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Environment Canada

Water Science and
Technology Directorate

Direction générale des sciences
et de la technologie, eau

Environnement Canada

Release of Phosphorus from Sediments in Lake

Biwa

By:

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NWRI Contribution # 01-211

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226
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no.
01-211

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Rejet de phosphore des sédiments dans le lac Biwa - Limnology 2 :119 -- 128.

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Sommaire à l'intention de la direction

Nous avons déterminé que le minéral vivianite (phosphate ferreux) se dissout dans les sédiments du lac Biwa (Japon). Cet lac est en voie d'eutrophisation, et les changements notés dans ses sédiments font partie du problème. À une certaine époque, la formation de ce minéral a dû réduire la disponibilité naturelle du phosphore dans le lac, ce qui a contribué à améliorer la qualité de l'eau. La charge naturelle de fer des eaux souterraines était vraisemblablement la principale source de fer requis par ce mécanisme naturel de protection. La dissolution de la vivianite est facilitée par la charge de soufre dans les sédiments, qui est actuellement de 4 à 5 fois supérieure aux valeurs préindustrielles, ce qui a pour effet de stopper la réaction naturelle de complexation du phosphore. Les pluies acides causées par le soufre constituent un problème local connexe, et on observe des changements marqués dans l'écosystème. Au cours des dernières années, on a noté une colonisation des sédiments de surface par des couches de bactéries du soufre. On n'observe toutefois pas de signes de changement du pH dans les eaux du lac Biwa, probablement à cause de la production d'alcalinité par la réduction du sulfate dans les sédiments. Malheureusement, cet effet tampon dissout aussi le phosphore. Une grande partie de la charge de soufre semble provenir de l'Asie continentale et sa limitation devrait être difficile dans le contexte actuel. Le traitement direct des sédiments est techniquement possible, mais il s'agit d'une technique innovatrice coûteuse. Au Japon, les efforts actuels de remise en état des sédiments utilisent surtout des techniques de dragage, une technique coûteuse et limitée. La profondeur du lac Biwa dépasse 100 m; comme la dissolution de la vivianite est plus rapide en eau profonde, des opérations de dragage dans la partie profonde du lac Biwa, en plus de présenter d'énormes difficultés, exposeraient de la vivianite non altérée à la charge de soufre, qui commencerait à la dissoudre. Bien que nous ayons déterminé la contribution des sédiments à l'eutrophication du lac Biwa, il y a encore des questions sans réponse. Par exemple, quelle est l'ampleur du flux relatif du phosphore provenant des sédiments et des sources externes? Quelle est l'ampleur du flux de soufre provenant de l'atmosphère et d'autres sources? Étant donné que la vivianite est commune dans un grand nombre de lacs, notamment dans le lac Érié, et que l'accroissement de la charge de soufre est un problème mondial, les résultats de ces travaux pourraient bien s'appliquer à un grand nombre de lacs du Canada. Ce projet est financé par le Lake Biwa Research Institute et la Préfecture de Shiga.

Résumé

Deux réactions favorisées par le soufre entraînent l'eutrophication du lac Biwa (Japon). Le minéral vivianite – formé de phosphate fer (II) – se dissout dans les sédiments enrichis en sulfure, ce qui, à certains endroits, donne des concentrations de phosphate supérieures à 3 mg L^{-1} dans les eaux interstitielles. La dissolution du phosphate est évidente dans les profils du phosphore total, où l'on observe des zones de dissolution, ainsi qu'une zone de précipitation dans des sédiments de surface plus oxygénés. Parfois, la réduction du sulfate dans ces sédiments de surface hausse le pH jusqu'à 9,9, ce qui est suffisant pour dissoudre le phosphate de fer (III). Cette libération de phosphore par les sédiments est au moins partiellement responsable de proliférations récentes d'algues bleues.

RESEARCH PAPER

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Release of phosphorus from sediments in Lake Biwa

Received: August 4, 2000 / Accepted: March 19, 2001

Abstract Two sulfur-mediated reactions are resulting in the eutrophication of Lake Biwa, Japan. The iron (II) phosphate mineral vivianite is dissolving in sulfide-enriched sediments that in places results in porewater concentrations of phosphate exceeding 3 mg l^{-1} . The dissolution of phosphate is evident in profiles of total phosphorus where zones of dissolution and a zone of precipitation in the most oxic surface sediments are visible. At times sulfate reduction in these surface sediments results in pH values as high as 9.9, which can dissolve phosphate adsorbed to iron (III). This release of phosphorus from sediments is at least partially responsible for the recent appearance of blue-green algal blooms.

Key words Sediments · Phosphorus · Eutrophication · Lake Biwa · Vivianite

Introduction

Lake Biwa is the largest lake in Japan, contains many endemic species, and is the drinking water supply for about 14 million Japanese. Unfortunately, Lake Biwa is becoming more productive (Hirayama et al. 1993; Tezuka and Nakano 1993). Recent studies indicate that sediment mixing during typhoons results in the release of phosphorus into the water column (Frenette et al. 1996; Robarts et al. 1998). Analysis of sediments from Lake Biwa at different times of the year indicates dissolution of phosphorus associated with in-

creased sulfide and decreased redox potential in summer (Murphy et al. 1998). The rationale for the large dredging program in Lake Biwa to control eutrophication was based on the recognition of sediments as an important source of phosphorus. However, the duration of the beneficial effects of dredging is uncertain (Yoshida 1982). The mechanisms responsible for release of phosphorus from sediments in Lake Biwa are not fully resolved. It appears that the sediments might have lost some of their capacity to retain phosphorus. Without insights into the mechanisms of phosphorus dissolution and precipitation in sediments, effective lake management is difficult.

Tezuka's (1992) analysis of the nutrient budget of Lake Biwa indicated that it was less productive than would be expected from the phosphorus loading that it received. He proposed that the high iron loading enhanced sedimentation of phosphorus and was responsible for the low productivity of Lake Biwa. Probably, the high iron concentrations also minimized sediment release of phosphorus.

