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Citation	Nuclear Instruments and Methods in Physics Research Section B : Beam Interactions with Materials and Atoms, 259(1), 552-557 https://doi.org/10.1016/j.nimb.2007.01.199
Issue Date	2007-06
Doc URL	http://hdl.handle.net/2115/28633
Type	article (author version)
File Information	NIMP259-1-552.pdf



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Variations in $\Delta^{14}\text{C}$ of humic substances in the Lake Biwa waters

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Keywords: Carbon-14; Humic substances; Lake water; Lake Biwa; delta carbon-13

Abstract

Carbon isotopes (^{13}C and ^{14}C) were used to study the characteristics and origin of humic substances in water samples from Lake Biwa in Japan. Humic substances were isolated from surface lake waters in each season by the XAD extraction method and their carbon isotopic ratios were measured by accelerator mass spectrometry. The $\Delta^{14}\text{C}$ values of Biwa humic and fulvic acids indicate that these substances consist mainly of pre-bomb ^{14}C . There is a negative correlation between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values for the Biwa fulvic acids. The fulvic acid consists of younger organic materials with lower $\delta^{13}\text{C}$ value in January, but older organics with higher $\delta^{13}\text{C}$ in April and October. The major part of fulvic acid may be supplied from soil solution and/or groundwater in the watershed and their contribution varies with season.

1. Introduction

Humic substances (humic and fulvic acids) are complex polymeric organic acids with a wide range of molecular weights and sizes, ranging from a few hundred to several hundred thousand, and are ubiquitous in natural environment. They are the largest fraction of dissolved organic materials (DOM) in river and lake waters, and play an important role in both pollutant chemistry and the biogeochemistry of natural waters and soils [1,2]. Humic substances in most aquifer systems affect the behavior of metals and radionuclides by different processes such as sorption, complexation and dissolution/precipitation [3-5]. The presence of humic substances can also promote the solubilization of nonpolar hydrophobic compounds such as PCB and DDT [6-8]. This acts to decrease the sorption of these materials to soil and sediment. Researchers have been studying the role of humic substances as a precursor in the formation of trihalomethanes [9-11]. Humic substances contain 40~60% carbon and are refractory because of their heterogeneous mixture of relatively poorly biodegradable matter [2,12]. Therefore, these substances are considered to be one of the global reservoirs of organic carbon. The investigations on characteristics of aquatic humic substances have yielded insight into the production and turnover of soil organic materials, and their transport behavior within natural watersheds.

Radiocarbon (^{14}C) is a useful tool for studying the dynamics of DOM in terrestrial environments [13]. It can provide unique information on the sources, ages, and residence times of organic materials in aquatic environments. There have been a

number of studies that have incorporated ^{14}C measurements in the oceans and soils [14-16]. However there has been little application of ^{14}C to dissolved and particulate organic materials in rivers and lakes [17-19]. This study applied a combined $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ approach to lake humic substances for better understanding of the geochemical behavior of aquatic humic substances in a lake and its watershed.

2. Study area

Lake Biwa is located in the central part of Honshu Island and the largest freshwater lake in Japan (Fig. 1). Lake Biwa has a surface area of 670 km^2 , a storage capacity of 275 km^3 , and is a typical harmonic lake. The lake is divided into north and south basins. The north basin has a mean water depth of 43 m and accounts for 90% of the entire lake area. The south part has an averaged water depth of 3.5 m. The main inflow rivers of Lake Biwa are the Nosu River, Ane River and Ado River with a watershed area of more than 300 km^2 . Total watershed of the lake is approximately 3170 km^2 . About 60% of this area is forested mountains (Ibuki, Suzuka, and Hira mountains), while 18% is in agriculture and the balance in other land uses such as urban and industrial development. A mean annual precipitation at Hikone is 1584 mm during 1980-2001 [20].

The north basin is a mesotrophic condition and a monomictic nature. The south basin is eutrophic due to human activity [21]. The peak chlorophyll-a concentration in the surface water column was observed in May and autumn in the north basin [22]. The DOC concentration in surface water at Kitakomatsu ranged from 1.1 to 1.6 mg/l in 2002 [23].

