Reviewer 1

As the reviewer correctly pointed out, our study utilized extensive datasets and advanced modelling tools at the national scale—resources that are both rare and valuable. These data and tools enabled us not only to investigate the linkage between groundwater chemistry and hydrogeological structures but also to quantify CO2 emissions resulting from denitrification in groundwater. Therefore, in revision, we will change the title to "A national scale quantification of CO2 emissions from groundwater denitrification through redox clustering".

We fully acknowledge the reviewer's point that CO2 emissions from groundwater denitrification represent a relatively small fraction (~1%) of the total greenhouse gas emissions (CO2, CH4, and N2O) from the agricultural sector. However, according to the *IPCC guidelines for national greenhouse gas inventories*, it states that:

"*Each greenhouse gas emitted from each category should be considered separately, unless there are specific methodological reasons for treating gases collectively.*" (IPCC guidelines for National Greenhouse Gas Inventories, Chapter 4.2. General rules for identification of key categories).

Therefore, CO2 emissions from denitrification should be compared directly to other CO2 sources under the same category i.e., managed soils defined as "*land where human interventions and practices have been applied to perform production, ecological and social functions*". The current guidelines for the managed soils category include CO2 emissions from three sources i.e., liming, urea, and other CO2-containing fertilizers. Our findings demonstrate that CO2 emissions from groundwater denitrification are a significant and previously overlooked source—equivalent to approximately half of the current estimates of CO2 emissions from managed soils. We believe this insight is highly relevant to the broader biogeoscience community, as it highlights a substantial but often overlooked source of CO2 emissions within agricultural systems. To better reflect this significance, we will emphasize this point more clearly in the revised manuscript.

3. Complete denitrification to N_2 is assumed in all calculations presented in this manuscript. The topic of indirect N_2O emissions that could result from incomplete denitrification in groundwater systems (additionally to nitrification) is not mentioned at all. While admittedly not the focus of this study, given the potency of N_2O as GHG, I would like to suggest inserting a brief justification why complete denitrification was assumed, and references to a few studies on indirect N_2O emissions (e.g. by Clough, Weymann, Jahangir, Jurado).

We assumed complete denitrification to ensure simplicity and consistency of the analysis in the national-scale assessment. While our dataset and modeling tools are extensive, analyses at this scale inevitably need a certain level of simplification. We fully acknowledge the reviewer's important point that Incomplete denitrification plays a critical role in greenhouse gas emissions from agricultural systems, particularly through the production of the highly potent greenhouse gas, N2O. However, it is also reported that a substantial portion of N2O produced in groundwater can be further reduced to N2 before discharging into the surface waters, especially when groundwater passes through reduced zones such as riparian zones or deeper reduced layers.

Moreover, N2O in groundwater is highly variable across both in space and time, and our current understanding of controls governing N2O dynamics still remains limited. This spatial and temporal heterogeneity introduces considerable uncertainty when attempting to incorporate incomplete denitrification into large-scale, quantitative assessment like ours. We appreciate the reviewer's suggestion and will incorporate relevant references in the revised manuscript to justify our assumption of complete denitrification as well as the potential of N2O emissions.

4. 2a suggests that Cluster 3 is dominant in most of DK, followed by Cluster 7 in the areas not covered by ice sheets during the last glaciation. Pyrite has been identified as the key electron donor in both of these clusters, while organic carbon only appears to serve this role in clusters 1 and 6 (with minor spatial extent), while no clear dominance was evident in clusters 4 and 8. Oxic conditions (Clusters 2 and 5) seem to have insignificant spatial coverage. Given the importance of these findings, I would suggest to explicitly provide information on the spatial extent (km^2) of each cluster, the area of pyrite-driven vs. organic carbon-driven denitrification, and references to any field research on electron donors that may underpin these results.

