EXPRESS LETTER

Apparent increase in Mn and As accumulation in the surface of sediments in Lake Biwa, Japan, from 1977 to 2009

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An apparent temporal increase in Mn and As in a thin surface layer (*ca.* 2 cm) of sediments in Lake Biwa, Japan, was observed by comparing depth profile data from 1977 and 2009. By our estimation, several thousand tonnes of Mn and a few hundred tonnes of As newly accumulated during the 32 years to 2009. Given various methodological concerns and geochemical factors associated with Mn and As dynamics, this phenomenon is believed to have been caused by increased Mn and As influxes to the lake rather than by redistribution induced by the intra-annual decrease in the level of dissolved oxygen. Mass balance calculations indicated that it is unlikely that the recently accumulated quantities of Mn and As were supplied via rivers as dissolved phases; rather, ground-water is the more likely source of these quantities. Further monitoring surveys will be important for assessing the environmental impact of this temporal change.

Keywords: Lake Biwa, manganese, arsenic, temporal variation, environmental change

INTRODUCTION

Accumulation of redox-sensitive elements, such as Mn and As, in surface sediments has been reported from various lakes around the world (Davison, 1993). Lake Biwa, the biggest lake in Japan, is a typical example. In 1976–1977, the geochemistry of trace elements in Lake Biwa was intensively studied through measurements of 36 trace elements in cored sediments collected from 24 stations in the northern basin of the lake (Takamatsu, 1985). Clear Mn and As enrichment within a thin surface layer (<2 cm) was observed in that survey. The enriched layer was possibly formed through precipitation of MnO_2 and adsorption of arsenate, which diffused from deeper sediments as a more mobile phase, in the presence of dissolved oxygen (DO) (Takamatsu, 1985).

In June and December 2009, we investigated the trace element profile in the sediments from seven stations in the northern basin to determine the cycling of trace elements under different DO conditions (Itai *et al.*, 2012). However, quite apart from seasonal variations, we found a clear increase in Mn and As levels in the enriched layer, compared with 1977. Six of the seven stations investigated (B, C, D, E, F and G) are close to the spots (Y, X,

L, G, T and E) investigated in 1976–1977 (Fig. 1), and in five of these, a clear increase in Mn was observed in the surface sediments; an increase in As was observed in all stations (Fig. 2). The thickness of the enriched layer was 2–6 cm. As both this study and a previous study by Takamatsu (1985) expressed concentrations on a dry weight basis, comparison of these data is meaningful. Given the magnitude of the apparent increase in Mn and As since 1977, it is important to clarify the source of these elements. Unlike other trace elements, Mn and As in cored sediments are strongly affected by diagenetic remobilization. Hence, various factors have to be considered when comparing depth profiles between years. In this study, we first clarified various methodological concerns to compare the results between 1977 and 2009. Following this validation, we made some assumptions on the sources of these elements using available geochemical data.

MATERIALS AND METHODS

The sampling method was described in a previous report (Itai *et al.*, 2012). Briefly, sediment cores and lake water samples were collected from seven stations in the northern basin in June and December 2009. Approximately 30 cm of sediment core was collected in an acrylic column (internal diameter (ID) = 10 cm) fitted to a sedi-

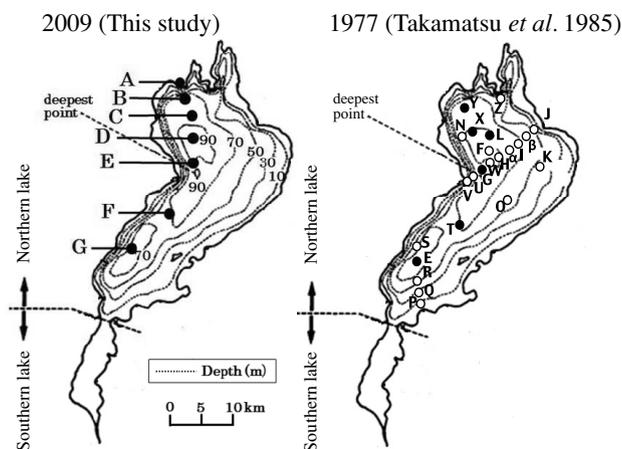*Corresponding author (e-mail: itai@sci.ehime-u.ac.jp)

Fig. 1. Sampling stations in this study and Takamatsu (1985). Solid circles show the stations that were used to compare the depth profiles of Mn and As in the two studies.

ment core sampler (Rigosha, Tokyo, Japan). The sediment cores were sliced into 5 mm sections within a day of sampling. The samples were freeze-dried, ground, digested with concentrated HNO_3 and HF in a microwave oven (Ethos D, Milestone General, Italy) and analysed by Inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500cx, Agilent Technology, Tokyo, Japan).

