First real-time isotopic characterization of N$_2$O from chemodenitrification

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Chemodenitrification is the main abiotic nitrous oxide (N$_2$O) source in soils, its N$_2$O 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$_2$O, $^{14}$N$^{14}$N$^{16}$O, $^{15}$N$^{14}$N$^{16}$O ($^{15}$N$^\alpha$-N$_2$O), $^{14}$N$^{15}$N$^{16}$O ($^{15}$N$^\beta$-N$_2$O), 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$_2$O from chemodenitrification in both aqueous solutions and soils. Contrary to the previous assumption that SP values are constant for distinct abiotic N$_2$O 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$_2$O might be explained by the multiple reaction pathways involved. These findings provide important new information for N$_2$O source partitioning using intramolecular N$_2$O isotopic signatures, e.g. end-member maps of SP vs. $\delta^{15}$N$_{bulk}$ and $\delta^{18}$O.