Reviewer's comments on ACPD-2016-259 manuscript "Trends in atmospheric ammonia at urban, rural and remote sites across North America" by X. Yao and L. Zhang

General comments

The paper presents an analysis of temporal trends, and to some extent spatial patterns, of long-term (>10 years) ambient atmospheric ammonia (NH3) concentrations measured across Canadian and US air pollution monitoring networks. Temporal trends are compared between a selection of 14 urban, rural and remote sites by using statistical trend analysis tools (Mann-Kendall, M-K and Ensemble Empirical Mode Decomposition, EEMD). The paper provides a useful and original study of NH3 trends at the N. American continental scale, and fits well within the scope of Atmospheric Chemistry and Physics, even though one may deplore the fact that not all sites and data available in the networks were analyzed.

Long-term trends are interpreted in terms of changing emission patterns and changing pollution climate and temperature, but some of the arguments and hypotheses are less than compelling. In particular the argument that increasing NH3 concentrations at some sites may be explained by a significant upward trend in mean temperatures on such short time scales - from a climatological viewpoint (only 10 years) - does not sound convincing, especially since no long-term temperature data are shown alongside the NH3 concentration time series.

Generally the paper could be improved by a better description of the methods used, both in terms of measurement techniques and statistical methods, and the figures should be re-arranged to combine the actual measured time series with the trends analysis to better illustrate the arguments.

Specific comments

<u>Methods</u>

p6, l96-100: please provide more details of the sampling and measurement techniques used in NAPS and CAPMON: which PM2.5 sampler is used (name/manufacturer), are the denuders wet or dry, what is the sample flow rate, are the data hourly or daily integrated values, how is NH4+ measured in the lab after extraction, or is it in-situ online analysis, etc...??

p6, l100-107: I agree that missing data are an important problem when dealing with the analysis of long term temporal trends, especially if the downtime periods are not randomly distributed but might tend to coincide with specific weather patterns, eg very cold or very wet, etc. Thus it would be useful to indicate the monthly/annual data capture rates (eg number of days per month of available data, or rates of missing data, whichever) alongside the measured concentrations in Figs. 2-3, on a separate axis with a different color or symbol. For example show the missing data rate as a vertical bar for each month, so the figure wouldn't be too cluttered.

p8, l133-141: please provide very briefly the mathematical basis of the statistical method (in which way

does it differ from a parametric procedure?)

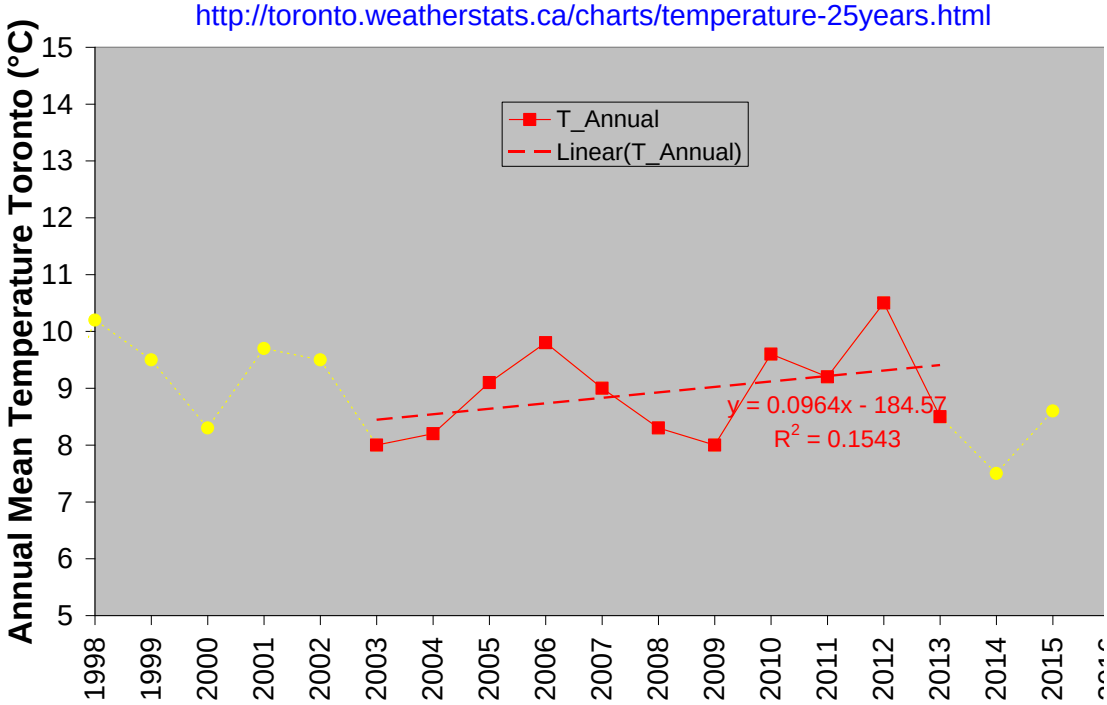
Results and discussion

p10, l189-193: is there any actual evidence from on-site observations that fertilization takes place in the fall at or around Site 3? Why should there be any fertilizer application after harvest and just before winter, when there is no longer any nitrogen demand from crops?

p13, l259-263: I think it highly unlikely, from a thermodynamic viewpoint, that freezing conditions would boost NH3 emissions from green areas. In cold conditions the Henry coefficient will not favour a shift to the gas phase, but to the condensed phase, and cold temperatures also reduce (micro-)biological activities. I don't actually recall that Flechard et al. (2013) made the argument that higher NH3 emissions from grasslands could be expected under freezing conditions. However, higher NH3 concentrations may occur in the atmosphere in very cold weather for two reasons, i) surface/canopy resistance to dry deposition is higher for a frozen surface, and thus the dry deposition sink strength is reduced and the atmospheric lifetime of NH3 is higher, and ii) if cold weather is associated with a shallow boundary layer and stable conditions (temperature inversion) then NH3 accumulates in the boundary layer at the Earth's surface.

