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Historical Change in Primary Productivity in Ishikari Bay Reconstructed from Biogenic Si Content in the Sediment

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Abstract

Organic C, N, and biogenic Si (BSi) content, as well as C and N stable isotopes, in sediment cores were measured to elucidate the historical change in primary productivity at Ishikari Bay. The bay is characterized as an oligotrophic coastal water considerably influenced by riverine discharge from the Ishikari River, the second largest river in Japan. Layers with a high C content of 50 mg g^{-1} and a high C : N ratio of 25 were found in several cores, which coincided with a sedimentation age between the 1960s and 1970s. This was attributed to peat exposure to land surface and the delivery to the bay due to the intensive exploitation of land in the catchment area of the Ishikari River and the frequent floods of that time period. BSi content in the sediment layer may reflect change in the diatomaceous primary productivity in the surface euphotic zone. BSi content increased up to the present at the station nearest to the river mouth, indicating an increase in primary productivity by diatoms. However, the total nitrogen flux from the river has not changed significantly since the 1970s. The transparency in the river water has increased, suggesting a decrease in the loadings of suspended solids from the river due to the construction of revetment walls. Thus, light limitation has been relieved in the area near the river mouth. In semi-enclosed coastal areas, the sedimentary record of organic matter and BSi content may reflect historical changes in primary productivity and riverine influence.

Key words: Diatom, Nutrient, BSi, Land-ocean interaction

Introduction

Primary production plays an important role in the transfer of carbon from the atmosphere to the sediments through the biological pump (Berger et al., 1989). The organic matter in marine sediments is mostly derived from exported material photosynthesized by autotrophic organisms in the surface euphotic zone. Terrestrial organic matter is also exported to coastal regions and some of this deposits in the sediments. The flux of organic matter to marine sediments is controlled by several factors, such as the extent of primary production, efficiency of export, degree of heterotrophic degradation, and advective transport (Hedges and Keil, 1995 ; Sepúlveda et al., 2005). The preservation of organic matter in the sediment is a combined function of mass and organic matter accumulation rates, oxygen content in the bottom water, and composition of organic matter. The biological signatures preserved in the sediment are useful proxies to reconstruct past changes in primary productivity and to elucidate possible causes for its variation (Zimmerman and Canuel, 2000, 2002 ; Ruiz-Fernández et al., 2002 ; Sepúlveda et al., 2005 ; Reuss et al., 2005 ; Szymczak-Zyla et al., 2011).

Diatoms usually become the dominant species in subarctic coastal environments and the contribution of diatoms to total primary production accounts for about 75 % in these areas (Nelson et al., 1995). Thus, biogenic silica (hereafter BSi) originated from diatom frustules may serve as a good indicator for the abundance of diatoms. However, surface seawater is undersaturated with opal (silica) and most of the BSi produced in the euphotic zone may dissolve during sinking in the water column. Though BSi reaching the seafloor and preserved in the sediment is a small fraction of the total BSi produced in the euphotic zone (Kamatani and Riley, 1979 ; Nelson et al., 1995), BSi content in the sediment has been utilized as a proxy for reconstructing the change in past primary productivity by diatoms (Mortlock et al., 1991 ; Bernárdez et al., 2005 ; Kauppila et al., 2005 ; Sepúlveda et al., 2005).

Ishikari Bay is located in a subarctic region, but is oligotrophic due to the influence of the subtropical Tsushima warm current (Yoshida et al., 1977). However, the bay receives discharges from the Ishikari River, the second largest river in Japan. The catchment area is 14,330 km^2 and the total length is 268 km (https://www.hkd.mlit.go.jp/ky/kn/kawa_kei/ud49g70000001a6b.html Accessed 4 Sept. 2024). The annual average discharge is 481 m^3 s^{-1}. The population of the catchment area is 3.5 million and the land usage of the

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upper area is farming ground developed intensively since the 1950s. Agboola et al. (2009, 2010) reported a spatial and temporal distribution of salinity, nutrients, and chlorophyll *a* at the 26 gridded sampling stations in Ishikari Bay and elucidated a seasonal change in the influence of riverine nutrients to primary productivity in Ishikari Bay. Thus, the bay is characterized as an oligotrophic coastal water with considerable influence from riverine discharge by the Ishikari River (Agboola et al., 2010).

In this study, several sediment cores were sampled and analyzed for sedimentation rate, organic C and N, and BSi contents, as well as C and N stable isotopes, at Ishikari Bay. From the vertical profiles of these proxies of primary productivity, we tried to elucidate the historical change in the environment of primary productivity in the bay, especially focused on the riverine influence to the bay.

Materials and Methods

Sampling

Oceanographic observations were conducted on 9 cruises during 2006 and 2008 aboard T/S *Ushio Maru* and T/S *Oshoro Maru*. Salinity and temperature were monitored with a Sea-Bird 19 plus or 911 plus CTD sensor. Water samples were collected with 12 1.7-L Niskin samplers attached to a CTD-CMS. Sediment core samples were collected at 10 stations with an undisturbed core sampler (Type GS, Rigosha) (Fig. 1) in August 2007. Sediment cores were sliced at 1 cm intervals on board, stored frozen, and then freeze-dried (DC41, Yamato).

