Surface NOx Measurements in Northern Alabama During and After DC3

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Abstract: A residual gas nitrogen oxides (NOx) analyzer was employed for the purpose of measuring surface NOx in Huntsville, Alabama during the Deep Convective Clouds and Chemistry (DC3) campaign. Measurements were taken during a variety of conditions, including storm-free days and nights, non-thunderstorm outflow, and several thunderstorm outflows. In addition to the regular diurnal cycle in NOx caused by local anthropogenic activity, thunderstorm outflows produced small but measurable increases in surface NOx. The magnitude of NOx increase is supportive of the "backwards C" model profile of lightning NOx.

1. INTRODUCTION

Nitrogen oxide production by lightning has been studied using a multitude of techniques. These include aircraft, satellite, laboratory, chambers capturing rocket triggered lightning, and modeling studies (Table 1). Largely missing from these studies are surface observations of NOx before and after thunderstorms to measure the impact of lightning on surface NOx.

The Franzblau et al. (1989) study included measurements of surface NOx. They found that NOx from thunderstorm outflows was primarily nitric oxide. Since their spectroscopic measurements of lightning NOx were solely an NO2 measurement, the surface measurements were used to apply a correction factor, thus increasing their estimates of NOx per lightning flash.

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First author	Year	Methodology	Molecules/flash	Moles/flash
Levine	1981	Laboratory	5.00E+24	8.30
Kumar	1995	Field study	5.00E+24	8.30
Dawson	1980	Theoretical	8.00E+24	13.28
Beirle	2010	Satellite	1.00E+25	16.61
Tuck	1976	Theoretical	1.10E+25	18.27
Hill	1980	Theoretical	1.20E+25	19.93
Koshak	2010	Theoretical	1.41E+25	23.40
Cooray	2009	Theoretical	2.00E+25	33.21
Lawrence	1995	Review	2.30E+25	38.19
Nesbitt	2000	Field study	2.67E+25	44.25
Huntrieser	2002	Field study	2.70E+25	44.84
Wang	1998	Laboratory	3.10E+25	51.48
Peyrous	1982	Laboratory	3.20E+25	53.14
Ridley	2004	Field study	3.20E+25	53.14
Beirle	2006	Satellite	5.40E+25	89.67
Koshak	2011a	Theoretical	6.09E+25	101.17
Koshak	2011b	Theoretical	7.23E+25	121.61
Sisterson	1990	Theoretical	8.20E+25	136.17
Noxon	1976	Field study	1.00E+26	166.06
Chameides	1977	Theoretical	1.00E+26	166.06
Kowalczyk	1982	Theoretical	1.00E+26	166.06
Bucsela	2010	Satellite	1.05E+26	174.36
Schumann	2007	Review	1.50E+26	249.09
Huntrieser	2011	Field study	1.51E+26	250.00
DeCaria	2000	Theoretical	1.56E+26	258.39
Fehr	2004	Field study	2.10E+26	348.72
Rahman	2007	Field study	2.40E+26	398.54
Chameides	1979	Theoretical	2.50E+26	415.14
DeCaria	2005	Theoretical	2.77E+26	460.00
Martini	2011	Theoretical	2.89E+26	480.00
Ott	2010	Theoretical	3.01E+26	500.00
Jourdain	2010	Theoretical	3.13E+26	520.00
Drapcho	1983	Field study	4.00E+26	664.23
Franzblau	1989	Field study	3.00E+27	4981.73

Table 1: A comparison of lightning NOx production from previous studies, adapted from Peterson and Beasley (2011).

2. METHODOLOGY

Nitrogen oxides were detected using a residual gas analyzer, the function of which is described in Peterson et al. (2009). The purpose of this method is not to reproduce the high speed reactions in lightning, but rather to obtain the overall contribution of lightning to NOx (Peterson et al. 2010). The residual gas analyzer was obtained on loan from the Tennessee Valley Authority, who also performed a calibration of the instrument prior to loaning it to us. Measurements were initially taken during the Deep Convective Clouds and Chemistry (DC3) field campaign (Carey et al. 2013), and continued through the rest of 2012.

3. RESULTS

To establish the role of lightning among all sources of NOx the background must first be known. Figure 1 shows a typical non-thunderstorm summer day in Huntsville. Here the primary source of NOx is vehicular traffic on Interstate 565 about 1 km south of the measurement site. There tends to be an increase in NOx around the time of the morning commute, and a smaller increase in NOx around the time of the afternoon commute. The morning peak is larger due to a shallower boundary layer in the morning.

