An uncertainty methodology for solar occultation flux measurements: ammonia emissions from agriculture

By Johan Mellqvist et al.

The authors give a detailed description of the issue of measuring ammonia (NH3) emissions from the agricultural sector. Using the solar occultation flux (SOF) method, which is a remote sensing technique with mobile FTIR, the conducted measurements of NH3 from a validation experiment and three case studies are used in combination with different combinations of wind measurements and an in situ FTIR to infer NH3 emission fluxes and their uncertainties.

The paper is appropriate for publication in AMT because it provides a new methodology to infer plume height prior to estimating emission fluxes. However, the specific comments in the next section need to be addressed by the authors beforehand.

Specific Comments:

1. The structure of the paper is not well outlined:
    a. In section 2 the authors introduce a validation and three case studies, but then in the results section are not very specific about the order of how these were introduced. This leads to confusion when e.g. in section 4 it becomes less clear that MeFTIR was only used during C3. It is also confusing when in the results section suddenly specific plume transects are discussed but it is not clear which case study these relate to. I suggest restructuring section 2 and better introducing the measurements and studies. It would help to have a designated subsection for the wind related instruments as well as one for the MeFTIR such that it doesn't first appear in a subsubsection describing plume height.
2. Unclear description about the novelty of the methodology:
    a. In the abstract as well as the main text it is not clear where the novelty is. Is the novel methodology the SOF method? Or is it the plume height estimation? Or is it the expanded method to estimate uncertainty? I suggest reducing the frequency of words such as "novel", "first-time" or "first" and only using in conjunction with the introduction of what is new to the science community.
    b. While the SOF method is not widely used up to this time, it is not novel.
    c. Stationary ground-based applications using FTIR are widespread and well published. Thus, it is generally well known to carefully account for systematic and random spectroscopic uncertainty in the FTIR community.
    d. After several reads through the paper, I believe the sole novelty here is the plume height estimation using the MeFTIR in situ in combination with the SOF columns. This means that only C3 contributes to this novel flux estimation. It is great to have the validation case study and others to further support the range of uncertainty an emission flux has but warrants clearer description within the paper.
    e. What kind of implications do the findings have (Line 26)? In other applications an aircraft or drone *in situ* instrument might measure the vertical distribution of the plume as well as wind speed which would even further constrain flux uncertainty.

3. Similarities to Vechi et al. (2023):
    a. Vechi et al. (2023) only used C3 data. But also already discussed expanded uncertainty and also obtained 37% uncertainty on the flux and used the same LIDAR for wind data. However, plume height estimation used distance between measurement road and source as well as horizontal and vertical winds. I suggest being more clear about the published C3 results in the Vechi et al. (2023) paper and that various information is shown here again but with the difference in plume height estimation.
4. Doublecheck listed uncertainties in Abstract and Results section agree with each other:
    a. The abstract lists the validation test measurement errors from -31 to +14%, estimated expanded uncertainty as 12 to 17% and application to farms as 21 to 37%. However, in the results the expanded uncertainty is listed as 15 to 37% with a median of 27% and Table 2 lists values from 12 to 37%. So I'm not sure if for example the 21% listed in the abstract are correct…

Minor comments:

Line 14: Currently reads as if SOF is the novel methodology. Suggest removing "introduces a novel methodology" such that the sentence becomes "This study for evaluating uncertainties in NH3 emissions measurements uses the Solar Occultation Flux (SOF) method."

Line 59ff: The SOF technique has also been demonstrated from aircraft (Kille et al. 2022)

Line 61, 77, 84, 104, and more: Suggest using terms and abbreviations slant column density (SCD) and vertical column density (VCD) instead of "slant columns" or simply "columns". Other literature uses the established terms SCD and VCD for slant and vertical columns as well as air mass factor (AMF) as the term describing their relation (to name a few, see e.g. Eq 1 in Griffin et al. (2021) or Eq 1 and 2 in Kuhlmann et al. (2022))

Line 73: While the measurement column is being driven through the gas plume, I might consider changing the sentence to "driving below the gas plume" as the vehicle and instrument detectors are below the (majority) of the plume.

