Composition and vertical profiles of photosynthetic pigments in the sediment of Lake Kasumigaura

YUKO SOMA, ATSUSHI TANAKA and MITSUYUKI SOMA

The National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305, Japan

(Received July 7, 1994; Accepted October 11, 1994)

Phytoplankton pigments in the sediment of Lake Kasumigaura were analyzed by HPLC. The depth profiles of echinenone and myxoxanthophyll, which are characteristic carotenoids of blue-green algae, showed an increase after the lock gate (Hitachigawa-suimon) was constructed 30 years ago to prevent seawater coming into the lake. The depth profile of B-carotene suggests that the algal biomass in the lake decreased 30 years ago, being consistent with the period of the construction of the lock gate, and then increased with the increase of freshwater phytoplankton such as blue-green algae.

INTRODUCTION

Pigments in plants, especially chiorophylls and carotenoids have long been investigated, and the development of HPLC technique has facilitated the analysis of pigments, including phytoplankton pigments in sediments (Mantoura and Lleywellin, 1983; Wright and Shearer, 1984; Goodwin and Britton, 1988).

Phytoplankton pigments provide important information on trophic states of lakes. Chlorophyll a has been used as a measure of algal biomass and carotenoids as biomarkers of algal taxa. Therefore, pigments preserved in lake sediments have been considered to contain detailed information about lake history (Watts et al., 1975; Züllig, 1981; Engstrom et al., 1985; Swain, 1985; Sanger, 1988). Profiles of oscillaxanthin and myxoxanthophyll in sediment cores of Esthwaite Water have been shown to indicate the onset of eutrophication of the lake (Griffiths, 1978). Inorganic elements, pigments and fossil diatoms in sediments were used to reconstruct the limnological history of Harvey’s Lake over the last 1000 years (Engstrom et al., 1985).

The pigment composition in sediments does not always reflect the phototrophic populations in the overlying water column, due to degradation of pigments. Demetallation of chlorophyll to pheophytin occurs through biotic and abiotic processes. Pheophorbide has been known as a grazing indicator (Hurley and Armstrong, 1990), and is the dominant degradation product of chlorophyll a found in sediment traps (Carpenter et al., 1986). Fucoxanthin or peridinin which has epoxide group in its xanthophyll structure has been found to be transformed to alcoholic derivatives in sediment traps and in sediments (Repeta and Gagosian 1984; Repeta, 1989). However some xanthophylls degrade at extremely slow rates and can be indicators of changes in the past phytoplankton communities (Griffiths, 1978; Leavitt and Carpenter, 1990; Yacobi et al., 1991).

In this paper we report the vertical profiles of phytoplankton pigments in the sediment of Lake Kasumigaura. It will be shown that the change of algal composition due to the environmental change of the lake in the past 50 years is reflected in the pigment profiles in sediment cores.

METHODS AND MATERIALS

Study site and sampling

Lake Kasumigaura is a shallow eutrophic lake, located in Ibaraki Prefecture, eastern Japan. The area is about 167 km² and the maximum depth is
7 m. Lake Kasumigaura is connected to Pacific Ocean through the Hitachi-Tone river and the main Tone river, and sea water had invaded in the southern part of the lake in dry season until the lock gate (Hitachigawa-suimon) was constructed in 1963. Since 1974, the gate has been closed to preserve freshwater in the lake for irrigation and industrial uses (Dept. Agricul., Ibaraki Univ., 1977).

Sediment core samples (2 core samples, 17 cm long) were collected from the central part, near the point of maximum depth in 1992. Sediment cores were obtained using a gravity corer with clear acryl tube (50 mm diameter).

The core was sliced into 2 to 2.5 cm intervals immediately after sampling and each slice was transferred to glass jars. The sliced samples were stored at -20°C until extraction.

