Characterization ascertained from δ^{13}C and Δ^{14}C of particulate organic matter in surface water from a shallow and semi-closed Lake Kiba

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Concentrations of stable and radioactive carbon isotopes of organic matter were determined for suspended solids in surface water from the shallow and semi-closed Lake Kiba, Japan during June 2014 – March 2016. Particulate organic carbon (POC) concentrations were 0.44–5.01 mg L^{-1}, and δ^{13}C and Δ^{14}C values were, respectively, −30.3 to −22.8 % and −156 to −33 %. The organic matter in suspended solid samples consistently showed depleted ^{14}C, with an average Δ^{14}C value of −81 ± 37‰. The carbon isotopes showed seasonal variation, being higher in summer, and with a positive correlation to POC contents. These results suggest that the POC characteristics are controlled by a mixture of two endmembers, organic matter produced by phytoplankton activity within the lake and the watershed organic matter, under a shallow and semi-closed environment.

1. Introduction

Radiocarbon abundance increased in the natural environment after nuclear weapons testing in the 1950s and 1960s injected large quantities of ^{14}C into the atmosphere [1,2]. The Δ^{14}C values of organic matter in river suspended particles are −980 to +75‰, but plankton and particulate organic carbon in marine environments have enriched ^{14}C values of −45 to +110‰ [1-3]. Radiocarbon is useful as a tracer of the dynamics of organic matter in river systems and lake environments because of differences in the contribution of each source with a wide range of Δ^{14}C values [4-6]. The paired Δ^{14}C versus δ^{13}C distributions vary among river systems. The distributions are categorized into three groups based on watershed conditions such as land-use type of wetlands, forest-paddy fields, and permafrost watersheds [7-9]. Riverine particulate organic matter (POM) from wetlands has lower δ^{13}C and higher Δ^{14}C than those of rivers in forests and fluvial plains, which indicates a greater contribution of apparently younger organic matter in wetland river systems. In lake environments, carbon isotopes have been applied to elucidate biogeochemical cycles and freshwater reservoir effect ranges and variations over time [6,10,11]. The phytoplankton Δ^{14}C reflects the Δ^{14}C of dissolved CO_{2}, which might be a mixture of aged and modern carbon [12-14]. Particulate organic carbon (POC) has a wide range of Δ^{14}C extending from −443 to +68‰ in these lakes. Such Δ^{14}C values have been useful in assessing the age, reactivity, and sources of carbon in lake systems. Oguri et al. [15] and Ueda et al. [16] have demonstrated that radiocarbon behavior in the Lake Obuchi and Lake Hamana ecosystems is influenced strongly by environmental factors.

Lakes play important roles in the carbon cycle through carbon sequestration in sediments and efflux of CO_{2} to the atmosphere [17-20]. Some lake environments in economically developing countries have sustained significant organic pollution during the last decade because of rapid economic development and increased human populations around watersheds. Organic pollution also has been observed in lake environments at past and present in developed countries. In Japan, water quality survey results for lakes and reservoirs in 2014 indicated that the compliance rate of environmental quality standards for living environmental items is 55.5% for chemical oxygen demand (COD) concentrations [21]. Another water quality problem is the slight increase of COD concentrations in lakes, although total nitrogen, phosphorus, and biochemical oxygen (BOD) concentrations are constant or decreasing with time [22-24]. The increasing annual measurements of COD appear to result from accumulation of refractory organic matter in the lakes. Therefore, the characterization of organic matter is important to elucidate organic matter dynamics, geochemical roles and organic pollution mechanisms in lake systems.

Lake Kiba (Kiba-gata) is located in Komatsu City, Ishikawa Prefecture, Japan (Figure 1) and is classified as a lagoon. The lake has a mean water depth of 1.7 m, area of 1.14 km², and water volume of 1.7 × 10^6 m³. Its watershed area is 38 km². In 1932, a sluicegate was constructed at the conjunction of the Kakehashi River to protect against inflow of water from the river during flood events (Figure 1). Lake Kiba was affected by changes in the drainage system and land consolidation around the lagoon during 1954–1969 [25]. One example in that period was construction of the Maekawa sluicegate and drainage pump station at the Mae River to control the Lake Kiba water level. The organic matter flux recorded in the sediment core increased from 1.1 to 2.3 and from 3.9 to 7.5 mg C cm^{-2} y^{-1}, respectively, during 1903–1974 and 1989–2012, although these values were similar to the flux recorded for 1974–1989 following reclamation [26]. The COD concentration was at a maximum, 11 mg L^{-1} in 1990, corresponding to the second worst value seen in Japan at that time. It has remained about double the national standard of this lake class

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(Class A, COD concentration < 3 mg L⁻¹ [27]) during the last
decade [28], although treatments for water quality improve-
ment have been conducted since 1991.

