Quantifying spatial and seasonal variability in atmospheric ammonia with in situ and space-based observations

Robert W. Pinder,[1] John T. Walker,[1] Jesse O. Bash,[1] Karen E. Cady-Pereira,[2] Daven K. Henze,[3] Mingzhao Luo,[4] Gregory B. Osterman,[4] and Mark W. Shephard[5]

[1]   Ammonia plays an important role in many biogeochemical processes, yet atmospheric mixing ratios are not well known. Recently, methods have been developed for retrieving NH_3 from space-based observations, but they have not been compared to in situ measurements. We have conducted a field campaign combining co-located surface measurements and satellite special observations from the Tropospheric Emission Spectrometer (TES). Our study includes 25 surface monitoring sites spanning 350 km across eastern North Carolina, a region with large seasonal and spatial variability in NH_3. From the TES spectra, we retrieve a NH_3 representative volume mixing ratio (RVMR), and we restrict our analysis to times when the region of the atmosphere observed by TES is representative of the surface measurement. We find that the TES NH_3 RVMR qualitatively captures the seasonal and spatial variability found in eastern North Carolina. Both surface measurements and TES NH_3 show a strong correspondence with the number of livestock facilities within 10 km of the observation. Furthermore, we find that TES NH_3 RVMR captures the month-to-month variability present in the surface observations. The high correspondence with in situ measurements and vast spatial coverage make TES NH_3 RVMR a valuable tool for understanding regional and global NH_3 fluxes. **Citation:** Pinder, R. W., J. T. Walker, J. O. Bash, K. E. Cady-Pereira, D. K. Henze, M. Luo, G. B. Osterman, and M. W. Shephard (2011), Quantifying spatial and seasonal variability in atmospheric ammonia with in situ and space-based observations, *Geophys. Res. Lett.*, *38*, L04802, doi:10.1029/2010GL046146.

1. Introduction

[2]   Ammonia (NH_3) is the atmosphere's most abundant alkaline compound and plays an important role in several biogeochemical processes [*Seinfeld and Pandis*, 1998]. In the presence of nitrate or sulfate, ammonia enhances the formation and growth of particles [*Napari et al.*, 2002], which impact the earth's climate [*Abbatt et al.*, 2006] and are statistically correlated with human health effects [*Pope*, 2000]. When deposited in sensitive ecosystems, ammonia contributes to acidification [*Pearson and Stewart*, 1993] and eutrophication [*Paerl et al.*, 2002].

[3]   Despite the importance of ammonia, the sources, sinks, and transport are poorly understood [*Schlesinger*, 2009]. Ammonia emissions are largely from agriculture and are driven by farming practices and weather. The largest removal process is deposition to surfaces; however, the biosphere can re-emit ammonia in complex ways [*Massad et al.*, 2010]. Furthermore, ammonia is difficult to measure in situ at relevant mixing ratios (<10 ppbv) [*von Bobrutzki et al.*, 2010]. The in situ measurements that are available show high levels of spatial and temporal variability [*Carmichael et al.*, 2003; *Walker et al.*, 2004].

[4]   Recent efforts have used remote sensing techniques to measure NH_3 from the Tropospheric Emission Spectrometer (TES) [*Beer et al.*, 2008] on the Aura satellite and the Infrared Atmospheric Sounding Interferometer [*Clarisse et al.*, 2009, 2010] on the MetOp-A satellite. TES orbits the Earth in 98 minutes, advancing 22 degrees westward on every orbit and returning to the same location every sixteen days. The solar time of overpass is approximately 1:30 and 13:30. Each observation has a viewing area of approximately 5.3 km × 8.3 km, providing a dataset that far exceeds the spatial and temporal coverage of any in situ monitoring efforts. However, much of the NH_3 is near the surface, which is challenging to detect from space. To use the vast TES dataset for environmental monitoring, it is critical to test it using in situ measurements.

[5]   Accordingly, for ten months we have co-located in situ surface NH_3 measurements and TES transects over a region of high ammonia emission variability in eastern North Carolina in the United States. Our goal is to quantitatively test if the spatial and temporal patterns found in the remote sensing data match the in situ NH_3 measurements. Our analysis shows, for the first time to our knowledge, a high level of correspondence between space-based and in situ observations of NH_3.