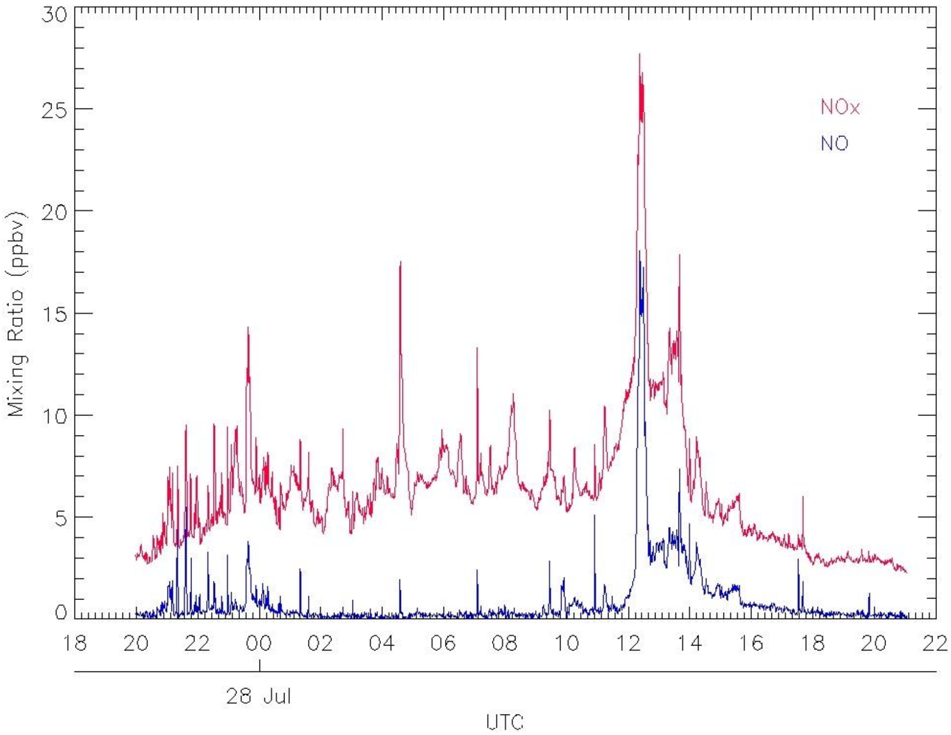


Figure 1: Summer background. Times on the bottom are UTC time. Concentrations on the left hand side are in ppb.

Figure 2 shows how the pattern changes for the cool season months. Two competing effects are at work: 1) a shallower boundary layer in the cooler months leads to higher surface concentrations of NOx, and 2) northerly winds due to passing cold fronts cuts off the I-565 source of NOx, leading to lower surface concentrations of NOx. In this example southerly winds were present in the afternoon, with an overnight cold frontal passage leading to northerly winds in the morning. As a result the relative strength of NOx peaks was reversed, with a higher concentration in the afternoon.

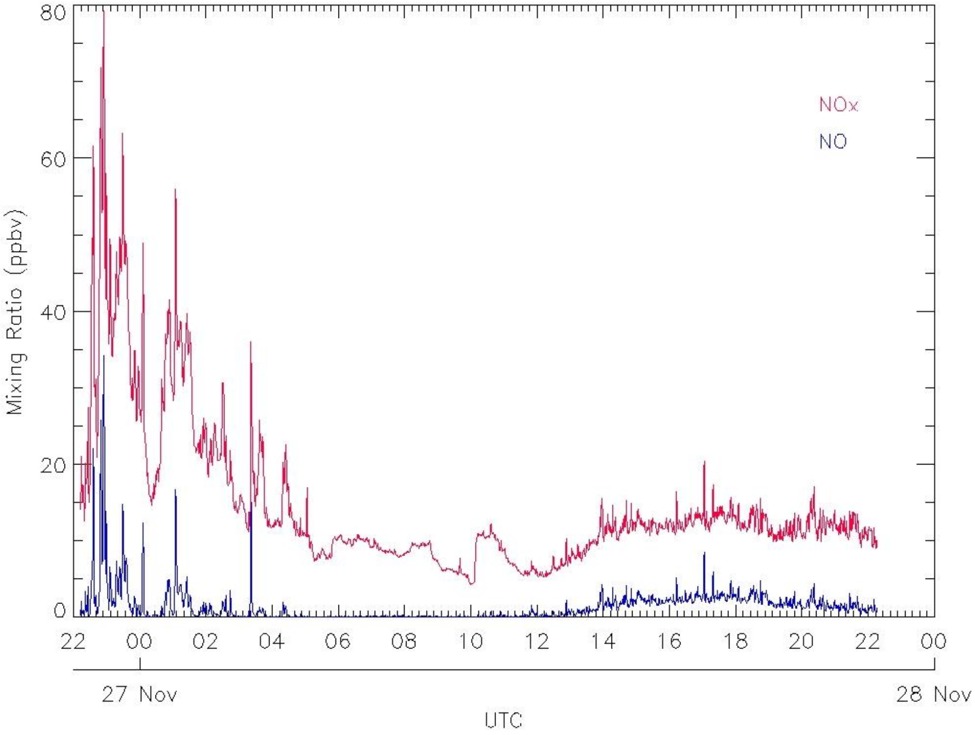
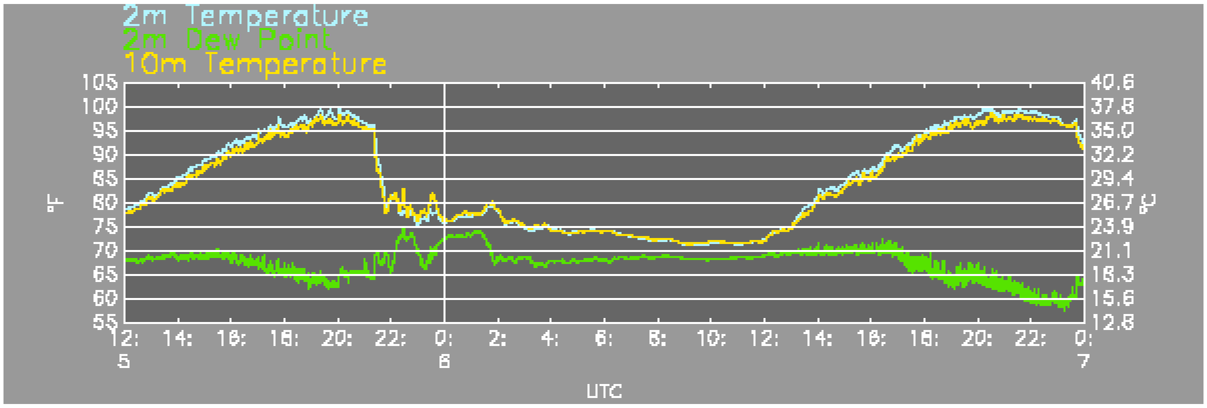


