# Reactive nitrogen budget during the NASA SONEX Mission

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Abstract. The SASS Ozone and Nitrogen Oxides Experiment (SONEX) over the North Atlantic during October/November 1997 offered an excellent opportunity to examine the budget of reactive nitrogen in the upper troposphere (8 - 12 km altitude). The median measured total reactive nitrogen (NOy) mixing ratio was 425 parts per billion by volume (ppbv) (NOy sum; slope >0.9 and r2 > 0.9). The total reactive nitrogen budget in the upper troposphere over the North Atlantic appears to be dominated by a mixture of NOx, HNO3, and PAN. In tropospheric air median values of NOx/NOy were 0.25, HNO3/NOy =0.35 and PAN/NOy =0.17. Particulate NO3, and alkyl nitrates together composed <10% of NOy, while NO3, N2O5, CH3C(O)OONO2 (PAN), RONO2 (alkyl nitrates), and particulate NO3 constitute important controls on O3, oxidant, and acidity levels on a global scale. The collective sum of these species, commonly referred to as total reactive odd-nitrogen (NOy) [Fahey et al., 1986; Ridley, 1991; Sandholm et al., 1994; Atlas et al., 1992a; Crosley, 1996; Kondo et al., 1997a] have been proposed as explanations.

In this paper we present a summary comparison between NOy measured directly with a gold catalytic converter [Kondo et al., 1997b] and the sum of the individually measured species NO, HNO3, PAN, PPN, alkyl nitrates, plus modeled NO2, HONO, N2O5, and NO3 over the North Atlantic during October/November 1997. The SONEX data represent the most complete set of measurement and model estimated parameters collected to date for the upper troposphere, and provide a good basis for examining our understanding of the NOy budget in this region of the troposphere. The data were obtained in or near the North Atlantic flight corridor where ~700 commercial aircraft traverse it each day at 9 - 12 km altitude between North America and Europe. Air parcels sampled in this region should represent a combination of processed continental and “fresh” aircraft emissions.

1. Introduction

Reactive nitrogen compounds in the Earth’s troposphere, primarily believed to be present as NO, NO2, HONO, HNO3, HNO4, NO3, N2O5, CH3C(O)OONO2 (PAN), RONO2 (alkyl nitrates), and particulate NO3, constitute important controls on O3, oxidant, and acidity levels on a global scale. The sum of the individually measured species NO, HNO3, PAN, PPN, alkyl nitrates, plus modeled NO2, HONO, N2O5, and NO3 over the North Atlantic during October/November 1997. The SONEX data represent the most complete set of measurement and model estimated parameters collected to date for the upper troposphere, and provide a good basis for examining our understanding of the NOy budget in this region of the troposphere. The data were obtained in or near the North Atlantic flight corridor where ~700 commercial aircraft traverse it each day at 9 - 12 km altitude between North America and Europe. Air parcels sampled in this region should represent a combination of processed continental and “fresh” aircraft emissions.

2. Methods

The SONEX mission was conducted aboard the NASA Ames DC-8 research aircraft with the majority (>95%) of the data collected at 8 - 12 km altitude. The aircraft operated from three base stations: Bangor, Maine (four flights), Shannon, Ireland (four flights), and the Azores Islands (one flight) and transits in between these locations. The details of the mission are summarized in the companion overview paper [Singh et al., this issue]. All of the data collected on these flights was used in this analysis to constitute a total of 15 science missions (= 120 flight hours of data).

Nitric oxide (NO) and NO2 were sampled through a rear-facing (to help exclude aerosols >1 μm diameter) heated (50°C) PFA teflon tube (6 mm ID) at 1 standard liter per minute (SLPM) flow rate and detected as NO using chemiluminescence [Kondo et al., 1997b]. NOy was catalytically converted to NO at 50 hPa on the surface of a gold tube heated to 300°C with addition of CO. The precision of 10 second NO and NOy measurements at 10 km altitude estimated from two sigma photon count fluctuations was 6 and 19 pptv at 100 and 800 pptv respectively. The absolute accuracy was estimated to be 8 and 10% for NO and NOy.

Nitric acid was measured using the mist chamber (MC) technique [Talbot et al., 1997, 1999]. The instrument utilized a heated (35°C) fast flowing (1000-3000 SLPM) fused-silica coated manifold (≈50 mm ID) with the capability to conduct standard
3. The NO$_x$ Budget

The NO$_x$ sum compared to NO$_x$ meas. showed a high degree of correlation over the range of NO$_x$ mixing ratios from 70 - 1500 pptv [Figure 1]. Here NO$_x$ sum represents the measured species NO,
probably reflect inputs from aircraft, lightning, and surface pollution uplifted by convection [Thompson et al., this issue]. At O₃ mixing ratios greater than 100 ppbv stratospheric influence was evident based on concomitant ⁷Be concentrations >1000 femtocuries (10⁻¹⁵ Ci) per standard cubic meter and CO mixing ratios <50 ppbv [Dibb et al., 1999]. The fraction of HNO₃ in these air parcels (i.e., HNO₃/NOₓ) progressively increased from the middle troposphere to the lower stratosphere comprising as much as 80% of NOₓ.

