

We thank both referees for their valuable comments and appreciate the associated improvements to the manuscript.

Referee#1:

“1. Despite continuous monitoring of N₂O fluxes (Fig. 3) the 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”

Answer: We addressed this comment by including a corresponding paragraph in section 4.7 (see below in the response to the specific comment “Section 4.7”).

“2. The authors use the relationship between isotope values (average d¹⁵N, d¹⁸O and SP) to estimate and discuss possible N₂O reduction. While this is justified, it should be better illustrated. Instead of showing isotope maps of d¹⁸O vs d¹⁵N_{bulk} only, they should also show SP vs d¹⁸O and also illustrate their postulated reduction events. Here I suggest to give isotope maps (SP/d¹⁸O and d¹⁵N_{bulk}/d¹⁸O) 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.”

Answer: We changed the manuscript accordingly and included a SP/d¹⁸O map (see below in response to the specific comment “P1590, Section 4.4”).

P1576 L 13.14: this reasoning is not exactly correct here: independence of SP from precursors is due to the fact that N₂O is the first molecule with two N atoms and thus SP is not existent in precursor compounds

Answer: in order to be unequivocal we reworded to “..., as SP remained constant in the de novo produced N₂O even though ...”

L 26 suggest to address N₂O isotopocules (or isotopologues) instead of SP since d¹⁵N_{bulk} and not SP is used in the cited examples

Answer: Agreed and changed to “In addition, N₂O isotopocules can be used for ...”

P1577 L 5see previous comment

Answer: Agreed and changed to “N₂O isotopomers can be ...”.

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

Answer: We agree that measurements in the surface layer cannot be replicated and that for some experimental designs (e.g. different treatments on an experimental field), a chamber setup is indispensable. However, we want to raise the point that chamber measurements are representative for the usually small chamber area and are therefore limited in spatial representation. As a consequence, we changed the section to “... is limited in temporal resolution and spatial representation of a given site”.

L 21 how about soil properties?

Answer: In this study, measurements were made above one intensively managed grassland site for which soil properties are assumed to be constant on the timescale of this study. Therefore, an analysis with respect to variations in soil properties is not possible.

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

Answer: We agree and removed (iii) from the objectives.

Study site: please report numbers on soil texture, Corg, C/N, pH and bulk density since these are very important to compare findings to other sites.

Answer: We included information on bulk density, texture, pH as well as C and N content in section 2.1

P 1579 L 16 suggest "(increase of 0.31: : : per mil.."

Answer: Changed to "(increase by 0.31 per mille ...")

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

Answer: The term surface layer is now explained at the beginning of section 3.2: "Air samples were taken at 2.2 m height which is in the lowest 10% of the atmospheric boundary layer (ABL) where mechanical generation of turbulence exceeds buoyant generation or consumption. This part of the ABL is called surface layer, hence corresponding air samples are referred to as surface layer air samples."

