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# Distribution of reactive nitrogen species in the remote free troposphere: data and model comparisons

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#### Abstract

The available reactive nitrogen measurements from the global free troposphere obtained during the period of 1985–1995 have been compiled and analyzed. The species of interest are NO,  $NO_x$  (NO + NO<sub>2</sub>), NO<sub>y</sub>, PAN, HNO<sub>3</sub> and  $O_3$ . Data extending to 13 km have been gridded with a 5° × 5° horizontal and 1 km vertical resolution. The data have been divided into two seasons, namely "Winter" and "Summer" depending upon the time and location of the observations. Data described here as well as additional analysis have also been archived and are accessible on-line through the World Wide Web at: http://george.arc.nasa.gov/ ~athakur. Global maps of the reactive nitrogen species distribution are produced in a form that would be most useful for the test and evaluation of models of tropospheric transport and chemistry. Limited comparisons of the observed reactive nitrogen species data with predictions by 3-D global models were performed using three selected models. Significant model to model as well as data to model differences were frequently observed. During summer, models tended to underpredict NO (-25 to -60%) while significantly overpredicting HNO<sub>3</sub> (+ 250 to + 400%) especially in the upper troposphere. Similarly, the seasonal HNO<sub>3</sub> variations predicted by some models were opposite to those observed. PAN was generally overpredicted, especially in the upper troposphere, while NO<sub>v</sub> was underpredicted. Ozone on average was better simulated but significant deviations at specific locations were evident. By comparing model predictions with observations, an overall quantitative assessment of the accuracy with which these three models describe the global distribution of measured reactive nitrogen species is provided. No reliable trend information for any of the reactive nitrogen species was possible based on the presently available data set. The reactive nitrogen data currently offer only a limited spatial and temporal coverage for the validation of global models. © 1999 Elsevier Science Ltd. All rights reserved.

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#### 1. Introduction

Nitrogen oxides  $(NO_x = NO + NO_2)$  play a central role in the chemistry of the troposphere via the production

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and destruction of ozone (O<sub>3</sub>), regulation of hydroxyl radicals (OH), and formation of acid rain (Haagen-Smit, 1952; Leighton, 1961; Crutzen, 1979; Logan et al., 1981). Depending on the availability of  $NO_x$ , any given tropospheric region can be a net producer or a destroyer of  $O_3$ . By controlling the abundance of  $O_3$  and OH, reactive nitrogen compounds exert a control on the overall oxidizing capacity of the atmosphere and therefore influence its ability to cleanse itself of many compounds of man-made as well as natural origin. Nitrogen oxides are emitted to the atmosphere primarily in the form of nitric oxide (NO), which is a major exhaust product from fossil fuel and biomass combustion, and is also produced from soil bacteria as well as electrical activity in the atmosphere. Although other forms of nitrogen are also released from the Earth's surface (e.g.  $N_2O$ , HCN,  $NH_3$ ), it is  $NO_x$  that primarily impacts ozone in the troposphere (Crutzen, 1995; Davis et al., 1996). Simulating and predicting the atmospheric distribution of  $NO_x$  has been a difficult task because of the extreme complexity of its sources and the intricacies of chemical reactions that describe its fate. For example,  $NO_x$  emitted to the atmosphere is slowly converted to species such as PAN (CH<sub>3</sub>C(O)OONO<sub>2</sub>), HNO<sub>3</sub>, peroxynitric acid (HO2NO2), N2O5, RONO2, organic pernitrate (RO<sub>2</sub>NO<sub>2</sub>), and aerosol nitrate (Singh, 1987; Roberts, 1995; Thompson et al., 1997). A full understanding is made further difficult by the fact that many of these products are hard to measure, have varying removal mechanisms and lifetimes, and under certain conditions can act as reservoirs which provide secondary sources of  $NO_x$ .

Major sources of atmospheric NO<sub>x</sub> (Tg N yr<sup>-1</sup>) are derived from fossil fuel combustion ( $\approx 21$ ), lightning  $(\approx 5)$ , biomass burning  $(\approx 7)$ , soil emissions  $(\approx 6)$ , subsonic aircraft (  $\approx 0.5$ ) and stratospheric injections (  $\approx 0.5$ ) (Levy et al., 1996; Price et al., 1997a, b; Baughcum et al., 1996 and references therein). Each one of the sources has significant uncertainties associated with it although gridded emissions inventories are available (Lee et al., 1997 and references therein). Some 85% of NO<sub>x</sub> is injected near the surface of the earth and nearly 60% is as a result of human activities. Because of rather active chemistry and fast removal in this region, only a small fraction of the surface emissions make it into the upper troposphere. One of the most uncertain sources of NO<sub>x</sub> is from electrical activity (lightning) with estimates ranging from 1 to  $220 \text{ Tg N yr}^{-1}$ . Recent analyses of old data and new satellite information have been used to conclude that the magnitude of this source is likely to be  $2-25 \text{ Tg N yr}^{-1}$ (Price and Rind, 1994; Lawrence et al., 1995; Levy et al., 1996; Price et al., 1997a, b). Lightning events are also typically associated with rapid convective movement of surface air upwards to the middle and upper troposphere, adding additional complexity to the distribution of this  $NO_x$ .

