IX dimethyl ester, was added to the extract. Carotenoids and chlorophyll *a* and its derivatives in this solution were analyzed by high-performance liquid chromatography (HPLC) according to Soma *et al.* (1996) and Tani *et al.* (2002). The HPLC system consists of two programmable gradient pumps (Shimadzu, LC-1-AD) and a diode array detector (Shimadzu, SPD-M10AVP). A reversed-phase column (Wako Pure Chemical Industries, Ltd., Japan, Navi C30-

5) was used for the separation of carotenoids and chlorophyll *a* and its derivatives, and the absorption spectrum at 470 nm wavelength for carotenoids and at 660 nm for chlorophyll *a* and its derivatives was monitored for the determination. Their identifications were based on the HPLC retention time and the absorption spectrum of standard samples (DHI) or taken from literature data (Jeffrey *et al.*, 1997) when standards were not available.

The concentrations of TOC and TN in the sediments were measured by using a CN analyzer (Sumika Chemical Analysis Service, SUMIGRAPH NC-1000) for dry

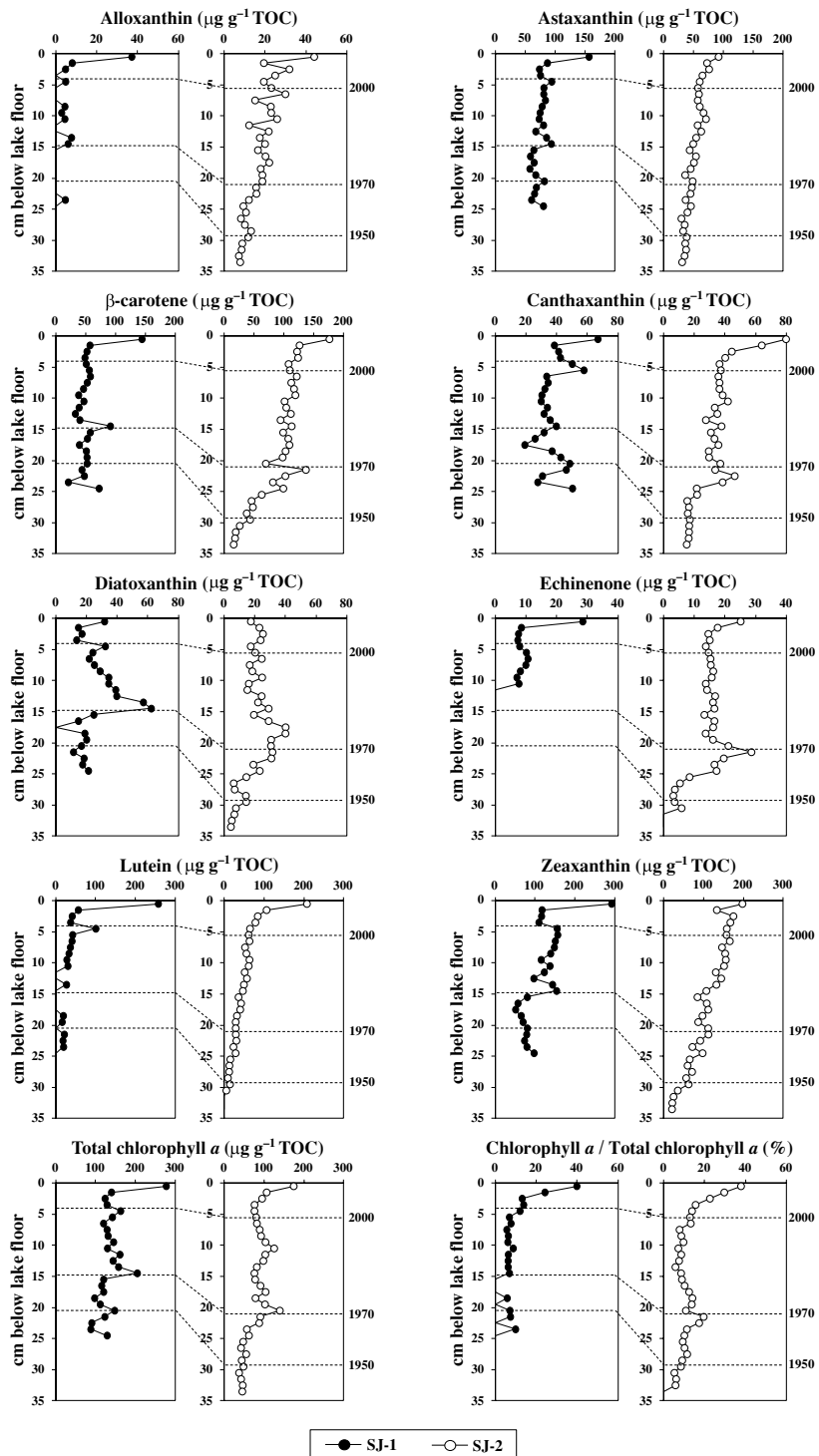


Fig. 3. Vertical profiles of concentrations of carotenoids and total chlorophyll *a* (=chlorophyll *a* + pheophytin *a* + pyropheophytin *a*) in sediment cores. The figure also includes the percentage of the primary chlorophyll *a* concentration for the total chlorophyll *a* concentration. Data was not plotted for concentrations of less than the quantification limit ($1 \mu\text{g g}^{-1} \text{TOC}$).

samples treated with 1 M HCl to remove carbonates according to Itoh *et al.* (2003). For the determination of TS concentrations in the sediments, the powdered samples were digested using HF–HNO₃–HClO₄. After evaporation to dryness, the residue was dissolved in 0.2 M HNO₃. The sulfur concentration in this solution was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, VARIAN, 730-ES). The concentrations of TOC, TN and TS in the sediments were normalized to dry-sample weight, whereas the concentrations of carotenoids and chlorophyll *a* and its derivatives were expressed by mass normalized to TOC. The quantification limits of carotenoids and chlorophyll *a* and its derivatives were approximately 1 μg g⁻¹ TOC.