**Pigment analysis**

After the centrifugation of the wet sediment samples at 2000 rpm to remove water, the pigments were extracted twice by sonicating in methanol/acetone (1:1) at 0°C. The combined extract was filtered through a 0.5 μm pore size Millipore FH Column-Guard for HPLC analysis. The liquid chromatograph system consisted of two HPLC programmable gradient elution pumps (GL

![HPLC chromatograms of pigments in the surface sediment of Lake Kasumigaura detected by 440 nm absorbance (a), and fluorescence (b) (excitation: 440 nm, emission: 660 nm).](image-url)
Science Co. model 576), Hewlett Packard 1040 diode array detector and a Hitachi 650-10S fluorescence spectrophotometer. Wakosil 5C18N column was used. The HPLC analysis procedure, identification and quantification of pigments were the same as reported by Soma et al. (1993).

β-Carotene was quantified using 440 nm absorbance, whereas the contribution of overlapping pheophytin a2 (Fig. 1) separately determined by fluorescence detection was subtracted. Pigment concentrations shown in all the figures are the average values of the two core samples. Relative differences in the analytical values between the two core samples were about 17% for lutein and 14% for β-carotene.

RESULTS AND DISCUSSION

Chromatograms of the pigments in the surface sediment are shown in Fig. 1. Major pigments detected in the sediment of Lake Kasumigaura were alloxanthin, diatoxanthin, lutein, zeaxanthin, echinenone and β-carotene. Several small peaks were possibly due to degradation products of fucoxanthin. Chlorophyll derivatives, pheophorbide a1, a2 and pheophytin a1, a2, b were determined by fluorescence spectroscopy.

The relative composition of pigments in the surface sediment were compared with average values in lake water obtained by monitoring over the period from 1989 to 1991 (Soma et al., 1993). The ratio of each pigment to β-carotene is shown in Fig. 2, because β-carotene is considered most stable among these pigments. Amounts of Chlorophyll a and fucoxanthin, the major pigments in water column, are comparatively less in the surface sediment, reflecting their rapid degradation, while alloxanthin, diatoxanthin and zeaxanthin are preserved well in the sediment. Therefore the past biomass of phytoplankton in Lake Kasumigaura is possibly reflected in the vertical distribution of stable carotenoids, whereas chlorophylls and labile carotenoids such as fucoxanthin are not suitable indicators.

The carotenoids in the sediment cores are classified into two groups in depth profiles. The depth profiles of carotenoids in the first group exhibit a minimum at the depth between 4.5 and 9.5 cm. These pigments are diatoxanthin, lutein, zeaxanthin and β-carotene. Contents of sedimentary lutein, diatoxanthin and zeaxanthin are shown in Fig. 3. Diatoxanthin is the major carotenoid in diatoms and Euglenophyceae, and lutein is in green algae, while zeaxanthin is contained in several kinds of algae such as green algae or blue-green algae. Contents of the second group carotenoids show increases above 9.5 cm and are rather constant above 4.5 cm, as shown in Fig. 4. Both echinenone and myxoxanthophyll (in the figure, the sum of myxoxanthophyll and oscillaxanthin is

![Fig. 2. Pigment composition in lake water (average values in 1988–1991) and in the surface sediment, given as ratios of the concentrations of pigments to that of β-carotene.](image-url)
described as myxoxanthophyll+) are characteristic carotenoids of blue-green algae. Acetylenic carotenoid, alloxanthin, is a characteristic carotenoid of Cryptophyceae.

The vertical distribution of echinenone is different from that of lutein or diatoxanthin. Accumulation of echinenone, myxoxanthophyll and alloxanthin apparently started at the period when the accumulation of diatoxanthin and lutein diminished temporally. Dating analysis using $^{210}$Pb of a core sample collected at the central part of the lake revealed that the sedimentation rate was 3.4 mm/year (Tanaka et al., 1991). The lock gate (Hitachigawa-suimon) to the Hitachi-Tone River was constructed 30 years ago. Change of salinity according to the construction of the lock gate presumably caused the alteration of phytoplankton taxa grown in brackish water to those in freshwater, being correlated to the temporal decrease of some pigments such as lutein and diatoxanthin. Diatoms observed between 7 and 13 cm layers by a microscope were broken fragments only, suggesting a low production of diatoms in these years. The accumulation of echinenone or myxoxanthophyll found in the layer above 10 cm is considered to have begun after the construction of the lock gate. Recent accumulation rates of echinenone and myxoxanthophyll decreased a little comparing with those 10 years ago.