There is evidence that the O<sub>3</sub> mixing ratios in the troposphere have increased significantly since the preindustrial era and this change is attributable to increasing man-made emissions of  $NO_x$  (Volz and Kley, 1988; Logan, 1994; Crutzen, 1995). Accurate model simulation of the distribution of reactive nitrogen is key to our ability to understand the past and future impact of human activities on the oxidative capacity and the ozone forming potential of the atmosphere. This requires that global models be tested and validated before they can provide credible predictions. In recent years (1985-1997), a number of airborne process studies have been performed with reactive nitrogen as a focus. Many of these studies are in different geographical locations and the data are hard to access. We have archived and analyzed this global database of reactive nitrogen measurements (and  $O_3$ ) from the period of 1985–1995 for the remote free troposphere. Data extending to 13 km have been gridded with a  $5^{\circ} \times 5^{\circ}$  horizontal and 1 km vertical resolution to make them suitable for purposes of model testing and evaluation. Limited comparisons of the observed reactive nitrogen species data with predictions by 3-D global models were made using three selected models. All data described here as well as additional analysis are accessible on-line through the World Wide Web at: http:// george.arc.nasa.gov/~athakur.

#### 2. Data acquisition, processing and analysis

#### 2.1. Sources of data

Table 1 lists the expeditions from which the measured data were gathered. The detailed description of the individual expeditions including flight plans, meteorology, instrumentation and uncertainties, and data collection have been previously reported in many publications which are also noted in Table 1. The duration and location of the expeditions are listed in Table 1. Each expedition has been assigned a "summer" or "winter" season. The Amazon Boundary Layer Experiment (ABLE 2B) was categorized as winter because it was wet season (April–May) in southern hemisphere. We are aware that this summer/winter seasonal breakdown is inadequate, but the limited amount of available data did not permit a more refined seasonal classification. This study also focused on the free troposphere where anthropogenic influence and localized variations are expected to be minimized. We expand on the earlier work of Emmons et al. (1997) which was limited to only NO<sub>x</sub> and NO<sub>y</sub> and in which individual campaigns were compared with model results. Here we have attempted to combine all recent measurements to create a single free tropospheric global data set for a more complete set of reactive nitrogen species before comparing with model results. Vertical,

Table 1										
Description	of	Expeditions,	their	area	of	coverage	and	species	of in	terest

Expedition <sup>a</sup>	Date	Season <sup>b</sup>	Location (main)	Altitude (km)	Main species of interest	Reference <sup>c</sup>
AASE-I	1/3-2/21 1989	W	Arctic, N. America	16–21	NO, NO,, NO,, NO,, O,	1
AASE-II	10/4 1991-3/26 1992	W	Arctic, N. America	16-21	NO, NO, NO, NO, NO, O3	2
ABLE 2A	7/11-8/13 1985	S	Amazon	0.15-3.5	NO, O <sub>3</sub>	3
ABLE 2B	4/1-5/13 1987	W	Amazon, Atlantic	0–6	NO, PĂN, O <sub>3</sub>	4
ABLE 3A	7/7-8/17 1988	S	Arctic, sub-Arctic	0–6	NO, NO <sub>x</sub> , NO <sub>y</sub> , NO <sub>2</sub> , HNO <sub>3</sub> , PAN, O <sub>3</sub>	5
ABLE 3B	7/6-8/15 1990	S	E. Canada	0–6	NO, NO <sub>x</sub> , NO <sub>y</sub> , NO <sub>2</sub> , HNO <sub>3</sub> , PAN, O <sub>3</sub>	6
CITE-1	11/4-11/26 1983	W	Pacific;	0.9–9.7	NO, Ŏ,	7
CITE-2	8/11-9/5 1986	S	E. Pacific, USA	0.15–6.1	NO, $NO_x$ , NO <sub>y</sub> , NO <sub>2</sub> , HNO <sub>3</sub> , PAN, O <sub>3</sub>	8
CITE-3	8/22-9/22 1989	S	W. Atlantic	0–6	NO, NO, NO, NO, O,	9
INSTAC	3/5-3/10 1989	S	Pacific	3–8	NO, NO, O,	10
MLOPEX-II <sup>d</sup>	1/15-5/15 1992	W,S	Hawaii	3	NO, NO <sub>x</sub> , NO <sub>y</sub> , NO <sub>2</sub> , HNO <sub>3</sub> , PAN, O <sub>3</sub>	11
PEM-West A	9/7-10/22 1991	S	Pacific	0–13	NO, $NO_x$ , $NO_y$ , $NO_2$ , $HNO_3$ , PAN, O,	12
PEM-West B	1/15-3/14 1994	W	Pacific	0-13	NO, NO, HNO, PAN, O,	13
SPADE	11/16 1992	W	N. America	15-20	NO, NO, NO, NO, HNO,	14
SPADE	4/26-5/18 1993	S	N. America	15-20	NO, NO, NO, NO, HNO,	15
STRATOZ-III	6/4-6/26 1984	S	Atlantic, S. America	0-12	NO	16
TRACE-A	9/24-10/11 1992	S	Atlantic	0–13	NO, NO <sub>x</sub> , NO <sub>y</sub> , NO <sub>2</sub> , HNO <sub>3</sub> , PAN, O <sub>3</sub>	17
TROPOZ-II	1/9-2/1 1991	W	Atlantic, S. America	0-12	NO, $NO_y$	18