Figure 2: Winter background, with labeling the same as Figure 1.

The afternoon of July 5 (Figure 3) had numerous thunderstorms in north-central Alabama. Initial increases in NOx around 4:15 p.m. corresponded to the passage of an outflow boundary from a storm to the south. Wind speeds died down later in the afternoon/early evening and shifted to generally northerly, allowing additional advection of NOx from storms to the north of Huntsville. While not visible in the wind speed/direction data, a careful examination of temperature and dewpoint data show the sudden dropoff in NOx after 8 p.m. corresponded to advection of non-thunderstorm air into the area, characterized by higher temperatures and lower dewpoints. Therefore the difference between the maximum and minimum NOx concentrations represents the total lightning NOx measured at the site, about 27 ppb. It should also be noted that air masses containing lightning NOx are primarily NO2, while NOx generated by traffic is a mix of NO and NO2.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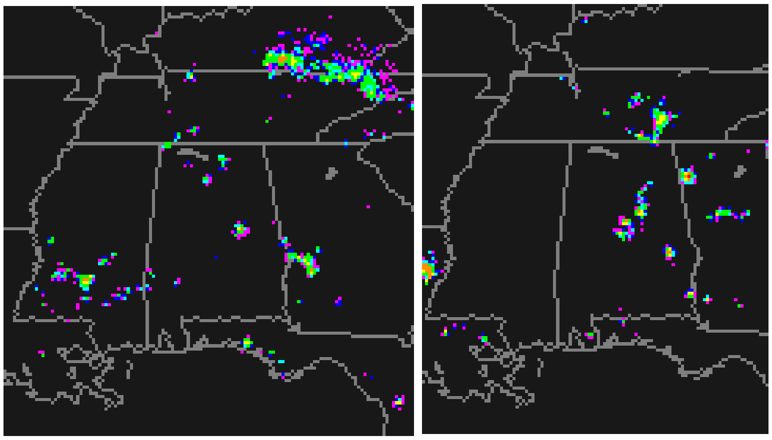

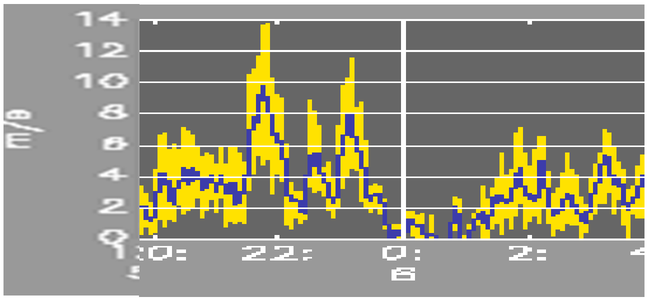
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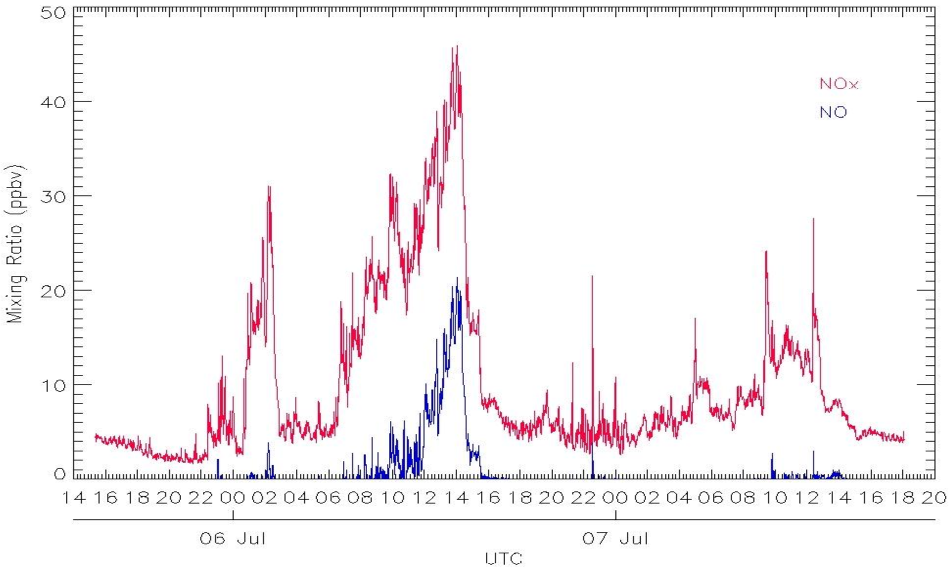
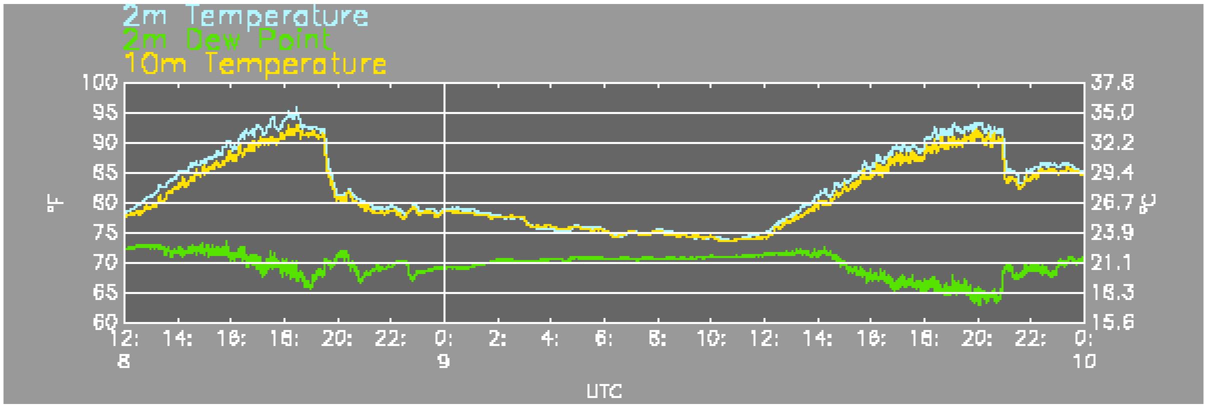