The spatial extent of the reduced clusters will be explicitly provided in the revised manuscript. For example, at the cluster level, Cluster 3 is dominant, covering 61% of Denmark (2.5 million ha), followed by cluster 7 (15%), cluster 4 (14%), cluster 8 (7.5%), cluster 6 (2%), and cluster 1 (0.5 %).

We had cited relevant field studies in our original manuscript: however, to improve the clarity, we will add a map showing the locations of these study sites, facilitating a more direct comparison between our model prediction and field observations.

Regarding the limited spatial coverage of oxic clusters, this is primarily due to the role of CH4 in the cluster analysis. Methane was included as a variable to help delineate redox conditions, but it is not always measured in oxic groundwater. As a result, some oxic groundwater screens lacking CH4 measurements were excluded during data processing. In this study, we assumed that denitrification does not occur in oxic groundwater; therefore, the exclusion of these oxic groundwater screens without CH4 data is unlikely to significantly impact the overall results or conclusions.

We will ensure that these clarifications, along with the requested spatial information and additional references, will be included in the revised manuscript.

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5. The results suggest that substantial nitrate reduction occurs in most groundwater systems in DK (Fig. 3a). Nevertheless, CO_2 emissions attributable to denitrification were estimated to add a maximum of 0.9% to the total emitted CO_2 equivalents (see below). While DK has excellent availability of relevant data and scientific expertise, most other countries utilising the IPPC scheme will be less well equipped (and often will have smaller fractions of reduced groundwater). Accordingly, I suggest that most countries are not in a position to credibly estimate what might be a very small contribution relative to all other processes contributing GHG emissions in agricultural landscapes (please see below for detail). I would like to suggest that resources might be more usefully employed in combatting GHG emissions, rather than in adding small new components to the IPCC accounting system. Please consider these points when revising your Conclusions.

As highlighted earlier, CO2 emissions from denitrification should be compared to other CO2 sources within the agricultural sector. In addition, we, as researchers, provide our best knowledge to policy- and decision-makers to properly tackle urgent challenges such as climate change. Our results showed that CO2 emissions from groundwater denitrification is a clearly overlooked agricultural CO2 source, which is important information for the IPCC committees as well as biogeoscience communities.

We fully acknowledged the reviewer's point that conducting a national-scale assessment, like the one we present for Denmark, may be not feasible in many countries due to limited data availability and differences in hydrogeological conditions. However, it is important to note that denitrification is one of the most extensively studied processes in agricultural landscapes. Studies have been conducted at multiple scales in 1D profiles, 2D transects, catchment studies

as well as regional assessments. As such, the quantification of CO2 emissions from denitrification can be adapted at different spatial and data contexts.

In line with the IPCC guidelines, there are three tiers of emissions factors. Tier 1 is based on large-scale modelling results, such as those presented in our study. Tier 2 uses local data while employing the emission factors from Tier 1. Tier 3 is based on the local data as well as local emissions factors for higher accuracy. Our study provides foundational data that could support Tier 1 assessment and inform the development of more localized studies under Tier 2 and Tier 3, where it is feasible to assessment.

We fully agree with the reviewer's perspective that efforts should primarily focus on mitigating GHG emissions. Importantly, the data and modeling tools developed in this study have broader applications beyond CO_2 accounting. For example, they can be employed to improve understanding of N_2O emissions in groundwater—an area where further research could yield significant insights. We will revise the Conclusions section to emphasize both the potential broader applications of our findings and the priority of directing resources toward impactful GHG mitigation strategies.

