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R. Talbot

University of New Hampshire, robert.talbot@unh.edu

Jack E. Dibb

University of New Hampshire, jack.dibb@unh.edu

Eric Scheuer

University of New Hampshire - Main Campus, Eric.Scheuer@unh.edu

Y Kondo

Nagoya University

M Koike

Nagoya University

See next page for additional authors

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Authors

R. Talbot, Jack E. Dibb, Eric Scheuer, Y Kondo, M Koike, H B. Singh, L Salas, F Fukui, J O. Ballenthin, R F. Meads, T M. Miller, D E. Hunton, A A. Viggiano, D R. Blake, N J. Blake, Elliot Atlas, F Flocke, D J. Jacob, and L Jaegle

Reactive Nitrogen Budget During the NASA SONEX Mission

R. W. Talbot,¹ J. E. Dibb,¹ E. M. Scheuer,¹ Y. Kondo,² M. Koike,² H. B. Singh,³
 L. B. Salas,³ Y. Fukui,³ J. O. Ballenthin,⁴ R. F. Meads,⁴ T. M. Miller,⁴
 D. E. Hunton,⁴ A. A. Viggiano,⁴ D. R. Blake,⁵ N. J. Blake,⁵ E. Atlas,⁶
 F. Flocke,⁶ D. J. Jacob,⁷ and L. Jaegle⁷

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 (NO_y) mixing ratio was 425 parts per trillion by volume (pptv). A data set merged to the HNO_3 measurement time resolution was used to calculate NO_y (NO_y sum) by summing the reactive nitrogen species (a combination of measured plus modeled results) and comparing it to measured NO_y (NO_y meas.). Comparisons were done for tropospheric air ($\text{O}_3 < 100$ parts per billion by volume (ppbv)) and stratospherically influenced air ($\text{O}_3 > 100$ ppbv) with both showing good agreement between NO_y sum and NO_y meas. (slope > 0.9 and $r^2 \approx 0.9$). The total reactive nitrogen budget in the upper troposphere over the North Atlantic appears to be dominated by a mixture of NO_x ($\text{NO} + \text{NO}_2$), HNO_3 , and PAN. In tropospheric air median values of NO_x/NO_y were ≈ 0.25 , $\text{HNO}_3/\text{NO}_y \approx 0.35$ and $\text{PAN}/\text{NO}_y \approx 0.17$. Particulate NO_3^- and alkyl nitrates together composed $< 10\%$ of NO_y , while model estimated HNO_4 averaged 12%. For the air parcels sampled during SONEX, there does not appear to be a large reservoir of unidentified NO_y compounds.

1. Introduction

Reactive nitrogen compounds in the Earth's troposphere, primarily believed to be present as NO , NO_2 , HONO , HNO_3 , HNO_4 , NO_3 , N_2O_5 , $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ (PAN), RONO_2 (alkyl nitrates), and particulate NO_3^- , constitute important controls on O_3 , oxidant, and acidity levels on a global scale. The collective sum of these species, commonly referred to as total reactive odd-nitrogen (NO_y) [Fahey *et al.*, 1985], is a quantity useful for general characterization of air parcels in rural and remote atmospheres. Direct measurements of NO_y 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_x , HNO_3 , and PAN

comprise $> 90\%$ of total NO_y [Parish *et al.*, 1993; Sandholm *et al.*, 1994].

At remote locations comparison of NO_y meas. and NO_y 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 NO_y meas. due to non-reactive nitrogen compounds [Crosley *et al.*, 1996; Bradshaw *et al.*, 1998] and possible inclusion of unidentified NO_y compounds (e.g., alkyl nitrates) in NO_y meas. [Fahey *et al.*, 1986; Atlas *et al.*, 1992a] have been proposed as explanations.

In this paper we present a summary comparison between NO_y measured directly with a gold catalytic converter [Kondo *et al.*, 1997b] and the sum of the individually measured species NO , HNO_3 , PAN, PPN, alkyl nitrates, plus modeled NO_2 , HONO , HNO_4 , N_2O_5 , and NO_3 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 NO_y 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 NO_y were sampled through a rear-facing (to help exclude aerosols $> 1 \mu\text{m}$ 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]. NO_y 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 NO_y 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 NO_y .

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

¹Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham

²Solar-Terrestrial Environmental Laboratory, Nagoya University, Toyokawa, Japan.

³NASA Ames Research Center, Moffett Field, California.

⁴Air Force Research Laboratory/VSBP, Hanscom Air Force Base, Massachusetts.

