

Interactive comment on “Predicting long-term denitrification capacity of sandy aquifers from incubation experiments and sediment properties” by W. Eschenbach and R. Well

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Dear Anonymous Referee,

thank you for your decision and comments on our manuscript bg-2012-136. We greatly appreciate the detailed and constructive comments of the two reviewers which helped us to improve the manuscript.

Overall, we addressed all comments of the reviewers and hope that we adequately solved the requests.

With kind regards

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Wolfram Eschenbach

Responses to reviewer 1

Referee(s)' Comments to Author:

Predicting long-term denitrification capacity of sandy aquifers from incubation experiments and sediment properties by W. Eschenbach and R. Well

This paper addresses relevant scientific questions within the scope of Biogeoscience. It includes a rather large data set and analysis that should be helpful to the scientific community on aquifer denitrification. However, I have several comments and concerns:

1. 1.1 In the first three pages I noted two apparent typographical errors. On line 11 of the abstract it indicates that the “long-term” denitrification capacities ranged from 0.18... However, in Table S2 it appears that this lower range value should be 0.19. Furthermore on page 8810, line 10 “amphiboles” is misspelled as “amphibols.” I encourage the authors to review the manuscript again for errors.

We have reviewed the manuscript thoroughly and hope to have eliminated all remaining errors. At the end of the introduction we now provide a small paragraph, which introduces the limitations of this research. In this paragraph we also refer to the sections 4.4 and 4.5 where the mentioned limitations are discussed in more detail.

2. 2.1 The stated goals of the research included (page 8811, line 28) “to quantify exhaustibility of long-term denitrification capacity in aquifers.” What is “long-term” in the authors' view? As mentioned above, long-term seems to be until the denitrification capacities of the sediment are exhausted. This idea is repeated in the paragraph beginning on page 8811, line 16. However, “long-term” from the methodology seems to mean 1 year incubation experiments [page 8812, line 4; page 8814, line 14, Dcap is the “cumulative amount of denitrification... at the end of one year of incubation (page 8817, line 26 and following)]. Assuming that using data from incubating sediment samples for one year will result in reliable estimates for minimum lifetimes of denitrification

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(page 8818, line 21 and following) of up to 66.5 years (Table S2) is a big assumption. In my view, “long-term” from the perspective of aquifer denitrification needs to be > 10 years. Again, I think the data provided are helpful, but the assumptions made and the related limitations of this research need to be more clearly stated.

We agree, long-term denitrification capacity is the capacity until the denitrification capacity of the sediment is exhausted. Therefore we changed the phrase denitrification capacity (Dcap) to cumulative denitrification after one year of incubation (Dcum(365)) throughout the whole manuscript.

We rewrote section 4.4 and included following sections into the manuscript in order to make the underlying assumptions and limitations of this study more clearly. (see also our response to question 2.2) We added the following to section 4.4: “Two key assumptions were made for the assessment of the lifetime of denitrification in both aquifers from our incubation experiments. There are relations between (i) the measured Dcum(365) and the stock of reduced compounds (SRC) and (ii) between the SRC and the denitrification capacity. (i) The measured Dcum(365) was a good predictor for the SRC for the whole data set and GKA samples. The SRC was also predictable for sulphidic and NO₃–free samples. Contrary, Dcum(365) was a poor indicator of the SRC for aquifer material from already oxidized parts of both aquifers with relatively low amounts of SRC (Table 6). Since the conducted incubations were not able to exhaust the denitrification capacity of the aquifer samples, the real fractions of the SRC available for denitrification (aFSRC) in the incubated samples and even more so the in situ aFSRC remained unknown.”

(see also our response to comment 1 of reviewer 2)

2.2 How do we know that all of the organic C and sulphur present in the sediments is able to be oxidized?

We don't know and we didn't assumed this. We assumed that only 5 % of the stock of reduced compounds (SRC) in the samples was able to be oxidized during microbial

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denitrification. This value was estimated from the intensive incubations. We added the following sentences to the beginning of section 4.4 of the manuscript: “Since the conducted incubations were not able to exhaust the denitrification capacity of the aquifer samples the real fractions of the SRC available for denitrification (aFSRC) in the incubated samples remained unknown. . .” In sediments I am familiar with, we have organic C in the unsaturated zone (below the soil zone), but little to no pyrite. Knowing that both organic C and pyrite exists below the water table suggests that the organic C above the water table is resistant to oxidation. Could it be that organic C below the water table is also resistant to oxidation?