2. Methods

[6]   To understand the extent to which the TES NH_3 retrievals can characterize the spatial and temporal variability in NH_3 mixing ratios, we conduct our comparison with in situ measurements over eastern North Carolina. As shown in Figure 1, this region has substantial variability in NH_3 emissions [*Walker et al.*, 2004]. Eastern North Carolina is a major agricultural production area with more than 9 million hogs, 30 million turkeys, and 100 million chickens produced in 2007 [*U.S. Department of Agriculture*, 2009]. However, counties surrounding the major agricultural areas are much less developed, feature designated wilderness

[1]U.S. EPA Office of Research and Development, Research Triangle Park, North Carolina, USA.
[2]Atmospheric and Environmental Research, Inc., Lexington, Massachusetts, USA.
[3]Department of Mechanical Engineering, University of Colorado at Boulder, Boulder, Colorado, USA.
[4]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA.
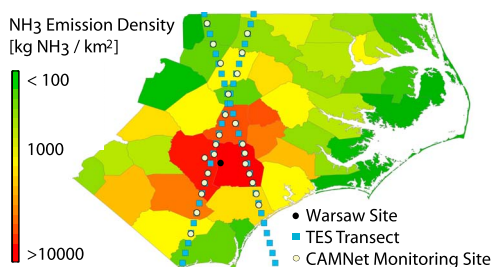[5]Environment Canada, Toronto, Ontario, Canada.

Figure 1. Counties in Eastern North Carolina are color-coded by emission density. The co-located TES transects and in situ measurements range from areas of low to high ammonia emission density. These transects span 300 km.

areas, and have much lower ammonia emissions. The region has significant seasonal changes in temperature – the mean July temperature is 27°C and the mean January temperature is 6°C. For these reasons, we expect large spatial and temporal gradients in the NH$_3$ mixing ratio.

[7] We have designed a sampling strategy to capture these gradients. As shown in Figure 1, we have scheduled TES transects to range from the low emission areas to regions of high emission density. We have co-located the in situ samplers with the locations of the TES observations and named this surface measurement network CAMNet. The study began in February 2009 and continued until November 2009.

2.1. Space-Based Measurements

[8] The vertical sensitivity of TES tropospheric ammonia retrievals vary from profile-to-profile depending on temperature contrast, cloud cover, and NH$_3$ amount, but the region of maximum sensitivity is usually between 700–900 hPa. Since ammonia has a limited amount of vertical information (typically ~1 piece of information), we compute for comparison purposes a Representative Volume Mixing Ratio (RVMR), which is the average NH$_3$ mixing ratio over the region of the atmosphere where TES is sensitive. A complete discussion and evaluation of the RVMR retrieval approach is available from M. Shephard et al. (TES Ammonia Retrieval Strategy and Observations: Global and Regional Examples of the Spatial and Seasonal Variability of Ammonia, manuscript in preparation, 2011). Briefly, the TES retrieval has a positive mean bias of 0.5 ppbv and the minimum detection limit of 1 ppbv. We limit our study to cases where the cloud optical thickness <1.

2.2. In Situ Measurements

2.2.1. Carolina Ammonia Monitoring Network (CAMNet)

[9] Two-week integrated ground-level NH$_3$ concentrations were measured at 25 sites (Figure 1) using the ALPHA passive sampler [*Tang et al.*, 2001]. The sampler consists of a 6 mm long, 21 mm inner diameter FEP Teflon tube. One end contains a 5 μm PTFE membrane, through which NH$_3$ gas diffuses and is adsorbed onto an acid-coated collection filter located at the other end of the diffusion path. The membrane prohibits particle collection and forms a quasi-laminar layer of air adjacent to its outer surface which serves to establish a turbulence-free diffusion path between the membrane and the collection filter. Samplers were deployed in duplicate at each measurement location in an open bottom

rain shelter fixed at a height of 1.5 m above ground. A complete description is available in the auxiliary material.[1]

2.2.2. Warsaw

[10] Our analysis also includes higher temporal resolution (30-minute average) NH$_3$ concentrations measured during a previous study near Warsaw, NC (Figure 1), conducted between June 18 and August 22, 2002 [*Walker et al.*, 2006]. Briefly, NH$_3$ concentrations were measured using a Thermo Environmental Instruments Model 17C chemiluminescence NO$_x$/NH$_3$ analyzer [*Thermo Environmental Instruments, Inc.*, 2002]. *Walker et al.* [2006] provides a detailed description of the experiment.