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

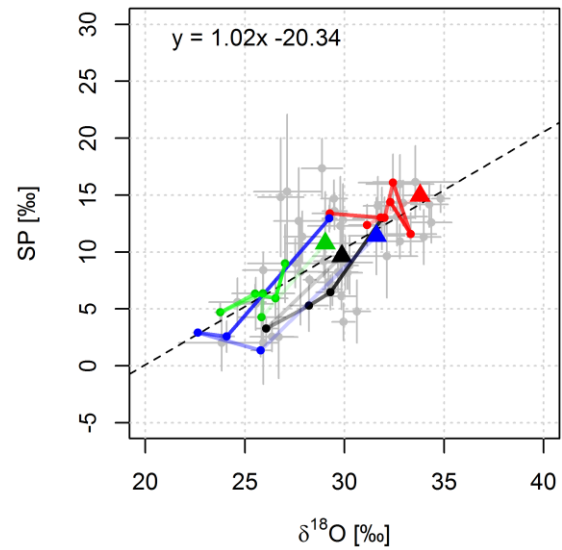
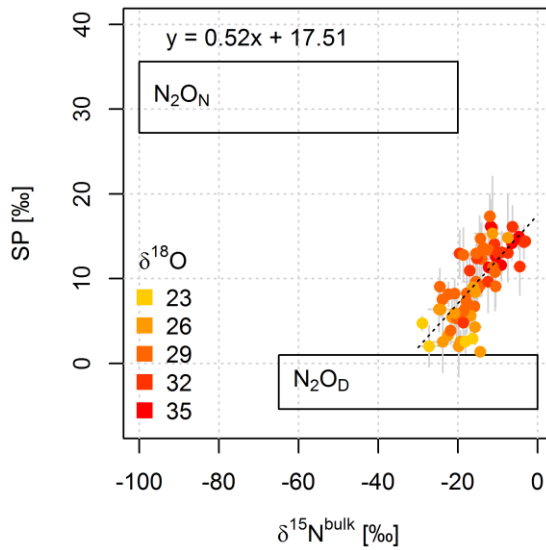
Answer: This sentence was meant to explain that simple averages do not represent the isotopic composition of any given treatment, site or ecosystem, but we agree that our wording might be misleading. Therefore we changed to a more general term: "Representative isotopic composition of N₂O emitted from a given site or treatment can be"

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

Answer: The explanation is included now: "However, in the terminal step of denitrification, namely the reduction of N₂O to N₂, N-O bonds between lighter isotopes are cleaved preferentially, leading to an increase in SP, $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ in the remaining 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.

Answer: We agree with the referee and figure 7's right panel was substituted by a panel showing SP as a function of $\delta^{18}\text{O}$ (see uploaded figure). We also indicated the development of isotopic composition during management events and the rewetting event as suggested by the referee in the general comments to the manuscript. The text in section 4.4 was adapted accordingly.



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.

Answer: Zou et al. give endmember areas in a SP/d15N map for the processes “Nitrification”, “Nitrifier-denitrification”, “Fungal denitrification” and “Denitrifier-denitrification”. While the SP-values representing the areas’ corner nodes are literature values, the corresponding d15N-values were calculated from the analyzed isotopic composition of N2O precursors (NO3- / NH4+) and the range of fractionation factors derived from literature for the four process groups (see table below). As our isotopocule measurements integrate over a large and (depending on wind direction) variable area, it was not possible within the scope of the presented study to sample and analyze the isotopic composition of N2O substrates. We appreciate the referee comment and the approach chosen by Zou et al., but due to the lack of knowledge on the substrate’s isotopic composition, we had to decide for a more general approach. To cover the whole range of potential d15Nbulk values, minimum and maximum values of fractionation factors reported in literature for the process groups N2O_N (nitrification and fungal denitrification) and N2O_D (denitrification and nitrifier denitrification) were selected and combined with the endpoints of literature values reported for the N2O precursors. Overall, as can be derived from the table below, these approaches are very much alike, but the lack of the substrate’s isotopic composition does not allow for an application of the approach chosen by Zou et al..

Study	SP _{nit}	SP _{fungalDen}	SP _{N2ON}	SP _{den}	SP _{nit-den}	SP _{N2OD}
Zou	31.4 (31.4-35.6)	37 (34.1-39.6)		-2 (-6.9-1.4)	-3.8 (-13.6-5)	
This study			32.8 ± 4			-1.6 ± 3.8
	ε _{nit}	ε _{fungalDen}	ε _{N2ON}	ε _{den}	ε _{NH3/NO2} , ε _{NO2/N2O}	ε _{N2OD}
Zou	-68 to -46,9	-36.2 to -24.1		-37 to -11	-39.8 to -10.6 -39.5 to 31.4	
This study			-90 to -40			-40 to -15

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

Answer: "bacterial" was added to revoke the unclear wording.

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.

Answer: Reference was added

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 3989-96,. Rohe et al., 2014 *Rapid communications in mass spectrometry*, 28, 1893-1903, please discuss).

