Authors response to referees and interactive comments on the BGD manuscript:

"Advances in understanding, models and parameterisations of biosphere-atmosphere ammonia exchange""

by C. R. Flechard, R.-S. Massad, B. Loubet, E. Personne, D. Simpson,
J. O. Bash, E. J. Cooter, E. Nemitz, and M. A. Sutton,

with an additional contribution to this response by Y. Fauvel, INRA, Rennes, France.

We are grateful to the two anonymous referees and to A. Neftel for their positive and constructive comments on the manuscript, which are addressed in detail in the following sections. A common and important issue raised by both reviewers and by A. Neftel concerns the availability and uncertainty of Γ values, representing the $[NH_4^+]/[H^+]$ ratios for soil and vegetation, which are needed as parameters of bi-directional NH_3 models. Both referees also suggest a few useful recommendations to be added to our lists in Sections 4.1 and 4.2, which will highlight specific needs for further research.

We have used a different font and colour (Arial blue) to distinguish comment from reply. Proposed additions to the original text are shown in *underlined italics*.

Reply to Anonymous Referee #1

"As field work is usually labour-intensive it is often restricted to some periods, usually periods where interesting phenomena occur (e.g. just after spreading of manure, during senescence when higher emission rates occur) are investigated.. This is very logical. Moreover, it is also more difficult to do measurements when concentrations are low. This means that large periods of the year are underrepresented. The reality is that even in Western-Europe there are sometimes no gamma-values available at all for important crops (and these can be cereals too)… …there is a tendency to develop scientifically sound models for which the input data not are available and will not become available in the near future. So I would propose that under 4.2. also the fact is addressed that gamma-values for different regions/agricultural practises should be obtained."

We agree that measured Γ values reported in the literature for different sites in supposedly similar conditions (plant or ecosystem type, crop stage, season) can differ very significantly, and that reconciling a wide range of Γ measurements into a coherent set of data (ie explaining the observed variability using proxies such as N nutrition, atmospheric N deposition, etc) can be extremely challenging (e.g. Massad et al, Atmos. Chem. Phys., 10, 10359–10386, doi:10.5194/acp-10-10359-2010, 2010).

To some extent the first five recommendations of Section 4.2 already do recommend measurements of Γ in a wide range of conditions, either explicitly or implicitly through flux measurement campaigns. We will add a clear recommendation (see proposed text further down) advocating the measurement of Γ values for different regions and agricultural practices, with a view to both i) developing empirical parameterisations for bi-directional models and ii) validating process-based ecosystem model predictions of Γ, while also

stressing the need for long-term (annual) flux datasets to better represent background conditions.

" - Measurements of Γ values for the dominant crops, ecosystems and land uses in different climates and for different agricultural practices. These experimental Γ estimates should be collected with a view to both i) underpinning the development of empirical parameterisations for bi-directional models and ii) validating process-based ecosystem model Γ predictions. Long-term (e.g. annual, growing season) flux and Γ datasets are needed to better represent background conditions, as campaign-based measurements over fertilised systems have traditionally tended to focus on emission events. Wherever possible, the determination of Γ_s values should be attempted using different techniques (micrometeorological surface concentration extrapolation; controlled gas exchange chamber experiments; apoplastic extraction), as they tend to yield different results and the discrepancies between techniques are as yet poorly understood, given the current paucity of parallel measurements."

"As far as I know long-range atmospheric transport models do not a good job in addressing local dry deposition of NH3. This is logical, as they focus on the larger scale, but I fear that they could have some systematic error, which leads to an underestimation of the local dry deposition and therefore maybe an overestimation of the long-range transport. The first long-range transport models had only one layer and all emissions were instantaneously distributed over this layer, leading to a larger underestimation of the local dry deposition, as in reality the low-level plume is not diluted instantaneously. To overcome the error made correction factors were introduced by which a fraction of the emission was assumed to be dry deposited in the grid cell where the emission occurred (Janssen and Asman, 1988). Nowadays multi-layer models are used. In these models the emission is instantaneously diluted over the lowest layer (maybe up to 50 m), making the error somewhat smaller. Moreover, a vertical concentration profile is calculated, which results in somewhat higher concentrations near the surface and hence somewhat higher dry deposition, but the effect of that the dilution of the emission does not proceed instantaneously near the source is not taken into account and for that reason I fear that the dry deposition near the source is systematically underestimated. So maybe a point could be added: Improvement the description of the local dry deposition in long-range atmospheric transport models."

