Dear Editor,

Below, there is a list with our replies and changes to the points raised by the reviewers. In addition, we will send you by e-mail (since the online-routine only allows one pdf upload) a pdf of the revised manuscript where all relevant changes have been marked.

Kind regards, Jörg Sintermann and co-authors.

Reviewer1:

reviewer:

p.6521 last paragraph: details such as “Federal Research Station”, the location and the long parentheses with instrument names should not be in Introduction. They appear in Methods section anyway.

- authors: agreed; we leave out this paragraph since its content is given in the method section. The introduction now ends: “The focus lies on TMA emission pathways in dairy systems, investigated by ambient trace gas concentration as well as laboratory dynamic chamber measurements. We further discuss the fate of the identified agricultural TMA emissions and their role in secondary aerosol particle formation.”

reviewer:

p.6525 r2: Schallhardt et al. “in preparation” is not a valid reference. If this is not submitted to a journal by the time of revision, then I suggest to provide an outline of the calibration and calculation procedures here as “Supplementary Material”.

- authors: The manuscript is currently in preparation, therefore we provide a short PTR-TOF calibration/calculation scheme in the supplement.

Supplement:

“This text originates from a manuscript by Schallhart et al. (in preparation).

The PTR-TOF was used for the amine measurements because of its high mass resolution, which allows for TMA (C3H10N1+, 60,0808 Th) measurements with almost no influence of the acetone/propanal isotope (C2[13C]1H7O1+, 60.0525 Th) (Fig. A1). Its high measurement frequency enables to follow emissions from cattle and separate different activities such as breathing and ruminating. The PTR-TOF and CIMS TMA sensitivities were calculated by a cross calibration with impinger samples, which were analyzed by ion chromatography. The PTR-TOF calibration was done by pumping VOC free air (produced by a catalytic converter) through a semipermeable tube connected to the two instruments and the impinger. The semipermeable tube was submerged in an aqueous solution of TMA and NaOH (pH of 10.7), which was inside a temperature controlled bath. The TMA diffused through the membrane and by keeping the TMA mixture temperature and the zero air flow constant, therefore produced a continuous TMA source. The influence of the inlet-line walls, temporarily adsorbing TMA, was mitigated by using equally long tubing between the source and the

PTR-TOF as well as between the source and the impinger. The PTR-TOF spectra were monitored in order to ensure that the TMA signal was stable. We integrated the signals of the mass spectrometers for the same time period as the impinger sampling. After the calibration the variation of the sensitivities, potentially caused by ambient temperature and humidity variations and changes of inlet line behavior, were considered: sensitivity changes over time were determined from several parallel ambient TMA measurements by impingers and PTR-TOF and were then used for the whole measurement period using linear interpolation. The median sensitivity was 4.2 ± 1.1 ncps/ppb.

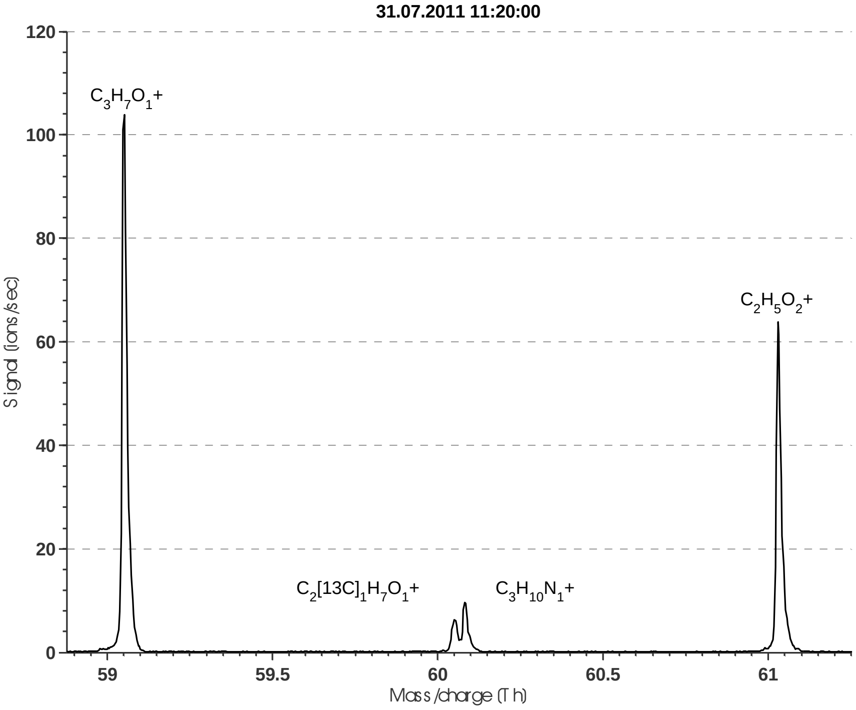

Figure A1: Part of the PTR-TOF mass spectrum with a 1 minute integration time. The high mass resolution of the instrument, allows to separate the acetone/propanal isotope peak (C2[13C]1H7O1+) from the TMA peak (C3H10N1+)”

reviewer:

p.6525 r25: “sticky molecules” is too casual, replace with “concentration”.

