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Interactive comment on "N_2O and N_2 losses from simulated injection of biogas digestate depend mainly on soil texture, moisture and temperature" *by* Sebastian Rainer Fiedler et al.

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Dear Sir or Madam

Thank you for your careful reading and your supportive suggestions. We agree with most of them. Indeed, the large amount of factor combinations was traded-off against a relatively short incubation duration which did not allow for the observation of the dynamics following the application of the biogas digestate (BD). But, as explained in our response to referee no. 2, our aim was not to study the dynamics, rather the effect of the different factors. We also argue in the other reply why we think the duration was appropriate to detect the peaks of the N2O and N2 emissions. However, because you

acknowledged our efforts to get such rare data, we assume that you agree with our study design (in opposite to the second referee). Basically, we follow your suggestion to include the data of all days into the statistical analysis and to the figures of the emissions. We also included the DOC content after the incubation into the step wise regression selection. As a result, DOC replaced NO3- content in the model for N2O and completed the models for N2 and CO2. However, the resulting models failed the Shapiro-Wilk test on normal distribution of the model residues. This might be a consequence of the increased number of data points which tend to reduce the reliability of tests on normal distribution in general. Hence, we decided to apply the skewness of the respective distributions as a measure, whereas a skewness of smaller than two is acceptable for normality assumptions (West et al., 1995) and all new models meet this assumption. Thank you for your clue about the possibility of NO formation and loss, which we acknowledge now with the mechanism of NO2- accumulation in our discussion as you elucidated in lines 327 – 337. In the following, we will reply to your specific comments. All corresponding changes are highlighted throughout the supplement pdf.

L. 1: Tune down the "simulated injection" story. I do not know how a band of injected slurry looks like in situ, but mixing it (evenly?) into dry (?) soil and packing it in a 200 cc cylinder does not seem to simulate conditions in a band of injected slurry at all. I get the point that different intensities of slurry (per cylinder) are a faint proxy for different row spacing in the field, if you look at it at the ha-scale. However, the study is conducted at the cm-scale and should be treated like this. Therefore, "simulated" should be removed from the title and the whole story should be tuned down throughout the text. It does not add much, anyway, because the study does not lend itself to making extrapolations to field-scale N losses. If you prefer to keep the stress on "simulated injection", much more detail would be needed about how the slurry was mixed into the soil (soil moisture at mixing, bulk densities before and after mixing, etc.).

→ We agree that our set-up was inadequate to "simulate" injection and revised the story accordingly. Rather, we point now to the high nutrient concentration occurring in injection bands which we reproduced in our repacked soil cores. To focus our manuscript more to "the cm-scale", we changed the differentiation from the application rates per ha to mL per soil core, though, still referred to a hypothetical application of 160 kg BD-N ha-1 by different row spacing: "Hence, we performed an incubation experiment with soil cores in a helium-oxygen atmosphere to examine the influence of soil substrate (loamy sand, clayey silt), water-filled pore space (WFPS; 35, 55, 75%) and application rate (0, 17.6 and 35.2 mL BD per soil core [250 cm^3] as a proxy for 'narrow' and 'wide' spacing, respectively, between injection rows) on the emissions of N2O, N2 and CO2 after the application of high loads of BD" (lines 14 – 18). Throughout the MS, the terms "160 kg N ha-1" and "320 kg N ha-1" are substituted by "LOBD" (low BD concentration) and "HIBD" (high BD concentration), respectively.

L. 15. Insert "the latter" between application rate and proxy. Otherwise, the sentence does not make sense.

→ We alternatively separated the respective sentence into two sentences: "[...] and application rate (0, 17.6 and 35.2 mL BD per soil core [250 cm^3]) on the emissions of N2O, N2 and CO2 after the application of high loads of BD. The application rate was used as a proxy for 'narrow' and 'wide' spacing, respectively, between injection rows." (16 – 18)

L. 16. Remove "these"

→ removed

L. 21. "Content in"

→ replaced (23)

L. 31: "emission and deposition ... are of environmental concern" & L. 32: rephrase: "e.g., through acidification and conversion to N2O"

→ rephrased to: "emission of ammonia (NH3) is of environmental concern, e.g., due to acid deposition or conversion to N2O" (33 – 34)

L. 39: Slurry? Animal slurry?

→ specified to "animal slurry" (41)

L. 40: mention NO here

→ done (42)

L. 41: how can an "overall effect ... [be] under debate"? What is under debate? The mechanism behind the effect, the "sign" of the effect, the effect strengths, or all together? Clarify.