<sup>a</sup>See Appedix A.2 for acronyms.

<sup>b</sup>W: Winter, S: Summer. <sup>c</sup>Special Issues of: (1) GRL Vol. 17, No. 4, 1990 (2) GRL Vol. 20, No. 22, 1993 (3) JGR Vol. 93, No. D2, 1988 (4) JGR Vol. 95, No. D10, 1990 (5) JGR Vol. 97, No. D15, 1992 (6) JGR Vol. 99, No. D1, 1994 (7) JGR Vol. 92, No. D2, 1987 (8) JGR Vol. 95, No. D7, 1990 (9) JGR Vol. 98, No. D12, 1993 (10) Not Available (11) JGR Vol. 97, No. D10, 1992 (12) JGR Vol. 101, No. D1, 1996 (13) Not Available (14, 15) GRL Vol. 21, No. 23, 1994 (16) Atm. Env. Vol. 24A, No. 11, 1990 (17) JGR Vol. 101, No. D19, 1996 (18) J. Atm. Chem. Vol. 22, No. 3, 1995. <sup>d</sup>Surface-based study.

latitudinal and longitudinal distributions and their comparisons with 3-D models are emphasized in this study.

#### 2.2. Data gridding

All data were carefully inspected to eliminate numerical errors. The impact of extreme outliers was minimized by using low frequency (notch) statistical filters and by manually inspecting these on a case by case basis. All data were merged into a single global set with a basic grid size of 5° latitude x 5° longitude and 1 km vertical resolution, starting at 0.5 km from the surface. This was selected as a most useful compromise between model resolution and data availability. When appropriate, coarser vertical resolutions (e.g. 3 km) were also considered. The data were processed to obtain mean, median, 25 and 75% tiles at each location. If the number of data points, within any given grid, was less than six for NO or less than three for other species, it was not accepted. This was done to minimize local atmospheric and instrumental fluctuations. The sampling frequency, which varied between a few seconds to a few minutes, was also taken into consideration before averaging. Small measured NO values during nighttime were considered instrumental measurement blanks and were rejected. All reported NO data are for daytime based upon solar zenith angles of  $> 70^{\circ}$ . Measured values of NO<sub>2</sub> were taken where available. Model calculated values of NO<sub>2</sub> were used for several expeditions when either no  $NO_2$ was measured or it was reported to be an unacceptable measurement. The calculation of NO<sub>2</sub> from observed NO requires the use of simple box models that have been extensively described in the literature (e. g. Davis et al., 1996). Recent measurements of NO and NO<sub>2</sub> have shown that the calculation of NO<sub>2</sub> from measured NO is a reasonable approach (Bradshaw et al., 1998). In general however, NO should be favored over  $NO_x$  for purposes of comparison with models. Since much of the daytime  $NO_x$  in the upper troposphere is present as NO, these difficulties would be minimized in this region.

#### 2.3. Maps showing data coverage

The median values of the species NO, NO<sub>x</sub>, NO<sub>y</sub>, PAN, HNO<sub>3</sub>, and O<sub>3</sub> between altitudes 0.5 and 12.5 km for the two seasons are shown in Figs. 1–3. A large number of other maps at other selected altitude bins (0.5–3, 3–6, 6–9 and 9–12.5 km) were also produced and can be accessed using the World Wide Web as described in the Appendix. It is evident from Fig. 1–3 that total available data are limited and do not provide adequate global coverage.

