

Release of trace oxyanions from littoral sediments and suspended particles induced by pH increase in the epilimnion of lakes

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Abstract

We measured the vertical distributions of dissolved vanadium (V), molybdenum (Mo), and tungsten (W) during a stratification period in Lakes Biwa, Ikeda, and Unagi-ike, which are located in the temperate zone of Japan. The concentrations of V and W in the epilimnia were 1.6–3.7 times (V) and 1.8–2.9 times (W) higher than those in the hypolimnia. The concentrations of V and W in the epilimnia were 2.94 ± 0.09 nmol L⁻¹ and 76.1 ± 5.7 pmol L⁻¹ in Lake Biwa, 10.5 ± 0.3 nmol L⁻¹ and 19.2 ± 1.3 pmol L⁻¹ in Lake Ikeda, and 18.4 ± 0.35 nmol L⁻¹ and 26.3 ± 1.8 pmol L⁻¹ in Lake Unagi-ike. The vertical distributions of Mo were homogeneous in all the lakes and its average concentration was 3.45 ± 0.21 nmol L⁻¹ in Lake Biwa, 1.18 ± 0.08 nmol L⁻¹ in Lake Ikeda, and 1.93 ± 0.09 nmol L⁻¹ in Lake Unagi-ike. We suggest that the higher concentrations of V and W in the epilimnia during the stratified period result from the release of these elements from the littoral sediments and suspended particles in response to the rise in pH, which is induced by high biological production. To test this mechanism, a laboratory experiment using lake water and sediment was carried out. The pH of the lake water was controlled by bubbling air with different CO₂ concentrations, and the experiment demonstrated that V and W were released from the sediments in response to the increasing pH.

In aquatic environments, the distributions and biogeochemical behaviors of vanadium (V), molybdenum (Mo), and tungsten (W) are controlled by various factors. These three elements exist as oxyanions (HVO₄²⁻, MoO₄²⁻, and WO₄²⁻) demonstrating the highest oxidation states (+V, +VI, and +VI) in oxic and neutral (or slightly alkaline) water (Brookins 1987). In oxic seawaters, lake waters, and river waters, the distributions of Mo and W exhibit conservative profiles or conservative behaviors (or both) along the flow (Sohrin et al. 1987; Johannesson et al. 2000). Vanadium also exhibits conservative behavior in well-oxygenated lakes and rivers (Nojiri et al. 1985; Johannesson et al. 2000); however, its uptake by phytoplankton or its adsorption onto biogenic particles can occur at the surfaces of the oceans and in some estuaries (Collier 1984; Shiller and Boyle 1987; Middelburg et al. 1988). In contrast, the behaviors of these three elements drastically change in deoxygenated (anoxic) water. The oxidation state of V changes from +V to +IV [VO(OH)⁺] with a decrease in the redox potential (Eh) (Szalay and Szilágyi 1967; Breit and Wanty 1991; Wanty and Goldhaber 1992). In contrast to V (+V), V (+IV) is readily moved from the water phase into the sediment phase (Breit and Wanty 1991; Wanty and Goldhaber 1992; Viollier et al. 1997), because V (+IV) is adsorbed onto various oxides and

forms complexes with organic matter (Szalay and Szilágyi 1967; Wehrli and Stumm 1989). The chemical form of Mo is converted from MoO₄²⁻ to thiomolybdate MoS₃²⁻ in anoxic and sulfidic water (Erickson and Helz 2000). MoS₃²⁻ is easily moved into the sediment phase by adsorption onto particles such as pyrite (Helz et al. 1996). Furthermore, Mo adsorbed on the surface of pyrite is reduced to +V or +IV by polysulfides in anoxic and sulfidic water (Vorlicek et al. 2004). Studies on W in anoxic water are very limited compared to those on V and Mo. However, it has been reported that W is released from the sediment along with the reductive dissolution of iron oxides (Miyauchi et al. 1998).

An interesting behavior of V has been observed under oxic conditions (Sugiyama 1989; Okamura 1994). On the basis of monthly observations at Lake Biwa, Japan, Sugiyama (1989) has reported that the dissolved V concentration in the well-oxygenated epilimnion (dissolved oxygen = 5.4–11.4 mg L⁻¹ = 170–356 μmol L⁻¹) during the stratification period significantly increased from 1.8 nmol L⁻¹ in May to 5.0 nmol L⁻¹ in October, and decreased thereafter. However, the concentration of V in the hypolimnion was constant throughout the year. He also suggested the potential factors that affect the increase in the V concentration in the epilimnion—inflow of river water; fallout from the atmosphere; secretion from limnetic organisms; and release from sediments and suspended particles. However, the mechanism for this increase in V concentration has not yet been identified. Additionally, to our knowledge, no increase in the V concentration in epilimnionlike environments has been reported during the summer in other lakes and seas.

In this paper, the vertical profiles of dissolved V in the well-oxygenated layers of three Japanese lakes, including Lake Biwa, will be presented to examine whether the phenomenon is specific to Lake Biwa. In addition, the profiles of dissolved Mo and W, which also exist as oxyanions in oxic water, will be reported for comparison. We will also show that the increase in the amount of dissolved V in the

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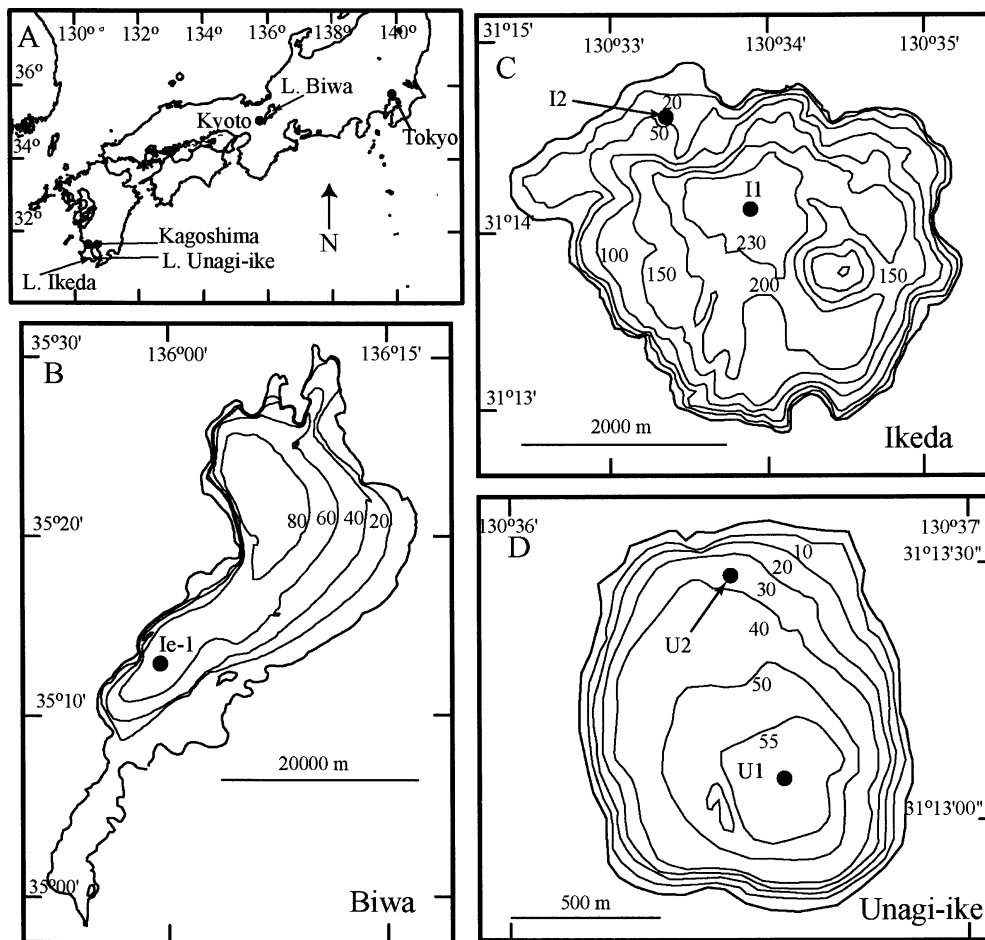


Fig. 1. Locations of the studied lakes: (A) Lakes Biwa, Ikeda, and Unagi-ike and (B–D) sampling site for each lake.

well-oxygenated epilimnion occurs not only in Lake Biwa but also in other lakes, and that the amount of dissolved W also increases in the layers. Furthermore, from a laboratory experiment, we will demonstrate that increasing pH is a key factor for the increase in the V and W concentrations in the epilimnion during the summer stratification period.

