Study on geochemical behavior of nutrients and trace metals in freshwater lakes with impact of human activities

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学　位　論　文　概　要
Dissertation Summary

学位請求論文（Dissertation）

題名（Title）　Study on geochemical behavior of nutrients and trace metals in freshwater lakes with impact of human activities

（邦訳又は英訳）（Title in Japanese or in English）　**人間活動の影響を伴う淡水湖における栄養塩と微量金属の地球化学的挙動に関する研究**

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学位論文概要（Dissertation Summary）

Eutrophication and organic matter pollution in lakes have become more serious with increasing human impacts and climate change. Therefore, many reports on water quality, biogenic elements (N, P, Si, Fe, Mn) and organic matter (DOC, POC) in lake water have been produced. However, research on the effects of climate change on the biogeochemical processes in small freshwater lakes in temperate regions has not yet been undertaken. We had the following three specific purposes: (a) to define the seasonal variation and vertical profile concentration of the biogenic elements in a small artificial lake, Lake Bulan; (b) to monitor the spatial and temporal variation of the trace metals and to identify the source of Fe (II) in a semi-closed lake, Lake Kibagata; and (c) to investigate the relationship between DOC and POC in the surface and bottom layers of the lake. Firstly, nutrients, trace metal, and DOC concentrations were observed in Lake Bulan via spatial and temporal observation from September 2019 to September 2021. The nutrient concentrations exhibited the cyclic behavior, because the concentration in the water surface increases during the winter season while decreases in the summer season. Our study is the first report on

the nutrient concentration and its profile in a small freshwater lake with eutrophication in a time series observation in Mongolia. The Lake Bulan shows the amplitude of seasonal fluctuations in the dissolved inorganic nitrogen (DIN) concentration and the percentage of the composition can serve as an indicator of the eutrophication of a water body. The DIN concentration reaches the maximum (1.44 ± 0.08 mg/l) in January and the minimum (0.26 ± 0.11 mg/l) in August in Lake Bulan. The trace metals Fe and Mn concentration showed no observable seasonal variation in the surface. The DOC concentration ranged from 5.82 ± 0.13 mg/l in January 2020 to 9.44 ± 0.68 mg/l in September 2021. The seasonal values of phosphorus ranged from 0.028 to 0.288 mg/l, while the phosphate concentration range was 0.001–0.199 mg/l, and the highest concentrations were measured in January 2021. Nutrient availability by molar mass ratios of DIN:PO_4^{3-} in Lake Bulan are 117, 1083, 192 and 118 in January, April, August, and September, respectively. Based on molar ratios of DIN:PO_4^{3-}, Lake Bulan phytoplankton is phosphorus-limited during the year. In interannual changes, the average ratio of phosphate/total phosphorus (TP) was 0.04 in April, 0.11 in August, and 0.49 in January. This increase showed the intense biochemical processes in the ecosystem leading to the production of nutrients and decomposition of organic matter in the bottom layer in winter. The vertical profile $NO_3^- - N$ concentration and were like those of $NH_4^+ — N$ and showed the evidence of active metabolism in lake bottom water during winter. The results indicate that the summer and winter stratifications occur for organic matter decomposition in the bottom layer and lead to the generation of the nutrients. Therefore, these processes are important to biochemical cycling in the ice-covered lake. An early time formation and long duration of summer stratification may be caused for the further increased nutrient concentration, while the shorter duration of winter stratification led to a lower productivity of phytoplankton in spring. The C/N ratio has been used as a representative proxy to reconstruct the depositional environment of freshwater lake sediments. TOC content significantly decreased from the surface to the sub – surface of 3 cm depth in core. TN content also decreased with depth until 3 cm depth, but $\delta^{13}C$ and $\delta^{15}N$ were almost constant with depth. The C/N ratio increased from 6.8 to 9.2. The result can be evidence that eutrophication occurs in Lake Bulan.

