Supplementary materials for Kim et al. (Nitrate reduction in groundwater as an overlooked source of agricultural CO₂ emissions)

Hyojin Kim[1]*, Julian Koch[2], Birgitte Hansen[1] and Rasmus Jakobsen[1]

[1]Department of Geochemistry, Geological Survey of Denmark and Greenland, Øster Voldgade 10. 1350 Copenhagen, Denmark.
[2]Department of Hydrology, Geological Survey of Denmark and Greenland, Øster Voldgade 10. 1350 Copenhagen, Denmark

* Corresponding author: Hyojin Kim (hk@geus.dk)

Contents:

Supplementary figures

Figure s1. Maps of the mode clusters from the 100 realizations of the denitrification processes based on the criteria of screen tops deeper than 5 (top left), 10 (top right), 15 (bottom left) meters below the redox interface. The black dots in the maps represent groundwater cluster data used for each criterion. The numbers of data points (n) are shown in the parenthesis in each map. The bottom right panel shows histograms of the DIC production estimates for these criteria. The depth criteria of 5, 10, and 15 meters are labeled as D5, D10, D15, respectively, in the histogram. The mean values are shown above the histogram, with standard deviations in parenthesis.

Figure s2. Locations of two oxic clusters i.e., cluster 2 and cluster 5. The sizes of circles represent the depths to the screen tops.

Supplementary tables

Table s1. Input parameters for NMF and K-means clustering analysis

Table s2. PHREEQC results of denitrification by organic C oxidation cases

Table s3. PHREEQC results of complete pyrite oxidation coupled with carbonate dissolution.