6. The **Specific comments** listed below are largely of a minor or technical nature, but addressing them should improve the clarity of the manuscript.	
Thanks for your suggestions. We will incorporate the specific comments in the revised manuscript as follows	
15: what is meant by 'dominant denitrification processes'? Different electron donors driving denitrification?	Yes, dominant denitrification processes mean different electron donors. In the revised manuscript, it will be revised as: "We identified dominant electron donors of denitrification in groundwater.... "
Table 1: Equations 1 and 2 are both assuming complete denitrification to N_2. Could you please add a sentence on the effect incomplete denitrification would have.	Incomplete denitrification would release less DIC because it requires fewer electrons. In addition, it produces N2O. We will add a few sentences to state both aspects of incomplete denitrification.
65 ff: The calculations marked by * and ** in Table 1 are valid for situations where calcite saturation occurs. Could you please provide the reader with information on how common such conditions are within the groundwater system and where groundwater discharges	In general, it will depend on underlying geology, particularly the content of calcite. For our study system, it is a theoretical upper limit of CO2 emissions due to denitrification.

into surface water bodies? Could it be argued that the CO_2 emissions estimates represent an upper limit?	
68: 'triggered by anthropogenic nitrate input'. Not all N in groundwater originates from fertiliser application. Is the fraction of the denitrified N that might have come from natural sources considered negligible?	Yes, other sources of N such as natural sources of N or wastewater were considered insignificant.
92: 'map of denitrification processes' seems a misnomer. The map is showing the distribution of six clusters with reduced groundwater redox chemistry.	The main objective of the clustering analysis was to identify the dominant denitrification processes at the redox interface. In addition, in this part, we did not mention specific ML methods that we employ i.e., MNF and K-means clustering. Therefore, in this section, we will keep "map of denitrification processes", but after the methods section, we will refer it to cluster map.
93: Please make sure you clearly define in Section 3.4 what exactly you mean by 'agriculture GHG inventory'.	We will revise it to "quantification of the CO2 contributions from denitrification in groundwater to the national CO2 gas emissions from agriculture in Demark."
106: Given that at least five measurements were required over the entire period (1890-2022), can you please provide the reader with a summary statement from which period most of the used data originate (e.g. 80% of the data were collected between 2001 and 2022)? Can we assume that the analysis is not affected by concentration trends during this period?	The final data that were used to the cluster analysis were primarily from 1990-2020. The concentrations change over time, which might explain the variability (or wide ranges) of some of the constituents that we included in the analysis. However, because we were interested in the stoichiometric ratios of products of denitrification reactions, the effects of the temporal trends of groundwater chemistry assuming the dominant reactions are not changing will be minor. If dominant reactions are changing it will result in less clear clustering.
Sections 2.2 and 2.3: I would like to disclose that my understanding of ML techniques is very limited, and therefore cannot evaluate the choice of methods. Another reviewer may be able to fill this gap.	We wanted to mention that the ML methods employed in here is widely used in similar applications. In addition, both Matlab and python codes for these analyses are readily available.

107: Numbers are reported for 'screens' rather than bore/well sites. Does this account for multiple screens possibly being located at different depths at one site?	Yes, some wells have multiple screens. Therefore, we referred to them as screens instead of wells or boreholes. In the revised manuscript, we will specify why we used 'screens' instead of borehole or wells.
112: 'The cleaned dataset was analyzed to categorize redox conditions and to identify dominant processes by combining two machine learning techniques'. 1) Does 'dominant processes' refer to nitrate reduction processes (e.g. driven by pyrite vs organic carbon)?; 2) Before embarking on ML techniques, have you tried to characterise the redox conditions using the 'classical' framework by McMahon & Chapelle (2008)?	1) We first identified redox conditions and processes that are responsible for the cluster's chemical signature, not only denitrification process. For instance, cluster 6 was characterized by high methane and we identified methanogenesis may be responsible for this cluster's chemistry. 2) No, we did not use pre-defined redox conditions. Our approach was to employ data-driven techniques, i.e., MNF and K-means clustering to identify different redox conditions.
134: The oxic clusters 2 and 5 are shown in Fig. s2, not Fig. s1 as stated.	We will correct it in revision.
158: 'the redox interface' is defined as 'the bottom of the nitrate-reducing zone'. Maybe specify 'the first redox interface', as Koch et al. (2024) makes it clear that more complex vertical stratification occurs widespread in DK.	We will change it to the first redox interface and add a couple of sentences of the complexity of the redox interface in Denmark.
169/170: Could you please provide the absolute number or percentage of screens excluded?	That excludes 16% of screens. Cluster 2(619), cluster 5(221) and 814 screens from the reduced clusters but with silhouette score less than 0. We will add this information in the revised manuscript.
172: 'depths of groundwater screens shallower than the depths of redox interface minus 5 (D5), 10 (D10), and 15 (D15) meters' is unclear; please reformulate this explanation. The caption to Fig. s1 suggests that e.g. D5 stands for wells with 'screen tops deeper than 5 (...) meters below the redox interface'. However, the corresponding well numbers given for D5 (235), D10 (566), and	Yes, D5 means that the top of the screen is not deeper than 5 m below the redox interface. We will revise this including Fig.s1 in revision.