RESULTS

The vertical profiles of the water content (% dry basis) and the TOC, TN and TS concentrations (mg g⁻¹, dry basis) in the sediment cores are shown in Fig. 2, along with that of the TOC/TN atomic ratio. The depth in the cores corresponding to 1950, 1970 and 2000, which was estimated on the basis of ²¹⁰Pb dating by Kanai *et al.* (1997), is indicated in the figures (also shown in Figs. 3 and 4; Details are discussed in the discussion section). The water content of the sediment cores at both sites decreased rapidly with depth within the upper 5 cm. There were minimal differences in the TOC and TN concentrations in those dates between SJ-1 and SJ-2. Moreover, their concentrations in the cores have been increasing since *circa* 1970. On the other hand, the TS concentration in the sediment cores at both sites was higher during the 1980s–1990s, and then decreased toward the present. The sulfate concentration in the sediments was only 1–4% of the TS concentration even when the sulfate concentration of pore water was assumed to be equivalent to that of lake water (approximately 3.5‰ of average salinity; Kanai *et al.*, 1997). Thus, sulfur in the sediments is regarded to be primarily in the form of sulfides. The TOC/TN atomic ratio (=8.8–15) in the sediment cores has been continuously decreasing toward the top of the cores, and was much closer to the ratio of marine phytoplankton (C/N = 6.6; Redfield *et al.*, 1963) than those of terrestrial plants (C/N > 15; Kendall *et al.*, 2001). This supports the idea that organic matter in the sediments is primarily derived from the sedimentation of dead phytoplankton.

Figure 3 indicates the vertical profiles of the concentrations (μg g⁻¹ TOC) of carotenoids and total chlorophyll *a* (=chlorophyll *a* + pheophytin *a* + pyropheophytin *a*) in the sediment cores. The figure also includes the percentage of the primary chlorophyll *a* concentration relative to the total chlorophyll *a* concentration. Eight types of carotenoids, i.e., alloxanthin, astaxanthin, β-carotene, canthaxanthin, diatoxanthin, echinenone, lutein and ze-

