Biogeosciences Discuss., 5, S951–S962, 2008
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Biogeosciences Discussions

Interactive comment on "Assessment of excess N_2 and groundwater N_2O emission factors of nitrate-contaminated aquifers in northern Germany" *by* D. Weymann et al.

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Received and published: 30 June 2008

The comments are repeated here and our responses are inserted after each comment. We numbered the comments according to our responses. Responses are marked with R (number).

1. P1264 L18-20 - Suggest replacing the sentence "According to denitrification intensity..." with a more straight-forward definition of EF2. L25 - The Abstract seems to lack a concluding statement that highlights the most important finding(s) of this study and gives the reader a sense of the implications of these results. The current closing sentence is a site specific result with unclear implications.

R (1): The sentence was replaced and a modified definition of EF2 was given. Further-

more, we inserted 2 concluding statements (marked with (i) and (ii)) in the following sentence. Lastly, we added a final sentence to the abstract.

2. P1265 L3 - Why "layers"? Suggest a more general term like "zones".

R(2): We argue that "layers"is a suitable expression from a geological view reflecting variable distributions of reactive substrate and heterogeneity better than a general expression like “zones”.

3. L6-16 - The introduction jumps too quickly to details of methods of study without first establishing why this sort of study and this particular study are important contributions. Much of this information could probably be omitted or moved to the methods section.

R(3): The structure of the introduction was changed. We focussed the first part on N2O and potential indirect emissions. Introductive sentences characterizing the method were moved to the second part of the introduction.

4. L21 - suggest"result from" in place of "are associated with"

R(4): Done.

5. L21-26 - This is a good concise statement of the context of this study in the existing literature.

R(5): We think no further comment or changes are necessary.

6. P1266 L6 - omit "presumably" L9 - spell out "IPCC" L12 - Suggest "Typically" in place of "Principally" L15 - "and" instead of "und" L18 - "reactions" instead of "change"

R(6): Done.

7. P1267 A map would be helpful to show the locations of the sites.

R(7): We decided to insert geographical coordinates (latitude and longitude) of the sites in Table 1.

8. L18-21 - This sentence is confusing. "respectively" appears twice.

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R(8): The sentence was divided into three shorter sentences in order to support a better comprehension.

9. L23 - Please provide depth to the water table at these sites.

R(9): The depth of the groundwater table was added to Table 1.

10. P1268 L2 - Suggest "pumping" instead of "suction". It seems unlikely that reducing the rate of pumping would make much difference. Perhaps move this comment to below the discussion of comparison of results from different pump types.

R(10): We argue that "suction" is a conventional, frequently used expression (see Blicher-Mathiesen et al., 1998). Furthermore, the suction rate can be in fact relevant (discussion in Blicher-Mathiesen et al., 1998; dissertation of M. Stute, 1989) and we tested different rates to check whether gas bubbles occur during sampling. Thus, no changes in the text were carried out.

11. L6 - Suggest using SI units instead of inches, and "in these wells" instead of "here"

R(11): Done.

12. L11 - "proves" is too strong a word. Maybe "indicates" or "implies". Comparing treatments is a good approach, but the reader needs to know the vertical distance from pump to water table at each site to evaluate the validity of extrapolating the comparison from one site to another.

R(12): "Proves" was replaced as suggested and a depth intervall (distance to the water table) is given.

13. L27 - What does "quantitatively removed" mean? Please clarify.

R(13): The meaning is "completely" removed. We replaced "quantitatively".

14. P1270 L5 - Suggest omitting "Principally" L9 - "in excess of..."

R(14): Done.

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15. L10 - Suggest "near the water table" instead of "at the groundwater surface"

R(15): Done.

16. P1271 L12 - Please clarify which value is meant by "this value". L24 - Suggest "to assess" instead of "assessed"

R(16): Done.

17. P1272 L4 - What are the units for these standard deviations?

R(17): The unit is L L-1. The information was added.

18. L8 - Please explain or provide a reference for "Gaussian error propagation"

R(18): A reference was provided.

19. L10 - Suggest "Intial NO3-concentration at a given location on the aquifer surface is defined by the NO3- concentration of the recharging water before alteration by denitrification in groundwater."