Most sediment studies have stressed the importance of iron (III) adsorption of phosphorus (Mortimer 1941, 1971; Williams et al. 1971; Krom and Berner 1981). Iron (III) adsorbs and precipitates more phosphorus than iron (II). Thus, when eutrophication results in sediments becoming more reduced, phosphorus is dissolved and can be released to the surface water (Murray 1995). This scenario is important but overly simplistic, because it ignores important sulfur chemistry, which can greatly influence phosphorus release. Sulfate loading can enhance formation of iron sulfides, leading to iron limitation, phosphorus dissolution, and eutrophication (Smolders and Roelofs 1993).

Although iron (III) reactions control the solubility of phosphorus in the surface sediments, the flux of phosphorus from deeper sediments is probably controlled by vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] formation. Iron (II) is well known to react with phosphorus to form the mineral vivianite, which can be an important sink for phosphorus in lakes. Usually the presence of vivianite is detected indirectly by using geochemical calculations and chemical analyses of sediment extractions or porewaters (Emerson and Widmer 1978), but it has also been identified with microscopic and X-ray

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diffraction methods (Cornwell 1987) and Mössbauer analysis (Manning et al. 1991). It has been demonstrated in lakes (Olsson et al. 1997; Hupfer et al. 1998) and groundwater (Griffioen 1994) that the formation of vivianite is partly controlled by the ratio of iron to phosphate, and that as long as the iron concentration exceeds sulfide formation, vivianite will be stable. The observations that porewater can at times be supersaturated with respect to vivianite without precipitation occurring indicates that vivianite formation and stability in sediments is not completely understood (Boers and Bles 1991).

The release of phosphorus from sediments into the overlying water has been related to physical factors such as currents, waves, storms, and boats. Diffusion is too slow to explain the observed phosphorus release rates. Holdren and Armstrong (1980) observed in laboratory studies that bioturbation had the greatest effect on phosphorus release rates, but other physical forces may be more important. For example, fluxes of phosphorus were shown to be highly dependent on water circulation in Norwegian studies (Skogheim and Erlandsen 1979), and phosphorus release from sediments increased 20- to 30-fold during resuspension events in a shallow Danish lake (Sondergaard et al. 1992). Of course, the luxury assimilation of phosphorus by algae temporarily lying on the sediment surface has the potential to greatly influence both resuspension of phosphorus and growth of algae (Nalewajko and Murphy 1998).

The main intent of the 1997–99 studies was to resolve whether the sediment chemistry was changing and whether it could enhance phosphorus release into the water column.

Methods

Site

Lake Biwa is composed of the south and north basin (Fig. 1). The south basin is shallow (<5m) and eutrophic. Akanoi Bay is an extremely eutrophic part of the south basin. Toxic blooms of *Microcystis* in Akanoi Bay resulted in closure of pearl farms. The north basin is much deeper, up to 104m in places, and much less productive. The north basin is deeper on the western side and contains several sub-basins that differ in depth and water circulation.

North basin sample collection

Sediment samples were collected from the north basin of Lake Biwa in June and September of 1999 (Fig. 1). Positioning was obtained with a differential Global Positioning System. Dissolved oxygen, conductivity, redox potential, and temperature of the water column were measured with a Fine Scale CTD probe. A modified mini box corer was used to collect sediment bulk samples with minimal vertical disturbance of sediments. It was equipped with a removable liner that was placed in a glovebag filled with nitrogen

gas. The top 2cm of sediment was then extruded into plastic freezer bags. The sediment was homogenized, and subsamples were placed in plastic 50-ml centrifuge tubes. The air was displaced from the plastic bags, and the samples were placed in a cooler immediately and frozen the same day. All subsampling procedures were conducted in the glovebag under nitrogen atmosphere. Porewater for nitrate and sulfate analysis was extracted by centrifugation on site for 20min at 3750rpm, immediately placed back into a glovebag with nitrogen, and filtered through 0.45- μ m cellulose acetate membranes in the same glovebag.

Porewater subsamples were frozen immediately for later anion analysis (sulfate and nitrate-N) on a Dionex model 2010i ion chromatograph. The relative standard deviation of the triplicate analyses was typically less than 5% for nitrate and 11% for sulfate. The remaining filtered porewater samples were brought to a pH of 2 with concentrated nitric acid and were then analyzed for iron and manganese by atomic absorption spectrophotometry. The total reactive phosphorus in the acidified porewater samples was measured by the ascorbic acid method 4500-P E (American Public Health Association 1989).