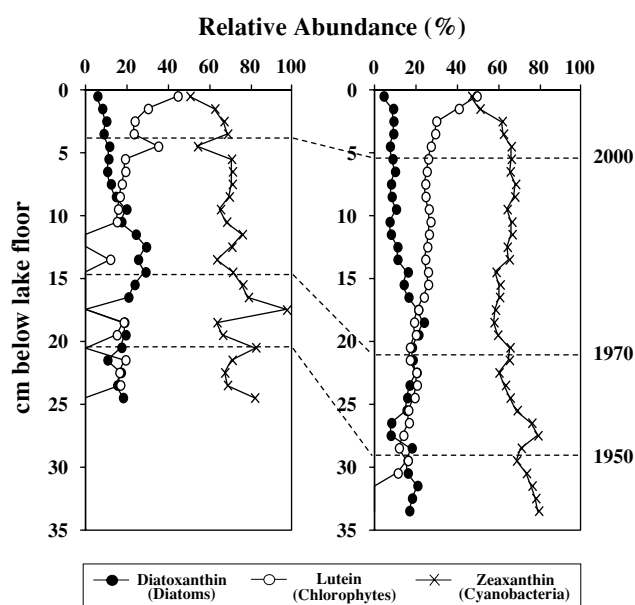


Fig. 4. Vertical profiles of relative abundances of diatoxanthin, lutein and zeaxanthin in sediment cores. Data was not plotted for concentrations of less than the quantification limit (1 μg g⁻¹ TOC).

axanthin, were detected in the sediments. The concentrations of carotenoids, other than diatoxanthin, and the total chlorophyll *a* concentration of sediment cores at both sites decreased rapidly with depth within the upper 5 cm. Moreover, the percentage of the primary chlorophyll *a* concentration relative to the total chlorophyll *a* concentration reduced markedly within this zone, suggesting that labile chlorophyll *a* is transformed diagenetically to more stable pheophytin *a* and pyropheophytin *a* in surface sediments. In the cores lower than 5 cm below lake floor, the carotenoid and total chlorophyll *a* concentrations showed a decreasing or fixed trend with depth.

DISCUSSION

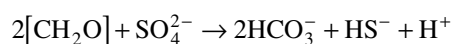
Chronology of sediment cores

The ages of the sediment cores were estimated on the basis of ²¹⁰Pb dating by Kanai *et al.* (1997) at sites adjacent (<1 km) to our study sites. There were no marked differences (approximately <20%) in the sedimentation rates between two sites, being 2–3 km from each other on the basis of the measurement at 15 sites by Kanai *et al.* (1997). Kanai *et al.* (1997) also measured the sedimentation rate using the ¹³⁷Cs dating methods for the same cores and found that the values obtained by both methods are similar ($r^2 = 0.92$). Except for the surface sediment layers, the vertical profiles of the water content in our cores (Fig. 2) were similar to those in the cores mea-

sured by Kanai *et al.* (1997) at sites adjacent to our study sites. The water content in the surface layers depends strongly on the degree of compaction, which is due to the difference in the sampling methods between the two sets of cores. Moreover, the dates (i.e., *circa* 1970) of the start of the increase in the TOC and TN concentrations in our sediment cores (Fig. 2) were similar to those in the ^{210}Pb -dated sediment cores reported by Yamamuro and Kanai (2005). All the above-mentioned facts tend to support the conclusion that the chronology of the cores obtained at sites adjacent to our study sites is useful (Kusunoki *et al.*, 2012).

Analysis of historical trend of TOC and TN concentrations in sediment cores

The following two factors are considered as possible reasons why the TOC and TN concentrations in the cores have increased: (1) increase in the primary production in the lake and (2) decomposition of organic matter in diagenetic processes within the sediment. Identifying which factor primarily controls the observed historical changes in the TOC and TN concentrations of sediment cores is important for a better understanding of the historical change in carotenoid concentrations. The concentration of TS, which is primarily composed of sulfides, has tended toward the opposite change (Fig. 2). These sulfides were not those produced in the bottom water and then deposited to the sediments, because bottom water is oxygenated even in summer owing to the shallowness of the lake (Sampei *et al.*, 1994). The presence of sulfides in the top 1 cm of the layer (Fig. 2) suggests anoxia near the sediment-water interface. If the recent increase in the TOC concentration is entirely owing to the decomposition of organic matter by sulfate reduction in the sediments, a stoichiometric relation of $\text{TOC}/\text{TS} = 2$ is expected to be realized between the amount of TOC decomposed and the amount of TS produced in the sediment column according to this equation



