Short Communication

Isotopic ($\delta^{13}$C) evidence for the autochthonous origin of sediment organic matter in the small and acidic Lake Katanuma, Japan

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Abstract. Sources of sediment organic matter from the strongly acidic Lake Katanuma (0.14 km$^2$; average pH 2.2), in Japan, were determined from an analysis of carbon stable isotope ratios ($\delta^{13}$C). Organic carbon was derived mainly from the benthic diatom, *Pinnularia braunii*, and particulate organic matter (POM) primarily from the phytoplankton, *Chlamydomonas acidophila*, and not from emergent or terrestrial C3 plants such as *Phragmites australis*, *Sasa kurilensis* or *Fagus crenata*. Although the sediment organic matter of most small lakes, especially strongly acidic lakes, is commonly thought to be of allochthonous origin, the sources of sediment organic matter in the small and acidic Lake Katanuma were clearly autochthonous.

Extra keywords: benthic diatom, C:N ratio, particulate organic matter, terrestrial plant.

Introduction

Lake sediment contains a mixture of organic matter from a variety of sources (Meyers and Ishiwatari 1993). Organic matter is usually derived from two main sources: (i) autochthonous components derived from plankton and benthic primary producers; and (ii) allochthonous components from terrestrial plants (Meyers and Ishiwatari 1993).

Lake sediment organic matter is generally derived from autochthonous sources (Meyers and Ishiwatari 1993; Ostrom et al. 1998a, 1998b), yet most studies have been undertaken on large lakes. The few studies of small lakes have shown that sediment organic matter is derived from mainly terrestrial sources (Rau 1980; Gu et al. 1997; Laskov et al. 2002).

There are many acidic volcanic lakes throughout Japan and the Kurile Islands. These low pH lakes are generally disharmonic (Ueno 1958); that is, there is an imbalance between the supply of allochthonous organic matter and its decomposition rate. This is because the strong acidity reduces primary production and organic decomposition (Pedrozo et al. 2001; Laskov et al. 2002). So, allochthonous organic supplies tend to exceed in-lake decomposition rates and, consequently, excess organic matters from outside the lake can accumulate.

Several natural tracers, including carbon stable isotope ratios ($\delta^{13}$C) and organic C:N ratios, have been used to identify the origins of sediment organic matter. The use of these tracers is dependent on there being differences between autochthonous and allochthonous organic matter pools. $\delta^{13}$C values of sediment have often been used to distinguish between autochthonous and allochthonous sources of organic matter in marine sediments (e.g. Rashid and Reinson 1979; Thornton and McManus 1994; Müller and Mathesius 1999), but few studies have used $\delta^{13}$C values to identify the sources of sediment organic matter in lake environments (Gu et al. 1997; Ostrom et al. 1998a, 1998b; Laskov et al. 2002). Phytoplankton in temperate lakes tend to exhibit lower carbon isotope values than do marine phytoplankton; these lower values are similar to those caused by terrestrial plants (France 1995a). Although C:N ratios have been used to
determine the relative contributions of allochthonous and autochthonous sources to organic matter in lake sediments (e.g., Meyers 1994; Ostrom et al. 1998a, 1998b; Laskov et al. 2002), these ratios could change during decomposition (Rice and Tenore 1981; Meyers 1994). Lake sediment organic matter is of complex origin (Meyers and Ishiwatari 1993) and derived from many species of microalgae and aquatic and terrestrial plants. The variety of organic sources, with different stable carbon isotope ratios, would make it difficult to determine the exact origin of lake sediment organic matter using δ13C as a tracer.

Lake Katanuma is a small, acidic volcanic lake in north-eastern Japan (38°14′N, 140°44′E; 0.14 km²; average pH of 2.2). The primary producers in Lake Katanuma are limited to two dominant species of microalgae: (i) the benthic diatom, *Pinnularia braunii*; and (ii) the planktonic green alga, *Chlamydomonas acidophila*. The simplicity of the primary producer community allows a more precise determination of sediment organic material origins using carbon isotope ratios. In the present study the sources of organic matter in Lake Katanuma sediments are determined using carbon stable isotope ratios.