R(19): Done. We additionally add a reference. Consequently, the following sentence was deleted.

20. L13-18 - Suggest revising this sentence for clarity.

R(20): We replaced "at" with "and" for claryfying the sentence.

21. L23 - Suggest omitting "is generally correlated with excess N2 in denitrifying aquifers"

R(21): Done.

22. P1273 L7 - Suggest defining EF2 with an equation in the same fashion as EF1.

R(22): Done.

23. L16 Suggest simplifying this header

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R(23): Done. "Controlling factors O2 and pH" was omitted because of redundancy.

24. L18 - Suggest "Groundwater temperatures at these sites were relatively constant..."

R(24): Done.

25. L22-24 - Is there any obvious explanation of why pH varies among these sites?

R(25): See the sub-clause "suggesting heterogeneous conditions...". The reason for pH variation are likely different geological conditions (i.e. occurrence of the hydraulic active sediments sand or gravel) among the sites, but partly also their heterogeneous distribution within each site. However, giving detailed and satisfactory information about these points would go beyond the scope of our study what is focussed on the EFs linked with NO3 t0. Therefore, we are content with interpreting the role of pH as a controlling factor without questioning the reasons for its variation among and within the aquifers.

26. P1274 L2 and Table 2 - please explain the meaning of these mean, min and max values. Are they all "means from the minimum and maximum values" (P1271, L25)? This is confusing. For example, some readers will likely assume that the "min" values of excess N2 are calculated using Eqs 1 and 3.

R(26): Firstly, we would like to clarify that the values described in L2 are - as we reported – median values (not means) for the sites. These values are a result of the means from minimum and maximum estimates (P1271, L25) taking the uncertainty connected with excess air fractionation into account (section 2.3). Thus, every single value is a mean from minimum and maximum estimates for excess N2 and results finally in ranges (Min-Max) and medians for the sites. However, it could be a problem for the reader to distinguish between "means" as specified in section 2.3 and "median" values what are shown in the results-section in Table 2 and L2. Therefore, we replaced minimum and maximum estimates with "lower" and "upper" estimates and the mean of both is called "best estimate".

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27. L2-3 - It seems unnecessary and convoluted to say that lowest values of excess N2 coincided with low RP, and that high values of excess N2 coincide with high RP. This is more a mathematical implication of the definition of RP than a result of this study.

R(27): We completely agree and deleted two sentences.

28. L9 - Should this say "denitrification is complete in parts of the Fuhrberg aquifer"?

R(28): Indeed, this is true for the deeper aquifer. We changed the sentence as suggested.

29. L12-13 - Is this difference statistically "significant"? What is the p-value?

R(29): We did not conduct a statistical analysis to compare the differences between measured and initial NO3 concentrations. We argue that a comparison of the mean values (Table 2) in a descriptive way shows clearly significance, because NO3 concentrations represent only 37 - 71 % of the initial NO3 concentration depending on the study sites. We replaced "significantly" in L13 with "substantially" in order to emphasize that here no statistical comparison is given.

30. L14-15 - Suggest "The presence of excess N2 demonstrates that..."

R(30): We think that the difference between measured and initial NO3 concentrations (=NO3 consumption) as a parameter to stress denitrification activity is more suitable in a final sentence for the section here. Starting with Line 10, the results of these terms are introduced, but not excess N2. Excess N2 is more related to the first part of the section.

31. L21 - These EF values were highly variable among the sites, or within each site? Please explain.

R(31): Done.

32. L22-23 - Suggest "was in agreement"

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R(32): Done.

33. L25 - By definition, EF2>EF1 at sites with denitrification, so this seems unnecessary to report as a result. Is there something more to say about this?

R(33): Although EF2>EF1 results already from the equations, we argue that this is one of the main results of the study and that it is necessary to mention this additionally in the text, also as a requirement for the discussion. We would like to point out that using EF1 is an improved approach and that EF2 can lead to overestimation of indirect N2O emissions from groundwater with increasing denitrification rates (i.e. NO3 consumption).