Line 74: Photons or solar light is captured by the solar tracker and spectra by the spectrometer. Suggested rephrasing to something such as "A solar tracker, containing several mirrors, follows the sun as the car moves and transmits solar light to the spectrometer where spectra are captured during sunny or low cloud coverage conditions." Please note that I suggested changing "follows the light" to "follows the sun" as light could refer to either scattered or direct light.

Line 84: I believe you mean "calculated enhanced column" instead of "calculated column"? The spectrum outside a plume is not necessarily equal to 0 especially if there are upwind contributions.

Line 85: How is that sentence on "low gas concentration should be chosen as the reference" to be understood? The reference or background should be representative of the external condition and not the one point with the lowest measurement.

Line 86: How is the "new reference spectrum" created?

Line 86: What is meant by “absolute column”?

Figure 1b: Is the residual multiplied by a factor? The difference between “Fit” and “Meas” looks negligible at the two peaks but shows visibly in the residual. The colors red and orange are too similar.

Figure 1d: Labels on inset are too small.

Figure 2: Does panel b have the same value range on the y axis? It appears that y = 0 here intersects at the x axis instead of y = -25 as in panel a.

Line 138: At which height above ground did SOF and MeFTIR measure from the vehicle?

Line 145: Should the solar angle not be contained in the integral with the column similar to Eq 1 as the angle changes over time and is somewhat unique to each measurement?

Line 217: You state this is “the first time that uncertainties in NH3 SOF emission measurements from livestock production have been established”, but in Line 61 you state that SOF “has been recently used to measure agricultural NH3 emission sources (Kille et al., 2017, Vechi et al., 2023)”. Vechi et al., 2023 uses the same data so this is not the first time and Kille et al., 2017 also measured concentrated animal feeding operations. I suggest rewriting this sentence to include the plume height as what has been contributed the first time.

Line 225: It is unclear what is meant by “novel method to assess spectroscopic uncertainties”. Spectroscopic uncertainties are well documented in FTIR publications such as from stationary FTIR networks. See for example Table 3 in Viatte et al. (2014).

Line 226: Whereas the previous sentence focused on spectroscopic uncertainty, which is also a measurement, this new paragraph seems to imply that measurement means emission flux measurement. I suggest explicitly stating “Emission flux random uncertainty” instead of “Measurement uncertainty”. Additionally, in Line 224 the words “superior results” are chosen when purely assessing spectroscopic uncertainty but in Line 226 (shifting to the emission flux uncertainty) it is stated that wind is the strongest influencer. I suggest modifying the sentences as this immediately seems to weaken the claim that these will be superior results.

Line 238: How is the number 1.96 derived? Wouldn't most of the contribution be from right where the NH3 fingerprints are, so despite your window being smaller than the full band would it not be better to assume the full absorption strength uncertainty?

Line 248ff: In lines 81ff you describe the retrieval window for NH3 to be the broad range from 900-1000 cm-1. Why do you calculate the error for a subregion of the retrieval’s spectral range? How do the lines outside this subregion contribute to the retrieval error?

Figure 4a: Be more specific about what uncertainty is portrayed in the panel. Is it the systematic uncertainty? Is column error the least-square sum of random and systematic spectroscopic errors?

Figure 4a: The 1:1 line does not appear dashed except for the last bit whereas the legend indicates dashes.

Figure 4b: Is the residual multiplied by a factor? The difference between “Fit” and “Meas” looks negligible at the two peaks but shows visibly in the residual. The colors red and orange are too similar.

Line 291 and Figure 5: The sentence describes it like Acol is the integrated column area across the plume, but in the figure caption it says the grey-shaded area is the integrated area in Eq 9. Unclear whether you meant the uncertainty is derived from the difference in the two sides’ background columns or the area between the columns and temporal/spatial distance of the plume?

Line 336: What is meant by effective degree of freedom? What is meant by “were considered”? Were they applied or found unnecessary?

Line 353: What is “a large number of transects”?