**Materials and methods**

Lake Katanuma has an average pH of 2.2 owing to high sulfate concentrations; the sulfates are products of oxidation of hydrogen sulfide from fumaroles on the lake bottom (Sato 1995). The lake (*Zma* < 20 m) is hydrologically closed [i.e. it has no overland inflow or outflow]. The biotic community of Lake Katanuma includes only a few dominant species, including the midge, *Chironomus acerbiophilus* (Chironomidae), and the two algal taxa, *Pinnularia braunii* (Bacillariophyceae) and *Chlamydomonas acidophila* (Chlorophyceae). There are other heterotrophic and chemotrophic microorganisms, but zooplankton and fish have not been observed (Fujimatsu 1938). Lake Katanuma is dimictic and is primarily covered with ice from January to March (Doi et al. 2001).

Lake sediments for carbon stable isotope analysis were collected monthly from four stations at water depths of 1 m, 2 m, 4 m and 10 m from April to December 2000. Surface sediment samples (0–1 cm depth) were collected with an Ekman–Birge grab. Large terrestrial leaves and woody debris were removed from sediment samples. *Pinnularia braunii* were separated from the sediment using a modification of the method of Coach (1989); the phototactic movement of *P. braunii* were used. For the separation, sediment samples were spread in Petri dishes to a depth of 1 cm, and a 75-µm nylon mesh net was used to separate the sediment samples from the water body. Samples of three common species of emergent or terrestrial plants, *Phragmites australis*, *Sasa kurilensis* and *Fagus crenata*, were collected from the shore of Lake Katanuma. All samples were freeze-dried and preserved at −20°C until stable isotope analyses could be completed.

The C:N ratios of the samples were measured using an elemental analyser (NA2500; CE Instruments, Milan, Italy). Carbon stable isotope ratios were measured using a mass spectrometer (DELTA plus; Finnigan Mat, Bremen, Germany). Isotope ratios are reported in standard delta notation.

$$\delta^{13}C = \frac{\text{R}_{\text{Sample}} - \text{R}_{\text{Standard}}}{\text{R}_{\text{Standard}}} \times 1000 (\%)$$

Peedee Belemnite (PDB) for δ13C was used as a standard. Accuracy of the entire procedure was within ±0.2‰ for δ13C.

Lake water was collected for measuring dissolved inorganic carbon (DIC) at 0 m, 1 m, 2 m, 5 m, 10 m and 15 m depths in April, May, July, September and October 2001, and measured with a total organic carbon (TOC) analyser (TOC 5000; Shimadzu Co., Tokyo, Japan). Accuracy of the entire DIC procedure was within ±5%.

**Results**

Figure 1 compares the δ13C values of lake sediment to values from *P. braunii*, POM (i.e. *C. acidophila*) and terrestrial plants (*P. australis*, *S. kurilensis* and *F. crenata*), which are potential organic carbon sources for Lake Katanuma. The δ13C values of sediments at 1 m, 2 m and 4 m depths were closer to those of *P. braunii*, and the δ13C value of sediment at a depth of 10 m was closer to that of POM in Lake Katanuma. Terrestrial plants (i.e. potential allochthonous sources of organic carbon) had significantly different δ13C values to the Lake Katanuma sediments (*P < 0.001, Scheffe’s F-test*).

Table 1 shows the C:N ratio of sediment, *P. braunii*, POM (i.e. *C. acidophila*) and terrestrial plants (*F. crenata*) from Lake Katanuma. The C:N ratios of sediments were slightly higher than 10 and tended to decrease with lake water depth. The C:N ratios of sediments taken from depths of 1 m and 2 m were significantly higher than those taken from depths 4 m and 10 m (*P < 0.01, Scheffé’s F-test*). The C:N ratios of *P. braunii* and POM were significantly lower than those of the sediments, but the C:N ratio of *F. crenata* was significantly higher than that of sediment (*P < 0.001, Scheffé’s F-test*).

The DIC ranged from 0.48 to 125 mg C L⁻¹ from April to December 2001 (*n = 24*). In stratification periods (April to July), DIC in the upper layers (0–2 m depth) was significantly lower than DIC in lower layers (5–15 m depth); that is, 1.36 ± 0.52 mg C L⁻¹ (mean ± 1 s.d.; *n = 7*) and 81.1 ± 36.6 mg C L⁻¹ (*n = 6*) respectively (*P < 0.01, Student’s *t*-test). During circulation periods (September and October), DIC of upper and lower layers was not significantly different; that is, 7.00 ± 2.52 mg C L⁻¹ (*n = 6*) and 6.41 ± 2.28 mg C L⁻¹ (*n = 5*) respectively (*P > 0.05, Student’s *r*-test).
Discussion

The δ13C values of the sediment organic matter in Lake Katanuma were closer to the values of *P. braunii* at 1 m, 2 m and 4 m depths, and to the values of POM at 10 m depth. These results indicated that the organic carbon of sediments in Lake Katanuma was derived primarily from *P. braunii* at 1 m, 2 m and 4 m depths, and from POM at a depth of 10 m. The POM of Lake Katanuma was considered to be composed mainly of phytoplankton (*C. acidophila*).