Samples and methods

Studied lakes—Sampling was performed in three Japanese lakes (Lakes Biwa, Ikeda, and Unagi-ike). Location details and major characteristics of the lakes are shown in Fig. 1 and Table 1, respectively. All these lakes are located in the temperate zone between 31.2°N and 35.5°N (Fig. 1). Lakes Biwa and Unagi-ike are monomictic lakes, which are stratified stably in the summer and whose waters completely circulate in the winter. Lake Ikeda is deep (max. depth: 233 m) and its water is circulated completely only in the coldest winters. Okuzono et al. (1979) studied Lake Ikeda and found that the water mass above a minimum depth of 100 m was circulated in February. Lakes Biwa and Ikeda are in a mesotrophic state, whereas Lake Unagi-ike is in a eutrophic state.

Sampling—All observations were carried out in 1997: Lakes Biwa (18 July), Ikeda (22 October), and Unagi-ike (23 October). The sampling sites are shown in Fig. 1. The observation at Lake Biwa was carried out at Ie-1 (depth: 73 m), where the seasonal variations of dissolved V were previously observed by Sugiyama (1989) and Okamura (1994). In each of the other lakes, the observation was carried out at the deepest site (Ikeda: 233 m; Unagi-ike: 57 m) and at other sites (Ikeda: 41 m; Unagi-ike: 30 m). For trace element analysis, water samples were collected using a 2.5-liter Niskin water sampler suspended by a polyethylene rope. Within 12 h after the samplings, the samples were filtered through the 0.2- μ m Nuclepore filters (Whatman). The filtrates were acidified with ultrapure HNO₃ (Kanto Kagaku) to pH < 2 and stored in low-density polyethylene bottles (Nalgene) under refrigeration. For the analysis of particulate metals, the filters and trapped suspended particles were stored in 30-ml polytrifluorochloroethylene (PTFE) vessels and covered with screw caps.

All the apparatuses and vessels used for the sampling, filtration, and storage were previously cleaned by soaking them successively in 10% Scat detergent (Nacalai Tesque) and 4 mol L⁻¹ HCl, followed by rinsing them thoroughly

Table 1. Major characteristics of the investigated lakes.

| Lake | Trophic state | Altitude (m) | Lake area (10 ⁶ m ²) | Lake volume (10 ⁹ m ³) | Max. depth (m) | Drainage area (10 ⁶ m ²) |
|-----------|---------------|--------------|---|---|----------------|---|
| Biwa | Mesotrophic* | 85.6‡ | 674‡ | 27.50‡ | 104‡ | 3174‡ |
| Ikeda | Mesotrophic* | 66.0‡ | 10.95‡ | 1.47‡ | 233‡ | 12.34‡ |
| Unagi-ike | Eutrophic* | 122* | 1.20* | 0.04‡ | 56.5* | 2.1‡ |

* Tanaka (2002).

‡ Data determined on basis of 1:25,000 scale topographic maps.

‡ LBRI and NIRA (1984).

with water purified by a Milli-Q (Millipore) system (hereafter called MQW). The filters were precleaned by soaking in 1 mol L⁻¹ HCl/HNO₃ solution at 60°C for 5 h, followed by a thorough rinsing with MQW.

The water temperature was measured on board using a thermistor (NWT, Nichiyu Giken Kogyo), and the dissolved oxygen (DO) and pH were measured on board using a water quality multichannel sensor (U-10, Horiba).

Analytical methods of dissolved elements—The concentration of dissolved V was determined by a catalytic method using the oxidation of Bindschedler's green leuco base (Sugiyama and Hori 1992). The concentration of dissolved Mo was determined by a catalytic method using the oxidation of ascorbic acid (Harita et al. 2003). In both these methods, an air-segmented continuous-flow analysis system (Auto-Analyzer II, Bran Luebbe) was used to ascertain a sensitive and accurate analysis of the dissolved V and Mo. The detection limits for V and Mo were 21 pmol L⁻¹ and 17 pmol L⁻¹, and accuracies at the level of 10 nmol L⁻¹ were 0.6% ($n = 10$) and 0.2% ($n = 10$), respectively.

The concentration of dissolved W was determined by isotope dilution inductively coupled plasma-mass spectrometry (ICP-MS). Isotopically enriched ¹⁸³WO₃ powder was obtained from the Oak Ridge National Laboratory. A stock solution of the enriched isotope was prepared by the complete dissolution of an accurately weighed quantity of the powder in 0.5 mol L⁻¹ NH₃ solution. A working spike solution was prepared by diluting the stock solution using MQW. The concentration of the spike solution was verified by reversed spike isotope dilution ICP-MS. After adding the required amounts of the spike solution to the lake water samples, they were allowed to stand for 1 d. In the samples, the ratio ¹⁸³W:¹⁸⁴W was determined by ICP-MS (VG Plasma Quad II, VG Elemental) using an ultrasonic nebulizer (U-5000AT+, CETAC). The concentrations of dissolved W in the lake water samples were calculated using this ratio. The detection limit was found to be 0.8 pmol L⁻¹.

Analytical method for total particulate metals—Total particulate concentrations of iron (Fe), manganese (Mn), and aluminum (Al) were measured using Sugiyama's method (1996). All the reagents used for the digestion of the suspended particles were of ultrapure grades and were purchased from Kanto Kagaku. All the samples were manipulated in a clean box having a 0.1- μ m air filter. First, the polycarbonate filter, trapping the suspended particles, was hydrolyzed in a PTFE vessel with 0.5 ml of 28% NH₃ so-

lution by allowing it to stand for 12 h. The solution was then heated at about 120°C on a hot plate until completely dry. Subsequently, 0.3 ml of 60% HClO₄, 1 ml of 60% HNO₃, and 1 ml of 48% HF were added to the dried cake. The vessel cap was loosely placed and the mixture was heated at 120°C for 2 h, followed by heating at 140°C for 2 h and at 170°C for 8 h. Thereafter, the mixture was heated until completely dry by removing the cap. After cooling, 0.5 ml of 60% HClO₄ and 1 ml of 60% HNO₃ were added, and the mixture was heated at 170°C until completely dry. The residue was completely dissolved in 4 ml of 0.1 mol L⁻¹ HNO₃ in an ultrasonic bath. The concentrations of Fe, Mn, and Al in the solution were determined by ICP-atomic emission spectrometry (AES) (ICAP-96-953, Nippon Jarrell-Ash).