Line 359: Suggest expanding section title to state this is specifically for C3. Otherwise it sounds like MeFTIR and SOF were always operated simultaneously whereas before it was stated that MeFTIR was only used in C3 (Line 204, and Table 1 also shows it only for C3).

Figure 6: Caption for panel b is somewhat confusingly structured. Suggest something like “Examples of plume height calculation using the two methods VCGC (light red bar; error bars correspond to the variation in the plume height calculation – variation in plume height calculation and resulting wind speeds) and PTVS (dark red bar; the error bars correspond to the variation of the HP calculation – variations in wind speed and measured distance).”

Figure 7b: Suggest adding legend for the lines (1:1 and ?)

Line 392ff: Does “lack of vertical wind profile measurements” imply that wind uncertainties should be increased to remain conservative with flux estimates?

Line 399: Was only NH3 released? Could a second, more stable in behavior, gaseous species be released simultaneously to better determine whether or not NH3 deposition or loss is taking place?

Figure 8: Please also add wind arrows for panels c and d.

Line 427 and 430: What does “for the house only” mean?

Line 443: I usually understand a transect to be a straight line. However, since you state the feedlot had an “18 km perimeter” and that it took “an hour to measure one box transect”, did you mean one loop/ circle around the box capturing upwind and downwind or did you mean one side of the box?

Line 448: Please add the range of meteorological factors and time of year for each to support your statement about “High fluctuations”.

Line 457ff: Suggest adding a little summary as to what is documented in Vechi et al. (2023). How is the EF estimated in Vechi et al. (2023) if in the previous sentence you stated “the number of animals was not known” and hence EFs “could not be established”.

Line 472f: See also Rowe et al. (2022), where CO from airborne SOF was compared to the TROPOMI satellite data product.

Technical comments:

Line 46: CSDR should be CRDS

Line 48: close-path should be closed-path

Line 49f: It is not clear what “its” refers to in this sentence. Should this be “their” or “the instruments’”?

Line 86f: “it” in “it results in” could be misinterpreted. Does “it” represent absolute column or calculated enhanced column or something else?

Line 105f: Eq 1 includes wind, so I suggest removing the mention of Eq 1 in Line 105 and keeping it only in Line 106.

Line 135: “Fig. Case II” should be “Fig. 3 Case II”

Line 148: Sentence is unclear with comma between “height, distance”. Should it be “available height and distance” or something similar?

Line 201: “concentrate animal” should be “concentrated animal”

Line 249: “AVG-abs960-968um” should be “AVG-abs960-968cm-1”

Line 249 and Eq 6: Should the term in the denominator of Eq 6 be the same as “(AVG-abs960-968cm-1)” in Line 249?

Eq 7: What is “abs” in the denominator here? Should it be the same as in Line 249 and Eq 6?

Line 270: Missing a word after “random” in “1000 random such as these were conducted”

Line 361: “compare, this” should be “compare this”

Figure 7: Is the time in the caption local time or UTC?

Line 441: “quantified” should be “quantify”

References:

Griffin et al. (2021): Biomass burning nitrogen dioxide emissions derived from space with TROPOMI: methodology and validation. https://doi.org/10.5194/amt-14-7929-2021

Kille et al. (2022): The CU Airborne Solar Occultation Flux Instrument: Performance Evaluation during BB-FLUX. https://doi.org/10.1021/acsearthspacechem.1c00281

Kuhlmann et al. (2022): Mapping the spatial distribution of NO2 with in situ and remote sensing instruments during the Munich NO2 imaging campaign. https://doi.org/10.5194/amt-15-1609-2022

Rowe et al. (2022): Carbon Monoxide in Optically Thick Wildfire Smoke: Evaluating TROPOMI Using CU Airborne SOF Column Observations. https://doi.org/10.1021/acsearthspacechem.2c00048

Viatte et al. (2014): Five years of CO, HCN, C2H6, C2H2, CH3OH, HCOOH and H2CO total columns measured in the Canadian high Arctic. https://doi.org/10.5194/amt-7-1547-2014