

## Effect of DO fluctuation on the manganese cycle around the sediment water interface in bottom of the Lake Biwa

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Enrichment of Mn and As in the surface of sediment has been reported from various lakes in the world. This enrichment is generally caused by the precipitation/adsorption of MnO<sub>2</sub> and arsenate after upward diffusion of Mn<sup>2+</sup> and arsenite. Lake Biwa is a typical example, in which clear enrichments of Mn and As within thin surface enriched layer (<2 cm) of sediment were observed. However, progressive hypoxia recently reported from the lake can induce release of these elements into water column (Yoshimizu et al. 2010, Itai et al. 2012). In order to reveal the dynamics of Mn and As in the lake bottom, we made geochemical survey through determination and speciation of Mn and As in sediment, porewater and lake bottom water. According to our estimation, total Mn and As in the enriched layer of Lake Biwa was roughly 10000 and 240 tons, respectively (Itai et al., 2012). These amounts are ca. 1800 and 12 times respectively higher than the inventory of these elements in Lake water, suggesting that releasing a portion of Mn and As from enriched layer can be a cause of large increase of these in lake water. The speciation of Mn and As in sediment determined by X-ray absorption fine structure (XAFS) indicated that predominant species of Mn from surface to 2 cm depth was MnO<sub>2</sub> while divalent Mn, likely ionic form, was predominant below enriched layer. Similar to Mn, oxidation state of As was gradually changed with depth, i.e., arsenate was predominant in surface, then arsenite and As in sulfide becomes predominant toward deep. These results suggested that Mn and As in enriched layer should be reduced when DO level in lake bottom becomes lower. The flux of Mn and As from the lake sediment to water column estimated by porewater profile were 3400 - 16000 and 400 - 1800 mg m<sup>-2</sup> year<sup>-1</sup>, respectively. The fluxes were higher in deeper part of the lake in which sediment character was more reducing than shallower part. With progressive hypoxia, this flux should increase. The monthly monitoring of DO and Mn level in lake water suggested that Mn level in water above 1 m of the lake floor increased from August to December with the highest level was ca. 100 times higher than the baseline level. This trend is consistent with the gradual decrease of DO during thermal stratification period. In the bottom water, the threshold DO level where apparent Mn release started was estimated to be 5-6 mgO<sub>2</sub>/L. This value is higher compare to the inter-annual DO minimum ever reported (<4 mgO<sub>2</sub>/L). If 40% of Mn released from enriched layer then completely mixed in whole lake, the Mn level becomes 0.6 mg/L which corresponds to lethal levels of some crustaceans and insects. Although such an extreme situation is unlikely, continuous monitoring Mn and As levels is important to safeguard the lake ecosystem and food supply.

Keywords: Lake Biwa, dissolved oxygen, manganese, arsenic, pore water, speciation