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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.

Anonymous Referee #4

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GENERAL COMMENTS

The manuscript of Weymann and others addresses a highly relevant scientific question, which is within the scope of BG. The study uses advanced methods to derive new insight into the process of denitrification and the related formation of N2O in aquifers. Overall, the methods and their underlying assumptions are described clearly and in detail. 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 cal-

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culation of N2O emission factors EF(1) and EF(2) makes little sense. 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. 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? Overall, I recommend publication of the manuscript following the amendments and revisions, that are suggested above and in the following.

SPECIFIC COMMENTS

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'.

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?

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

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 groundwater 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.

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

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).

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.

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?

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).

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

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.

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?

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