The cored sediment at station D, collected in December 2008, was dated using ^{210}Pb and the constant initial concentration dating model (Robbins and Edington, 1975). The ^{210}Pb dates were verified using the ^{137}Cs activity peak (Roberts, 1998).

Statistical analysis was performed using the data analysis tool contained in the KaleidaGraph software package (Hulinks, Inc., Tokyo, Japan). The Mann–Whitney non-parametric test was used to detect statistically significant differences between the two groups. A value of $p < 0.05$ was considered significant.

RESULTS AND DISCUSSION

Accuracy and precision of measurements

When comparing data sets, accuracy and precision are of primary concern. We used acid digestion by the microwave system using a mixture of HF and HNO_3 followed by the determination of trace elements by ICP-MS. The certified reference material of marine sediment (PACS-2), provided by the National Research Council Canada, was always measured alongside each set of samples. The difference in results relative to the certified value was 91% to 118% for Mn (mean 106%, $n = 7$) and 105% to 126% for As (mean 118%, $n = 7$). The positive systematic error for As is possibly derived from differences in the sensitivity of As species during ICP-MS analysis
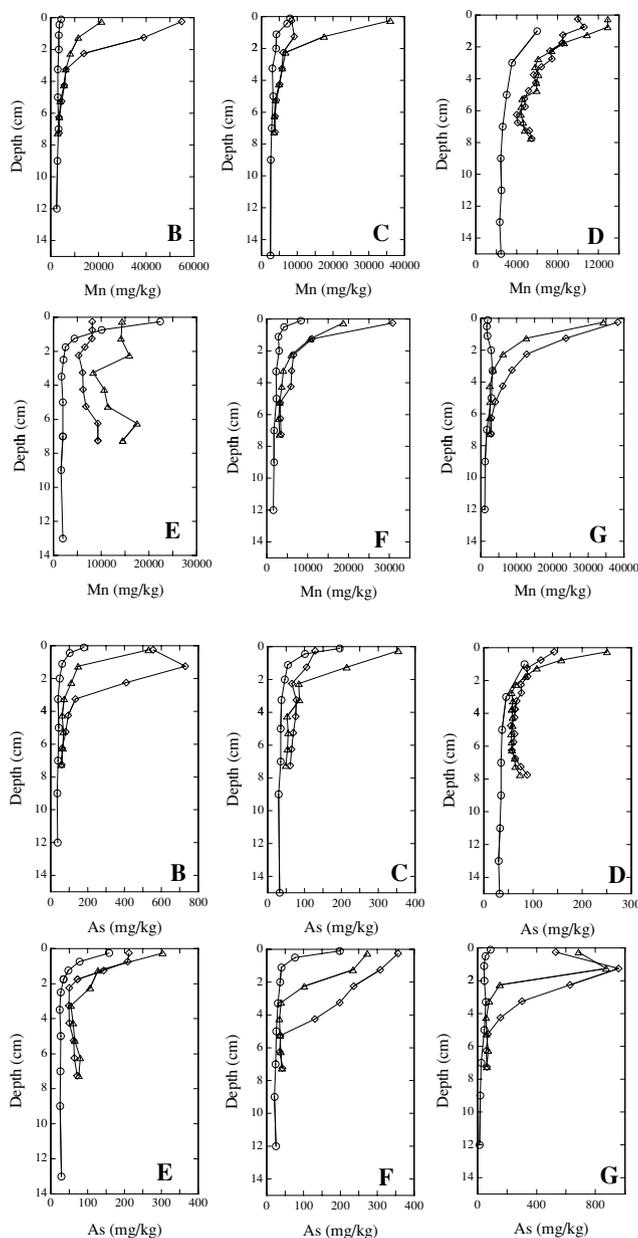

Fig. 2. Comparison of the depth profiles of Mn and As in the sediment between 1977 (open circles: XRF results by Takamatsu, 1985) and 2009 (ICP-MS results: open rhombuses, June; open triangles, December). Samples used in Takamatsu (1985) were collected in November 1977 (B, C, F), April 1977 (D, E), and August 1976 (G). The sampling depth of station B, C, D, E, F, and G were 78, 89, 91, 98, 67, 73 m, respectively.