34. L25-26 - Should this say "Among the sites"?

R(34): We chose the suggested expression instead of "within the sites".

35. P1275 L13-26 - The first half of this first paragraph of discussion repeats much introductory material. Suggest omitting or moving to the introduction.

R(35): We would prefer to keep this paragraph. In this first paragraph of the discussion the role of excess air and its fractionation is discussed. Furthermore, we discuss the uncertainty of excess N2 according to excess air fractionation. In the introduction, only one part of a sentence (L13-16) refers to the excess air phenomenon without mentioning the term directly. Thus, we can not find any repetition of introductory material here. We agree that the first half of this first paragraph is written in a more or less introductory style, but argue that it is necessary to give the reader this as a requirement for the following methodical discussion. Furthermore, we prefer not to move this point to the introduction, because we do not want to confront readers with details on uncertainty assessment in the introduction.

36. L3 - Please relate these values to the "UN2" term defined by equation 4.

R(36): Realized.

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37. P1276 L7 "the uncertainty of RP is relatively small and does not affect"

R(37): Done.

38. L1-14 - At this point in the discussion, it is distracting to read a defense of results that were given earlier in a separate section. I suggest including these calculations in the results section and including error bars on Figs 2 & 3 to show the reader the potential importance (or lack of importance) of the error associated with assuming total dissolution of entrapped bubbles. Also, Figure 3 should be introduced in the results section. The "relationship" shown in Figure 3 is mentioned here, but it hasn’t been mentioned previously and it is not explained here. I agree that the topic of uncertainty in these estimates worthy of discussion, but a discussion section should provide a broader perspective on how these results are relevant to the existing literature. For example, what does this say about previously published values of excess N2 and associated denitrification rates? Are the errors small enough that we can trust the published values, or should we be concerned about a potentially significant bias?

R(38): The calculations / value were included in the results section. However, we argue that it is necessary to discuss these data in this "methodical-discussion-section". Therefore, a short part of discussion the uncertainty data remained in the discussion section. To our opinion, error bars in Figure 2 would be obsolete, because every data point enables to distinguish between minimum and maximum value and to assess the difference between them and the resulting uncertaintiy, respectively. We tried to provide error bars as suggested for Figure 3. As we already indicated in L13, uncertainties connected with excess N2 are hardly of consequence for EF1. Thus, error bars would be more "error points" and very difficult to read. Furthermore, these error "bars" would downgrade the clarity of the figure and hamper identification of the differences between EF1 and EF2. Therefore, we decided to provide Figure 3 without error bars. The results-section 3.3 was extended by introducing Figure 3 and clarifying the increasing difference between the emission factors with increasing RP. To our best knowledge, there is a lack of studies related to uncertainty of excess N2 estimates connected with

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excess air fractionation. Therefore, it is quite difficult to link our results with comparable literature in the discussion. At page 1275, L15-19, we have already provided references which we extended by an additional one (Heaton et al., 1983). Indeed, Heaton et al. (1983) determined also excess N2 and initial nitrate concentrations, but they did not take excess air fractionation and the connected uncertainties into account. On the other hand, Aeschbach-Hertig et al. (2002) characterized excess air fractionation by analysing several noble gases, but this study did not aim in determining excess N2. In conclusion, and despite a lack of comparable experiences, we argued that our EF(1) data are robust results (see P1276, L11-13).

39. L14-26 - This paragraph seems tenuous. If it is an important point, maybe the data (e.g. sum of partial pressures versus hydrostatic pressure) should be shown.

R(39): We modified this section in the revised version, also with respect to reviewer 1. Please note that degassing what was observed by Blicher-Mathiesen et al. (1998) was clearly subject to special conditions (considerable production of excess N2 in surface groundwater and a simultaneous decrease of the hydrostatic pressure due to a partly upward groundwater flow direction). In the majority of comparable studies mentioned in the text, degassing is not a significant mechanism.

40. P1277 L1-20 - The point made by this paragraph seems very weak. Giving this much space and attention to a comparison with a previous modeling estimate (not even real data) distracts from more important points raised by this study. One sentence in the results section should be sufficient for this point.

R(40): We agree and deleted this paragraph.