Surely, there are parts of organic carbon below the water table that are resistant to oxidation. To make this point clearer we added the following to section 4.4:

“(ii) The low total-S values in the upper parts of both aquifers (Table S1) suggest that most of the sulphides present in both aquifers (see section 4.3.1) are not resistant to oxidation. Moreover, sulphides are supposed to be the dominant reduced compound supporting denitrification in the FFA (Kölle et al. 1983). Both aquifers (FFA and GKA) still contain reduced compounds in form of organic matter in their oxidized upper parts. So obviously, certain fractions of the whole SRC are resistant to oxidation. But it is unknown how the ratio of oxidizable to none-oxidizable Corg may change with depth in both aquifers. During this study we found that the Cl/Corg ratio was higher for deeper (sulphidic) aquifer samples compared with non-sulphidic samples from the upper region in both aquifers. This suggests that the proportion of organic C which is recalcitrant is higher in the already oxidized zone (see section 4.3.1). A reason for this might be that the proportion of mineral associated organic carbon to total organic carbon is higher in this zone. (Mineral association of organic matter is assumed to increase the recalcitrance fraction of total organic matter (Eusterhues et al., 2005). Eusterhues et al. (2005) reported for a dystric cambisol and a haplic podzol from northern Bavaria that 80 – 95 % of the total organic carbon content of the particle size fraction (< 6.3 μm) in the C horizon is mineral associated organic matter and Fe oxides were identified

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as the most relevant mineral phases for the formation of organo-mineral associations.) Fe oxides can form during autotrophic denitrification with pyrite and they are known to exist frequently in oxidized aquifers.)”

3. With the comments of #2 above, I recommend that the title be changed to “Predicting long-term denitrification capacity of sandy aquifers from shorter-term incubation experiments and sediment properties.

We followed this suggestion and changed the title accordingly.

4. 4.1 Sulphur was measured as total S (page 8815, line 20) and assumed to be pyrite (page 8818, line 11). Is this a good assumption?

We believe this is as a sufficiently good assumption for both aquifers, especially for the reduced parts. In these deeper parts the occurrence of sulphate minerals are not reported. The total S values of aquifer samples from the reduced parts of both aquifers are at least 10 times higher than the ones measured in the upper oxidized region of the FFA and GKA. See also our replies below.

4.2 Why not measure inorganic S instead of total S?

On this issue, we replied the following to one of the reviewer (during the first short review process). Hopefully this answers the question sufficiently:

We used total-S as an inexpensive estimate for sulphide content. This is reasonable because previous investigations in comparable aquifers and the Fuhrberger Feld aquifer showed that total-S values were to a large extent identical with sulphides. In Line 776 to 779 of the submitted manuscript (open discussion paper) we referred to this: “Bergmann (1999) and Konrad (2007) investigated the distribution of S species in aquifer material from sandy aquifers in North Rhine-Westphalia and Lower Saxony, Germany, respectively, and found that 80 to over 95% of the total-S value is represented by sulphide-S.” Kölle et al. (1982) reported from 23 aquifer samples from different locations in the Fuhrberger Feld Aquifer a mean lignin content of 0.26 % by weight and

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a pyrite content of lignin of 5.6 % (chemical and x-ray analysis) giving 77.7 mg FeS₂-S kg⁻¹. The median total-S values of 72 mg S kg⁻¹ of our Fuhrberg samples (Table S1, supplementary material) are comparable to the values given by Kölle et al. (1983). We assume that in the deeper parts of both aquifers aluminium hydroxide and aluminium hydroxysulfates minerals are negligible. Gypsum mineral are for different reasons unlikely in the investigated sediments. The SO₄²⁻ and Ca concentrations in the groundwater of both aquifers are far below equilibrium concentration with gypsum of approximately 2 g L⁻¹. Precipitation of gypsum minerals in the groundwater is therefore unlikely. Gypsum rock fragments are not reported for both aquifers and microcrystalline gypsum minerals if initially present should have already dissolved since deposition of the unconsolidated rock aquifers. Because of this we are relatively sure that the gypsum content is negligible.

4.3 On line 6 on this same page it mentions that the possible sulphate produced by dissolution of sulphate minerals was accounted for, but were the amounts significant?

