

Short comment:

We read with great interest the manuscript “Soil-atmosphere exchange of ammonia in a non-fertilized grassland: measured emission potentials and inferred fluxes” by G. R. Wentworth et al. It provides an observational large scale characterization of NH₃ (and other chemicals) during a 50-day campaign over a non-fertilized grassland in Ontario, CA. The results show that the emission potential for non-fertilized grasslands is way below (up to 2 orders of magnitude) the values proposed in previous studies for fertilized lands. The NH₃ fluxes obtained during the campaign were also validated against previous literature showing a relative good agreement. An analysis using a Lagrangian model assesses the air parcel history and therefore identifies the possible impact of various emission sources on the chemical composition. The authors have found that NH₃ – contrarily to all the other chemicals investigated - does not show a bias due to the different air mass directions, suggesting that the NH₃ near surface is mainly controlled by emission/deposition rather than horizontal advection or entrainment. This is somewhat surprising since non-fertilized grasslands have a lower emission potential if compared to fertilized lands – as also mentioned in this manuscript. Maybe some extra clarification can be given.

Despite the characterization, the authors have discussed only qualitatively the morning increase of NH₃. Several explanations are suggested – dew evaporation, volatilization of NH₄NO₃, surface emission and NH₃ rich-air entrainment at the top of the boundary layer – however, the contribution of the various processes to the diurnal variability of NH₃ have not been well quantified. We believe these features can be explored more carefully – and in a quantitative fashion - by the use of mixed-layer theory (Barbaro et al 2013 and references therein). This type of analysis has also been performed for other chemical species (see van Stratum et al 2012 – Figure 6). By doing so, the specific contributions to the diurnal variability of NH₃ driven by turbulent mixing, advection and chemistry are quantified on time.

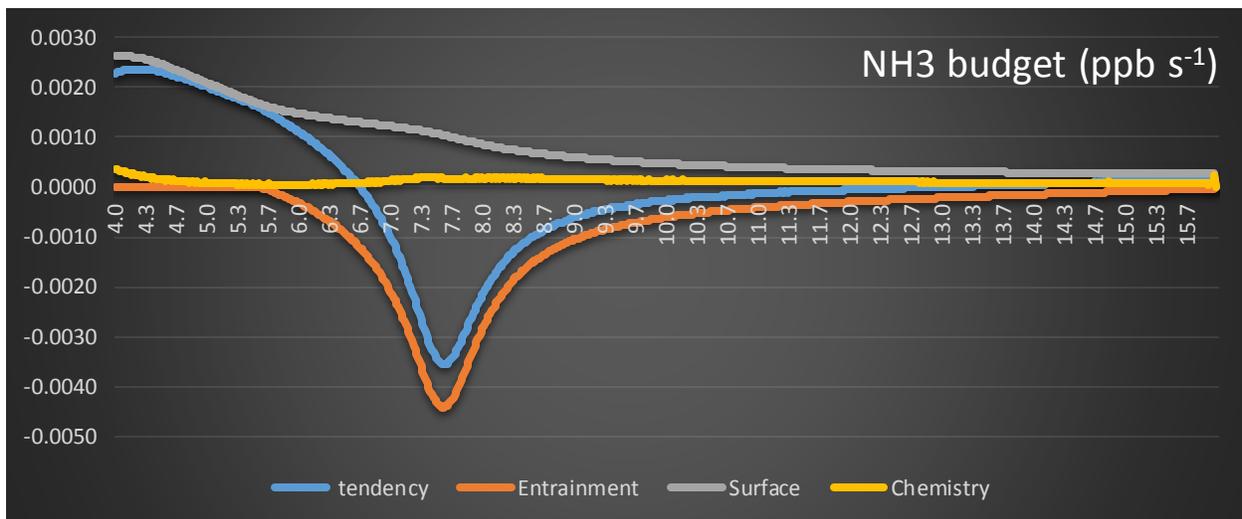
Specifically, in Sect 3.2 and in Sect. 3.4 the role of the boundary layer dynamics (entrainment and CBL growth) and chemistry on the morning increase of NH₃ can be fully quantified. In that context, we would suggest the authors to analyze the NH₃ budget.

The conservation equation for NH₃ assuming horizontal homogeneity and neglecting advection – as suggested in the manuscript, reads:

$$\frac{\partial \overline{NH_3}}{\partial t} = \frac{\overline{w'NH_3'_s} - \overline{w'NH_3'_e}}{h} + CHEM$$

where the first term on the right hand side is the divergence of the NH_3 vertical flux. Note that the flux divergence contains (i) the surface flux ($\overline{w'NH_3}'_s$ emission and deposition) controlled by plant and soil processes and (ii) the entrainment flux, controlled by NH_3 rich/poor-air entrained from the nocturnal residual layer or free troposphere. The last term stands for the chemical NH_3 formation/destruction. By calculating the budget it will be possible to better explore (quantify) the role of the NH_3 bidirectional exchange.

To further support our argument, we include here a time evolution of the budget analysis (for NH_3) during the convective period over grassland for the Netherlands (manuscript in preparation). Here, the free tropospheric NH_3 concentration (around 1 ppb) is much lower than the CBL values (ranging from 10-20 ppb during the day). The CBL depth ranges from 150 m in the morning up to around 1500 m in the afternoon. We observe that during the morning the bulk-averaged NH_3 tendency is explained both by the emission/deposition of NH_3 and the entrainment of NH_3 -poor air from the free-troposphere. Note the role of the CBL growth on the time evolution of the NH_3 tendency. The chemistry contribution remains small during the whole convective period but can be relevant depending on specific chemical conditions (e.g. NH_4NO_3 volatilization and HNO_3).



Lastly, the discussion of the results shown in Figures 3-5 can also greatly benefit by the use of mixed-layer theory. For instance, the atmospheric concentrations shown in Fig. 5 can be modeled with a mixed-layer model providing an extra validation component to the manuscript. In case the authors are interested, the mixed-layer code (MXLCH) used in the two references provided here is freely available including a complete documentation.

References:

Van Stratum et al (2012): Case study of the diurnal variability of chemically active species with respect to boundary layer dynamics during DOMINO: *Atmos. Chem. Phys.*, 12, 5329–5341.

Barbaro et al (2013): Impacts of Aerosol Shortwave Radiation Absorption on the Dynamics of an Idealized Convective Atmospheric Boundary Layer *Boundary-Layer Meteorol* (2013) 148:31–49 DOI 10.1007/s10546-013-9800-7.