D15 (1019) seem to contradict this information. Does D5 stand for all wells where the screen is a maximum of 5m below the redox interface?	
174: First time 'wells' is used rather than 'screens'. Maybe consider using one term throughout the manuscript or clarify why different terms are used if there is a reason for it.	We will change it to screens.
187: The 1990-2010 period was used for nitrate reduction estimates. Were the measurements from the 6,273 screens (line 108) also predominantly from this period?	It is predominantly from 1990 to 2020. Most data are from 1990-2010, which is synchronized with the N reduction estimation.
208 ff: Could you please provide the number of wells in each of the eight identified clusters. Would it be useful to apply the USGS redox classification scheme to the wells in these clusters? Also, could the clusters interpreted as reflecting heterotrophic denitrification be grouped (and presented) according to the redox sequence (weakly to strongly reduced: 2,5<4<8<1<6)?	The cluster numbers will be added in revision. For instance, "two oxic clusters (cluster 2 (n= 619) and cluster 5 (n=221)) and six reduced clusters i.e., cluster 1 (246), cluster 3 (1235), cluster 4 (1940), cluster 7 (252), and cluster 8 (1012)." In this section, we discuss the redox condition of each cluster, it may not be necessary to order them in the sequence of the redox ladder. Instead, from line 260-268, where we summarized our interpretations, we introduced the clusters in the sequence of redox condition. In revision, we will explain it more clearly. We will employ a conceptual model of the sequence of reduction processes in Appelo and Postma (2005). We did not used pre-defined, deterministic classification such as USGS redox classification, thus it may not be directly comparable.
Please also consider if the key cluster information provided in Sections 3.1 and 3.2 could usefully be presented in a Table? This would facilitate direct comparison between clusters, both concerning their chemistry and spatial distribution.	We will add a summary table showing the number of screens, redox stage, and primary denitrification processes of each cluster.

Given the variability in the data within a cluster (e.g. Fig. 1c), could some variability be interpreted as indicating that nitrate may have been reduced along its flowpath to the well screen by a combination of heterotrophic and autotrophic denitrification?	Yes, that is possible. Although we identified one dominant denitrification process for each cluster, it is absolutely possible that different denitrification processes occur along the pathways. In addition, groundwater mixing and variation in time can contribute to the variability. Our interpretations of dominant denitrification process, however, was based on not only groundwater chemistry but also hydrogeological features; thus, it enabled us to identify the most probable process for denitrification.
270 ff: It would seem useful to start here with info on the spatial extent (km^2 or % of DK area) of the clusters, as Cluster 3 appears to be dominant, followed by Cluster 7, and all others well behind. Accordingly, pyrite would appear to provide much more widespread denitrification potential in DK than organic carbon.	We will add each cluster area in the beginning of this section. Yes, according to our prediction, pyrite oxidation plays an important role in reducing nitrate in Denmark.
273: Final 'maps of denitrification processes' (Fig. 2a). I find the use of the term 'process' somewhat misleading. As I understand it, Fig. 2a represents a spatial prediction of groundwater chemistry clusters. As outlined in Section 3.1, these clusters are thought to reflect the prevalence of one or more of the reactions listed in Table 1. Accordingly, I would suggest replacing 'denitrification processes' with 'denitrification clusters' or even wider 'redox clusters' (as denitrification reactions are only a subset of the reactions defining the clusters).	We will change it to redox clusters.
Fig. 2a: Maybe move the label 'Main stationary line' out of the black square that indicates the enlarged area, to make it clear that it refers to the somewhat inconspicuous dotted line, not the more prominent square. I also wonder, how to better present the less prominent clusters? Maybe colours could be swapped	The label will be moved out of the box. We tried different color combinations, but this was the best one to represent all the clusters. The area of cluster 1 was too small (only 0.5% of the total area); therefore, it is difficult to present. Cluster 6 and 8 were the next

