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 trillion by volume (pptv). A data set merged to the HNO3 measurement time resolution was used to calculate NOy (NOy sum) by summing the reactive nitrogen species (a combination of measured plus modeled results) and comparing it to measured NOy (NOy meas.). Comparisons were done for tropospheric air (O3 <100 parts per billion by volume (ppbv)) and stratospherically influenced air (O3 >100 ppbv) with both showing good agreement between NOy sum and NOy meas. (slope <0.9 and r^2 = 0.9). The total reactive nitrogen budget in the upper troposphere over the North Atlantic appears to be dominated by a mixture of NOx (NO + NO2), 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 model estimated HNO4 averaged 12%. For the air parcels sampled during SONEX, there does not appear to be a large reservoir of unidentified NOy compounds.

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 collective sum of these species, commonly referred to as total reactive odd-nitrogen (NOy) [Fahey et al., 1985], is a quantity useful for general characterization of air parcels in rural and remote atmospheres. Direct measurements of NOy and its suspected dominant components show good agreement at most continental sites at part per billion by volume (ppbv) mixing ratios where a simple mixture of NO, HNO3, and PAN comprise >90% of total NO [Parish et al., 1993; Sandholm et al., 1994].

At remote locations comparison of NOx meas. and NOx sum at hundreds of parts per trillion by volume (pptv) typically show disagreement of 30-50% [Fahey et al., 1986; Ridley, 1991; Sandholm et al., 1994; Atlas et al., 1992a; Crosley, 1996; Kondo et al., 1997a]. Measurement problems at low mixing ratios for individual reactive nitrogen species, overestimation of NOx meas. due to non-reactive nitrogen compounds [Crosley et al., 1996; Bradshaw et al., 1998] and possible inclusion of unidentified NOy compounds (e.g., alkyl nitrates) in NOy meas. [Fahey et al., 1986; Atlas et al., 1992a] 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, HNO4, 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 Azore 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]. NO3 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
additions of HNO₃ down = 95% of the entire length of the inlet. At mixing ratios above 100 pptv the overall uncertainty is 15-20%, increasing to 25-30% below 100 pptv. Nitric acid was also measured by a new chemical ionization mass spectrometer (CIMS) instrument [Miller et al., 1999]. Calibration and offset issues are currently being resolved for this instrument, so associated measurement uncertainties have not been fully assessed. Thus, these data have not been included in this analysis of the NOy budget, but in general the two data sets for HNO₃ agreed within 25%.

Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) were measured through a rear-facing inlet (6 mm ID) composed of heated (20°C) PFA teflon tubing with a flow rate of 5 SLPM. PAN and PPN were cryogenically trapped from ambient air and quantified subsequently by electron capture gas chromatography [Singh and Salas, 1983]. The uncertainty for PAN and PPN is 20%.

Alkyl nitrates (methyl nitrate, ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, and 2-butyl nitrate) were sampled through a 6 mm ID stainless steel tube into passivated stainless steel canisters and pressurized to 2750 hPa with a metal bellows pump. The canisters were shipped back to the laboratory where the alkyl nitrates were cryogenically trapped and measured using electron capture and mass spectrometry detection coupled with gas chromatography [Atlas et al., 1992b]. The overall uncertainty in the alkyl nitrate data is 20%. In addition, alkyl nitrates were measured along with PAN and PPN in near real-time and agreed within 20% with the canister method. For this paper we utilized the canister data set which had better overlap with the time base used in our budget analysis.

A diel steady-state model [Jaegle et al., this issue] was used to calculate the unmeasured species NO₂, NO₃, N₂O₅, HONO, and HNO₄. The model was constrained with observed NO, CO, H₂O, CH₄, hydrocarbons, pressure, temperature, aerosol surface area, and UV actinic flux. Modeled NO₂ was used to calculate NO₃. The error in evaluating NO₂ could be as large as 50%, which is derived from the uncertainties in measured NO, O₃, and the rate constants for NO + O₃ and NO₂ photolysis.

2.1 Database

Although each of the participating groups reported individual flight data files to the SONEX archive (publically available on Cloud1.nasa.ames.gov at NASA Ames Research Center), we used data files merged to the HNO₃ time resolution for the analyses reported in this paper. This provided measurements and associated model-estimated NO₂, HONO, HNO₄, N₂O₅, and NO₃ on the same time base [Jaegle et al., this issue]. Since particulate-NO₃ was measured during SONEX with approximately 10 minute time resolution, we did not include it in the data analysis. The median value of particulate-NO₃ was 15 pptv [Dibb et al., 1999] which represented <5% of the NOy and its omission for our budget analysis does not significantly influence the conclusions presented here.

We further narrowed the selected data set based on two criteria: (1) a solar zenith angle < 85° and, (2) measurement intervals where NO, HNO₃, PAN, and NOy were all reported with a time overlap of >50%. This reduced the data points for our analysis from several thousand to 700. We believe that this final breakdown provides a reasonably consistent set of measurement and model products to evaluate the upper tropospheric NOy budget over the North Atlantic.

3. The NOy Budget

The NOy sum compared to NOy meas. showed a high degree of correlation over the range of NOy mixing ratios from ~70 - 1500 pptv [Figure 1]. Here NOy 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 ⁷³Be 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 NO₃ 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 HNO₃ 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 NOₓ meas. by non-reactive nitrogen compounds

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
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