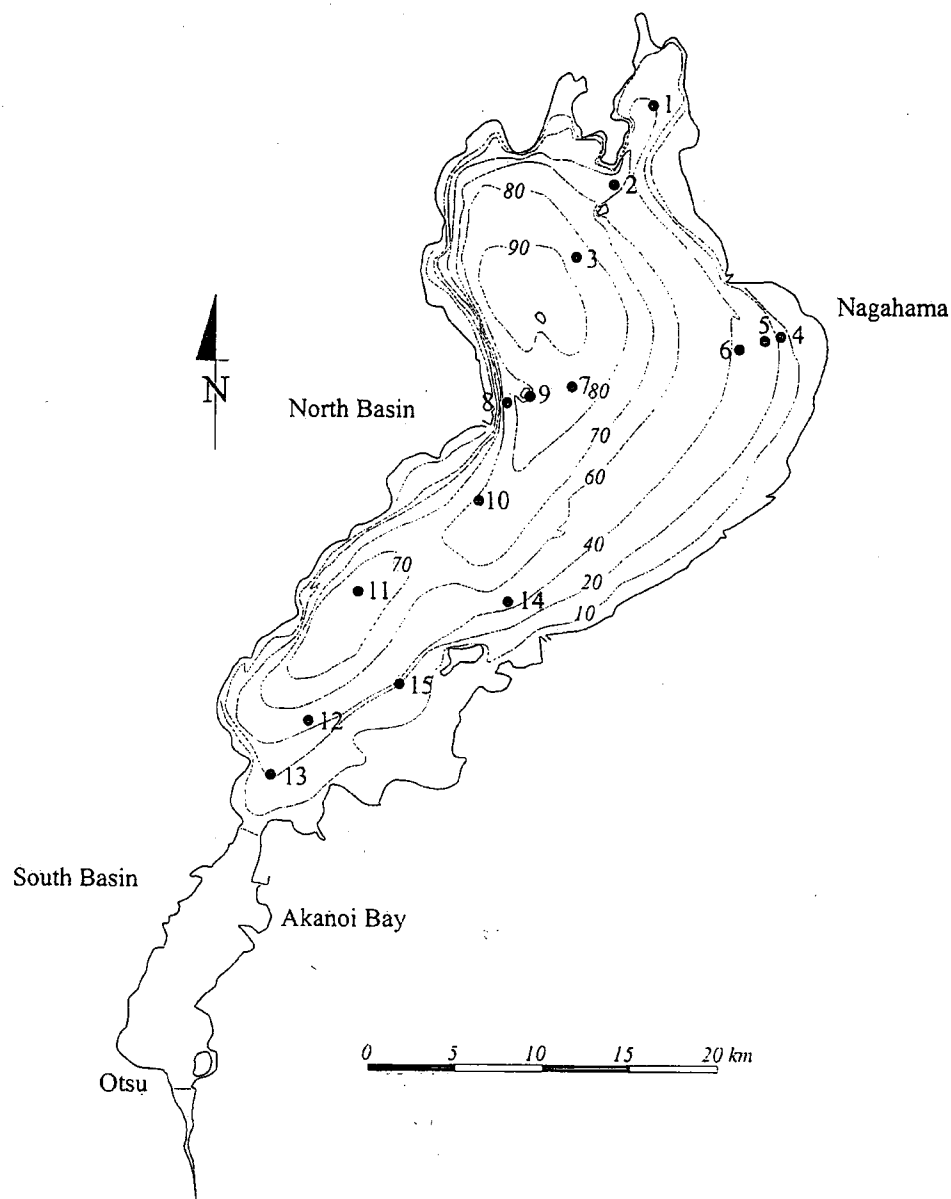
A gravity sediment core was taken at each station, and visual observations were recorded. The core was extruded at 2-cm intervals for the first 10 sections, and the redox potential of each section was measured with an Orion platinum electrode. Core sections were homogenized, and AVS was measured by ion-selective electrodes using a diffusion method (Brouwer and Murphy 1994). Freeze-dried sediments were analyzed by converting the sulfur and carbon content of the sediments into SO_3 and CO_2 , respectively, with a Leco furnace system at 900°C and an infrared detector. X-ray fluorescence, X-ray diffraction, and Mössbauer analysis of iron species in sediments were done with a fully automated Philips PW2400 sequential X-ray fluorescence spectrometer and a Philips PW3710 powder diffractometer, respectively (Rancourt 1994).

Interstitial water samplers (peepers)

Where the depth of water allowed divers to work, diffusion chambers (peepers) were used to collect sediment porewater samples. The peepers were made of two Plexiglas components: a bottom reservoir with six cells of approximately 12ml capacity each and a cover, which were secured together by screws to hold polysulfone dialysis paper (Gelman HT 450) firmly in place over the reservoir. The six cells were arranged in three rows of two cells, separated horizontally by 1 cm and vertically by 0.5 cm. The cover had holes corresponding to the cells to allow diffusion of chemicals from the sediment, across the dialysis membrane, and into the reservoirs containing distilled water. Peepers were prepared to avoid contamination with oxygen, which could affect the analyses. The peepers were filled with deionized distilled water that had been deoxygenated by purging with nitrogen gas for several hours.

Once assembled, the peepers were checked for trapped gas bubbles and bubbled with nitrogen for at least 48 h prior

Fig. 1. 1999 sample stations, north basin, Lake Biwa



to deployment (Hesslein 1976; Rosa and Azcue 1993). Divers quickly attached a surrounding baffle and then inserted the peepers into the sediment with one cell above the sediment-water interface. The baffle acted as a stabilizer to minimize movement of the peeper. Two weeks later, the peepers were removed individually, the porewater was extracted from the cells with syringes, and subsamples were acidified immediately.

Pilot scale treatment in Aka-noi Bay (1997)

In situ treatments took place in two 10-m-square enclosures with a 1-m metal deck around the perimeter. Divers in-

serted the curtain chain 30 cm into the sediments to prevent water exchange between the enclosures and the lake. A water pump was used to fill the enclosures until the sides of the curtain bowed outward, allowing the required clearance for injection and ensuring a sealed container. A walkway was moved to act as a guide for the injector positioning.

The injector was built by the Engineering Services Section of the National Water Research Institute. It was a 1-m-square aluminum plate with internal plumbing to feed the oxidant liquid to 100 rods projecting 17 cm from the bottom of the plate. Each rod had three 0.8-mm holes at 5, 10, and 15 cm from the base of the plate. A peristaltic pump was used to inject 175 kg of calcium nitrate (Murphy et al. 1998).

Results

Total phosphorus in sediments

The concentration of total phosphorus in sediments provides insight into long-term limnological changes. The >80% increase in total phosphorus in the surface (0–2 cm) relative to 18–20 cm of 13 sediment cores in the North Basin (1999, Fig. 2) could represent increased external loading, but the results of the next section indicate some of this surface enrichment reflects mobilization of phosphorus from deeper sediments.