The objectives of this study were to elucidate the character-
istics of POM for the shallow and semi-closed Lake Kiba
throughout a year based on monthly observations obtained
using data for carbon isotopes, δ¹³C and Δ¹⁴C. The simultane-
ous use of Δ¹⁴C and δ¹³C values adds a second dimension to
observations of carbon cycling in surface aquatic environ-
ments [1, 8, 19]. During the sampling period, the fundamental
physicochemical parameters, POC concentrations, and carbon
isotope concentrations were ascertained. Results of this study
are expected to provide basic and useful information to clarify
organic pollutants affecting shallow lakes and lagoons.

2. Materials and methods

Figure 1 shows sampling sites KB1 to KB6 in Lake Kiba.
Water sampling was done at KB3 and all six sites were used
for surface sediment sampling.

Water sampling was conducted monthly during June 2014 –
March 2016 at KB3, in the central part of the lake. Collection
of the surface water samples was done from a boat using a
bucket. During 18 November – 16 December 2016, sampling
was also conducted weekly to elucidate changes in water qual-
ity during water quality improvement experiments using the
Maekawa sluiceway and drainage pump station, as presented
in Figure 1 [29]. Detailed results of those experiments will be
reported elsewhere.

Water characteristics such as water temperature (WT), pH,
conductivity, and turbidity in the surface water were measured
using a portable water quality meter (WQC-24; DKK-TOA
Corp.). Chlorophyll-a concentration was photometrically
quantified using the trichromatic absorption method after
extraction of particles using a 0.45 μm membrane filter
(Advantec MFS Inc.) with 90% acetone [30]. Samples of chlo-
rophyll-a were collected at a site close to KB3 during monthly
research conducted by the Komatsu City Government.
About 60 L of water was taken into polyethylene containers and these were then transferred to the laboratory. Suspended particles in lake water samples were concentrated with a single-bowl continuous-flow centrifuge with a flow rate of 15 L h⁻¹ [7]. The inside temperature was maintained at 10–20°C to avoid transformation of solids. Solid samples were dried at room temperature or freeze-dried. The suspended solids (SS) concentration was measured using the weight of the suspended solids.

Surface sediments were collected at the six stations (Figure 1) using an Ekman–Birge grab sampler in 2012 and 2013. The sediment samples were freeze-dried and ground in an agate mortar after sieving with a 2-mm mesh size sieve.

Organic carbon contents in suspended solids and sediment samples were determined using an elemental analyzer (NA2500, CE Instrument or Flash EA1112; Thermo Fisher Scientific Inc.). Before analysis of the suspended solids, carbonates were removed by adding 1 M HCl solution. The respective levels of precision of TOC and TN analyses were ± 0.009% and ± 0.003%. The POC concentration is calculated by POC content divided by lake water volume at continuous flow centrifugation. Stable carbon isotopes were assessed for sub-samples of the CO₂ gas generated during graphite production for radiocarbon analysis using a mass spectrometer (Delta V Plus; Thermo Fisher Scientific Inc.), or were measured using an EA-IRMS analyzer (Delta V coupled to Flash EA1112; Thermo Fisher Scientific Inc.). The δ¹³C value is expressed as follows.

δ¹³C = [(¹³C/¹²C) sample / (¹³C/¹²C) standard – 1] × 1000. (1)

Here, (¹³C/¹²C) sample is the abundance ratio of ¹³C to ¹²C of the sample. (¹³C/¹²C) standard is the ratio of VPDB: ANU-Sucrose (δ¹³C = –10.80‰) and L-Alanine (δ¹³C = –19.6‰).