Median values of the ratios of NOₓ, HNO₃, and PAN to NOₓ meas. in tropospheric air showed that overall NOₓ composed ≈25% of NOₓ, HNO₃ ≈35%, and PAN ≈17%. The alkyl nitrates collectively averaged about 10 pptv, and represented <5% of NOₓ. Particulate reactive nitrogen was sampled to some (unknown) degree by the NOₓ instrument, some of which could have been present in unidentified forms. Our model calculations predict from 0.1 - 100 pptv of various unmeasured reactive nitrogen species, with HNO₄ being the most important one accounting for an average of 12 ± 9% (i.e., 55 ± 30 pptv) of NOₓ sum. In addition, positive interference in NO₂ meas. by non-reactive nitrogen compounds

Figure 2. (a) Average value of various reactive nitrogen species as a function of binned O₃ mixing ratios. The height of the stacked groupings represent the sum of the individual components and the value above it is average NOₓ meas. The uncolored area includes model calculated HNO₄ plus the remaining difference in NOₓ meas. and NOₓ sum. (b) Fraction of each species as shown in (a) to NOₓ meas. as a function of binned O₃ mixing ratios.

HNO₃, PAN, PPN, methyl nitrate, ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, 2-butyl nitrate, plus modeled NOₓ, HONO, HNO₄, N₂O₅, and NOₓ. The dashed lines depicted in Figure 1 indicate ±20% values for the regression relationship, with 98% of the data falling within these bounds.

As presented in Figure 1, the data was broken into two groups based on the O₃ mixing ratio to generally separate tropospheric (O₃ <100 ppbv) from stratospherically influenced air parcels (O₃ >100 ppbv). The correlation between NOₓ sum and NOₓ meas. was the same in both types of air parcels indicating no significant bias in comparing regions comprised of numerous reactive nitrogen species (troposphere) with another dominated by HNO₃ (stratosphere). The few large mixing ratios of NOₓ for the tropospheric case represent sampling of recent aircraft emissions where NO comprised > 80% of the NOₓ species. The lowest mixing ratios of NOₓ denote tropical air parcels sampled south of the Azores where mixing ratios (pptv) of the various species were about 10 (NO), 3 (NO₂ calc.), 35 (HNO₃), 10 (PAN), 5 (sum of alkyl nitrates), and 5 (HNO₄ calc.).

In Figure 2 the median values of the various reactive nitrogen species are shown as a function of binned O₃ mixing ratios. In tropospheric air NOₓ had a median mixing ratio of 150 pptv, HNO₃ 130 pptv, and PAN 80 pptv. The relatively high values of NOₓ

Figure 3. Difference between NOₓ sum and NOₓ meas. as a function of solar zenith angle (a) and NO mixing ratio (b).
To look for likely factors which may have contributed to systematic differences in NO$_3$ sum and NO$_2$ meas., we plotted the difference, NO$_3$ sum - NO$_2$ meas., as a function of various parameters including HNO$_3$, PAN, O$_3$, CO, C$_2$H$_4$/CO and modeled HNO$_4$. No significant trends were identified. This suggests that measurement bias or chemical environments sampled during SONEX were not a major factor influencing the agreement between NO$_3$ sum. and NO$_2$ meas. An interesting result was found with regard to solar zenith angle (Figure 3a); the difference in NO$_3$ sum. and NO$_2$ meas. increased with larger solar zenith angles. A possible explanation for this trend is that at high solar zenith angles NO is at mixing ratios <20 ppt (Figure 3b) due to slowed photolysis of NO$_2$. The uncertainty in measured NO is greatest here (~25-30%), which then propagates to larger variability in important model calculated species such as NO$_2$ and HNO$_3$. Thus, NO$_3$ sum. has greatest uncertainty at low mixing ratios of NO, and propagation of the associated errors in NO$_3$ sum makes it potentially as large as ±80%. The increased scatter in the agreement between NO$_3$ sum and NO$_2$ meas. at high solar zenith angles (or low NO) is attributed to this effect. The rather even distribution of positive and negative values of NO$_3$ sum - NO$_2$ meas. suggests that this is variation due to random errors rather than a serious bias in one of the terms.

Collectively the SONEX results indicate that NO$_3$, HNO$_3$, and PAN constitute about 80% of reactive nitrogen in the middle and upper troposphere over the North Atlantic. To narrow uncertainties in this type of budget analysis further, it requires development of techniques for reliable measurement of species such as NO$_2$ and HNO$_3$ in the remote troposphere. It is also necessary to continue to assess the conversion efficiency of NO$_3$ instruments for reactive and non-reactive nitrogen compounds under actual field conditions to better characterize the utility of NO$_3$ measurements in the troposphere.

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References


J. E. Dibb, E. M. Scheuer, and R. W. Talbot, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham 03824. (e-mail: jack.dibb@unh.edu; eric.scheuer@unh.edu; robert.talbot@unh.edu)

Mikoike and Y. Kondo, Solar-Terrestrial Environmental Laboratory, Nagoya University, Honohara, Toyokawa, Aichi, 442 Japan. (e-mail: koike@stelab.nagoya-u.ac.jp; kondo@stelab.nagoya-u.ac.jp)

Y. Fukui, L. B. Salas, and H. B. Singh, NASA Ames Research Center, Moffett Field, CA 94035. (e-mail: hisingh@arc.nasa.gov)

J. O. Ballenthin, D. E. Hunton, R. F. Meads, T. M. Miller, and A. A. Viggiano, Air Force Research Laboratory/VSSB, Hanscom Air Force Base, MA 01731. (e-mail: ballenthin@phf.af.mil; viggiano@phf.af.mil).

D. R. Blake and N. J. Blake, Department of Chemistry, University of California - Irvine, Irvine, CA 98107. (e-mail: dBlake@orion.oac uiuc.edu; nblake@uci.edu)

E. Atlas and F. Flocke, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80303. (e-mail: atlas@aci.ucar.edu).

D. J. Jacob and L. Jaegle, Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138. (e-mail: dj@europa.harvard.edu; lj@io.harvard.edu)

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