(Narukawa et al., 2007). Although this effect is not negligible, the degree of this effect is generally <10% when using He as collision gas. Furthermore, duplicate measurements of these elements in core samples indicated that reproducibility was generally within ±5%. Hence, we regard the results of our sediment analysis as acceptable for comparison with previous data after correction for

systematic error(s). Takamatsu (1985) cross-checked de-structive and non-destructive methods in their experiments. In their study, they used atomic absorption spectroscopy (AAS) after complete acid digestion and X-ray fluorescence spectroscopy (XRF). The difference in Mn content between AAS and XRF (AAS–XRF) was 5.14 ± 12.5% (2s). In the case of As, they used XRF and neutron activation analysis (NAA). The difference in As content between XRF and NNA (XRF–NAA) was –4.73 ± 12.0% (2s). Given the range of error, the results of Takamatsu (1985) are acceptable for comparison.

Effect on diagenetic remobilization

Given that sediments are continuously supplied to aquatic systems, the sedimentation rate also should be considered. ^{210}Pb dating was applied to a core recovered from station D in 2008. The mass accumulation rate of the sediments was found to be 0.15 g/cm^2/yr, with an average sedimentation rate of 3.6 mm/yr. This is consistent with the mass accumulation rates determined by other studies, which varied in the range 0.01–0.22 g/cm^2/yr (Kamiyama *et al.*, 1982; Taishi and Okuda, 1989; Otsuka *et al.*, 2001; Tsugeki *et al.*, 2003; Minami *et al.*, 2005). According to the comprehensive data table provided by Taishi and Okuda (1989), the general ranges of accumulation and sedimentation rates were 0.035–0.072 g/cm^2/yr and 1.4–2.3 mm/yr, respectively. Based on these estimates, the sediments deposited in 1977 would have been 4.6–7.3 cm below the surface in 2009. If the peaks observed in 1977 were not moved as a result of the diagenetic process, the peaks should have appeared at around 4.6–7.3 cm. However, these peaks did not appear, and the Mn and As levels reported in the present study are mostly background levels below 6 cm except for stations D and E, indicating that Mn and As have continuously moved upwards as a result of the diagenetic process (Fig. 2), as suggested in previous studies (Takamatsu, 1985; Kawashima *et al.*, 1988). In other words, Mn and As are of natural origin and their accumulation has been caused by the upward diffusion of reduced species (Mn^{2+} and arsenite) and subsequent oxidation in the surface sediments (Balzer, 1982; Balistrieri *et al.*, 1992). That this mechanism occurred is partly supported by our solid-phase speciation approach (Itai *et al.*, 2012), which suggested that the dominant oxidation state of As in the enriched layer was arsenate, whereas arsenite becomes stable in deeper layers (Itai *et al.*, 2012). Although MnO_2 was not always detected even in the top sediment layer (0–0.5 cm), it was possibly formed in a very thin surface layer. These results are consistent with the proposed natural accumulation scenario. Therefore, comparing the enriched layers on the surface of the sediments of different ages is a reasonable approach.

So far, the reasons for the different trend of Mn between 1977 and 2009 in stations D and E below 6 cm are not clear. Since this is impossible to compare the results in 1977 and 2009 in exactly same location, it cannot be ruled out that inconsistent trend below 6 cm is due to spatial heterogeneity. Another explanation is different speciation of Mn in sediment. While Mn^{2+}, after deposition, could be mobilized by molecular diffusion, formation of secondly minerals such as rhodochrosite ($MnCO_3$) prevented the mobilization of Mn^{2+} from deeper sediment. Although supporting evidence for this hypothesis is insufficient, we have noted oversaturation of rhodochrosite in porewater from stations C–E in 2012 (unpublished data).

Handling of samples

A clear comparison also requires that differences in sampling methods be considered. Both studies used sediment cores but the samplers were different. Takamatsu (1985) used an acrylic column sampler with a 3.5 cm ID; we employed a similar sampler, but with a 10 cm ID. In both cases, contamination of the lower layer by a portion of upper-layer sediments might occur during vertical insertion of the column sampler. If this contamination effect was significant in this study, it could have led to the overestimation of the Mn and As levels in each layer and the finding that the enriched layer had thickened between 1977 and 2009. To avoid the potential disturbance of lateral structures during core recovery, the outer layer of the sediment core (*ca.* 1 cm from inner wall) was removed before the sediment was sliced. Had contamination been the major factor behind the thicker enriched layer in 2009, the Mn and As profiles would likely have been similar. However, the thickness of the enriched layer was often clearly different for the Mn and As concentrations (e.g., station F), suggesting that the cause of the difference between the 1977 and 2009 profiles was not just an artefact.