Core processing and analysis

Grain size

Frozen sediment core samples were thawed at room temperature, then sieved using 2, 1, 0.5, 0.25, 0.125 and 0.063 mm mesh sieves sequentially. The sieved sediment samples were dried at 60°C and weighed.

^{13}C and ^{15}N stable isotopes

Freeze-dried samples were homogeneously ground and mixed, and then immersed in 1 M HCl for 24 h to remove inorganic carbon. The samples were washed several times with Milli-Q water. Ten to 50 mg of the sample were weighed and put in a tin capsule. Samples were analyzed for bulk contents and stable isotope ratios of C and N using a Thermo Electron Delta V Plus Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS ; Bremen, Germany) coupled with a Thermo Electron Flash Elemental Analyzer 1112 Series (Milan, Italy). Stable isotope ratios were expressed in delta notation ($\delta^{13}C$ or $\delta^{15}N$) and are reported in per mil (‰) using the following equation :

$$\delta^{13}C_{sample} \text{ or } \delta^{15}N_{sample}\ (‰) = (R_{sample}/R_{standard} - 1) \times 1000 \quad (1)$$

where R is the corresponding ratio of $^{13}C/^{12}C$ or $^{15}N/^{14}N$ for the sample (R_{sample}) and standard ($R_{standard}$). Vienna Pee Dee Belemnite (for C) and atmospheric nitrogen gas (for N) were used as international reference standards. The analytical precision for both C and N isotope measurements was < 0.2‰.

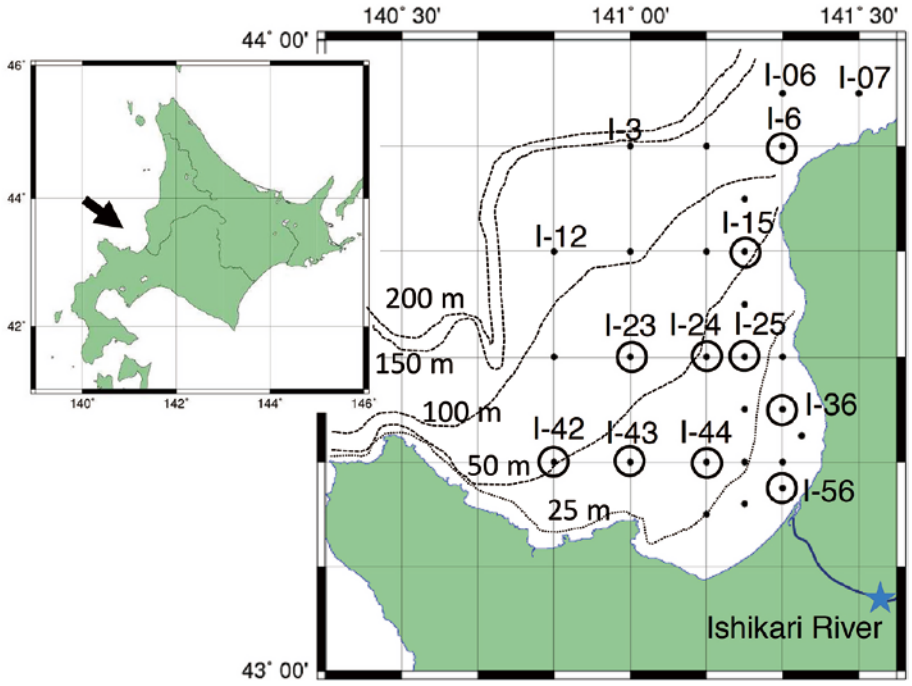

Fig. 1. Map showing the sampling stations at Ishikari Bay. The stations with a circle indicate where the sediment core was sampled. The star in the Ishikari River indicates Ishikari Ohashi where the river water monitoring was conducted.

^{137}Cs, ^{210}Pb, and sedimentation rate

Sediment samples were dried at 60°C for more than 24 h, and ground with a mortar and pestle. A well-mixed sediment sample was put in a styrene container for three weeks to attain a radioactive equilibrium. Gamma activity was measured using an ultra-low background Ge semiconductor detector and a multichannel analyzer (MCA-7700, SEIKO EG&G). Distributions of ^{137}Cs in sediments show a typical fallout peak in 1963, due to their emission to the atmosphere by nuclear bomb experiments in that time period (Peirson, 1971). Thus, a layer showing a ^{137}Cs peak was identified as having sedimented in 1963. Assuming a constant sedimentation rate since then, the rate was calculated from the depth and elapsed time. Sedimentation rate was calculated based on the excess ^{210}Pb profile applying CIC (Constant Initial Concentration) and CRS (Constant Rate of Supply) models (Appleby and Oldfield, 1978). The excess ^{210}Pb was calculated by subtracting the background level from the total ^{210}Pb. The background level (originating from ^{226}Ra in the sediment) was assumed to be the ^{210}Pb activity at the deepest layer for each core where the activity becomes constant.

