First real-time isotopic characterization of N_2O from chemodenitrification

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Chemodenitrification is the main abiotic nitrous oxide (N_2O) source in soils, its N_2O isotopic signatures could be applied for source attribution, but are currently not known in sufficient detail. To overcome this limitation, the intramolecular isotopic composition of N_2O: $^{14}N^{14}N^{16}O$, $^{15}N^{14}N^{16}O$ ($^{15}N^\beta$-N_2O), $^{14}N^{15}N^{16}O$ ($^{15}N^\alpha$-N_2O), and $^{14}N^{14}N^{18}O$, produced by the reaction of sodium nitrite with lignin, five lignin derivatives, and three types of soils, was analyzed online with a quantum cascade laser absorption spectrometer (QCLAS). Thereby, we present the first continuous dataset of $\delta^{15}N^{bulk}$ ($\delta^{15}N^{bulk} \equiv (\delta^{15}N^\alpha + \delta^{15}N^\beta)/2$), $\delta^{18}O$, and SP (site preference, SP $\equiv \delta^{15}N^\alpha - \delta^{15}N^\beta$) of N_2O from chemodenitrification in both aqueous solutions and soils. Contrary to the previous assumption that SP values are constant for distinct abiotic N_2O source processes, our results reveal a considerable shift along time in SP from 5.6 to 29.0 ‰ in the reactions of sodium nitrite with organic substances. The large SP variability of N_2O might be explained by the multiple reaction pathways involved. These findings provide important new information for N_2O source partitioning using intramolecular N_2O isotopic signatures, e.g. end-member maps of SP vs. $\delta^{15}N^{bulk}$ and $\delta^{18}O$.