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Comment

Interactive comment on "Inter-comparison of ammonia fluxes obtained using the relaxed eddy accumulation technique" *by* A. Hensen et al.

A. Hensen et al.

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Replies to the reviewer comments

Interactive comment on "Inter-comparison of ammonia fluxes obtained using the re-laxed eddy accumulation technique&"; by A. Hensen et al. Anonymous Referee #1 Received and published: 14 November 2008 General comments This paper pro-vides a unique intercomparison of 4 REA systems for NH3, showing mixed results. The comparison is a useful exercise, and the characteristics, performances,pros and cons of each system are compared adequately and with enough detail, without over-elaborating unnecessarily. Some REA flux measurements can be convincing when compared with the AGM, but the overall impression is that such systems are unlikely ever to be used successfully to measure vertical flux divergence, which is stated as the main objective and motivator for developing REA systems.

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One problem in the interpretation of results is that the AGM flux is used throughout as a "reference" for intercomparison with the REA: to what extent should the REA actually agree with the AGM, given that there may be significant vertical flux divergences and that ideally the purpose of developing REAs is precisely to quantify this vertical flux divergence? There is potentially a problem of logic here.

Perhaps the term "reference" is slightly misleading as it implies that the AGM provides the "true" flux.

Reply: The AGM flux and it's uncertainty is discussed extensively in the paper by Milford et al. (BGD, this special issue). It is a "reference" flux in the sense that the AGM setup was used over the last decade for this type of exchange measurements. It is assumed to be the best estimate for the exchange with the current available technique. The reviewer is right that also this reference flux has significant uncertainties (as discussed by Milford et al.) which is the main reason for development of other techniques, for example the REA technique.

As for the evaluation of flux divergence. Two main reasons may lead to vertical flux divergence: a) errors caused by advection from nearby ammonia sources, b) reactions of ammonia with particulate ammonium compounds. In most studies it is difficult to quantity these effects due to the resources required. In particular a direct measurement would require determination of ammonia fluxes at several heights, such as by REA or EC methods. To avoid the possible circularity mentioned by the referee, independent measurements quantified both these effects during the Braunschweig Experiment. Loubet et al. (BGD, this special issue) report the measurement of horizontal ammonia profiles across the study field, their simulation using a dispersion model, and the quantification of advection errors. Nemitz et al. (BGD, this special issue), report on the measurement of aerosol fluxes and their interactions with ammonia, leading to quantification of gas-particle conversion rates. In both cases, the effects were found to be rather small compared with the measurement differences between the REA systems reported here. These demonstrate that, while the REA method is suitable to measure

net ammonia fluxes, it currently remains a challenge to apply it directly to quantify flux divergence in the conditions of this experiment.

Reviewer 1: Also, REA fluxes were measured at different zREA heights (between 1 and 2 m) above ground, but they are all compared with a common AGM flux, which results from concentration measurements at different heights (and thus different footprints). Thus, if there is a vertical flux divergence then there cannot be an agreement of ALL REA systems with one common reference. Please comment.

Relpy The potential uncertainty due to horizontal flux divergence is discussed in the paper by Benjamin Loubet et al. (this issue) He showed that the advection error due to the farm between 0 and 1 m height was of the magnitude ˜ 10-20 ng m-2 s-1. However the farm was at 600 m. Measurement closer to the farm or with a larger farm may lead to larger advection errors (see Figure 7 of Loubet et al., BGD, this special issue). The advection error due to the field itself (at 1 m height) reached up to - 50 to -100 ng m-2 s-1 following fertilization, which may become measurable by the REA technique. (Figure 5) Of course increasing the height difference will increase the flux divergence. A quick simulation with FIDES shows that if we look at the flux difference between z = 5 m and z = 1 m, we get this (fluxes in ng m-2 s-1):

Conclusion: This calculation shows that with increasing height the advection is expected to increase. For 1-5 m with roughly a factor of 2. The maximum height between the REA systems was (2.09-1.14) about one m. So a rough estimate would be that we can expect a difference in flux divergence of 20-30% between the systems. The divergence error at 1-2 m height is relatively small compared with the fluxes observed. A 30% difference of this effect is then not likely to explain the differences observed between the systems. When REA systems will be used (in future) to evaluate the flux divergence measurements, a setup would use identical systems at say 1- 5- 10 m height in that case the divergence effect will be larger and might be detectable (with increased analytical precision.)