We corrected for pore water SO₄²⁻ and possible dissolution of sulphate minerals. The amounts were significant. We added the following sentences at the relevant point at the manuscript (section 2.5): “For the aquifer samples from the NO₃⁻ free zone of both aquifers and for non-sulphidic samples these initial SO₄²⁻-S concentrations accounted for 25,4 % and 90 % of the final SO₄²⁻-S concentrations in the batch solutions. These initial SO₄²⁻-S concentrations originated supposedly mainly from pore water SO₄. The SO₄²⁻ concentrations of the groundwater at the origin of the samples reached 5 to 60 mg S l⁻¹ in both aquifers (data not shown).”

5. In section 3.6.1 (page 8824), the authors noted that D_{cap} was not predictable by the seven-day denitrification rate (except for non-sulphidic samples) (see also page 8832, line 11 and following); however, D_{cap} was predicted well with the eighty-four-day denitrification rate. If goal c (page 8812, line 1 and following) is to use push-pull tests to check “long-term” denitrification this presents a problem because push-pull tests generally cannot be used for 84 days?

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That is true and a result of this as well as a second study to follow, were we conducted push-pull test at the origin of the sampled aquifer material. During this second study we also tested push pull test with pre conditioning of the aquifer material. These tests resulted in a better agreement between measured laboratory and in situ denitrification rates. In the conclusions we already referred to this problem: "In the deeper zones that had not yet been in contact with NO₃⁻, Dcum(365) was poorly related to initial denitrification rates. Only after prolonged incubation of several weeks denitrification rates could predict Dcum(365) of these samples."

6. On page 8828 (line 8 and following) the authors write, "The ultimate goal of our research is to predict long-term denitrification capacity (Dcap) from initial denitrification rates." But this assumes that a one-year long Dcap effectively predicts "long-term" denitrification capacity (as in quantifying its exhaustability).

To emphasize our assumptions and the limitations of this research more clearly, we changed the beginning of section 4.2 to:

"An important goal of denitrification research is to predict long-term denitrification capacity of aquifers from initial denitrification rates. The conducted incubations showed that there are significant quantitative relations between Dcum(365) and the SRC of the incubated aquifer samples (Table 6) and it can be assumed that the SRC represents a maximum estimate of the long-term denitrification capacity of aquifer material. Taking this into account it was tested if initial denitrification rates can predict Dcum(365)."

7. The question discussed in section 4.5 (page 8840, line 4 and following) are very good. However, I don't find compelling the authors' responses. The only way I know to adequately answer these questions is to have in situ studies. And push-pull tests Apparently won't help achieve the authors' goal (see my comment 5 above). Apparently, the only long-term in situ tests that would work appear to be like those described by Korom et al. (2005). They could be used to test in situ some estimated minimal lifetime of denitrification values given on Table S2 (2-5+ years). They also may help determine

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what electron donors take part in the denitrification and for how long.

To emphasize the limitations in drawing conclusions from laboratory incubations to the in situ process, we rewrote the section 4.5.3 to clarify the limitations of our approach and added: "Linear regressions showed that there are quantitative relations at least between Dcum(365) and the SRC of the incubated aquifer samples from the reduced zone in both aquifers (Table 6) and it can be assumed that the SRC in a certain degree determines the long-term denitrification capacity of aquifer material. From this, one-year incubations may give minimum estimates of the denitrification capacity of aquifer sample. Furthermore one year of incubation seems long enough to overcome microbial adaptation processes encountered at the beginning of the conducted incubations (see section 4.2)." But we think the questions as well as the associated conclusions drawn from this study, are nonetheless helpful for future studies.

References: Bergmann, A.: Hydrogeochemische Untersuchungen anoxischer Redoxprozesse in tiefen Porengrundwasserleitern der Niederrheinischen Bucht - Im Umfeld des Tagebaus Garzweiler I, Bochumer geol. geotechn. Arb. 51, 59. Abb., 27. Tab.; Bochum, Germany, 167, 1999. Eusterhues, K., Rumpel, C., and Kogel-Knabner, I.: Organo-mineral associations in sandy acid forest soils: importance of specific surface area, iron oxides and micropores, Eur. J. Soil Sci., 56, 753-763, 10.1111/j.1365-2389.2005.00710.x, 2005. Kölle, W., Werner, P., Strebel, O., and Bottcher, J.: DENITRIFICATION BY PYRITE IN A REDUCING AQUIFER, Vom Wasser, 61, 125-147, 1983. Konrad, C.: Methoden zur Bestimmung des Umsatzes von Stickstoff für drei pleistozäne Grundwasserleiter Norddeutschlands, 161, 2007.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/9/C6812/2012/bgd-9-C6812-2012-supplement.pdf>

Interactive comment on Biogeosciences Discuss., 9, 8807, 2012.

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