41. Section 4.2 - Here it would be nice to see some comparisons with previous studies. Have these sorts of correlations been seen elsewhere? A broader context would make these arguments more compelling.

R(41): This section was slightly extended in the light of similar correlations found in

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previous studies.

42. P1278 L3 - Does "partial" refer to a part of the entire data set or a part of the Fuhrberg data set?

R(42): It refers to the entire data set. "Partial" was deleted.

43. L5 - Temporal and spatial or just spatial? Suggest omitting "which implies that the relationship between reaction progress and residence time was more variable."

R(43): We think that spatial distribution is dominating here, because the Fuhrberg aquifer (what delivers the correlation) is characterized by relatively homogeneous distribution of two denitrification zones: heterotrophic denitrification with organic carbon as an electron donor dominates in shallow groundwater, whereas chemolithotropic denitrification (reduced sulfur compounds as an electron donor) is the main process in depths $>$6 m below the soil surface. We omitted in L6-7 as suggested.

44. L13 - "found" instead of "evaluated"

R(44): This was changed.

45. L16-17 - Is it possible that N2O correlates with pH because N2O correlates with NO3- and NO3- correlates with pH? Acidification due to greater fertilizer applications explains the NO3- / pH correlation.

R(45): This would be possible, but we think that this argumentation could be too hypothetical. We argue that it is more likely that the correlation between N2O and pH is a result of the effect of low pH on denitrification enzymes (here especially N2O reductase). This was demonstrated in laboratory and field studies, which reported increasing N2O:N2 ratios when the pH is reduced.

46. L19-20 - Omit "This regulation is illustrated... in our study."

R(46): Done.

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47. P1279 Section 4.3 - Again, a more thorough comparison with existing studies would strengthen this discussion section. Is the result of higher emissions between RP=0.2-0.6 a new finding? Does it agree or disagree with previous results in other studies?

R(47): Additional references were added. Higher emissions between RP = 0.2 – 0.6 agree with the studies of Almeida et al. (1997) and Well et al. (2005b). This has been already reportet starting with L20.

48. L27 - The assertion that emission is negligible at RP close to zero appears not to hold true at Thulesfelde. Is there anything unique about this site that would explain the difference?

R(48): We did not state an assertion, that N2O emission has to be always negligible at RP close to zero. We formulate that “this emission can be expected”. We derived our expection from the whole data set, being aware of possible exceptions against the background of heterogeneous conditions governing denitrification and N2O accumulation. However, we inserted one sentence which includes the possibility that the range of RP connected with highest N2O concentrations might be even more variable.

49. P1280 L13-14 - Earlier in the paper (P1274 L23) a comment is made that EF2 values are similar to EF5-g. Given the large range of both EF estimates among the sites, can a stronger case be made that one is any better than the other? Or are these EF values more or less random. Are EF values worth calculating, or should a different approach be used?

R(49): Despite the large range of both emission factors, what implies a high uncertainty, our study clearly shows that EF1 is a more realistic approach for denitrifying aquifers than EF2, which tends to overestimate indirect emissions. More or less large ranges for EF estimates were found in many studies (Deurer et al., 2008; Reay et al., 2005; Well et al., 2005) due to the high heterogeneity of N2O in ground- or drainage water.

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Thus, uncertainties will remain with respect to a single emission factor. We argue that taking in account metabolism of N2O during transport could be an improvement and reduce uncertainties connected with EF calculation.

50. L26 - "was" instead of "could be"

R(50): Done.

51. P1281 L7 - "EF(1)" instead of "EFs(1)" L17 - Are there any important conclusions about uncertainty of excess N2 / N2O / initial NO3- estimates? Any conclusions about regulating factors for N2O production?

R(51): We have already provided one sentence about uncertainty of excess N2 und the consequences for the concept of EF1 (L5-7). We extended the conclusions with respect to regulating factors.

General responses:

Due to the general comments,

(i) excess air concentrations measured in this study were added to section 4.1 and compared with the findings of Heaton et al. (1983) and

(ii) the title of Table 2 was related to the relevant equations in order to give the reader information how the values were calculated.

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