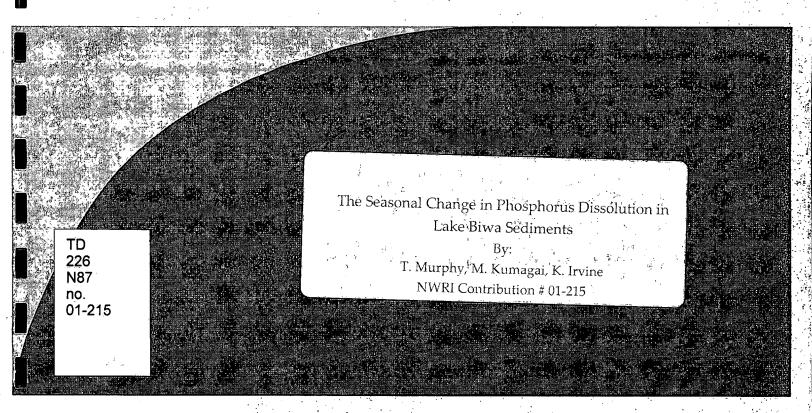
Environment Canada

Water Science and Technology Directorate

Direction générale des sciences et de la technologie, eau Environnement Canada



The Seasonal Change in Phosphorus Dissolution in Lake Biwa Sediments

Tom Murphy, Michio Kumagai and Kim Irvine

Management Perspective

Lake Biwa is the largest lake in Japan. It is the drinking water supply for 15 million people and has many endemic species. Unfortunately it is becoming more eutrophic and part of the problem is related to the release of phosphorus from sediments. We identified that the mineral vivianite (ferrous phosphate) is dissolving in the sediments of Lake Biwa, Japan. The dissolution of vivianite is enhanced by sulphur loading, largely from continental Asia. Direct treatment of the sediments is technically possible but would be expensive and innovative. Current sediment restoration in Japan is centered on sediment dredging. It is also expensive and has major limitations. In this paper we review how the concentration of dissolved phosphorus in lake sediments increased substantially from June to October, 2000. We used large in situ sediment diffusion chambers to measure this seasonal increase in phosphorus. Some of the important aspects of this reaction are influenced by weather, especially typhoons. To collect more data associated with storm events would require further modification of the equipment to match the hardware of Japanese vessels. Although we have determined how sediments are contributing to the eutrophication of Lake Biwa, there are still unresolved questions: What is the relative flux of phosphorus from sediments and external sources? What is the flux of sulphur from atmospheric and other sources? Vivianite is common in many lakes, including Lake Erie, and enhanced sulphur loading is a global concern. The results of this work apply to many lakes in Canada. The Lake Biwa Research Institute and the Shiga Prefecture funded this project.

Changement saisonnier de la dissolution du phosphore dans les sédiments du lac Biwa

Tom Murphy, Michio Kumagai et Kim Irvine

Sommaire à l'intention de la direction

Le lac Biwa, le plus grand lac du Japon, sert d'approvisionnement en eau de boisson à 15 millions de personnes, et abrite un grand nombre d'espèces qui lui sont propres. Malheureusement, il devient de plus en plus eutrophe, et une partie du problème est due à la libération de phosphore par les sédiments. Nous avons établi que de la vivianite (un minéral de phosphate ferreux) des sédiments de ce lac se dissolvait. La dissolution de ce minéral est accélérée par la charge de soufre, qui provient surtout de l'Asie continentale. Le traitement direct des sédiments est techniquement possible, mais il s'agit d'une méthode coûteuse et peu connue. Au Japon, les activités actuelles d'assainissement des sédiments sont surtout des opérations de dragage également coûteuses, dont l'application comporte de fortes limitations. Dans cet article, nous examinons comment les concentrations de phosphore dissous dans les sédiments des lacs ont augmenté fortement de juin à octobre 2000. Pour mesurer ces augmentations saisonnières de phosphore, nous avons utilisé de grandes chambres de diffusion de sédiments sur place. Certains des aspect les plus importants de cette réaction sont influencés par les conditions météorologiques, et notamment les typhons. Pour obtenir plus de données sur les épisodes de tempête, il faudrait apporter d'autres modifications aux équipements pour faciliter leur adaptation au matériel des bateaux japonais. Bien que nous ayons déterminé comment les sédiments contribuent à l'eutrophisation du lac Biwa, il y a encore des questions qui n'ont pas reçu de réponses, par exemple : quels sont les flux relatifs du phosphore des sédiments et des sources de l'extérieur? Quels sont les flux du soufre des sources atmosphériques et des autres sources? La vivianite est un minéral commun présent dans un grand nombre de lacs, notamment dans le lac Érié, et l'accroissement de la charge de soufre est un problème mondial. Les résultats de ces études pourraient s'appliquer à un grand nombre de lacs du Canada. Ce projet était financé par l'Institut de recherche du lac Biwa et par la préfecture de Shiga.