#### 2.4. Super-grids for vertical profiles

There were generally insufficient data within a given  $5^{\circ} \times 5^{\circ}$  grid to provide a detailed description of the vertical structure of species for the entire troposphere. Standard grids were thus combined to form super-grids for the explicit purpose of creating a statistically valid profile up to 12 km with a 1-km resolution. These super-grids thus provided the best opportunity for comparison of observations with the output from 3-D global models. All 17 super-grids are rectangular boxes in shape and varied in size as shown in Fig. 4. Table 2 provides the latitude, longitude and the type of available data for each supergrid. Since the measured data were limited, some profiles remained inadequate for specific seasons or specific chemicals even within these super-grids. Many meaningful comparisons, however, could be made for the two seasons. Some of the vertical profiles for specific chemicals are presented for selected super-grids and seasons in Figs. 5-10. Additional material can be found on-line at the WWW site.

#### 2.5. Latitudinal and longitudinal distributions

As is evident from Fig. 4, longitudinal and latitudinal data are sparse and are certainly not available with a 1-km vertical resolution. For these comparisons we have selected a coarser vertical resolution of 0.5–3, 3–6, 6–9 and 9–12.5 km. In some cases data are only available for the upper troposphere and that too for a limited number of species. We, however, wish to point out that latitudinal/longitudinal profiles derived from these sparse data may not be climatologically representative (see the WWW site).

#### 3. Model outputs

Evaluation of the ability of a model to reproduce observed features of the atmosphere is a prerequisite for use in an assessment mode. We describe here a limited comparison of three models: (1) BISA/NCAR IMAGES Model, (2) Harvard/GISS Model and (3) MPI-Ch MATCH Model (see Appendix A for acronyms) with the observational record collected in this study. Salient features of these models are given in Table 3 and are briefly described below. Model output was obtained in all cases to represent winter (December–January–February, DJF) and summer (June–July–August, JJA) average conditions. The models were evaluated against the data from the 17 super-grids (Table 2).

#### 3.1. IMAGES model

The IMAGES model is a 3-D CTM for the troposphere. It calculates the monthly averaged distributions of 56 chemical species, including ozone, hydrogen oxides, nitrogen oxides, sulfur oxides, methane, and several non-methane hydrocarbons. Its horizontal resolution is  $5^{\circ}$  in latitude and  $5^{\circ}$  in longitude. In the vertical, the model has 25 layers extending between the Earth's surface and the lower stratosphere (50 mbar) (Müller and Brasseur, 1995; Pham et al., 1995). A semi-Lagrangian scheme (Smolarkiewicz and Rasch, 1991) is used to calculate the advection by monthly averaged winds. The wind fields, as well as temperature and water vapor are a 1985-1989 average taken from an analysis of the European Center for Medium-Range Weather Forecasts (ECMWF). The impact of wind variability at time scales smaller than one month are taken into account by the introduction of a diffusion term in the continuity equation. The diffusion coefficients are estimated from the ECMWF wind variances. Vertical mixing in the planetary boundary layer is also represented as diffusion. Convection intensity is adjusted so that the model reproduces the observations for radon (Rn) at mid-latitudes in summer.

The chemical scheme includes more than 150 reactions, including simplified oxidation schemes for ethane, propane, isoprene, etc. The photodissociation rates are interpolated from a look-up table. The effect of clouds in the model is parameterized following Chang et al. (1987) and using the cloud cover and optical depth estimated by ISCCP. The surface emissions and deposition velocities used in IMAGES are based on an inventory of the sources (Müller and Brasseur, 1995), with minor modifications (private communication). Global N sources used in this model are listed in Table 3. The production of NO by lightning discharges in the basic model is  $5 \text{ Tg N yr}^{-1}$ globally, distributed as the satellite-derived flash frequencies of Turman and Edgar (1982). The emission is assumed to be constant with altitude between the surface and the top altitude of Cumulonimbus. The washout scheme is based on the ISCCP cloud data set and climatological precipitation rates. The conversion of  $N_2O_5$  to HNO<sub>3</sub> on aerosols is parameterized using the modelcalculated sulfate distribution. Additional details on the IMAGES model can be found in Müller and Brasseur, (1995) and Brasseur et al. (1996).













Fig. 3. Median NO<sub>y</sub> (ppt) and O<sub>3</sub> (ppb;  $10^{-9}$  v/v) mixing ratios, for summer and winter. Same as Fig. 1.