Biogenic Si (BSi)

The alkaline extraction method by Kamatani and Oku (2000) was applied to the BSi measurements in this study. Approximately 10 mg of dried sediment was added into a polypropylene spit with 4 mL of 0.2 M NaOH and extracted Si and Al at 100°C for 40 min. Then, the extracts were neutralized by adding 1 mL of 1 M HCl and centrifuged at 2500 rpm for 10 min. One mL of the supernatant was dispensed into another spit and then measured for Si and Al concentrations as the first extract. Residue was dried at 60°C and re-extracted Al and Si as described above (second extract). The Si concentration was measured with an auto-analyzer (QuAAtro, Bran-Luebbe) and the Al concentration was measured with a Flameless Atomic Absorption Spectrometry (Perkin Elmer). BSi concentration was calculated by the following equation :

$$BSi = [Si]_1 - [Al]_1 \times ([Si]_2/[Al]_2) \quad (2)$$

where $[Si]_1$ and $[Al]_1$ are Si and Al concentrations in the first extract and $[Si]_2$ and $[Al]_2$ are those in the second extract.

Results

Grain size distribution and water content

Grain size at I-56 and I-6 was mostly < 63 μm, and that at I-36 and I-15 was dominated by 63-125 μm and 250-500 μm, respectively (Fig. 2). The spatial distribution of grain size suggested that the sediment at the western side of the bay was sandy. Water content of the sediment at I-56 and I-6 was high at 0.7 and that at the other stations was lower at < 0.4.

^{137}Cs and ^{210}Pb profiles, and sedimentation rate

^{137}Cs was detected at I-6 and I-56 (Fig. 3). The ^{137}Cs peak was found at I-6 between 18 and 24 cm, resulting in an average sedimentation rate of 0.325 g cm^{-2} y^{-1}. No obvious peak was found at I-56, indicating the ^{137}Cs peak might be present below 39 cm, the deepest layer of the core. Hamahara et al. (2003) reported a clear ^{137}Cs peak in the 19-20 cm layer of I-26 (Fig. 3) and calculated an average sedimentation rate of 0.58 g cm^{-2} y^{-1}.

^{210}Pb decreased exponentially with depth at each station, but the absolute values were different — higher at I-6 and lower at I-56 (Fig. 3). Taking the background level at the deepest layer (38-39 cm) of I-6, the average sedimentation rate calculated by the CIC model was 0.33 g cm^{-2} yr^{-1}. This rate was the same as calculated by the ^{137}Cs profile. The average sedimentation rate by the CIC model at I-56 was 0.65 g cm^{-2} yr^{-1}, almost the identical rate by the CRS model (Fig. 4).

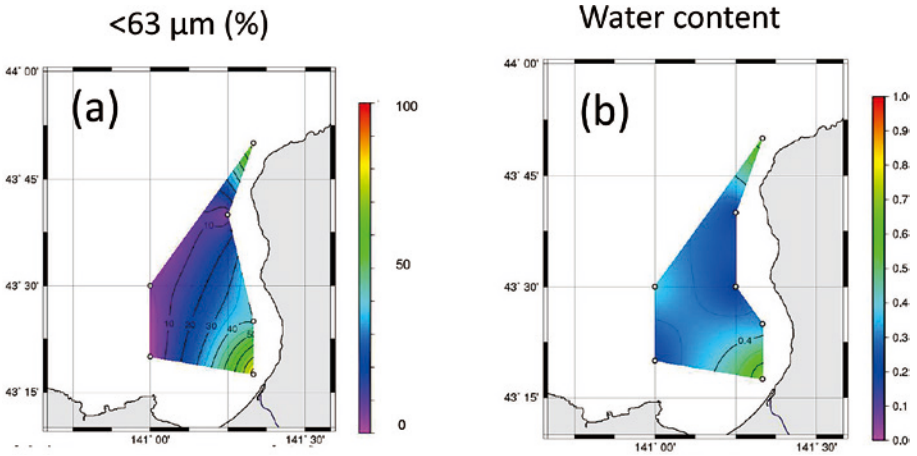

Fig. 2. Contour plots showing (a) the percentage of grain size < 63 μm and (b) the water content of the surface sediment from Ishikari Bay.

