

## ***Interactive comment on “Advances in understanding, models and parameterisations of biosphere-atmosphere ammonia exchange” by C. R. Flechard et al.***

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The authors compiled an impressive review on the subject of biosphere-atmosphere exchange of ammonia. For a long time ammonia was not in the focus of atmospheric research as it is chemically spoken a not very reactive compound or with other words a boring constituent, but nevertheless notoriously difficult to measure due to its stickiness. Also its various interactions with the different biological substrates make a quantitative description of exchange processes difficult as the review by Flechard et al. perfectly shows.

We would like to comment on two points discussed in the review.

C1521

Our review of European emission factors (Sintermann et al, 2012) of  $\text{NH}_3$  related to application of liquid manure (slurry) revealed a shift to lower emission by approx. half that seems to be correlated with the used plot size. Circular plot size with a diameter of around 40m as used mainly in the 90ies showed in average the highest emission, whereas newer measurements on larger fields showed smaller emissions. The current state-of-the-art empirical emission model by Sogaard et al. (2002), based on the Alfam database, could not predict the comparatively low emission levels from our recent field scale experiments. Hence, the current empirical knowledge insufficiently accounts for major influencing factors in some cases. As discussed in Sintermann et al, 2012, a strong dependence of the emission level on the plot size cannot be explained for comparable application conditions (meteorology, slurry conditions, soil conditions) as already pointed out by Genermont and Cellier (Agricultural and Forest Meteorology (1997) 145-167, Figure 8). The compiled data for medium sized plots consisted to a large part of published datasets from the Netherlands (Huijsman et al, 2001, 2003) and from Switzerland (Katz, 1996 Phd-thesis ETH-Zürich).

The Dutch trials are characterized by slurry with a dry matter content around 7 and application rates between 15 to 20  $\text{m}^3 \text{ha}^{-1}$ , whereas in the Swiss trials diluted slurry with a dry matter content between 2 to 4% and application rates around 30  $\text{m}^3 \text{ha}^{-1}$  have been used. In the meantime we reassessed the raw data from the Swiss trials from the 90ies and found three factors that led to a systematic overestimation of these EF's.

- Over-speeding of the custom made cup anemometers used for the wind measurements near the ground.
- Cross-interference of the plots located at distances of 70m between each other (advection errors which were not accounted for).
- ZINST scaling factor: recalculation of the ZINST relationship (first determined by Wilson et al. (1981) with a 2D bLS with only vertical wind velocity fluctuations) using

C1522

WindTrax (3D bLS, 3D turbulence) showed differing ZINST heights and factors. Applying these to the old Swiss setup would yield systematically lower emissions.

Additionally, it is possible that the used ammonia sampling device (passive diffusion samplers in an actively ventilated sample volume) overestimated concentrations in situations with strong temporal fluctuations, due to potential deposition of NH<sub>3</sub> onto internal surfaces during periods with high concentrations, followed by remobilization from the surfaces during phases with cleaner air. An ongoing new measurement series in Switzerland using both medium and large scales clearly confirms the lower levels and also shows no differences between different plot scales.

We feel that the interaction of ammonium with soil particles play a key role in driving ammonia emissions. As shown in the review the  $\Gamma$ -concept is very successful in explaining potential emissions. In case of  $\Gamma_{soil}$  there are analytical difficulties as both the pH and the NH<sub>4</sub><sup>+</sup> concentrations do depend on the used extraction technique. At our institute the default methodology to determine NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentration in soil samples is a rather weak extraction using 0.01m CaCl<sub>2</sub> that deliver values that reflect plant available inorganic N. Soil extractable NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> are determined with 2M KCl, thus a much stronger extraction solution. The values that were indicated in Felber et al. (2012) were done with 0.01m CaCl<sub>2</sub>. With this method only a minor fraction of added fertilizer- N could be extracted. The fast disappearance of NH<sub>4</sub><sup>+</sup> is therefore only an indication for fast nitrification, but not a proof. Further experiments showed that even with the stronger KCl extraction for our soil type, added ammonium with slurry could not be fully extracted.

The following table shows an example of the extraction efficiency with different methods. 3 ml slurry (TAN content 0.6 g N l<sup>-1</sup>, DM content 3%, pH =7.7) was added either directly to the extraction solutions or first to 20g fresh soil from Reckenholz (mineral soil with a clay content of 19%, pH = 6.3). We compared 0.01m CaCl<sub>2</sub> and 2M KCl extraction solutions.

C1523

Slurry applied (mg NH <sub>4</sub> -N)	Extraction solution	Soil	Type elapsed before extraction	Extracted amount of ammonium (mg NH <sub>4</sub> -N)
1.9	0.01M CaCl <sub>2</sub>	none	none	1.68 / 1.74
1.9	2 M KCl	none	none	1.64 / 1.79
1.9	0.01M CaCl <sub>2</sub>	Reckenholz	1 min	1.1 / 1.1
1.9	2 M KCl	Reckenholz	1 min	1.4 / 1.6
2.85	0.01M CaCl <sub>2</sub>	Reckenholz	1 hour	0.33 ± 0.12
2.85	2 M KCl	Reckenholz	1 hour	0.75 ± 0.01

Given the incomplete extraction by either method, it seems likely that  $\Gamma_{soil}$  derived  $\chi_{zo}$  are not reliable. Generally we feel that ammonium - soil particle interactions and microbial processes in the soil must gain more attention in explaining biosphere-atmosphere exchange processes of ammonia.

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C1524

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