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# ***Interactive comment on “Kinetics of N<sub>2</sub>O production and reduction in a nitrate-contaminated aquifer inferred from laboratory incubation experiments” by D. Weymann et al.***

**Anonymous Referee #1**

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## **Comments to authors**

The manuscript of Weymann et al. (2010) in BGD 7, 503–543, dealing with the ‘kinetics of N<sub>2</sub>O production and reduction’ tackles a scientifically and environmentally interesting topic. Without doubt the production and reduction of greenhouse gases needs intensive considerations and research. As a first conclusion, the topic is relevant and fits to the scope of the journal. However, the manuscript is, to my opinion, not (yet) ready for publication. There are a number of weak points with regard to the scientific content as well as the style/language. To get the manuscript ready for BG it will need

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a rigorous revision. I will try to highlight the weak points (I detected) in detail in the following.

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When reading the abstract I already asked myself (the microbiologist) how can a kinetic from nitrate to di-nitrogen oxide be modelled without considering nitrite. There is so many nitrate reducing bacterial strains that first (or exclusively) reduce nitrate to nitrite. The prerequisite for a further reduction of nitrite often is nitrate dropping below a certain threshold concentrations or other strains to take over. The authors shortly mention the 'complexly' control of  $N_2O$  production in the environment (P 505, L: 19-25). Moreover, the authors show (Fig. 3) that  $N_2O$  accumulates in their batch experiments as long there is plenty of nitrate. From a certain threshold on,  $N_2O$  starts to disappear. Identical patterns as often observed for nitrate reduction to nitrite and subsequent conversion to  $N_2O/N_2$ . From a microbiological point of view, evaluation of first or zero order kinetics for nitrate reduction to  $N_2O$  only makes sense if it can be shown that there is no reaction limiting step between nitrate and  $N_2O$  (e.g. accumulation of nitrite). This information is not found in this manuscript.

A point which confused me, is the differentiation between a 'shallow' heterotrophic and a 'deeper' autotrophic denitrification zone. The manuscript does, to my opinion, not provide sufficient information to substantiate this differentiation. Indeed, the authors refer to other papers. But as this is a crucial point with respect to the grouping of batch incubations, I would ask for additional information supporting this differentiation given in the paper.

I appreciate that the authors could prove the different potentials for denitrification in the shallow (what they called heterotrophic) and less shallow ('autotrophic') zone of the aquifer. But this is not a new finding, as it was already shown earlier (see citations in the manuscript). The data presented and the interpretation are sometimes confusing and misleading. Example given, only in the autotrophic denitrification zone, there is a

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significant correlation between denitrification rates and organic matter. I am willing to follow the argumentation of the authors that the combination of low (available) organic matter, high nitrate concentrations and a low pH favours  $\text{N}_2\text{O}$  accumulation (P 520, L 5-20). However, the data presented from the multi-level well do (1) not show a coincidence of high nitrate and high  $\text{N}_2\text{O}$  (it is more the other way round, Table 3 also says there is no correlation in the heterotrophic zone between  $\text{D}_i$  and  $\text{N}_t$ ), (2) not show a link to organic matter (DOC data are missing and OM data in Table 1 indicate no clear patterns of OM with respect to  $\text{N}_2\text{O}$ ), and (3) not provide any spatially resolved pH data. I also do not clearly see how the calculated denitrification rates fit to the data of groundwater samples from the multi-level wells. At Well B1, most sulphate (originating from autotrophic denitrification coupled to the oxidation of reduced sulphur species) is found in the shallow groundwater. Also in Well I1, where sulphate is more prominent in less shallow areas (the so called 'autotrophic' zone) there is a similar pattern for sulphate and  $\text{N}_2\text{O}$  obvious. Is this just by chance?

I come to the conclusion that the two distinct  $\text{N}_2\text{O}$  peaks detected in both vertical profiles at B1 and I1 can not be explained by denitrification rates, organic matter, pH, nitrate concentrations at the moment. Maybe microbial community data could help. Or maybe there are more supportive data not shown so far.