Figure 3: July 5-6. The top figure shows temperature and dewpoint, the second row shows NLDN lightning strikes from 4:15-4:30 p.m. (left) and 7:00-7:15 p.m. (right) local time, the next row shows wind speed for the evening of the 5th, with times in UTC, and the bottom row shows NO (blue) and NOx (red) concentration in UTC time.

For July 8 storms, temperature and dewpoint data are needed instead of wind data in order to determine thunderstorm vs. non-thunderstorm air masses. In this case (Figure 4) weak thunderstorms were present just south of Huntsville, which generated a drop in temperature of about five degrees Celsius but not an increase in wind speed. The result was a 5 ppb increase in NO2. Note that July 5 was a Sunday, so commuter NOx was much less of a factor than during the week.



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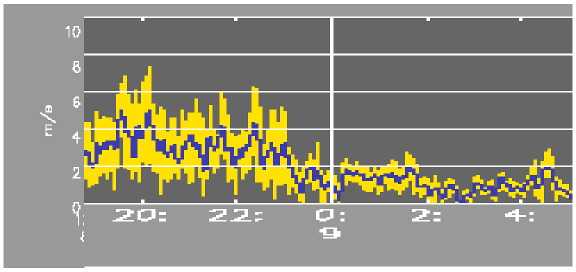

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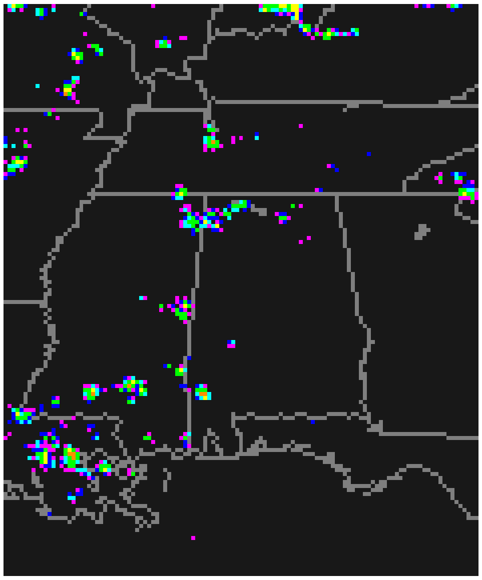