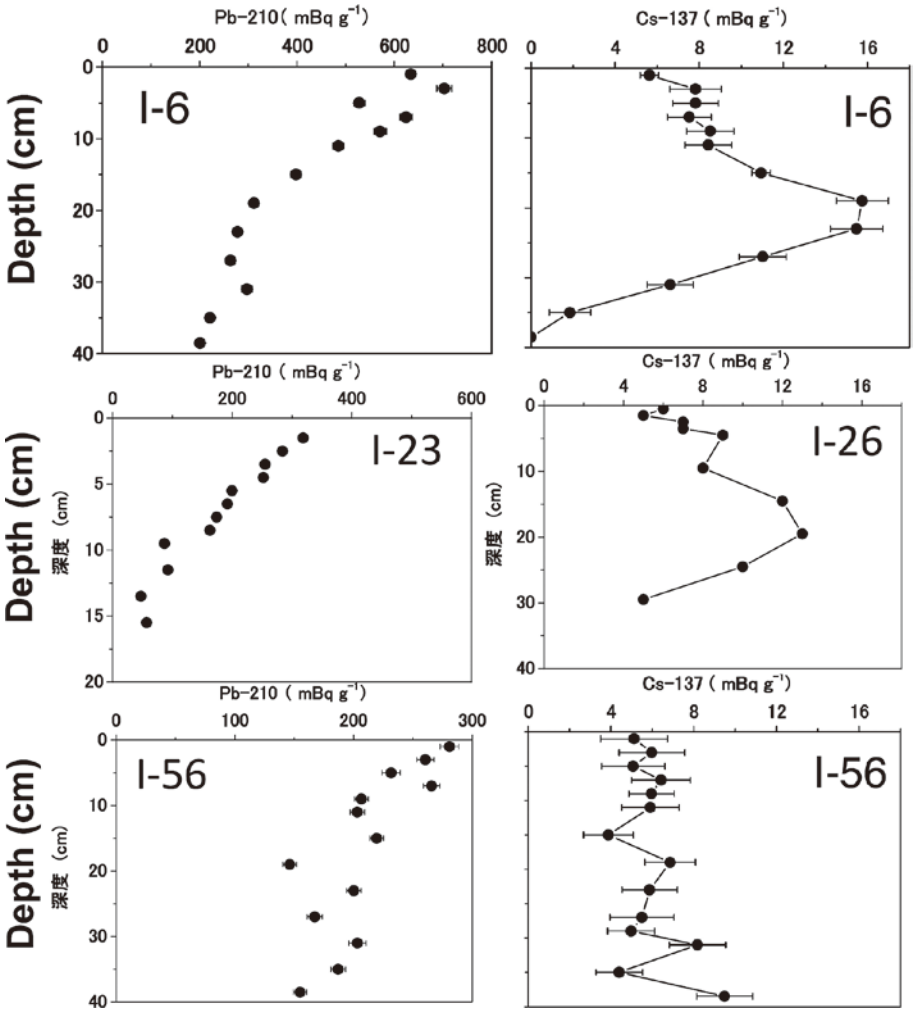

Fig. 3. Vertical distribution of ^{210}Pb and ^{137}Cs activities in the sediment from Ishikari Bay.

TOC and TN

TOC and TN at I-56 ranged from 14.9 to 41.2 mg C g^{-1} and from 1.0 to 2.5 mg N g^{-1}, respectively (Fig. 5). TOC and TN at I-6 ranged from 22.2 to 48.4 mg C g^{-1} and from 1.7 to 2.3 mg N g^{-1}, respectively. A sharp peak in C was observed at I-6 from 1960 to 1970 (18–21 cm layer), coinciding with a peak in TOC : TN of 24. The ratio of TOC : TN increased with depth at I-56, with the two peaks corresponding to sedimentation ages of 1990 and 1974, respectively.

$\delta^{13}C$ and $\delta^{15}N$

The $\delta^{13}C$ values at I-56 were constant at −25.5‰ in the surface layer and dropped to −26‰ in the layer for 1990 (Fig. 6). The $\delta^{13}C$ values at I-6 were relatively constant from −24.6 to −24.3‰. The $\delta^{15}N$ values at I-6 showed a decreasing trend with depth from 3.0‰ at the surface to 2.3‰ in the layer for 1940. The $\delta^{15}N$ values at I-56 showed a fluctuation with depth ranging from 1.8 to 2.6‰.

BSi

BSi content decreased with depth at I-56 from 12.7 mg Si g^{-1} at the surface to 0.3 mg Si g^{-1} at the 29–30 cm depth (Fig. 7). The distribution of BSi at I-26 was relatively constant at 5.1–15.8 mg Si g^{-1} while that at I-6 showed several peaks, ranging from 8.2 to 28.3 mg Si g^{-1}. At I-23, offshore station BSi content was the lowest at 5 mg Si g^{-1} at the surface and under the detection limit below 8 cm depth.

Discussion

The origin of sedimentary organic matter

The endogenous organic matter produced by phytoplankton and the exogenous terrestrial riverine organic matter are the primary candidates for the origin of the organic matter in the sediment of Ishikari Bay. It is important to elucidate the origin of the organic matter in the sediment of the bay for the objectives of this study — reconstruction of the historical change in primary productivity in the bay through the sedimentary record. The $\delta^{13}C$ value is generally higher in

