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Unveiling the Hidden Dynamics: How Production and Consumption Pathways Influence N_2O Emissions in Estuaries

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Estuaries play an important role in reducing nitrogen transport from rivers to the ocean and have become hotspots for global N_2O emissions. However, the complex hydrological and topographic characteristics of estuaries result in significant spatiotemporal heterogeneity in N_2O emissions. We quantitatively identified the N_2O production pathways and consumption processes in the Yangtze River estuary in China by combining molecular approaches and isotopocule analyses. The N_2O fluxes and N_2O isotopocule ratios ($\delta^{15}N^{bulk}$, $\delta^{18}O$, and SP) of the estuary exhibited significant spatiotemporal heterogeneity, with N_2O fluxes decreasing and N_2O isotopocule ratios increasing with the rise in sediment salinity. The Monte Carlo modelling tool FRAME was used to quantitatively discriminate the N_2O production pathways and consumption processes of the Yangtze River estuary, and the results were verified by a dual N_2O isotope mapping approach (MAP) and the $^{15}N–^{18}O$ double tracer technique. The fractional contribution of nitrifier denitrification (nD) and bacterial denitrification (bD) to total N_2O production in the estuary ranged from 18% to 83%, with nitrifier denitrification contributing about half. Approximately 15% to 80% of N_2O was reduced throughout the year. Temperature, salinity, and sediment NO_2^- concentration were the key factors affecting N_2O production and consumption, with NO_2^- playing a more significant role. Unexpectedly, we found that the $^{15}N–^{18}O$ double tracer technique for analyzing key N_2O production processes in sediments is limited by environmental temperatures, as it cannot effectively analyze the fraction of N_2O produced by nitrifier denitrification under low-temperature (e.g., winter) incubation conditions. Considering that NO_2^- concentration in the sediments of the estuary primarily originates from anthropogenic sources, this strongly suggests that controlling human reactive nitrogen inputs is crucial for reducing N_2O emissions in estuaries.