where $[\text{CH}_2\text{O}]$ denotes organic matter. Under the assumption of a steady state, those amounts were estimated from the vertical profiles of TOC and TS after 1970 in the sediment cores (Fig. 2), using

$$\text{TOC} \left(\text{mmol cm}^{-2} \right) = \sum_{i=1}^n (\text{TOC}_1 - \text{TOC}_i) l_i \rho_i,$$

$$\text{TS} \left(\text{mmol cm}^{-2} \right) = \sum_{i=1}^n \text{TS}_i l_i \rho_i,$$

where TOC_i and TS_i denote the TOC and TS concentrations (mmol g^{-1}) in layer i , and TOC_1 is the TOC concentration in the top 1 cm of the layer. Also, l_i and ρ_i are the thickness (i.e., 1 cm) and dry density (g cm^{-3}) of layer i . Layer n corresponds to 1970. The calculated TOC/TS ratio was 2.0 at SJ-1 and 2.4 at SJ-2. Thus, these values were significantly close to the stoichiometric relation of $\text{TOC}/\text{TS} = 2$, which is expected for the decomposition of organic matter by sulfate reduction in the sediments. This suggests that the historical changes in the TOC concentration in the upper layers of the sediment cores are attributable to the decomposition of organic matter rather than the increase in the primary production.

As can be seen in Fig. 2, the TOC/TN ratio (=8.8–15) of the sediment cores has decreased toward the present, which may be explained by the fact that organic nitrogen compounds (e.g., protein, peptides and amino acids) are easily decomposed compared with bulk organic compounds in diagenetic processes within sediments (Rosenfield, 1981). Actually, Sampei *et al.* (1994) observed a lower C/N ratio (=4.9–6.7) in the sediment trap material (i.e., fresh organic matter originating from various algae) collected from the lake for one or two months from summer to winter. It has been reported that the annual average concentrations of chemical oxygen demand (COD) and chlorophyll a in Lake Shinji did not change significantly in 1984–2009 (COD, $4.6 \pm 0.4 \text{ mg L}^{-1}$; chlorophyll a , $17 \pm 4 \mu\text{g L}^{-1}$), on the basis of monthly monitoring at 7 sites in the lake (Shimane Prefecture, 1985–2010). This also supports the idea that the increase in the TOC and TN concentrations in the cores since *circa* 1970 is not due to an increase in the primary production in the lake.

Analysis of historical trend in algal composition inferred from carotenoid concentrations in sediment cores

It has been clarified that among the eight types of carotenoids detected in the sediments in Lake Shinji, alloxanthin, canthaxanthin, diatoxanthin, echinenone and zeaxanthin originate specifically from the following major algal groups (Leavitt, 1993; Soma *et al.*, 2007): alloxanthin—cryptophytes; canthaxanthin—cyanobacteria; diatoxanthin—diatoms and dinoflagellates; echinenone—cyanobacteria; zeaxanthin—cyanobacteria. In Lake Shinji, a red tide of dinoflagellates is occasionally observed when the water salinity increases (Akiyama, 1996), but chlorophytes, cyanobacteria and diatoms are usually the dominant algal groups (Nakamura, 1998). Thus, diatoxanthin in the sediments is considered to originate primarily from diatoms, but not from dinoflagellates.

On the other hand, it is known that lutein and astaxanthin are specific to chlorophytes, and β -carotene is found in many major algal groups (Leavitt, 1993; Soma

et al., 2007). However, those carotenoids may not necessarily be specific to the respective algal groups in the lake, because they also exist in the higher terrestrial plants growing around the lake. As described in the Results section, however, the TOC/TN ratio in the sediments (Fig. 2) was much closer to the ratio of marine phytoplankton than those of terrestrial plants. Moreover, it is likely that the bulk of carotenoids contained in the detritus of the higher terrestrial plants is decomposed by various factors, including wetting and drying by the atmosphere, a wide temperature variation, oxidization, and feeding by creatures, before burial into the sediment (Sanger, 1988). Hence, lutein, astaxanthin and β -carotene in the sediments are considered to originate primarily from phytoplankton in the lake. Table 1 summarizes the correspondence between the carotenoids detected in the sediments from Lake Shinji and the major algal groups from which those carotenoids originate.