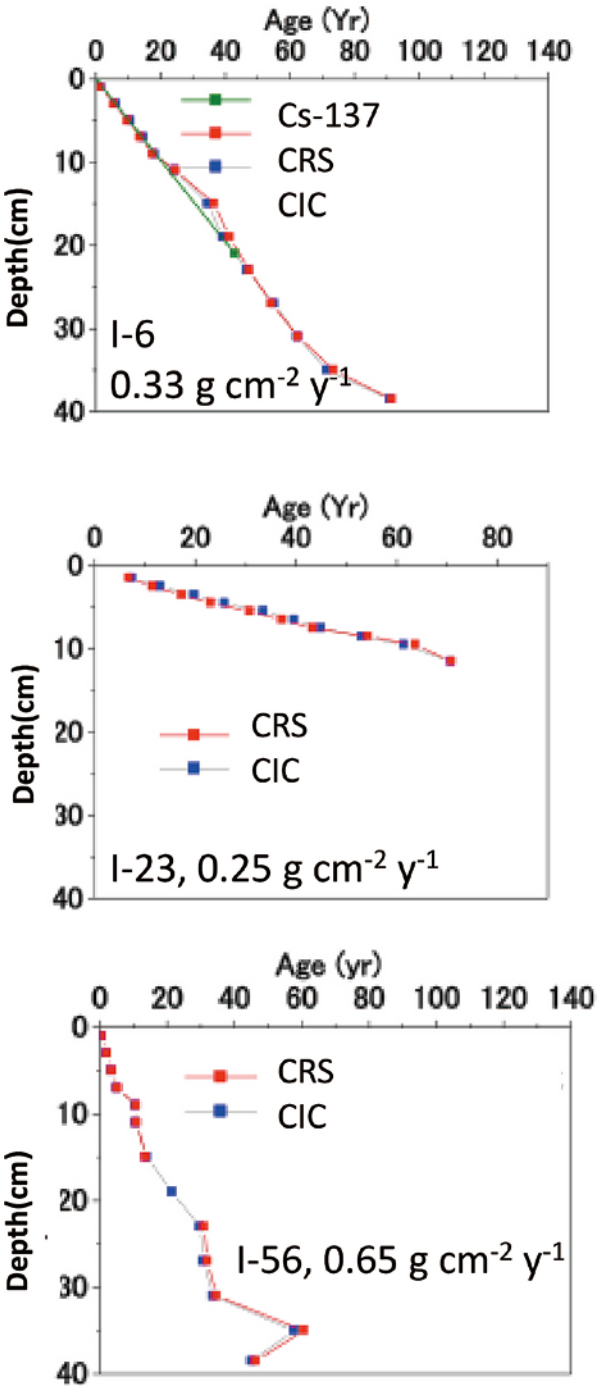

Fig. 4. Relationship between depth and sedimentation age before 2007 estimated from ^{137}Cs, CRS and CIC models.

marine organic matter than in terrestrial organic matter (Thornton and McManus, 1994 ; Cloern, et al., 2002 ; Usui et al., 2006). The δ^{13}C in POM of the Ishikari River ranges from −30.6 to −25.9‰, with the minimum value occurring in the thawing season (Alam et al., 2007). The δ^{13}C in plankton collected by a 100 μm net ranged from −22.16 to −20.72‰ with an average of −21.3‰ (Kudo unpublish.). The contribution of the riverine organic carbon to the surface sediment was calculated taking these values as the end-member of δ^{13}C for the riverine and marine organic carbon. The riverine contributions at I-56 and I-23 were estimated as 44 and 27%, respectively, indicating a higher contribution of the riverine organic carbon at the station nearest to the river mouth compared to the offshore station. The horizontal distribution of δ^{15}N in the surface sediment showed a lower value along with the eastern near-shore stations, coinciding with the distribution of the river plume (Fig. 8). The δ^{15}N of phytoplankton in the bay was about 5‰ (Kudo unpublish.). The δ^{15}N in marine and terrestrial organic matter ranges from 3 to 8‰ and from 0 to 5‰, respectively (Thornton and McManus, 1994 ; Usui et al., 2006). Thus, the lower δ^{15}N at I-56 seems influenced by riverine organic matter.

Historical change in organic matter concentration in the sediment core

The variation of TOC and TN concentrations at I-56 was relatively large, with the peak TOC concentration occurring in the 1970s (Fig. 5). The TOC : TN ratio was high at > 20 in the 1970s and decreased to the present value of about 12. Similarly, the TOC : TN ratio at I-6 showed high values in between the late 1950s and early 1970s. The same trend is observed at I-26 (Hamahara et al., 2003). They explain that the high C : N ratio in this layer originates from peat that was exposed to land surface due to the exploitation of land in the catchment area of the Ishikari River and delivered to the bay by the frequent floods of that time period. The decrease in C : N ratio after the 1970s is also explained by the decrease in floods due to the improvement of the river bank and flood management system.

The δ^{13}C and δ^{15}N in peat obtained from Hokkaido ranged from −29 to −28‰ and from 1 to 2‰, respectively (Nagao pers. comm.). The δ^{15}N in the I-6 core showed low values of 2.2‰ in between the late 1950s and early 1970s, suggesting the influence of peat from the catchment area of the Ishikari River.

Historical change in diatomaceous primary productivity estimated from the BSi content in sediment

BSi content in the core increased with the sedimentation age at I-23 and I-56 while it showed no apparent trend with fluctuations at I-26 (Fig. 7). BSi content at I-6 showed an increasing trend with several peaks in 1944, 1963, and 1982. The influence of the Ishikari River discharge at I-6 is apparent only in the spring thaw season or at the time of high discharge after a heavy rain event because the station is > 50 km from the river mouth (Agboola et al., 2009). Thus, these sharp peaks may relate to a temporal enhancement of the BSi productivity due to frequent rain events.