Seasonal variation

It is possible that the profile change depended on the seasons, given that the DO level at the bottom of the lake is at maximum in spring and at minimum in winter (Yoshimizu *et al.*, 2010). Lake Biwa is a monomictic lake and vertical mixing occurs annually during winter. The minimum DO level is generally observed just before the vertical mixing event, i.e., December to February. The sampling by Takamatsu (1985) was performed in August 1976 (station E) and in April (stations L, G) and November 1977 (stations Y, X, T), whereas our samples were taken in June and December. In our samples, the DO level at the bottom of each station was always higher in June than in December (Itai *et al.*, 2012). Hence, we expected that the lower degree of Mn accumulation in December than in June could be attributable to the progress of reductive dissolution during low DO levels (Table 1). However, the Mn and As levels in the enriched layer were

Table 1. pH and DO levels in the water collected from 1 m above the sediment surface in June and December 2009

|	pH	DO (mg/L)		pH	DO (mg/L)
Station B			*Station E*		
June	7.8	5.4	June	7.8	7.4
December	7.8	3.7	December	7.9	4.7
Station C			*Station F*		
June	7.8	6.0	June	8.0	8.3
December	7.8	2.4	December	—	—
Station D			*Station G*		
June	7.8	6.7	June	7.9	7.8
December	7.8	3.7	December	—	—

Fig. 3. The enrichment factors of Mn and As vs. depth of the lake floor in 1977 and 2009. The results of each station were specified in the plot of 2009.

not always higher in December (Fig. 2). Besides, the results in both seasons of 2009 were clearly higher than in 1977 except for station C in June 2009, suggesting that seasonal variation was not the primary factor behind the large difference between 1977 and 2009.

Spatial variation

Finally, spatial variation should be considered. If the increase in Mn and As was not observed in samples from the entire lake, we would not be able to confirm the presence of a temporal increase in the influxes of these elements into the lake, and redistribution of these elements within the lake could have another explanation. Mn and As apparently increased in five and six of the six stations, respectively. However, the degree of enrichment differed among the locations. The most notable increase was observed at stations B, F and G. These stations are located in relatively shallow areas (e.g., 67–78 m). In contrast, the enriched layer was not observed in station E (98 m), which is the deepest part of the northern basin. To compare this spatial variation with that in 1977, the surface enrichment factor (EF) was defined as follows.

$$EF_{Mn} = \text{average Mn in 0–2.5 cm/average Mn below 2.5 cm.}$$

$$EF_{As} = \text{average As in 0–2.5 cm/average As below 2.5 cm.}$$

The relationship between EF_{Mn}, EF_{As} and water depth indicated apparently different trends. EFs increased with increasing water depth in 1977, whereas peak values of EFs were observed at around 70 m in 2009 (Fig. 3). This shift suggested a possible redistribution of Mn and As from deeper to shallower regions. This is likely attributable to the intra-annual decrease in the DO level in the deep part of the northern basin (Yoshimizu *et al*., 2010). In contrast to station E in this study, the enriched layer was observed in the deepest part (>90 m) in the report by Takamatsu (1985) possibly due to higher DO level than 2009. When released from the enriched layer, Mn is oxidized in the DO-rich depth followed by the return to the
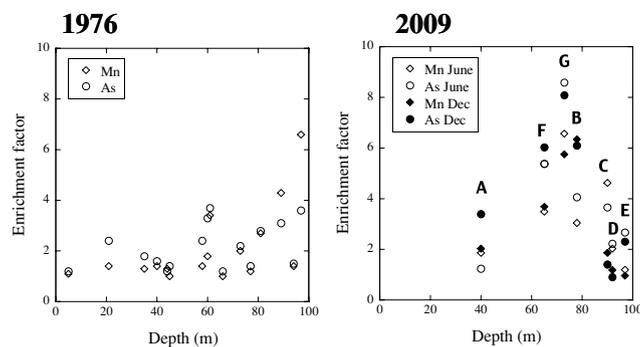
sediments. Through this process, Mn likely accumulates more in an oxic than in a reducing region. Hence, the redistribution of Mn from deep to shallow areas is plausible. However, quite large increase in stations B, G, and F seems difficult to explain by just redistribution from deeper areas.

