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Position-specific kinetic isotope effects for nitrous oxide: A new expansion of the Rayleigh model and its application to nitrous oxide source tracing

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Nitrous oxide (N_2O) is produced by multiple (bio)geochemical processes as part of the global nitrogen cycle via processes such as nitrification and denitrification. Unfortunately, N_2O is also a potent greenhouse gas and a significant ozone-depleting substance. Because at least 70% of annual anthropogenic N_2O emissions in the US result from agricultural practices (*e.g.*, use of nitrogen-containing fertilizers), understanding the soil microbial processes involved in N_2O formation and consumption is critical. Stable isotope techniques are ideally suited to studying sources and sinks of N_2O because the central (N^{α}) and outer (N^{β}) nitrogen atoms in N_2O are non-exchangeable, and the difference in the relative abundance of ^{15}N at these positions is determined primarily by the kinetic isotope effects of the microbial enzymes that produce or consume N_2O. Here we summarize our use of stable isotope measurements to study the isotopic signatures of enzymes that synthesize or reduce N_2O. Importantly, we show that our new expansion of a widely-used isotopic model (the Rayleigh distillation equation) is necessary to accurately quantify *position-specific* kinetic isotope effects for N_2O synthesis. Our Expanded Rayleigh model provides an improved description of N_2O biosynthesis by accounting for the fact that fractionation at the α position affects the isotopic composition of substrate available for the β position (and vice versa) because both N atoms are typically drawn from the same substrate pool.

Application of our Expanded Rayleigh model to experimental datasets representing multiple N_2O biosynthesis pathways (*e.g.*, bacterial nitrification and denitrification, and fungal denitrification) illuminates differences between these processes by providing insight into the diverse underlying enzymatic mechanisms. Ultimately, determining the isotopic signatures for enzymes that produce or consume N_2O will aid in identifying environmental sources and sinks of N_2O.