The loss of BSi due to dissolution in the sediment with time has to be considered using the BSi content to estimate the historical change in the diatomaceous primary productivity. The BSi content in the sediment generally

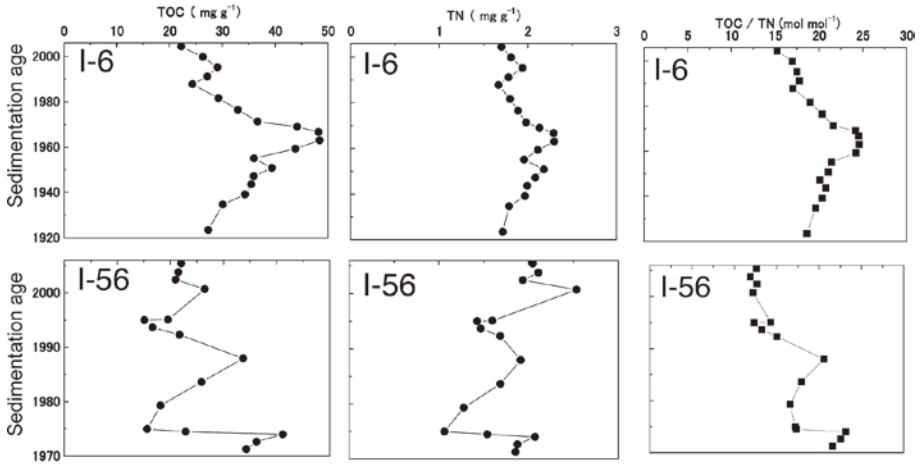

Fig. 5. Relationship between sedimentation age and TOC, TN, and TOC/TN in the sediments for I-6 and I-56.

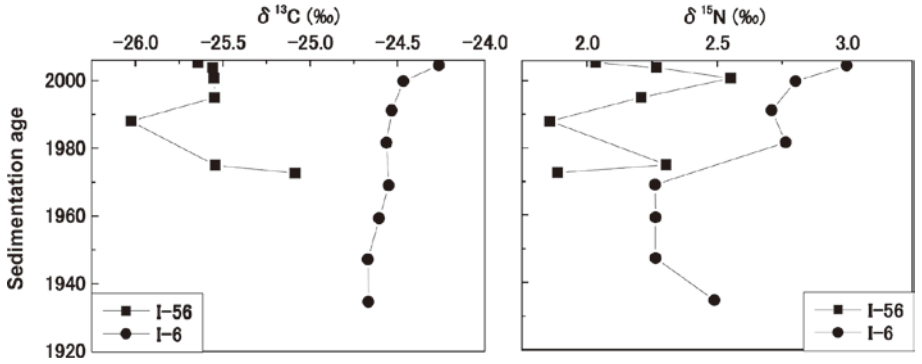

Fig. 6. Relationship between the sedimentation age and the $\delta^{13}C$ and $\delta^{15}N$ in the sediments for I-6 and I-56.

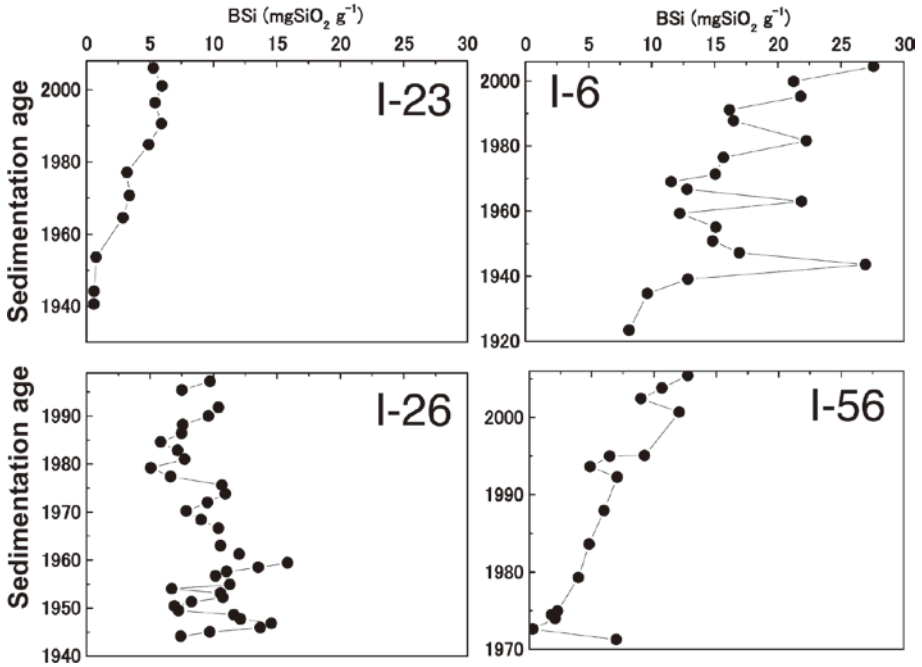

Fig. 7. Relationship between the sedimentation age and the BSi content in the sediments for I-23, I-6, I-26, and I-56.