- authors: we leave out “of the sticky NH3 molecules”

reviewer:

p.6526 r19: CH4 background of 7 ppm is very high. Is this a typo (Fig. 2 would suggest that)? Or is there a strong CH4 source permanently upwind of the experiment location?

- authors: the expression “CH4 background” is, in our context, indeed misleading and a value of 7 ppm would be too high for conditions without additional source influence. In our case, however, the measurements took place in a situation with several CH4 sources rather close by, for example: the slurry pit, silage storage, polluted surfaces. Such sources elevate the local CH4 concentration, and on top of that we identified concentration increase associated with the action of present cattle. Periods without strong cattle CH4 emissions were before the morning milking, between milkings, and mainly during night, which is the reason for the given 7 ppm value (CH4 concentrations increased in the stable nocturnal boundary layer). In the manuscript the expression “Background concentration levels” is replaced by “Typical concentration levels without the direct influence of animals” and we specify the corresponding concentration as a range between approx. 3 and 7 ppm.

reviewer:

p.6527 r11: At what height were wind speeds measured? Was temperature measured, too? Temperature affects NH3 emission rates; those of TMA as well?

- authors: Wind speed was measured at 1.5 m above ground, as was air temperature. Temperature was lowest in the early morning with 13 to 15 °C, and peaked during daytime with 23 to 26 °C. Temperature affects NH3 and also TMA solubility. This argument is used in the discussion, p. 6530, l.4-7.

reviewer:

p.6529 r11-15: There is nothing wrong in these sentences about CH4 release, but it may be worthwhile pointing out more clearly that the CH4 peaks are less frequent than those of acetone, because CH4 release occurs with every “burp” while acetone release (apparently) occurs with every breath. Hence, correlation of the two time series is actually quite poor (Fig. 3a).

- authors: Yes, we will state this more clearly with an additional statement:

“The high CH4 peaks appear less frequent than those of acetone, because CH4 is more related to eructation while acetone is rather associated with exhalation. Both time series are hence not well-correlated.”

reviewer:

p.6536 r9-14: If the lifetime is only 1 min, why is dispersion considered for 8.4 min? How was the dilution “down to 1 ppt” obtained, from a model calculation or a reference? Why is “mixing … with cleaner air” considered separately, when it is the very same process of turbulent mixing that spreads a plume and entrains air from outside its initial boundaries to the inside? Please rework this passage.

- authors: We agree with the reviewer that it would be desirable to consider all processes within one consistent dispersion-chemistry model. For simplicity, however, we split the reduction of the TMA concentration into dilution and condensation, the latter representing the lifetime given in the manuscript. The TMA lifetime is between 30-1000 seconds due condensation to pre-existing aerosol particles. The lifetime of 1 minute was chosen as the best estimate for typical central European conditions and the very long lifetimes is estimated only for very clean environments. As stated on page 6535 line 18, when amine concentrations exceed the sulphuric acid concentration nucleation rates will be increased substantially. Lifetime is defined as the time it takes for the concentration c to be reduced to a concentration of 1/e*c. On average we measured approx. 10 ppb TMA. In central Europe the concentration of sulphuric acid is in the order of 0.01 ppt. On the one hand, we calculated the time of 8.4 minutes which it takes for the typical TMA concentration to be depleted below 1 ppt sulfuric acid concentration by the condensation on particles. On the other hand, the 1 : 100 dilution is an estimate based on dispersion modelling during typical daytime boundary layer conditions over the travel time of 8.4 minutes. This exercise is supposed to give an impression of the possible dispersion time window for TMA availability of a farm source to contribute to particle formation. We will rephrase the paragraph in the manuscript for clarification.

"Given a lifetime of 60 s, estimated to reflect a typical condensation sink with respect to central European aerosol particle concentrations, TMA and other aliphatic amines cannot travel far in the gas phase. For example, a plume with 3 m s-1 wind speed would advance 1.5 km within 8.4 min, while the condensation sink would reduce the initial 10 ppb down to 1 ppt. In addition to the loss on particles, the TMA plume is diluted with cleaner air during dispersion. Assuming typical boundary layer conditions, dilution of that plume over 8.4 min would downmix the concentration of a (conservative) gas by roughly 1 : 100 (calculated by bLS dispersion modelling: Flesch et al. (2004)). In the case of TMA, concentrations would have fallen below values typical for sulphuric acid. Consequently, gas-phase TMA could determine aerosol particle formation relatively close to the source while the further away NH3 begins to dominate the formation."

reviewer:

Fig. 2: Nice display of some essential results. The NH3 time series looks rather messy, though, not as convincingly affected by excretion and scraping as the TMA time series. Also, there is no clear diurnal cycle.