2.3. Chemical Transport Modeling

[11] To further interpret the comparison between the in situ and space-based measurements, we analyzed a five year simulation (2002–2006) from the Community Multi-scale Air Quality (CMAQ) Model. CMAQ includes advection, dispersion, gas and aqueous chemistry, aerosol thermodynamics and deposition on an Eulerian grid spanning the continental United States with 36 km horizontal resolution. A description and evaluation of this simulation are provided by *Appel et al.* [2010].

2.4. Comparing In Situ and Space-Based Measurements

[12] Because the TES retrieval and the in situ measurements are not sampling the same airmass, we would not expect perfect agreement using a direct comparison of the paired data. A more nuanced approach is necessary. Each of the differences between the two sampling methods are described below.

[13] First, the CAMNet measurements are an integrated average of the ammonia concentration over a two-week period, while TES instantaneously samples the atmosphere at the time of overpass at approximately 1:30 and 13:30 solar time every 16 days. There is substantial daily variability in the NH$_3$ concentration, so we examined in situ measurements [*Walker et al.*, 2006] conducted for all of 2002 at half-hourly time intervals at Warsaw, North Carolina. We calculated the correlation between the measurement at the time of overpass with the average of all measurements one week before and after the time of overpass. At the daytime overpass, we find the correlation between the Warsaw half-hourly surface measurement and the Warsaw two-week average surface measurement to be 0.40. However, during the night, the variability increases considerably, and the correlation decreases to 0.07.

[14] We extend this analysis across the range of conditions found in our study area, by sampling the NH$_3$ mixing ratio from the CMAQ simulation at the same location, month, day and hour as TES and CAMNet, for all instances when TES and CAMNet overlap. Although the CMAQ simulation does not include the same year as the observations, we have analyzed five years of simulation in order to estimate the climatological properties. We find the correlation between the CMAQ NH$_3$ mixing ratio at the daytime TES overpass and the CMAQ two week average is 0.68. This correlation is higher than at Warsaw, in part because it includes the spatial and seasonal variability present across
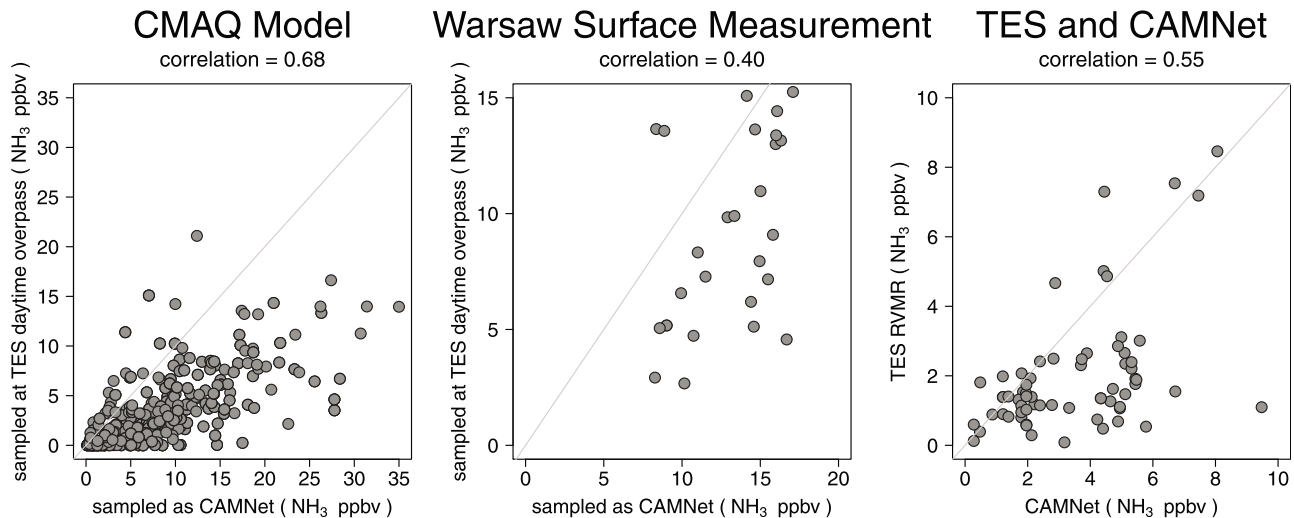