Figure 5 shows the annual variation of chloride ion and annual sum of Chlorophyll $a$ in lake water of the central part of Lake Kasumigaura over

---

**Fig. 3.** Depth profiles of lutein, diatoxanthin and zeaxanthin in the sediment.

**Fig. 4.** Depth profiles of alloxanthin, echinenone and myxoxanthophyll in the sediment. Myxoxanthophyll+: sum of myxoxanthophyll and oscillaxanthin.
the period from 1966 to 1991. The values in the figure were cited from Annual Reports of Water Quality (The Ministry of Construction, 1966–1991) and from Environmental Data for Lake Kasumigaura (National Institute for Environmental Studies, 1984, 1988, 1990, 1994). The concentration of chloride ion approached to freshwater level in 1977, 3 years after the lock gate was closed. The concentration of Chlorophyll $a$ increased abruptly in 1979 soon after the concentration of chloride ion dropped to freshwater level, and the concentration of Chlorophyll $a$ showed a maximum between 1979 and 1983. The concentration of chlorophyll was low for some years after the lock gate was closed, although data of Chlorophyll $a$ before 1973 are not available. The increase of Chlorophyll $a$ in water would correlate with the increase of echinenone and myxoxanthophyll in Fig. 4.

Figure 6 shows the depth profiles of β-carotene and Chlorophyll $a$, both of which are contained in all algae. Degradation rate of Chlorophyll $a$ is so fast that the profile shows a maximum at the top layer and a monotonous decrease with the depth. The profile of β-carotene shows a dip in the depth between 7 and 9.5 cm depth, and a maximum was in the depth between 2 and 4.5 cm. The dip closely corresponds to that found in

---

**Fig. 5.** Annual variations of chloride ion and annual sum of Chlorophyll $a$ in lake water of the central part of Lake Kasumigaura. The values in the graph were calculated from Annual Reports of Water Quality (The Ministry of Construction, 1966–1991) and Environmental Data for Lake Kasumigaura (National Institute for Environmental Studies, 1984, 1988, 1990, 1994).

---

**Fig. 6.** Depth profiles of β-carotene and Chlorophyll $a$ in the sediment.
the profile of lutein, zeaxanthin and diatoxanthin. The vertical distributions of carotenoids suggest that the algal biomass in the lake increased with the growing of blue-green algae and Cryptophyceae due to the construction of the lock gate 30 years ago. The concentration of β-carotene in the surface is lower than deeper layers, which may reflect the recent decrease of blue-green algae in summer.

Contribution of green algae, blue-green algae, Cryptomonas and diatoms to Chlorophyll a in each depth was calculated, using the pigments/Chlorophyll a ratios (Soma et al., 1993), which could be regarded as constant for the combination of the carotenoid and the designated algae. Figure 7 shows the amounts of Chlorophyll a calculated from the concentrations of lutein, echinenone, alloxanthin and diatoxanthin, respectively. As these carotenoids are not readily degraded in sediments as Leavitt and Carpenter (1990) and others have observed, the sum of calculated Chlorophyll a in each layer is regarded to reflect the past phytoplankton biomass. The depth profile of β-carotene included in the figure is consistent with the reconstructed profile of Chlorophyll a in Fig. 6.

Acknowledgments—A part of the research was supported by Grant-in-Aid for General Scientific Research from the Ministry of Education, Science and Culture.

REFERENCES


