



Non-homogeneity of isotopic labelling in ^{15}N gas flux studies: theory, some observations and possible lessons

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Quantifying dinitrogen (N_2) and nitrous oxide (N_2O) fluxes from different soil N pools and processes can be accomplished using the ^{15}N tracer technique but this is subject to four different sources of bias (i. – iv.). This approach includes ^{15}N labelling of selected N pools in soil and subsequent isotope analysis of all relevant N pools as well as of gas samples from enclosures, i.e. mixtures of soil-derived and atmospheric N_2 and N_2O . Depending on the processes of interest, there may be ^{15}N labelling of one or several N pools, were several labelling treatment are needed in the latter case (e.g. Müller et al., 2004). Measuring pool-derived N_2 or N_2O has been shown to include two calculation problems, (i.) arising from multiple pools (e.g. Arah, 1992) and (ii.) dealing with the non-random distribution of N_2 and N_2O mole masses (Hauck et al., 1958). Non-randomness can be solved if m/z 28, 29 and 30 are correctly analysed and the ^{15}N enrichment of one (to distinguish two pools, i.e. soil and atmosphere) or two pools (in case of three pools) is known (Spott & Stange, 2008).

Moreover (iii.), NO_3^- pools generating N_2 and N_2O via denitrification can be identical or different, e.g. if N_2O evolved from higher enriched NO_3^- in deeper soil was more reduced to N_2 compared to N_2O evolved from N_2O from shallow soil with lower enrichment, or vice versa.

Apportioning N_2O fluxes to NH_4^+ (nitrification and/or nitrifier denitrification) and NO_3^- (denitrification) is often conducted by NO_3^- labeling, measuring $\delta^{15}\text{N}$ of emitted N_2O and applying mixing equations were the measured ^{15}N enrichment of NH_4^+ and NO_3^- pool is used. However, this assumes that the average ^{15}N enrichment of NH_4^+ and NO_3^- in the soil is identical to the enrichment in the active soil domain producing N_2 and/or N_2O . Violation of this precondition must lead to bias in source apportionment (iv.), but to our knowledge this has not been investigated until now.

Here we present conceptual models and model calculations addressing cases iii. and iv.. Furthermore we present some experimental data illustrating this. These include two data sets from denitrification experiments exhibiting substantial deviations in ^{15}N enrichment between the N pools producing N_2 and N_2O . Moreover, results from a lab incubation study to quantify NH_4^+ -derived N_2O with increasing NH_4^+ amendment under conditions favouring nitrification are shown, were non-labelled NH_4^+ was added together with ^{15}N labelled NO_3^- . Here we found large deviations between the ^{15}N enrichment of NO_3^- in extracted soil water and the ^{15}N enrichment of the labelled N pool as calculated from N_2O isotopologues (Bergsma et al., 2001). We think that this reflects type iv. bias, probably because enrichment of NO_3^- in anoxic micro-sites was less diluted by non-labelled NO_3^- from nitrification compared to NO_3^- in oxic zones. Our data analysis provides a means to overcome bias iv. and thus to obtain correct source apportionment.

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