

## In situ estimation of new and regenerated production in lakes using triple oxygen isotopes as tracers

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The gross primary production rate is an essential parameter to study biogeochemical processes in hydrosphere, having strong relations with environmental changes in lakes and oceans, such as eutrophication and global warming. Supplying rates of fixed nitrogen, especially dissolved nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ), to each hydrospheric environment often control each gross primary production rate. As a result, the primary production is often divided into the following two categories: “new production” that uses  $\text{NO}_3^-$  supplied either from atmosphere or from aphotic layer, and “regenerated production” that uses a recycled nitrogen in the form of  $\text{NH}_4^+$  or dissolved organic nitrogen excreted or produced during biogeochemical processes within photic layer.

All the above-mentioned parameters had been traditionally estimated based on incubations of sampled water in bottles by adding isotope-labeled compounds such as  $^{13}\text{CO}_2$  or  $^{14}\text{CO}_2$  for the primary production rates and/or  $^{15}\text{NO}_3^-$  or  $^{15}\text{NH}_4^+$  for nitrogen uptake rates. In these approaches, however, sampled water in bottles is incubated under artificial conditions that must be somewhat different from actual in-situ conditions and the results could represent different rates from the original in aquatic environments. Moreover, the estimated values based on the incubation corresponds to instantaneous uptake rates when sampling was done so that large errors could be expected for the hydrospheric environments with significant temporal variations, otherwise we must increase a number of observations using time and costs.

In this study, we determined the parameters using natural isotopes in lake-dissolved materials instead of using incubations. Most of the oxygen-containing molecules on earth show mass-dependent relative variation between  $^{17}\text{O}/^{16}\text{O}$  ratios and  $^{18}\text{O}/^{16}\text{O}$  ratios. On the other hand, atmospheric  $\text{O}_3$  photochemically produced from  $\text{O}_2$  shows an anomalous enrichment in  $^{17}\text{O}$ , so that residual atmospheric  $\text{O}_2$  is slightly depleted in  $^{17}\text{O}$  in comparison with the mass-dependent relative relation. Besides, at least one of the O atoms in atmospheric  $\text{NO}_3^-$  is derived from atmospheric  $\text{O}_3$  owing to the contribution of O atoms from  $\text{O}_3$  during the photochemical oxidation processes of  $\text{NO}_x$  in atmosphere, so that the triple oxygen isotope ratios ( $\Delta^{17}\text{O}$  values) of  $\text{NO}_3^-$  also deviate from the mass-dependent relative relation. Since  $\Delta^{17}\text{O}$  value does not vary during the general mass-dependent reactions such as decompositions, we can estimate the mixing ratio between atmospheric  $\text{O}_2$  and photosynthetic  $\text{O}_2$  from  $\Delta^{17}\text{O}$  value of  $\text{O}_2$  and that between atmospheric  $\text{NO}_3^-$  and remineralized  $\text{NO}_3^-$  from  $\Delta^{17}\text{O}$  value of  $\text{NO}_3^-$ . If we determine the  $\Delta^{17}\text{O}$  values of both dissolved  $\text{O}_2$  and  $\text{NO}_3^-$  in a hydrospheric environment as well as supplying rates of atmospheric  $\text{O}_2$  and  $\text{NO}_3^-$ , we can determine both the primary production rate and  $\text{NO}_3^-$  uptake rate simultaneously. One of the priorities of this  $\Delta^{17}\text{O}$  method is that the estimated rate corresponds to the average value of each rate, so that the values can be a more reliable and accurate than the values estimated from the incubation methods.

In this study, we determined both gross primary production rate and new primary production ( $\text{NO}_3^-$  uptake) rate simultaneously based on the  $\Delta^{17}\text{O}$  value of dissolved  $\text{O}_2$  and  $\text{NO}_3^-$  in two oligotrophic lakes (Lake Shikotsu and Lake Kuttara) and one mesotrophic lake (Lake Biwa) in Japan. The regenerated production rate was then calculated by deducing the later from the former. Water samples were collected twice (spring and summer) in a year for each lake. Both primary production rates and  $\text{NO}_3^-$  uptake rates were determined from the vertical distribution of  $\Delta^{17}\text{O}$  values of  $\text{O}_2$  and  $\text{NO}_3^-$  and their difference between the seasons. We found that the f-ratios (relative use of  $\text{NO}_3^-$  among the total use of nitrogen) were lower in oligotrophic lakes than in the mesotrophic lake.

Keywords: new production, regenerated production, gross primary production, lakes, triple oxygen isotopes, hypolimnion