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Session 5b) Novel Methodology 2: Technical Development

Vertical distribution of phosphate oxygen isotopes during algal blooms in thermally stratified reservoirs

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Phosphate oxygen isotope composition ($\delta^{18}O_p$) is an effective tool to tracing phosphate sources in eutrophic lakes, but biological processes such as intensive algal growth can also cause oxygen isotope fractionation on phosphate (PO_4^{3-}), bringing in large uncertainties in source determination [1]. A large impact of active algal growth and decomposition on the $\delta^{18}O_p$ in lake surface water in both space and time is expected. Particularly, under PO_4^{3-} limited condition, algal surface proteins preferentially transport PO_4^{3-} with lower $\delta^{18}O_p$ value, and thus, a kinetic fractionation process is expected to occur at places of or during intensive algal growth or decomposition, resulting in increase or decrease in the $\delta^{18}O$ of the PO_4^{3-} in the water. However, due to difficulty in sampling a sufficient amount of dissolved PO_4^{3-} for $\delta^{18}O_p$ measurements in high spatial and temporal resolutions, this prediction has never been tested.

The recently developed ESI-Orbitrap-MS method can measure $\delta^{18}O_p$ using small sample sizes (25 nmol) [2], which is two orders of magnitude smaller than the conventional method through silver phosphate decomposition to CO via the TC/EA-IRMS technique. In this study, we sampled 500 mL of water at 2 m resolution during an algal bloom season in two thermally stratified lakes (Lake Hongfeng (19 m depth, n = 21) and Lake Aha (20 m depth, n = 12)). We developed a new ZrO gel-Anion resin method modified from a previous study [3,4] to concentrate and purify the dissolved phosphate from the natural waters. We successfully isolated nmol-level pure PO_4^{3-} solutions for Orbitrap-MS analysis, and confirmed negligible isotopic fractionation (< 0.3‰) during the separation and purification processes. The $\delta^{18}O_p$ in Hongfeng Lake and Aha Lake ranged from 13.7‰ to 20.5‰ and 13.7‰ to 19.3‰, respectively. The highest $\delta^{18}O_p$ values were found at 0-1 m depth, where the $\delta^{18}O_p$ is apparently more positive than the equilibrium value with the ~-7‰ $\delta^{18}O$ value of the lake water. The lowest $\delta^{18}O_p$ values were found at 8-9 m depth where algal organic mass accumulated at the thermocline and the anoxic condition facilitated the remineralization of organic phosphorus into inorganic phosphate. The high-resolution vertical distribution of the dissolved $\delta^{18}O_p$ during algal blooms in thermally stratified reservoirs has revealed the dynamics of phosphorus cycling in phosphorus-limited lakes during an algal bloom season.

References:

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