¹⁴C measurements were done using an accelerator mass spectrometer at the Beta Analytic Radiocarbon Dating Laboratory. For this study, δ¹⁴C is defined as the deviation in parts per thousand from the modern standard (NBS oxalic acid: SRM-4990C):

δ¹⁴C = [(¹⁴C/¹²C) sample / (¹⁴C/¹²C) standard – 1] × 1000. (2)

The ∆¹⁴C value is expressed as follows [31]:

∆¹⁴C = δ¹⁴C – 2(δ¹³C + 25) (1 + δ¹⁴C/1000). (3)

The ∆¹⁴C values are normalized to the base value of δ¹³C –25‰ of standard carbonate (VPDB) to correct for isotopic fractionation of ¹²C and ¹³C. A positive ∆¹⁴C value reflects the presence of ¹⁴C released from nuclear weapon tests in the 1950s and 1960s.

3. Results and discussion

Water quality

Water quality data during the sampling period (June 2014 – March 2016) are shown in Figure 2. Water temperature (WT) and pH show seasonal variation. They are higher in summer. Increased pH results from utilization of CO₂ for phytoplankton activity [32]. Suspended solids (SS) and particulate organic carbon (POC) concentrations are higher in summer (July–August) and lower in winter (December-February). The chlorophyll-a concentration has two peaks in April and August 2015. The POC concentration in the unit of mg L⁻¹ is correlated with water temperature and pH (r = 0.67–0.70, p < 0.05), but the POC content in unit of %, as portrayed in Figure 3, shows a stronger positive correlation with water temperature and pH (r = 0.87, p < 0.0001). This result suggests that the increase in POC concentration is related to phytoplankton activity within the lake.
Carbon isotopes of particulate organic matter

To understand organic matter dynamics through a year, focus was placed on POC content and its characteristics. The POC contents were 4.9–27%, showing a maximum in July–September (Figure 3). The maximum value in 2014 is higher than that of 2015. The C/N ratio varies from 5.0 to 9.8, except for the sample on 2 December 2015. The highest value indicates a larger contribution of soil organic matter and land plant in the watershed [33]. The δ13C value of organic matter in the suspended solids was –30.3 to –22.8‰. The maximum value in 2014 is higher than that of 2015. These values show similar variation as the POC contents \( (r = 0.80, p < 0.0001) \) do. The δ13C values also correlate with pH of the lake water \( (r = 0.75, p < 0.0005) \). Similar results have been reported for a shallow lake environment [32,34]. The δ13C values of phytoplankton increase because of the reduced isotope fractionation of 12C and 13C during photosynthesis, when the phytoplankton biomass increases or the supply of dissolved inorganic carbon is limited [32,35].

The ∆14C value of POC in the Lake Kiba water is more depleted than in the present atmospheric CO2, ca. 30‰ in 2012 [36], exhibiting an average value of –81 ± 37‰, although the maximum ∆14C value is observed in summer with higher pH, POC, and chlorophyll-a concentration. The lake water POC has lower ∆14C than inorganic carbon, plankton, and present biota in the river and lake watershed [16,37]. Increases in δ13C and ∆14C values of dissolved organic carbon have been observed in the water of Lake Kasumigaura during spring because of the primary production of phytoplankton, although ∆14C-DOC was more depleted than atmospheric CO2 [38]. Lake Kasumigaura is classified as a shallow water lake and it shows depleted 14C of organic matter, similar to the situation for Lake Kiba. The bulk POC in a large lake, Lake Superior, had a mean ∆14C value of +10 ± 29‰ ranging from −55 to +39‰. The ∆14C of dissolved inorganic carbon (DIC) was +36 ± 62‰ [39]. However, some lake water was reported to have low ∆14C values (−443 to −80‰) of POC together with low DIC (−718 to −20 ‰) [13,14]. The results suggest that ∆14C of organic matter in dissolved and particulate phases depends on that of DIC in lake water. Therefore, the depleted ∆14C value of POC in Lake Kiba might be caused by lower ∆14C inorganic compounds in lake water.

Factors controlling characteristics of particulate organic matter

Radiocarbon of POC in lake water is derived from primary production within the lake system, resuspension of sedimentary particulate matter, and inputs from the watershed. To elucidate the contribution of radiocarbon in Lake Kiba, relationships between radiocarbon and characteristics of organic matter must be discussed. Figure 4 presents the relationship between ∆14C values of organic matter and its contents in suspended solids in Lake Kiba. With the increase of POC contents in the suspended solids, ∆14C values increase \( (r = 0.82, p < 0.005) \). Similar variation of chlorophyll-a concentration represents the contribution of phytoplankton activity within the lake.