The referee is correct that deposition near the source is problematic, and may be systematically underestimated, in some cases at least, but the issue is complex. The phenomena of bi-directional exchange, discussed extensively in this paper, may result in emissions rather than deposition close to sources, and so model errors may be either over- or under-predictions. Section 3.3 has dealt with many of these issues, and given many references to further information, while Section 3.4.2 "Improved treatment of sub-grid variability…" provides the example of the "…Danish Ammonia Modelling System (DAMOS) [which] has been established as a coupled system consisting of the Danish 3-D Eulerian Hemispheric Model (DEHM) CTM covering the Northern Hemisphere (6×6km2 resolution) and of the local-scale (up to ca. 20 km) Gaussian plume dispersion and deposition model OML-DEP (400×400m2 resolution) (Geels et al., 2012)."

We have added a rather short comment on vertical gradients near the end of our manuscript (p5460), and we have re-phrased and expanded the latter to address the referees comments:

"– Development of methods for sub-grid assessments. *The accuracy and evaluation of models close to sources is a source of uncertainty, since especially NH$_3$ deposition can occur at scales substantially smaller than the horizontal and vertical extent of CTMs (e.g. Section 3.3, and Loubet et al., 2009a).* Even where network data are available, the *application and* evaluation of CTMs for NH$_3$ concentrations is hindered by *such* local scale gradients and variability (Wichink Kruit et al., 2012). *Use of plume or Lagrangian 1-D models close to the source (see Asman, 2001; Hertel et al., 2006, 2011) or* coupling of *sub-grid dispersion* models to CTMs (e.g. Geels et al., 2012) should help bridge the gap between ground-based, single point observations and spatially-averaged CTM outputs, *and could be used to help parameterise larger scale CTM models in future*."

Additional reference:

Asman, W.: Modelling the atmospheric transport and deposition of ammonia and ammonium: an overview with special reference to Denmark, Atmos. Environ., 35, 1969-1983, 2001.

"Gamma-values can be determined in different ways, e.g. from chamber measurements and from measurement of the NH4+ and H+ concentration in the apoplast. There are only a few publications where both methods were used and differences where found (e.g. Massad et al., 2009). This should be addressed and information should be given on which method should be preferred"

This point is alluded to briefly in the manuscript p5442, l12-18, in the context of modelling choices made by Wichink Kruit et al., Atmos. Environ., 44, 945–957, 2010:

"Two linear regressions were proposed, either based on literature Γ_s values derived from micrometeorological flux measurements, to be used in 1-layer χ_s/R_w or $\chi_s/\chi_w/Rw$ models; or based on Γ_s values from apoplastic extraction, to be used in 2- or multi-layer (e.g. $\chi_s/\chi_g/R_w$) models (see Fig. 7). This distinction was based on the recognition that bioassay-derived Γ_s values were typically a factor of 3 lower than micrometeorologically-derived values (e.g. Figure 1d), presumably due to additional contributions by litter and soil emissions to the latter estimates."

On the other hand, in their comprehensive review of published Γ_s mesurements / estimates, based on i) micrometeorological measurements, ii) controlled gas exchange (chamber) experiments, and iii) apoplastic extraction, Massad et al., Atmos. Chem. Phys., 10, 10359–10386, 2010, note that : "…For the compiled data, none of the three measurement methods gave a tendency towards higher or lower values compared with the other. However, the gas exchange measurements seem to give higher Γ_s values for semi-natural vegetation but this is probably due to measurements being done in high N input semi-natural ecosystems."

We agree with the referee and feel that there are too few parallel measurements of Γ_s using the different techniques and that such endeavours should be encouraged in future experiments. For this reason, however, we also feel that no single method should be singled out and preferred over the others for Γ_s estimates; rather, a combination of the different methods is advocated until enough data have been assembled from the different techniques and differences can be plausibly explained. This will be made clear in the revised manuscript in Section 4.2 as an additional item to the "Need for more Γ measurements" recommendation already mentioned above and outlined as follows:

" - Measurements of Γ values for the dominant crops, ecosystems and land uses in different climates and for different agricultural practices. These experimental Γ estimates should be collected with a view to both i) underpinning the development of empirical parameterisations for bi-directional models and ii) validating process-based ecosystem model Γ predictions. Long-term (e.g. annual, growing season) flux and Γ datasets are needed to better represent background conditions, as campaign-based measurements over fertilised systems have traditionally tended to focus on emission events. Wherever possible, the determination of Γ_s values should be attempted using different techniques (micrometeorological surface concentration extrapolation; controlled gas exchange chamber experiments; apoplastic extraction), as they tend to yield different results and the discrepancies between techniques are as yet poorly understood, given the current paucity of parallel measurements."

p. 5395. Is it possible to give reliable values for Kh and Ka? This would be better for the reader who now only gets confused.

