Discussion of “What matters when? Temporal development of drivers and sources of nitrous oxide emissions in winter wheat”

Author (Turco et al.) response to Referee 2 comments

In the following, *reviewer comments are given in blue italics*, author comments are given in normal font.

General and specific comments

The study reports GHG fluxes by ECT in winter wheat following 2-3 year grass clover cropping and measurement of vegetation dynamics, soil moisture, and mineral N to (i) quantify GHG fluxes, .(ii) identify drivers of N2O fluxes (iii) and determine N2O pathways.

A novel machine learning (ML)-based modeling approach was used to identify drivers for N2O peak events and to model N2O fluxes.

The ECT approach was state of the art and together with the soil and vegetation parameters determined the data-set is probably unique and well suited for model testing. Isotopic fluxes were determined during 3 weeks after early spring fertilization with mineral and organic fertilizer to determine N2O pathways and reduction to N2.

While the evaluation of ECT data and the measured control factors using the KI model is certainly innovative and helpful to identify drivers of N2O in that study.

Thank you for your favorable feedback.

But the study presents only data one site and one under soil conditions and fertilization regies which are quite special (one-year, one soil, without replicates, special case of grass-clover as preceding crop with very high expected N-mineralisation and mixed organic/mineral fertilization, in a clay loam soil which is quite prone to intense denitrification), the study thus does not expand our knowledge on the processes and their control. It only confirms with several observations the well-known regulation of N2O fluxes by the interplay of fertilization, soil moisture, mineral N and crop growth. Similarly, the determination of emission factors and of the GHG budget must be seen as individual observation of that site and year that add little to regional or global estimates of these values.

Thank you for this comment. We agree that our study represents one site and one winter wheat season under specific soil and management conditions, and we will make this limitation clearer in the revised manuscript. Accordingly, we will clarify that the emission factor and GHG budgets should be interpreted as site- and year-specific estimates, rather than as values intended to directly improve regional or global inventories. However, as noted by the reviewer, our study provides a unique combination of data streams, and as the second reviewer noted “*the paper employs strong and novel methods to demonstrate this idea through use of spatio-temporally integrated flux measurements and frequent measurement of crop growth dynamics to estimate soil nitrogen dynamics, plant nitrogen uptake, and N2O emissions over time”.* Thus, despite working in a well-researched field, we are confident that our results can shed new light on N_2O fluxes and their drivers.

We thus agree that the individual controls of N_2O emissions, such as fertilization, soil moisture, mineral N availability, and crop development, are well established. However, our objective was not to identify these drivers in isolation, but to investigate how they interact temporally under field conditions. This is relevant because N_2O fluxes are highly episodic and often controlled by short-lived combinations of management events and environmental conditions, but the nature of these controls is still not understood.

In this context, the XGBoost-SHAP analysis provided insights into why elevated N_2O emissions occurred during specific periods, by showing how combinations of management events, soil moisture/temperature conditions, and crop activity contributed to flux variation under winter wheat, the main crop in Central Europe. In addition, we compared our findings with other regional studies, which generally supported the main patterns identified by our ML analysis.

We will revise the manuscript to better emphasize the main contributions of our study, i.e., resolving the temporal interplay among N_2O drivers at high temporal resolution, rather than a general identification of already known N_2O controls.

The new ML-model was used to identify drivers of N2O fluxes. Traditionally, this is done by conventional statistical models or using process-based biogeochemical model like, e.g., DNDC. There were no attempts to compare the new model to traditional approaches. Moreover, the model is not addressed in the discussion. From my view the data-set and the evaluation reported in the paper are suitable for a methodical paper that focusses on the new model and how it relates to previous models. But the discussion largely neglects the new model and focusses on the question (1.) how the fluxes were regulated, (2) how the magnitude of N2O fluxes relates to previous studies and (3.) what we can learn from the data on N2O mitigation strategies. While the first aspect, as said before, does not add any new insights, the study does ono add any basis for the third aspect.