Résumé

On a utilisé des chambres de diffusion des sédiments pour détecter l'augmentation de la dissolution de phosphore lors d'épisodes de conditions réductrices dans les sédiments du lac Biwa. Dans plusieurs échantillons, une faible diminution de la différence de potentiel moyenne Eh (de +85 mV à-9 mV, de juin à octobre) causait une augmentation d'un facteur de 3,8 du phosphore (par rapport au fer), si on compare ces valeurs à celles observées dans les eaux de porosité en juin. La dissolution de la vivianite semble expliquer les concentrations supérieures de phosphore dans les eaux de porosité des sédiments.

The Seasonal Change in Phosphorus Dissolution in Lake Biwa Sediments

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Abstract

Sediment diffusion chambers were used to detect enhanced dissolution of phosphorus when sediments of Lake Biwa became more reduced. A minor decrease in the mean Eh potential from +85 mV in June to -9 mV in October resulted in several samples having 3.8 times more phosphorus (relative to iron) than observed in the June porewater. The dissolution of vivianite appears to account for the higher concentrations of phosphorus in sediment porewaters.

Introduction

The dissolution of vivianite a ferrous phosphate mineral [Fe₃(PO₄)₂.8H₂O] in sediments of Lake Biwa, Japan is enhancing eutrophication (Murphy et al. 2001). Decades ago in Lake Biwa, vivianite was stable and little or none of this phosphorus compound dissolved. In part the naturally high iron loading stabilized the vivianite. Now the enhanced loading of sulphur with organic matter results in sulphide in sediments which preferentially reacts with iron and indirectly results in dissolution of vivianite. The release of the dissolved phosphorus into the water column is difficult to measure in part because it is controlled by currents generated by storms (Frenette et al. 1996, Robarts et al. 1998). The lake sediments have lost some of their capacity to retain phosphorus.

The purpose of this study was to use sediment diffusion chambers to further resolve the seasonal change in the processes controlling the dissolution of vivianite.

Keywords phosphorus, sediments, vivianite, redox

Methods

Sediment Sample Collection

Peepers (sediment diffusion chambers) were inserted on June 20 and October 17 at a depth of 5 metres in the South Basin of Lake Biwa (35° 03' 35.3" N 135° 54' 18.0" W). The peepers were allowed to equilibrate for two weeks. Preparation of the peepers is outlined in Hesslein 1976, Rosa and Azcue 1993. The peeper moorings were hit by ships which tilted the peeper tripod and resulted in a larger number of surface sediment replicates than had been planed. Nonetheless, the seasonal differences in surface porewater chemistry are strong and interesting.

Immediately after retrieval, one set of bottles from each peeper frame was preserved with 0.6 ml of 50% HNO₃. Samples were cooled and then shipped to the Canada Centre for Inland Waters (CCIW) for analysis for total phosphorus, iron and manganese ion by automated inductively coupled argon plasma emission spectroscopy with ultrasonic nebulisation and direct aspiration (NLET, Method 02-2051).

Another set of porewaters samples were frozen for shipment to CCIW for anion analysis (sulphate 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 sulphate. Acid volatile sulphide (AVS) analysis by ion selective electrodes used a diffusion method (Brouwer and Murphy 1994).

A benthos sediment core was taken at each site and visual observations were recorded. The core was extruded at 2 cm intervals for the first 10 cm and the redox potential of each sample was measured with an Orion platinum electrode.

Results

Porewater Analysis

In June the correlation between dissolved iron and phosphorus concentrations was very high with one simple linear relationship (Figure 1, y = 0.05 x + 8.36, $r^2 = 0.94$). It is obvious that phosphorus solubility was closely coupled to iron concentrations. In June, there was about 20 times as much iron as phosphorus. In October, the relationship between iron and phosphorus was similar but there was a significant difference in 8 samples. In these samples there was 3.8 times more phosphorus (relative to iron) than observed in the June porewater samples (y = 0.19 x - 1145, $r^2 = 0.86$, Figure 2). The higher proportion of phosphorus is expected if vivianite was dissolving (Figure 2). The surface 6 cm of sediments were oxic in both June and October (12 and 60 mV, respectively). The redox of the deeper sediments (6-56 cm) was relatively constant on each sampling date, but the Eh potential decreased from a mean of +85 mV in June to a mean of -

9 mV in October. Since the redox potential was much lower in October than in June, and we have observed dissolution of vivianite in these sediments (Murphy et al. 2001), it is highly likely that these 8 samples represent dissolution of vivianite. These sediments were only slightly reduced and the AVS content of the deeper sediments (6-56 cm) did not change significantly between June and October (mean surface 0-6 cm sediments 0.9 and 1.5 µg/g; mean 6-56 cm sediments 39 and 42 µg/g, in June and October, respectively). Much higher concentrations of sulphide have been observed in deeper areas of Lake Biwa (not shown), so potentially the dissolution of phosphorus can be much faster. Also, difficulties with the peeper incubation suggest that the number of samples with potential vivianite dissolution and the degree of vivianite dissolution may have been underrepresented.