There were other minor suppressions of surface phosphorus in the surface of some cores in Lake Biwa (i.e., near Nagahama City), but these cores were not replicated, and

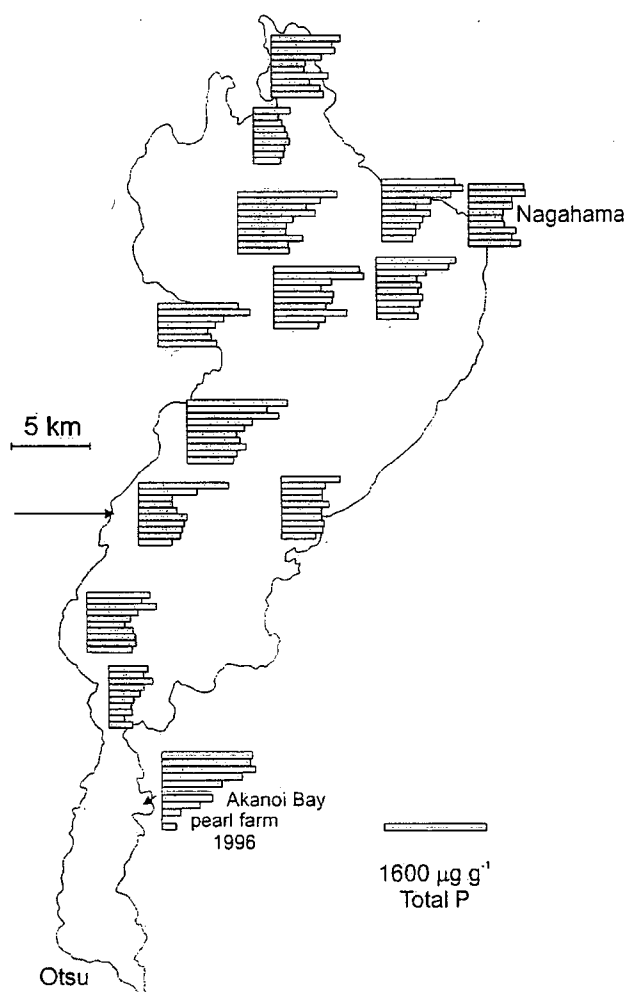


Fig. 2. Depth profiles of total phosphorus in Lake Biwa sediments (2-cm intervals), 1999

the reductions are statistically uncertain. If these minor changes in the sediments were reflecting sediment release of phosphorus, they could represent major impacts on the water column. Minor changes in the concentration of total phosphorus at 10–12 cm, such as at station 11 (see arrow in Fig. 2), also suggest changes in loading or dissolution. In 1997, station 11 had the highest concentration of sulfides observed in the sediments. The AVS concentrations of triplicate samples from station 11 in 1997 are shown in Table 1.

Station 11 appears to be impacted by organic loading from the south basin. The stations further to the south (Fig. 1) are in shallower water, and the loss on ignition (indirect measurement of organic content) decreased from 13.4% at station 11 to 12.9% at station 12 to 9.6% at station 13. AVS changes seasonally and year to year; therefore, a direct comparison of AVS to more stable variables, such as total phosphorus, is difficult. By themselves the decreases in total phosphorus at 6–12 cm at station 11 and near Nagahama could represent a change in external loading or natural variability. However, the data presented in the following section suggest that the decrease indicates dissolution of vivianite.

Vivianite dissolution

Studies of vivianite crystals and sulfur chemistry indicate that some of the increase of phosphorus in surface sediments reflects movement of phosphorus from deeper sediments. Electron micrograph analysis of the crystals of vivianite from sediments with high sulfide concentrations showed that the vivianite crystals were pitted from dissolution (Fig. 3). Deeper in the sediments where the AVS concentration was 40 times lower (Fig. 4), the vivianite crystals were dense and smooth. A magnetic isolation of vivianite from samples indicated that most of the total phosphorus was vivianite (Rancourt, personal communication).

Sulfide

Sulfide analysis showed anoxia of sediments in two areas, the deeper basin in the far north and the southern part of the north basin (Fig. 5). These results must indicate an interaction between currents and organic loading. Potential sources of organic matter include Nagahama City and the south basin via density currents. The area with by far the greatest sulfide concentration in 1999 was station 3, the station with the highest sediment pH (9.9, Fig. 6). There was a general tendency for sulfides to be associated with sediments in deeper water, but the relationship changed near the tips of peninsulas on the east shore where the water was deep but there were strong currents (Endoh and Okumura 1993). The relationship of redox potential to sulfide was

Table 1. Acid volatile sulfide (AVS) concentrations at station 11 in 1997

Depth (cm)	0–2	2–4	4–6	6–8	8–10
AVS (µg/g)	51 ± 6	247 ± 25	1748 ± 118	1768 ± 236	1073 ± 226

Fig. 3. Vivianite crystals collected in 1996 in Lake Biwa sediments. Sample A was collected from sulfide-rich sediments from the pearl farm of Akanoi Bay. Sample B was collected from station 9, 35 cm deep from the sediment surface in the north basin and below the level where the sulfide concentrations increased

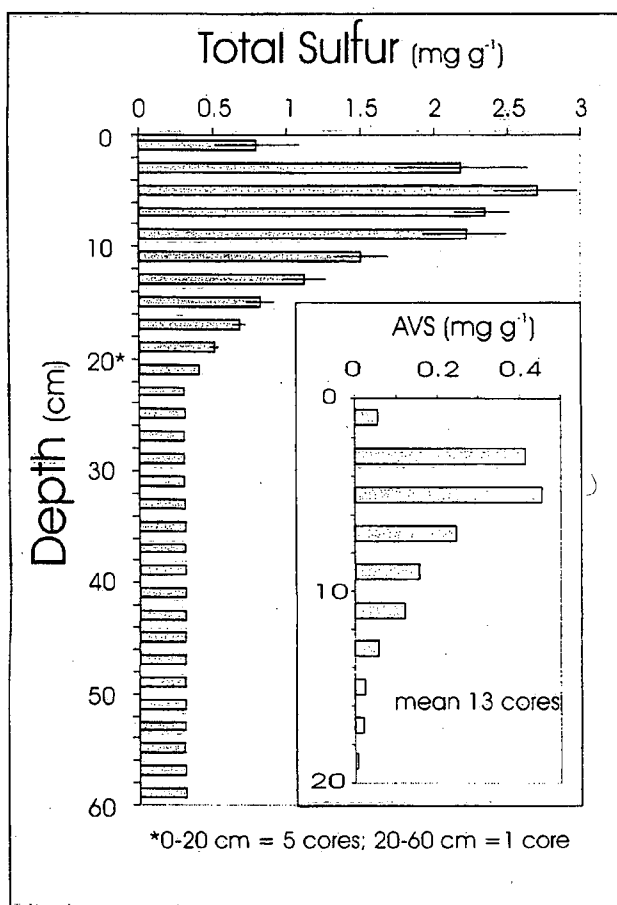
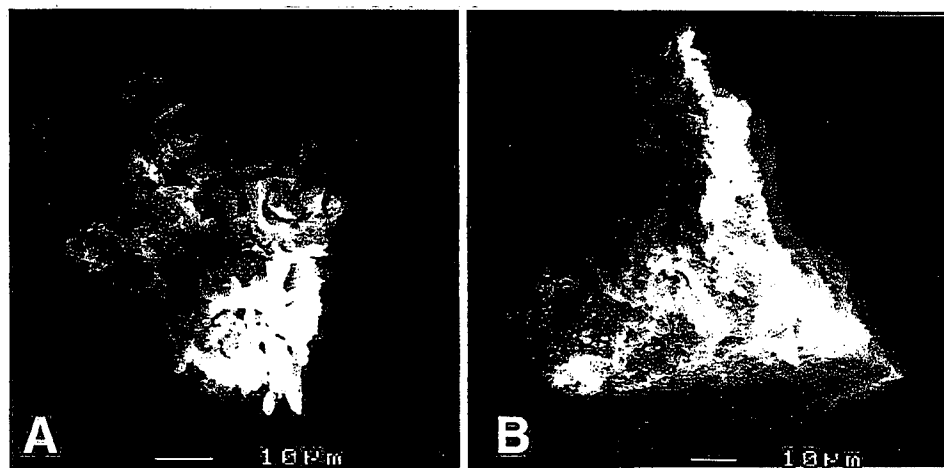