Figure 2. Comparison of CMAQ modeling results from 2002–2006 and Warsaw surface measurements sampled at the same frequency as TES and CAMNet. The correlation between two-week average and ammonia mixing ratio at time of TES daytime overpass are shown for each dataset.

the measurement sites. Because TES and CAMNet are sampling the atmosphere in different ways, we do not expect a pair-wise comparison to yield a correlation of one.

[15] Second, the ammonia surface concentrations have substantial diurnal variability. From the Warsaw data, the median ratio of the two-week average concentration to the concentration at the daytime overpass is 1.4 (95% confidence interval 1.1–1.7). Hence, we would expect the TES NH₃ to be lower than the two-week average concentration. To address this concern, we scaled the TES NH₃ by 1.4 for the seasonal and spatial comparisons below.

[16] Third, the in situ measurements are sampling a single location, while the TES observations include a viewing window 5.3 km × 8.3 km. The in situ samplers are intentionally located far enough from any livestock facility such that the measurement is representative of the average concentration over a region at the same spatial scale as the TES window. However, the viewing area does not cover exactly the same place every time, so we remove cases when the surface observation is not located within a TES window. To further address this issue, for each surface monitor and centroid of the TES viewing window, we classify the CAMNet and TES observations by number of livestock production facilities located within 10 km.

[17] Fourth, the TES RVMR is not an estimate of the NH₃ mixing ratio at an exact elevation, nor is it the integrated NH₃ column density. Rather, the RVMR estimates the mixing ratio averaged over a portion of the atmospheric column where the instrument is sensitive. Most of the daytime sensitivities peak between the surface and 800 hPa, which is usually within the turbulent boundary layer for this region. We expect the NH₃ concentration to be well mixed across the turbulent boundary layer, so we expect a high level of correspondence between CAMNet and TES RVMR daytime overpasses.

[18] Most nighttime retrievals have maximum sensitivity near the surface. At night, vertical mixing declines, causing larger NH₃ concentrations near emissions sources and

greater spatial and temporal variability [*Walker et al.*, 2004]. This increased variability is not resolved by the two-week integrated average CAMNet measurements, so we restrict the rest of our analysis to daytime TES retrievals that have maximum sensitivity between the surface and 800 hPa.

[19] Finally, to compare the in situ NH₃ concentration to the TES NH₃ mixing ratio, we convert the in situ measurements to a mixing ratio (ppbv) using standard pressure and monthly mean temperature measured at Warsaw, NC.

3. Results

[20] There are 78 overlapping pairs of CAMNet and TES NH₃ observations. Figure 2 shows the relationship between NH₃ at the time of TES overpass and the two-week average for the CMAQ model, Warsaw measurements, TES, and CAMNet datasets. The correlation between the daytime TES and the two-week averaged CAMNet NH₃ is 0.55, between the correlation in the Warsaw and CMAQ datasets. Also, the median ratio of the CAMNet NH₃ to the daytime TES RVMR is 1.6, where at Warsaw the 95% confidence interval for this ratio is 1.1–1.7.

[21] It is challenging to draw meaningful conclusions from this pair-wise comparison between CAMNet and TES, because they are sampling the atmosphere in different ways. Accordingly, we examine the seasonal and spatial patterns by grouping these data in time and space.