Estimation of the concentrations of authigenic particulate Fe and Mn—Various trace elements, including V, can be removed from water by the authigenic hydrous Fe and Mn oxides, which are freshly formed in oxic natural waters by the oxidation of Fe²⁺ and Mn²⁺ transported from anoxic waters (Viollier et al. 1997). To examine the extent of V removal in oxygenated hypolimnion ("oxygenated" will be defined later), the concentrations of the authigenic hydrous Fe and Mn oxides in all the studied sites were estimated using the method of Sholkovitz and Copland (1982) with a slight modification. According to their method, the concentrations of the authigenic hydrous Fe (or Mn) oxides can be obtained by subtracting the concentration of detrital particulate Fe (or Mn) from the concentration of the total particulate Fe (or Mn). This calculation assumes that the detrital components are unreactive and primarily comprise aluminosilicates (i.e., clay minerals), which are derived from the river inputs and resuspension of bottom sediments. The calculation formula is as follows: [Authigenic hydrous Fe (or Mn) oxides] (nmol L⁻¹) = [total particulate Fe (or Mn)] - $R \times$ [total particulate Al], where the coefficient R represents the ratio of Fe (or Mn): Al in the detrital component. In this study, the R values for Fe and Mn were 0.0351 and 0.00835 mol mol⁻¹, respectively. These correspond to the average upper crustal abundance ratios in Japan, as determined from the detrital components of the 64 Japanese rivers (Sugiyama 2004).

Laboratory experiment of vanadium removal by hydrous iron and manganese oxides—A laboratory experiment was carried out to examine the extent of V removal from oxic lake water by the authigenic hydrous Fe and Mn oxides. Hydrous Fe oxide was synthesized by the dropwise addition

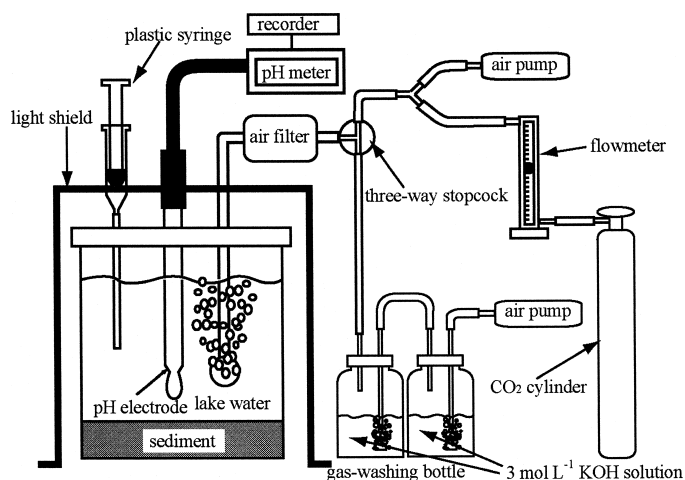


Fig. 2. Schematic diagram of the experimental setup for examination of the geochemical behaviors of oxyanions.

of 25% ammonia to an acidified 0.04 mol L^{-1} ferric chloride solution until the pH of the solution reached a value of 9.0. Hydrous Mn oxide was synthesized by mixing potassium permanganate and manganese chloride solutions (Murray 1975). Both hydrous oxides were repeatedly washed with MQW.

A water sample was collected from Lake Biwa and was filtered through the $0.2\text{-}\mu\text{m}$ Nuclepore filters. Different volumes of hydrous Fe (or Mn) oxide suspensions were added to 30-ml aliquots of the filtered lake water and appropriate volumes of MQW were added to the aliquots so that the final volume equaled 31 ml. The aliquots were shaken for 12 h under room temperature (about 20°C). They were then filtered through the $0.2\text{-}\mu\text{m}$ Nuclepore filters. The concentration of dissolved V in the filtrates were determined by the above-mentioned method.

Laboratory experiment for the analysis of the effect of pH on V, Mo, and W concentrations—A laboratory experiment was carried out to investigate the effect of pH variation on the dissolved concentrations of V, Mo, and W. A schematic diagram of the experimental setup is shown in Fig. 2. The setup comprised two main parts: a tank and a gas controller. In the tank, 700-cm^3 volume of sediment was placed, and 20-liter volume of lake water was gently poured on it. The sediment sample was collected from the bottom surface (0 to 5 cm) of a littoral area in Lake Biwa. The lake water was sampled at a depth of 40 m at the Ie-1 site of Lake Biwa. The tank was kept in the dark at a constant temperature (25°C). The pH of the water was controlled by bubbling CO_2 -free air or natural air mixed with CO_2 gas. The CO_2 -free air was prepared by passing natural air through 3 mol L^{-1} KOH solution. The experiment was carried out for 11 d. The pH of the lake water was continuously monitored using a pH electrode. Fourteen samples were collected during the experimental period and these were filtered through the $0.2\text{-}\mu\text{m}$ Nuclepore filters. The concentrations of dissolved V, Mo, and W in the filtrates were determined using the methods described above.

Results and discussion

Comparison of vertical profiles among the lakes—In this paper, we define an “oxygenated” layer as a water layer in which the dissolved oxygen concentration is higher than 3.0 mg L^{-1} ($94 \mu\text{mol L}^{-1}$). We will restrict our discussion to oxygenated layers, because the increase in the dissolved V concentration in the previous work (Sugiyama 1989) was recorded only in the oxic epilimnion. Moreover, the geochemical processes of V, Mo, and W in a deoxygenated (weakly oxic or anoxic) layer differ from those in an oxygenated layer, as mentioned above.

The vertical profiles of water temperature; DO; pH; and dissolved V, Mo, and W in the oxygenated layers at all the studied sites are shown in Fig. 3. On the basis of the water temperature profile, the oxygenated layer was further divided into three sublayers: oxygenated epilimnion, thermocline, and oxygenated hypolimnion. The depth-weighted average concentrations of V, Mo, and W in the oxygenated epilimnion and hypolimnion along with their ratios (epilimnion/hypolimnion) are listed in Table 2.

The distributions of V, Mo, and W in all the lakes can be classified into two types on the basis of their vertical profiles. The first type, which we will refer to as the epilimnion-high concentration type (EH-type), is characterized by a higher concentration of the elements in the oxygenated epilimnion when compared to that in the oxygenated hypolimnion. The distributions of V and W in all the lakes were classified as EH-type (Fig. 3). The concentrations of V and W in the epilimnia were 1.6 to 3.7 and 1.8 to 2.9 times higher, respectively, than those in the hypolimnia (Table 2). The second type is the homogenous type, characterized by the constant vertical profile. The Mo distributions in all the lakes were classified under this type. The Mo concentration ratio of the epilimnion/hypolimnion was approximately 1.1 for all the sites (Table 2).

The EH-type profiles of V observed in all the lakes in this study can be interpreted in two ways: One way is that the EH-type profiles were derived from the supplies of V to the epilimnia. The other way is that the EH-type profiles were derived from the removals of V from the oxygenated hypolimnia. The former appears to be more valid, because the removal of V from the oxygenated hypolimnia is unlikely.