Fig. 4. Acid volatile sulfide (AVS) and total sulfur in Lake Biwa sediments, 1999

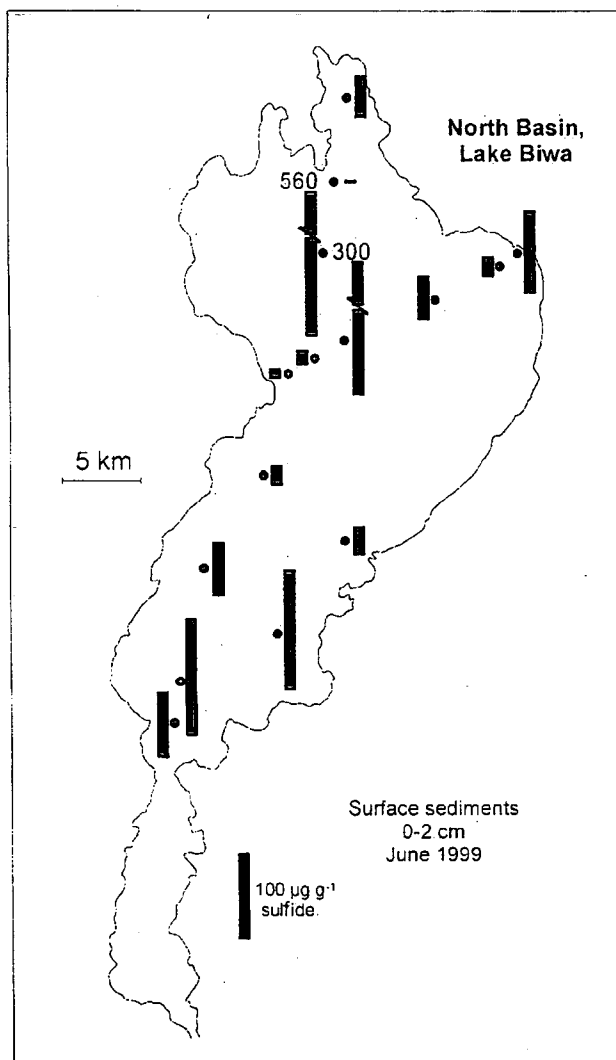


Fig. 5. Distribution of sulfide in surface sediments of Lake Biwa, June 1999

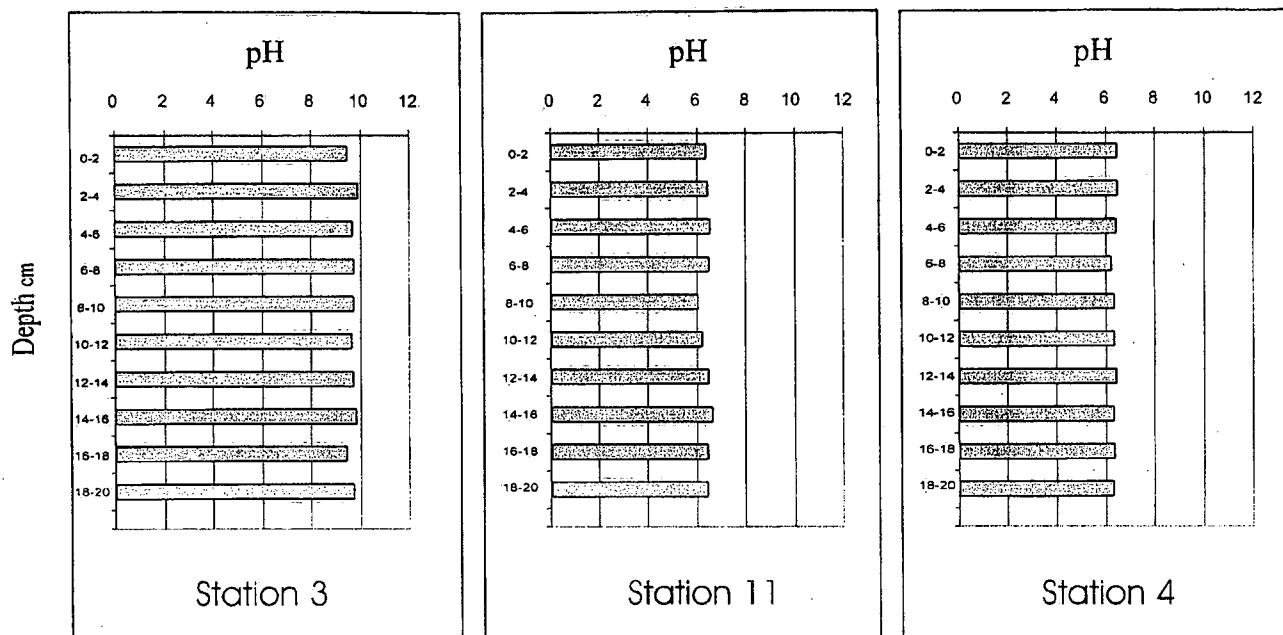


Fig. 6. Measurements of pH of three representative sediment cores from the North Basin, June 1999