Figure 5 presents ∆14C values of organic matter in the lake suspended solids, shown as a function of the C/N ratio and δ13C values together with relationship between C/N and δ13C of POC. They have been used as a simple tracer to distinguish inputs of aquatic phytoplankton from soil organic matter. The sedimentary C/N ratio has values of 6 to 9 for freshly deposited organic matter derived from phytoplankton and 20 higher for terrestrial vascular plants [40]. The δ13C of organic matter in lake sediments reveal dynamics of suspended particle organic matter derived from phytoplankton and soil organic matter with land plants [41,42]. As shown in Figure 5(a), δ13C of POC shows a negative correlation with C/N ratio of sus-

![Figure 4](image-url)  \( \text{Figure 4.} \Delta \text{^14C values of POC as a function of POC content in the Lake Kiba surface water. Error bars correspond to 1σ uncertainty on } \Delta \text{^14C measurements.} \)

![Figure 5](image-url)  \( \text{Figure 5.} \ \delta \text{^13C of POC versus C/N ratio (a), } \Delta \text{^14C values of POC as a function of C/N ratio (b) and } \delta \text{^13C value for the POC (c) in the Lake Kiba surface water. Error bars correspond to 1σ uncertainty on } \Delta \text{^14C measurements.} \)
suspended solids, indicating the mixture of two endmembers, phytoplankton within the lake and soil organic matter around the lake watershed [43]. A negative correlation is found between the C/N ratio and ∆14C of POC (correlation coefficient of 0.82, p < 0.005). Apparently, the higher ∆14C value results from the larger contribution of a newly produced organic matter from phytoplankton activity. The ∆14C of POC shows a positive correlation with δ13C (r = 0.73, p < 0.01). The δ13C and C/N in winter are within the range of soil organic matter in Ishikawa Prefecture, Japan (C/N ratio of 10.9 to 23.6; δ13C of −28.4 to −25.9‰; S. Nagao, unpublished data). The higher ∆14C of POC and the lower C/N ratio suggest an increase in signals of phytoplankton activity in the POC content variation, as presented in Figure 2.

The contribution of surface sedimentary organic matter by resuspension is discussed from C/N and δ13C. Table 1 summarizes carbon isotope data for organic carbon in surface sediments at Lake Kiba. The δ13C values are −26.1 to −27.0‰, with an average and standard deviation of −26.6 ± 0.3‰, and is narrower and higher than the average of surface water POCS (δ13C of −27.5 ± 2.1‰). The C/N ratios in surface sediment samples also have higher values (10.6–11.8) than the suspended POC in the lake water, as depicted in Figure 3. A discrepancy exists in δ13C and C/N ratio of organic matter between the suspended solids and surface sediments. Therefore, resuspension of sediment particles from the surface sediment exerts a weak effect on the increase in δ13C and C/N ratio of POC during spring–summer. The δ13C of −26.6 ± 0.3‰ and C/N ratio of 11.5 ± 0.5 on average from surface sediments might be controlled by selective degradation of newly produced particulate organic matter within the lake [43, 44] and/or a mixture with organic matter transported from the watershed fields and sandy fields.

4. Summary

Simultaneous use of ∆14C and δ13C values adds a second dimension to results of isotopic studies of carbon cycling in surface aquatic environments. This study applied the analysis of carbon isotopes to the lake environment of a shallow and semi-closed lake, Lake Kiba located in Komatsu City, Ishikawa Prefecture, Japan. The field research was conducted during June 2014 to March 2016. Surface water sampling was done at a monitoring station in the central area of Lake Kiba. Suspended solids were collected from these water samples using continuous flow centrifugation. Particulate organic carbon (POC) concentration and its contents were, respectively, 0.44–5.01 mg L−1 and 4.9–27%. Strong positive correlations of POC content were found with its ∆14C (−157 to −33‰) and δ13C (−30.3 to −22.8‰), and a negative correlation was found with the C/N ratio (5.0–14.7). These results indicated that organic matter in the surface water suspended solids consisted mainly of a mixture of organic matter produced by phytoplankton within the lake and watershed organic matter, although the ∆14C of POC was depleted to a greater degree than present atmospheric CO2.