## Supergrid Locations - (Summer/Winter) Standard Grid: 5° x 5° ; ALT: 0.5-12.5 km



Fig. 4. Location of the super-grids used for profile studies and model comparisons. The numerical coordinate values are identified in Table 2. Numbers indicated are used as super-grids numbers in the text.

Fable 2
Locations of the super-grids (SGs) selected for comparison of observations and models. The existence of measured data is indicated by
symbol

SG	Lat	Latitude Longit		gitude	ude HNO <sub>3</sub>		NO		1	NOx	1	NOv	(	$D_3$	P	AN
#	Min.	Max.	Min.	Max.	S	W	S	W	S	W	S	W	S	W	S	W
1	15	25	- 180	- 145	•	•	•	•	•	•	•	•	•	•	•	•
2	25	35	-160	-125	•		•	•	•	•	•	•	•	•	•	
3	35	50	-145	-125	•	٠		•			•	•	•	•	•	•
4	50	75	-170	-145	•	٠	•	•	•		•	•	•	•	•	•
5	0	20	150	175	•	•	•	•	•		•	•	•	•	•	•
6	10	30	130	150	•	٠	•	•	•		•	•	•	•	•	•
7	40	50	150	175	•	•		•			•	•	•	•	•	
8	-40	- 30	- 30	15	•		•		•		•		•		•	
9	-25	- 5	- 5	10	•		•		•		•		•		•	
10	-20	5	-25	-10	•		•		•		•		•		•	
11	- 5	10	-40	-25	•		•		•		•		•		•	
12	10	20	-60	- 45	•		•		•		•		•		•	
13	25	50	150	175												•
14	25	40	- 75	-60	•		•	•		•		•		•		•
15	70	85	-80	- 55	•		•		•		•	•	•	•	•	
16	-25	- 5	- 155	- 135				•		•		•		•		
17	- 5	15	- 145	- 120				•		٠		•		٠		



### SG #6 (Lat:10-30°N, Long:130-150°E)

Fig. 5. Vertical profiles of species NO, HNO<sub>3</sub>, and PAN at super-grid number 6 during summer and winter. Median, mean, 25 and 75% tiles are shown. Solid line joins measured median values. Model results of Harvard (dashed line), MATCH (dash-dot line), and IMAGES (dotted line) model for summer (June–July–August) and winter (and December–January–February) are compared. MATCH model does not simulate PAN chemistry.

#### 3.2. Harvard/GISS model

The Harvard CTM has a spatial resolution of  $4^{\circ} \times 5^{\circ}$ , with 9 vertical layers in sigma coordinates, extending from the surface to 10 mbar. Meteorological fields are from the NASA GISS GCM II (Hansen et al., 1983), and are updated every 4 h. Dry deposition is computed with a resistance-in-series scheme similar to that of Gao and Wesely (1995). Wet deposition of soluble tracers is computed with the scheme of Balkanski et al. (1993). The present version of the Harvard model (Wang et al., 1998 a; b) transports 15 reactive chemical tracers: odd oxygen ( $O_x = O_3 + O + NO_2 + HNO_4 + 2 \times NO_3 + 3 \times$  $N_2O_5$ ),  $NO_x$  ( $NO + NO_2 + NO_3 +$  nitrous acid ( $HNO_2$ )),  $N_2O_5$ ,  $HNO_4$ , PANs (peroxyacetyl nitrate and its homologues), alkylnitrates ( $\ge C4$  lumped as butylnitrate),  $HNO_3$ , CO, ethane, higher alkanes ( $\ge C4$  lumped as butane), alkenes ( $\ge C3$  lumped as propene), isoprene, acetone, higher ketones ( $\ge C2$  lumped as methylethyl ketone), and  $H_2O_2$ . The chemical mechanism is based on

NO



Fig. 6. Vertical profiles of species NO at four locations (super-grid numbers: 5, 9, 11 and 14) in summer and two locations (super-grids numbers: 2 and 7) in winter. Same as Fig. 5.

recent compilations. The chemical mechanism is parameterized for rapid computation following the procedure described by Spivakovsky et al. (1990). Global N sources used in this model are listed in Table 3. In sum, the total NO<sub>y</sub> source in the troposphere is 44 Tg N yr<sup>-1</sup>. HC emissions from fossil fuel combustion are based on Piccot et al. (1992), with the emission ratios from Middleton et al. (1990) and light alkane ratios derived from measurements at Harvard Forest (Goldstein et al., 1995). Biomass burning sources are scaled to the CO source based on observed emission ratios (Lobert et al., 1991; Hurst et al., 1994; Andreae, 1997). Additional details on this model structure and its validation can be found in Wang et al. (1998a–c).