In order to understand the carbon fixation as DOM in lake, we have chosen two reservoirs created by Zao Dam and Kawashiro Dam (Fig. 1). Zao dam was built to ensure the supply of water for agriculture upstream of Hino River, which is an inflow river to Lake Biwa, and assists the steady production of food regardless of meteorological conditions. The reservoir area is 0.33 km^2 and watershed area is 9.4 km^2 . Usable storage capacity is 4.6 km^3 [24]. Kawashiro dam is located in the Kako River system in Hyogo Prefecture. The dam consists of gates in a tributary of the River, and is channel storage and the smallest reservoir of this study. The usable storage capacity is $1.28 \times 10^{-3}\text{ km}^3$ [25].

Water quality is different from each other. Mean total nitrogen (T-N) concentration was 0.27 mg/l for the north basin of Lake Biwa, 0.30 mg/l for Zao Dam, and 1.23 mg/l for Kawashiro Dam [21,26,27]. Total phosphorous (T-P) was 0.009 mg/l for the Biwa, 0.01 mg/l for the Zao and 0.07 mg/l for the Kawashiro [21, 26, 27]. The concentration of nutrients is related to the primary production in surface layer of lake and reservoir.

3. Materials and methods

3.1 Sampling and isolation of humic substances

Humic substances from Lake Biwa were isolated from surface waters by the XAD extraction method [28] at the environmental standard sites at Kitakomatsu and Hikone from 1998 to 2003 and at Karasaki in 1998 (Fig. 1). The isolation and purification of humic substances was also carried out at Zao Dam in July and October in 1999. The Kawashiro Dam water was also collected in October in 1997.

The surface waters of 1~206 tons were collected by pump and adjusted using HCl to pH2 after removing suspended particles by cartridge filters (pore size of 10 μ m, 1 μ m and 0.45 μ m). The acidified waters were passed through a column containing DAX-8 resin. The humic substances were adsorbed on the DAX-8 resin. It desorbed from the resin using 0.1M NaOH solution and separated to humic and fulvic acids by adjusting the solution pH to 1.5. The humic and fulvic acids were converted to the hydrogen form by passage through a cation exchanger in the hydrogen form. The isolated humic and fulvic acids were freeze-dried. The isolation conditions are given in Table 1. The humic and fulvic acids from the Suwannee River and Nordic lake surface water were purchased from the International Humic Substances Society (IHSS). These reference materials were prepared by the similar method in this study.

3.2 Analyses

The $^{14}\text{C}/^{12}\text{C}$ measurements were performed by accelerator mass spectrometry at the Marine Research Laboratory of Japan Atomic Energy Research Institute [29]. Humic substances were first converted to CO_2 and purified cryogenically. The purified CO_2 was then reduced to graphite with H_2 over Fe and its $^{14}\text{C}/^{12}\text{C}$ ratio was measured with a Tandem AMS system using a NIST oxalic acid ^{14}C standard

(SRM-4990C; HoxII). The precision of ^{14}C measurement was typically less than $\pm 7\%$. Radiocarbon values are reported as $\Delta^{14}\text{C}$ values. The replicate determination of $\Delta^{14}\text{C}$ values was performed for humic substances in the Sakhan River. The averaged $\Delta^{14}\text{C}$ value was $-14 \pm 3 \text{ ‰}$ for the humic acid and $-46 \pm 6 \text{ ‰}$ for the fulvic acid.

The preparative cleaning and conditioning for the resin were carried out by soxhlet extraction at batch method, and by influent of NaOH solution and Milli-Q water to the column packed with the resin until the DOC concentration less than 1mg/l for the eluted solution [28]. The volume ratio of DAX-8 resin to lake water samples was not same as shown in Table 1, but there is no systematic variations in $\Delta^{14}\text{C}$ values of humic substances (Table 2). The $\Delta^{14}\text{C}$ values of Harp Lake DOC was almost similar with those of humic and fulvic acids isolated by similar method [17]. Therefore, artifact effects of sample preparation by the XAD extraction on the $\Delta^{14}\text{C}$ values may be negligible and /or small.