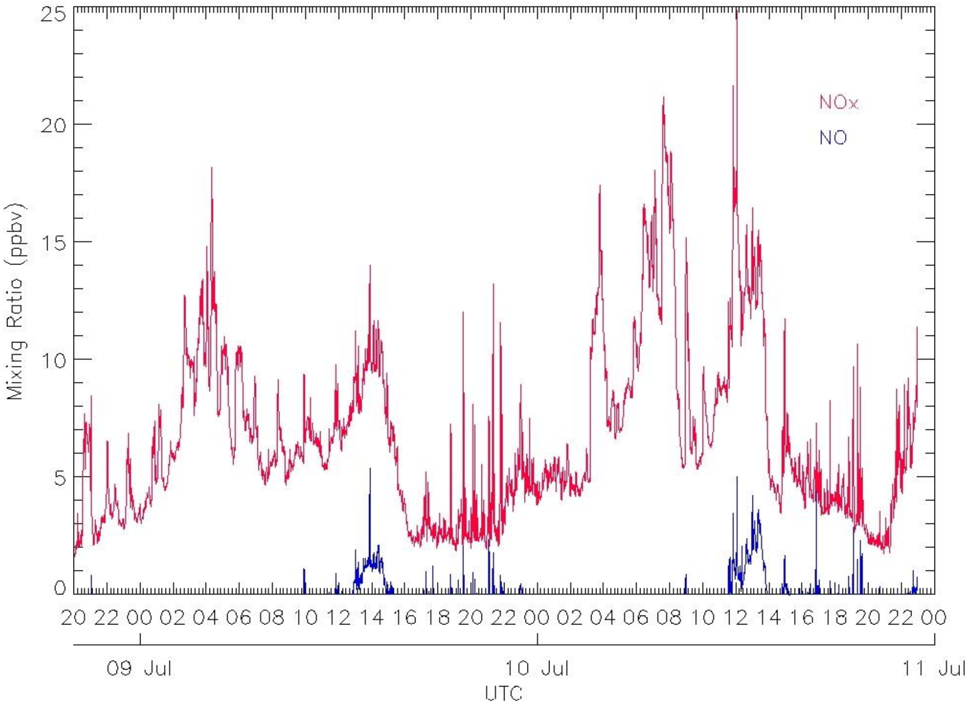
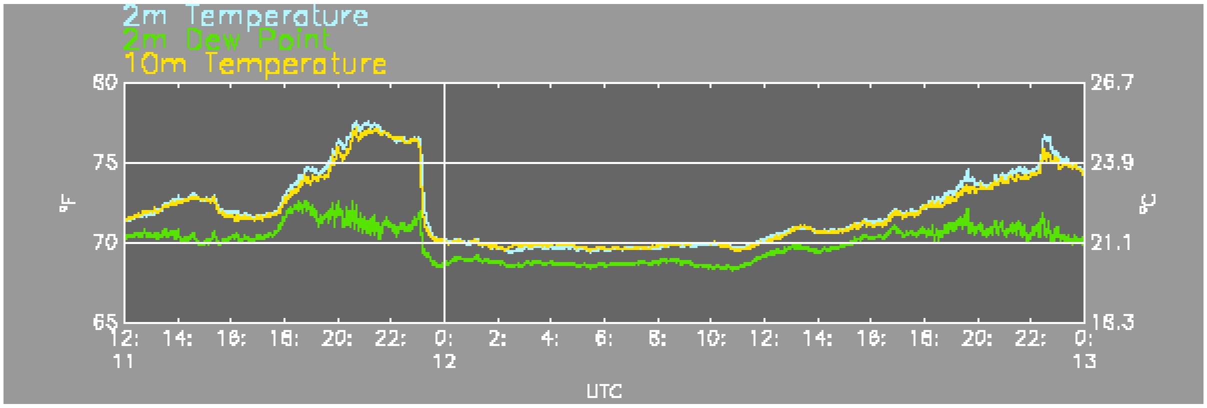


Figure 4: July 8-9. The top row gives temperature and dewpoint, the second row gives wind speed, the third row shows lightning from 2:30 to 2:45 p.m. CDT, and the bottom row shows NOx concentration.