The removal of dissolved V from the water phase is known to be facilitated by the formation of authigenic hydrous Fe and Mn oxides (Takematsu et al. 1985; Viollier et al. 1997) or by the reduction of vanadate (HVO_4^{2-}) to vanadyl [$\text{VO}(\text{OH})^+$] ions (Breit and Wanty 1991; Wanty and Goldhaber 1992). However, the concentrations of the authigenic hydrous Fe and Mn oxides in the oxygenated hypolimnion at all the sites were not sufficient to largely remove the dissolved V. The Fe and Mn oxide concentrations were estimated to be at the level of <180 and $<80 \text{ nmol L}^{-1}$, respectively, at all the sites. Figure 4 shows the effect of hydrous Fe and Mn concentrations on the removal of dissolved V (+V, vanadate). The Fe (180 nmol L^{-1}) and Mn (80 nmol L^{-1}) oxides were observed to scavenge only 4.5% and 1.1% of the initial concentration (2.5 nmol L^{-1}) of dissolved V, respectively. From these results, it is expected that the large

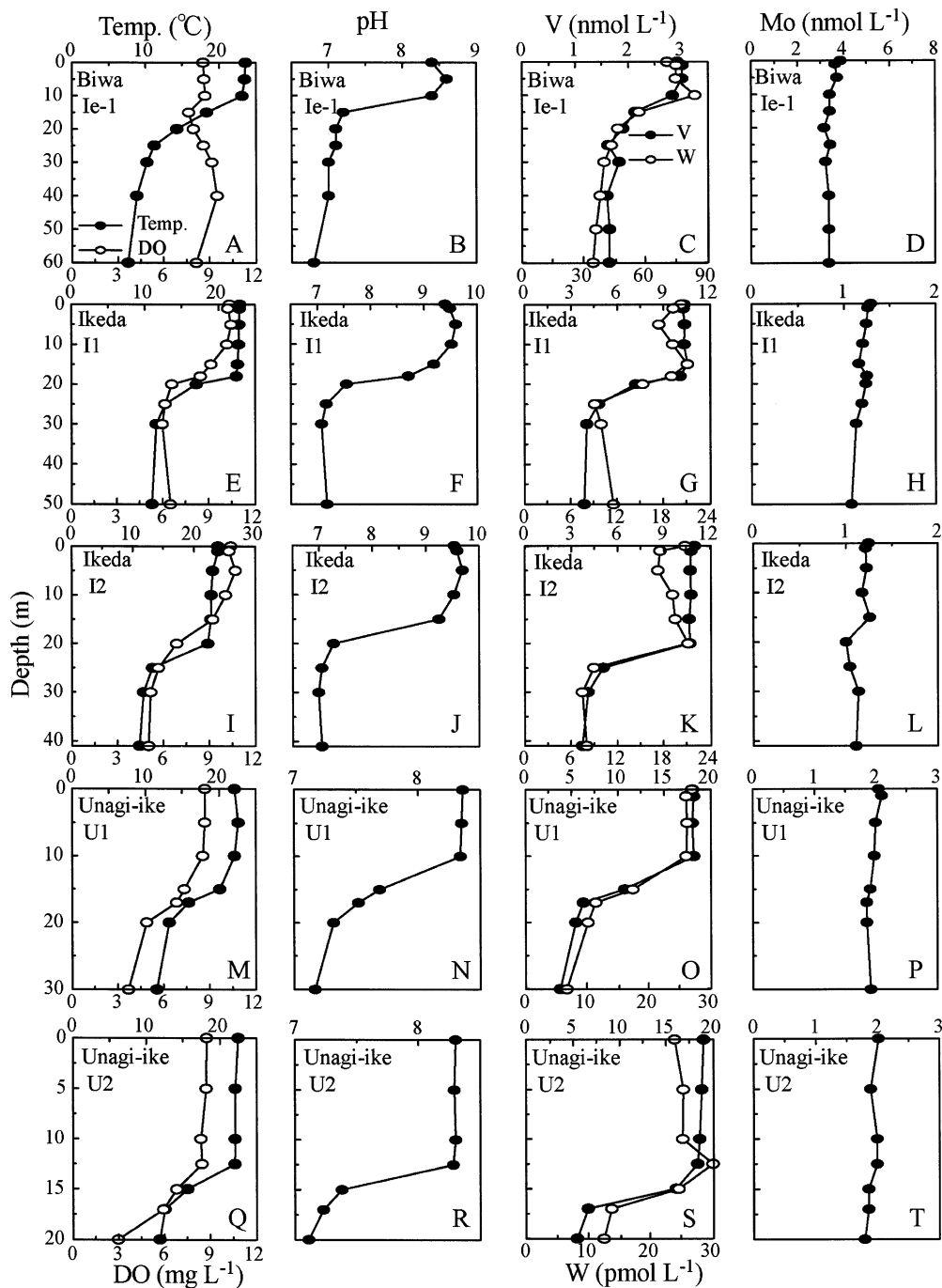


Fig. 3. Vertical distributions: (A, E, I, M, Q) temperature and dissolved oxygen; (B, F, J, N, R) pH; (C, G, K, O, S) dissolved vanadium and tungsten; and (D, H, L, P, T) dissolved molybdenum in the oxygenated layers at sites Ie-1 (A, B, C, D), I1 (E, F, G, H), I2 (I, J, K, L), U1 (M, N, O, P), and U2 (Q, R, S, T).

removal of vanadate from the oxygenated hypolimnia did not occur at all the sites. In addition, it is also expected that the reduction of vanadate ion to vanadyl ion hardly occurred in the oxygenated hypolimnia, because a thermodynamic calculation and a speciation analysis indicate that the concentration of the vanadyl ion is insignificant in water containing $>3.0 \text{ mg L}^{-1}$ ($94 \text{ } \mu\text{mol L}^{-1}$) of dissolved oxygen.

Assuming that the redox reaction $\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$ attains equilibrium, the concentration ratio of vanadate ion to vanadyl ion was estimated as 1.5×10^{16} at pH 7.0 and DO of 3.0 mg L^{-1} ($94 \text{ } \mu\text{mol L}^{-1}$) by the solution equilibrium computer program MINEQL+ (version 4.0, Environmental Research Software). In addition, although Okamura (1994) conducted a high-sensitive speciation analysis

Table 2. Depth-weighted average concentrations of dissolved V, Mo, and W in the oxygenated epilimnion (E) and hypolimnion (H), and the ratios of these average concentrations between the two layers.

| Site | V | | | Mo | | | W | | |
|------|-----------------------------------|------------------|-----------|-----------------------------------|------------------|-----------|-----------------------------------|-------------------|-----------|
| | Av. conc. (nmol L ⁻¹) | | E:H ratio | Av. conc. (nmol L ⁻¹) | | E:H ratio | Av. conc. (pmol L ⁻¹) | | E:H ratio |
| | E | H | | E | H | | E | H | |
| Ie-1 | 2.8 (0–15 m) | 1.7 (25–73 m) | 1.6 | 3.6 (0.15 m) | 3.3 (25–73 m) | 1.1 | 74.8 (0–15 m) | 37.7 (25–73 m) | 2.0 |
| I1 | 10.1 (0–20 m) | 4.0 (25–50 m) | 2.5 | 1.2 (0–20 m) | 1.1 (25–50 m) | 1.1 | 18.9 (0–20 m) | 10.5 (25–50 m) | 1.8 |
| I2 | 10.7 (0–20 m) | 4.1 (25–41 m) | 2.6 | 1.2 (0–20 m) | 1.1 (25–41 m) | 1.1 | 18.9 (0–20 m) | 7.9 (25–41 m) | 2.4 |
| U1 | 18.1 (0–10 m) | 4.9 (17–30 m) | 3.7 | 2.0 (0–10 m) | 1.9 (17–30 m) | 1.1 | 26.3 (0–10 m) | 9.0 (17–30 m) | 2.9 |
| U2 | 18.7 (0–12.5 m) | 6.0 (17–20 m) | 3.1 | 2.0 (0–12.5 m) | 1.8 (17–20 m) | 1.1 | 25.5 (0–12.5 m) | 13.2 (17–20 m) | 1.9 |

of V (+IV and +V) in the water of Lake Biwa, the vanadyl ion was not detected (<0.05 nmol L⁻¹) even in the lake water containing 1.0–3.0 mg L⁻¹ (31–94 μmol L⁻¹) of DO (Okamura et al. 2001). From the above discussion, we can conclude that the EH-type profiles of dissolved V at all the sites were formed by the supply of V to the epilimnia and not by its removal from the oxygenated hypolimnia.