As described in the preceding section, it is likely that the historical changes in the TOC and TN concentrations of sediment cores since *circa* 1970 have been attributable to the decomposition of organic matter by sulfate reduction, confirming the importance of diagenetic processes in Lake Shinji sediments. It was found that labile chlorophyll *a* is transformed diagenetically to more stable pheophytin *a* and pyropheophytin *a* within the upper 5 cm of the cores (Fig. 3). Similarly, the concentrations of carotenoids, other than diatoxanthin, in the cores decreased rapidly within this zone, and in the cores lower than 5 cm below lake floor, their concentrations showed a decreasing or fixed trend with depth. This suggests that these carotenoids have been degraded in sediments depending on their stability (Repeta and Gagosian, 1987; Millie *et al.*, 1993; Leavitt and Findlay, 1994; Itoh *et al.*, 2003; Hobbs *et al.*, 2010).

It is known that carotenoids, such as diatoxanthin, lutein and zeaxanthin, without the 5,6-epoxide structure, are fairly well preserved in sediments (Itoh *et al.*, 2003; Hobbs *et al.*, 2010). This allowed us to presume that the composition of these carotenoids essentially reflects the composition of the major algal groups from which they originate, i.e., chlorophytes for lutein, cyanobacteria for zeaxanthin, and diatoms for diatoxanthin, as the chemical structures of the three carotenoids are similar. Its effectiveness may be supported by the following reports. Itoh *et al.* (2003) observed a decrease in zeaxanthin level relative to lutein and diatoxanthin levels since *circa* 1960 in sediment cores from Lake Hamana, Japan. In this lake, the average salinity increased between 1950 and 1970 owing to the construction of training walls introducing direct tidal currents into the lake, and to the expansion and deepening of the shipping channel in the shallow southern part by dredging (Mazda, 1983). Thus, it is likely that the number of cyanobacteria (zeaxanthin) has de-

Table 1. Correspondence between carotenoids detected in sediments from Lake Shinji and major algal groups from which those carotenoids originate

Carotenoids	Major algal groups
Alloxanthin	Cryptophytes
Astaxanthin	Chlorophytes
β -carotene	Unspecified
Canthaxanthin	Cyanobacteria
Diatoxanthin	Diatoms
Echinenone	Cyanobacteria
Lutein	Chlorophytes
Zeaxanthin	Cyanobacteria

clined since *circa* 1960 in response to the increase in salinity. Conversely, an increase in the number of cyanobacteria (zeaxanthin) relative to those of chlorophytes (lutein) and diatoms (diatoxanthin) caused by a decrease in salinity was also observed for a sediment core from Lake Kasumigaura, Japan (Soma *et al.*, 1995).

Chlorophytes, cyanobacteria and diatoms are usually the dominant algal groups in Lake Shinji (Nakamura, 1998). Hence, we analyzed the historical changes in their composition on the basis of the vertical profiles of the relative abundances of diatoxanthin, lutein and zeaxanthin in the sediment cores. The vertical profiles of the relative abundances of diatoxanthin, lutein and zeaxanthin in the sediment cores from Lake Shinji are indicated in Fig. 4. The relative abundances of diatoxanthin and zeaxanthin at both sites have decreased since *circa* 1970 and 2000, respectively. Conversely, the relative abundance of lutein has increased since *circa* 1970. This suggests an increase in the number of chlorophytes (lutein) relative to those of cyanobacteria (zeaxanthin) and diatoms (diatoxanthin) in recent Lake Shinji. The annual average concentrations (\pm SD) of chemical constituents in the entire lake in 1984–2009 were 2100 ± 700 mg L⁻¹ for Cl⁻, 4.6 ± 0.4 mg L⁻¹ for COD, 17 ± 4 μ g L⁻¹ for chlorophyll *a*, 500 ± 50 μ g L⁻¹ for total N, 45 ± 8 μ g L⁻¹ for total P, and 4.4 ± 0.7 mg L⁻¹ for dissolved Si (Shimane Prefecture, 1985–2010). Thus, their levels did not change significantly in 1984–2009. Hence, the historical changes in algal composition are not caused by the changes in water quality, such as salinity change, progress in eutrophication and silica deficiency (Humborg *et al.*, 1997).