The most noteworthy feature of July 11 (Figure 5) is the drop in NOx concentration at 6 p.m. While wind, temperature and dewpoint data all point to an outflow boundary passing at this time, NLDN data show the origin of the outflow is a region not producing lightning. This decrease may be considered to be the effect of replacing boundary layer air with free tropospheric air on NOx concentration, leading to a 15 ppb (about 75%) drop in total concentration. Since precipitation is shown to cause a large decrease in NOx, the level of increase in NOx shown in the previous cases is above and beyond the amount needed to offset this decrease.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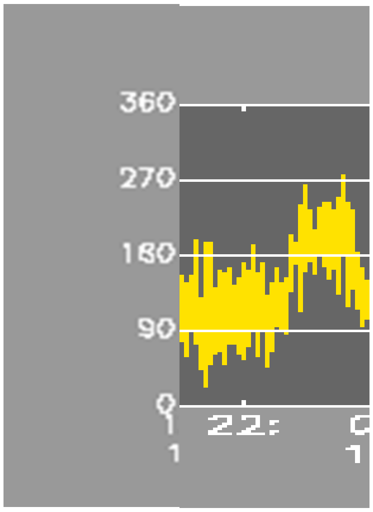
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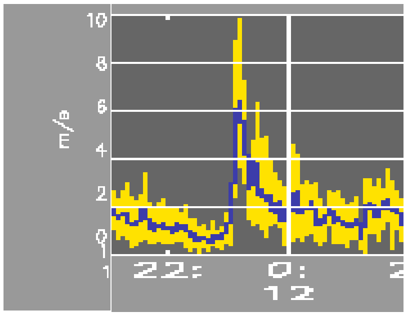
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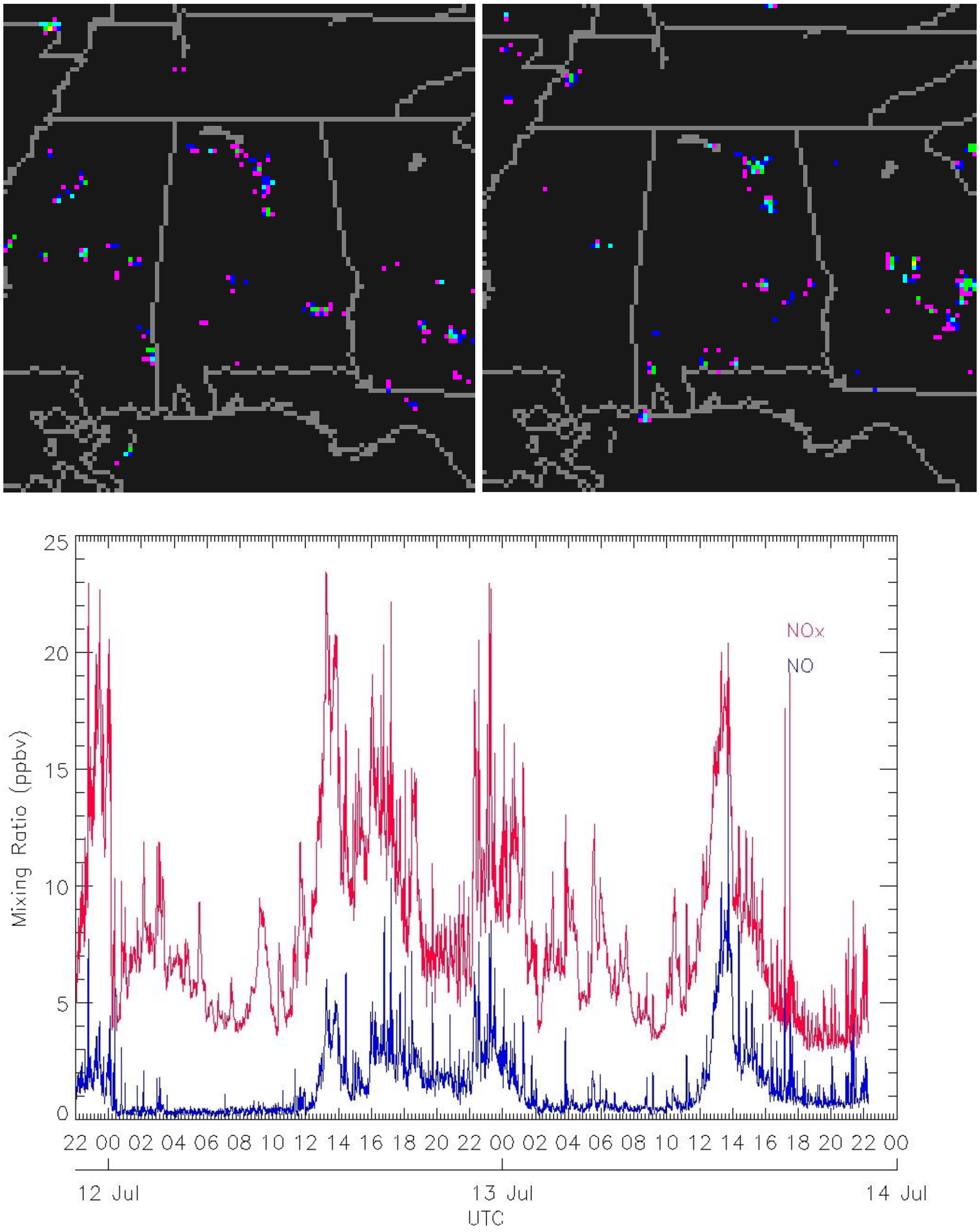

Figure 5: July 11-12. The top row shows temperature and dewpoint, the second row shows wind direction over UTC time, the third row shows wind speed over UTC time, the fourth row shows NLDN lightning at 5:00-5:15 (left) and 6:00-6:15 (right) p.m. CDT, and the bottom row shows NO (blue) and NOx (concentration over local time).

4. DISCUSSION AND CONCLUSIONS

These three cases show that lightning generates a measurable amount of surface NOx. The chemical composition of the air masses measured containing lightning-generated NOx were clearly distinguishable from anthropogenic NOx due to a much higher ratio of NO2 to NO; the cause of this higher ratio has not yet been determined. Winterrath et al. (1999) suggest ozone is introduced into thunderstorms by stratospheric intrusions and non-lightning electrical discharges; this ozone could titrate NO into NO2. Surface NO2 values compare favorably with Drapcho et al. (1983), who found a peak of 22 ppb following lightning discharges within 1.5 km; their NO2 to NO ratio was similarly high. The meteorological signature of air masses containing lightning NOx is a faster than normal decrease in temperature accompanied by surface winds tracing back to a lightning active region. Conversely, advection of warmer, less humid air following the advection of thunderstorm outflow leads to a decrease in NOx. Similarly, advection of non-thunderstorm outflow also leads to a decrease in NOx as free tropospheric air will remove much of the preexisting NOx from the air in the absence of lightning generated NOx.

It is noted that the Ott et al. (2010) model only produces about 1 ppb NOx in simulated midlatitude storms, nearly an order of magnitude less than the amount shown in the above figures as produced above and beyond urban NOx. They state that vertical transport is too strong in their model, indicating the difference comes from the amount of NOx injection near the surface.

It is further noted that our results indicate no correction factor should have been applied to the Franzblau et al. (1989) measurements. The new value would be 1660 moles/flash, much closer to the value found in other studies.

Acknowledgement: Special thanks to the Tennessee Valley Authority for loaning us a nitrogen oxides detector.