In contrast to Mn, the disappearance of the enriched layer was not observed for As. This is attributed to the difference in the standard redox potential (at 25°C) of MnO_2/Mn^{2+} (+1.23 V) and As^V/As^{III} (+0.56 V) (Aylward and Findlay, 2002). In fact, the peak of As appeared 1.5 cm below the surface at stations B and G (Fig. 2), suggesting that mobilized As from a deeper layer had been trapped in the depth because of the oxidation of arsenite to arsenate followed by the adsorption onto Fe oxyhydroxide (Dixit and Hering, 2003). The previous report showing that less As than Mn was mobilized into the water column from the sediments is consistent with the proposed process (Sugiyama *et al*., 2005; Itai *et al*., 2012). Hence, it is difficult to explain large increases in As at all stations using the redistribution hypothesis; therefore, a temporal increase of As flux to the lake should be considered.

Given that a redistribution process alone is not a plausible explanation for the large increases in Mn and As in the enriched layer, there must be some other processes that; increase Mn and As fluxes to the lake. To confirm the presence of a temporal increase in whole lake, we applied a statistical method. The Mann–Whitney unpaired non-parametric test using the geometric mean concentration of the upper layer (0–2.5 cm) measured by AAS in Takamatsu (1985) at 20 stations and the present results (corrected by dividing the Mn and As results by a factor of 1.18 and 1.26, respectively, to account for maximum overestimation due to analytical artefacts) at 7 stations (A–G in June and December 2009) indicated *p* values of Mn and As lower than 0.0001. Hence, the presence of

Table 2. *Parameters used for the estimation of Mn and As in enrich layer (EL)*

Parameters			Remarks
Surface area of lake bottom (<20 m)	458	km^2	Takamatsu (1985)
Thickness of EL	5	mm	Arbitrarily defined
Mean concentration of Mn in EL	10000	mg kg^{-1}	Data from this study
Mean concentration of As in EL	200	mg kg^{-1}	Data from this study
Density of dry sediment	2.62	g/cm^3	Takamatsu (1985)
Water content	78	%	Takamatsu (1985)
Bulk density	1.36	g/cm^3	Computed from dry density and water content
Volume of EL	5.0×10^{11}	cm^3	Computed from bulk density and thickness of EL
Mass of EL	6.78×10^8	kg	Computed from bulk density and volume of EL
Mass of total Mn in EL	1.2×10^8	mol	Equivalent to 6800 ton
Mass of total As in EL	2.7×10^6	mol	Equivalent to 20 ton

Table 3. *Budget of dissolved elements in Lake Biwa*

Basic parameters			
North basin			
Surface area	616	km^2	Somiya (2000)
Mean depth	44	m	Somiya (2000)
South basin			
Surface area	58	km^2	Somiya (2000)
Mean depth	3.5	m	Somiya (2000)
River input	2.8×10^9	m^3 year^{-1}	Somiya (2000)
Rain input	1.2×10^9	m^3 year^{-1}	Somiya (2000)
Groundwater input	0.2–1.3×10^9	m^3 year^{-1}	Somiya (2000)
River output	4.9×10^9	m^3 year^{-1}	Somiya (2000)

Badget of dissolved Mn and As (mol)			
	Mn	As	
Inventory	1.0×10^5	2.6×10^5	Mito *et al.* (2004)
Input rain	1.1×10^5	3.7×10^3	Mito *et al.* (2004)
Input river	1.9×10^6	4.2×10^4	Mito *et al.* (2004)
Input rain + river	2.0×10^6	4.6×10^4	Mito *et al.* (2004)
Output river	1.6×10^5	5.7×10^4	Mito *et al.* (2004)
Input–output	1.8×10^6	-1.1×10^4	Mito *et al.* (2004)

temporal increases in Mn and As in whole lake is statistically supported.

Given the various methodological concerns discussed above, we have confirmed the apparent increase of Mn and As in Lake Biwa surface sediments. Hence, the cause of this temporal increase in Mn and As influxes to the lake should be investigated.