The similarity between the vertical profiles of dissolved V and W (EH-type) indicates that W was also probably supplied to the epilimnia. On the other hand, the homogenous vertical profiles of Mo indicate that the dissolved Mo was conservative in the oxygenated epilimnia of all the lakes.

Sources of vanadium to the epilimnion—Pathways for influx of dissolved V into the epilimnion include riverine and groundwater inflows, precipitation, and release from the solid phase including sediment and suspended particles. Similarly, the pathways for the outflux of dissolved V include water outflow and diffusion across the thermocline from the epilimnion. The relation of these fluxes in the epilimnetic water column can be represented by the following mass balance equation of V:

$$F_{\text{river}} + F_{\text{groundwater}} + F_{\text{precipitation}} + F_{\text{solid}} = \frac{\Delta M}{\Delta t} + F_{\text{outflow}} + F_{\text{diffusion}} \quad (1)$$

where F_{river} = flux from the river, $F_{\text{groundwater}}$ = flux from the groundwater, $F_{\text{precipitation}}$ = flux from the precipitation, F_{solid} = release flux from the solid phase, $\Delta M/\Delta t$ = rate of change in the amount of dissolved V in the epilimnetic water column, F_{outflow} = leaving flux via the outflow, and $F_{\text{diffusion}}$ = turbulent diffusive flux from the epilimnion to the hypolimnion. In the following paragraphs, we will focus our discussion on Lake Biwa to evaluate the contribution of each of these potential sources to the increase in dissolved V in the epilimnion.

The average dissolved V concentrations in the epilimnetic water column (depth: 0–15 m) of Lake Biwa were 5.0 nmol L⁻¹ on 15 October 1986 (Sugiyama 1989), 3.6 nmol L⁻¹ on 6 September 1994 (Okamura 1994), and 2.8 nmol L⁻¹ on 18 July 1997 (this study). The mean rate of change ($\Delta M/\Delta t$) in the amount of dissolved V was estimated as 209 ± 48 nmol m⁻² d⁻¹, assuming that the V concentration in the epilimnion starts increasing from 1.7 nmol L⁻¹ (Sugiyama 1989) on 10 April of any year (Otsu Hydrobiological Station 1988; Ueda et al. 1998). The rates of water inflow from the river, precipitation, and groundwater have been reported as 5.56×10^6 , 3.32×10^6 , and 0.66×10^6 m³ d⁻¹ (Iwasa 1991), respectively. The dissolved V concentrations in the river water and precipitation around Lake Biwa have also been reported as 11 ± 4 nmol L⁻¹ (Okamura 1994; Mito et al. 2004) and 5.4 ± 3.1 nmol L⁻¹ (Okamura 1994; Mito et al. 2004; S. Tsukuda pers. comm.), respectively. On the basis of these rates and concentrations, we estimated the V fluxes from the river and precipitation (F_{river} and $F_{\text{precipitation}}$) as 93 ± 32 nmol m⁻² d⁻¹ and 27 ± 15 nmol m⁻² d⁻¹ (Table 3), respectively. The V flux from the groundwater will be discussed later. The leaving flux of V via the outflow (F_{outflow}) was estimated as 39 ± 8 nmol m⁻² d⁻¹ (Table 3), assuming that the sum of the water inputs from the river, precipitation, and groundwater was always equal to the amount of the water outflow.

We are able to estimate the vertical diffusive fluxes ($F_{\text{diffusion}}$)

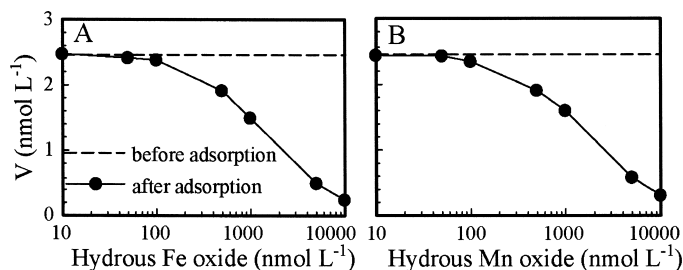


Fig. 4. Removal of dissolved vanadium by (A) hydrous iron oxide and (B) hydrous manganese oxide. The broken line shows the initial concentration (2.5 nmol L⁻¹) of dissolved vanadium and the filled circles show the concentrations of vanadium remaining in the water. The pH values of the samples after shaking were 7.1–7.2.

Table 3. Dissolved V fluxes in the epilimnetic water column in Lake Biwa during the stratification period.

| Dissolved V flux term | Flux (nmol m ⁻² d ⁻¹) |
|---|--|
| $\Delta M/\Delta t$ | 210 ± 50 |
| Σ influx | 260 ± 70 |
| F_{river} | 93 ± 32 |
| $F_{\text{precipitation}}$ | 27 ± 15 |
| $F_{\text{groundwater}} + F_{\text{solid}}$ | 140 ± 61 |
| Σ outflux | 51 ± 11 |
| F_{outflow} | 39 ± 8 |
| $F_{\text{diffusion}}$ | 12 ± 7 |

across the thermocline using the Fick's Law: $F_{\text{diffusion}} = -K_z \times \Delta C/\Delta z$, where K_z (m² d⁻¹) = turbulent diffusion coefficient and $\Delta C/\Delta z$ (mol m⁻⁴) = concentration gradient of dissolved V. The turbulent diffusion coefficient (K_z) was calculated as $K_z = 0.25 \varepsilon N^{-2}$ (Osborn 1980), where ε (m² s⁻³) is the rate of turbulent energy dissipation and N (s⁻¹) is the Brunt-Väisälä frequency. The rate of turbulent energy dissipation in the upper thermocline (13–17 m) of Lake Biwa has been reported to be in the range from 1×10^{-8} to 7×10^{-6} m² s⁻³ (Roberts et al. 1998). In the calculation, the rate of turbulent energy dissipation was set to the lowest value of 1×10^{-8} m² s⁻³. The values of K_z and the vertical gradient of V ($\Delta C/\Delta z$) across the thermocline (15–25 m), which were determined from the monthly vertical profiles of water temperature (Ueda et al. 1998) and dissolved V (M. Sugiyama unpubl.) from May to October, ranged from 0.04 to 0.54 m² d⁻¹ and from 40 to 310 nmol m⁻⁴, respectively. The average diffusive flux of dissolved V was calculated as 12 ± 7 nmol m⁻² d⁻¹ (Table 3).

The values of the fluxes from the groundwater and solid phase cannot be determined separately, because the dissolved V concentration has not been measured in the groundwater of Lake Biwa. Therefore, the sum of the fluxes from the groundwater and solid phase ($F_{\text{groundwater}} + F_{\text{solid}}$) was calculated by substituting the above values of F_{river} , $F_{\text{precipitation}}$, $\Delta M/\Delta t$, F_{outflow} , and $F_{\text{diffusion}}$ in the mass balance equation (Eq. 1); the sum was determined as 140 ± 61 nmol m⁻² d⁻¹ (Table 3). If the flux from the solid phase is negligible, then the groundwater must contain dissolved V at a high concentration (140 ± 60 nmol L⁻¹). However, such a high V concentration has not been measured even in the bottom water of Lake Biwa's littoral zone (Y. Harita, unpubl.). In addition, if the dissolved V concentration in the groundwater is assumed to be the same as that in the river water, then $F_{\text{groundwater}}$ and F_{solid} are determined as 11 ± 4 and 129 ± 61 nmol m⁻² d⁻¹, respectively, indicating that F_{solid} is the largest among the four influses. From these values, it appears that the solid phase, such as sediment and suspended particles, is the significant source of V to the epilimnion.