5. REFERENCES

Beirle, S., Spichtinger, N., Stohl, A., Cummins, K. L., Turner, T., Boccippio, D., Cooper, O. R., Wenig, M., Grzegorski, M., Platt, U. and Wagner, T., 2006: Estimating the NO_x produced by lightning from GOME and NLDN data: a case study in the Gulf of Mexico, *Atmos. Chem. Phys.*, **6**, 1075-1089.
Beirle, S., Huntrieser, H., and Wagner, T., 2010: Direct satellite observation of lightning-produced NO_x, *Atmos. Chem. Phys.*, **10**, 10965-10986.
Bucsela, E. J., Pickering, K. E., Huntemann, T. L., Cohen, R. C., Perring, A., Gleason, J. F., Blakeslee, R. J., Albrecht, R. I., Holzworth, R., Cipriani, J. P., Vargas-Navarro, D., Mora-Segura, I., Pacheco-Hernandez, A., and Laporte-Molina, S., 2010: Lightning-generated NO_x seen by the Ozone Monitoring Instrument during NASA's Tropical Composition, Cloud and Climate Coupling Experiment (TC^4), *J. Geophys. Res.*, **115**, D00J10, doi:10.1029/2009JD013118.
Carey, L., A. L. Bain, R. H. Rogers, D. Kozlowski, A. Sherrer, M. Saari, B. Bigelbach, M. Scott, E. V. Schultz, C. J. Schultz, P. N. Gatlin, M. T. Wingo, D. W. Phillips, C. Phillips, H. Peterson, J. Bailey, T. Frederickson, J. M. Hall, R. Blakeslee, W. Koshak, N. Bart, M. Becker, K. Pinkney, S. Rowe, M. Starzec, J. K. Weber, and G. L. Mullendore, 2013: Alabama ground operations during the Deep Convective Clouds and Chemistry experiment, *Proc. of the 93rd Ann. Am. Met. Soc. Meeting*, Austin, TX.
Chameides, W., Stedman, D., Dickerson, R., Rusch, D., and Cicerone, R., 1977: NO_x production in lightning, *J. Atmos. Sci.*, **34**, 143–149.
Chameides, W. L., 1979: Production of CO, H_2, and other trace gases by atmospheric lightning, *Transactions, Amer. Geophys. Un.*, **59**, 1150–1150.
Cooray, V., Rahman, R., and Rakov, V., 2009: On the NO_x production by laboratory electrical discharges and lightning, *J. Atmos. Solar-Terr. Phys.*, **71**, 1877-1889.
Dawson, G. A., 1980: Nitrogen-fixation by lightning, *J. Atmos. Sci.*, **37**, 174–178.
DeCaria, A. J., Pickering, K. E., Stenchikov, G. L., Scala J. R., Stith, J. L., Dye, J. E., and Laroche, B. A. R. P., 2000: A cloud-scale model study of lightning-generated NO_x in an individual

thunderstorm during STERAO-A, *J. Geophys. Res.*, **105**, 11 601–11 616.

DeCaria, A. J., K. E. Pickering, G. L. Stenchikov, L. E. Ott, 2005: Lightning-generated NOX and its impact on tropospheric ozone production: A three-dimensional modeling study of a Stratosphere-Troposphere Experiment: Radiation, Aerosols and Ozone (STERAO-A) thunderstorm, *J. Geophys. Res.*, **110**, D14303, doi:10.1029/2004JD005556.

Drapcho, D. L., Sisterson, D., and Kumar, R., 1983: Nitrogen fixation by lightning activity in a thunderstorm, J. Geophys. Res., **19**, 729–734.

Fehr, T., Holler, H., and Huntrieser, H., 2004: Model study on production and transport of lightning-produced NO_x in a EULINOX supercell storm, *J. Geophys. Res.*, **109**, D09 102, doi:10.1029/2003JD003935.

Franzblau, E. and Popp, C. J., 1989: Nitrogen oxides produced from lightning, *J. Geophys. Res.*, **94**, 11 089–11 104.

Hill, R. D., Rinker, R. G., and Wilson, H. D., 1980: Atmospheric nitrogen fixation by lightning, *J. Atmos. Sci.*, **37**, 179–192.

Huntrieser, H., Feigl, C., Schlager, H., Schroder, F., Gerbig, C., van Velthoven, P., Flatøy, F., Thery, C., Petzold, A., Holler, H., and Schumann, U., 2002: Airborne measurements of NO_x, tracer species, and small particles during the European Lightning Nitrogen Oxides Experiment, *J. Geophys. Res.*, **107**, 4113, doi:10.1029/2000JD000209.

Huntrieser, H., Schlager, H., Lichtenstern, M., Stock, P., Hamburger, T., Höller, H., Schmidt, K., Betz, H.-D., Ulanovsky, A., and Ravegnani, F., 2011: Mesoscale convective systems observed during AMMA and their impact on the NO_x and O_3 budget over West Africa, *Atmos. Chem. Phys.*, **11**, 2503-2536, doi:10.5194/acp-11-2503-2011.

Jourdain, L., Kulawik, S. S., Worden, H. M., Pickering, K. E., Worden, J., and Thompson, A. M., 2010: Lightning NO_x emissions over the USA constrained by TES ozone observations and the GEOS-CHEM model, *Atmos. Chem. Phys.*, **10**, 107-119.