between Clusters 4 and 6, so that Cluster 4 areas in the still fairly small enlargement can be more easily recognised? Making Cluster 4 more prominent would also help with the discussion of Fig. 3 (highest DIC production in northern Jutland).	smallest clusters. These bright colors display them well, we believe.
280/81: Maybe replace 'outside' with 'west and south' and 'behind' with 'east and north'?	It will be changed as suggested.
315ff: Please either add 'Jutland' and 'Zealand' labels on the map or provide more location info in the text (e.g. in the west of DK).	The map will be updated
324 ff: I would suggest emphasizing more that the spatial patterns of nitrate reduction and DIC production differ substantially, as the electron donors fuelling denitrification differ spatially.	We will revise the manuscript as suggested.
Section 3.4: Notwithstanding the GHG contributions by LULUCF, the 'agricultural contributions' in the narrow sense comprise CH_4, N_2O, and CO_2 from liming, urea, and other fertilisers. It would seem to me that the 90-104 kt estimated below almost pale into insignificance relative to the total GHG emissions attributed to 'agriculture' (amounting to 11,268 kt CO_2-eq. yr^{-1}, see Fig. 4).	We addressed this comment above. Again, for the total GHG, it is insignificant. However, CO2 emissions from denitrification should be compared among other CO2 emissions sources.
338: I'm unsure if 'excluding' is the right word here? Would 'after' be more suited?	It is "excluding" – meaning without contributions from the total national GHG inventories.
375: If I understand the numbers correctly, the upper limit of 104 kt (Fig. 4) would result in an increase of CO_2 equivalents of 0.9%; the CO_2 contribution to GHG emissions rising from 2.3 to 3.1% (358 out of 11,372 kt). While acknowledging that substantially smaller contributions are accounted for in the IPCC guidelines, these are more easily quantifiable	We have addressed this comment above: CO2 emissions from denitrification should be compared to other CO2 sources; extensive research on denitrification across the world may be able to provide reasonable estimates of CO2 emissions from denitrification at local and regional levels.

(e.g. from fertiliser sales statistics). I am unconvinced that estimating CO_2 resulting from denitrification could be added to the IPPC procedure in a credible manner. DK may be in the enviable position of being a virtual laboratory, but even under the favourable Danish conditions the estimates rely on a number of assumptions which introduce uncertainty. Estimates for most other countries around the world would inevitably be markedly less certain than the results presented here.	
405: I find the 38% number for 'agricultural emissions' misleading, as the 254 kt calculation basis refers in the IPPC system only to the minor contributions made by liming, urea and other fertilisers (254 kt), rather than the total of 11,268 kt CO_2-eq. attributed to agriculture (incl. 5132 kt arising from N_2O and the 5881 kt from CH_4, Fig. 4).	It will be revised as "total CO2 emissions". We estimated that up to 104 kt of CO2 is released by denitrification which is equal to about 40% of current estimates of CO2 emissions from agriculture. It is actually by 30% (104/(104+254)). We will correct this number in revision.