→ specified to "effect strengths" (43)

L. 44: Reduction of local O2 availability. What are the processes/factors reducing O2 availability? This paragraph seems to focus solely on denitrification. Mention also NH4+and nitrification, which is a strong O2 sink while being a potential source for N2O.

→ We rephrased the respective section: "On the one hand, high NH4+ concentrations in the injection band promote nitrification, which is a significantly O2 consuming process releasing N2O (Christensen and Rowe, 1984). On the other hand, increased amounts of C in the injection band also promote respiration and, thus, additionally deplete the O2 supply (Dell et al., 2011)." (48 – 51)

L. 46: skip "these"; in general restrict the use of "these"

→ OK

L. 55...and nitrification!

→ right, included (60)

L. 58 ff.: tune down the "row spacing". Your study does not address row spacing. See comment above.

→ We have revised the respective section and shortened it. However, though not investigated directly, we will use it discreet as explanation for the application different BD rates. It reads now: "However, though high within injection bands, nutrient concentrations and WFPS should theoretically increase further with the row spacing between the injection bands, if a given amount of BD per area is assumed. We are not aware of studies addressing the effect of such high BD concentrations." (66 – 69)

L. 66: not the least

→ OK

L. 66. Methodological issues; be a bit more specific

→ Specified: "The indicated knowledge gaps are caused not the least by methodological constrains with the direct determination of N2 fluxes due to the high background level of N2 in the atmosphere, while indirect applications like acetylene-based methods and 15N tracers are unfavourable since the former implicates serious underestimations and the latter has rather high detection limits (Groffman et al., 2006)." (72 – 75)

L. 69: generation = emission?

→ Yes, changed accordingly.

L. 70: CO2 as an indicator for O2 consumption. Not entirely free of problems. The slurry is full of bicarbonate, the soil is above pH 7. But better than nothing.

→ We added "[. . .] but with the restriction that inorganic sources could not be differentiated." in lines 80 – 81.

L. 73: not entirely clear from the introduction what you base your hypothesis 3 on.

→ We added the following sentence into the introduction section: "In general, fine textured soils exhibit a lower gas diffusivity compared to coarse textured soils, which result regularly in higher denitrification activity in the former with higher N2O emission rates, but also a higher probability for the consecutive reduction to N2 (Senbayram et al., 2014; Gu et al., 2013; Ball, 2013)." (62 – 65)

L. 76: treated with WFPS? Adjusted to WFPS

→ Changed accordingly (88)

L. 78: give volume of the cores

→ 250 cm3 (91)

L. 82 to "gather" soil. Like in Hunter and Gatherers? Replace by "collect"

→ replaced (94)

L. 84: give some reasoning for why you dry the soils

→ "to facilitate adjustment of WFPS" (97)

L. 97: "with the respective quantity of water calculated based on". Too many words!

→ We split the respective sentence into two: "For adjustment of WFPS, the dry and undisturbed soil cores were moistened dropwise. The respective quantities of water were calculated based on the bulk density, an assumed particle density of 2.65 g cm-1 and reduced by the expected moisture input from subsequent addition of BD." (110 – 112)

L. 99 ff.: see comment above. Does the mixing described here really simulate injection, the result of which I would figure as a band rather than a mixture?

→ No, you are right. As for your former comment, we adjusted the story towards the concentration of BD appearing in injection bands rather than simulating injection bands. We also added an explanation why we mixed the soil with BD: "The soil cores were then mixed with BD and finally repacked to reach nutrient concentrations comparable to that in injection bands. The mixing was done for methodical reasons since the available space in the incubation vessels was limited and, hence, 'real' injection not feasible. However, injection bands have actually a thickness comparable to the sample rings we used (Markfoged et al., 2011)." (112 – 116)

L. 109: wouldn't an apparatus like this typically involve the use of an additional empty reference chamber to infer N2 leak rates, blank values, etc.? Please comment.

→ We used all six chambers because the tightness of one individual one kept empty does not allow concluding about the individual tightness of each of the other five chambers. Generally, we calculated the fluxes from the concentration differences at the respective inlets and outlets. To reduce contamination with atmospheric air, the lids of every single chamber were purged permanently with helium. Additionally, we determined individual blank values every cycle before the measurements started by inserting aluminium blocks into the chambers. Since the obtained blank values were usually steady, we suggest that the chambers were tight. The blank values were subtracted from the values measured at the respective outlets (146 – 153).