As light intensity decreases with water depth, production of the benthic diatom *P. braunii* also declines with water depth in Lake Katanuma. Thus, differences in sources of sediment organic matter between the shallower (1 m, 2 m and 4 m) and deeper (10 m) areas of the lake are thought to depend on the production of *P. braunii*; namely, the production of *P. braunii* contributes to sediment organic matter in the euphotic zone (1 m, 2 m and 4 m depths), whereas POM (mainly *C. acidophila*) is the primary source of sediment organic matter in the aphotic zone (10 m depth).

The δ13C value of *P. braunii* was significantly higher than that of POM (mainly *C. acidophila*), even though these species presumably absorb the same DIC source, with the same isotopic signature. This may be explained by different boundary layers. Greater water turbulence for planktonic algae is known to reduce boundary layer thickness dramatically. Benthic microalgae tend to be more enriched in δ13C because of boundary layer effects that promote 13C-enrichment, which, in turn, is the result from the greater diffusional resistance of CO2 in less turbulent environments (France 1995b).

In strongly acidic lakes such as Lake Katanuma, CO2 gas is usually considered to be the predominant form of inorganic carbon and to be present in very low concentrations (Wetzel 2001). Under limited CO2 supply, the δ13C value of algae is expected to be higher because of reduced isotopic fractionation; however, δ13C values of POM (*C. acidophila*) in Lake Katanuma were not higher than values reported for other lakes (Yoshioka et al. 1989; Zohary et al. 1994).

Satake and Saijo (1973) measured the CO2 content and photosynthetic activity of water in Lake Katanuma and reported a CO2 content higher than that theoretically calculated, based on solubility in acidic water and the considerably high productivity of *C. acidophila*. In fact, DIC was more than 0.5 mg C L−1. The DIC in the lake is almost entirely from CO2 gas, as the lakeis pH is 2.2 (Wetzel 2001).

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Table 1. The δ13C values and C:N ratios of sediment, particulate organic matter (POM) (predominantly *Chlamydomonas acidophila*), *Pinnularia braunii* and emergent and terrestrial plants from Lake Katanuma (mean ± 1 s.d.)

<table>
<thead>
<tr>
<th>Samples in Lake Katanuma</th>
<th>δ13C (‰)</th>
<th>n</th>
<th>C:N</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment (1 m depth)</td>
<td>−23.1 ± 0.5</td>
<td>9</td>
<td>16.6 ± 1.5</td>
<td>9</td>
</tr>
<tr>
<td>Sediment (2 m depth)</td>
<td>−22.2 ± 0.6</td>
<td>9</td>
<td>15.5 ± 1.8</td>
<td>9</td>
</tr>
<tr>
<td>Sediment (4 m depth)</td>
<td>−22.8 ± 0.7</td>
<td>9</td>
<td>14.4 ± 1.4</td>
<td>9</td>
</tr>
<tr>
<td>Sediment (10 m depth)</td>
<td>−24.4 ± 0.9</td>
<td>9</td>
<td>14.2 ± 3.0</td>
<td>9</td>
</tr>
<tr>
<td>Pinnularia braunii</td>
<td>−22.8 ± 0.5</td>
<td>6</td>
<td>6.9 ± 1.7</td>
<td>5</td>
</tr>
<tr>
<td>POM</td>
<td>−25.3 ± 1.0</td>
<td>36</td>
<td>11.6 ± 0.5</td>
<td>5</td>
</tr>
<tr>
<td>Phragmites australis</td>
<td>−28.0 ± 0.9</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sasa kurilensis</td>
<td>−27.9 ± 0.8</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fagus crenata</td>
<td>−29.2 ± 1.2</td>
<td>3</td>
<td>77.9 ± 1.0</td>
<td>3</td>
</tr>
</tbody>
</table>

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Fig. 1. The δ13C values of sediment, particulate organic matter (POM) (predominantly *Chlamydomonas acidophila*), *Pinnularia braunii* and emergent and terrestrial plants from Lake Katanuma. The bars indicate the range of values, white squares indicate ± 1 s.d., and black squares indicate mean values. Assigned letters a, b and c indicate significant differences among δ13C values (*P* < 0.001, Scheffe’s F-test).
The concentration of free CO$_2$ in most freshwater bodies is approximately 0.1 mg C L$^{-1}$, which is in approximate equilibrium with the atmosphere (Wetzel 2001). Thus, the concentration of CO$_2$ in Lake Katanuma is higher than concentrations found in most fresh waters, irrespective of pH. This high concentration is probably because of the continuous supply of DIC from fumaroles on the lake bottom. Therefore, *C. acidophila* may be fairly depleted in $\delta^{13}$C despite the low pH in Lake Katanuma.