The epilimnetic concentration of dissolved V decreases in Lake Biwa from October to January (Sugiyama 1989; Okamura 1994). This decrease may be reasonably explained by assuming that the solid phase acts as the sink as well as the source for V.

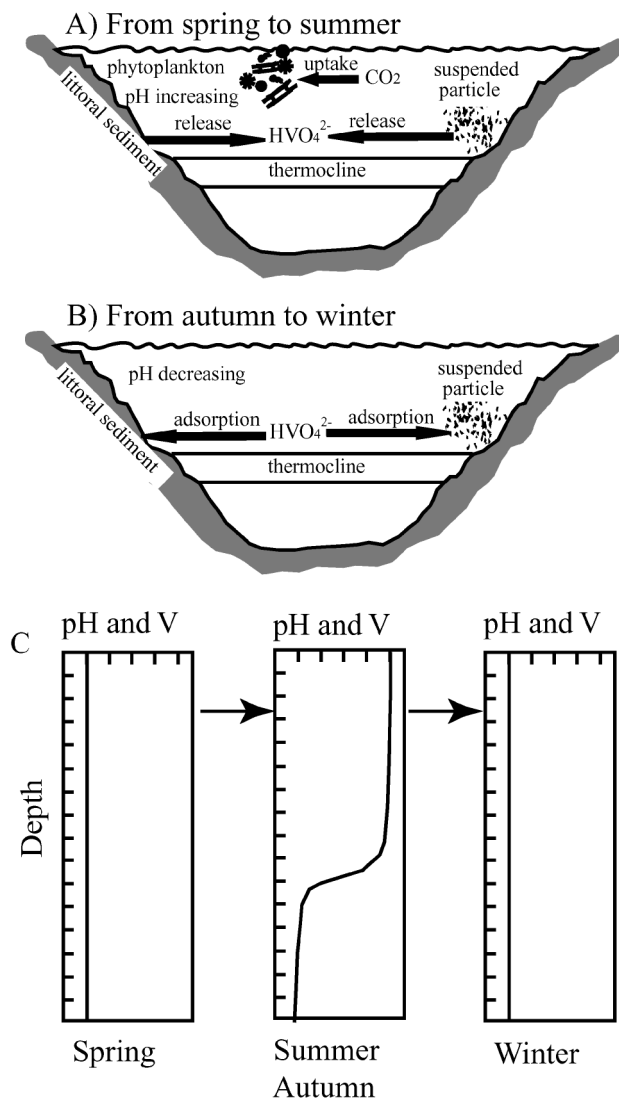


Fig. 5. (A and B) Mechanism of vanadium increase and decrease in the epilimnion, and (C) seasonal variation in the profiles of pH and dissolved vanadium from spring to winter.

Hypothetical mechanism for the geochemical behaviors of V—The pH profiles in all the sites studied were similar to those (EH-type) of dissolved V (Fig. 3). In addition, on the basis of the monthly observations reported by Sugiyama (1989) and Okamura (1994), it has been shown that the dissolved V concentration in the epilimnion of Lake Biwa appears to vary in response to the pH variation, which increases from April to October and decreases from October to January. On the basis of these observations, the transportation of V between the solid phase and water appears to be influenced by the pH variation.

Here, we propose the following hypothetical mechanism (Fig. 5) to account for the seasonal variation in the dissolved V concentration. Vanadium is adsorbed onto minerals contained in the littoral sediment and suspended particles at neutral pH during the winter circulation period. The epilimnion pH increases owing to biological metabolism from spring to summer (Stumm and Morgan 1994). Along with the rise in

pH, V is desorbed from the mineral surfaces to the epilimnetic water, resulting in an increase in the dissolved V concentration (Fig. 5A,C). During the middle stage of the stratification period, the pH and dissolved V in the epilimnion reach their maxima. In autumn, the epilimnetic pH starts to decrease in response to the decline in the biological activity (Fig. 5B). With the decrease in pH, the dissolved V in the lake water is adsorbed onto the surface of littoral sediment minerals and suspended particles, and the dissolved V concentration decreases (Fig. 5B,C). Fuller and Davis (1989) have also suggested a similar mechanism to account for diurnal variations in the dissolved arsenate concentration in stream water.

The factors controlling the transportation of V between the solid phase and lake water might include a redox reaction. It is possible that even in the littoral zone, a temporary lowering of the redox potential at the surface of the sediment will occur owing to a high microbial activity (Murase 2002). The lowering of the redox potential may lead to the reductive dissolution of the Fe and Mn oxide phases in the sediment and the release of V that was adsorbed onto the oxide phases. However, the dissolved Fe(II) and Mn(II) that diffuse in well-oxygenated water will be immediately reoxidized (Stumm and Morgan 1994), and the freshly formed Fe and Mn oxides will again scavenge the dissolved V (Fig. 4). Therefore, it is likely that the redox reaction occurring in the littoral sediment is not the primary factor for the increase of V in the epilimnion.

Testing the hypothetical mechanism—A laboratory experiment was carried out to examine the hypothetical mechanism using the setup shown in Fig. 2. This experiment was designed to simulate the natural pH variations that are observed in the littoral environment and the epilimnion. In natural environments, the pH of lake water is controlled mainly by the $\text{CO}_2(\text{aq})$ uptake by phytoplanktons for photosynthesis and the $\text{CO}_2(\text{aq})$ release due to respiration (Stumm and Morgan 1994). The setup is designed to control the pH by regulating the $\text{CO}_2(\text{aq})$ concentration.

The experimental period (11 d) was divided into three subperiods (Fig. 6). In period I (0–1.8 d), the pH was maintained at approximately 7.0 by bubbling a mixture of natural air (2.5 L min^{-1}) and CO_2 gas (6 ml min^{-1}) (Fig. 6A). In period II (1.8–7.2 d), the pH was raised to approximately 8.7 by bubbling CO_2 -free air (2.5 L min^{-1}) that was made by passing air through 3 mol L^{-1} KOH solution (Fig. 2). In period III (7.2–11 d), the pH value was decreased to 7.0 as in period I.

The results (Fig. 6A, B) show that the dissolved V concentration changed with the pH variation. In period I, the concentration of the dissolved V was constant ($6.4 \pm 0.2 \text{ nmol L}^{-1}$). In period II, its concentration increased in response to the increase in pH. Further, the result indicates that V was released from the sediment owing to the rise in pH. In period III, the pH value decreased to 7.0 and the concentration of dissolved V decreased, suggesting that V was transported to the sediment. From the above results, it is possible to conclude that the mechanism mentioned above is reasonable.