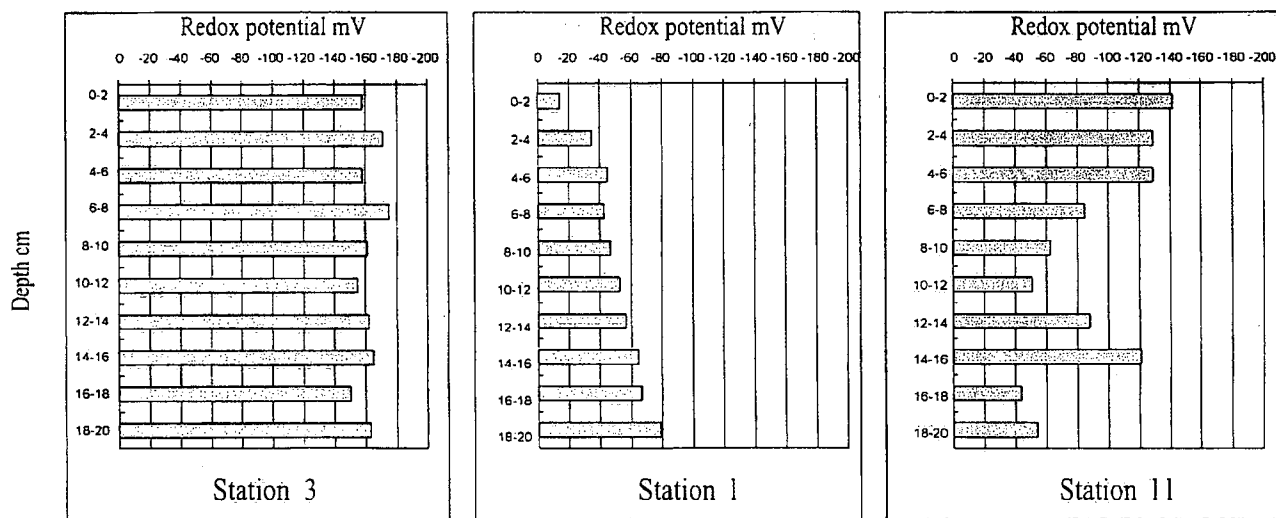


Fig. 7. Redox potential (mV) of three representative sediment cores from the North Basin, June 1999

nonsignificant ($r^2 = 0.09$, $n = 13$, surface samples). The effects that occurred during storms changed the sediments and obscured relationships that otherwise would be stronger. The changes in pH and redox potential that were observed between early and late summer samplings were apparent throughout the sediment core. For example, station 3 developed a similar pH and redox potential throughout the core that was not found earlier or in other cores. The temporal and depth changes indicate equilibration to a depth of at least 20 cm (Fig. 7). The high pH did not persist

over our entire sampling period (<3 months). The mean pH of 12 sediment cores in 1999 was 7.03.

The lower AVS content of the surface sediments was supported by physical observations. None of the sediments had an obvious odor of hydrogen sulfide, and all had a thin cap (usually <2 cm) of brown mud overlying darker gray to black sediments. The sediments from station 2 were firmer than others, and in June the first samples from this station had a surface iron-manganese crust. The organic content of the sediments, as measured by loss on ignition, was

relatively low in the north basin but varied from a low of 1% at station 2 to about 2% in the extreme south or east side of the lake, and to about 3% in the deeper areas. The generally low organic content of the sediments indicates a combination of low organic matter loading, rapid organic biodegradation, and high mineral inputs.

Sulfate/nitrate

The degree of anoxia can be more accurately measured by other redox-sensitive ions, such as sulfate and nitrate. Both analyses are more sensitive and seem to equilibrate faster than redox potentials. The seasonal changes in sulfate provide great insights into redox processes. In 1999, the sulfate concentrations of the surface sediments of three stations (1, 3, and 4) increased by $6.3 \pm 1.7 \text{ mg l}^{-1}$ (Table 2). These stations were sampled and analyzed in triplicate, so the significance is extremely high. Furthermore, these three stations were all in the north end of the lake. Wind mixing and associated sediment oxygenation is the only likely explanation for these results. In 1999, nitrate was consistently present (5 mg l^{-1}) only at station 2, an area with manganese nodules. This station was consistently much more oxic than other stations. Presumably either water currents were much faster here or groundwater upwelling was substantial. This area of the lake was frequently windy, so water currents were probably important.

Total sulfur

The distribution of total sulfur in the sediment cores was very similar to AVS distribution (Fig. 4). The 10-fold increase of AVS and sulfur just below the sediment surface must represent a combination of increased sulfur loading and diagenesis within the sediments, i.e., movement of sulfate to a zone of sulfide precipitation. There may be other factors influencing the decrease in the concentration of total

sulfur in the sediment surface, but diffusion of sulfate to a zone of sulfide precipitation is the most likely explanation.

Porewater phosphorus

The mean concentration of phosphate in sediment porewater in midsummer at stations where divers could use peepers (Akanoi Bay) was about 3.4 mg l^{-1} . As a lake becomes eutrophic, one might expect to see increased porewater concentrations of phosphorus that would form new equilibria with surface water and solids in the sediments. Seasonal changes and storms mask much of the anticipated changes associated with eutrophication that porewater and most bulk-phase analysis (i.e., total phosphate) might provide. Furthermore, analysis of phosphorus in porewater from centrifuged sediments underestimated the concentrations of phosphorus. Geochemical calculations (Minteqa2) were flawed in that the anion-cation balance was poor. "Corrections" to the results from certified laboratories were made by increasing chloride concentrations, but the model predicted precipitation of manganese phosphate. This water is very soft; presumably the dissolved organic matter provided the missing anion charge required for cation-anion balance, and either the organic matter or bacteria influenced the precipitation of vivianite.