The C:N ratio has been used as an indicator of sediment organic matter source in many investigations (Bordovskiy 1965; Rashid and Reinson 1979; Prahl et al. 1980; Silva and Rezende 2002). In general, sediment organic matter with low C:N indicates microagal origin, whereas higher C:N is indicative of terrestrial plant origin because the C:N values of microalgae are usually lower (i.e. C:N 4-10) than those of terrestrial vascular plants (i.e. C:N > 20) (Meyers 1994). The C:N of *P. braunii* and POM were 6.7 ± 1.7 and 11.6 ± 0.5 (mean ± 1 s.d.; n = 5), respectively, whereas the C:N of *F. crenata* was 77.9 ± 1.0 (mean ± 1 s.d.; n = 3), which is higher than both the microalgae and POM (Table 1).

In Lake Katanuma, the C:N of sediments ranged from 14.4 ± 2.1 to 16.6 ± 1.4 (mean ± 1 s.d.; n = 9) (Table 1); these values were higher than those from other lakes (Meyers and Ishiwatari 1993). The C:N values from 14.4 to 16.6 may indicate the large contributions of organic matter originating from allochthonous sources (Meyers and Ishiwatari 1993; Meyers 1994). Yet the $\delta^{13}$C values of the sediments suggest that the main organic source for the sediment organic matter was microagal.

The value of natural organic tracers as indicators of origin lies in their ability to faithfully record the original source of organic matter. During the degradation of vascular plant detritus with high C:N, the C:N tends to decrease with time and to asymptotically approach 10 (Rice and Tenore 1981; Meyers 1994). Conversely, $\delta^{13}$C compositions of organic detritus have been reported to be stable, even following extensive and prolonged microbial decomposition (Haines 1976; Schwinghamer et al. 1983; Gearing et al. 1984; Fenton and Ritz 1988). Thornton and McManus (1994) used $\delta^{13}$C, $\delta^{15}$N, and C:N to determine sources of sediment organic matter in an estuarine system and concluded that only $\delta^{13}$C is reliable as a provenance indicator because $\delta^{15}$N and C:N record not only the organic matter origin but also the degree of diagenetic alteration.

The small amount of fresh plant litter in Lake Katanuma was supplied from the surrounding vegetation because there is no overland inflow to the lake. The terrestrial plants had extremely high C:N (C:N F. crenata = 77.9) (Table 1). Only a small amount of this allochthonous material would be needed to shift the C:N of surface sediments away from algal values and to increase the sediment C:N. Thus, the C:N ratios of Lake Katanuma sediments were probably not contradictory to the results of the carbon isotope ratios.

In general, sediment organic matter in lake ecosystems is derived from numerous sources, with a range of $\delta^{13}$C values. This complicates the determination of the exact origin of sediment organic matter using $\delta^{13}$C as a natural tracer; however, the organic sources for Lake Katanuma are limited. They are, primarily, the phytoplankton *C. acidophila* and the benthic diatom *P. braunii* as autochthonous sources, and terrestrial vascular plants as allochthonous sources. In addition, each source has discretely different $\delta^{13}$C values (Fig. 1). Therefore, $\delta^{13}$C values are more reliable as provenance indicators of sediment organic matter in Lake Katanuma. The $\delta^{13}$C values in the present study indicate that sediment organic matter in Lake Katanuma is derived primarily from the microalgae *P. braunii* and *C. acidophila* despite the continuous supply to the lake of fresh plant litter from surrounding terrestrial vegetation.

Sediment organic matter has been thought to be derived primarily from allochthonous sources in small lakes (Rau 1980; Gu et al. 1997) and to be especially the case in small, acidic lakes (Laskov et al. 2002). In contrast, the sediment organic matter in Lake Katanuma was derived mainly from autochthonous sources, despite the small size and low pH of the lake.

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**References**


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