Reviewer1: All REA datasets do show a deviation from the AGM at one point or another over the course of the experiment, which might be interpreted as a sign of vertical divergence, but the problem is that their divergences with respect to the AGM are not always mutually compatible (e.g. one may over-estimate while the other may under-estimate, etc...) and may be a result of sampling biases and lack of analytical precision and stability.

While the discussion and conclusion make these points adequately, the abstract is rather optimistic with respect to the applicability of the REA technique for quantifying vertical NH3 flux divergence in the future.

Reply: Indeed the REA samplers were not co-located so also horizontal divergence effects will have been different at the different locations. The point is that the scatter in the REA systems is bigger than the estimated flux divergences for both advection (at site 1) and chemistry. This means that we must improve analytical precision. Only in the case of extreme divergence (e.g. much closer to sources, would we detect the differences using REA at multiple heights),

We will change the abstract to : significant improvements in sampling precision are essential to allow robust determination of flux divergence in future studies.

Reviewer 1: Specific Comments p 3972, line 19, is the liquid flow rate of NaHSO4 really 1 l/min i.e. 60 l/hr, or rather 1 ml/min? Table 1 gives 0.8 l/min as the liquid flow for the CEH/UMIST system. Please check.

Reply: This will be changed

p 3973, line 12: "...32 mm diameter tube as inlet close to the sonic anemometer that splits into two sample tubes..." : Fig.1 does not show this, rather 2 parallel tubes all the way, one for each up- and downdrafts, thus more prone to potential sample biases.

Reply: This is an error indeed, the diameter is 1/8"; and the length is 32 cm. This will be modified.

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p 3974, line 26: "the NH3 concentrations should be equal..." Changed

p 3975, section 2.3.4: in the CEH/UMIST system the small deadband of <0.05ms-1 resulted in only a small fraction of time being spent on the deadband and thus this was deactivated. However the ECN used the same deadband (<0.05ms-1) (see line 17) but did sample into a third denuder. Presumably the time spent on deadband must have been identical to that in CEH/UMIST, so why the difference in approach (implementation vs. non-implementation of a deadband) ?

Reply: The third denuder for the ECN system was not used for the deadband so this will be removed.

p3976, lines 25-13, and Fig.2: why are AGM and REA concentrations compared at 4 different heights (zREA) rather than at one common reference height i.e. zRef= 1m above d? All that is required is to apply Eq.5 not to C(AGM) but to C(REA), scaling from zREA down to 1m using REAflux. This would allow for a better comparability of concentration levels between the 4 REA systems.

Reply: The concentration comparison is made versus the AGM level not between the different REA's. Reason is that the REA sensors might not have the >95% capture efficiency that the AGM systems have. Then the correction in concentration is also used to correct the REA flux levels. When using the REA flux to correct the REA concentration this would mean circularity in the calculations .

p3977, line 21, section 3.3: Why call this "auto"-reference mode? This was called "reference mode sampling" in Section 2.33, but also called "auto-referencing" in the abstract, and "auto-calibration" on p 2984, line 23. What is the meaning of "auto", i.e. do the authors mean that this is an automated/automatic system, or a self-referencing system?

Reply: Ok. The same term will be used everywhere: "reference sampling"; and we will add that this was implemented in to the software to operate automatically for 1 hour

every 7 hours.

p3978, line 4: a systematic difference of 15% between up- and downdrafts in the reference mode seems rather alarming, even if this can be corrected for. The text does not specify whether the down-channel over- or under-estimated relative to the up-channel, and no explanation is offered for the phenomenon.

Reply: Both the inlet and the sampler blocks might have slightly different behaviour in terms of collection efficiency. Although the flow is controlled with a MFC the two different samplers might still have had small difference in sample flow the MFC has a limited response time and switching occurs roughly at 0.5-3 Hz. This is exactly why the reference sampling is needed.

p 3979 and Table 4: the authors first compare "unselected" REA fluxes with AGM data, and then filter flux data for "proper micrometeorological conditions" (optimal fetch and u>1 ms-1) to show that the agreement is better. However, flux data that do not satisfy basic micrometeorological requirements such as fetch, turbulence and a well developed surface turbulent layer should not be displayed in the first place, and the comparison between REA and AGM should only take place for adequately selected (filtered) flux data. The text does not say whether the data shown on fig.4 and fig.5 are selected or unselected data, but they must contain micro meteorologically suitable fluxes only.