Supplementary text

Text s1. Estimation of molar ratio of CO₂ emission per nitrate reduction using PHREEQC
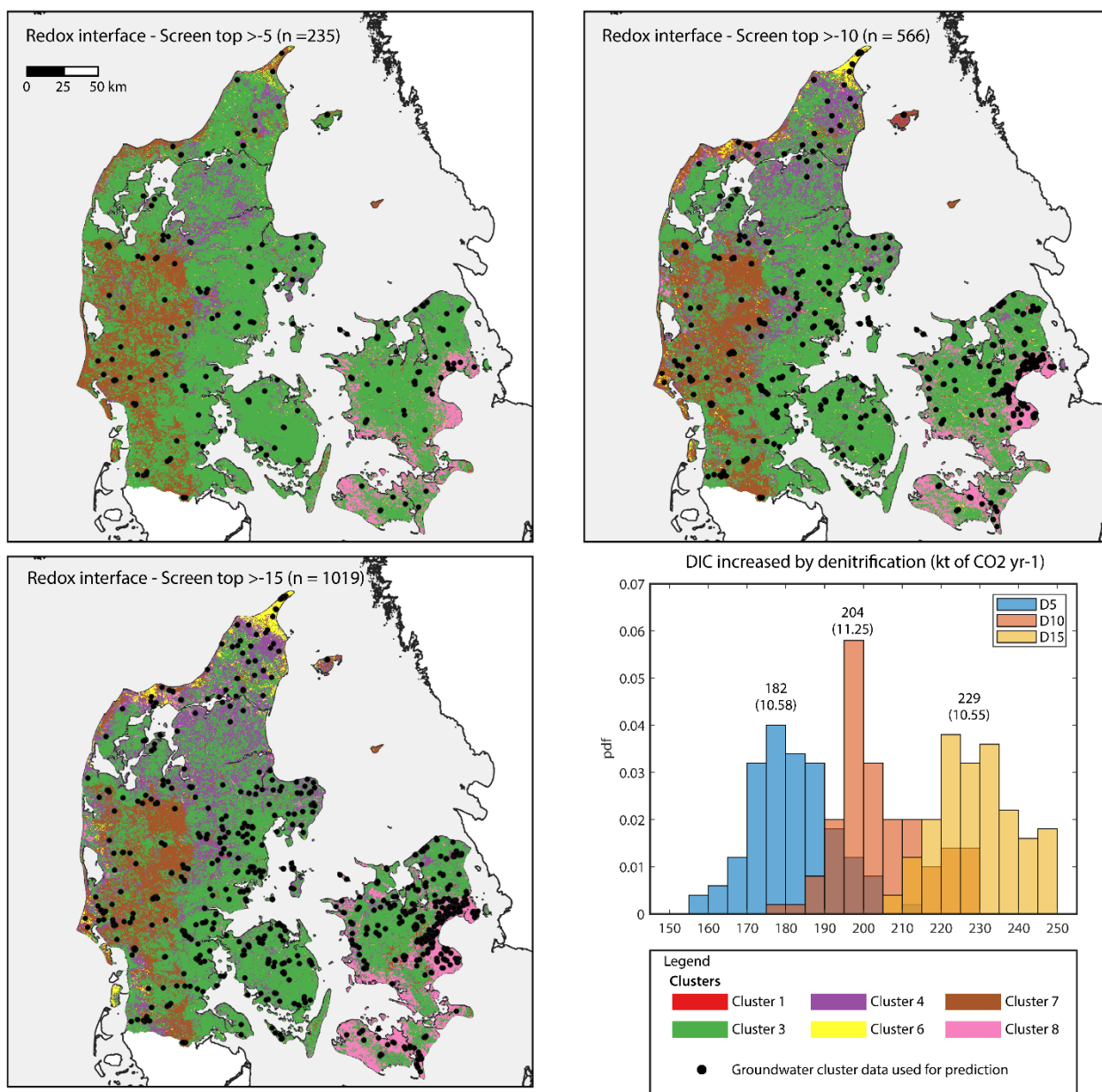
Figure s1. Maps of the mode clusters from the 100 realizations of the denitrification processes based on the criteria of screen tops deeper than 5 (top left), 10 (top right), 15 (bottom left) meters below the redox interface. The black dots in the maps represent groundwater cluster data used for each criterion. The numbers of data points (n) are shown in the parenthesis in each map. The bottom right panel shows histograms of the DIC production estimates for these criteria. The depth criteria of 5, 10, and 15 meters are labelled as D5, D10, D15, respectively, in the histogram. The mean values are shown above the histogram, with standard deviations in parenthesis.
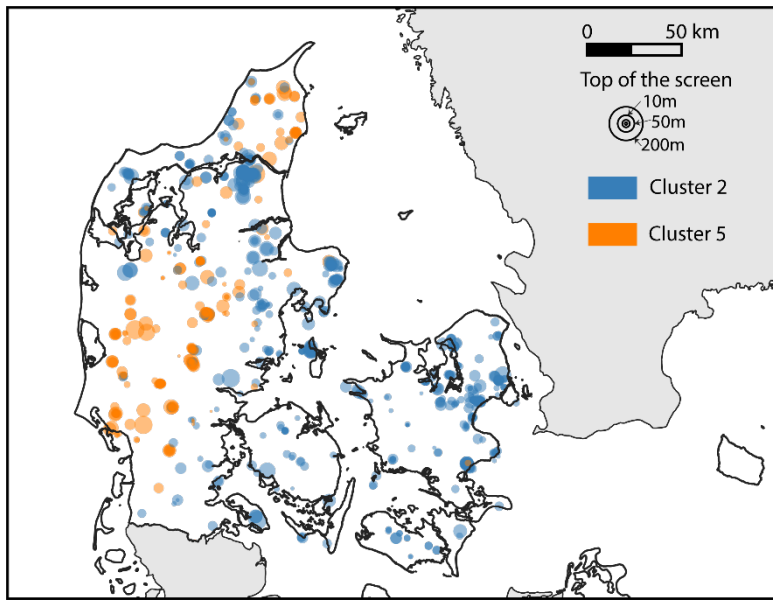
40   **Figure s2. Locations of two oxic clusters i.e., cluster 2 and cluster 5. The sizes of circles represent the depths to the screen tops.**