Answer: The section was corrected to "...due to increased contribution of nitrification or fungal denitrification, ...".

P1593 L18 please show linearity of Keeling plots

Answer: Keeling plots for each single day are provided as supplementary file S1, and a corresponding reference to the supplementary material was placed in the text.

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

Answer: An explanation was added in section 4.6: "Alternatively, the variation in isotope values associated with small overnight concentration increase may result from other land use or land cover. The EC fluxes are calculated from the turbulent fluctuation of concentration and vertical wind speed (i.e. the covariance of the concentration and wind speed deviations from the half-hourly mean) and therefore account for the modulation of concentration around a short term (30 min) mean caused by locally emitted N₂O. Isotopic composition based on Keeling plots, however, is determined from total N₂O accumulated in the nocturnal boundary layer and, thus, this approach also contains molecules that had been emitted outside the flux footprint, which almost exclusively comprised our grassland site (Zeeman et al. 2010), within the larger concentration footprint (Griffis et al., 2007)."

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.

Answer: We address this issue at the end of section 4.6: "Secondly, the CHA grassland can be characterized as a site with vigorous N₂O emission and therefore may dominate the determined N₂O isotopic composition as the influence of a source area increment scales with the source strength. The grassland was restored in 2012 which lead to extraordinary high N₂O-N emission of 29.1 kg ha⁻¹ year⁻¹ (Merbold et al 2014). In the following year, 2.5 kg N ha⁻¹ were released. This value is still in the range of maximum emissions reported for another intensively managed Swiss grassland, emitting 1.5-2.6 kg N ha⁻¹ year⁻¹ and at least a factor of five compared to an extensively managed grassland with less than 0.5 kg N ha⁻¹ year⁻¹ (Ammann et al 2009). With regard to distant land use and land cover, the 2.5 kg N ha⁻¹ are also more than double the median of all reported values for cultivated temperate sites and higher than the maximum value reported for forests presented in a study containing 1008 N₂O emission measurements from agricultural fields (Stehfest and Bouwman, 2006)".

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

Answer: fungal denitrification was added.

Referee#2:

The manuscript reports a technical feat: the on-line isotopic characterisation of N₂O emitted from an agricultural area. All descriptions, data and discussion relating to the isotopic characterisation are excellent science. A weak point is the relation of isotopic compositions to N₂O flux (and soil parameters) measured on the experimental grassland plot. There are probably something like four orders of magnitude in size difference between the concentration footprint (in the order of 10 x 10 km; from which isotopic compositions were derived) and the N₂O flux footprint (in the order of 0.1 x 0.1 km).

By relating changes in isotopic composition to N₂O flux (and soil conditions) on the experimental grassland plot, the implicit assumption is made that N₂O emitted from the grassland plot is representative, in terms of isotopic composition, for a much larger area. Looking at aerial photographs of Chamau (e.g. Google Earth), it seems there is a large proportion of arable crops and also forest within the concentration footprint (I am not familiar with this site, but think to have located it at 47 degrees 12' and 24" N and 8 degrees, 24' and 32" E). This mix of different landuse constitutes the concentration footprint and is the source of observed changes in the isotopic composition observed during nocturnal inversions. In contrast, the N₂O flux measured by eddy covariance relates to the grassland site, where also the soil parameters (soil temperature and moisture, inorganic N) were measured. I would propose to drop the N₂O flux part of the manuscript and relate observed changes in isotopic composition during nocturnal inversions solely to meteorological parameters ("wet phase" and "dry phase", as in section 3.5), which are much more likely to have been homogenous within the concentration footprint, than N₂O flux or soil parameters (in particular NH₄⁺, NO₃⁻, DOC,) or management events.

