**Biogeosciences
Discussions**

Interactive
Comment

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.

D. Weymann et al.

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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. A critical issue in my eyes is a discrepancy or conflict between the applied concept of emission factors on the one hand and NO3-(t0) on the other hand. The concept of NO3-(t0) relies on the assumption that N2O and N2 do not degas and escape from groundwater during transport. However, if this assumption holds, then the current calculation of N2O emission factors EF(1) and EF(2) makes little sense.

R(1): The authors agree that there are uncertainties with regard to the fate of the

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gaseous denitrification products - especially of N2O - during transport in groundwater. In the first paragraph of section 4.3 (lines 3-15), we stated our position related to this issue. This is valid for both concepts of EF calculation. However, we think that the EF(1)-approach is a first step to improve estimation of those emission factors in comparison to the EF(2)-approach, although N2O metabolism is not taking into account. Furthermore, we argue that the concept of NO3 t0 delivers robust results: for the large majority of data, excess N2 is the dominant product of denitrification, whereas N2O concentrations are negligible compared with excess N2 concentrations. Significant degassing during transport has been only reported by two studies using the "N2-Ar technique" (Blicher-Mathiesen et al., 1998; Mookherji et al., 2003). In both studies, conditions were favourable for degassing. High denitrification potentials were observed in the shallow groundwater of the investigated riparian wetlands under the presence of low hydrostatic pressures (see section 4.1, lines 16-17 on page 1276). In the case of Blicher-Mathiesen et al. (1998), hydrostatic pressure even partly decreased along the hillslope down to the wetland where upwelling of groundwater was observed. In our study, oppositional conditions are dominating: we mainly obtained low denitrification potentials in the shallow groundwater of the sandy and gravel aquifers combined with a downwards groundwater flow direction. Under these conditions, degassing is unlikely due to increasing hydrostatic pressure. Therefore, we think that N losses during transport are negligible for the concept of NO3 t0 and that the EF(1) calculation based on this concept is reliable.

2. As the authors state on page 1266, lines 12-13, emission factors are commonly defined as a ratio between N2O emission and N input. I completely acknowledge that the EF(1) proposed by the authors is a better approximation to this definition than the old EF(2). However, I believe that the authors could do an even better job. To my knowledge, the Fuhrberger Feld is one of the best explored aquifers in Germany. There should be quite good information regarding the groundwater age in different depths and the travel times of groundwater for this aquifer. By using this information the authors might be able to translate their reaction progress RP into reaction rates

for the formation and consumption of N2O. These reaction rates would allow them to calculate the N2O concentration at the point of groundwater abstraction or exfiltration into rivers.

R(2): We completely acknowledge that this approach would make the manuscript much more sophisticated. Indeed, for the Fuhrberg aquifer a lot of data with regard to groundwater age and travel times of groundwater would be available. However, analysing the whole data set in the same way would be a problem due to incompletion of these data. Furthermore, we think that the aspect of N2O reaction rates and the consequences connected with this aspect would overload a manuscript which already contains a non trivial method linked with the comparison of emission factors. Hence, we have already planned a case study what will include reaction rates and results from reactive transport modeling of the Fuhrberg aquifer with an upscaling of N2O emissions from groundwater as an ambitious aim. Therefore, we would prefer to publish these data in an upcoming paper what is focused on the Fuhrberger Feld aquifer.

3. According to table 2, RP approaches values of 1 in all four aquifers. Does this mean that emission factors would be even lower than EF(1) or almost zero if the N2O consumption by denitrification is extrapolated to the point of groundwater abstraction or groundwater exfiltration?

R(3): Theoretically, EF(1) at RP=1 would be zero if N2O is completely consumed. According to our results, a last bit of N2O remains in groundwater if denitrification comes to a standstill due to complete NO3 consumption. We observed low N2O concentrations in groundwater slightly above the ambient level, although NO3 was completely removed and RP was actually 1. This is not an inconsistensy, because low N2O concentrations are practically negligible for the calculation of RP. Therefore, we hypothesize that EF(1) is always different from zero and the minimum values shown in Table 3 are the lowest limits. We inserted a sentence covering this phenomenon in the last paragraph of section 3.3 in order to clarify this question.

4. Page 1263: In my opinion the title of the paper could be improved. The current title starts with two low-impact words that are followed with a quite specific term, which might be common to a limited number of experts only. I would suggest ‘Denitrification in North-German aquifers and related N2O emission factors as derived from accumulation of excess N2‘.

R(4): The title was changed, but we preferred to avoid "Denitrification" as the first term, because we focussed on the emission factors. Hence, the title starts with "Groundwater N2O emission factors".

5. Page 1269, lines 19-26: Was the total pressure equal to the sum of partial pressures of Ar, N2O, and O2? According to Daltons law, the total pressure of a gas mixture equals the sum of partial pressures of all single gasses. I would have expected that for example CO2 would contribute significantly to the total pressure. Were the water samples free of dissolved CO2?

R(5): CO2 was measured and we determined its contribution to the total pressure. We add this information on page 1269 and enlarged the paragraph starting with line 10 (GC analysis).

6. Page 1269, lines 29ff: It would have been nice to have a similar information for recoveries of N2O as well.

R(6): We conducted this test for N2 only, in order to guarantee the precision of our excess N2 estimates. Unfortunately, we can not give any information for recovery of N2O.

