Supplementary material

pyisotopomer: A Python package for obtaining nitrous oxide isotopocules from isotope ratio mass spectrometry

Colette L. Kelly,[1*] Cara Manning,[2] Claudia Frey,[3] Noah Gluschankoff,[1] and Karen L. Casciotti

1. Stanford University, Department of Earth System Science, Stanford, CA 94305, USA
2. University of Connecticut, Department of Marine Sciences, Groton, CT 06340, USA
3. Department of Environmental Science, University of Basel, Basel, Switzerland.

*** Correspondence to:** Colette L. Kelly (clkelly@stanford.edu).

Table S1: Different pairings of reference materials. Pooled standard deviations of γ and κ calculated from different pairings of reference materials, and the corresponding pooled standard deviations of $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, and SP, are shown for tests performed on the Lab 1 and Lab 2 IRMS. Pooled standard deviations are also shown for scrambling and isotopomer calculations done in the MATLAB and Python versions of the software.

Test	Pooled standard deviations				
	γ (% uncertainty*)	κ (% uncertainty*)	$\delta^{15}N^{\alpha}$ (‰ $vs. Air N_2$)	$\delta^{15}N^{\beta}$ (‰ $vs. Air N_2$)	SP (‰ $vs. Air N_2$)
Lab 1 three ref. pairings, no extreme values	0.39	0.16	0.47	0.44	0.91
Lab 2 three ref. pairings, incl. extreme values	0.77	1.17	2.54	2.29	4.83
Lab 2 one ref. pairing, excl. extreme values	0.15	0.61	(see section 4.7 for precision between replicates)		
MATLAB vs. Python	0.44	0.93	0.028	0.026	0.054

*Percent uncertainties represent pooled SD as a percentage of the mean

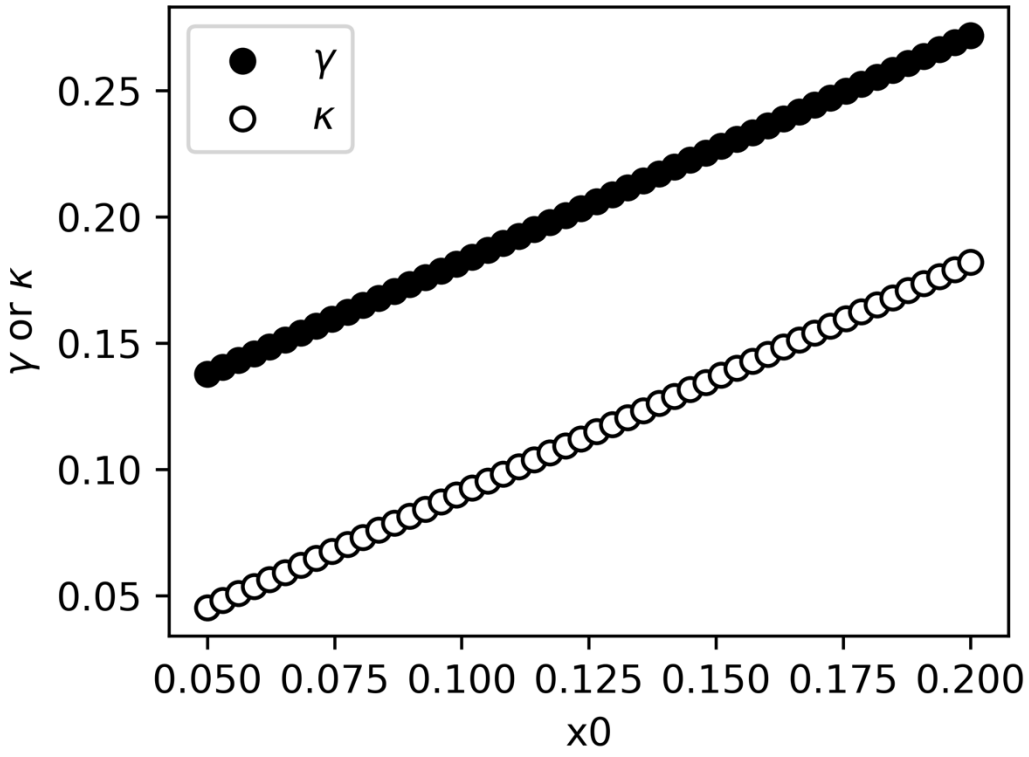

Figure S1. Solutions for γ and κ calculated across a range of initial guesses (x0) for the least squares solver function at the core of pyisotopomer. The default values for x0 are γ=0.17 and κ=0.08, based on the performance of the ThermoFinnigan Delta V mass spectrometer at Lab 1.