Reply: The conclusions are based on the comparison of selected data the other data under less favorable conditions is shown as a starting point and to demonstrate how subsequent steps in data evaluation improve the correlation between the AGM and REA data. We will keep the unselected data in the table. The process of selection can create a a bias in the dataset, since the conditions of selected and rejected data (esp night, cool etc) are different. We will comment on this in the text and explain that the purpose of also showing the unselected data is to show the scale of difference that the selection process makes to the overall numbers. In the figures the difference between

the total available REA data and the selected data is now shown explicitly

p 3981, line 20: could the large bias of 30% be due to differences in T or RH between up and downdrafts in very warm and presumably dry conditions, leading to different evaporation rates of the stripping solution and different capture efficiencies in the 2 denuders?

Reply: This is possible, another option is the position of the denuder in sunlight with one denuder in the sun and the other in the shadow (a shading effect) or any other technical cause that will result in a difference wetting of the two denuders.

p 3982, line 8-9, and rest of the paragraph: if the micromet / fetch conditions are un-suitable for flux measurements then these fluxes should be discarded (see comment above) for both AGM and REA. The authors seek explanations in the analytical pro-cedures for the difference in flux between REA and AGM, but if fetch or stability are a problem ("low windspeed from the east") then there could be differences in footprints of the AGM and the four REA systems (measuring at different heights). Also, errors due to advection are likely to be greatest on the first day after fertilising, and advection errors will also be height-dependent, and therefore measurement system-dependent. Again, either the fluxes satisfy micrometeorologiocal requirements, or they dont, in which case there is no case for arguing about differences between systems.

Reply: The data in the figures is now clearly markes in selected and not selected. The referee is right to say that in imperfect micromet conditions, we would not expect the different systems to agree. But we do not agree that there is no merit in data when the micromet conditions are not perfect (i.e. comments above).

p 3982, line 25: "the AGM flux estimates might actually show levels that are too high" : compared with what reference flux?

Reply: This question relates to the first point raised by referee 1(see above). The AGM flux on based on four measurements systems is the best available estimate of the flux

and used as a reference here. But as stated by the referee, also the gradient system has uncertainties. On most days the four systems agree but on a small number of days (in the text) a best and an alternative estimate are available. The remark that the AGM flux (best estimate) might be to high refers to this point discussed in the paper by Milford et al.

p 3984, paragraph 4.3.2 on sampling height: these are theoretical considerations, but in practice could these explain observed differences between the REA systems during the experiment? Please comment.

Reply: No. These considerations are of importance when chosing between 1-10-30 meter height sampling locations. It would have been nice to check for differences in the switching frequencies at the different inlet heights. This was not done.

p3984, line 23: do the authors mean "reference sampling mode"? (see comment above). My understanding is that this is not a "calibration" mode (there are no reference concentration standards applied). "Auto-calibration" should probably not be used in this context and paragraph.

Reply: Correct. We will adjust this to reference sampling throughout the text.

Typographical or language errors

Reply: (will be changed) p 3970, line 10: "...leads to the fast instrument response times BEING necessary..."

p 3970, line 20, "...estimated from measurements of fluxes OF other scalars..."

p 3971, line 18: "...other details of SITE conditions..."

p 3974, line 24 "operateD"

p 3994, the table header is missing (Table 3...)

p 3995, Table 3 is Table 4

p 3981, line 23: "the REA fluxes ... agree (no S) remarkably well"

p 3982, line 2: "seem (no S) to show.."

p 3983, line 7: "time delay" rather than "delay-time"

p 3984, line 3: an inlet cannot be "fast", but it can be "long" or "short" or "thin"...

Interactive comment on "Inter-comparison of ammonia fluxes obtained using the relaxed eddy accumulation technique" by A. Hensen et al. Anonymous Referee #2

Received and published: 31 October 2008 General Comments: The paper details an inter-comparison of four relaxed eddy accumulation(REA) systems to measure ammonia flux with an aerodynamic gradient method (AGM) used as an independent reference. The authors focus on the robustness of the REA techniques while analysis and discussion of ammonia fluxes are addressed in companion papers (as listed in footnotes). Quantification of ammonia flux using the REA technique requires consideration of both theoretical and practical issues. The authors appropriately address such issues as beta coefficient determination, deadband implementation, and detector specifications. This reviewer had initial questions concerning the individual analytical methods utilized by each REA system. Most questions were subsequently answered in latter portions of the paper.