The $\delta^{13}\text{C}_{\text{PDB}}$ measurements of a sample and the standard used for normalization were made by analyzing sub-samples of CO_2 gas generated during graphite production using a triple collector mass spectrometer (DeltaPLUS; Thermo Electron Corp.) with a precision of $\pm 0.05\%$.

4. Results and discussion

4.1 Variations in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values

The results of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values are shown in Table 2. The $\Delta^{14}\text{C}$ values of humic substances in surface waters from Lake Biwa and Zao Dam are less than 0‰. The fulvic acids range from -316 to -55% . The humic acids have $\Delta^{14}\text{C}$ values of -55% and -122% . On the other hand, the $\Delta^{14}\text{C}$ values of the Kawashiro Dam are greater than 0‰. The IHSS aquatic reference samples from the Suwannee and Nordic sites in 1986 are 149~209‰. Similar results were found in Harp Lake [17]. The $\Delta^{14}\text{C}$ values of the Biwa humic substances are ca. 400‰ lower than the IHSS reference samples. The surface water humic substances from Lake Biwa and Zao Dam consist mainly of pre-bomb carbon, and the IHSS and Kawashiro Dam samples must contain a substantial amount of bomb carbon. The $\Delta^{14}\text{C}$ values of humic substances reflect the average production and turnover time scale in lake environment [17]. Comparison of $\Delta^{14}\text{C}$ values of humic substances in the Biwa and IHSS samples suggests that the

presence of a rapidly cycling component can not be recognized for the Biwa samples. The $\delta^{13}\text{C}$ values exhibited a wide range from -25.6 to -29.4‰ , indicating C_3 plant and freshwater planktons as the original sources [12,30].

Figure 2 shows the variations in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values for humic and fulvic acids from Lake Biwa together with data of Zao and Kawashiro Dams. The Biwa fulvic acids have the lower $\Delta^{14}\text{C}$ values for the samples collected in October-November in 2001 and April-May in 2002. The fulvic acids from other Biwa and Zao Dam samples range from -32 to -80‰ , and the averaged value is $-49\pm 17\text{‰}$. These data suggest that the $\delta^{13}\text{C}$ values of fulvic acids have maximum values in early summer, from June to July.

4.2 Relationship between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values

As shown in Fig. 3, there is a negative correlation between the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values ($-25.6\text{‰} \sim -27.8\text{‰}$) of fulvic acids from Lake Biwa ($r=0.94$). The negative relationship is also found in fulvic acids from Lake Biwa, Zao Dam, Kawashiro Dam and the IHSS samples ($r=0.84$) with the similar slope. This result indicates the mixture of two end members of fulvic acids; newly formed fulvic acid with lower $\delta^{13}\text{C}$, and older fulvic acids with higher $\delta^{13}\text{C}$.

The $\Delta^{14}\text{C}$ values of Biwa humic acids have a positive correlation with the $\delta^{13}\text{C}$ values. The $\delta^{13}\text{C}$ values of Biwa and Zao Dam humic acids indicate a wide range of variation from -30.4 to -24.0‰ in comparison with the fulvic acids. On the other hand, $\Delta^{14}\text{C}$ values of humic acids from the IHSS, the Kawashiro and two Biwa samples negatively correlate with $\delta^{13}\text{C}$ values, ranging from -28‰ to -27‰ . The major sources of humic acids, therefore, may be different from the fulvic acids. This hypothesis is consistent with the results of Py-GC/MS (S. Yamamoto, unpublished data). The relative composition of fatty acids to the sum of fatty acids and lignin phenol, important fractions of humic substances, was $5.2\sim 37.1$ for the fulvic acids and $74\sim 79\%$ for the humic acids. These results indicate difference in sources of humic and fulvic acids, but we can not recognize them from the present data set.