The paper is thus not suitable for publication in the present form. I suggest major review which should include model comparison as explained above and removal of the current discussion on emission factors, flux regulation and N2O mitigation.

Thank you for this comment. We agree that comparing the XGBoost-SHAP approach with conventional statistical models or process-based models such as DNDC would be valuable. However, such a comparison was not the aim of this study. A rigorous evaluation across modelling approaches would require a larger multi-site and multi-year dataset to assess model transferability across contrasting soils, climates, crops, and management regimes, which is beyond the scope of our one-site, one-season dataset. Our objective was not to develop or benchmark a new N_2O model, but to use an explainable machine-learning approach as an interpretative tool to assess how environmental and management drivers contribute to temporal variation in EC-derived N_2O fluxes. We chose XGBoost because N_2O fluxes are highly episodic and exhibit non-linear responses to interacting drivers such as soil moisture, temperature, and soil N availability. This approach further allowed us to incorporate management history as predictors and to explore the complex interplay of N_2O drivers directly from our high-frequency dataset.

More generally, we respectfully disagree that this study does not add new insights on how N_2O fluxes were regulated. The study we present is, to our knowledge, among the first to explicitly investigate how multiple drivers contribute to N_2O fluxes over time, rather than focusing only on average seasonal relationships, and to combine eddy covariance fluxes with isotopic analyses to resolve underlying processes. Given the site-specific nature of the study, we placed emphasis on comparing our findings with existing process understanding and published field studies to assess their plausibility and potential broader relevance.

We acknowledge that our ML approach was not sufficiently discussed and we will expand the Discussion with a dedicated subsection clarifying the role, strengths, and limitations of the XGBoost-SHAP framework. At the same time, the current section “4.4 Implications for N_2O mitigation in cropland” will be removed, and relevant content will be integrated into other parts of the Discussion. Finally, while we do not think that the discussion of flux regulation and emission factors should be removed entirely, we will streamline these sections to ensure that greater emphasis is given to the modelling approach and its interpretation.

There are some further shortcomings in the paper regarding the GHG budget calculation, the determination of emission factors, the calculation and interpretation of the isotopic data, the presentation and discussion of the N budget and of NUE. These points are addressed in the detailed comments below.

Details:

Line 45f pH as control of denitrification product ratio missing

Role of N2 related to total N loss, yield and GHG cost for replacing loss of fertilizer N and role of N2O reduction to N2 to understand N2O regulation is missing in introduction and also in the evaluation of the N2O drivers

We thank the reviewer for this comment. We will revise the Introduction to clarify that environmental controls of nitrification and denitrification also affect the reduction of N_2O to N_2, the final product of denitrification. While pH is an important control of N_2O reduction, we avoid presenting it as the sole regulator because other factors are relevant for this step. We also agree that N_2 losses are relevant for total N loss, yield, and the GHG costs of replacing fertilizer N. However, our study focuses on N_2O emissions and their drivers, and N_2 losses were not directly measured.

L90 relevance for isotopocules to determine rN2o missing

We have revised the sentence, which now reads:

“Combined with N and O stable isotope ratios ($\delta^{15}N$ and $\delta^{18}O$), SP can be used to trace the temporal development of N_2O-producing processes and constrain the extent of N_2O reduction to N_2 (Verhoeven et al., 2019; Yu et al., 2020).”

L91-96 need to stress that process identification with stable isotope was only for a few weeks.

We will revise objective (iii) to clarify that isotope-based process identification was conducted during the weeks following a fertilization event, not throughout the full study period.

L103 supply full soil info: pH, bulk density, total C, total N, soil classification.

We will complement the site description with the requested soil information, including pH, bulk density, and C and N stocks, while retaining the existing soil classification and soil texture information.

L110-118 give more details on tillage technique and straw management after wheat as this is a key control of N_2O

We thank the reviewer for this suggestion. We will add further details on the tillage technique after winter wheat harvest. Straw management was already specified in the manuscript (line 115), where we stated that wheat straw was removed from the field.

