The microbial nitrogen pump in the ocean: Role of heterotrophic bacteria in the ocean DON pool indicated by compound-specific  $\delta^{15}$  N analysis of amino acids

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Dissolved organic nitrogen (DON) is one of the most important - but perhaps least understood components of the modern ocean nitrogen cycle. We explored the use of compound-specific nitrogen isotope analysis of amino acids ( $\delta^{15}N_{AA}$ ) of DON as a new approach to examine relative sources and transformation processes of the main detrital organic nitrogen form in the ocean water column. We measured  $\delta^{15}N_{AA}$  distributions in high-molecular-weight DON (HMW DON) and suspended particulate organic nitrogen (PON) samples from various oceanic regions including the oligotrophic open ocean (the North Pacific Subtropical Gyre) and a coastal upwelling system (the California Current System). A new analytical approach using HPLC purification of amino acids achieved far greater  $\delta^{15}N_{AA}$  measurement precision for DON than earlier work, allowing us to resolve previously obscured differences in  $\delta^{15}N_{AA}$ signatures, both with depth and between ON pools. The  $\delta^{15}N_{AA}$  values of DON in the various oceanic regions and depths (surface to mesopelagic) suggest mainly heterotrophic sources, with the mesopelagic and upwelled DON bearing signatures of far more degraded material. These results contrast with a previous proposal that DON are essentially "pre-formed" in the surface ocean, undergoing little further change with depth. Together with the results of amino acid enantiomers (D/L), these results suggest that transformation by heterotrophic bacteria is the main source for DON in the ocean.

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