Sintermann discussion measurement of ammonia emission from field-applied manure

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During the1990's the measurement methods for ammonia (NH_3) emissions got much attention in research. Field experiments were carried out to assess the NH_3 emission from field-applied manure. Most measurements focused on the relative effects of application methods, soil or crop conditions and manure characteristics on the NH_3 emission when applying manure on grassland and arable land. Results from different measuring campaigns within EU countries were published as emission factors (EF's) and results were used to model and unravel parameters that influence the NH_3 emission from field applied manure. In the Netherlands the mass balance method or integrated horizontal flux method (IHF) was selected.

Within Europe, different measuring methods were applied to assess the NH_3 emission from field applied manure. These measurement methods were recently described in a discussion paper (Sintermann et al., 2012) and further discussed in an international workshop held in Bern, Switzerland (12-13 February 2013). In this note we will provide a summary of the Sintermann paper and highlight the main results of the Bern workshop. Attached are:

- the full version of the Sintermann paper
- the proceedings of the Bern Workshop and the presentations by the Dutch participants
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Discussion paper Sintermann et al. (2012)

In Sintermann et al. (2012), different methods used to measure the ammonia volatilization of field applied manure are described, and their main advantages and limitations are discussed in detail. A large set of peer reviewed and published experiments all over Europe were collected and analysed. Two important conclusions emerged from this analysis:

- The collected data seem to show a downward trend in the emission from splash plate application over the years.
- The reported emission factors in Europe seem to show different results when different measurement methods are used.

A review was done of the different methods used for emission measurements thus far. The focus in that review was to identify potential sources of non-random errors in each measuring method. Every data set in the EU, independent of what measurement method is used, shows large variations in the derived emission factors (for one manure type - application type combination). This is caused by different factors, including:

- The accuracy of the method used to measure the emissions and calculate emission factors. This includes both random as systematic (non-random) variations. Regarding random errors, by performing a significant number of experiments the random uncertainty in the measurement method will itself average out to zero. Non-random errors, however, will shift the whole dataset up or down and thus change the average EF accordingly.
- Spatial and temporal variations in emissions are related to random variations in weather conditions (rain, wind speed, solar radiation,…), manure characteristics, and soil and crop type between measurements (within and between different measurement sites). Similar to the accuracy of the method, by performing a significant number of measurements, this random uncertainty will average out to zero.
- Not explicitly mentioned in the Sintermann paper but also important are uncertainties associated to non-proper use of the machinery needed to apply the manure into the field when using low ammonia emission techniques in combination with the application rate. This may both have a random error (some farmers will apply the manure in a proper way, some others will not) and a systematic error (if not applied properly, the emission reduction will be lower than when applied in the right way).

In the paper, potential sources of bias (systematic errors) were identified for different measurement methods.

- Chamber method, used for small scale tests
- Wind tunnel method, used for small scale tests
- Mass balance method (IHF), used in the Netherlands on 50 m diameter plots
- Zinst method, simplification of IHF, used among others and in Switzerland
- Atmospheric gradient method (AGM), preferably used for large fields
- Eddy covariance method (EC), also applied for large fields
- Plume measurements

Each measurement method has its advantages and limitations. There is no golden standard on how to do this, which is mainly due to the complexity of the ammonia emission process from applied manure:

- up to 3 orders magnitude change in the emission level over a few hours time span,
- dependency on pH, temperature, wind, soil, crop, manure etc.
- potential deposition of NH_3 anywhere outside the manured plot
- NH_3 is a very sticky gas, meaning that caution should be taken in avoiding NH_3 to be absorbed on parts of the measurement equipment during measurements

Chamber and wind tunnel measurements are conceptually simple and may be used to compare emission data on small plots from different treatments (for example using different manure types). Due to the limitations of these methods (interference with the emission process, difficulties dealing with sticky gases such as NH_3), they are not recommended to determine absolute emissions and therefore not recommended to determine emission factors (EF).
At the other end of the spectrum, plume AGM or EC measurements are in concept much more difficult to perform and require relatively expensive measurement sensors. Plume measurements are difficult to operate 24 hours a day- 7 days a week, and both EC and AGM methods in theory need multiple hectare fields to work properly.