Table 1: unit of Nin/out missing

We thank the reviewer for pointing this out. We have revised Table 1 by moving the unit from the caption to the corresponding table heading, so that the units for Nin/out are now explicitly stated.

Intersting that NH4NO3 and slurry were applied simultaneously. Consider that labile C of slurry might create hot spots of denitrification from NO3 of min. fertilizer. And that O2 consumption during nitrification of NH4 might also cause short-term anaerobic hot spots.

We thank the reviewer for this comment. We agree that the near-simultaneous application of NH_4NO_3 and slurry is relevant for interpreting post-application N_2O dynamics, which was also pointed out by Referee 1. This practice can occur in integrated farms (i.e., farms combining livestock and arable crop production), which are common in Switzerland, and is compliant with Swiss agricultural regulations. We agree that this practice sets favorable conditions for denitrification. We will provide additional context to clarify this management practice and discuss its relevance in detail in the Discussion section.

More details on slurry needed(volume Norg and NH4 content, and "+18" is not clear to me

We will add additional information to the table, including slurry application volume. Available information on slurry N composition was already provided, but we will clarify it directly in the table by removing the previous explanation of *"+18"* from the caption where the explanation was provided originally (i.e., for slurry, +43 refers to total N input and +18 to NH_4^+-N input).

2.2 skipped, not my expertise

L185-190 background flux calculation not clear. I think it is not possible to get a robust estimate of N2O fluxes with zero fertilization from the EC data of one field. Please discuss uncertainty arising from this simplification and clarify in all parts of the paper that the reported EF is an approximation.

As noted in our response to Referee 1, after careful consideration of the methodological concerns raised, we decided to remove the background-flux estimation from the revised manuscript. We therefore no longer report a background-corrected emission factor. Instead, we report an apparent emission factor, calculated as cumulative N_2O-N emission divided by fertilizer N applied, and will clearly define it as such throughout the manuscript. A more detailed explanation is provided in our response to Referee 1, where the same issue was discussed in detail.

L199-207 one moisture profile is not enough for one field due to variability. Not adequate to use old data for BD in top soil. Please discuss these limitations

As noted in our response to Referee 1, we agree that one soil moisture profile cannot fully represent spatial variability across the EC footprint. We will acknowledge this limitation and clarify that our conclusions rely mainly on temporal co-variation between fluxes and soil drivers, rather than on footprint-mean soil moisture estimates. We refer the reviewer to our detailed response to Referee 1 on the soil moisture representativeness issue, including **Figure R1.1**.

In response to the additional point raised here, we will also discuss the uncertainty introduced by converting SWC to WFPS using bulk density values from previous measurements.

L 243 need to calculate uncertainty of soil emitted isotopes ((Wu et al., 2019). SD of isotope analysis should be reported

We did not run technical replicates for individual samples and therefore cannot report a standard deviation for each measurement. Instead, instrument performance was assessed during each analytical run through several quality-control procedures following Mohn et al., (2014).

Specifically, two standards with different isotopic compositions were analyzed at the beginning, middle, and end of each run and treated as samples following the identical treatment principle (Werner and Brand, 2001). In addition, these standards were analyzed at lower concentrations to account for potential linearity effects across all m/z. Lastly, a third standard is run and treated as sample to test for across run instrument stability. We will clarify these procedures in the revised Methods section.

L254 need to report results of all scenarios and uncertainty given by Frame

We thank the reviewer for this comment. The full distribution of the FRAME outputs, including associated uncertainties, is already shown in Fig. 7 as violin plots. To improve clarity, we will explicitly report the corresponding uncertainty in the text of Sect. 3.5.

L423 better keep consistent wording (N2O fluxes) to avoid misunderstanding

We thank the reviewer for this suggestion. We will revise the terminology accordingly and replaced "net ecosystem N_2O fluxes" with "N2O fluxes". Throughout the revised manuscript, "fluxes" will be used to refer to both positive (emissions) and negative (uptake) N_2O fluxes, and "emissions" when referring to N_2O losses.