4.3 Factors controlling variations in carbon isotopes

The humic substances produced and flushed from watershed are a mixture of compounds with varying $\Delta^{14}\text{C}$ contents depending on the humic substances parent

materials and the residence time in the aquifer [17]. The geochemical behavior of humic substances in lake also is important for the variations in $\Delta^{14}\text{C}$. The $\Delta^{14}\text{C}$ values of fulvic acids are in the order of the Kawashiro > the Zao \geq the Biwa samples. The Kawashiro fulvic acid has the $\Delta^{14}\text{C}$ value of +3‰. Kawashiro Dam has the highest T-N and T-P concentrations, and the smallest size of reservoir than the Biwa and Zao. These results indicate that eutrophication, primary production and size of reservoir may be related to the variations in $\Delta^{14}\text{C}$, that is, reflecting differences in contribution of newly formed humic substances.

The north basin is monomictic, and water temperature becomes uniform throughout the water column in January. Thermal stratification begins to develop in April and is well established in mid-summer and early autumn [31]. The Biwa fulvic acids collected in January in 2000 and 2003 have $\Delta^{14}\text{C}$ values of -50‰. This value reflects averaged features of fulvic acids though the water column due to the vertical mixing of lake waters. On the other hand, $\Delta^{14}\text{C}$ values were -186‰ in October 2001 and -316‰ in April 2002, and the corresponding ^{14}C ages were 1650 yr B.P. and 3050 yr B.P., respectively. The variations in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of Biwa humic substances reflect phenomena in surface water environments. The range in organic matter ages in the top meter of soil is from modern to > 5,000 yr [15, 32]. Tomita [33] has shown that the concentration of humic substances in waters from the Seta River, which is an outflow river for Lake Biwa, increased due to heavy rain. Horii et al. [34] have shown that no sign of diffusion of DOC from the bottom sediment was observed from the DOC measurements in the lake water. Therefore, older fulvic acids in soil and groundwater may be transported from rivers to the lake in April and October.

As shown in Fig. 3, there is a positive correlation between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values for the Biwa humic acids. Miyajima et al. [35] have shown that particulate organic materials of the size fractions of 40-70 μm and 70-150 μm in surface waters from Lake Biwa consisted mainly of phytoplankton (>90% in volume), and their $\delta^{13}\text{C}$ values were $-18 \pm 4\text{‰}$ and $-20 \pm 3\text{‰}$, respectively. The $\delta^{13}\text{C}$ of the 20-40 μm fraction, which consisted mainly small cyanobacteria and detritus, was intermediate ($-24 \pm 2\text{‰}$) between those of plankton and sediment. There are seasonal variations in $\delta^{13}\text{C}$ values of POM. The $\delta^{13}\text{C}$ values reached their lowest value during winter through early spring and tended to increase toward summer [36]. If dissolved organic materials derived from decomposition of phytoplanktonic algae, i.e., autochthonously

produced organic materials, are precursors of humic acid, it appears that the variation in $\Delta^{14}\text{C}$ may be explained by the addition of newly formed humic acid originated from phytoplankton. However, we must measure $\Delta^{14}\text{C}$ values of phytoplankton and particulate organic matter in the lake waters to understand these variations clearly.

Summary

The geochemical behavior of humic and fulvic acids in waters from Lake Biwa was studied with a combined use of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values. Humic substances were isolated and purified from surface waters at standard environmental monitoring sites from 1998 to 2003. The humic and fulvic acids have almost $\Delta^{14}\text{C}$ values less than 0‰. These substances consist mainly of organic matter created before nuclear weapon testing during the 1950's and 1960's. Seasonal variations in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values occur for fulvic acids during the year. A strong negative correlation exists between the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of fulvic acids. There is a positive correlation for Biwa humic acids. These results indicate that the lake humic substances consist of a mixture of two sources, and humic acids may form from different sources than fulvic acids.

Acknowledgments

The authors thank the Department of Lake Biwa Environment, Shiga Prefecture in Japan and members of Laboratory of Soil Chemistry of Kyoto Prefectural University for the lake water sampling. We also thank Dr. O. Togawa of Japan Atomic Energy Research Institute (present: Japan Atomic Energy Agency) for the ^{14}C measurements of these samples. The research described in this paper was funded by a Grant-in-Aid for Scientific Research, No. 13460033 and No. 1531002 from the Ministry of Education, Science, Sport and Culture in Japan.