Potential sources

To explain the increases in Mn and As influxes to the lake, the source and pathways of these elements must be clarified. To determine the source, we performed simple mass balance calculations. First, we estimated that the total mass of Mn and As in the enriched layer increased after 1977. A similar estimation was made by Takamatsu (1985); we followed the same assumptions to facilitate comparison (Tables 2 and 3). To determine the average mass accumulated after 1977, the geometric mean concentrations of Mn and As in the upper (0–2.5 cm) and lower (5–7.5 cm) layers were calculated. The concentrations of recently accumulated Mn and As were determined as the difference in the geometric mean concentrations between the upper and lower layers. The average concentrations of the recently accumulated Mn and As at the seven stations were 8280 and 190 mg/kg, respectively. The estimated total mass of Mn in the enriched layer was 1.9×10^9 mol (*ca.* 10000 t) and that of As was 3.1×10^7 mol (*ca.* 240 t) when we considered only the regions at a depth below 20 m (*ca.* 458 km^2) when accounting for the total surface area. These levels are higher than the estimates by Takamatsu (1985), which were 4350 and 73 t of Mn and As, respectively. Hence, several thousand tonnes of Mn and a few hundred tonnes of As have been supplied to the bottom of the lake since 1977.

Given the average composition of the dissolved trace elements in Lake Biwa provided by Mito *et al.* (2004), it seems impossible that the large amounts of Mn and As were supplied from the overlying lake water. Their re-port suggested that river flow is the dominant source of Mn and As in the lake water, with an annual influx of Mn and As through the river and rainfall of 2.0×10^6 and 4.6×10^4 mol/yr, respectively (Table 3). Since the outflow of Mn and As was 1.6×10^5 and 5.7×10^4 mol/yr, the net input of these elements was 1.8×10^6 and -1.1×10^4 mol. When these amounts are multiplied for 32 years, the cumulative masses of Mn (5.8×10^7 mol) and As (-3.5×10^5 mol) are much smaller than the 32-year accumulated mass found in this study.

Because of its anaerobic characteristics, ground-water generally contains much higher concentrations of Mn and As than surface water. We analysed the pore water from seven stations in January 2012 and found 1000–12000 μg/L of Mn and 5–110 μg/L of As (unpublished). Given that the estimated influx of ground-water to Lake Biwa is 0.2–1.3×10^9 m^3/yr^{-1} (Somiya, 2000), the cumulative Mn input can be 0.2–1.5×10^9 mol during those 32 years, if we assume that the mean of dissolved Mn in the ground-water is 2000 μg/L (36 μmol/L). Similarly, the cumulative As input was found to be 0.4–2.8×10^7 mol when we assumed that the mean of dissolved As in the ground-water is 50 μg/L (0.67 μmol/L). Since the maxima of the estimates are comparable to the amounts of recently accumulated Mn and As, a likely source of these elements are subsurface materials. However, considering the long depositional history of Lake Biwa, the changes in the influx of Mn and As through ground-water after 1977 should be verified to explain the large increase during the past three decades. A recent increase in ground-water influx or in dissolved Mn and As in ground-water is a possible factor. Recently, using an autonomous underwater vehi-

cle, a curious vent activity was discovered in the northern basin. The nature of this vent is still a matter of debate; it is likely that the number of the vent spots is increasing with time (unpublished). Some other pathways also could be considered, e.g., the large Mn and As release in the southern basin could be due to eutrophication-induced anoxia in 1994 (Sohrin *et al.*, 1997) or to the transport of particulate matter to the northern basin caused by intensive dredging in the southern basin. Although the water flow in Lake Biwa is generally north to south, exchange of water occurs annually by interchanging current. A possible influx from the southern basin should be another focus in future monitoring surveys.

CONCLUSIONS

Based on various methodological concerns and geochemical features, it is concluded that large amounts of Mn and As have accumulated on the surface of lake sediments in Lake Biwa since 1977. Since the Mn and As in the enriched layer are most likely in the form of MnO_2 and arsenate, respectively, these can be reduced to more mobile species, i.e., Mn^{2+} and arsenite (Itai *et al.*, 2012). Because the intra-annual decrease in DO levels has been apparent since the 1960s, a further decrease may have triggered the release of Mn and As into the lake water. Considering the total volume of water in Lake Biwa (27.6 km^3), the concentrations of dissolved Mn and As could reach 3700 and 87 μg/L if all the Mn and As in the enriched layer dissolves and is completely mixed into the lake water. Although such an extreme situation is unlikely, ongoing monitoring of DO and the Mn and As levels is important to safeguard the lake ecosystem and food supply.

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