Answer: We agree with referee#2 that there is a remarkable difference in size between flux and concentration footprint and therefore the concentration footprint associated with our measurements of N₂O isotopic composition certainly comprises adjacent areas differing in land use or land cover. In summary, however, we are confident, that the grassland represents a major contribution to the analyzed isotopic signature of the N₂O accumulated above the grassland in the nocturnal boundary layer. To better illustrate our argumentation, but also to present potential limitations, we added the following changes to the manuscript:

- 1) *The manuscript title was changed from "First on-line isotopic characterization of N₂O emitted from intensively managed grassland" to "First on-line isotopic characterization of N₂O above intensively managed grassland".*
- 2) *As given above in response to referee#1 (see comment to P 1994 L 6-9) an explanation was added why flux and concentration footprint are different and how this could influence N₂O isotope analysis. In addition we added the following wording to the end of section 4.6: "However, it cannot be excluded that N₂O isotopic signatures analyzed above the grassland were influenced by adjacent ecosystems". As well as section 4.7: "One has to keep in mind, however, that part of the observed variability may be attributed to the fact that the footprint area of the N₂O isotopic composition includes areas with other land use or land cover".*
- 3) *As detailed above in response to referee#1 (see comment to section 4.7) the weight of influence scales with source strength and distance so that areas of high source strength and low distance to the sample inlet have a higher influence on the determined isotopic composition. The grassland on which our measurements were carried out was restored in 2012 which caused extraordinary high N₂O emission in 2012 (29.1 kg ha⁻¹). Emissions during the measurement campaign were also distinctly elevated with up to 500 µg m⁻² h⁻¹ and the grassland site CHA can be considered as a site with vigorous N₂O emission. In the study by Griffis et al. (2007) the shift of source signature was calculated for different concentration footprint sizes, assuming an increasing area of contributing C3 canopy. However, Griffis et al. postulated a constant source strength for C3 and C4 canopy, which is certainly not the case for CHA.*
- 4) *In addition, the linearity of the Keeling plots, given in the supplementary file S1, indicates a constant source process. During the overnight concentration increase, which was used for the Keeling plots, wind speed and direction were not constant over the several, approx. 16 minute*

intervals during which surface layer air was pre-concentrated. Consequently, influences from other grasslands, land use or land cover with different isotopic composition would result in Keeling plots that show a deviation from a linear relation of isotopic composition with 1/concentration. This is especially the case for $d^{15}N_{bulk}$ as this value is most variable due to its dependence on precursor composition which can be expected to vary significantly in space. To highlight this, the following phrase was added to the text: “However, two facts indicate a major influence of the studied grassland on the determined N_2O isotopic composition: First, the N_2O isotopic composition is very stable for a noon-to-noon period as indicated by a linear relationship between individual measurements (supplementary file S1). This relationship persists even though wind speed and direction are changing and, therefore, individual N_2O isotope measurements integrating over 16 minutes sampling interval originate from different source areas.”

Owing to the considerable source strength in combination with the strictly linear Keeling plots (given as supplementary material), we assume that the grassland studied has a major influence on the determined isotopic composition. Nonetheless, we clearly give credit to the possibility that adjacent regions may have influenced the determined N_2O isotopic composition.

Page 1575, lines 13-15 state: “Hence, the development of adequate mitigation strategies is pertinent and requires a better understanding of the processes driving N_2O fluxes.”

Please return in your discussion to this statement and try to show how the study has contributed to this goal (maybe as a follow-up to sections 4.4 and 4.5).

Answer: As stated at the end of section 4.4, a better understanding of processes driving N_2O emission cannot be reached to date by determination of N_2O isotopic composition alone, but will need to be combined with other methods determining isotopic composition in the substrates and quantification of N_2 emission.

Minor:

Page 1576, line 22: insert space between “in” and “Toyoda”.

Answer: done

Page 1579, line 18, and page 1594, line 22: maybe “comparability” instead of “compatibility”?

Answer: The term “compatibility” is used to refer to the agreement between results from different laboratories, in accordance with the vocabulary for metrology (see GAW report No. 213, 2013).

Page 1584, line 22: Results of DOC measurements are presented here, without the DOC measurements having been explained in the Methods section.

Answer: Section 2.7 was supplemented by a corresponding paragraph