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Table 1 Isolated conditions for humic substances in lake waters by XAD extraction.

Site	Sampling period	Column (mmφ)	Treated lake water (t)	Isolated humus HA (mg) FA(mg)	
Lake Biwa					
Kitakomatsu	1999/6/15-20	150	5.4	n.d.	372.5
	2000/1/26-31	150	4.4	82.4	1243.4
	2001/10/17-11/9	480	155.8	9.6*	18.0*
	2002/4/16-5/6	480	151.2	12.4*	14.7*
	2003/1/15-2/3	480	205.6	7.4*	22.0*
Hikone	1998/10/2	70	1.0	3.5	136.5
Karasaki	1998/11/4	70	1.0	5.1	283.9
Zao Dam	1999/7/6-8	150	2.0	209.0	991.7
	1999/10/29-11/3	150	2.3	46.3	226.3
Kawashiro Dam	1997/10/29-11/3	150	1.2	66.5	580.4

n.d.=not determined.

* unit is gram.

Table 2 $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of humic substances isolated from water samples in Lake Biwa, Zao Dam, and Kawashiro Dam.

Sample		Sampling period	$\Delta^{14}\text{C}$ (‰)	$\delta^{13}\text{C}$ (‰)
Humic acid				
Lake Biwa	Hikone	1998/10/2	-55 ± 5	-27.0
	Kitakomatsu	1999/6/15-20	-16 ± 7	-26.0
2000/1/26-31		-53 ± 4	-27.1	
2003/1/15-2/3		-122 ± 4	-29.1	
Zao Dam		1999/7/6-8	-47 ± 5	-24.0
		1999/10/6-12	-52 ± 6	-29.4
Kawashiro Dam		1997/10/29-11/3	$+18 \pm 5$	-27.2
IHSS Suwannee River		1982-83	$+167 \pm 6$	-28.1
IHSS Nordic		----	$+149 \pm 7$	-27.9
Fulvic acid				
Lake Biwa	Kitakomatsu	2000/1/26-1/31	-46 ± 9	-26.7
		2001/10/17-11/9	-186 ± 5	-25.6
		2002/4/16-5/6	-316 ± 6	-25.6
		2003/1/15-2/3	-55 ± 4	-26.8
Zao Dam	Karasaki	1998/11/4	-32 ± 4	-27.0
		1999/7/6-8	-80 ± 6	-27.1
		1999/10/6-12	-56 ± 7	-27.8
Kawashiro Dam		1997/10/29-11/3	$+3 \pm 5$	-27.4
IHSS Suwannee River		1982-83	$+209 \pm 7$	-27.7
IHSS Nordic		----	$+170 \pm 6$	-27.8

Figure captions

Figure 1 Location of the sampling sites in Lake Biwa, Zao Dam and Kawashiro Dam.

Figure 2 Variations in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of aquatic humic substances (HA: humic acid, FA: fulvic acid) from Lake Biwa (\circ : north and south basin HA, \bullet : north basin FA, \blacktriangle : south basin FA), Zao Dam (\diamond :HA, \blacklozenge :FA), and Kawashiro Dam (\square :HA, \blacksquare :FA).

Figure 3 Relationship between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of humic substances in water samples from Lake Biwa, Zao Dam, Kawashiro Dam, and IHSS reference samples (∇ :HA, \blacktriangledown :FA).