Koshak, W. J., Peterson, H. S., McCaul, E. W., and Biazar, A., 2010: Estimates of the lightning NO_x profile in the vicinity of the North Alabama Lightning Mapping Array, *Proc. of the 2010 Int. Lightning Detection Conf.*, Orlando, FL.

Koshak, W., Peterson, H., Khan, M., Biazar, A., and Wang, L., 2011: The NASA Lightning Nitrogen Oxides Model (LNOM): application to air quality modeling, *Proc. of the 2011 Int. Conf. on Atmos. Elec.*, Rio de Janiero, Brazil.

Koshak, W., Peterson, H., 2011: A summary of the NASA Lightning Nitrogen Oxides Model (LNOM) and recent results, *Proc. of the 10th Ann. CMAS Conf.*, Chapel Hill, NC.

Kowalczyk, M. and Bauer, E., 1982: Lightning as a source of NO_x in the troposphere, *Technical Memorandum ORNL/TM-2001/268*, Federal Aviation Administration, Oak Ridge, Tenn.

Kumar, P. P., Manohar, G. K., and Kandalgaonkar, S. S., 1995: Global distribution of nitric-oxide produced by lightning and its seasonal variation, *J. Geophys. Res.*, **100**, 11,203–11,208.

Lawrence, M. G., Chameides, W. L., Kasibhatla, P. S., Levy II, H., and Moxim, W., 1995: Lightning and atmospheric chemistry: The rate of atmospheric NO production, Vol. I, 189–202, *CRC Press*, Inc., 1995.

Levine, J. S., Rogowski, R. S., Gregory, G. L., Howell, W. E., and Fishman, J., 1981: Simultaneous measurements of NO_x, NO and O_3 production in a laboratory discharge: Atmospheric implications, *Geophys. Res. Lett.*, **8**, 357–360.

Martini, M., Allen, D. J., Pickering, K. E., Stenchikov, G. L., Richter, A., Hyer, E. J., Loughner, C. P., 2011: The impact of North American anthropogenic emissions and lightning on long-range transport of trace gases and their export from the continent during summers 2002 and 2004, *J. Geophys. Res.*, **116**, D07305, doi:10.1029/2010JD014305.

Nesbitt, S. W., Zhang, R., and Orville, R. E., 2000: Seasonal and global NO_x production by lightning estimated from the Optical Transient Detector (OTD), *Tellus*, **52B**, 1206–1215.

Noxon, J. F., 1976: Atmospheric nitrogen-fixation by lightning, *Geophys. Res. Lett.*, **3**, 463–465.

Ott, L. E., Pickering, K. E., Stenchikov, G. L., Allen, D. J., DeCaria, A. J., Ridley, B., Lin, R.-F., Lang, S., and Tao, W.-K., 2010: Production of lightning NO_x and its vertical distribution calculated from three-dimensional cloud-scale chemical transport model simulations, *J. Geophys. Res.*, **115**, D04301, doi:10.1029/2009JD011880.

Peterson, H., M. Bailey, J. Hallett, and W. Beasley, 2009: NOx production in laboratory discharges simulating blue jets and red sprites, *J. Geophys. Res.*, **114**, doi:10.1029/2009JA014489.

Peterson, H., M. Bailey, J. Hallett, and W. Beasley, 2010: Reply to comment by S. Nijdam et al. on "NOx production in laboratory discharges simulating blue jets and red sprites", *J. Geophys. Res.*, **115**, A12306, doi:10.1029/2010JA015946.

Peterson, H. and W. Beasley,2011: Possible catalytic effects of ice particles on the production of NO_x by lightning discharges, *Atmos. Chem. Phys.*, **11**, 10259-10268, doi:10.5194/acpd-11-10259-2011.

Peyrous, R. and Lapyere, R. M., 1982: Gaseous products created by electrical discharges in the atmosphere and condensation nuclei resulting from gaseous-phase reactions, *Atmos. Environ.*, **6**, 959–968.

Rahman, M., Cooray, V., Rakov, V. A., Uman, M. A., Liyanage, P., DeCarlo, B. A., Jerauld, J., and Olsen III, R. C., 2007: Measurements of NO_x produced by rocket-triggered lightning, *Geophys. Res. Lett.*, **34**, L03816, doi:10.1029/2006GL027956.

Sisterson, D. L. and Liaw, Y. P., 1990: An evaluation of lightning and corona discharge on thunderstorm air and precipitation chemistry*, J. Atmos. Chem.*, **10**, 83–96.

Schumann, U. and Huntrieser, H., 2007: The global lightning-induced nitrogen oxides sources, *Atmos. Chem. Phys.*, **7**, 3823-3907.

Tuck, A. F., 1976: Production of nitrogen-oxides by lightning discharges, *Q. J. R. Meteorol. Soc.*, **102**, 749–755.

Wang, Y., DeSilva, A. W., Goldenbaum, G. C., and Dickerson, R. R., 1998: Nitric oxide formation by simulated lightning: dependence of current, energy, and pressure, *J. Geophys. Res.*, **103**, 19,149-19,159.

Winterrath, T., Kurosu, T. P., Richter, A., and Burrows, J. P., 1999: Enhanced O3 and NO2 in thunderstorm clouds: convection or production?, *Geophys. Res. Lett.*, **26**, 9, 1291-1294.