#### 3.3. MATCH model

MATCH (Model of Atmospheric Transport and Chemistry) is being jointly developed by C4 (UCSD), NCAR, and MPI-Ch (Rasch et al., 1997). The resolution

### HNO<sub>3</sub>



Fig. 7. Vertical profiles of species HNO<sub>3</sub> at four locations (super-grid numbers: 1, 2, 5 and 9) in summer and two locations (super-grid numbers: 5 and 7) in winter. Same as Fig. 5.

of MATCH is dependent upon the input meteorological winds used. The transport in the model can be driven by either GCM (CCM2 or CCM3) or forecast center analyses ("observed winds") from ECMWF or NCEP. Convection also depends on the input meteorological data: CCM2 – Hack scheme, CCM3 – Zhang/Hack scheme, ECMWF – Tiedtke scheme, NCEP – Pan/Wu scheme. Advection in MATCH is done using the Semi-Lagrangian Transport scheme, and vertical diffusion uses the same scheme as in the CCM2.

Several chemistry schemes are being used in MATCH. For CH<sub>4</sub>–CO–O<sub>3</sub>–NO<sub>y</sub>–HO<sub>x</sub> tropospheric photochemistry, a version has been developed at C4 and MPI (Lawrence, 1996). The tropospheric chemistry version driven by NCEP data (Lawrence, 1996) was used to produce the model output that was made available to us for the comparison. In this version, the only explicit sources are for CO (2260 Tg CO yr<sup>-1</sup>), CH<sub>4</sub> (540 Tg CH<sub>4</sub> yr<sup>-1</sup>), and NO<sub>x</sub> (see Table 3). The photochemical mechanism contains about 40 reactions and is integrated based





Fig. 8. Vertical profiles of species PAN at four locations (super-grid numbers: 2, 5, 9 and 15) in summer and two locations (super-grid numbers: 4 and 13) in winter. Same as Fig. 5.

on the quasi-steady-state assumption (QSSA). Photolysis rates are also updated each time step, based on the method of Landgraf and Crutzen (1997). Loss by dry deposition is based on globally gridded monthly deposition velocities from Ganzeveld and Lelieveld (1995). Wet deposition is based on the cloud water amounts and formation and evaporation rates of precipitation computed by the model convection and microphysics schemes (Rasch and Kristjansson, 1998). A current shortcoming is the absence of NMHC chemistry.

#### 4. Data and model comparisons: results and discussion

When comparing observations with models, it is important to keep in mind that both have inherent weaknesses. Basic model assumptions and parameterizations introduce several shortcomings in the simulation of chemistry, transport, emissions, and removal processes. On the other hand, observations of the chemical species are usually sparse in space and time and even intensive measurement campaigns have only a one to two month





Fig. 9. Vertical profiles of species  $NO_y$  at four locations (super-grid numbers: 1, 2, 5 and 9) in summer and two locations (super-grid numbers: 4 and 14) in winter. Same as Fig. 5.

duration, precluding diagnosis of seasonal variations. In this work, we have attempted to minimize this problem by combining all recent measurements into one global data set before comparing it to model results. Nevertheless, the data available are generally insufficient for a complete evaluation of models.

The measured vertical distribution of key species for the seventeen super-grids (SG) shown in Fig. 4 was compared with models. Only limited comparisons will be discussed here but additional information on model and data comparison can be found on the WWW. Fig. 5 shows the summer and winter vertical distribution of NO, HNO<sub>3</sub> and PAN for super-grid #6. Figs. 6–10 show data and model comparisons for individual species from a variety of super-grids in both selected seasons.

To gain a quantitative assessment of the differences between observations and models we selected 5465 grids where measurements, were available. For comparison purpose, these data for the selected species (reactive nitrogen and ozone) were grouped by season



Fig. 10. Vertical profiles of species  $O_3$  at four locations (super-grid numbers: 1, 2, 5 and 11) in summer and two locations (super-grid numbers: 2 and 4) in winter. Same as Fig. 5.