There are several alternative parameterisations for both constants, as shown by the Montes et al., T. Am. Soc. Agr. Biol. Eng., 52, 1707–1719, 2009 review paper, or by R. Sander's Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, Max-Planck Institute of Chemistry, 1999 report (cited by Seinfeld and Pandis, Atmospheric Chemistry and Physics, John Wiley and Sons, 2006).

The Dasgupta and Dong, Atmos. Environ. 20, 565-570, 1986 parameterisation for Kh and the Bates and Pinching, Am. Chem. J. 72, 1393-1396, 1950 parameterisation for Ka tend to be used often in NH_3 exchange models (eg Nemitz et al., Q. J. Roy. Meteor.Soc. 127, 815–833, 2001).

Reply to Anonymous Referee #2

1) "…With respect to integrating current knowledge into a common modeling framework, the authors summarize a list of realistic NH_3 exchange frameworks for CTMs in section 4.1. While I agree with this list, perhaps a schematic summary would help the reader better visualize how a model containing these improvements would differ from the current NH_3 frameworks used in CTMs"

Sect. 4.1 lists a number of complex concepts which models will have to deal with. It is difficult to draw one figure which can encompass all of these concepts, it would either be very simple (similar to Fig. 4) or very complex - a mixture of the processes included already in Figs. 5, 7 and 8, with additions. The overlap of these concepts at different spatial and temporal scales (e.g. dynamic emissions and soil/litter emission potential) also complicates a simple summary figure.

We feel that the possibilities mentioned in Sect. 4.1 are best presented as text, and for this reason prefer to leave Sect. 4.1 as it is.

2) "With respect to the need for more flux measurements (Section 4.2), I think it should be mentioned that the temporal extent of the measurements should also be sufficient for the development of representative annual (semi-natural ecosystems) or growing season (crops) cumulative fluxes. Cost and logistical considerations make long-term deployments of micrometeorological NH3 flux measurement platforms extremely difficult. However, while relatively short intensive studies are highly valuable for process level investigation, development of robust flux parameterizations and datasets sufficient to understand net annual or growing season fluxes requires measurements over longer periods of time. Further development of lower cost flux measurement platforms will surely be beneficial in this regard."

The need for long-term (annual, seasonal, growing season) flux measurements was also suggested by Referee#1; see our suggestion above for an additional recommendation.

We will add a further recommendation related to the development, testing, validation and application of low-cost, long-term NH_3 flux measurement setups:

" – Development, testing, validation and deployment of low-cost instrumentation for long-term NH_3 flux estimates. Given the complexity and elevated costs associated with intensive and high-resolution NH_3 flux measurement campaigns, there have been endeavours to develop robust "low-cost, low-tech" methods for long-term flux estimates and parameterisations, such as the COTAG (COnditional Time-Averaged Gradient) system (Famulari et al., 2010). However, such systems have been successfully deployed at only a handful of sites to date, and further they lack consistent validation against established reference methods."

Additional reference:

Famulari, D., Fowler, D., Nemitz, E., Hargreaves, K.J., Storeton-West, R.L., Rutherford, G., Tang, Y.S., Sutton, M.A. and Weston, K.J.: Development of a low-cost system for measuring conditional time-averaged gradients of SO_2 and NH_3, Environ. Monit. Assess., 161, 11–27, doi:10.1007/s10661-008-0723-6, 2010.

3) ” The authors provide a rather comprehensive list of ancillary data needed to properly interpret flux measurements and parameterize flux models. There are a couple of items within the list that are important enough to warrant additional detail. First, I strongly agree with A. Neftel's comments on this manuscript regarding the need to better understand NH4+/soil interactions as related to quantification of soil emission potential (gamma). As I and others have seen, Neftel points out that the magnitude of soil gamma depends on the NH4+ extraction technique used. The literature on this point, as related to soil gamma, is not yet mature enough to provide guidance on the most appropriate extraction method for the development of representative soil gamma values. There is fundamental work to be done here, which I believe should be a high priority for further development of NH3 emission algorithms for agricultural soils. Secondly, as regional and global NH3 modeling progresses, soil chemistry data from long term ecological sites, agricultural experiment stations, soil surveys, etc will see more use. A better understanding of the relationships between extractable NH4+ and soil gamma will be needed to properly apply these data.”

We thank both A. Neftel and Referee #2 for pointing out the tricky soil extractable NH_4^+ issue and the resulting uncertainty in soil Γ values. We also concur with A. Neftel on the analytical difficulty for soil pH, which adds a further uncertainty in Γ.