The authors should give some consideration to reorganizing the Materials and Methods section to improve the flow of the paper. After the initial discussion of REA theory and site description, the REA systems (and their specifications) should be introduced individually within separate subsections. Discussing each REA system entirely within four subsections would provide a clearer depiction of individual system specifications. Additionally, such a restructured section would better complement Table 1 and Figure 1.

Reply: We discussed this among the authors but decided that we want to keep the

current set up. The per-setup description will indeed be easier to read but the items: inlet, sensor, deadband will be repeated in different paragraphs. Then when differences between approaches are discussed this is either fragmented across the chapter or appears double. Table 1 tells both stories either per row or per column of course.

The acronyms used by the authors to identify the REA systems are not consistent throughout the paper. For example, the ECN is referred to as ECN, ECN REA, and REA-ECN The authors should select a single acronym for each REA system and use such in the text and accompanying figures/tables.

Reply: Good comment this will be modified.

Specific Comments: Page 3968 Line 22: The addition of references for REA application on aircraft and in urban areas would be beneficial for interested readers. The literature lists previous airborne REA measurements of VOCs (Zhu et al., 1999) and isoprene (Delon et al., 2000). However, REA application in urban areas is admittedly less well documented.

Reply: We will check these articles and see where they would add info.

Lines 23-24: NH3's adsorptive properties are a direct result of its polarity. The authors should consider providing a brief explanation of this, especially as a lead in to the next sentence concerning NH3’s source/sink relationship with H2O covered surfaces.

Reply: We will add:&Like water, ammonia is a highly polar molecule, with the result that it is extremely soluble in water.However, this only explains a small part of the adsorption and desorption of ammonia with water covered surfaces. Under typical pH values of leaf surfaces ($<$pH 7), almost all NH3 reacts to form NH4+ ions (Sutton et al., 1993), thereby substantially increasing the overall amounts of ammonia that are dissolved.

Page 3969 Line 12: Quantify the approximate uncertainty range in the flux estimates. Reply: We will refer to the Milford paper here and give an indicative range.

Page 3971 Equation 3: Define all variables. Clarify the use of b0=0.4 and b1=1.9 (specifically for the coefficient for T since other variables may be utilized). Reply: Ok, this will be done.

Lines 16-17: Although Sutton et al., 2008 provides detailed site characteristics, this paper should list some key details (e.g. type of fertilizer application, vegetation height pre- and post-cutting) that are relevant to flux measurements but can be included in a concise manner. Reply: Ok a sentence will be added.

Page 3977 Line 4: Reference to CEH/UMIST usage throughout the campaign is at odds with Sec. 2.2 (page 3971) where experimental period is listed as 21 May-15 June. From Table 2, CEH/UMIST ran from 25 May -14 June. Reply: Ok, sentence will be modified

Line 11: The ECN and RISOE deadbands are specifically mentioned, but the CEH/UMIST deadband is not. Is it due to CEH/UMIST’s larger sample flow rate?

Reply: The ECN system used a deadband of 0.05 ms-1 and a correction was applied to the data according to Eq. (3). Will be modified to: The CEH/UMIST and ECN systems used a deadband of 0.05 m s-1 and a correction were applied to the data according to Eq. (3)

Page 3978 Line 4: Is there a technical issue that caused the 15% difference for ECN in upward versus downward channels during reference measurements? Reply: Yes but there are several potential reasons why this might occur. The most likely part is the sampling part where two membrane blocks are used to trap the up and down sample air. The exact cause was not found. The reference sampling episodes are used to correct for this.

Line 7: Were relative differences variable for FAL and RISOE? Reply: Yes: CEH/UMIST will be replaced with ;the other three systems;.

Line 15: r2 values in Fig. 3 range from 0.66-0.79. Why the discrepancy? Reply: The table is right. Sorry for this.

Page 3979 (13) Lines 12-14: The RISOE and ECN data have small changes in slope due to the correction factor, but the change in r2 is considerable, especially for ECN (0.11 increase). Reply: We will look in the data and see if we can find an explanation. If so this will be added in the text.

Line 17: The improvement for CEH and ECN data is substantial, but not necessarily proven significant unless statistically tested. Reply: This is true but we will not add extra stat test here.

Page 3982 Lines 6-8: Earlier in the manuscript, the fertilization date is listed as 5 June. However, these lines refer to the first day after fertilization as 5 June. Which is correct?