(summer/winter) and four altitude levels (0.5–3, 3–6, 6–9 and 9–12 km). The number of measurements, in individual bins thus created, varied from 10 to 345. The measured data (mean, median and standard deviation) and the results of the statistical comparison of Harvard, Mainz and IMAGES model predictions are summarized in Table 4. For reasons of simplicity, model results are given as a percent of the observed mean value. The main purpose of information provided in Table 4 is to provide an overall assessment of the predictive capability of these models. One of the first observations that can be quickly made from Fig. 5 (and Table 4) alone is that model to model differences are nearly as large as model to data differences. The level of agreement is both variable as a function of altitude and season. It is also clear that these differences are not systematic in nature. For example, NO is underpredicted in summer while  $HNO_3$  is greatly overpredicted. These model to model uncertainties are in large part due to different transport parameterizations, as shown in Friedl et al. (1997), based on a comparison of Table 3

Description of global three-dimensional chemistry-transport models used in this study

Properties	IMAGES	HARVARD/ GISS	MATCH
Resolution			
Horizontal	$5^{\circ} \times 5^{\circ}$	$4^{\circ} \times 5^{\circ}$	$1.88^{\circ} \times$ $1.88^{\circ}$
Vertical layers	25	9	18-44
Temporal	1 month	4 h	30 min
Sources (Tg N yr <sup>-</sup>	<sup>1</sup> )		
Industry	21.0	21.0	21.3
Biomass burning	4.9	11.6	8.5
Soil	5.5	6.0	5.5
Lightning	5.0	3.0	2.2
Aircraft	0.46	0.46	0.5
Stratosphere	$0.4(NO_x) + 0.6 (HNO_3)$	0.5	1.1
Chemistry			
NMHC	Yes	Yes	No
Reference	Müller and Brasseur,1995	Wang et al., 1998a, b	Lawrence, 1996

tracer runs, as well as due to differences in the simulation of the production and removal rates of these reactive species. Extensive model to model intercomparisons are required before the true nature of these differences can be elucidated.

#### 4.1. NO and $NO_x$

Every expedition, used in this compilation, had measured NO. A typical NO (and NO<sub>x</sub>) profile showed extremely low mixing ratios in the lower troposphere (10-20 ppt; ppt = pptv =  $10^{-12}$  v/v) increasing significantly in the upper troposphere (20-200 ppt) (Figs. 5 and 6). Part of the reason for this NO profile is due to the fact that NO should make up a high fraction of  $NO_x$  in the upper troposphere (model calculated NO<sub>2</sub>/NO  $\approx$  0.3 at 10 km). Additionally, the total burden of  $NO_{x}$  available in the upper troposphere is maintained due to its slow removal there as well as the presence of primary (lightning, aircraft) and possibly secondary (recycling) atmospheric sources. In general, models show an overall tendency to underpredict NO at all levels in the troposphere (Table 4). To a degree this could be attributed to an underestimation of the lightning source. As can be seen from Figs. 5 and 6, the nature of disagreement is a function of location and season. NOx data-model comparisons show even larger disagreements extending to the lower troposphere (Table 4). This is also due to the fact that measured NO<sub>2</sub> values have traditionally been over

estimated (Crawford et al., 1996; Bradshaw et al., 1998). Of the three models, the MATCH model provides the largest deviation from measured data. We note that the prediction of NO (and  $NO_x$ ) by the MATCH model may be impaired by the fact that this model does not contain NMHC chemistry and cannot simulate the synthesis of PAN and its role in the storage and transport of  $NO_x$ .

#### 4.2. HNO<sub>3</sub>

The observed HNO<sub>3</sub> mixing ratios were highly variable. In the upper troposphere, median HNO3 concentrations in winter were 136 ppt, nearly twice as large as in summer (Table 4). In general, models tended to overpredict HNO<sub>3</sub> at all levels in summer (Figs. 5, 7 and Table 4) but the level of disagreement among models could vary greatly. This is particularly surprising as the  $NO_x$  field to support this HNO<sub>3</sub> reservoir is generally underpredicted. This discrepancy is not entirely due to a poor simulation of the HNO<sub>3</sub> sink processes (washout and dry deposition). The Harvard and MATCH models generally showed higher HNO3 concentrations in the lower half of the troposphere, while IMAGES showed higher concentrations in the uppermost troposphere. The Harvard model generally predicts larger abundances of HNO<sub>3</sub> in summer compared to winter while actual observations tend to show the opposite. Of the three models tested here IMAGES tended to describe the HNO<sub>3</sub> observations best in much of the troposphere. However, the implementation of a new and more realistic washout scheme in IMAGES would bring the HNO3 results much closer to the other model results (J.-F. Müller, private communication) and deteriorate this ostensible agreement.