3.1. Seasonal Variability

[22] When the daytime TES RVMR and CAMNet NH₃ are paired and averaged for each month, both datasets have higher values in the Summer and lower values in the Spring and Fall. Figure 3 shows the monthly-averaged values for each dataset, as well as the 95% confidence interval for the mean, calculated using the student t-test. Comparisons for June, September, and October are not available due to cloudy conditions that prevented valid retrievals. We find
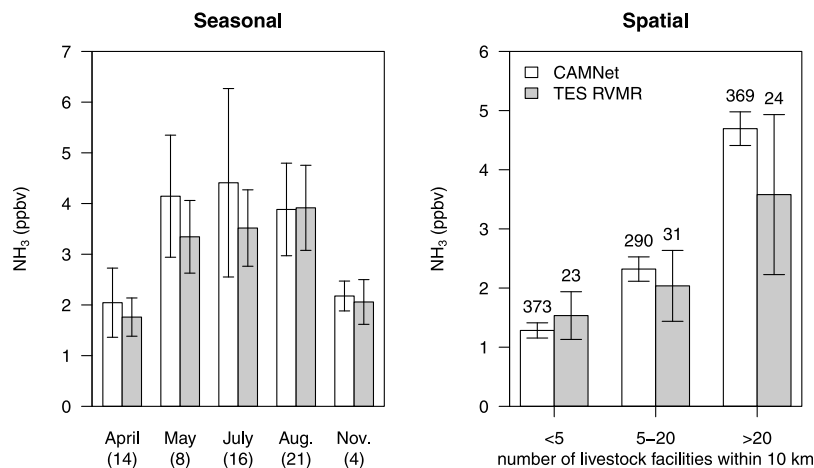
Figure 3. (left) Average daytime TES RVMR and CAMNet NH$_3$ observations by month of year for all months with more than three TES observations. The number of overlapping pairs for each month is shown in parenthesis. (right) Average daytime TES RVMR and CAMNet NH$_3$ binned by number of animal facilities within 10 km. Error bars denote the 95th percentile confidence interval for the mean.

that the April and November mean values are statistically different than the mean values for May–August.

3.2. Spatial Variability

[23] We also find a strong correspondence between the number of livestock facilities and both the TES RVMR and CAMNet observations. Figure 3 shows the average daytime TES RVMR and CAMNet NH$_3$ binned by number of animal facilities within 10 km. This includes hog and poultry production facilities, which are the largest sources of ammonia emissions in this region. There are also considerable fertilized crop lands, but these are spatially correlated with livestock operations. The observations with less than 5 animal facilities have NH$_3$ mixing ratios statistically different than the observations with more than 20 animal facilities.

4. Conclusions

[24] It is critically important to evaluate space-based observations using in situ measurements, yet this requires a nuanced approach. Because the in situ measurements in this study have an integrated sampling period of two weeks, we are not able to evaluate the large mixing ratios during night observed by TES. Future studies comparing nighttime in situ and space-based measurements of NH$_3$ should focus on sampling at greater temporal frequency to better understand this phenomenon.

[25] During the day, we find there is a strong correspondence between the region of the atmosphere observed by TES and the surface measurements. For the first time, our analysis reveals that the TES observations are able to capture the seasonal and spatial patterns found in the surface measurements. The vast amount of information available from TES NH$_3$ is a valuable tool for understanding spatial and temporal patterns of NH$_3$.

References

Abbatt, J. P. D., S. Benz, D. J. Cziczo, Z. Kanji, U. Lohmann, and O. Mohler (2006), Solid ammonium sulfate aerosols as ice nuclei: A pathway for cirrus cloud formation, *Science*, *313*(5794), 1770–1773, doi:10.1126/science.1129726.

Appel, K. W., K. M. Foley, J. O. Bash, R. W. Pinder, R. L. Dennis, D. J. Allen, and K. Pickering (2010), A multi-resolution assessment of the community multiscale air quality (cmaq) model v4.7 wet deposition estimates for 2002–2006, *Geosci. Model Dev. Discuss.*, *3*(4), 2315–2360, doi:10.5194/gmdd-3-2315-2010.

Beer, R., et al. (2008), First satellite observations of lower tropospheric ammonia and methanol, *Geophys. Res. Lett.*, *35*, L09801, doi:10.1029/2008GL033642.