L436 keep consistent wording. This sentence suggests that net ecosystem flux is different from emission, but you use both expression for the same flux. So what do you mean by "indicating"

As for N_2O, we will revise the terminology throughout the manuscript for consistency. In this sentence, "indicating" was intended to clarify that a positive net CH_4 flux corresponds to a net emission of CH_4. However, we agree that this wording may be confusing, so we will simplify the terminology and revise the sentence accordingly to ensure clarity and consistency.

Section 4.3.4: why was there continuous positive CH4 flux? The soil was mostly rel. low in WFPS, eg clearly above 0.8 and N2o flux was low. Thus it would be expected that the soil acts mostly as CH4 sink. This questions validity of EC results. Or was there evidence for positive CH4 fluxes from the chambers? An explanation might be the decay of the grass-clover sward in the clay loam leading to CH4 production. But this would indicate strong reducing conditions which would be highly relevant for the N2O production and reduction. So this should be discussed.

The magnitude of CH_4 fluxes was very low in both directions, with a mean measured flux over the measurement period of $+0.77\pm8.57$ nmol m^{-2} s^{-1} and a median signal-to-noise ratio of 1.55, indicating that the flux was only marginally distinguishable from instrumental noise and thus near the detection limit.

Nevertheless, periods with positive CH_4 fluxes coincided with relatively high soil moisture (high WFPS; Fig. 2b), conditions which are known to favor CH_4 production. As soils dried (WFPS decreasing in May–June), we observed a transition from a weak source to a weak sink, consistent with increasing aerobic conditions and enhanced CH_4 oxidation.

We are therefore confident that the EC fluxes successfully captured the temporal dynamics of CH_4 fluxes, although we acknowledge the higher uncertainty associated with CH_4 fluxes. This is further supported by the small overall contribution of CH_4 to the total GHG budget (Table 2). Our observations are in line with previous studies showing that agricultural soils in temperate regions can act as small net CH_4 sources (Cowan et al., 2021) and a shift from sink to source of upland cropland soils over the past three decades (Li et al., 2025).In the revised manuscript, we will better contextualize the conditions that could have led to the observed weak CH_4 source, while also explicitly acknowledging the higher uncertainty of CH_4 fluxes to improve transparency.

L450 please check units: 0.8 nM/m2/sec gives 5.6 g N/ha/282 days so your numbers seem to be mMol/m2/sec

We have rechecked the unit conversion and confirm that the reported fluxes are correct and expressed in nmol N_2O m^{-2} s^{-1}.

The cumulative emission over the 282-day period is calculated as:
0.81 [nmol N_2O m^{-2} s^{-1}] * 282 [days] * (60*60*24 [seconds per day]) * 10^{-9} [nmol to mol] * 28.014 [molar weight N_2] * 10^4 [m^2 in 1 ha] * 10^{-3} [g to kg]

Resulting in values expressed in kg N_2O-N ha^{-1} in 282 days.

L278 need to explain how the root simulators are different in estimating plant available N, since Nmin is plant available. Also explain why 0-0.1 m was chosen as rooting depth is much deeper

We thank the reviewer for this comment. Plant root simulators provide an integrative measure of plant-available N over time by capturing nutrient supply through ion exchange, whereas soil mineral N (Nmin) represents a snapshot of extractable inorganic N at the time of sampling. We will clarify this distinction in the Methods.

Regarding depth, we used the 0–0.1 m layer to represent the zone most strongly affected by management and where root density and nutrient uptake are highest. We will add this rationale to the manuscript.

L 303 not clear why N fertilization was used as a proxy for N availability instead of measured Nmin in cores or accumulators. To train models of N2o, typically Nmin is measured in top soil at each gas sampling event.