**Table s 1. Input parameters for NMF and K-means clustering analysis**

parameters	Unit	Log-transformation
$HCO_3^-/Ca^{2+}+ Mg^{2+}$	mM/mM	yes
$SO_4^{2-}/Ca^{2+} + Mg^{2+}$	mM/mM	yes
Fe^{2+}	mg/L	yes
Mn^{2+}	mg/L	yes
CH_4	mg/L	yes
SO_4^{2-}	mg/L	yes
HCO_3^-	mg/L	yes
NH_4^+	mg/L	yes
NO_3^-	mg/L	yes
Na^+/Cl^-	mg/L	yes
Ca^{2+}	mg/L	yes
Mg^{2+}	mg/L	yes

45

Text s1. Estimation of molar ratio of CO$_2$ emission per nitrate reduction using PHREEQC
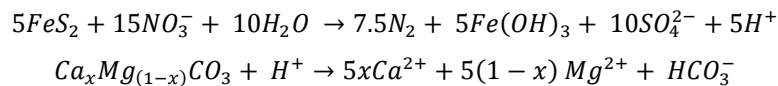
Introduction

Denitrification leads to an increase of dissolved inorganic carbon (DIC) in groundwater. When denitrification is driven by organic C oxidation, 1.25 moles of DIC are produced per 1 mole of N reduced:

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + H_2CO_3 + 2H_2O$$
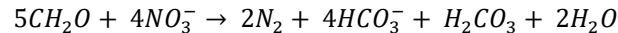
In contrast, complete denitrification by pyrite oxidation coupled with carbonate dissolution will produce 0.33 moles of DIC per 1 mole of N reduced:

$$5FeS_2 + 15NO_3^- + 10H_2O \rightarrow 7.5N_2 + 5Fe(OH)_3 + 10SO_4^{2-} + 5H^+$$
$$Ca_xMg_{(1-x)}CO_3 + H^+ \rightarrow 5xCa^{2+} + 5(1-x)Mg^{2+} + HCO_3^-$$

The partial pressure (pCO$_2$) of groundwater is naturally 1-2 orders of magnitude higher than in the atmospheric, making denitrification in groundwater as a potential contributor of higher CO$_2$ emissions. As groundwater discharges at the surface, calcite precipitation may occur, releasing half of the increased DIC into the atmosphere with the remaining half precipitating as calcite:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3(s) + CO_2(g) + H_2O$$
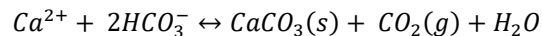
Consequently, denitrification by organic carbon will result in a ratio of 0.63 moles of CO$_2$ emissions per 1 mole of N reduced while pyrite oxidation yields a ratio of 0.17 mole of CO$_2$ emissions per 1 mole of N reduced. However, factors such as pH and buffering effects of elevated DIC concentrations may also play a role in determining the fate of the increased DIC. We evaluated these theoretical estimations using PHREEQC with data from the oxic cluster groundwater.

Methods and materials

We took cluster 2 (oxic cluster) to represent initial groundwater conditions. For simplicity, the dissolved oxygen levels were set to zero. Three groundwater samples at three different levels of nitrate (i.e., low, medium and high) from cluster 2 were chosen. Nitrate reduction was simulated in two scenarios: denitrification via 1) organic C oxidation; and 2) complete pyrite oxidation coupled with carbonate dissolution. After denitrification, the groundwater samples were equilibrated with atmospheric CO$_2$ (400 µatm) to simulate CO$_2$ emissions from groundwater as groundwater discharges to the surface ($\uparrow CO_{2,d}$). For comparison, the initial groundwater samples were equilibrated with atmospheric CO$_2$ without any geochemical reactions

($\uparrow CO_{2,i}$). The denitrification's contribution to CO_2 emissions were then calculated as the differences in CO_2 emissions between the denitrification and initial cases, normalized by the initial nitrate concentration ($NO_{3,i}^-$):

$$\frac{+\Delta CO_2}{-\Delta N} = (\uparrow CO_{2,d} - \uparrow CO_{2,i}) \Big/ NO_{3,i}^-$$