CONCLUSIONS

The results presented here suggested a relative increase

in the number of chlorophytes and a relative decrease in the number of diatoms since *circa* 1970 in Lake Shinji on the basis of the relative abundances of the corresponding carotenoids in sediment cores. The catch of *C. japonica* in the lake has decreased since the 1970s (Shimane Agricultural Administration Office, 1953–2008). *C. japonica* feeds through filtration by holding its inhalant siphon above sediment surface. Hence, changes in food sources directly affect the growth and survival rates of *C. japonica*. Diatoms and chlorophytes are rich in neutral lipids, accounting for nearly 70% of their total lipids (Borowitzka, 1988), but only a small percentage of chlorophytes exhibit a high total lipid content (Chen, 2012). Thus, diatoms are a staple food for many organisms, including zooplankton, shellfish and shrimp larvae, owing to their high lipid content (Chen, 2012). In particular, long-chain polyunsaturated fatty acids, such as eicosapentaenoic acid (EPA, C20:5 *n* – 3) and docosahexaenoic acid (DHA, C22:6 *n* – 3), are needed for good growth and survival because of a limited capacity for synthesizing their fatty acids (Beninger and Stephan, 1985; Wenne and Polak, 1989; Hayashi and Kishimura, 1991; Pazos *et al.*, 1996; Galap *et al.*, 1999). These suggest that the relative decrease in the number of diatoms in Lake Shinji may have some effect on the decrease in the population of *C. japonica* since the 1970s. The feeding habit of *C. japonica* in Lake Shinji remains to be clarified. It is likely that feeding experiments using cultured algae from the lake (e.g., Yamaguchi *et al.*, 2008) are useful to obtain knowledge on the nutrition and growth of *C. japonica*. This will enable us to clarify the relationship of the observed changes in the algal composition to the reduction in the catch of *C. japonica* in Lake Shinji.

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REFERENCES

- Akiyama, Y. (1996) *Algae in Lakes Shinji and Nakaumi*. Shimane University (in Japanese).
- Beninger, P. G. and Stephan, G. (1985) Seasonal variations in the fatty acids of the triacylglycerols and phospholipids of two populations of adult clam (*Tapes decussates* L. and *T. philippinarum*) reared in a common habitat. *Comp. Biochem. Physiol.* **B81**, 591–601.
- Bianchi, T. S., Johansson, B. and Elmgren, R. (2000) Break-down of phytoplankton pigments in Baltic sediments: effects of anoxia and loss of deposit-feeding macrofauna. *J. Exp. Mar. Biol. Ecol.* **251**, 161–183.
- Borowitzka, M. A. (1988) Fats, oil and hydrocarbons. *Micro-Algal Biotechnology* (Borowitzka, M. A. and Borowitzka, L. A., eds.), 257–287, Press Syndicate of the University of Cambridge, Cambridge.
- Chen, Y.-C. (2012) The biomass and total lipid content and composition of twelve species of marine diatoms cultured under various environments. *Food Chem.* **131**, 211–219.
- Engstrom, D. R., Swain, E. B. and Kingston, J. C. (1985) A palaeolimnological record of human disturbance from Harvey’s lake, Vermont: geochemistry, pigments and diatoms. *Freshwater Biol.* **15**, 261–288.
- Furlong, E. T. and Carpenter, R. (1988) Pigment preservation and remineralization in oxic coastal marine sediments. *Geochim. Cosmochim. Acta* **52**, 87–99.
- Galap, C., Netchitailo, P., Leboulenger, F. and Grillot, J. (1999) Variations of fatty acid contents in selected tissues of the female dog cockle (*Glycymeris glycymeris* L., Mollusca, Bivalvia) during the annual cycle. *Comp. Biochem. Physiol.* **A122**, 241–254.
- Griffiths, M. (1978) Specific blue-green algal carotenoids in sediments of Estwaite Water. *Limnol. Oceanogr.* **23**, 777–784.
- Griffiths, M. and Edmondson, W. T. (1975) Burial of oscillaxanthin in the sediment of Lake Washington. *Limnol. Oceanogr.* **20**, 945–952.
- Hayashi, K. and Kishimura, H. (1991) Seasonal changes in the contents of eicosapentaenoic acid-containing triacylglycerides in hepatopancreas of scallop. *Nippon Suisan Gakkaishi* **57**, 1397–1401.
- Hobbs, W. O., Lalonde, S. V., Vinebrooke, R. D., Konhauser, K. O., Weidman, R. P. Graham, M. D. and Wolfe, A. P. (2010) Algal-silica cycling and pigment diagenesis in recent alpine lake sediments: mechanisms and paleoecological implications. *J. Paleolimnol.* **44**, 613–628.
- Humborg, C., Ittekkot, V., Cociasu, A. and Bodungen, B. v. (1997) Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. *Nature* **386**, 385–388.
- Hurley, J. P. and Armstrong, D. E. (1990) Fluxes and transformations of aquatic pigments in Lake Mendota, Wisconsin. *Limnol. Oceanogr.* **35**, 384–398.
- Itoh, N., Tani, Y., Nagatani, T. and Soma, M. (2003) Phototrophic activity and redox condition in Lake Hamana, Japan, indicated by sedimentary photosynthetic pigments and molybdenum over the last ~250 years. *J. Paleolimnol.* **29**, 403–422.
- Jeffrey, S. W. and Vesk, M. (1997) Introduction to marine phytoplankton and their pigment signatures. *Phytoplankton Pigments in Oceanography* (Jeffrey, S. W., Mantoura, R. F. C. and Wright, S. W., eds.), 37–84, UNESCO, Paris.
- Jeffrey, S. W., Mantoura, R. F. C. and Bjørnland, T. (1997) Data for the identification of 47 key phytoplankton pigments. *Phytoplankton Pigments in Oceanography* (Jeffrey, S. W., Mantoura, R. F. C. and Wright, S. W., eds.), 449–559, UNESCO, Paris.
- Kanai, Y., Inouchi, Y., Yamamuro, M. and Tokuoka, T. (1997)