We thank the reviewer for this comment. While soil mineral N (Nmin) measurements are commonly used in chamber-based studies, their sampling frequency cannot match the high temporal resolution of EC measurements (10–20 Hz aggregated to 30 min). Interpolating a limited number of Nmin measurements (seven in this study) would therefore not adequately resolve short-term variability in N availability at the daily scale.

Instead, we used fertilization-derived variables as a proxy for the effect of fertilization on N availability, as they represent the primary driver of changes in substrate supply for N_2O production in agricultural systems. This approach allowed us to better capture the effects of management-induced N inputs at the temporal scale relevant for EC flux dynamics. We will clarify this in the revised manuscript and further discuss the implications of this approach in the Discussion section.

``L 308 cumulative N is a rough predictor of Nmin. Because this was strongest parameter it is not clear why measured Nmin was not included. Please explain or remove.

See the explanation to the previous point.

Unit nM/s2/sec: please refer to identical units: fertilized area is kg /ha.N2o should be reported accordingly. t

We are not sure what this comment refers to in the manuscript. We use nmol m^{-2} s^{-1} when referring to instantaneous or average fluxes and kg N_2O-N ha^{-1} for cumulative fluxes. We will check again in the revised version of the manuscript.

L326,327 not clear what these variables mean

These values correspond to parameters of the XGBoost model. To avoid confusion for readers not familiar with these parameters, we will move them to the Appendix/Supplement, where they are provided for completeness.

``L450: cumulated flux in kg N/ha does not fit avg value in nM/m2/s. apparently the data shown are in µMol.

See our response above on the same doubt. The units are correct.

L453 – 450 Calculation of EF based on estimation of unfertilized N2O fluxes from phases of background flux is not adequate as this is affected by seasonal effects (temp, moisture, Nmin of unfertilized from mineralization-nitrification-immobilisation. Please delete estimation or explain that a very rough approximation was used to get an EF estimate.

As noted above, we have removed the background-flux estimation from the revised manuscript. Accordingly, we no longer report background fluxes or derive emission factors based on this approach.

L 466 CO2 uptake during cropping is not a climate benefit as the fixed C is not stable unless grain and straw were long-term deposited which is quite improbable. Thus it does not make sense to be compared with GHG effect of N2o flux. Clearly, not NEE but NEE minus net C export must be used in GHG budgets.

Please correct or delete paragraph and delete last line of Table with the GHG budget and report only the fluxes. Please double check the CH4 fluxes. Positive flux in wheat is not plausible. Please explain reasons for net source (shallow groundwater, stagnic soil properties?)

We thank the reviewer for this comment. As noted in our response to Referee 1 regarding the same concern, we will revise the wording to clarify that we refer to EC-based fluxes only, without accounting for additional C imports or exports. We acknowledge that the term "GHG budget" is used inconsistently across studies and can therefore be interpreted as including lateral C imports and exports, which may lead to confusion. While we already indicated in the table that C imports and exports were not considered, we will further reduce ambiguity by replacing "GHG budget" with "net GHG exchange"(Wall et al., 2023) throughout the manuscript when referring to the EC-based sum of CO_2, CH_4 and N_2O fluxes expressed in CO_2 equivalents.

For completeness, we will additionally calculate and report the full GHG budget, accounting for C imports and exports, in the revised manuscript.

Regarding the concern about CH_4 fluxes, we have addressed this point above. Positive CH_4 fluxes in arable systems (even for wheat) are not implausible, as also shown e.g. by Cowan et al. (2021).

We will further clarify the site-specific conditions that may explain the observed weak CH_4 source in the revised manuscript.

L512 avoid unclear interpretations in results. PS is not a direct regulator of N2O. It is not PS itself but the multitude of plant growth effects (exudation, rhizosphere respiration, water uptake, Nmin uptake, etc.), please address in discussion accordingly

We thank the reviewer for this helpful suggestion. As noted in our response to Referee 1 regarding the same point, we will revise the wording and expand the Discussion to better contextualize the observed association between GPP and N_2O fluxes. Specifically, we will emphasize that GPP is used as a proxy for plant activity and that the relationship likely reflects indirect plant-mediated effects (notably N uptake and thus change in soil N availability), rather than a direct control of N_2O emissions.