Tungsten was also released from the sediment in response

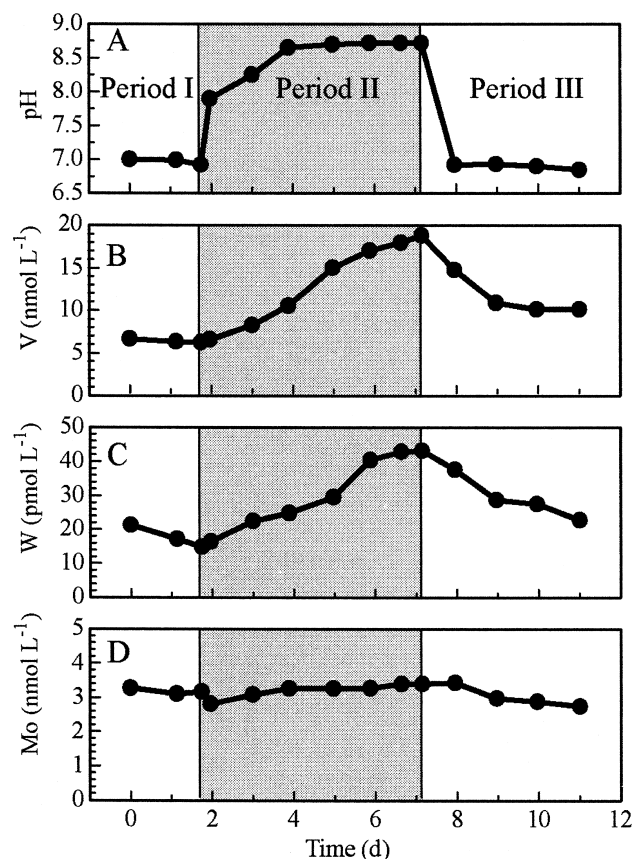


Fig. 6. (A) Changes in pH, and (B–D) concentrations of dissolved V, W, and Mo in the lake water during the laboratory experiment.

to the rise in pH (Fig. 6C). This result indicates that the vertical profiles of dissolved W, which were EH-type and similar to those for V, can be explained by the same mechanism (Fig. 5A). It also implies that the seasonal variation of dissolved W in natural lakes may display a pattern similar to that observed for dissolved V. The observations of the seasonal variation in the vertical profile of W pose an interesting challenge for future studies.

The concentration of the dissolved Mo was nearly constant ($3.1 \pm 0.2 \text{ nmol L}^{-1}$) throughout the experiment (Fig. 6D). This indicates that the concentration of the dissolved Mo is not affected by the pH variation, and is consistent with the homogeneous Mo profiles found in all the lakes (Fig. 3).

Importance of hydrous Fe oxide in oxyanion cycling—Among various solid phases composing the littoral sediment and suspended particles, the hydrous Fe oxide phase seems to play an essential role in catching and releasing oxyanions corresponding to pH variations. Hydrous Fe oxide is one of the major components in lake sediment (Nakashima 1982). As shown in Fig. 7, hydrous Fe oxide adsorbs vanadate and tungstate under a lower pH, but releases them to the water phase when the pH increases. Similar processes are expected to occur in natural lakes. In the case of molybdate, hydrous Fe oxide does not adsorb molybdate even under the neutral

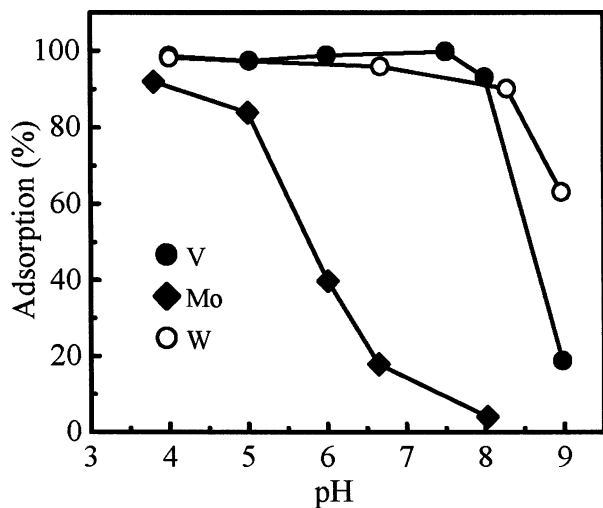


Fig. 7. Adsorption ratios of vanadium, molybdenum, and tungsten onto hydrous iron oxide as a function of pH. This figure was constructed using the data of Ishibashi et al. (1958, 1960) and Kuwamoto (1960). Total concentrations of adsorbate and adsorbent were $20 \mu\text{mol L}^{-1}$ and 0.45 mmol L^{-1} in V, $0.52 \mu\text{mol L}^{-1}$ and 0.18 mmol L^{-1} in Mo, and $50 \mu\text{mol L}^{-1}$ and 1.8 mmol L^{-1} in W.

pH and does not have an influence on the variations in the molybdate concentrations (Fig. 7). Such differences among the geochemical behaviors of V, W, and Mo are in agreement with the work of Pokrovsky and Schott (2002). They performed a fractionation analysis for aquatic environments and found that large portions of Mo were present in the form of truly dissolved inorganic species, whereas large portions of V and W remained strongly adsorbed onto the colloidal iron oxide.

Phosphorus (P) and arsenic (As) are also speculated to be mobilized from solid phase, such as the lake and creek sediments, in response to an increasing pH (Andersen 1975; Fuller and Davis 1989). Andersen (1975) and Fuller and Davis (1989) suggested that the hydrous Fe oxide phase plays an important role in controlling the release of P and As. Similar to vanadate and tungstate, large amounts of phosphate and arsenate are contained in the hydrous Fe oxide phase in aquatic environments (Filippelli and Delaney 1996; Pokrovsky and Schott 2002; Koschinsky and Hein 2003). The adsorption properties of phosphate and arsenate on hydrous Fe oxide are very similar to those of vanadate, because the chemical structures are analogous among vanadate, phosphate, and arsenate (Rietra et al. 1999). Phosphorus and As have +V oxidation states under oxic conditions (Brookins 1987) and exist, like V, as oxyanions (PO_4^{3-} and AsO_4^{3-}). The above information appears to suggest that during the stratification period P and As are also released from the hydrous Fe oxide phase of littoral sediment and suspended particles under high pH.

References

ANDERSEN, J. M. 1975. Influence of pH on release of phosphorus from lake sediments. *Arch. Hydrobiol.* **76**: 411–419.
BREIT, G. N., AND R. B. WANTY. 1991. Vanadium accumulation in