- authors: it is our experience that, in a high concentration regime caused by local sources such as the farm itself, it can be common that the concentration at one location fluctuates strongly around the mean value within a given time period of, say, 10 to 30 minutes (e.g. Sintermann et al., 2011, Atmos. Meas. Tech. 4, 599-616). In Fig. 2 of the present manuscript, the anyway high NH3 concentrations at the farm are even more increased by the NH3 emissions from the cow's excrements during and subsequent to their presence in the stable. It seems like the related concentration increase and considered temperature dependence is less pronounced for NH3 than for TMA. On the baseline of these peaks (occurring in the morning and afternoon) the NH3 concentrations do increase slightly again in the night, associated with a stable nocturnal boundary layer frequently forming in that area.

reviewer:

Also Fig. 2: Why is acetone elevation higher and more prolonged after the afternoon milking than it is after the morning milking? I find this counter-intuitive because stronger accumulation should occur in the morning when stratification tends to be stable, rather than in the afternoon when I would expect good mixing due to unstable stratification. This is not really the topic of this paper, but I'm still curious.

- authors: This has to do with the time period the animals spend in the stable, which was longer in the afternoon than in the morning. Also, the typical management (here: gathering of animals) resulted in a higher animal density at the open-air waiting yard in the afternoon, thus more concentrated emissions. The difference is not so pronounced for CH4. It might be the case that the animal behavior varied during the day, e.g. that the cows ruminated/eructated differently during the course of the day.

Technical comments have all been considered in the revised manuscript, see attached pdf

Reviewer2:

reviewer:

1) The authors should make it clear that this study is only a case study, that its results should be used with cautions when scaling to a global level.

- authors: We fully agree with this remark and we will add a statement pointing this out. However, as amine measurements, especially flux measurements, are rare our up-scaling exercise is intended to give the case of an order of magnitude.

"This upscaling, based on our individual flux measurement experiments, provides a case-study. Yet, it concurs well with the broad knowledge about agricultural TMA volatilisation as discussed above. Flux measurements under a wide range of environmental conditions would be required for a more detailed assessment."

reviewer:

2) The discussions on TMA influences on particle formation are a bit skeptical as all the discussions are based on previous studies, without a clear connection with the findings of this work. The authors give no details on their estimated lifetime of 30-1000s using the model of Kulmala et al. (2012). TMA and other amines may have a longer life time as it neutralizes the acids rather than being attacked by oxidants (such as OH radicals), its partitioning may be influenced by the RH, temperatures, etc.

- authors: It is right that our discussion on TMA influencing particle formation is based on previous studies. We point out how the identified emissions of agricultural TMA, and according ambient concentrations, which are at maximum only a few percent than that of ammonia, behave in the atmosphere according to recent findings. This discussion, which has not been elaborated with focus on agricultural emissions elsewhere, sets the context of how to interpret the relevance of the presented agricultural TMA emissions and we thus consider it relevant. The abundance of TMA in the gas phase is crucial for enhanced aerosol particle formation rates and the lifetime of gas-phase-TMA is determined by both oxidization and condensation. We agree with the reviewer and state that it amounts to 4.6-7.7 hours due to oxidation in atmospheric conditions. This is orders of magnitude slower than the calculated loss due to condensation and thus we neglect it in the lifetime calculations. Changes in RH and temperature influence e.g. the OH oxidation capacity and evaporation rate. However, they do not affect the condensation sink. Formation of amine salts is indeed a possibility to promote transport of amines further downwind. However, after TMA has formed a cluster with a neutralizing acid, re-evaporation of the TMA it is thought to be unlikely. The lifetime of TMA due to condensation is determined by 1/CS (condensation sink). The CS itself can be calculated as stated in Kulmala et al. (2012), PROCEDURE, Step 9: Calculate the size distribution–dependent particle loss parameters.

We clarified the calculation method and slightly changed the text to:

"The lifetime due to condensation is the reciprocal of the condensation sink, which is determined by the aerosol number size distribution. The TMA lifetime due to condensation on aerosol particles was calculated according to the condensation sink method calculation by Kulmala et al. (2012), using the diffusion coefficient of TMA. We derive a TMA lifetime due to condensation in the range of 30 to 1000 s: half a minute for the case of a number size distribution (aerosol load) as found in the plume of a German cattle farm (Schneider et al., 2008), several minutes in cleaner environments such as in a boreal forest in Finland (Dal Maso et al., 2007)."

reviewer:

3) The correlation coefficients should be provided for Figure 3.

- authors: as suggested we provide the correlation coefficients

Other changes:

We unfortunately misspelled our Co-author, without noticing… His real name is Schallhart and we have corrected this. We have added thanks to Markku Kulmala in the acknowledgments.