Using semi-continuous, in-situ measurements of nitrous oxide isotopic composition at a suburban site to track emission processes

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Nitrous oxide (N_2O) is a potent greenhouse gas and the strongest ozone-destroying substance emitted this century. The atmospheric N_2O mole fraction has been increasing at a rate of 0.2-0.3% per year over the past decades due to anthropogenic emissions; in addition, recent results suggest that the rate of increase is rising – therefore effective mitigation of N_2O emissions is a critical point for environmental policy. However, N_2O sources are poorly defined and disperse, complicating the development of targeted mitigation strategies.

Online isotopic measurements using preconcentration and laser spectroscopy [1,2,3] have great potential to unravel spatial and temporal variations in sources, sinks and chemistry of trace gases such as N_2O. Semi-continuous, real-time measurements of N_2O isotopic composition ($\delta^{18}O$, site preference [SP = $^{14}N^{15}N^{16}O$ - $^{15}N^{14}N^{16}O$] and $\delta^{15}N^{bulk}$) were performed at the suburban site of Dübendorf, Switzerland, for 19 months between July 2014 and February 2016. The data precision reached 0.1‰ in the final months, thus the results could clearly identify nocturnal build-up of N_2O, with a corresponding decrease in $\delta^{18}O$, SP and $\delta^{15}N^{bulk}$ due to isotopically depleted anthropogenic sources.

Daily mean source isotopic composition was calculated by considering the measured and the background mole fraction and isotopic composition. Delta values of the mean emission source were highest in winter, with a seasonal cycle of 12, 8 and 5‰ for $\delta^{18}O$, SP and $\delta^{15}N^{bulk}$ respectively. The chemical and meteorological parameters controlling source isotopic composition were considered using data from the Swiss National Air Pollution Monitoring Network (NABEL) as well as a transport regime cluster analysis. A clear spatial distribution for source isotopic composition was observed for $\delta^{18}O$, as well as a significant relationship with the level of urban pollution, indicating $\delta^{18}O$ may be a strong indicator of combustion/industrial vs. agricultural N_2O. In contrast, $\delta^{15}N^{bulk}$ and particularly SP appear to vary too strongly in response to other factors affecting emission processes to provide a useful distinction between source categories on a regional scale – these isotopocules may however be useful to distinguish emission pathways on a local scale.

For comparison, FLEXPART-COSMO transport simulations [4] were combined with emissions from the EDGAR inventory and estimates of source isotopic composition from literature, to simulate N_2O isotopic composition at the sampling site. The model was able to capture variability in N_2O mole fraction adequately (R^2 = 0.34; p <<0.01). However, the measured variability in source isotopic composition was 1-2 orders of magnitude larger than simulated, illustrating that our knowledge of isotopic source signatures – in particular technical N_2O sources – is still too limited to successfully model variations in ambient N_2O isotopic composition.

[1] Mohn et al. (2012) *Atmospheric Measurement Techniques*, doi:10.5194/amt-5-1601-2012

[2] Harris et al. (2014) *Analytical Chemistry*, doi: 10.1021/ac403606u.

[3] Röckmann et al. (2016) *Atmospheric Chemistry and Physics,* doi:10.5194/acp-16-10469-2016.

[4] Henne et al. (2016) *Atmospheric Chemistry and Physics*, doi:10.5194/acp-16-3683-2016.