p15, l303: Was there really a significant and steady temperature increase in Downtown Toronto over the 10-year measurement period, that could explain the increasing NH3 trend? How large was the corresponding temperature trend, what was the interannual mean temperature range? From Fig. 4 (right-hand Y axis of upper panel) it looks as though the minimum annual mean temperature was around 8°C, and the maximum value was around 13°C, ie an interannual range of around 5°C, which seems rather large. According to the website weatherstats.ca, the mean annual temperatures in Toronto only ranged from 8 to 10.5 °C during the period 2003-2013 (see below), with no systematic or significant upward trend. I therefore wonder about the accuracy of the temperature data used in producing Fig.4: is it likely that the Toronto mean annual temperature may have been as high as 13°C over that period? In my view this casts some doubt over the argument that an increasing temperature trend was responsible for the increasing NH3 trend. I would encourage the authors to double-check the time series of annual mean temperatures and to show the data in the revised version alongside the mean annual NH3 data.

http://toronto.weatherstats.ca/charts/temperature-25years.html



However, I find the argument of the decreasing SO2 emission more convincing, for two reasons: a decreasing SO2 concentration would lead to less NH3 uptake by acidic (sulphate) aerosols, which is duly mentioned in the paper, but also because less SO2 dry deposition would make the surface less acidic, or more alkaline, which could increase the surface resistance for NH_3 (eg Fowler et al., Atmos. Chem. Phys., 15, 13849–13893, 2015, www.atmos-chem-phys.net/15/13849/2015/).

p19, l375-376: "... the long-term change in ambient T possibly dominated the long-term trend in atmospheric NH3 at the site." Again, I don't deny that there is a strong positive correlation between ambient NH3 and temperature on a seasonal or annual basis, or between sites across a continental temperature gradient; this has been shown elsewhere many times, and the reasons for this are mainly thermodynamics and biological. However, what I don't really believe is that there was such a large and systematic increasing temperature trend from year to year over the 10-yr time period considered.

I do however agree that over the long term, climate change and the forecast temperature increases of a few °C will likely result in increased emissions and atmospheric concentrations (See Sutton et al., 2013), but the present dataset is unlikely to show this conclusively, the noise in the signal being likely too high.

Conclusion

p21, l437 onwards: I expect that the "significant decreases in anthropogenic NH3 emissions from main sectors" were calculated on the basis of activity data and related emission factors, which are notoriously highly uncertain and which do not necessarily reflect the true impacts of meteorology and other controls on the NH3 emission processes, if at all. We could therefore argue that the large expected decreases in

agricultural NH3 emissions (as shown in Fig.3) may not necessarily have occurred to the extent they were supposed to. For example, some supposedly "low-emission" slurry spreading techniques that have been introduced over the last 20 years (in Europe, but probably also in N. America?) may not be that efficient after all, and there are also strong methodological issues to be examined regarding the published emission factors (eg Sintermann et al., 2012, http://www.biogeosciences.net/9/1611/2012/bg-9-1611-2012.pdf). The issue of the Dutch ammonia gap, mentioned at the start of the paper, may in part have been a consequence of large uncertainties in NH3 emission inventories and their temporal evolution over the last 20 years.

p21, l440: in addition to changes in biogenic emissions (which may or may not have happened as a consequence of changes in temperatures, as discussed above) and to the changed gas/aerosol NH3/NH4+ partitioning, I would add the possible decrease in NH3 dry deposition rates caused by lower SO2 deposition rates and impact on surface chemistry (eg Fowler et al., Atmos. Chem. Phys., 15, 13849–13893, 2015, www.atmos-chem-phys.net/15/13849/2015/)

Technical corrections

In the methods section, there should be two sub-sections, 3.1 NH3 concentration measurements, and 3.2 Statistical methods

p3, l43-44: suggest change to "...the long-term trend in atmospheric NH3 observed in some countries **didn't reflect the** dramatic decrease in NH3 emissions..."

p6, l89: suggest change to "... compiled from three data sources, i.e., the **Canadian** National Air Pollution Surveillance (NAPS,..."

p6, l91: suggest change to "... (CAPMoN), and the **U.S.** Passive Ammonia Monitoring Network..."

p7, l127: change to "...were **referred** to as Site 7-14..." (not "*refereed*")

p8, l135-137: change to "... Campata et al., 2008). Considering **that** the data flaws aformentioned were indeed **present** in our selected datasets to different extents, the M-K analysis..."

p9, l167: change "*Whitehand*" to "**Whitehead**"

p11, l217: "**Texas**", not "*Taxes*"

p13, l243: "...was much small**ler**..."

p17, l347: I believe the figure referred to is **Fig S3c**, not *S3b* ?

p20, l417: "...This increase **alone** is not enough to explain..."

p21, l431-432: "respectively, across ~~**the**~~ North America..."

In Fig S3 (all three panels) in the supplement, change "*Argriculture*" to "**Agriculture**"

Figures and Tables

In Figures 2 and 5, and also in Figs S1 and S2, the letters "a,b,c,d, e,f,g,h" in each panel should be changed to Site 1, Site2, .. Site 14

Figure 1: Rather than the split American/Canadian, it would be useful to differentiate and identify sites on the basis of the NAPS, CAPMON and AMON split

For clarity, it would be better to merge Figs 2 and 5, and also Figs 3 and 6, to show both the measured data and the derived trend lines on the same figures.

Table 1: For each site please provide Lat, Long, Elevation, name of network (NAPS, CAPMON or AMON), land use (urban, agric, remote)