L. 118: why "possibly"? N2 measured by a TCD is by a factor 10ËĘ3 to 10ËĘ4 less precise than N2O by an ECD. That's a fact.

→ We omitted "possibly" (133)

L. 118: So, what was the precision? Please give precision in ppm and in mg N2 m-2 h-1

→ We refer to Eickenscheidt et al. (2014) (133). See also our reply about precision/blank values obove.

L. 128: Difference of gas concentrations. Between what? Inlet and outlet?

→ Yes, changed accordingly (145)

L. 130: How comes that the detection limit for N2 in this study is one order of magnitude higher than the one given by Eickenscheidt et al. (2014)?

→ The "detection limits" given in the manuscript are actually derived from the blank values and, thus, do not represent the detection limit of the TCD. The actual detection limits are in accord with Eickenscheidt et al. (2014), see comment above on precision/blank values.

L. 130: Entirely unclear to me how you can check a detection limit daily in vessels filled with soil. Please explain.

→ Same misunderstanding about detection limit and blank values as above. The respective section was deleted.

L. 134: Any reasoning behind the use of 0.01 M KCl as an extractant? Wouldn't it be more interesting to look at total exchangeable NH4+?

→ No special reasoning since this was the standardised extraction method of the commissioned laboratory at Leibniz Centre for Agricultural Landscape Research e. V., annotated now. (157 – 158)

L. 143: Just out of curiosity: the "technical reasons" for omitting all these fluxes would be what? Influx of N2 from the atmosphere?

→ No, the soil cores where not adjusted to the right WFPS and were, thus, not coherently useful.

L. 177: Replace "from" with "in"

→ Replaced (192)

L. 185: Why not moving the CO2 subchapter here?

→ OK (200 – 210)

L. 191: ". . .the other treatment means emitted between. . .". Means cannot emit!

→ That's true. Rephrased to: "[. . .] treatments emitted in mean between 1.0 and 3.0 mg [. . .]" (217) L. 207 Fig. 4: Insert a line in figure 4, denoting the average detection limit for N2. No N2 fluxes could be detected = N2 fluxes were under the detection limit.

→ Inserted.

L. 210: Negligible amounts of N2. What is negligible? Replace by "small rates". It is actually rates you are reporting.

→ Replaced (245)

L. 212: Awkward phrasing

→ Rephrased: "[. . .] were detected in the clayey silt. However, the clayey silt showed also no fluxes in all BD treatments with 35% WFPS." (246 – 247)

L. 214: Can a soil "present" emissions?

→ Rather not. Rephrased to: "emitted" (249).

L.254 ff.: Not so strange that temperature "shows . . . significant influences" if one warms a soil from 2 to 15oC. Did you ever consider to use the temperature difference to tentatively distinguish between chemical and biological processes? I would actually exclude temperature from the mixed model. It's too obvious.

→ No, we did not consider to use the temperature for such a tentatively distinction, because it is out of the scope of our study. However, aren't chemical processes also driven by temperature? We tentatively set temperature as a random effect in the model for N2, which then had been eliminated during the step-wise regression section. But the resulting model had only a slightly improved AIC (decreased from 121 to 118). Thus, we decided to keep the temperature as a fixed effect, because its omitting resulted in virtually unchanged effects of the independent variables. However, we reduced the discussion about temperature in the revised manuscript.

L. 256. Q10 is just a metrics for temperature response. It is not reserved to biological processes.

→ We now omit Q10 and rephrased to: "increased metabolic activity" (280)

L. 257: Temperature is not a proxy. It's a driver!

→ Changed accordingly (281)

L. 258: CO2 is not a product of O2!

→ rephrased to: "resulting from respiration of O2" (282)

L. 267: "many N2-producing processes". How many are there?

→ Not so many. Actually it's denitrification as coupled nitrification-den., nitrifier den., co-den. and chemo-den. (Butterbach-Bahl et al., 2013). We rephrased: "N2O is the direct precursor of N2 in denitrification" (291).

L. 274: 35% WFPS should be more than enough for substrate diffusion in the soil. This is not a good argument for explaining low fluxes at this soil moisture.