In the Netherlands, emissions factors are determined using the IHF method, which is conceptually simple and does not have the wall effects that hampers the use of chambers. Besides, it may be relatively low cost when using time integrated samplers instead of the continuous monitors as required for EC and AGM, but as it is applied it is labour intensive. In Switzerland, Denmark (DK) and the UK similar IHF methods were used, although measurements were either done at one height only (Zinst method; Switzerland) or using wind speed dependent samplers (DK & UK).

Sintermann et al. (2012) discusses some theoretical sources of error associated to the use of all different techniques. For the Netherlands the IHF technique is relevant, for this the Sintermann paper has the following hypotheses:

Potential sources of overestimation:

- When wind speed measurements at the lowest level are suffering from overspeeding due to wind gusts wind meters (small cup anemometers).

- When the manure emission would be enhanced due to an “oasis effect”: a manured 50m diameter plot in a non-manured surrounding might emit NH_3 easier than the same area in the middle of a fully manured field.
- Backward turbulence correction, known from theory and potentially 5-20% but not measured thus far.

Potential sources of underestimation:

- When wind speed measurements at the lowest level are stopping in low wind conditions.
- When part of the emitted NH_3 passes over the top height of the measurement tower (height of the tower too low to capture the whole NH_3 plume).

It is important to point out that, apart from these effects, there are several potential sources of random error that are already tackled with the experimental work done thus far. These errors were therefore not discussed in Sintermann et al. (2012). As an example, the acid traps (impingers) used to trap NH_3 can have a <100% efficiency, which can be tested with by using a second acid trap (this is done and reported in the measurement experiments performed using the IHF method). Also, there are different integration schemes that can be used to make a combination of measured wind speeds and concentration levels (also described). Besides, calibration of the gas flow through the acid traps is done to get the proper concentration levels. The laboratorial analyses of the NH_4^+ concentration are done under proper accreditation. The wind meters need to be calibrated (and clean).

The conclusion of Sintermann et al. (2012) was that the whole EU dataset which is now used does not seem to be consistent and that still some important non-random effects in the measurement technique applied thus far might cause part of this inconsistency.
For their discussion they used Swiss field data in relation to measuring method over the past years. They concluded that the higher emissions measured in Switzerland in the past may be related to the different measurement techniques used in Switzerland.

Sintermann, J., Neftel, A., Ammann, C., Häni, C., Hensen, A., Loubet, B., Flechard, C.R. 2012. Are ammonia emissions from field-applied slurry substantially over-estimated in European emission inventories? Biogeosciences 9: 1611–1632.

International workshop Bern 12-13 February 2013

February 12-13 an international workshop was held in Bern to discuss internationally the findings presented in Sintermann et al. (2012) (Kupper et al, 2013). Participants of the workshop were mainly researchers in the field of ammonia losses from field-applied manure coming from Denmark, France, The Netherlands, United Kingdom and Switzerland.

Comments on the Sintermann paper

The Dutch WUR-team pointed out that the decreasing trend in ammonia emissions by surface application of manure, as shown in Sintermann et al. (2012), may not be real since more data from the Netherlands (NL), Denmark (DK) and UK is available. In order to verify this, available data from NL, DK and UK should be added to the database, and a new analysis should be performed. Sintermann et al. (2012) focusses on the effect of the measuring method on NH_3 emissions. Other factors such as dry matter (DM) content, total ammonium nitrogen (TAN), application rate and weather conditions may explain the large variability found in emission factors. The number of experiments aimed to measure emissions at the full scale (manure applied into a large field) is much smaller than the number of experiments done with Zinst or IHF method. If the other explaining conditions mentioned above would be different between these two data sets this may explain part of the difference in the average EF. Exchange of data sets among the participating countries can provide insight in this.

