Seasonal variations in surface water nitrogen cycle in the western subarctic North Pacific revealed by nitrogen isotope ratios of amino acid from the settling particles

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The nitrogen isotopic composition ($\delta^{15}N$) of nutrients in the surface ocean transfer to the $\delta^{15}N$ of phytoplankton, settling particles, and eventually benthic sediment. The $\delta^{15}N$ of settling particles and sediment can therefore be used to trace the past nitrogenous nutrient environment. Previous observations have revealed that there is an inverse relationship between seasonal $\delta^{15}N$ and flux of settling particles. In winter at high latitudes, the settling particles have high $\delta^{15}N$ and low flux as compared with other seasons. In contrast, the surface water nitrate in winter has the lowest $\delta^{15}N$ in a year due to convective mixing. The winter settling particles should also have the lowest $\delta^{15}N$, if winter phytoplankton assimilates only nitrate. Previous studies pointed out three reasons why $\delta^{15}N$ of settling particles from autumn to winter increases despite the decrease in $\delta^{15}N$ of surface nitrate: (1) the increase in contribution of zooplankton, which have a $\delta^{15}N$ about 3 ‰higher than that of phytoplankton; (2) the contribution of old particles most degraded with isotope fractionation in a year; and (3) the winter phytoplankton assimilates not only nitrate but also ammonium, which has higher $\delta^{15}N$ than nitrate due to nitrification. In this study, to clarify the reason we applied the compound-specific stable isotope analysis of amino acid and a marine nitrogen isotope model. Sediment trap experiment was conducted at 1000 m depth at station K2 (47°N, 160°E) from June 2014 to July 2015. The bulk $\delta^{15}N$ was determined by a sensitivity-improved EA/IRMS. The $\delta^{15}N$ of glutamic acid and phenylalanine were determined by GC/C/IRMS. The bulk $\delta^{15}N$ show relatively low values around 2‰ from July to August and increases to 5‰ from September to June, which is a typical seasonal variation observed at high latitudes. Surprisingly, the apparent trophic positions of settling particles estimated from the $\delta^{15}N$ of glutamic acid and phenylalanine are 2.0±0.1 both in summer and winter. This is the first evidence that the winter high-$\delta^{15}N$ of settling particles does not reflect the increase in contribution of zooplankton. Our model result suggested that the winter high-$\delta^{15}N$ value of settling particles mainly reflects the winter high-$\delta^{15}N$ of ammonium due to nitrification, which was strongly supported by the nitrogen isotopic compositions of amino acids.

Keywords: Marine nitrogen cycle, Nitrogen isotope, Marine ecosystem model