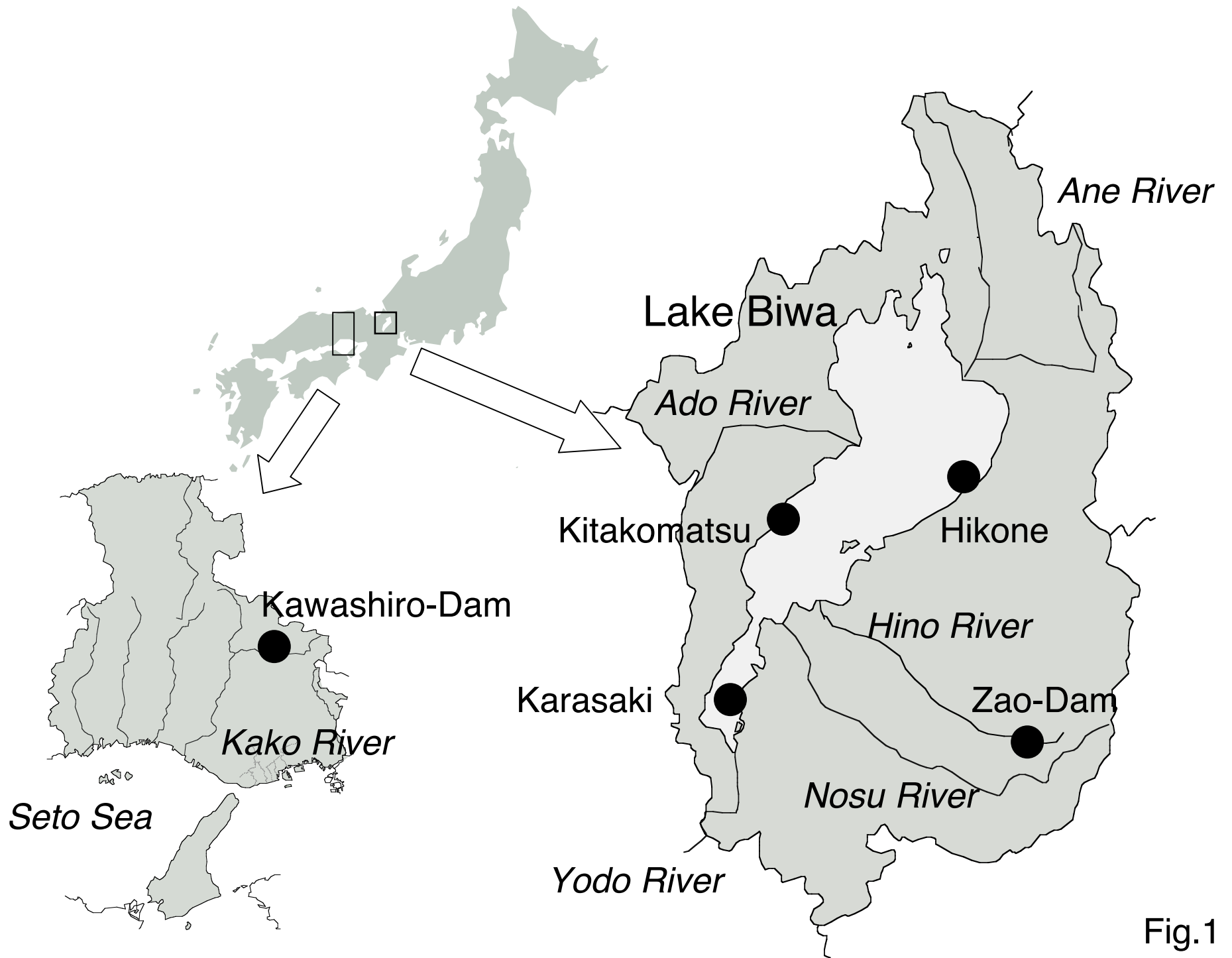


Fig.1