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References

(1) P. A. Raymond, and J. E. Bauer, Organic Geochemistry 32, 469 (2001).

### Table 1: TOC content, C/N ratio and δ13C of organic matter in surface sediments from Lake Kiba.

| Sampling site | Depth (cm) | TOC (%) | C/N | δ13C (%) |
|---------------|------------|---------|-----|----------|
| St. KB1        | 0-2        | 2.86    | 10.6 | −27.0    |
| St. KB2        | 0-2        | 5.61    | 11.2 | −26.7    |
| St. KB3        | 0-2        | 7.24    | 11.5 | −26.1    |
| St. KB4        | 0-2        | 5.27    | 10.6 | −26.5    |
| St. KB5        | 0-2        | 4.77    | 11.1 | −26.9    |
| St. KB6        | 0-1        | 7.32    | 11.8 | −26.5    |

(2) A. P. McNichol, and L. I. Aluwihare, Chemical Review 107, 443 (2007).
(3) J. I. Hedges, J. R. Ertel, P. D. Quay, P. M. Groote, J. F. Richey, A. H. Devol, G. W. Farewell, F.W. Schmidt, and E. Salati, Science 231, 1129 (1986).
(4) C. A. Masieelo, and E. R. M. Druffel, Global Biogeochemical Cycles 15, 407 (2001).
(5) P. A. Raymond, J. E. Bauer, N. F. Caraco, J. J. Cole, B. Longworth, and S. T. Petsch, Marine Chemistry 92, 353 (2004).
(6) S. Nagao, H. Kodama, T. Aramaki, N. Fujitake, and K. Yonebayashi, Nuclear Instrument and Methods in Physical Research Section B 259, 552 (2007).
(7) S. Nagao, T. Aramaki, O. Seki, M. Uchida, and Y. Shibata, Nuclear Instrument and Methods in Physical Research Section B 268, 1098 (2010).
(8) S. Nagao, T. Usui, M. Yamamoto, M. Minagawa, T. Iwatsuki, and A. Noda, Chemical Geology 218, 63 (2005).
(9) L. Guo, and R. W. Macdonald, Global Biogeochemical Cycles 20, GB2011 (2006) doi: 10.1029/2005GB002593.
(10) M. B. Abbott, and T. W. Stafford Jr., Quaternary Research 45, 300 (1996).
(11) F. W. Nara, A. Imai, M. Uchida, K. Matsushige, K. Komatsu, N. Kawai, Y. Shibata, K. Amano, H. Mikami, and R. Hanaishi, Radiocarbon 52, 1078 (2010).
(12) P. K. Zigah, E. C. Minor, and J. P. Werne, Global Biogeochemical Cycles 26, GB1023 (2012) doi:10.1029/2011GB004132.
(13) P. Albéric, D. Jézéquel, L. Bergonzin, E. Chapron, E. Vioillier, M. Massault, and G. Michard, Radiocarbon 55, 1029 (2013).
(14) E. M. Keaveny, P. J. Reimer, and R. H. Foy, Radiocarbon 57, 407 (2015).
(15) K. Oguri, E. Matsumoto, A. Hino, H. Kurokura, and K. Okamoto, In Summaries of Researches Using AMS at Nagoya University (VII) (Dating and Materials Research Center, Nagoya University, 1996) pp. 184-192.
(16) S. Ueda, K. Kondo, and J. Inaba, Radiocarbon 49, 161 (2007).
(17) J. J. Cole, N. F. Caraco, G. W. Kling, and T. K. Kratz, Science 265, 1568 (1994).
(18) J. J. Cole, N. F. Caraco, G. W. Kling, and T. K. Kratz, Ecosystems 10, 172 (2007).
(19) G. Gupta, V. Sarma, R. Robin, A. Raman, M. J. Kumar, M. Rakesh, and B. Subramanian, Biogeochemistry 87, 265 (2008).
(20) A. J. Heathcote, and J. A. Downing, Ecosystems 15, 60 (2012).
(21) Ministry of the Environment, Water quality data for public waters, http://www.env.go.jp/water/suiiki/h26/h26-1.pdf (accessed 30 November 2016).
(22) National Institute for Environmental Studies, Ecosystem Management Studies in Lake Towada. Report of Special Research R-146-99 (National Institute for Environmental
(23) National Institute for Environmental Studies, Studies on Mass Balance of Dissolved Organic Matter in Lake and its Functions and Effects on Lacustrine Ecosystems and Water Quality. Report of Special Research SR-62-2004 (National Institute for Environmental Studies, Japan, Tsukuba, 2004) p. 59.

