

Reviewer 2

The manuscript “Nitrate reduction in groundwater as an overlooked source of agricultural CO₂ emissions” provided an estimation of CO₂ emissions by heterotrophic Denitrification from groundwater, based on monitoring data of Danish groundwater and come up with the hypothesis that heterotrophic Denitrification is a significant source for DIC and outgassing CO₂ and should be taken into account for the national GHG emissions estimations and that this may also important for other countries.

Generally, to conduct an entire GHG budget the emissions from groundwater have to be taken into account and a robust estimation is necessary, nevertheless some questions arise.

- At which point and time the exchange of the GHG including CO₂ between groundwater and atmosphere happened. After the leaching to river systems and marine waters, or at a earlier point. So maybe to CO₂ from submarine groundwater discharge (SGD) already count for the general GHG budget

This is an important question. Our study specifically focused on the subsurface processes, aiming to quantify CO₂ emissions resulting from denitrification in groundwater. However, we fully acknowledge the fate of DIC in groundwater as it moves into different water bodies such as streams, lakes, and coastal areas is complex and requires further investigation. Degassing of CO₂ in streams, lakes, and coastal waters is influenced by multiple factors such as water turbulence, wind speed, relative humidity and temperature. However, CO₂ degassing from groundwater will likely occur when groundwater discharges into surface waters i.e., streams, wetlands, riparian zones, where it comes into direct contact with the atmosphere. It is largely driven by the fact that groundwater’s pCO₂ levels are significantly higher than atmospheric CO₂ concentrations, creating a natural gradient that promotes CO₂ degassing to reach equilibrium. In the revised manuscript, we will add a few sentences explaining where CO₂ in groundwater will be emitted into atmosphere.

We acknowledge that in Denmark, we have not quantified the contribution of submarine groundwater discharge (SGD) to the national water budget. While SGD might be an important contributor at a local scale water and nutrient budgets, its contribution at larger scales will be minor. Therefore, we concluded that SGD is a minor pathway to release CO₂ emissions from denitrification in groundwater.

- You just mentioned heterotrophic denitrification, because that produced CO₂. But what is the percentage of autotrophic denitrification in the systems and does that play a role for CO₂ fixation?

In this study, we considered both heterotrophic (i.e., organic carbon mediated) and autotrophic (i.e., pyrite-oxidation mediated) denitrification. These two processes have been identified as the dominant denitrification reactions in Danish groundwater as well as in other regions with similar geological setting.

In case of autotrophic denitrification by pyrite oxidation, the process contributes to an increase of DIC. This occurs because pyrite oxidation generates protons, which promotes calcite dissolution if calcite is present. While some other form of autotrophic denitrification processes that fix CO₂ (such as driven by oxidation of sulfur or H₂) occur under more strongly reduced conditions. Our analysis showed that these reactions may be limited in spatial extent at the redox interface. For instance, Cluster 1 (sulfur-reducing conditions) and 6 (methanogenesis) were predicted to account for only 0.5 % and 2% of the total area at the redox interface. We interpreted that these conditions typically occur in organic-rich environments, where organic-mediated denitrification would likely dominate and reduce nitrate at shallower depth before groundwater reaches these deeper, more reduced zones.

In the revised manuscript, we will provide a table of summarizing cluster prediction results including predicted areas, numbers of screens, redox conditions of each cluster, and dominant denitrification processes. This table will provide information of the relative importance of autotrophic and heterotrophic denitrification.

- Anaerobic denitrification also produced TA, how that was taken into account and maybe increase the capability to store DIC and emit less. See: Middelburg, J. J., Soetaert, K., and Hagens, M.: Ocean Alkalinity, Buffering and Biogeochemical Processes, Reviews of Geophysics, 58, e2019RG000681, <https://doi.org/10.1029/2019RG000681>, 2020.

Yes, both heterotrophic and autotrophic denitrification reactions considered in this study contribute to an increase in dissolved inorganic carbon in groundwater. The increase in DIC also elevates pCO₂ in groundwater, resulting in CO₂ degassing when the supersaturated groundwater encounters the atmosphere. Therefore, while denitrification does temporally increase DIC in groundwater, this acts as a short-term C storage, typically on the order of years to decades, before the CO₂ is eventually released into the atmosphere. It is also important to highlight that denitrification in groundwater mineralize and mobilize both organic and inorganic C pools that would otherwise remain stored over a geological time scale.

The suggested reference, on the other hand, focuses on total alkalinity in ocean systems, where the residence times of both water and carbon are significantly longer than in groundwater systems. This extended residence times allows for long-term carbon storage and buffering in the ocean, which contrast with the more dynamic and short-term nature of the C cycle in

groundwater. Therefore, while the oceanic context provides valuable insights into global carbon cycling and buffering, its direct comparison to groundwater systems may not be fully applicable. Therefore, we will not implement any changes to the revised manuscript.

Some specific comments:

<p>L 18/19: Why you mention CO₂-eq. and not just CO₂ although is it as DIC. Where and when the 50% emitted to the atmosphere</p>	<p>It is displayed as CO₂-eq because this number can be compared to the amount of CO₂ emissions. Therefore, we will keep CO₂-eq as the unit to express DIC. The second question was addressed above.</p>
<p>L 35/41: this paragraph raises some questions. Nitrogen fertilizers are more than nitrate, so that also organic nitrogen and ammonium is part of that. So in consequence nitrification plays also a crucial role and can be a significant source of N₂O. The references for the N₂O sources Ritchie et al, 2023 just focused on “anthropogenic” Sectors. So that natural processes and sources with is maybe also anthropogenic impacted are not negligible. Especially ODZ and also groundwater discharge can be source of N₂O and other GHGs</p>	<p>“Nitrogen fertilizers” was used to infer both synthetic fertilizers and organic fertilizers as well i.e., manure. We will clarify it in the revised manuscript.</p> <p>We fully acknowledge the importance of N₂O as a greenhouse gas, particularly for the agricultural sector. However, this study focused on CO₂ emissions. Because CO₂ emissions from denitrification has never been quantified, and our study demonstrated that it is a significant but overlooked CO₂ source. In addition, N₂O emissions in groundwater is highly heterogeneous in space and time. Therefore, it is too uncertain to quantify the national budget.</p> <p>In the revised manuscript, we will explain why we assumed complete denitrification and provide justification of our assumption.</p>
<p>L50: what is the ratio of autotrophic and heterotrophic denitrification?</p>	<p>We will provide a summary table of cluster analysis results including the numbers of screens used for the prediction and the predicted area at the cluster level. Organic C-mediated clusters represent heterotrophic denitrification, and pyrite-mediated denitrification represent autotrophic denitrification.</p>

L360: When and where is will outgassing to atmosphere?

We addressed this comment above: Further research will be required but it will likely occur when groundwater discharges back to the surface waters.