Carmichael, G. R., et al. (2003), Measurements of sulfur dioxide, ozone and ammonia concentrations in Asia, Africa, and South America using passive samplers, *Atmos. Environ.*, *37*(9–10), 1293–1308, doi:10.1016/S1352-2310(02)01009-9.

Clarisse, L., C. Clerbaux, F. Dentener, D. Hurtmans, and P.-F. Coheur (2009), Global ammonia distribution derived from infrared satellite observations, *Nat. Geosci.*, *2*(7), 479–483.

Clarisse, L., M. W. Shephard, F. Dentener, D. Hurtmans, K. Cady-Pereira, F. Karagulian, M. Van Damme, C. Clerbaux, and P.-F. Coheur (2010), Satellite monitoring of ammonia: A case study of the San Joaquin Valley, *J. Geophys. Res.*, *115*, D13302, doi:10.1029/2009JD013291.

Massad, R.-S., E. Nemitz, and M. A. Sutton (2010), Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere, *Atmos. Chem. Phys. Discuss.*, *10*(4), 10,335–10,398, doi:10.5194/acpd-10-10335-2010.

Napari, I., M. Noppel, H. Vehkamaki, and M. Kulmala (2002), An improved model for ternary nucleation of sulfuric acid-ammonia-water, *J. Chem. Phys.*, *116*, 4221–4227.

Paerl, H., R. Dennis, and D. Whitall (2002), Atmospheric deposition of nitrogen: Implications for nutrient over-enrichment of coastal waters, *Estuaries*, *25*(4), 677–693.

Pearson, J., and G. R. Stewart (1993), Tansley Review No. 56: The deposition of atmospheric ammonia and its effects on plants, *New Phytol.*, *125*, 283–305.

Pope, C. A. (2000), Epidemiology of fine particulate air pollution and human health: Biologic mechanisms and who's at risk?, *Environ. Health Perspect.*, *108*, 713–723.

Schlesinger, W. H. (2009), On the fate of anthropogenic nitrogen, *Proc. Natl. Acad. Sci. U. S. A.*, *106*(1), 203–208, doi:10.1073/pnas.0810193105.

Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Wiley-Intersci., New York.

Tang, Y. S., J. N. Cape, and M. A. Sutton (2001), Development and types of passive samplers for monitoring atmospheric NO$_2$ and NH$_3$ concentrations, *Sci. World*, *1*, 513–529.

Thermo Environmental Instruments, Inc. (2002), *Model 17C Chemiluminescence NH3 Analyzer Instruction Manual*, Franklin, Mass.

U.S. Department of Agriculture (2009), 2007 Census of Agriculture, United States Summary and State Data, *Tech. Rep. AC-07-A-51*, Washington, D. C.

von Bobrutzki, K., et al. (2010), Field inter-comparison of eleven atmospheric ammonia measurement techniques, *Atmos. Meas. Tech.*, *3*(1), 91–112, doi:10.5194/amt-3-91-2010.

Walker, J. T., D. R. Whitall, W. Robarge, and H. W. Paerl (2004), Ambient ammonia and ammonium aerosol across a region of variable ammonia emission density, *Atmos. Environ.*, *38*(9), 1235–1246, doi:10.1016/j.atmosenv.2003.11.027.

Walker, J., W. Robarge, Y. Wu, and T. Meyers (2006), Measurement of bi-directional ammonia fluxes over soybean using the modified bowen-ratio technique, *Agric. For. Meteorol.*, *138*(1–4), 54–68, doi:10.1016/j.agrformet.2006.03.011.

J. O. Bash, R. W. Pinder, and J. T. Walker, U.S. EPA Office of Research and Development, Mail Drop E243-01, Research Triangle Park, NC 27711, USA. (pinder.rob@epa.gov)

K. E. Cady-Pereira, Atmospheric and Environmental Research, Inc., 131 Hartwell Ave., #4, Lexington, MA 02421, USA.

D. K. Henze, Department of Mechanical Engineering, University of Colorado at Boulder, Boulder, CO 80302, USA.

M. Luo and G. B. Osterman, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, USA.

M. W. Shephard, Environment Canada, 4905 Dufferin Street, Toronto, ON M3H 5T4, Canada.