80 **Results and discussion**

s1.1 CO_2 emissions from denitrification by organic C

This scenario applied to cluster 1, 4, 6 and 8, where denitrification is primarily mediated by organic C oxidation. Results indicated that CO_2 emissions increased with increasing nitrate concentrations while the amount of calcite precipitated did not show such as dependency (Table s2). This difference may be likely due to the initial concentrations of Ca^{2+} and Mg^{2+} in the

85 groundwater.

The average molar ratio of CO_2 emitted per N reduced was 0.65, which was slightly higher than the theoretical estimate. This deviation is attributed to minor CO_2 degassing that occurs without precipitating calcite likely due to the initial high pCO_2 and increased DIC without corresponding increase of Ca^{2+} and Mg^{2+}. Overall, about half of the increased DIC was emitted into the atmosphere, 30 % precipitated as calcite, and the remaining DIC stayed in the solution, primarily as bicarbonate.

90

Table s2. PHREEQC results of denitrification by organic C oxidation cases

Organic C mediated cases (Cluster 2 evolves to cluster 1, 4, 6 and 8)								
Nitrate conc. (ppm)	N reduction (mmole)			Initial groundwater (mmole)		Difference between N reduction and initial groundwater		$\Delta CO_2/N$ (mole /mole)
	Total increase of DIC	CO_2 emissions	$CaCO_3$ precip.	CO_2 emissions	$CaCO_3$ precip.	CO_2 emissions	$CaCO_3$ precip.	
11	0.23	2.44	1.84	2.33	1.77	0.12	0.07	0.64
40	0.81	2.39	1.66	1.97	1.40	0.42	0.26	0.67
100	2.07	2.88	2.06	1.81	1.43	1.07	0.63	0.64

s.1.2. CO_2 emissions from denitrification by complete pyrite oxidation coupled with carbonate dissolution

95 This scenario was associated with cluster 3, where denitrification is likely mediated by pyrite oxidation. The molar ratio of CO_2 emitted per mole N reduced was 0.17, closely aligning with the theoretical estimate (Table s3). About half of the increased

6

DIC was emitted as CO_2, while the 54-66 % of the increased DIC precipitated as calcite, indicating 5-16 % of reduction of the DIC. This reduction can be explained by acid production during pyrite oxidation, which lowers the groundwater pH as well as reduces the total DIC concentration after CO_2 degassing.

100

Table s3. PHREEQC results of complete pyrite oxidation coupled with carbonate dissolution.

Complete pyrite oxidation coupled with carbonate dissolution (Cluster 2 evolves to cluster 3)								
Nitrate conc. (ppm)	N reduction (mmole)			Initial groundwater (mmole)		Difference between N reduction and initial groundwater		ΔCO_2/N (mole /mole)
	Total increase of DIC	CO_2 emissions	$CaCO_3$ precip.	CO_2 emissions	$CaCO_3$ precip.	CO_2 emissions	$CaCO_3$ precip.	
11	0.06	2.36	1.81	2.33	1.77	0.030	0.04	0.18
40	0.21	2.08	1.52	1.97	1.40	0.111	0.12	0.17
100	0.55	2.08	1.70	1.81	1.40	0.277	0.30	0.16

Conclusion

Our findings suggest that denitrification increases DIC in groundwater, contributing higher CO_2 emissions from groundwater.
105 In both scenarios i.e., organic C oxidation and pyrite oxidation roughly half of the increased DIC was emitted as CO_2, with the remainder partitioned between calcite precipitation and bicarbonate in solution. The concentrations of Ca^{2+} and Mg^{2+} and pH of groundwater may play a role in distributing the remaining DIC between solid (calcite precipitation) and solute (DIC) phases. Overall, our results confirms that the simple theoretical estimates of the molar ratios of CO_2 emitted per N reduced were reasonable.