The trace metal concentrations, especially dissolved Fe, display temporal and spatial variation in the surface water. The highest Fe and Mn concentrations were observed at surface water site KB1 in February 2018, at 335 μg/l and 131 μg/l, respectively. On the other hand, Fe and Mn concentrations in Hiyou River, which contributes to the lake, were 112 μg/l and 50.1 μg/l, respectively. The concentration of dissolved Fe at all stations was relatively low in the summer, but there were a few cases where concentrations of dissolved Fe were high (179 μg/l and 107 μg/l), such as in August 2016 and August 2018. This could be related to there being a large amount of precipitation before sampling. As the concentration of dissolved Fe had high temporal variability, we examined the behaviour of Fe in winter and summer conditions. The concentration of dissolved Fe had a positive linear correlation with NH_4^+ (r = 0.62) and

Mn (r = 0.83, $p < 0.05$) in the summer season, plus a positive linear correlation with NH_4^+ (r = 0.65), Mn (r = 0.80), Al (r = 0.96), Ca (r = 0.62), and negative linear correlation with Si (r = -0.89, $p < 0.05$) in the winter season. To better understand the spatial and temporal variation of Fe and its source in the lake, additional research was carried out from 2019 to 2021. Dissolved Fe and Fe (II) concentrations from the surface water in Lake Kibagata (KB1 – KB4) had high spatial variation in February 2020, November 2020, and January 2021. The highest Fe (II) concentration was observed at station KB1. This result was related to the previously observed maximum concentration of Fe, which was observed in February 2018 at station KB1. To identify the source of dissolved Fe, additional sampling at sites KB-1 and KB-2 were performed on the bottom water in Lake Kibagata. Fe concentrations over 80 μg/l were observed in June, July, and September, but lower concentrations for $NH_4^+ - N$ were observed. Higher $NH_4^+ - N$ and Fe concentrations were observed from November to March, though DO concentration was 11.1-12.2 mg/l. Small effects of organic matter decomposition were seen in the bottom water during the winter season. The study of the effects of river input on dissolved Fe concentration in the bottom water at KB-1 was obtained. results show the small contribution of river discharge to higher concentrations of Fe in the bottom water. Higher Fe (II) concentrations suggest that Fe (II) is input from the lake bottom to the oxic bottom water. Sub-bottom groundwater discharge is a possible source of Fe (II), due to higher Fe (II) and $NH_4^+ - N$ concentrations in the bottom layer. The differences in flush intensity and residence time of the groundwater before discharge to the bottom water are related to the differences in Fe and NH_4^+ concentrations, and are also related to the concentrations in summer (rain events) and winter (snow cover and melting).

The DOC and POC concentration in surface water in Lake Kibagata have been observed from 2015 until the present. We started additional study from the bottom layer of Lake Kibagata to organic matter redox conditions, which are related to COD concentration. DOC concentration has a similar profile in surface and bottom water of Lake Kibagata, and Hiyou River. The POC concentration presents a different path between the river and lake water. Temporal variation of $\delta^{13}C$ of total organic carbon and $\delta^{15}N$ of total nitrogen in suspended solids from the inflow river water and the lake waters are different in winter months. Chemical functions and physical parameters such as temperature and precipitation are related to nutrient availability, the amount of available free oxygen, the redox activity, the microbial functions with microfloral succession patterns, and the availability of microorganisms (aerobic or anaerobic). The $\Delta^{14}C$ of POC in the surface and bottom water shows seasonal variation, but different in the summer season. The results suggest that summer stratification occurs, and the differences in $\Delta^{14}C$ values of POC are related to the production of phytoplankton in the surface and the bottom waters, though Lake Kibagata is a shallow (~2.4 m water depth) and small lake environment.

Two case studies were conducted to understand the effects of direct and indirect human activities on lake water quality and the ecosystem. Under climate change, thermal stratification development leads to changes and effects on water quality parameters, which consequently affects biogeochemical processes in small lakes. Lake systems are important for maintaining social activities, biodiversity, and aquatic ecosystems. To perform sustainable development in rural and urban areas, aquatic environments including lake systems require monitoring and assessment of their environments.