7. Page 1270, line 25, to page 1271, line 8: Is it really true that the maximum amount of N2 that can be dissolved in groundwater during the entrapment and subsequent complete dissolution of air bubbles at the groundwater surface is defined by the atmospheric concentration of N2? I would have expected that the N2 concentration of soil air or vadose zone air determines the maximum amount of N2 that enters groundwa-

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ter with entrapped air. Reducing conditions are quite common in the capillary fringe above the groundwater surface. Therefore I would expect that concentrations of N2 in air above the groundwater surface could be higher than atmospheric ones. If this is the case, the uncertainty analysis presented in equation 4 does not capture the upper limit correctly, which might be crucial for deriving accurate estimates of excess N2 according to equation 1.

R(7): We add references which confirm our statement (Heaton et al., 1983; Aeschbach-Hertig et al, 2002). We agree that N2 concentration of soil air could potentially differ from the atmospheric air concentration, but we argue that this effect is negligible due to the dominating amount of atmospheric air in the unsaturated zone.

8. Page 1275, lines 8-10: A correlation between EF(1) and N2O is trivial since the EF is derived from N2O concentrations.

R(8): This sentence was omitted.

9. Page 1275, lines 21ff: It is very difficult for me to derive the mean difference of 1.25 mg N/l from figure 2. I suggest to delete figure 2 and give minimum and maximum values of excess N2 in new figures of depth distributions of excess N2 (see below). 10. Figure 2: The message of this figure is not very plain to me. Is the ‘maximum distance to 1:1 line‘; equal to the greatest difference that was calculated between minimum and maximum excess N2? What is the meaning of the regression line? Is the intercept of the regression line equal to 1.25 mg N/l?

R(9+10): We add further information to the figure caption, in order to guarantee a better connection to the relevant paragraph in the text and to clarify the meaning of the 1:1 and regression line, respectively. Indeed, the mean difference of 1.25 mg N/l is not directly derivable from the figure. Thus, we gave the calculated value in the text. We show this figure to give an imagination how much minimum and maximum estimates differ for the whole data set. It is to be seen that a majority of data is very close to the 1:1 line where the difference between minimum and maximum estimates is zero. Furthermore, the

reader has the possibility to assess the uncertainty for the single values, because it is possible to compare minimum (x axis) and maximum (y axis) estimates for one sample directly in one figure. This would not be possible if minimum and maximum estimates would be separated and shown in two figures depending on depth. Furthermore, giving minimum and maximum estimates as results could be confusing because we used minimum and maximum values frequently in the manuscript, for example in table 2. For that reason, we prefer to add a new figure with means of the minimum and maximum excess N2 estimates depending on depth (Figure 1 A in the revised version).

11. Page 1276, line 4: Following equation (5), NO3-(t0) is the sum of excess N2, nitrate concentration, and N2O concentration. Accordingly, the error of excess N2 concentrations is only one part of the total error of NO3-(t0). Errors (variances) of nitrate concentrations and N2O concentrations have to be added to derive the total error of NO3-(t0) concentrations.

R(11): The intention of the authors here was to assess the uncertainty that is connected with the uncertainty of excess N2. We changed the sentence in line 4 for clarifying.

12. Page 1276, lines 14ff: Hydrostatic pressure might prevent the degassing of CO2, O2, N2, Ar etc. The question is what happened when water was pumped up from greater depths with the peristaltic pump or the GRUNDFOS submersile pump. How was degassing due to decreasing hydrostatic pressure prevented?

R(12): During pumping with a submersible pump there is no vertical distance between the depth of sampling and the pump. Therefore, degassing is unlikely because the hydrostatic pressure is not decreasing (see dissertation of M. Stute, University of Heidelberg, 1989). For pumping with the peristaltic pump, see our explanations on page 1268, lines 1-3 and 9-12, respectively: we compared gas concentrations which resulted from the different pumping types. Furthermore, we used a suitable low suction rate during pumping with the peristaltic pump according to Blicher et al. (1998).

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13.Page 1278, lines 12-13: A correlation between N2O concentrations and NO3- concentrations does not corroborate any relationship between N2O/N2 ratios and NO3- concentrations. Higher N2O concentrations at higher NO3- concentrations might also be a consequence of higher absolute denitrification rates, not of lower denitrification efficiency (reaction progress).

R(13): We strongly suppose that higher N2O concentrations at higher NO3- concentrations according to higher denitrification rates are unlikely for our data set. This is shown by data which we will present in an upcoming publication. For example, high denitrification rates result in very low N2O concentrations in the deeper groundwater of the Fuhrberg aquifer, whereas high N2O concentrations are a result of low denitrification rates in the shallow groundwater. In the first case, N2O is spontaneously reduced to N2 and is not accumulated. In contrast, the conditions in the shallow groundwater are favourable for N2O accumulation due to an inhibition of the N2O reduction step. However, we can not prove these assumptions for the more heterogeneous conditions of the other aquifers. Therefore, we deleted the sentence in line 10 to analyse the connection between NO3 and N2O correctly.

14. Page 1278, lines 19-20: This sentence is a repetition of ‘A significant negative correlation was found..‘ in lines 13-16.

R(14): We deleted tis sentence.

15.Tables 1 and 2: There is a big variation in the values that are presented in tables 1 and 2, which is probably not random, but dependent on sampling depth. The interdependency between sampling depth and reaction progress for example is reflected in a significant correlation in table 3. Instead of the tables 1 and 2, I would therefore prefer figures which present depth distributions of nitrate concentrations, NO3-(t0), excess N2, N2O, and reaction progress. I think that a two whole-page figures with four panels for the sites and five parameters per panel will be easier to read and interpret than the current tables.

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R(15): As mentioned in R(9+10), we added a figure containing the measured quantities excess N2, N2O-and NO3 concentrations depending on depth. The site specification was provided using different symbols.

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