

Interactive comment on “N₂O and N₂ losses from simulated injection of biogas digestate depend mainly on soil texture, moisture and temperature” by Sebastian Rainer Fiedler et al.

Anonymous Referee #1

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Fiedler et al. present a soil core incubation study, quantifying CO₂, N₂O and N₂ losses induced by different amounts of biogas digestate (BD) added to a loamy sand and a silty clay. Assessing the effects of organic amendments in general, and biogas slurry in particular on soil N cycling and N gas emissions is challenging but timely, given the growing importance of biogas as renewable energy source. The present study employs a He/O₂ apparatus to measure notoriously difficult to quantify N₂ emissions. As such, it adds to the sparse literature quantifying both N₂O-N and N₂-N losses after slurry application.

The study has a stringent design, mixing BD into the soil on Mondays, keeping the cores at 20°C while N₂ is removed until Wednesday, warming them up to 15°C under a

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He/O₂ atmosphere and switching to He on Fridays, before taking the weekend off. By running this scheme week after week, an incredible amount of factor combinations is investigated (2 soils x 3 soil moistures x 2 BD intensities x 3 replicates). This makes it an interesting piece of work, allowing for some mechanistic insight.

The downside of this design is that the factor time since “simulated injection” is not addressed. Much to the contrary, half of the gas measurements is deliberately discarded from the statistical analysis (L. 139), which is a pity! The authors argue that, by doing so, they would “. . .allow for establishment of a new flux equilibrium on day three after temperature change and, thus, minimising the effect of time”. (L 140-41). This is a truth with modifications, of course. To warm six ~200 cm³ soil cores from 2 to 15°C does not take 48 hours, and steady state conditions will not be reached anyway in BD amended soils within 3 days at 15°C. I find these data important and I would rather like to see them plotted over days than having them in a table in the Supplementary. There are some strong indications in the data that the effect of added labile C and N depended on the slurries’ interaction with the soil (as discussed in the para starting on L. 277) and I wonder whether showing gas data in between the ones used for stats could shed some light on this. In general, I would like to see the CO₂ data more actively used when discussing N gas data. For instance, did total N gas and CO₂ gas flux correlate?

Another shortcoming in terms of total N gas loss and mechanistic understanding is the lack of NO and NO₂⁻ measurements, respectively. N₂O-N losses under He/O₂ in the clayey silt were clearly larger than N₂-N losses, indicating that much of the N gas loss was driven by processes other than canonical denitrification. Given the high soil pH, NO₂⁻ may have accumulated which fuels NO and N₂O formation through a number of biological and chemical processes. Under such conditions, NO-N losses may exceed N₂O losses. This should at least be mentioned in the discussion, since N losses at large and fertilizer use efficiency in particular are invoked as a motivation for this study at several places in the manuscript.

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The likely accumulation of NO₂⁻ is intimately linked to the inhibitory effect of NH₃ mentioned in L. 283 ff. It is well known that excessive NH₃ inhibits nitrification, but actually, it is also the mechanism behind NO₂⁻ accumulation: NH₃ inhibits AOB less than NOB, which leads to the accumulation of NO₂⁻ (a fact known for long in the waste water treatment community). As NO₂⁻ accumulates, part of it protonates to HNO₂, which is toxic and unstable, driving biological (detoxification!) and chemical NO and N₂O production. The appropriate mechanistic study to cite would be Venterea et al., 2015 Scientific Reports DOI: 10.1038/srep12153.

Finally, the manuscript suffers from numerous, small linguistic imprecisions and would certainly benefit from a more straightforward language.

Specific comments:

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.).

L. 1. Consider inserting the term “short-term” or “instantaneous” at some place in the title, for obvious reasons.

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

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L. 16. Remove “these”

L. 21. “Content in”

L. 31: “emission and deposition . . . are of environmental concern”

L. 32: rephrase: “e.g., through acidification and conversion to N₂O”

L. 39: Slurry? Animal slurry?

L. 40: mention NO here

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.

L. 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.

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

L. 55 . . . and nitrification!

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

L. 66: not the least

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

L. 69: generation = emission?

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.

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

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- L. 76: treated with WFPS? Adjusted to WFPS
- L. 78: give volume of the cores
- L. 82 to “gather” soil. Like in Hunter and Gatherers? Replace by “collect”
- L. 84: give some reasoning for why you dry the soils
- L. 97: “with the respective quantity of water calculated based on”. Too many words!
- 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?
- 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.
- L. 118: why “possibly”? N₂ measured by a TCD is by a factor 10³ to 10⁴ less precise than N₂O by an ECD. That's a fact.
- L. 118: So, what was the precision? Please give precision in ppm and in mg N₂ m⁻² h⁻¹
- L. 128: Difference of gas concentrations. Between what? Inlet and outlet?
- 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)?
- L. 130: Entirely unclear to me how you can check a detection limit daily in vessels filled with soil. Please explain.
- 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⁺?
- L. 143: Just out of curiosity: the “technical reasons” for omitting all these fluxes would be what? Influx of N₂ from the atmosphere?
- L. 177: Replace “from” with “in”

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- I. 185: Why not moving the CO₂ subchapter here?
- L. 191: "...the other treatment means emitted between...". Means cannot emit!
- 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.
- L. 210: Negligible amounts of N₂. What is negligible? Replace by "small rates". It is actually rates you are reporting.
- L. 212: Awkward phrasing
- L. 214: Can a soil "present" emissions?
- L.254 ff.: Not so strange that temperature "shows ... significant influences" if one warms a soil from 2 to 15°C. 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.
- L. 256. Q10 is just a metrics for temperature response. It is not reserved to biological processes.
- L. 257: Temperature is not a proxy. It's a driver!
- L. 258: CO₂ is not a product of O₂!
- L. 267: "many N₂-producing processes". How many are there?
- 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.
- L. 278: such moderate amounts of N?
- L. 279: I see your point, but also you mixed the BD into the soil, didn't you'?
- L. 283: highly amended
- L. 284. Do not use "where" as a relative pronoun, unless it deals with a place

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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.

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

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

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

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

L. 302: it certainly was

L. 304: one verb too many

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

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

L. 315. Let*s*

L. 316. “inferior diffusion characteristics”, rephrase

L. 327: “reasonable establishment”, rephrase

L. 328: ensured a moderate diffusional constraint!

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

L. 246: “reasonable stocks of NO₃-“?

L. 349: proposed

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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?

L. 352. There is only one denitrification process that depends on the availability of organic carbon, namely denitrification.

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

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 15°C.

L. 380: claggy? Do you mean cloggy?

L. 388: larger loss and higher ratios

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

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