

Interactive comment on “First on-line isotopic characterization of N₂O emitted from intensively managed grassland” by B. Wolf et al.

Anonymous Referee #1

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General:

The authors present a first data set on the use of N₂O isotopes in free air in combination to Eddy Covariance measurements to estimate N₂O processes governing soil fluxes. This was successful and convincing due to the impressive precision of continuous in situ monitoring of isotope values. Previously N₂O isotope fluxes were only determined from lab or field chamber measurement with limited temporal and spatial resolution. From this aspect the present study is a big step forward. N₂O isotopes are promising to progress understanding of N₂O flux control. Hence this study is excellent in terms methodology. Moreover it is well written and results are adequately presented and discussed. Beside some minor details listed below, I have only two general points that should be addressed: 1. Despite continuous monitoring of N₂O fluxes (Fig. 3) the

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authors give no values of cumulative losses per year and don't address this aspect in the discussion (see also details below). However it is quite important to interpret the impact of their findings, i.e. to which extent observed isotope fluxes are representative to agricultural ecosystems. So these numbers should be reported and discussed. 2. The authors use the relationship between isotope values (average $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and SP) to estimate and discuss possible N_2O reduction. While this is justified, it should be better illustrated. Instead of showing isotope maps of $\delta^{18}\text{O}$ vs $\delta^{15}\text{N}_{\text{bulk}}$ only, they should also show SP vs $\delta^{18}\text{O}$ and also illustrate their postulated reduction events. Here I suggest to give isotope maps (SP/ $\delta^{18}\text{O}$ and $\delta^{15}\text{N}_{\text{bulk}}/\delta^{18}\text{O}$) showing the change in values during estimated reduction events. Reduction vectors could be added in these figures to show agreement or deviation of observed data from previously reported reduction dynamics. These figures might be given in the appendix.

Details

P1576 L 13.14: this reasoning is not exactly correct here: independence of SP from precursors is due to the fact that N_2O is the first molecule with two N atoms and thus SP is not existent in precursor compounds

L 26 suggest to address N_2O isotopocules (or isotopologues) instead of SP since $\delta^{15}\text{N}_{\text{bulk}}$ and not SP is used in the cited examples

P1577 L 5 see previous comment

L7 flask sampling with chambers is better in spatial resolution than atmospheric measurement ($N = 1$) which gives not info on spatial resolution at all

L 21 how about soil properties?

L 22 goal (iii) can clearly not be achieved with this approach as there is no way to check the process information from isotopomers independently. Please modify accordingly or explain how you can test this with your approaches

Study site: please report numbers on soil texture, Corg, C/N, pH and bulk density since

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these are very important to compare findings to other sites.

P 1579 L 16 suggest “(increase of 0.31... per mil..”

P 1583 L 21 please better explain “surface layer”, lowest ten of m is quite vague, maybe add a reference here?

P 1587 L 4 data are representative for this site, but not for agricultural land in general, please clarify

P1590 L 8 Please add that the preferred cleavage of N-O bonds between lighter isotopes leads to increasing d18O and SP in residual N2O

P 1590, Section 4.4 suggest to add an SP/d18O plots (see discussion on problems of SP/d15N plots in Well et al 2012, *Geochimica et Cosmochimica Acta* 90, 265–282 Lewicka-Szczebak et al., 2014 *Geochimica et Cosmochimica Acta*, 134, 55-73, Lewicka-Szczebak et al 2015 *Rapid Comm Mass Spectrometry* 29:269-282). The extremely large range in d15N of the endmember areas make the use of d15N really difficult. Moreover, these ranges might even be larger than reported in the literature due to the unknown d15N of NO3 in active microsites. Conversely, d18O of N2O produced by denitrification is mostly governed by O exchange with soil water and thus less variable.

L 15 to 20: please compare your endmember areas with those given and discussed in Zou et al. 2014 *Soil Biology and Biochemistry*, 77, 276–291.

L 28 here and elsewhere: BACTERIAL denitrification, since isotopologues of fungal denitrification are close to NH2OH-N2O.

P 1591 L 6-7 you might refer to the discussion of this aspect in Well et al 2012, *Geochimica et Cosmochimica Acta* 90, 265–282.

P1592 L10 note that N2O_N includes Nitrification AND fungal denitrification. You can't exclude the fungi (see Sutka et al., 2008 *Rapid Commun Mass Spectrom.* 2008 3989-

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96,. Rohe et al., 2014 Rapid communications in mass spectrometry, 28, 1893-1903, please discuss).

P1593 L18 please show linearity of Keeling plots

P 1994 L 6-9 not clear to me why the footprints are different, please explain

Section 4.7 please discuss cumulated N₂O fluxes of this site in comparison to other grassland sites in order to interpret to which extent flux weighted isotope values can be seen representative. In view of high mean fluxes it seems to me that this site is a real hot spot. . (rough look at Fig 3 suggests that flux level is at least higher than 5 kg N/ha and year). This needs to be taken into account in the discussion here or at least addressed somewhere.

P 1595 L 5 and elsewhere: add fungal nitrification since it is not distinguishable from NH₂OH oxidation.

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