Conclusions

There was a strong seasonal change in the concentrations of iron and phosphorus in the sediment porewater. The decrease in the redox in summer resulted in substantially more phosphorus in solution in October than would be expected from the relationship between iron and phosphorus that existed in June. There is likely sediment phosphorus release occurring in early summer but vivianite dissolution appears to be faster in autumn.

References

Brouwer, Henry and Tom P. Murphy. 1994. Diffusion method for the determination of acid volatile sulfides (AVS) in sediment. Envir. Toxicol. Chem. 13:1273-1275.

Hesslein, R.H. 1976. An in situ sampler for close interval pore water studies. Limnol. Oceanogr.

21: 912-914.

- Frenette, J.J., W.F. Warwick, L. Legendre, T. Nagata, K. Kawabata, and M. Kumagai. 1996.

 Biological responses to typhoon-induced mixing in two morphologically distinct basins in

 Lake Biwa. Jpn. J. Limnol. 4(2):501-510.
- Murphy, T.P, M. Kumagai, and C. Nalewajko. 2001. Phosphorus Release from Sediments in Lake

 Biwa. Limnology, in press.
- Robarts, R.D., M.J. Waiser, O. Hadas, T. Zohary, and S. MacIntyre. (1998) Relaxation of phosphorus limitation due to typhoon-induced mixing in two morphologically distinct basins of Lake Biwa. Japan. Limnol. Oceanogr. 43(6)1023-1036.
- Rosa, F.; Azcue, J.M.; Peeper Methodology A detailed procedure from field experience.

 National Water Research Institute contribution, 1993, 93-33.

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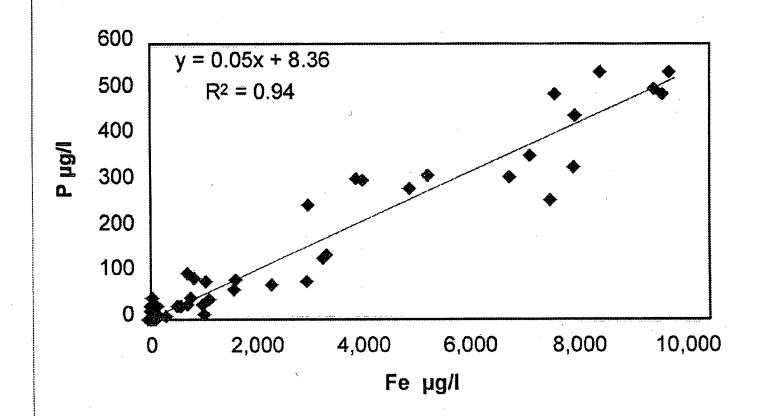
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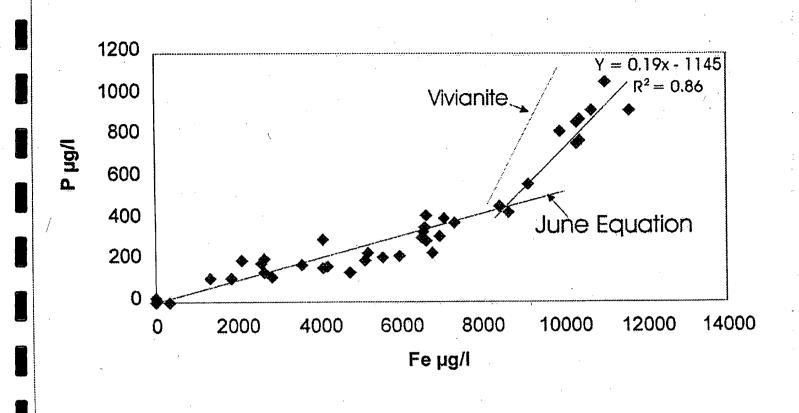
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Figure Legends

The concentration of total iron and total phosphorus in sediment porewaters in June,
 2000.

The concentration of total iron and total phosphorus in sediment porewaters in October,
 2000.





Tom Murphy, Michio Kumagai and Kim Irvine The Seasonal Change in Phosphorus Dissolution in Lake Biwa Sediments. Verh. Internat. Verein. Limnol.

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