Section 3.5: Stable isotopes also yield info on N2O reduction, thus this aspect should also be covered by the heading.

We thank the reviewer for this suggestion. Our study, as noted in a previous response, primarily focuses on identifying N_2O source processes, whereas N_2O reduction to N_2 is a secondary aspect relative to our stated aims. We therefore retain a process-focused heading and will rename Sect. 3.5 to "N_2O-producing processes identified by stable isotopes". Nevertheless, we will expand our explanation of the reduced fraction, when showing and later discussing the stable isotope results and the FRAME model.

Please state and discuss whether and why you use the mixing-reduction or reduction -mixing scenario in FRAME and how results would change if you assumed the other scenario. Please also discuss the rising uncertainty in isotopes of soil emitted with decreasing flux. As far as I know, the FRAME model does not yet add this effect to the reported uncertainty. But the effect is addressed in detail in Wu et al 2019. rN2O of march 17 might be highly uncertain due to the low flux.

We thank the reviewer for these helpful suggestions. We used the mixing–reduction (M–R) scenario in FRAME and will explicitly state and justify this choice in the Methods. Following the reviewer's request, we also ran the alternative reduction–mixing (R–M) scenario; it yielded very similar results and did not change our interpretation (new Fig. R2.1). We will add Fig. R2.1 to the Appendix with the corresponding figure for the mixing-reduction scenario (see Fig. R1.5 in our reply to Referee 1). We will briefly summarize the comparison in the Results/Discussion.

We will also expand the Discussion on the uncertainty at low fluxes, as this additional flux-dependent uncertainty is not accounted for by FRAME.

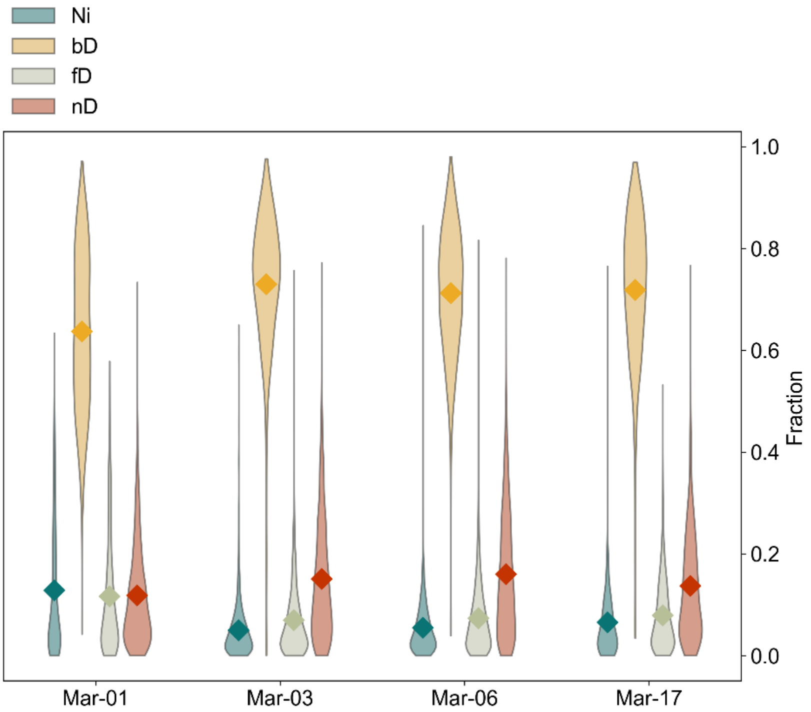

Figure R2.1. FRAME-estimated N_2O source fractions based on the reduction-mixing scenario in March 2023 following fertilization (27–28 February), shown as violin plots for denitrification, nitrifier denitrification, nitrification, and fungal denitrification (means indicated by diamonds).