- Sedimentation rate and environment in Lake Shinji, Shimane Prefecture. *Chikyukagaku (Geochemistry)* **32**, 71–85 (in Japanese).
- Kendall, C., Silva, S. R. and Kelly, V. J. (2001) Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. *Hydrol. Process.* **15**, 1301–1346.
- Kusunoki, K., Sakata, M., Tani, Y., Seike, Y. and Ayukawa, K. (2012) Evaluating the contribution of long-range transport of heavy metals from the Asian continent to their concentrations in sediment cores from Lake Shinji, western Japan. *Water Air Soil Pollut.* **223**, 1151–1160.
- Leavitt, P. R. (1993) A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. *J. Paleolimnol.* **9**, 109–127.
- Leavitt, P. R. and Findlay, D. L. (1994) Comparison of fossil pigments with 20 years of phytoplankton data from eutrophic lake 227, experimental lakes area, Ontario. *Can. J. Fish. Aquat. Sci.* **51**, 2286–2299.
- Mazda, Y. (1983) Marine environment of Lake Hamana—Temporal change in tides affected by the change in shape of the inlet channel. *Bull. Coast Oceanogr.* **20**, 178–188 (in Japanese).
- Millie, D. F., Paerl, H. W. and Hurley, J. P. (1993) Microalgal pigment assessments using high-performance liquid chromatography: a synopsis of organismal and ecological applications. *Can. J. Fish. Aquat. Sci.* **50**, 2513–2527.
- Nakamura, M. (1993) Creatures and fishery in brackish lakes. *Urban Kubota* **32**, 14–23 (in Japanese).
- Nakamura, M. (1998) Physico-ecological study on interrelationships between *Corbicula japonica* Prime and environment in Lake Shinji, Japan. *Report of Shimane Prefectural Fisheries Experimental Station No. 9*, 1–192 (in Japanese).
- Nakamura, M. (2000) *Corbicula Fisheries in Japan*. Tatarashobo, Yonago, Tottori (in Japanese).
- Nixon, S. (1988) Physical energy inputs and the comparative ecology of lake and marine ecosystems. *Limnol. Oceanogr.* **33**, 1005–1025.
- Pazos, A. J., Ruiz, C., Garcia-Martin, O., Abad, M. and Sanchez, J. L. (1996) Seasonal variations of the lipid content and fatty acid composition of *Grassostrea gigas* cultured in El Grove, Galicia, N.W. Spain. *Comp. Biochem. Physiol.* **B114**, 171–179.
- Rabalais, N. N., Atilla, N., Normandeau, C. and Turner, R. E. (2004) Ecosystem history of Mississippi River-influenced continental shelf revealed through preserved phytoplankton pigments. *Mar. Pollut. Bull.* **49**, 537–547.
- Redfield, A. C., Ketchum, B. H. and Richards, F. A. (1963) The influence of organisms on the composition of seawater. *The Sea, Vol. 2* (Hill, M. N., ed.), 26–77, Wiley-Interscience.
- Repeta, D. J. and Gagosian, R. B. (1987) Carotenoid diagenesis in recent marine sediments—I. The Peru continental shelf (15°S, 75°W). *Geochim. Cosmochim. Acta* **51**, 1001–1009.
- Reuss, N., Conley, D. J. and Bianchi, T. S. (2005) Preservation conditions and the use of sediment pigments as a tool for recent ecological reconstruction in four Northern European estuaries. *Mar. Chem.* **95**, 283–302.
