Seasonal variations in nitrogen isotope ratios of amino acid of settling particles in the western subarctic North Pacific

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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 two 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; and (2) the winter phytoplankton assimilates not only nitrate but also ammonium, which has higher $\delta^{15}N$ than nitrate due to nitrification. However the evidences for these hypothses have not been reported yet. In this study, to clarify the reason we applied the compound-specific stable isotope analysis of amino acid of settling particles 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 $\delta^{15}N$ of settling particles ($\delta^{15}N_{bulk}$) was determined by a sensitivity-improved EA/IRMS. The $\delta^{15}N$ of glutamic acid and phenylalanine of settling particles ($\delta^{15}N_{Glu}$ and $\delta^{15}N_{Phe}$) were determined by GC/C/IRMS. The $\delta^{15}N_{bulk}$ 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 $\delta^{15}N_{Glu}$ and $\delta^{15}N_{Phe}$ 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. Although the winter observation of $\delta^{15}N$ of amminim are needed to confirm this hyphosesis, the nitrogen isotopic compositions of amino acids strongly supported our model result.