Continuous Measurements of NOy and NOy Components during the Southeast Atmospheric Study, June 1-July 15, 2013

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Atmospheric dry deposition of oxidized nitrogen species (collectively known as NOy) is a complex function of chemistry and physics, including physical form (gas or aerosol), diffusivity, solubility and reactivity of individual species. Thus, information on individual components of NOy is needed to develop and/or constrain deposition estimates. This presentation will describe observations of NOy and its major components at a rural site in the southeastern US during the summer of 2013. Hourly and 5-minute average measurements of NOy, NO, NO_2, HNO_3, fine particulate nitrate (pNO_3), total peroxynitrates (tPANs) and total alkyl nitrates (tANs) were performed at the SEARCH Centreville, AL site during the multi-agency SAS/SOAS/SENEX campaign (June 1-July 15, 2013). All components were quantified via NO-O_3 chemiluminescence: NO directly, NOy via conversion to NO on 350C Mo, NO_2 via blue LED photolysis, HNO_3 via denuder difference, pNO_3 via denuder-filter difference, tPANs and tANs via thermal-photolytic conversion at 160C and 380C, respectively. Results show that the sum of components accounts for 98 +/- 11% of NOy (mean = 1250 +/- 810 parts per trillion) over the course of the study and that NO_x (NO_2 + NO) and NOz (others) each account for almost exactly 50% of NOy. HNO_3, tPANs, tANs and pNO_3 account for 12%, 10%, 21% and 4% of NOy, respectively. Each of the measured components has a more or less unique diurnal pattern. NOx accounts for >75% of NOy during nighttime hours and is exclusively NO_2 overnight, while HNO_3, NO_2, tPANs and tANs each account for roughly 25% of NOy during midday. HNO_3 concentrations generally peak around 1600 local standard time (LST), while tPANs and tANs generally peak around 0900-1200 LST. pNO_3 concentrations peak within +/- 2 hours of sunrise and are effectively zero from 1000-1600 LST. Inspection of time series data provides interesting clues to the physical-chemical characteristics of tPANs and tANs (recognizing, of course, that these are classes of compounds rather than individual compounds). For example, tPAN and tAN concentrations are very slightly affected by rainfall events, whereas HNO_3 and pNO_3 concentrations are rapidly reduced to zero or near zero. Similarly, nighttime concentrations of tPANs and tANs decline much more slowly than HNO_3. These observations suggest that tPANs and tANs have substantially different (slower) wet and dry removal rates than HNO_3, which, in turn, may provide useful information for estimating NOy deposition.

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