carbonaceous rocks. A review of geochemical controls during deposition and diagenesis. *Chem. Geol.* **91**: 83–97.
BROOKINS, D. G. 1987. Eh-pH diagrams for geochemistry. Springer-Verlag.
COLLIER, R. W. 1984. Particulate and dissolved vanadium in the North Pacific Ocean. *Nature* **309**: 441–444.
ERICKSON, B. E., AND G. R. HELZ. 2000. Molybdenum(VI) speciation in sulfidic waters: Stability and lability of thiomolybdates. *Geochim. Cosmochim. Acta* **64**: 1149–1158.
FILIPPELLI, G. M., AND M. L. DELANEY. 1996. Phosphorus geochemistry of equatorial Pacific sediments. *Geochim. Cosmochim. Acta* **60**: 1479–1495.
FULLER, C. C., AND J. A. DAVIS. 1989. Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters. *Nature* **340**: 52–54.
HARITA, Y., T. HORI, AND M. SUGIYAMA. 2003. Air-segmented continuous-flow analysis for molybdenum in various geochemical samples. *Microchim. Acta* **142**: 71–78.
HELZ, G. R., C. V. MILLER, J. M. CHARNOCK, J. F. W. MOSSELMANS, R. A. D. PATTRICK, C. D. GARNER, AND D. J. VAUGHAN. 1996. Mechanism of molybdenum removal from the sea and its concentration in the black shales: EXAFS evidence. *Geochim. Cosmochim. Acta* **60**: 3631–3642.
ISHIBASHI, M., T. FUJINAGA, AND T. KUWAMOTO. 1958. Chemical studies of the ocean. LXXVII: Coprecipitation of molybdenum with ferric hydroxide. *J. Chem. Soc. Jpn.* **79**: 1496–1499. [In Japanese.]
ISHIBASHI, M., T. FUJINAGA, AND T. KUWAMOTO. 1960. Chemical studies of the ocean. XXCIX: Coprecipitation of tungsten with ferric hydroxide. *J. Chem. Soc. Jpn.* **81**: 392–395. [In Japanese.]
IWASA, Y. 1991. Engineering limnology. Sankaido. [In Japanese.]
JOHANNESSON, K. H., W. B. LYONS, E. Y. GRAHAM, AND K. A. WELCH. 2000. Oxyanion concentrations in eastern Sierra Nevada rivers—3. Boron, molybdenum, vanadium, and tungsten. *Aquat. Geochem.* **6**: 19–46.
KOSCHINSKY, A., AND J. R. HEIN. 2003. Uptake of elements from seawater by ferromanganese crusts: Solid-phase associations and seawater speciation. *Mar. Geol.* **198**: 331–351.
KUWAMOTO, T. 1960. Chemical studies of the ocean. XXCIV: Coprecipitation of vanadium with ferric hydroxide. *J. Chem. Soc. Jpn.* **81**: 1669–1673. [In Japanese.]
LBRI AND NIRA. 1984. Data book of world lakes. The secretariat, LECS'84, Otsu.
MIDDELBURG, J. J., D. HOEDE, H. A. VAN DER SLOOT, C. H. VAN DER WEIJDEN, AND J. WIJSTRA. 1988. Arsenic, antimony and vanadium in the North Atlantic Ocean. *Geochim. Cosmochim. Acta* **52**: 2871–2878.
MITO S., AND OTHERS. 2004. The budget of dissolved trace metals in Lake Biwa, Japan. *Limnology* **5**: 7–16.
MIYAUCHI, T., M. IWASHITA, AND T. SHIMAMURA. 1998. Behaviors of trace elements in Tsukui Reservoir inferred from ICP-MS analysis. *J. Environ. Chem.* **8**: 13–21.
MURASE, J. 2002. Littoral and sub-littoral sediments in Lake Biwa: Division based on a thermal structure of the lake and their possible roles in the lake ecosystem. *Jpn. J. Limnol.* **63**: 249–254.
MURRAY, J. W. 1975. The interaction of metal ions at the manganese dioxide-solution interface. *Geochim. Cosmochim. Acta* **39**: 505–519.
NAKASHIMA, S. 1982. Partitioning of heavy metals (Mn, Fe, As, Cd, Pb, Cu, Zn, Co and Ni) into selective chemical fractions in sediment cores from Lake Biwa. *Jpn. J. Limnol.* **43**: 67–80. [In Japanese.]
NOJIRI, Y., T. KAWAI, A. OTSUKI, AND K. FUWA. 1985. Simultaneous multielement determination of trace metals in lake wa-

- ters by ICP emission spectrometry with preconcentration and their background levels in Japan. *Wat. Res.* **19**: 503–509.
- OKAMURA, K. 1994. Development of the automated separation and determination system of vanadium (IV) (V) and study on these behaviors in natural waters. MS. thesis, Kyoto Univ. [In Japanese.]
- , M. SUGIYAMA, H. OBATA, M. MARUO, E. NAKAYAMA, AND H. KARATANI. 2001. Automated determination of vanadium(IV) and (V) in natural waters based on chelating resin separation and catalytic detection with Bindschedler's green leuco base. *Anal. Chim. Acta* **443**: 143–151.
- OKUZONO, K., T. NAKAUCHI, T. SUNOSE, M. KORIYAMA, K. NAKAO, T. HAGI, AND T. KOKUSHO. 1979. Water qualities of Lakes Ikeda and Unagi-ike. *Rep. Kagoshima Pref. Inst. E. P. & P. H.* **15**: 125–142. [In Japanese.]
- OSBORN, T. R. 1980. Estimates of the local rate of vertical diffusion from dissipation measurements. *J. Phys. Oceanogr.* **10**: 83–89.
- OTSU HYDROBIOLOGICAL STATION. 1998. Seven report of the regular limnological survey of Lake Biwa during 1972–1987. *Contr. Otsu Hydrobiol. Stn., Kyoto Univ.* **327**: 1–56.
- POKROVSKY, O. S., AND J. SCHOTT. 2002. Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chem. Geol.* **190**: 141–179.
- RIETRA, R.P.J.J., T. HIEMSTRA, AND W. H. VAN RIEMSDIJK. 1999. The relationship between molecular structure and ion adsorption on variable charge minerals. *Geochim. Cosmochim. Acta* **63**: 3009–3015.
- ROBERTS 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**: 1023–1036.
- SHILLER, A. M., AND E. A. BOYLE. 1987. Dissolved vanadium in rivers and estuaries. *Earth Planet. Sci. Lett.* **86**: 214–224.
- SHOLKOVITZ, E. R., AND D. COPLAND. 1982. The chemistry of suspended matter in Esthwaite Water, a biologically productive lake with seasonally anoxic hypolimnion. *Geochim. Cosmochim. Acta* **46**: 393–410.
- SOHRIN, Y., K. ISSHIKI, T. KUWAMOTO, AND E. NAKAYAMA. 1987. Tungsten in North Pacific Waters. *Mar. Chem.* **22**: 95–103.
- STUMM, W., AND J. J. MORGAN. 1994. *Aquatic chemistry*, 3rd ed. Wiley.
- SUGIYAMA, M. 1989. Seasonal-variation of vanadium concentration in Lake Biwa, Japan. *Geochim. J.* **23**: 111–116.
- . 1996. Simultaneous multi-element analysis of aquatic suspended particulate matter. *Bunseki Kagaku* **45**: 667–675. [In Japanese.]
- . 2004. Analysis of aquatic suspended particle. *Bunseki* **355**: 412–414. [In Japanese.]
- , AND T. HORI. 1992. Air-segmented continuous-flow analysis for vanadium based on a catalytic reaction with Bindschedler's green leuco base. *Anal. Chim. Acta* **261**: 189–196.
- SZALAY, A., AND M. SZILÁGYI. 1967. The association of vanadium with humic acids. *Geochim. Cosmochim. Acta* **31**: 1–6.
- TAKEMATSU, N., Y. SATO, S. OKABE, AND E. NAKAYAMA. 1985. The partition of vanadium and molybdenum between manganese oxides and sea-water. *Geochim. Cosmochim. Acta* **49**: 2395–2399.
- TANAKA, M. 1992. *The lakes in Japan*. The University of Nagoya Press. [In Japanese.]
- UEDA, T., A. KAWABATA, T. KOITABASHI, AND T. NARITA. 1998. Data of regular limnological survey of Lake Biwa. *Cent. Ecol. Res. Kyoto Univ. Tech. Rep.* **1**: 1–60.
- VIOLLIER, E., G. MICHARD, D. JÉZÉQUEL, M. PÈPE, AND G. SARAZIN. 1997. Geochemical study of a crater lake: Lake Pavin, Puy de Dôme, France. Constraints afforded by the particulate matter distribution in the element cycling within the lake. *Chem. Geol.* **142**: 225–241.
- VORLICEK, T. P., M. D. KAHN, Y. KASUYA, AND G. R. HELZ. 2004. Capture of molybdenum in pyrite-forming sediments; role of ligand-induced reduction by polysulfides. *Geochim. Cosmochim. Acta* **68**: 547–556.
- WANTY, R. B., AND M. B. GOLDBABER. 1992. Thermodynamics and kinetics of reactions involving vanadium in natural systems: Accumulation of vanadium in sedimentary rocks. *Geochim. Cosmochim. Acta* **56**: 1471–1483.
- WEHRLI, B., AND W. STUMM. 1989. Vanadyl in natural waters: Adsorption and hydrolysis promote oxygenation. *Geochim. Cosmochim. Acta* **53**: 69–77.

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