In Switzerland, old Zinst data has been recently reanalysed and it is suggested that the Swiss EF for above ground manure application may be lower than the value currently implemented in Switzerland. Applying these new emission factors will result in lower EF's for above ground application of Swiss manure compared to Dutch manure. This may be partly explained by the large difference in weather conditions, DM content, TAN and application rate of manure between the two countries (Netherlands high TAN and DM, lower (volume) application rates and more windy conditions; EF findings in the Netherlands are well comparable with findings in Denmark).

Besides, the measurement method applied in Switzerland (Zinst) and in the Netherlands (IHF) may have different sources of error when applied in those countries: not all systematic errors that might have caused a bias in the Swiss data are applicable in the Netherlands.

The Swiss method (Zinst) used measured data at one height; in the Netherlands the full concentration and wind speed profile are used (IHF method). The Swiss setup is expected to be more sensitive to assumptions on the vertical profiles of wind and concentration, Low wind conditions in Switzerland are occurring more often than in the Netherlands. Furthermore, the effect of overspeeding of the very sensitive Swiss anemometers may not cause problems in the Netherlands, where another type of anemometers is used and wind conditions are different.

Conclusion:
The fact that the Swiss reanalyses of the method previously used in Switzerland may indeed lead to a significant change in the EF is an opening for an international discussion. It is not clear if and if so to what extent a similar change may be required in other countries. However, testing the hypotheses described in the Sintermann paper for the IHF method as used in the Netherlands is strongly advised.

Summary of the recommendations from the Bern Meeting:

- Reassessment of measurements of ammonia emissions after field application of slurry. Teams will send two datasets each.
- Extension of the data base on ammonia emissions after field application of slurry used in the Sintermann et al. paper by inclusion of hitherto unpublished data
- Conclusions on measurement methods and dispersion modelling
    - The group recognizes that micrometeorological methods are the only reliable measurement techniques for the determination of ammonia losses after field application of manure.
    - The IHF method, as used in the Netherlands, can be considered as the reference method, provided that sufficient attention is paid to critical parameters such as: integration height, background concentration, shape of profile (fitting), calibration of sensors.
    - The use of several short range dispersion models is a useful tool to assess the consistency and plausibility of the calculated emissions and the measured vertical concentration profiles.
- Recommendations for international methodological intercomparison field studies

  - An international coordinated field intercomparison experiment is recommended to investigate the potential discrepancies between emission measurement methods. This should take advantage of recent advances in instrumentation (e.g. open path DOAS sensors, LIDAR) and dispersion modelling in combination with the established reference methodology (e.g. IHF method). The inclusion of an artificial ammonia source is recommended to validate all methods used to quantitatively determine emissions from field applied slurry. The intercomparison experiments should include measurements to assess if results from different emission modelling methods differ with respect to the plot size. Specific experiments should be carried out to allow a differentiation in emissions between manures with low and high DM/TAN contents in interaction with application rates.
- Use of mechanistic models (e.g. Volt'Air)
  - The participants felt that the application and further development of mechanistic models such as Volt'Air would strengthen process understanding and may reveal the influence of soil processes and other influencing factors on the observed emission rates.

A full documentation on the proceedings of the Bern meeting and the contributed Dutch presentations:

Kupper, T., M. Hansen, C. Flechard, B. Loubet, A. Hensen, J. Huijsmans, J. Mosquera, T. Misselbrook, A. Neftel, J. Sintermann, C. Amman, , H. Menzi, C. Häni, B. Achermann, R. Weber, G. Theis and C. Zundel, 2013. Assessment of NH_3 emission factors for field application of slurry, Bern workshop summary.

Huijsmans, Jan and Julio Mosquera, 2013. Ammonia emissions The Netherlands. Workshop Bern, 12-13 February 2013.

Huijsmans, Jan and Julio Mosquera, 2013. NL measurements, characteristics and measuring heights. Workshop Bern, 12-13 February 2013

Huijsmans, Jan, 2013. Volt'air and The Netherlands. Workshop Bern, 12-13 February 2013

Hensen, Arjan, 2013. Intercomparison experiments The Netherlands. Workshop Bern, 12-13 February 2013