(24) K. Hayakawa, and T. Okamoto, In Lake Biwa: Interactions between Nature and People edited by H. Kawanabe, M. Nishino and M. Maehata, (Springer, Tokyo, 2012) pp. 441-446.

(25) Hokuriku Regional Agricultural Administration Office, Report of Reclamation and Construction Work for Kaga Sanko (Meiji Publishing Company, Kanazawa, 1970).

(26) S. Nagao, H. T. Bui, Y. Kawano, T. Suzuki, S. Ochiai, K. Yonebayashi, M. Okazaki, A. Goto, T. Hasegawa, and M. Yamamoto, In Geomorphology and Society edited by M. E. Meadows and J.-C. Lin (Springer, Tokyo, 2016) pp. 181-192. doi: 10.1007/978-4-431-56000-s_11.

(27) Y. Magara, Classification of water quality standards, Vol. 1, https://www.eolss.net/Sample-Chapters/C07/E2-19-01-02.pdf, (accessed on 28 December 2016).

(28) Komatsu City Government, Research of Natural Environment and Watershed Culture in and around Lake Kiba, http://www.city.komatsu.lg.jp/secure/15659/kiba_lake_report.pdf (accessed 30 November 2016).

(29) Komatsu City Government, Field demonstration for water quality improvement of Lake Kiba by use of the Maekawa sluicegate, http://www.city.komatsu.lg.jp/12055.htm (accessed 30 November 2016).

(30) Ministry of the Environment, Analytical method for suspended solids concentration, http://www.env.go.jp/kijun/wt_a09.html (accessed 1 December 2016).

(31) M. Stuiver, and H. A. Polach, Radiocarbon 19, 1127 (1977).

(32) T. Yoshioka, Journal of Plankton Research 19, 1455 (1997).

(33) Y. Sampei, and E. Matsumoto, Geochemical Journal 35, 189 (2001).

(34) H. Doi, E. I. Zuykova, E. Kikuchi, S. Shikano, K. Kanno, N. Yurlova, and E. Yadrenkina, Hydrobiologia 571, 395 (2006).

(35) B. Fry, Marine Ecology Progress Series 134, 283 (1996).

(36) Ministry of the Environment, Long-term observation of oxygen and isotopes of carbon dioxide in the atmosphere to evaluate the global budget of carbon dioxide, https://www.env.go.jp/earth/kenkyuhi/report/pdf/13_4_2.pdf. (accessed 28 December 2016).

(37) T. Nakamura, S. Kojima, T. Ohta, H. Oda, A. Ikeda, M. Okuno, K. Yokota, Y. Mizutani, and W. Kretschner, Radiocarbon 40, 933 (1998).

(38) F. Nara, A. Imai, M. Yoneda, K. Matsushige, K. Komura, T. Nagai, Y. Shiha, and T. Watanabe, Radiocarbon 49, 767 (2007).

(39) P. K. Zigah, E. C. Minor, J. P. Werne, and S. L. McCallister, Biogeosciences 9, 3663 (2012).

(40) P. A. Meyer, and E. Lavillier-Verges, Journal of Paleolimnology 21, 345 (1999).

(41) J. C. Finlay, and C. Kendall, In Stable Isotopes in Ecology and Environmental Science, Second edition edited by R. Michener and K. Lajtha (Blackwell Publishing Ltd., Malden, 2007) pp. 283-333.

(42) N. S. Khan, C. H. Vane, and B. P. Horton, In Handbook of Sea-level Research edited by I. Shennan, A. J. Long and B. P. Horton (John Wiley & Sons Ltd., New York, 2015) pp. 295-311.

(43) T. Yoshioka, H. Hayashi, E. Wada, Japanese Journal of Limnology 50, 313 (1989).

(44) B. J. Eadie, L. M. Jeffrey, Marine Chemistry 1, 199 (1973).