The most graphic illustration of porewater release from the sediments of Lake Biwa can be found in the results of an enclosure experiment which nitrate was injected into sediments to oxidize sulfides and precipitate phosphorus. Initially porewater phosphorus concentrations in sediments were similar in treated and control enclosures. Oxidation of sulfide in Lake Biwa sediments precipitated >80% of the porewater phosphorus (Murphy et al. 1999). The concentration of total phosphorus in the water column of the control enclosures increased to $45 \mu\text{g l}^{-1}$ but remained less than $10 \mu\text{g l}^{-1}$ in the treated enclosure (Fig. 8).

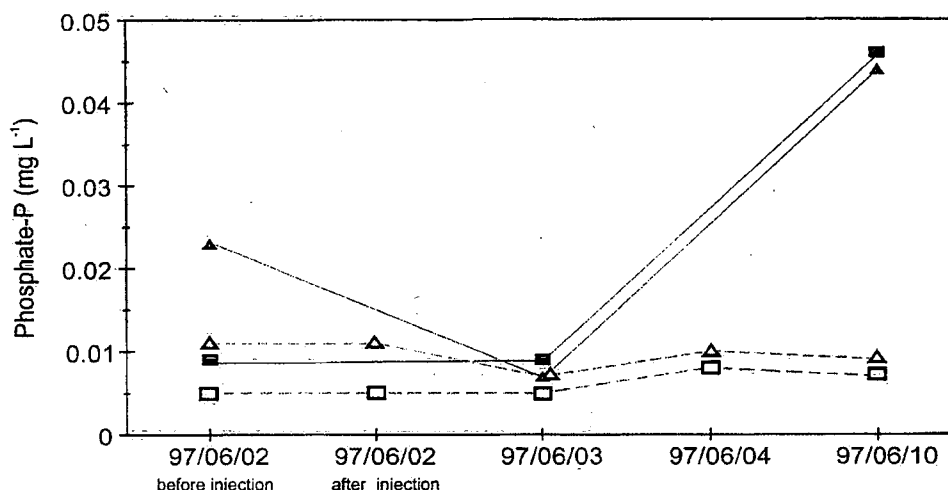
The Cs-137 sedimentation rate was about 1.5 mm year^{-1} (Kashiwaya, personal communication). Major changes in

Table 2. Porewater sulfate in Lake Biwa sediments^a

Samples collected June 1999			Samples collected September 1999			Change
Station no.	Sulfate (mg/l)	SD	Station no.	Sulfate (mg/l)	SD	
1	8.59	0.69	1	12.9	0.99	Increase
2	13.8	1.14	2	13.4	0.3	
3	5.04	0.96	3	12.5	1.16	Increase
4	7.06	2.06	4	14.1	1.4	Increase
5	7.03	1.89	5	6.55	1.41	
6	8.42	2.34	6	7.56	1.5	
7	7.73	1	7	7	1.9	
8	8.97	0.96	8	6.48	1.93	
9	8.67	0.24	9	8.66	1.15	
10	7.91	0.3	10	7.63	0.48	
11	7.04	0.8	11	7.09	0.54	
12	7.33	1.19	12	6.39	0.78	
13	7.92	1.47	13	7.59	0.12	
14	7.76	1.27	14	6.27	3.38	
15	5.92	1.5	15	0	0	Decrease

^aThree samples were collected from each station

Fig. 8. Release of phosphorus from sediments in enclosures, Akanoi Bay, 1997. (□) Treated surface, (■) control surface, (△) treated bottom, (▲) control bottom



the surface sediments that can influence eutrophication all took place in the top 23 cm that were deposited within the last 150 years.

Discussion

The porewater phosphate concentrations and sediment phosphorus release observed in the enclosures in Akanoi Bay must apply to the deeper areas. The total phosphorus and carbon contents of the Akanoi Bay pearl farm are similar to those in the deep basin. Moreover, in spite of a history of fertilization, the sulfide content of the sediments of the Akanoi Bay pearl farm is five times less than that in the deeper stations. Thus, if sulfide formation influences phosphorus, release rates could be higher in the deep basin. However, physical mixing of sediment is no doubt greater in the shallow areas, so the relative amount of phosphorus release in deep versus shallow water is uncertain.

There is a significant spatial variation in the amount of total phosphorus (Fig. 2), but the trends with depth are very consistent, which suggests that the forces acting on dissolution of vivianite are similar. It is expected that stations with a high concentration of sulfide reflect recent deposition of sulfur and that redox reactions are influenced by storm-driven currents. The results of studies of Lake Biwa in 1997 were similar to those in 1999 but very different from those in 1998, when we sampled between major typhoons (Murphy, unpublished). Thus, the stations with the most phosphate dissolution probably change from year to year, and the processes of phosphorus mobilization are not changing in synchrony.

