Constraining the atmospheric nitrous oxide cycle using triple oxygen isotopic compositions

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We developed a rapid, sensitive, and automated analytical system to determine the $d^{15}N$, $d^{18}O$, and $D^{17}O$ values of nitrous oxide (N_2O) simultaneously in nanomolar quantities for a single batch of samples by continuous-flow isotope ratio mass spectrometry (CF-IRMS) without any cumbersome and time-consuming pretreatments. The analytical system consisted of a vacuum line to extract and purify N_2O, a gas chromatograph for further purification of N_2O, an optional thermal furnace to decompose N_2O to O_2, and a CF-IRMS system. In addition, we used pneumatic valves and pneumatic actuators in the system so that we could operate the system automatically based on timing software on a personal computer. The analytical precision was better than 0.12 per mil for $d^{15}N$ with more than 4 nmol N_2O injections, 0.25 per mil for $d^{18}O$ with more than 4 nmol N_2O injections, and 0.25 per mil for D17O with more than 20 nmol N_2O injections for a single measurement. Besides, we were able to improve the precision (standard errors) to be better than 0.05 per mil for d15N, 0.10 per mil for $d^{18}O$, and 0.10 per mil for D17O easily through multiple analyses with four repetitions with 190 nmol samples using the automated analytical system. Using the system, the $d^{15}N$, $d^{18}O$, and $D^{17}O$ values of N_2O can be quantified not only for atmospheric samples but also for other gas or liquid samples with low N_2O content, such as soil gas or natural water. Here, we showed the first ever $D^{17}O$ measurements of soil N_2O.