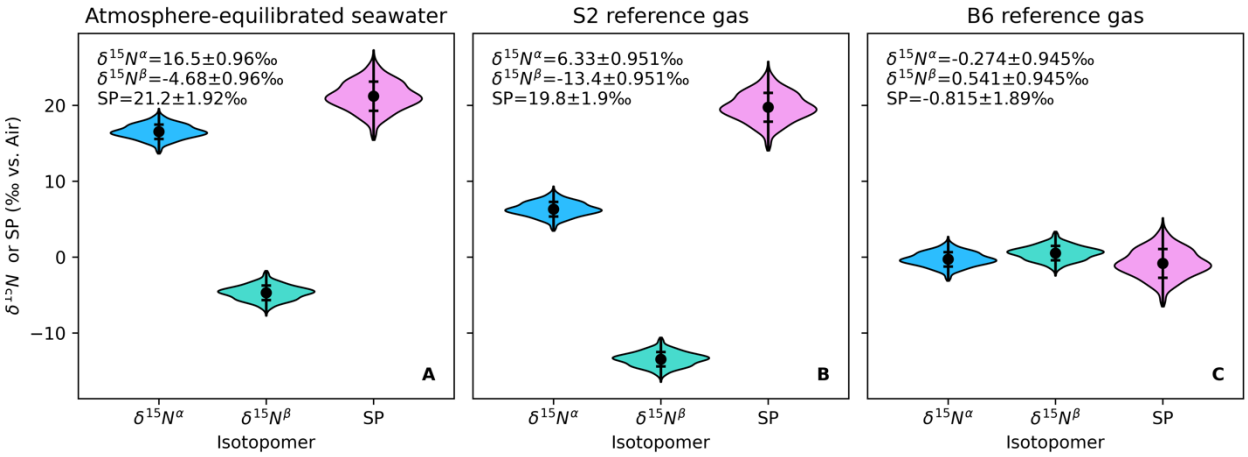

Figure S2: Isotopocule values and error associated with an uncertainty of ±6.83*10^{-4} in γ and ±1.48*10^{-4} in κ, based on Monte Carlo simulation results. The violin plots are based on a kernel density estimate of the distribution and show the mean value ±1σ.