Reply: Fertlized 0600 to 0700 on 5 June. We will cite Paper 1 (Sutton et al.) for experimental site description.

Technical Corrections:

Page 3967 Line 2: Identify chemical symbol at first use, i.e. exchange of ammonia (NH3); Reply: Ok

Line 9-10: Consider revising for clarification, i.e. before and after both cutting and fertilizing. Reply: Will be modified

Line 22: Consider using adsorptive instead of sticky. Reply: OK

Page 3969 Line 6: Delete comma between EC and measurements. Reply: OK

Line 7: Delete one use. Reply: OK

Line 15: Remove Sutton et al. from the parenthetical reference and place in a sentence such as An overview is given by Sutton et al. (2008). Reply: OK

Page 3970 Line 6: Reword to avoid double use of given. Reply: OK

Line 6: Remove redundancy of see and e.g. Reply: OK

Line 14: Replace e.g. with ˜. Reply: ??

Lines 18-19: Place derived from fast response measurement of w’ in parentheses. Reply: OK

Page 3971 Line 2: Show equation for beta calculation from H. Reply: OK

Line 12: Check accuracy of coordinates with Sutton et al., 2008. Reply: OK

Line 14: Replace second the with a. Reply: OK

Page 3972 Line 18 and in other places: Check consistency of chemical symbol or chemical name usage. Preferably use both at first use. Reply: OK

Page 3973 Line 10: Add ; or , and between distortion and the air flow. Reply: OK

Line 27: Add s to system. Reply: OK

Page 3974 Line 1: Ortho prefix for phthaldialdehyde should be lower case letter o. Looks like number 0. Reply: OK this will be changed

Line 9: Change to in a 10 min period. Reply: OK

Line 24: Instead of in the end of the field campaign use at (near) the end. Reply: OK

Page 3975 Line 8: Separate updraft and downdraft equation into 4a & 4b or 4 & 5. Reply: OK

Line 8: Include reference(s) for equations. Reply: OK

Line 17: Change moving to dynamic. Reply: OK

Page 3977 Line 11: Delete , after ECN. Reply: OK

Line 23: Instead of using Eq. (4) using a linear write using Eq. (4) with a linear. Reply: OK Page 3979 Line 5: Change is to are to agree with plural results. Reply: OK will be

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changed

Line 9: Add reference to Table 4. Reply: OK

Page 3982 Line 2: Delete s from seems. Reply: OK will be changed

Page 3983 Line 11: Add +; indicator for positive charge on NH4+. Reply: OK will be changed

Page 3987 Line 2: Consider using adsorptive instead of sticky. Reply: OK will be changed

Page 3992 Table 1: List reference modes for FAL and RISOE, possibly with footnotes. Reply: No changes made since I do not understand what the question is here.

Page 3993 Table 2: REA System, though not the header for the first column, is listed as such. Reply: OK will be changed

Table 2: Superscript 1 in unit for u*. Reply: OK will be changed

Page 3994 Table is not numbered. I assume it should be Table 3. Reply: OK will be changed

Table 3: Add - to m-3. Table 3: Add . after No. Reply: OK will be changed

Page 3995 Change number to Table 4. Table 4: Add decimal to 0.74 on 8th row, 3rd column. Reply: OK will be changed

Page 3996 Figure 1: Change and CEH/UMIST to , CEH/UMIST. Reply: OK will be changed

Page 3997 Figure 2: Add markers on each plot denoting 5 June (fertilization date). | Reply: OK will be changed

Page 3998 Figure 3: System names should appear in bold type and possibly in upper right corners of plots to be more noticeable. Reply: OK will be changed

References Reply: We will check the two articles and if relevant for this specific article add these at the appropriate place in the text.

Delon, C., Druilhet, A., Delmas, R. and Greenberg, J.: Aircraft assessment of trace compound fluxes in the atmosphere with Relaxed Eddy Accumulation: Sensitivity to the conditions of selection, J. Geophys. Res., 105(D16), 20,461/20,472, 2000.

Zhu, T., Wang, D., Desjardins, R.L., and Macpherson, J.I.: Aircraft-based volatile organic compounds flux measurements with relaxed eddy accumulation, Atmos. Environ., doi:10.1016/S1352-2310(98)00098-3.

Interactive comment on Biogeosciences Discuss., 5, 3965, 2008.

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