⁵Department of Chemistry, University of California - Irvine, Irvine, California.

⁶Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado.

⁷Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts.

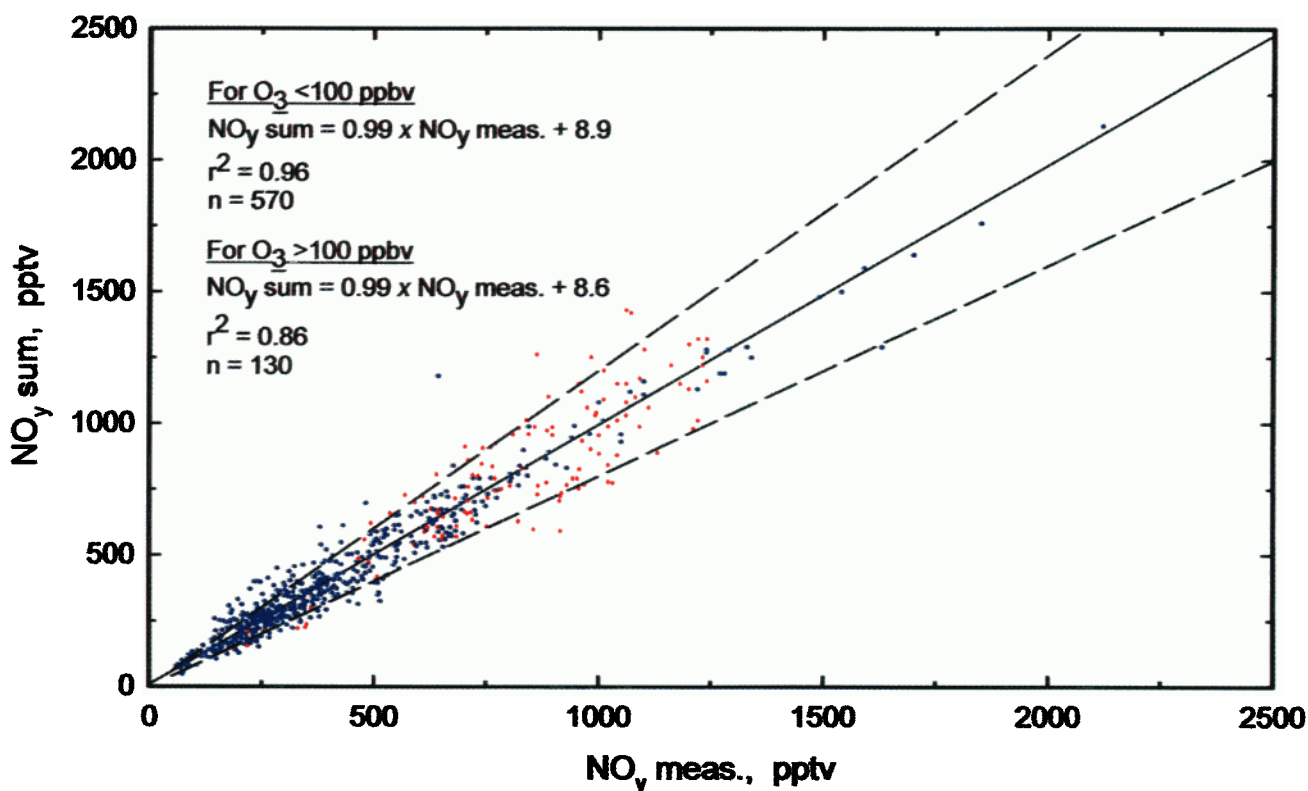


Figure 1. Linear least squares relationship between NO_y meas. and NO_y sum in the middle and upper troposphere (8 - 12.5 km altitude) over the North Atlantic. Blue solid circles represent the relationship for $\text{O}_3 < 100$ ppbv and the red $\text{O}_3 > 100$ ppbv. Only one regression line is shown since the two overlap identically, with $\pm 20\%$ bounds indicated by dashed lines.

additions of HNO_3 down $\approx 95\%$ 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 NO_y budget, but in general the two data sets for HNO_3 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 NO_2 , NO_3 , N_2O_5 , HONO, and HNO_4 . The model was constrained with observed NO , CO , H_2O , CH_4 , hydrocarbons, pressure, temperature, aerosol surface area, and

UV actinic flux. Modeled HO_2 was used to calculate NO_2 . The error in evaluating NO_2 could be as large as 50%, which is derived from the uncertainties in measured NO , O_3 , and the rate constants for $\text{NO} + \text{O}_3$ and NO_2 photolysis.