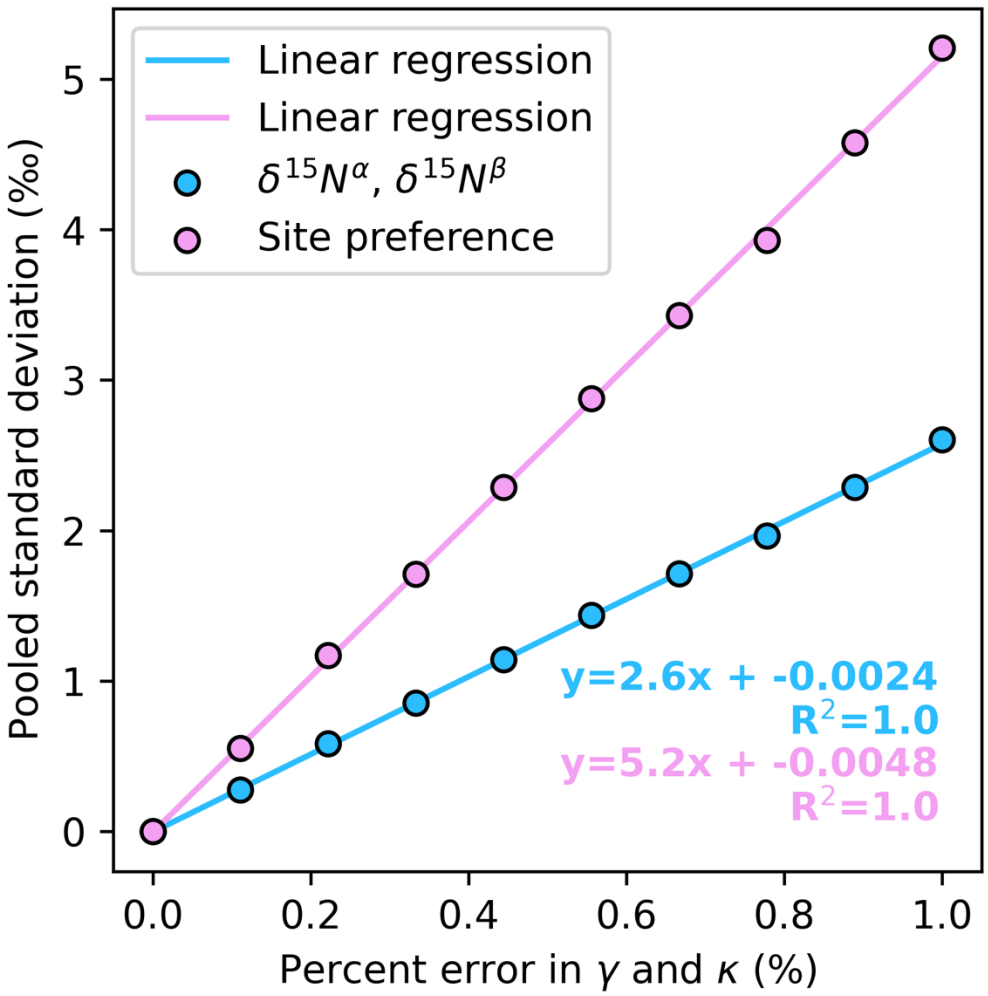

Figure S3: Pooled standard deviation of $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, and SP resulting from increasing relative uncertainties in γ and κ. Each point corresponds to 1,000 values of γ and κ sampled from a distribution with standard deviation equal to the given level of uncertainty, and the corresponding pooled standard deviation of 1,000 simulated values of $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, and SP.

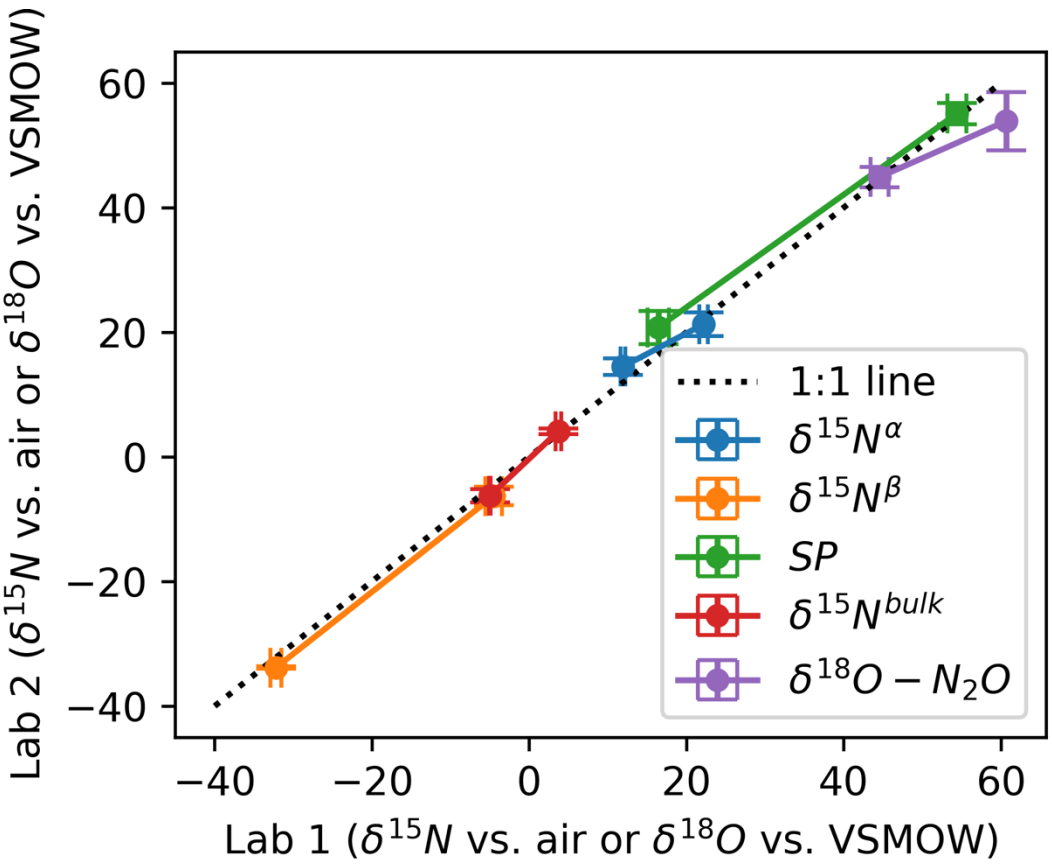

Figure S4: Intercalibration results for lake water unknowns taken at 10 meters and 90 meters depth from lake Lugano in Switzerland. Independent measurements of the isotopic composition of N_2O in each sample, performed by Lab 1 and Lab 2, respectively, are plotted against each other. Data points represent the mean from replicate bottles taken at the same depth (n=2-5) and error bars represent one standard deviation. A one-to-one line (black dashed line) is plotted for comparison.