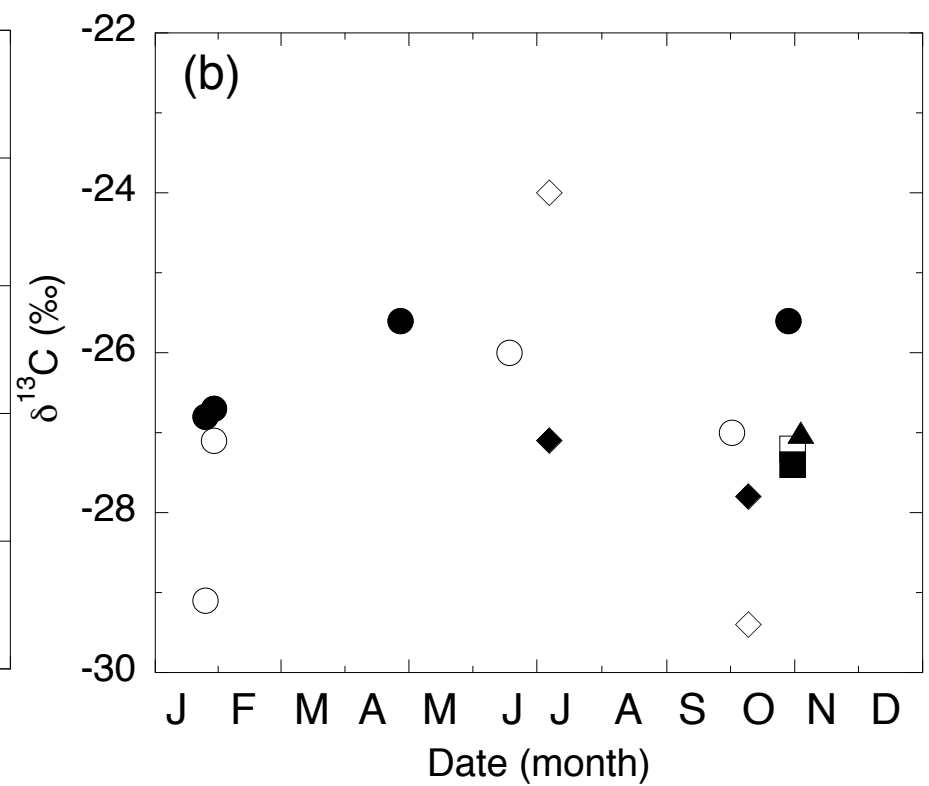
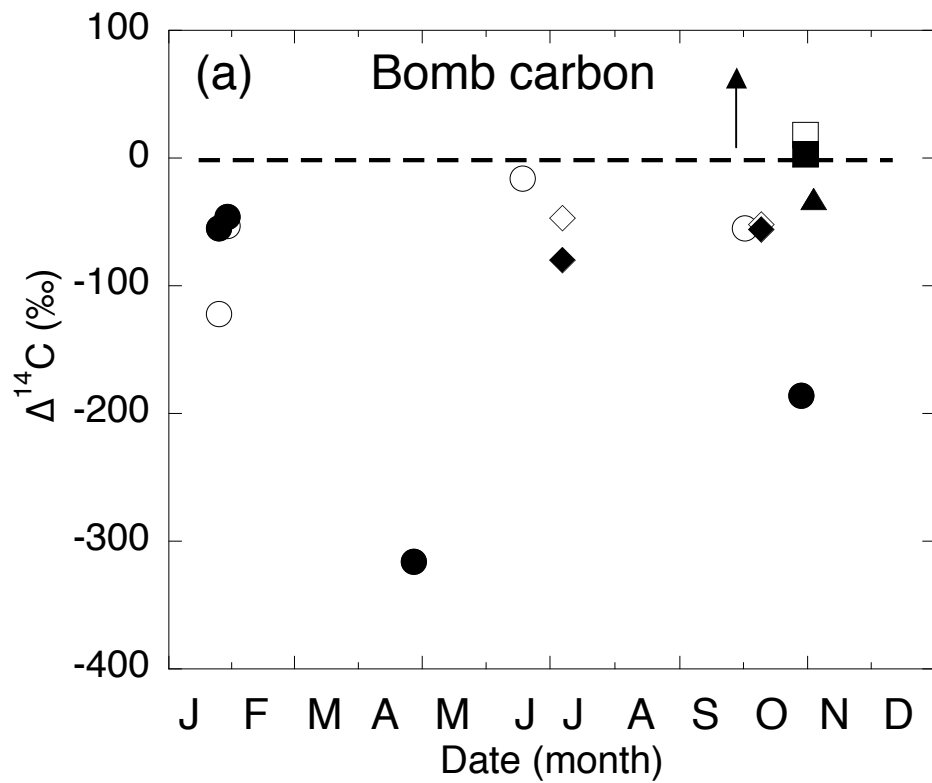


