

Reviewer 1

Suggestions for revision or reasons for rejection

(visible to the public if the article is accepted and published)

The authors are to be congratulated on their thorough and comprehensive response to the comments previously provided, which improved the manuscript significantly.

In my opinion, the only remaining weak point concerns the authors' recommendation to incorporate denitrification-induced CO₂ emissions into the IPCC framework. My reasoning is as follows:

Authors: 'In addition, we also provided a justification for the complete denitrification assumption: (Line 89-94) This study, therefore, aims to quantify CO₂ release from denitrification of nitrate derived from agricultural N fertilizer use, in the context of national GHG inventories. To enable this quantification, we assumed complete denitrification.'

However, to the best of my understanding, IPCC guidelines for national GHG inventories assume indirect N₂O emissions to occur from nitrate leached from agricultural soils (EF5). My concern is that the current IPCC methodology using the EF5 factor (implying some degree of incomplete denitrification) would be incompatible with introducing an additional new approach for accounting for denitrification-induced CO₂ emissions (assuming complete denitrification). Do you agree that one of the two options would have to be chosen?

The reviewer has a good point. Indeed, assuming complete denitrification would theoretically preclude N₂O emissions. However, N₂O emissions from groundwater represent only a small fraction of the total groundwater N retention. While the fraction may vary considerably across sites, global estimates suggest that only 1 % of total groundwater denitrification is emitted as N₂O (Bouwman et al., 2013). Similarly, the IPCC guidelines' emission factor for indirect N₂O via groundwater is 0.6% of leached N. N₂O is a potent greenhouse gas due to its high global warming potential, not because of large quantities emitted from groundwater.

Therefore, we believe that N₂O and denitrification-induced CO₂ emissions should be treated separately with different level of uncertainties. For CO₂ emissions from denitrification, a 1 % of uncertainty is acceptable, where as N₂O emissions require different types and levels of data and modeling approaches.

In the revised manuscript, we have strengthened our argument for the complete denitrification assumption:

Line 89-99:

This study, therefore, aims to quantify CO₂ release from denitrification of nitrate derived from agricultural N fertilizer use, in the context of national GHG inventories. To enable this quantification, we assumed complete denitrification. While incomplete denitrification can result in the production of N₂O, which has a substantial climate impact, this N₂O is typically

further reduced to N₂ in deeper anoxic aquifer (Jurado et al., 2017). As a result, the fraction of N₂O emitted from groundwater is generally insignificant compared to the total amount of nitrate denitrified in groundwater. For instance, Bouwman et al. (2013) estimated that about 1 % of total groundwater denitrification results in N₂O emissions, and the most recent IPCC guidelines suggest that 0.6% of leached N would be ultimately emitted as N₂O from groundwater (IPCC, 2019; Tian et al., 2019). Furthermore, N₂O production and reduction processes are highly heterogeneous in space and time (Clough et al., 2007; Jahangir et al., 2013; Jurado et al., 2017; McAleer et al., 2017). While these hotspots and hot moments may be relevant for local-scale assessment, they are unlikely to significantly influence large-scale GHG budgets. Therefore, we consider that assuming complete denitrification is a reasonable approximation for large-scale assessments such as this study.

Authors: 'Incomplete denitrification, which produces N₂O, is highly heterogeneous in space and time (Clough et al., 2007; Jahangir et al., 2013; Jurado et al., 2017; McAleer et al., 2017).'

This is correct, but per se not a justification for ignoring it. Despite its immense small-scale variability (hot spots, hot moments), incomplete denitrification could still be quantitatively very important in terms of GHG potential, especially when integrated over larger areas and longer time scales.

We disagree with the reviewer's point. In our view, hotspots and hot moments may influence short-term, local-scale budgets, but they are unlikely to have a significant impact on long-term, large-scale greenhouse gas budgets. Over larger spatial and temporal scales, these localized and transient events tend to average out, and the overall budget converges toward the system-wide mean. We have addressed this reasoning in our response to the previous comment.

Authors: 'In addition, N₂O produced in groundwater is likely converted to N₂, particularly in anoxic groundwater (Jurado et al., 2017). Therefore, we concluded that assuming complete denitrification is a reasonable approximation for large-scale assessments such as this study.'

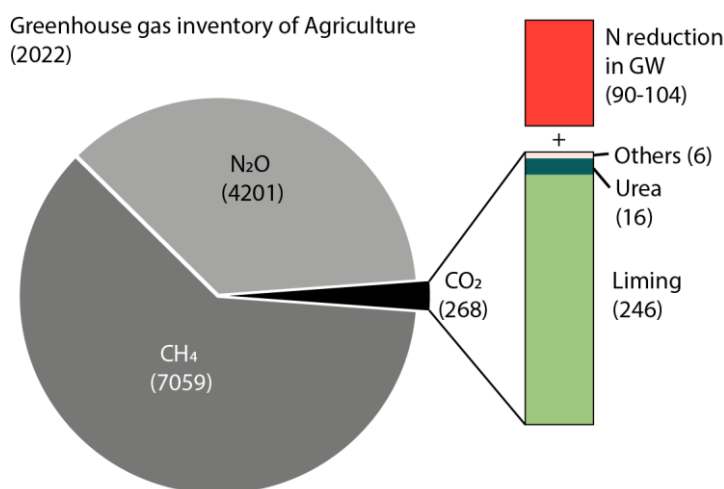
In many situations, groundwater denitrification will indeed almost quantitatively proceed to N₂ gas. However, given that N₂O is a GHG 298 times more potent than CO₂, I would like to encourage you to provide the reader with one or more example calculations that put your estimated complete denitrification-induced CO₂ emissions into perspective. E.g., how would the GHG effect of currently unaccounted for CO₂ emissions compare to that of N₂O emissions if only 90% of the nitrate was fully reduced to N₂ (and 10% to N₂O)?

As mentioned earlier, the fraction of N₂O emission from groundwater is generally estimated to be around 1% or less of the total groundwater denitrification. However, to put denitrification induced CO₂ emissions into perspective, we have added the following sentence to the revised manuscript:

Line 426-427:

For comparison, the national GHG inventories of Denmark estimates that 360 kt of CO₂-eq yr⁻¹ of N₂O would be emitted via groundwater in 2022 (Nielsen et al., 2024).

We also identified more recent national GHG inventory data and have updated figure 4 accordingly to reflect these new estimates.



L 448: Please change 205 kt to 204 kt.

Corrected to 204.

Reviewer 2

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The authors of the manuscript with the new title “A national scale redox clustering for quantifying CO₂ emissions from groundwater denitrification” put a lot of efforts in the revision of the paper according to the suggestions of the editor and the two reviewers. They have taken up the criticism and provided necessary explanations for some assumptions, such as the relationship between autotrophic and heterotrophic denitrification or the role of N₂O formation during incomplete denitrification. I can

understand the explanations and find the considerations a good addition to the GHG emission estimates.

Only one smaller issue I want to rise, is the relation to TA by anaerobic metabolisms. Sure, the suggested reference is about the situation in the Ocean, but that doesn't prove that it only plays a role in the ocean. You should at least discuss that.

Thank you for the comment. The process the reviewer refers to i.e., denitrification linked to anaerobic metabolism is already represented in our study. Denitrification coupled with organic carbon oxidation as analyzed in our study included the alkalinity effects associated with anaerobic heterotrophic metabolism. Therefore, we believe this process is already addressed in our analysis, and no changes have been made in response to this comment.