- Rosenfield, J. K. (1981) Nitrogen diagenesis in Long Island Sound sediments. *Am. J. Sci.* **281**, 436–462.
- Sampei, Y., Yomura, H., Otsuka, M., Yoshida, K. and Suzuki, N. (1994) Decomposition of organic matter and the organic carbon content of sediments in Lake Shinji, southwest Japan. *Earth Sci.* **48**, 317–332.
- Sanger, J. E. (1988) Fossil pigments in paleoecology and paleolimnology. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **62**, 343–359.
- Shimane Agricultural Administration Office (1953–2008) *Statistical Report on Agriculture, Forestry and Fisheries in Shimane Prefecture for 1952–2006* (in Japanese).
- Shimane Prefecture (1985–2010) *Monitoring Results of Water Quality of Public Water Areas and Groundwater Quality in 1984–2009* (in Japanese).
- Soma, Y., Tanaka, A., Soma, M. and Kawai, T. (1995) Composition and vertical profiles of photosynthetic pigments in the sediment of Lake Kasumigaura. *Geochem. J.* **29**, 107–113.
- Soma, Y., Tanaka, A., Soma, M. and Kawai, T. (1996) Photosynthetic pigments and perylene in the sediments of southern basin of Lake Baikal. *Org. Geochem.* **24**, 553–561.
- Soma, Y., Tani, Y., Soma, M., Mitake, H., Kurihara, R., Hashimoto, S., Watanabe, T. and Nakamura, T. (2007) Sedimentary steryl chlorine esters (SCEs) and other photosynthetic pigments as indicators of paleolimnological change over the last 28,000 years from the Buguldeika Saddle of Lake Baikal. *J. Paleolimnol.* **37**, 163–175.
- Swain, J. E. (1985) Measurement and interpretation of sedimentary pigments. *Freshwater Biol.* **15**, 53–75.
- Tani, Y., Kurihara, K., Nara, F., Itoh, N., Soma, M., Soma, Y., Tanaka, A., Yoneda, M., Hirota, M. and Shibata, Y. (2002) Temporal changes in the phytoplankton community of the southern basin of Lake Baikal over the last 24,000 years recorded by photosynthetic pigments in a sediment core. *Org. Geochem.* **33**, 1621–1634.
- Wenne, R. and Polak, L. (1989) Lipid composition and storage in the tissues of the bivalve, *Macoma balthica*. *Biochem. Sys. Ecol.* **17**, 583–587.
- Yamaguchi, K., Ko-uchi, A. and Fujioka, K. (2008) Experimental studies on relationship between feeding materials and increase of soft parts of *Corbicula japonica*. *Laguna* **15**, 49–55 (in Japanese).
- Yamamuro, M. (2000) Chemical tracers of sediment organic matter origins in two coastal lagoons. *J. Mar. Sys.* **26**, 127–134.
- Yamamuro, M. and Kanai, Y. (2005) A 200-year record of natural and anthropogenic changes in water quality from coastal lagoon sediments of Lake Shinji, Japan. *Chem. Geol.* **218**, 51–61.
- Züllig, H. (1981) On the use of carotenoid stratigraphy in lake sediments for detecting past developments of phytoplankton. *Limnol. Oceanogr.* **26**, 970–976.