Fig. 7 Not clear what is shown here residual N2O fraction or unreduced N2O fraction? r explained in the methods is: "The contributions of different N_2O production pathways and the residual fraction of unreduced N2O (r) were estimated with the FRAME software"

The residual N2O fraction is equivalant to the N2O/N2+N2O ratio, ie lowering values show increasing N2o reduction to N2.

But in Fig 7ba it can be seen from the smaller circles along the reduction line that rN2O sjould be is lowering over tie . Hence it seems you show 1-r which corresponds to the expression in the caption "reduced fraction".

We thank the reviewer for this comment. The reviewer is correct: Fig. 7b shows 1 − r (i.e., the fraction of N_2O reduced to N_2), whereas r denotes the residual (unreduced) N_2O fraction. Accordingly, in the Results text, as well as in Fig. 7 caption and legend, we refer to 'reduced fraction'. We will explicitly state "1 − r" in the text and Figure to avoid confusion.

L556: to be clear better state: d18O and SP of emitted N_2O

Thanks, we will clarify that these values refer to emitted N_2O by changing the sentence to "$\delta^{18}O$ and SP of emitted N_2O…".

L 557 better name it "heterotrophic bacterial denitrification" since AOB are also bacteria

Thank you for the suggestion, we will revise the text accordingly.

L 583 not plausible that GPP is a direct driver of N2O but rather its relation to N uptake, exudation and water uptake

We agree with the reviewer and note that this relationship is clarified in the following sentence. As mentioned in our response to the comment on L512, we will further clarify this point and expand the Discussion accordingly.

4.1 This descriptive discussion does not yield any new insights but just summarizes that N2O fluxes were controlled as known since long.

We will shorten this section in the revised manuscript. At the same time, we note that, to our knowledge, there are no published EC-based N_2O studies covering a full winter wheat season. Moreover, our driver analysis enables a temporally resolved assessment of controls, providing new insights into specific time periods rather than only overall relationships.

L 640-644 not clear which numbers are compared current study to Maier 2022? High NUE in this study is probably not related to wheat cropping but to previous crop (grassland conversion) delivering high amounts of Nmin from sward mineralization. Please note that 3 year grass-clover is often used in organic agriculture to feed 2 follow-up harvest of winter wheat without adding mineral fertilizer, which illustrate the high delivery of plant available N from this previous cropping season.

We thank the reviewer for this comment. We will specify that the NUE for maize from Maier et al. (2022) was derived from the values presented in their Table 1. In addition, we agree that the high NUE may be influenced by N supply from previous land use, and we will include a brief discussion on the potential contribution of sward mineralization following grassland conversion.

L646 revise CO2 in GHG budget (see above)

See our response above.

L 654 role of vegetation not new at all

We assume this refers to the statement around line 694 (not line 654), as vegetation is not discussed at line 654. The intention of this sentence is to emphasize that plant N uptake can act as an important N sink and thereby reduce the availability of mineral N for microbial N_2O production, a mechanism that is sometimes underemphasized in N_2O flux studies.

As noted above, we will restructure this subsection of the Discussion and move the relevant statements to the appropriate subsections, while keeping the key message in a clarified form.

L 700-703 only one peak event investigated thus not representative for the cropping period

Thank you for pointing this out. The stable isotope data were collected in March 2023, when the highest N_2O fluxes occurred. In the revised manuscript, we will clearly specify this time window and clarify its relevance by quantifying its contribution to total N_2O losses over the entire cropping season.

L703f not adequate to derive mitigation strategies based on a one year study with only treatment. A multitude of field plots studies has investigated this before. The current study may be in agreement with the previous ones, but this single observation can't be used to confirm the previous results, and certainly not to propose N2O mitigation strategies.

This subsection was intended to synthesize our results with the broader literature in terms of mitigation options, not to generalize from our dataset alone. To avoid overinterpretation, as mentioned above, we will remove this mitigation subsection and relocate only the relevant contextual text to other discussion subsections.

References

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