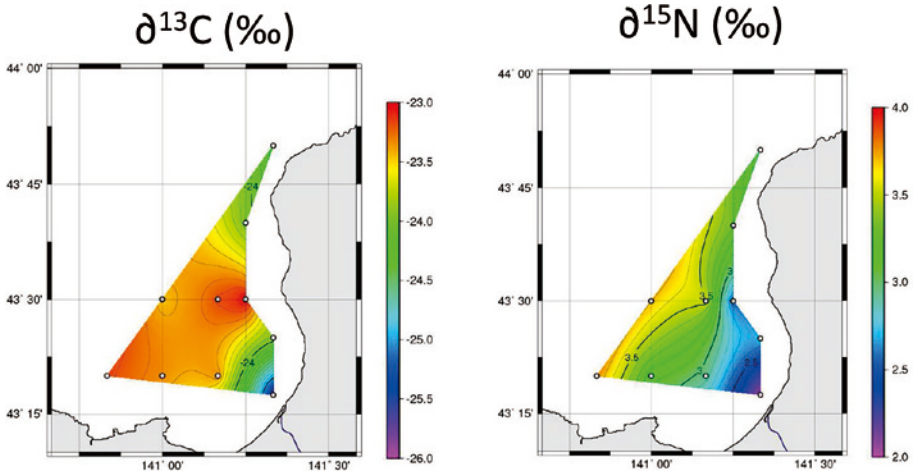

Fig. 8. Contour plots showing the (a) $\delta^{13}C$ and (b) $\delta^{15}N$ of the surface sediment in Ishikari Bay.

decreases exponentially with time (Khalil et al., 2007 ; Kamatani and Takeda, 2007). In this study, the initial BSi content was reconstructed assuming the dissolution rate follows a first order reaction :

$$A(x) = A_0 \exp(-\lambda x) \quad (3)$$

where A(x) is the BSi content in the layer x years before 2007, A_0 is the initial BSi content, and λ is a dissolution rate constant.

The λ is estimated from the BSi profile at I-6. The BSi production rate was assumed to be constant with time, because the environment for the BSi production at I-6 was assumed to be unchanged during the time period considered. The estimated λ value was 0.0086 y^{-1} (Fig. 9). Using this value and equation (3), the initial BSi content for each layer at I-26 and I-56 was reconstructed (Fig. 10). The initial BSi at I-56 was lowest in the 1970s and gradually increased up to the present, suggesting primary productivity by diatoms increased up to the present. Because this place is close to the Ishikari River mouth, this increase seems to reflect the historical change in the nutrient flux from the river. However, the river discharge and TN concentration (i.e., nutrient flux) have apparently not changed since 1973 (Fig. 11). On the other hand, the transparency of the river water has increased dramatically since the late 1970s (Fig. 12). Primary productivity in the Ishikari River plume is limited by light availability due to a high attenuation by suspended particles, not nutrients (Agboola et al., 2009). Thus, the increase in the initial BSi content toward the present layers of the area near the river mouth may be attributable to the decrease in the riverine suspended particle loadings, resulting in relieving light limitation. The improvement of the river bank by construct-

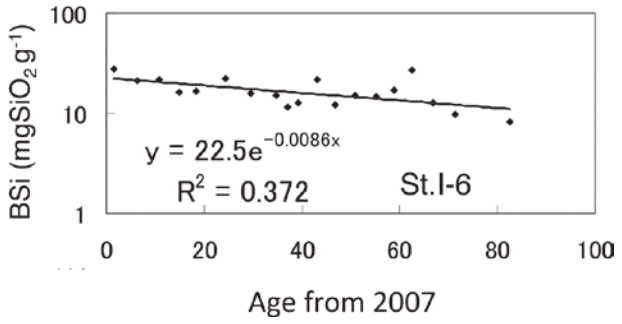

Fig. 9. Plots of the sedimentation age from 2007 vs the BSi content (log scale) for I-6.

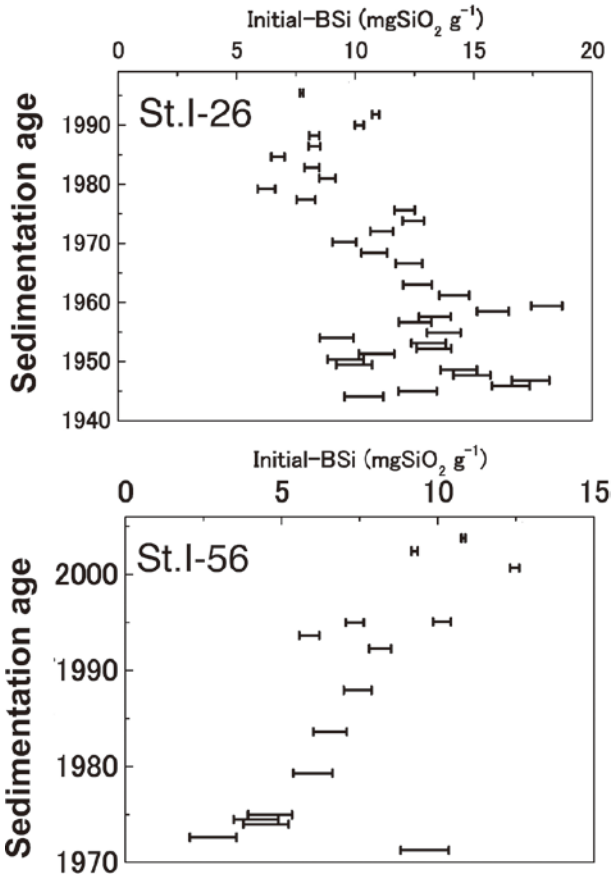

Fig. 10. Relationship between the estimated initial BSi and the sedimentation age for I-26 and I-56.