To illustrate the NH_4^+ measurement issue, we refer to a report by T. Sterckeman and H. Ciesielski, Principaux facteurs influant sur la détermination de l'azote minéral des sols, In: L'azote et le soufre dans le sol, edited by P. Duc, Groupe d'études méthodologiques pour l'analyse des sols, p101-121, Editions Frontières, Gif-sur-Yvette, France, ISBN 2-86332-095-5, 1991 (in French). The authors compared the soil NH_4^+ extraction efficiencies of 1M KCl and NaCl solutions, and of different KCl solution concentrations (0, 0.1, 0.25, 0.5, 0.75, 1 or 2 M), refering to 1M KCl as their standard method. They also tested different experimental protocols for soil weight to extraction volume ratios, stirring duration, etc.
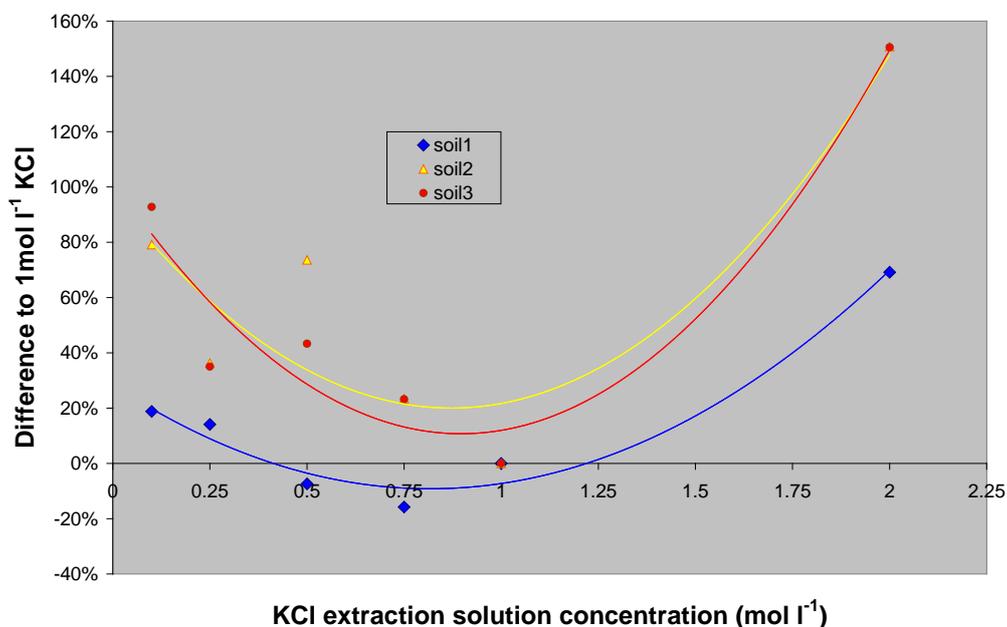
Fig. 1. Influence of the KCl extraction solution concentration (range 0.1 to 2 M) on the soil NH_4^+ extraction efficiency. The results are expressed as the percentage difference in extracted NH_4^+ relative to the 1M KCl extraction, which was the authors standard procedure.

The NH_4^+ extraction efficiency of the 1M NaCl solution was 35% to 65% lower than for 1M KCl for three silty loam soils. Further, Figure 1 shows the results of the experiment on different KCl concentrations applied to the same three soils; the NH_4^+ extraction efficiency was highest with 2M KCl in all three soils, which is consistent with A. Neftel's observations (http://www.biogeosciences-discuss.net/10/C1521/2013/bgd-10-C1521-2013.pdf), although intriguingly the extraction efficiency was also higher at 0.1 and 0.25 M (by 20 to 100%) than at 1M (which incidentally was the authors standard procedure in their laboratory). Given the U-shaped curves, one might thus conclude that the standard 1M KCl extraction systematically underestimates soil NH_4^+ (at least in this soil type).

On the other hand one might also question whether the whole soil NH_4^+ pool can actually take part in soil/atmosphere exchange and whether it is the whole NH_4^+ pool that one should target in soil extractions; or whether one should not consider two or more pools with different activities, e.g. NH_4^+ ions strongly bound to soil clay/humic colloids; NH_4^+ ions in water-filled microporosity; NH_4^+ in mesoporosity; etc. There may thus be not one but several soil Γ values with more or less relevance to NH_3 gas exchange, and the more or less aggressive NH_4^+ extraction techniques may draw from different pools.