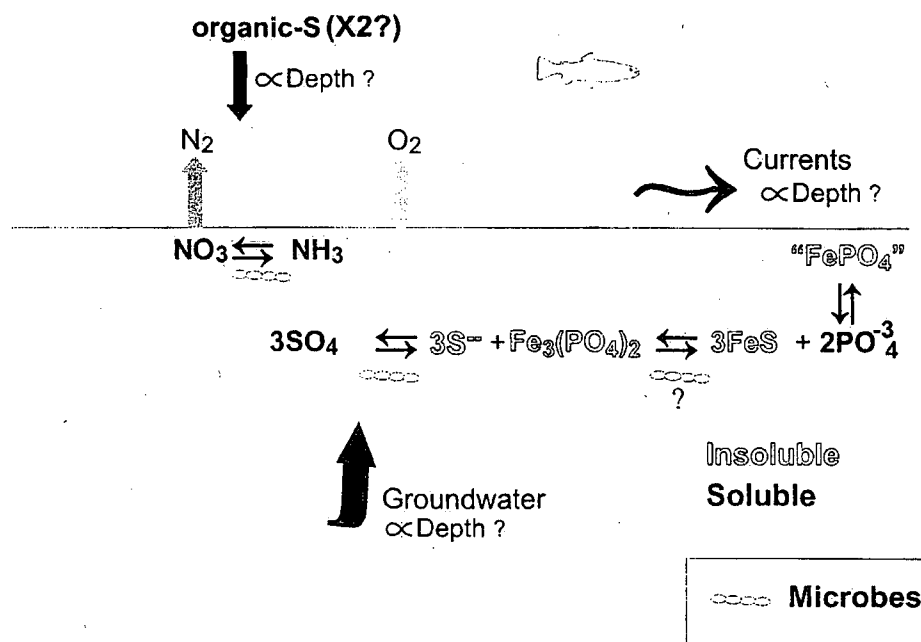
We have confirmed that phosphorus release is enhancing the eutrophication of Lake Biwa, but the uncertainty about current and future rates of release remains. Kurata (1994) estimated that in Akanoi Bay of Lake Biwa the rate of release was $2.8 \text{ mg m}^{-2} \text{ day}^{-1}$. The maximum rate that we observed in Akanoi Bay was $14 \text{ mg m}^{-2} \text{ day}^{-1}$, but this only lasted for a week. Attempts to measure annual phosphorus

release rates from sediments will be complicated by seasonal and storm-driven variability (Fig. 9).

The stability of the phosphorus that has been mobilized by dissolution of vivianite and precipitated on surface oxic sediments is critical and is controlled by the sulfur biochemistry. During periods of water stagnation, sulfate reduction in the surface sediments increased the pH to as high as 9.9, but the periods of high pH were short (<3 months). At stations of active sulfate reduction, the depth of pH increase was more than 20 cm (mean pH 9.7, $n = 10$, 2-cm intervals). This pH adjustment reflects the lack of buffering in these sediments and the production of alkalinity from microbial sulfate reduction. The amount of alkalinity produced depends upon the degree of reduction of the metabolized organic substrate. Two representative reactions are as follows: $\text{C}_{10}\text{H}_{22} + 7.75 \text{ SO}_4^{2-} + 5.5 \text{ H}^+ = 10 \text{ HCO}_3^- + 7.75 \text{ H}_2\text{S} + \text{H}_2\text{O}$ (Rueter et al. 1994) and $2\text{CH}_2\text{O} + \text{SO}_4^{2-} = \text{H}_2\text{S} + 2\text{HCO}_3^-$ (Elliott et al. 1998). Lake Biwa contains very soft water with little buffering (lakewater conductivity, $123 \mu\text{S cm}^{-1}$; sediment porewater alkalinity, $<34 \text{ mg l}^{-1}$). The mean pH of 12 sediment cores in 1999 was 7.03. The return of the pH in the porewater to near neutral appears to be driven in part by the dissolution of phosphate from the solid phase. Acid-base titrations with Lake Biwa sediments indicate that the change in pH associated with sulfate reduction represents about 1 mmolar exchange of H^+ for phosphate and other adsorbed anions. This change would represent as much as 10% of the total phosphorus. Dissolution of phosphate from iron (III) at pH 9.9 would be expected to dissociate about 50% of the phosphate adsorbed to iron (Stumm and Morgan 1981).

The shifting between stagnant periods with sulfate reduction and typhoon mixing resulted in movement of phosphorus into the water column. The physics in this scenario differs from that in similar studies on pH and sediments. Iron-rich sediments with low alkalinity are well known to release phosphorus into solution during periods of high pH (Jacoby et al. 1982; Boström 1984). Andersen (1975) observed maximal release of phosphorus at a pH around 9. These studies assumed that the primary process influencing

Fig. 9. Summary of reactions in water and sediments that control chemical species and solubility of phosphorus. The relationships of currents, sedimentation, and groundwater to depth are not clear and warrant analysis. It appears that the organic S loading has at least doubled over several decades



the pH of sediments was algal production. Even in shallow water (<3 m), our studies indicated minimal equilibration between bottom and surface water (Murphy, unpublished data); hence we are confident that sulfate reduction in sediments produced the high pH.

The enhanced concentrations of sulfide and sulfur near the sediment surface must represent a combination of both increased sulfur loading and diagenesis within the sediments, i.e., movement of sulfate to a zone of sulfide precipitation. Increased sulfur loading must in part be responsible for the recent increase in the concentration of *Thioploca*, a large, sulfur-oxidizing bacterium, in the surface sediments of Lake Biwa (Nishino et al. 1998). The colonization of *Thioploca* could also partly represent a recovery response from improved sewage treatment. If the decrease in total sulfur in the surface sediments reflects recovery, the signals are lost either in typhoon-mediated mixing or in inadequate organization of sulfur data.

The limited understanding of the importance of sulfur loading for the eutrophication of Lake Biwa prevents the development of a sulfur-loading budget. Certainly the concept that sulfur loading enhances eutrophication, demonstrated in New England (Caraco et al. 1989), Europe (Bellemakers and Maessen 1998), and Australia (Donnelly et al. 1997), applies to Lake Biwa. It is not clear whether the major Japanese sulfur sources are from agriculture, sewage, or combustion of fuels and wastes. Atmospheric loading of sulfur has probably increased in proportion to the increased amount of Japanese waste incineration and perhaps long-range transport of sulfur from sites in continental Asia. The potential for the involvement of similar mechanisms in enhanced eutrophication of other Asian lakes is high. The potential for continued or even more rapid release of phosphorus from the sediments of Lake Biwa is also high.

Acknowledgments The National Water Research Institute engineers and technicians built, serviced and provided, equipment for field experiments. Many individuals in the Lake Biwa Research Institute allowed us to use their laboratory. The vessel Hakken provided effective support for sediment sampling in the north basin. Dr. Denis Rancourt of the University of Ottawa did the X-ray fluorescence, X-ray diffraction, and Mössbauer analysis. Dr. Pierre Brassard of McMaster University provided advice on Minteqa2. This paper is dedicated to Professor Masahiko Higashi of Kyoto University.

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