→ We omitted this argument and refer to the presumably well aeration in these treatments (299). L. 278: such moderate amounts of N?

→ We rephrased to "commonly applied amounts of BD-N (i.e., 160 kg N ha-1)" (301 – 302).

L. 279: I see your point, but also you mixed the BD into the soil, didn't you'?

→ Yes, we mixed it into the soil, but we aim at the substrate concentration (in injection slits) which was comparable (see reply to your comment on line 1) (303).

L. 283: highly amended

→ revised (307)

L. 284. Do not use "where" as a relative pronoun, unless it deals with a place

→ OK, rephrased as a seperate sentence "Accordingly, Anthonisen et al. (1976) found an [. . .]" (308).

L. 286: "relatively high concentrations of NH3". Use the NH4 – NH3 partitioning coefficients given by Venterea et al. (2015) together with your slurry pH and calculate the apparent NH3 concentration.

→ We calculated the apparent NH3 concentration according to Emerson et al. (1975) with 15 °C under the assumption that all extractable soil NH4 is in solution, because we do not know the sorption capacity of our soils and, further, Equation (3) in Venterea et al. (2015) resulted in unrealistic high numbers. The corresponding section reads now: “The application rate in the treatments with HIBD amounted to approximately 500 mg NH4+-N (kg soil)-1 (Fig. 3) which correspond to 25.8 mg NH3-N (kg soil)-1 at 15 °C if we use the pH of the BD and assume that all extractable NH4+-N was in solution (Emerson et al., 1975).” (308 – 311)

L. 287: An argument? Or rather the reason?

→ Rather the reason (311)

L. 290: this is a good argument (clay fixation), which you probably would not observe to the same extent if the slurry was placed as a band in the soil

→ We discussed this issue in lines 316 – 317: “However, since we mixed the BD with the soil, we would expect a lower NH3 fixation in tubular injection slits in situ, resulting in probably lower N2O and N2 fluxes from clayey soils.”

L. 294: If you really think that nitrifiers reduce more NO2- than denitrifiers, then please cite the original literature, and not some review

→ This was a misunderstanding. We aimed at the preferred reduction of NO2- and NO3- compared to N2O during denitrification. We reformulated this section and give alternative references: “In general, NO2- and NO3- are preferably reduced compared to N2O during denitrification sequence since the energy yield of each reduction step decreases from NO3- to N2O (Koike and Hattori, 1975). Additionally, the reaction rate of reduction is higher for NO3- and NO2- than for N2O, which results in an accumulation of N2O, if NO3- concentration is not limited (Betlach and Tiedje, 1981). Hence, increasing application rates of BD increase the availability NO2- and NO3- from NH4+

oxidation which, consequently, decreases N2O reduction.” (320 – 325)

L. 299: Consider also AOB - NOB decoupling due to NH4 inhibition of NOB

→ We added a phrase about this important hint: “Since NO2- oxidising bacteria are less resilient against high concentrations of NH3 than NH3 oxidising bacteria (Anthonisen et al., 1976), the accumulation of NO2- is likely. This NO2- protonates then partly to the toxic and unstable HNO2, which drives biological and chemical production of NO and N2O for detoxification (Venterea et al., 2015). Hence, we suggest a dominant role of denitrification, i.e., NO2- reduction, in the generation of N2O during our experiment.” (329 – 333)

L. 302: it certainly was

→ This makes sense, we reformulated accordingly: “[...] it was certainly a substantial source [. . .]” (340).

L. 304: one verb too many

→ We added the relative pronoun “which” (343)

L. 302: How about writing: “Different effects of soil diffusivity on N2O and N2 fluxes”

→ Good idea, thanks!

L. 314: why do we need saturated conductivity here? You mixed the slurry into the soil. There shouldn’t be any gravitational flow

→ It is omitted now (352)

L. 315. Let*s*

→ changed accordingly (353)

L. 316. “inferior diffusion characteristics”, rephrase

→ rephrased to “relatively poor diffusion characteristics” (354)

L. 327: “reasonable establishment”, rephrase

→ rephrased to: “sufficient establishment” (365)

L. 328: ensured a moderate diffusional constraint!

→ rephrased accordingly (365)

L. 337: if you really think that NO3- availability affected the N2/(N2+N2) ratio, cite the original literature.

→ We refer now to Senbayram et al. (2012) (377).