Fig.2

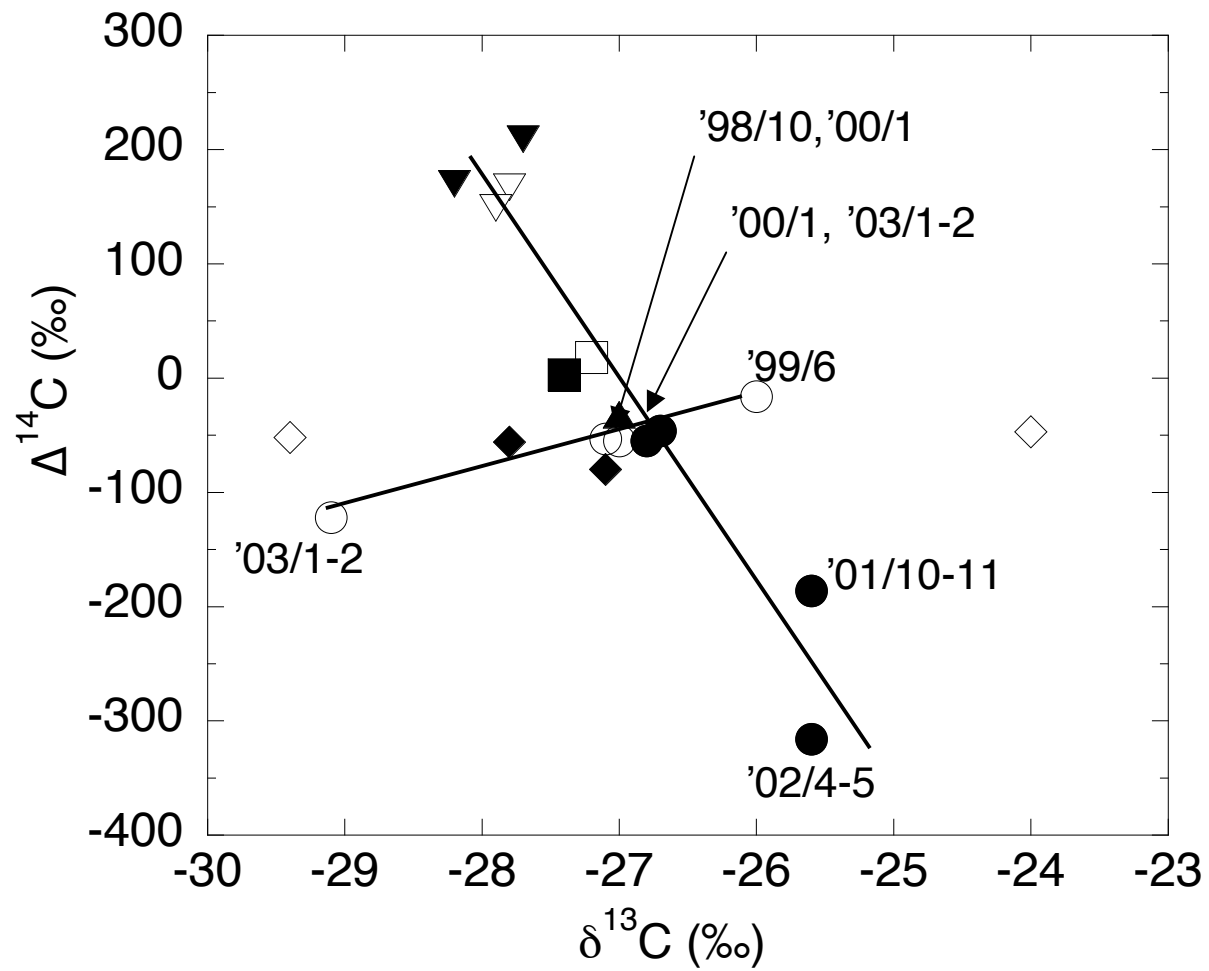


Fig.3