2.1 Database

Although each of the participating groups reported individual flight data files to the SONEX archive (publicly available on Cloud1.nasa.ames.gov at NASA Ames Research Center), we used data files merged to the HNO_3 time resolution for the analyses reported in this paper. This provided measurements and associated model-estimated NO_2 , HONO, HNO_4 , N_2O_5 , and NO_3 on the same time base [Jaegle *et al.*, this issue]. Since particulate- NO_3^- was measured during SONEX with approximately 10 minute time resolution, we did not include it in the data analysis. The median value of particulate- NO_3^- was 15 pptv [Dibb *et al.*, 1999] which represented $< 5\%$ of the NO_y 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 $< 85^\circ$ and, (2) measurement intervals where NO , HNO_3 , PAN, and NO_y 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 NO_y budget over the North Atlantic.

3. The NO_y Budget

The NO_y sum compared to NO_y meas. showed a high degree of correlation over the range of NO_y mixing ratios from ≈ 70 - 1500 pptv [Figure 1]. Here NO_y sum represents the measured species NO ,

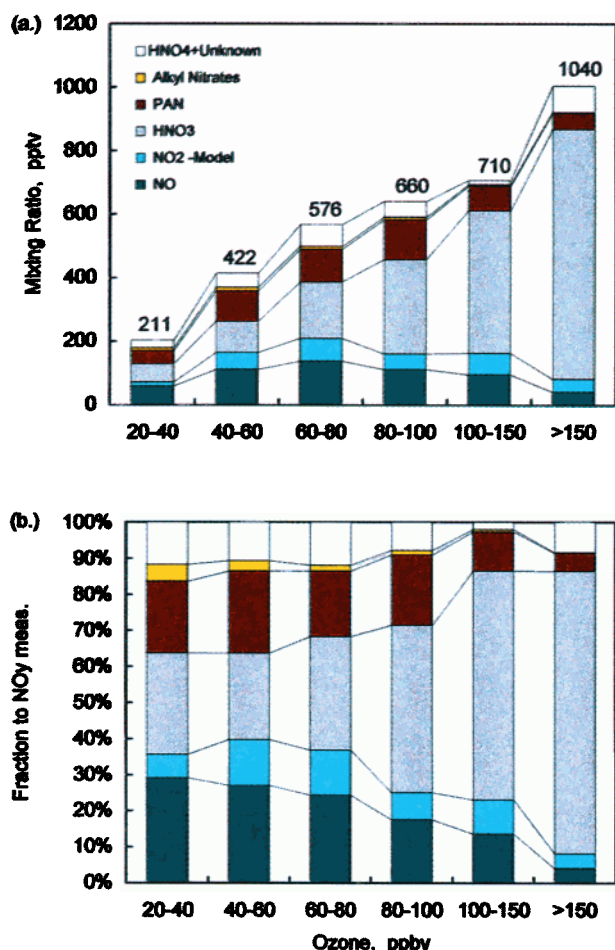


Figure 2. (a) Average value of various reactive nitrogen species as a function of binned O₃ mixing ratios. The height of the stacked groupings represent the sum of the individual components and the value above it is average NO_y meas. The uncolored area includes model calculated HNO₄ plus the remaining difference in NO_y meas. and NO_y sum. (b) Fraction of each species as shown in (a) to NO_y 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 NO₂, HONO, HNO₄, N₂O₅, and NO₃. The dashed lines depicted in Figure 1 indicate $\pm 20\%$ 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 NO_y sum and NO_y 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 NO_y for the tropospheric case represent sampling of recent aircraft emissions where NO comprised $\geq 80\%$ of the NO_y species. The lowest mixing ratios of NO_y 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 NO_x had a median mixing ratio of 150 pptv, HNO₃ 130 pptv, and PAN 80 pptv. The relatively high values of NO_x

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/NO_y) progressively increased from the middle troposphere to the lower stratosphere comprising as much as 80% of NO_y.