We therefore entirely agree with Referee #2 that this whole complex question needs to feature in the recommendations for future research. We will add the following recommendation to Section 4.2:

"- Fundamental analytical research is needed to provide guidance on the most appropriate soil NH_4^+ extraction method for the development of representative soil Γ values. Many studies have demonstrated the variability of extracted/extractable NH_4^+ depending on the electrolyte used (eg KCl, $CaCl_2$) and its concentration in the extraction solution. Provided a better understanding of the relationships between extractable NH_4^+ and soil Γ, historical soil chemistry datasets from long term ecological sites, agricultural experiment stations, soil surveys, etc, could be put to use within the context of soil/vegetation/atmosphere NH_3 modelling."

4)" Parameterization of dynamic leaf surface chemistry models currently relies on measurements of the bulk chemistry of relatively large droplets collected at night and early morning or after rain events. Further testing and development of these models is hindered by the fact that the chemistry of microscale cuticular water layers present on leaves and needles during the day cannot be measured. Thus, the extent to which existing bulk chemistry measurements may be used to parameterize models used to simulate conditions of much lower canopy surface water content during the day remains unknown. While such complex models may not be suitable for use within regional or global CTMs, with further improvement they may be very useful for understanding and improving simpler models which are more mechanistically representative than current empirical approaches for cuticular NH3 exchange yet are computationally feasible for CTMs. Environmental microscopy, such as the methods described by Burkhardt et al. (2012), may represent a useful set of tools for improving our fundamental understanding of the chemical dynamics of leaf surface water during the transition from wet to dry conditions. In the absence of suitable techniques for field measurements, such laboratory techniques should be encouraged."

The Burkhardt et al. (2012) paper referred to by the referee, as well as earlier work on micro-scale leaf surface moisture-particle interactions by the same author (e.g. Burkhardt, J. and Eiden, R.: Thin water films on coniferous needles, Atmos. Environ., 28, 2001–2011, 1994), certainly have contributed a great deal to our current understanding of external leaf surface pollutant gas and aerosol exchange processes, and of the crucial role played by very thin (microscopic) water layers on "macroscopically dry" leaves, although the transcription of these processes into mechanistic models remains a significant scientific challenge. We will add a further recommendation at the end of Section 4.2 as suggested by the referee:

"- Use of environmental microscopy (e.g. Burkhardt et al., 2012) as a powerful set of tools for improving our fundamental understanding of the chemical dynamics of leaf surface water during the transition from wet to dry conditions. Further testing and development of dynamic leaf surface chemistry models is currently hindered by the fact that the chemistry of microscale cuticular water layers present on leaves and needles during the day cannot be measured. In the absence of suitable techniques for field measurements, such laboratory techniques should be encouraged."

Additional reference:

Burkhardt, J., Basi, S., Pariyar, S. and Hunsche, M.: Stomatal uptake of aqueous solutions – an update involving leaf surface particles, New Phytol., 196, 774-787, 2012.

5) "I fully agree with the author's point that there is a great need for more ground based measurements, using low-cost techniques, to aid in the evaluation of CTMs and ground-truthing of satellite data. While surface layer measurements are certainly the highest priority, there is also a need for characterization of vertical concentration profiles, particularly in agricultural areas. Aircraft measurements provide such information but are expensive. The extent to which low-cost measurement techniques could be deployed on tall towers should be investigated."

The potential for deployment of low-cost NH_3 concentration measurements such as denuders and passive samplers should certainly be investigated in the context of vertical gradients in the atmospheric boundary layer and tall tower setups, with the potential caveat that they might well lack the precision required to resolve such vertical gradients in the context of low emission areas. We will extend the existing recommendation for low-cost measurements as suggested by the referee:

"- Spatial fields of measured atmospheric NH_3 and NH_4^+ concentrations. Satellite-derived column NH_3 data offer much promise for CTM evaluation at regional and global scales, but there are still large uncertainties in the retrieved concentrations. Ground-based monitoring networks for both NH_3 and NH_4^+ by low-cost denuder/filter methods (Tang et al., 2009; Flechard et al., 2011; Adon et al., 2011) are available in only a handful of countries worldwide and should be encouraged, both for CTM evaluation and for ground truthing of satellite data. *The vertical dimension of the concentration field in the atmospheric boundary layer should also be explored; aircraft measurements provide such information but are expensive; the extent to which low-cost measurement techniques could be deployed in profile configurations on tall towers should be investigated*".

<u>Minor additional change suggested by the authors</u>

- p5447, l10-11: change "…unified EMEP 50×50km2 model (Simpson et al., 2012)…" to "…*EMEP MSC-W model (Simpson et al., 2012)*…"