Besides these points, I suffered at several locations in the manuscript from the 'non-precise' information given. I will highlight some examples in the following. In the 'Study site' description, for example, the authors talk about 'substantial microbially mediated processes' such as denitrification and desulfurification. Is the later process referring to 'oxidation of reduced sulphur species'? Then this is probably not the right term. Moreover, when talking about autotrophic denitrification with reduced sulphur compounds, I would like to know which compounds are meant. It is like a red line through the paper. The authors continuously talk about reduced sulphur, without mentioning a speciation; e.g.  $\text{FeS}$ ,  $\text{FeS}_2$ ,  $\text{HS}^-$ ,  $\text{S}^0$ , etc. Table 1 provides useful information on the aquifer material sampled. However, the table clearly lacks some detailed information. Abbreviations

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such as 'Nt' and 'Sulfur' (total sulphur? Or what species?) are not explained in more detail, and units [ $\text{mgL}^{-1}$  or  $\mu\text{gL}^{-1}$ ] are missing. I miss detailed information regarding the pH, as this is an important point of argumentation later in the manuscript. I also miss the information on oxygen concentrations in the aquifer. The authors mention that there is not too much organic carbon, thus limiting heterotrophic denitrification (which may already take place at concentrations of  $\leq 2 \text{ mgL}^{-1}$  of dissolved oxygen). It is not clear if the saturated zone of the investigated aquifer is exhibiting reduced conditions already at the groundwater table. DOC concentrations, although available (at least) for the lab incubations are not shown.

Last but not least, depths 2-3m below the (relatively shallow) groundwater table, I would preferably not call 'deeper aquifer'. The term deeper aquifer is somehow restricted to aquifers or zones of aquifers  $< 50\text{m}$  below land surface (P 508, L 5). The authors should search for a more appropriate term.

Finally, the paper leaves several interesting points unanswered. What do the high  $\text{N}_2\text{O}$  values at or close to the groundwater table mean? Is the  $\text{N}_2\text{O}$  produced there or transported there, or only accumulating there?

As a concluding remark, I wonder if the presented manuscript contains sufficient new findings and has the critical mass for publication in BG. There is a pile of papers, dealing with similar and closely related research questions tackled at the same field site from the same authors. To my opinion, it will take the consideration and state of the art analysis of microbial communities and functional genes related to denitrification and sulphide oxidation at the extensively investigated aquifer. This would allow to draw new 'integrative' conclusions on what's going on in this system.

Besides these general comments there is a multitude of specific comments given below.

### Further points:

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P 504, L 5: 'in situ' should be given in *italic*

P 504, L 9: I suggest to replace the term 'deeper' groundwater. It is misleading. The authors deal with groundwater from a few meters below land surface.

P 504, L 14: Please further specify which 'sulfur' was measured.

P 504, L 26: replace the term 'goodness'.

P 505, L 8: choose 'up to' or 'more than', but not 'up to more than'

P 505, L 9: the term 'surface groundwater' sounds strange to me; consider to use 'shallow groundwater', 'surface near groundwater', etc.

P 505, L 16: replace 'By and large', also the 'two crucial subjects' sounds strange - please rephrase.

P 506, L 9-29: This section should move from the introduction to the discussion section. Moreover it is hard to read and sometimes confusing.

P 507, L 3-4: The study investigated the kinetics of N<sub>2</sub>O production and reduction in 'material' from an unconsolidated sandy aquifer, not in the aquifer.

P 507, L 25: delete 'its key function for'.

P 508, L 1: ... the other 'hand'?

P 508, L 12: what means 'schematically'? maybe 'exemplarily'?

P 508, L 17: Where does the high sulphate values in the shallow gw from B1 originate from, if it is assumed that the oxidation of reduced sulphur species is not anymore a relevant process. For high sulphate data from site I1 the authors argue that these are a result of autotrophic denitrification coupled to oxidation of reduced sulphur species. Sulfate values in shallow groundwater from B1 are in the same range than values from groundwater of zones below at I1.

P 508, L 18: unconventional formulation: '5C'

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P 509, L 16: I miss NO<sub>2</sub>- as an important denitrification related parameter.