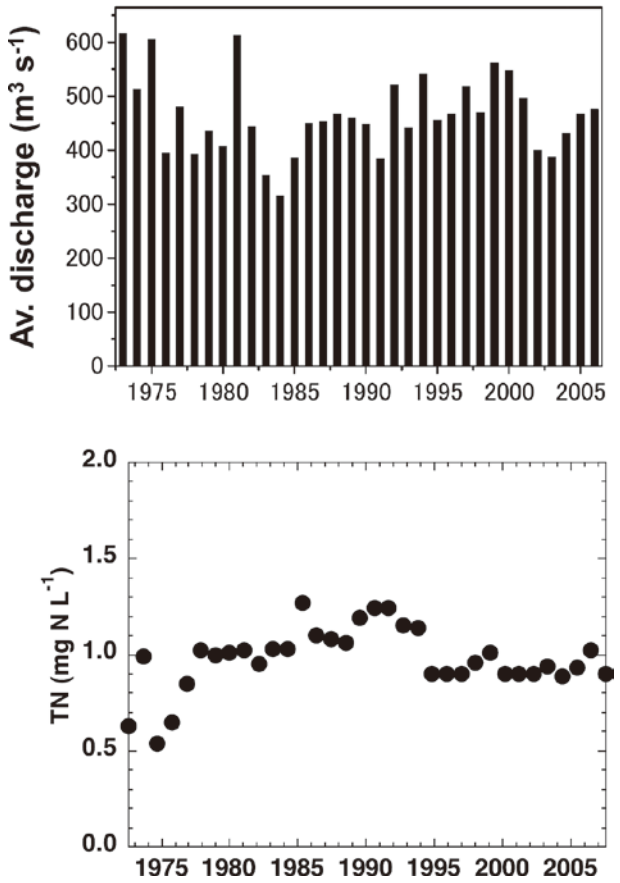

Fig. 11. Historical change in (a) the average discharge and (b) the total N concentration in the Ishikari River. Data were obtained from the data base of Ministry of Land, Infrastructure, Transport & Tourism (http://www1.river.go.jp). Sampling point : Ishikari Ohashi, Data : averaged from monthly data.

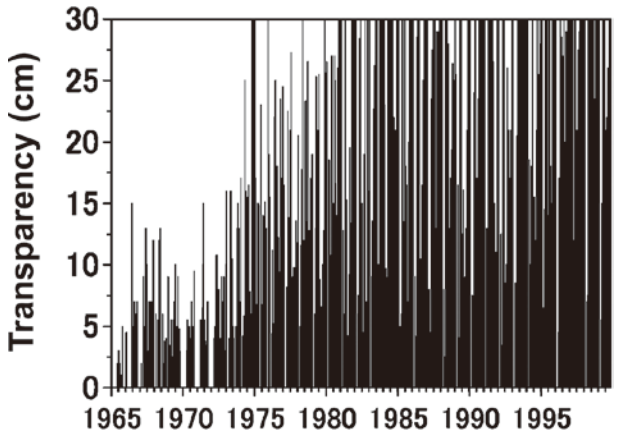

Fig. 12. Historical change in transparency in the Ishikari River. Data were obtained from the data base of Ministry of Land, Infrastructure, Transport & Tourism (http://www1.river.go.jp). Sampling point: Ishikari Ohashi. Data : averaged from monthly data. Transparency ranged from 0 to 30 cm.

ing the revetment walls seemed to lead to a decrease in suspended particles in the river water. The initial BSi at I-26 showed higher values in between the 1940s and 1960s, indicating that primary productivity by diatoms was higher than at present. This place is about 30 km from the river mouth, thus light limitation may not be a major factor because most of the riverine suspended particles sink below the euphotic zone within 10 km from the river mouth (Agboola et al., 2009). The increase in nutrient flux from the Tsushima warm current seems a plausible explanation (Yoshida et al., 1977)

Sepúlveda et al. (2005) reported primary productivity fluctuations reconstructed from the sediments in southern Chile using BSi and other productivity proxies. They suggest the influence of rainfall on the fluctuation at a local scale. Li et al. (2015) reported on the most recent 80 years of sediment records for the Changjiang River Estuary. The records have reconstructed the historical change in pollution since the 1950s and the recovery after the 1970s.

In conclusion, the sedimentary record of organic matter and BSi content could be used to reconstruct the historical change in primary productivity and the riverine influence in coastal areas.

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