Median values of the ratios of NO_x, HNO₃, and PAN to NO_y meas. in tropospheric air showed that overall NO_x composed $\approx 25\%$ of NO_y, HNO₃ $\approx 35\%$, and PAN $\approx 17\%$. The alkyl nitrates collectively averaged about 10 pptv, and represented $\leq 5\%$ of NO_y. Particulate reactive nitrogen was sampled to some (unknown) degree by the NO_y 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 $12 \pm 9\%$ (i.e., 55 ± 30 pptv) of NO_y sum. In addition, positive interference in NO_y meas. by non-reactive nitrogen compounds

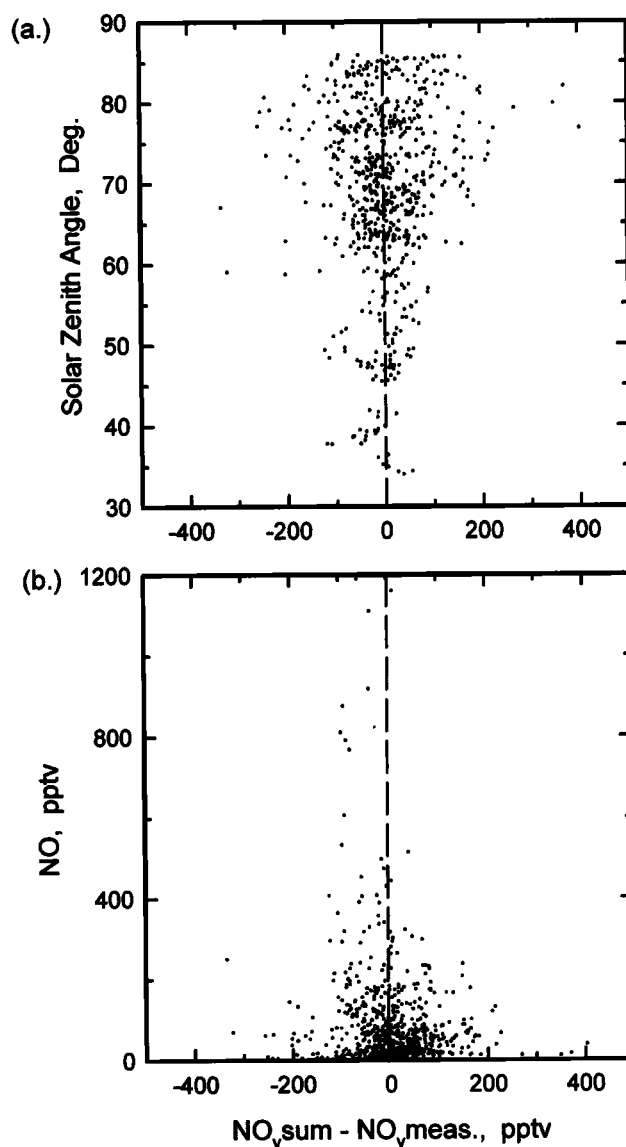


Figure 3. Difference between NO_y sum and NO_y meas. as a function of solar zenith angle (a) and NO mixing ratio (b).

(e.g., NH_3 and HCN) [Kliner *et al.*, 1997; Bradshaw *et al.*, 1998] is a general concern, but seemingly a small one with regard to the SONEX data [Koike *et al.*, 1999].

To look for likely factors which may have contributed to systematic differences in NO_y sum and NO_y meas., we plotted the difference, NO_y sum. - NO_y meas., as a function of various parameters including HNO_3 , PAN, O_3 , CO , $\text{C}_2\text{H}_2/\text{CO}$ 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_y sum. and NO_y meas. An interesting result was found with regard to solar zenith angle (Figure 3a); the difference in NO_y sum. and NO_y 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 pptv (Figure 3b) due to slowed photoysis 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_4 . Thus, NO_y sum has greatest uncertainty at low mixing ratios of NO , and propagation of the associated errors in NO_y sum makes it potentially as large as $\pm 80\%$. The increased scatter in the agreement between NO_y sum and NO_y 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_y sum - NO_y 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_x , 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_4 in the remote troposphere. It is also necessary to continue to assess the conversion efficiency of NO_y instruments for reactive and non-reactive nitrogen compounds under actual field conditions to better characterize the utility of NO_y measurements in the troposphere.

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- 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)
- M. Koike 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: hsingh@mail.arc.nasa.gov)
- J. O. Ballenthin, D. E. Hunton, R. F. Meads, T. M. Miller, and A. A. Viggiano, Air Force Research Laboratory/VSBP, Hanscom Air Force Base, MA 01731. (e-mail: ballenthin@plh.af.mil; viggiano@plh.af.mil)
- D. R. Blake and N. J. Blake, Department of Chemistry, University of California - Irvine, Irvine, CA 98107. (e-mail: dblake@orion.oac.uci.edu; nblake@uci.edu)
- E. Atlas and F. Flocke, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80303. (e-mail: atlas@acd.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; lyj@io.harvard.edu)

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