P 510, L 15: I did not get why the sampling of an undefined area of the same depth should reveal samples differing in texture and chemical composition. Was this the intention or the final result (= unexpected spatial heterogeneity) – please explain.

P 510, L 18: which water was used for filling the buckets containing the sediment? Reduced groundwater from the same depth?

P 510, L19-20: From an microbiological point of view, storage of aquifer material for a period of 4 weeks is not adequate, if later the intention is to transfer results to *in situ* conditions. Too many studies have shown fast changes within microbial communities and activities in the order of hours to days during storage. I ask the authors to mention this point in the discussion section and interpret the results (and the transferability) with caution. Related to the incubation time of 350 d, the 30 d of storage may be acceptable.

P 511, L 3: ... amended with 400 mL of a 'anoxic' (oxygen free) test solution?

P 512, L 17: you mean 'gas chromatograph'

P 513, L 18-20: Honestly, I am not very familiar with the modelling approach applied. However, to use the results from an analytical solution as fitting functions sounds to me as a 'double fitting' approach.

P 514, L 17-18: the authors talk about nitrate concentrations and give 'nitrogen' concentrations. Why not just provide the nitrate values. Same is true for P 514, L 26, where N<sub>2</sub>O concentrations are mentioned.

P 515, L 1-2: is there a better term for 'sharp-cut' peak, e.g. pronounced peak, or simply a sharp peak.

P 515, L 22: 'inbetween' instead of 'between'?

P 517, L 15-19. It si interesting that in the autotrophic zone the denitrification rate was positively correlated to organic matter, indicating heterotrophic denitrification?. The

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positive correlation with sediment sulphur is supportive, but it would be good to know what 'sulfur' we are talking about. Is it only reduced sulphur species? There is also a lot of sulphate in the system.

P 518, L 6: I am sorry, but the data presented in Fig 4 refer to the chart 'I1-S2 2.0-2.5' in Fig 2 not 'I1-S1 2.0-2.5' as mentioned in the text as well as in the Fig. 4 legend.

P 518, L 12-24: Can the reason for the 'bad' fit be caused by the different kinetic steps being presents when going from nitrate to dinitrogen oxide?

P 519, L 9-10: To my opinion, this separation is not sufficiently supported with data; sulphate data at least partly do not support this argumentation and DOC values are not shown. Organic carbon in the sediment material seems on average higher in the autotrophic zone.

P 521, L 16-18: ... indicate that the aquifer is recharged by water that infiltrated at forest or pasture areas.

P 521, L 16-18: Can the dilution of sulphate be estimated based on potassium concentrations by a simple dilution model? This would support the argumentation.

P 521, L 25-27: what is meant: 'O<sub>2</sub> had been kept constant in the anaerobic incubations'?

P 522, L 13-17: It is from a microbiological point of view quite strange that no microbial activity (consumption of DOC and nitrate) was measureable at these high DOC concentrations over a period of 350 days. There is no DOC which is 'not' bioavailable. To my opinion, it is only a matter of time.

P 523, L 2: What reduced sulphur species are we talking about? The authors mentioned that the test site is under investigation since more than two decades. There should be some information available what sulphur species are present in the aquifer. I ask the authors to be more precise.

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P 524, L 8: replace the word 'goodness'

P 524, L 12-17: The authors state that the model did not take into account the organic matter but nitrate as a limiting factor. Why did the authors not modify to test the alternative scenario; organic matter is limiting but not nitrate?

P 525, L 16-17: Rephrase the sentence.

P 525, L 24-25: The field data shown do not tell anything about denitrification rates *in situ*.

P 526, L 19: replace 'is exhibited by' by 'is evident from'

Fig. 1: unconventional labelling of the axes (mg SO<sub>4</sub> L<sup>-1</sup> = SO<sub>4</sub> [mgL<sup>-1</sup>]); follow the style of the journal. The paper would clearly benefit from incorporating DOC and pH values in Fig 1.

Fig. 2: It would be great to have DOC and sulphate data included. Only these can provide evidence if the denitrification was 'heterotrophic' or 'autotrophic'.

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Interactive comment on Biogeosciences Discuss., 7, 503, 2010.

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