L. 346: “reasonable stocks of NO3-“?

→ “sufficient stocks” (384)

L. 349: proposed

→ changed (388)

L. 351 ff. nice discussion about the role of C, but why did you not try to correlate total N gas flux with CO2 or DOC?

→ Honestly, we do not know ourselves why we have not correlated them. But we catch it up and found a very good correlation for the clayey silt (R^2 = 0.93, p = 0.001), when the treatments with 35 % WFPS (which showed virtually no N emissions) were omitted. We included this finding into the respective section: “Accordingly, there is also a good correlation between cumulated CO2 and N2O + N2 fluxes for the same period from the clayey silt (R^2 = 0.93, p = 0.001), when the treatments with 35 % WFPS (which showed virtually no N emissions) are omitted (Fig. 7). However, there was no such a correlation for the loamy sand. This confirms the interactive effect of diffusivity (induced by both the soils and WFPS) and C availability on the emissions of N2O and N2.” (403 – 407) L. 352. There is only one denitrification process that depends on the availability of organic carbon, namely denitrification.

→ That’s right, changed accordingly (390).

L. 368: “a tendency of fostered N2O reduction”; rephrase

→ rephrased to “a tendency of N2O reduction” (410).

L. 370: here Q10 pops up again. To what end? If you want to use Q10 values, then try to calculate them from your emission rates at 2 and 15oC.

→ We omitted the reference to Q10 (cf. L. 256)

L. 380: claggy? Do you mean cloggy?

→ Yes, cloggy (423).

L. 388: larger loss and higher ratios

→ Changed accordingly (456)

L. 392: Appropriate denitrifying community? Denitrifers are ubiquitous and comprise some 5 to 20% of any soil microbial community. Any reason why there should be no appropriate denitrifying community?

→ To be honest, no. So we omit this phrase now.

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Please also note the supplement to this comment:
https://www.soil-discuss.net/soil-2017-6/soil-2017-6-AC1-supplement.pdf

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Interactive comment on SOIL Discuss., https://doi.org/10.5194/soil-2017-6, 2017.

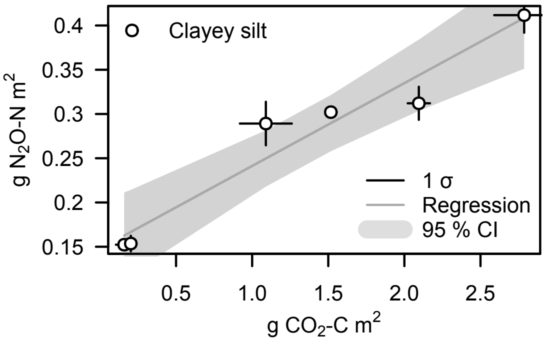

Fig. 1. Fig. 7: Fig. 7: Regression between cumulated CO2 emissions (g C m-2) and the respective cumulated N2O + N2 emissions (g N m-2) from the clayey silt with WFPS > 35 % during the period of aerobic headsp

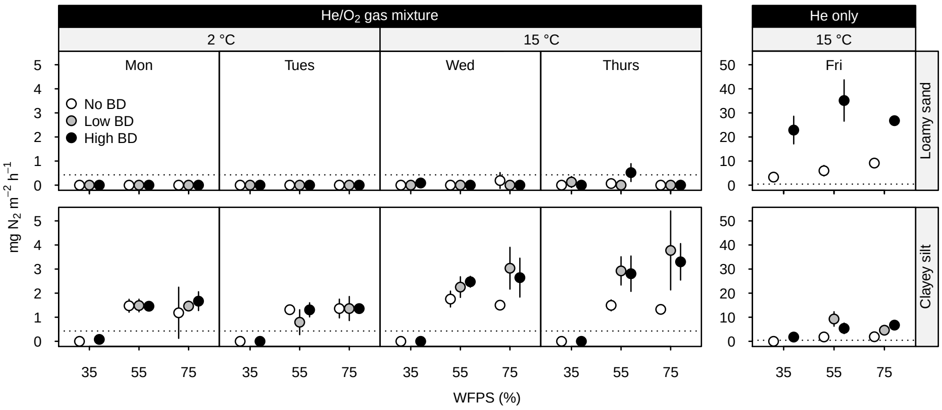

Fig. 2. Fig. 4: The dotted horizontal lines depict the average blank value; single flux rates lower than the respective lank value were set zero