In general, it is evident that models are significantly overpredicting HNO<sub>3</sub> and underpredicting NO<sub>x</sub> at least in the summer months (Figs. 5, 7 and Table 4). It also appears that the level of agreement between data and models is much improved for the winter period (Table 4). The prediction of too little NO and too much HNO<sub>3</sub> has led to the speculation that unknown processes, possibly involving particle reactions, might exist to rapidly convert HNO<sub>3</sub> to NO<sub>x</sub> (Chatfield, 1994; Fan et al., 1994; Singh et al., 1996; Dentener et al., 1996) and these are not being currently simulated by models. Reaction between HNO3 and aerosol black carbon or soot has been suggested as a mechanism for the rapid conversion of HNO<sub>3</sub> to  $NO_x$  (Larry et al., 1997; Hauglustaine et al., 1997). A possible reason for better agreement in winter as opposed to summer may be that HNO<sub>3</sub> removal by particles is significant only during summer when particle concentrations are high (Singh et al., 1998; Tabazadeh et al., 1998). The possibility that measurement difficulties for HNO<sub>3</sub> may exist can also not be ruled out (Crosley, 1994).

Species	Altitude	Summer				Winter			
	(1117)	Observed value <sup>a</sup>	Model-H (%) <sup>b</sup>	Model-I (%)	Model-M (%)	Observed value <sup>a</sup> (%)	Model-H (%)	Model-I (%)	Model-M (%)
ON	0.5 - 3	$22 \pm 39$ (9, 136)	$79 \pm 107$	$86 \pm 90$	$20 \pm 27$	$36 \pm 50 \ (16, 94)$	$32 \pm 30$	51 <u>±</u> 45	$6\pm 6$
	3–6	$17 \pm 24$ (11, 218)	$75 \pm 39$	$73 \pm 32$	$27 \pm 23$	$26 \pm 35 \ (16,  127)$	$34 \pm 21$	$46 \pm 26$	$24 \pm 15$
	69	$32 \pm 35 \ (21, 141)$	$72 \pm 37$	$56 \pm 23$	$45 \pm 35$	$45 \pm 52 \ (34,  125)$	$35 \pm 27$	$38 \pm 13$	$37 \pm 24$
	9–12	$90 \pm 91 \ (76, 185)$	$75 \pm 52$	$46 \pm 27$	$40 \pm 26$	$68 \pm 89 \ (55, 107)$	$73 \pm 71$	$58 \pm 28$	$59 \pm 48$
NOx	0.5 - 3	$85 \pm 172$ (38, 95)	$170 \pm 234$	$95 \pm 116$	$48 \pm 75$	$47 \pm 44$ (29, 13)	$41 \pm 19$	$36 \pm 21$	$26 \pm 5$
	3–6	$47 \pm 40 \ (36, 148)$	$79 \pm 35$	$61 \pm 33$	$45 \pm 31$	$48 \pm 40 \ (38, 28)$	$41 \pm 9$	$44 \pm 38$	$42 \pm 20$
	6-9	$70 \pm 35 \ (64, 80)$	$65 \pm 31$	$42 \pm 18$	$75 \pm 42$	$109 \pm 92 \ (60, \ 10)$	$23 \pm 5$	$37 \pm 17$	$78 \pm 38$
	9–12	$159 \pm 133 \ (133, 93)$	$55 \pm 40$	$31 \pm 16$	$61 \pm 28$	$104 \pm 62 \ (99, \ 20)$	$46 \pm 34$	$71 \pm 42$	$111 \pm 75$
HNO <sub>3</sub>	0.5 - 3	$258 \pm 387 \ (96,  90)$	$191 \pm 148$	$76 \pm 88$	$150\pm89$	$294 \pm 277 \ (143,36)$	$103\pm 63$	$118 \pm 99$	$99 \pm 69$
	3–6	$153 \pm 269 \ (70, 155)$	$275\pm137$	$101 \pm 64$	$216\pm57$	$178 \pm 107 \ (140, 46)$	$141\pm46$	$123 \pm 76$	$162\pm72$
	69	$124 \pm 241 \ (61, 98)$	$237 \pm 98$	$105\pm53$	$294 \pm 109$	$206 \pm 172 \ (150, 57)$	$90 \pm 27$	$127 \pm 71$	$187\pm74$
	9–12	$80 \pm 68 \ (64, 126)$	$247\pm91$	$271\pm177$	$408 \pm 251$	$326 \pm 533 \ (136, 33)$	$37 \pm 23$	$73 \pm 91$	$84\pm52$
PAN	0.5 - 3	$197 \pm 548$ (48, 92)	$93 \pm 102$	$22 \pm 26$		$307 \pm 311$ (230, 38)	$74 \pm 72$	$34 \pm 25$	
	3–6	$242 \pm 402 \ (196, 155)$	$73 \pm 41$	$36\pm17$		$175 \pm 153 \ (130, 60)$	$91\pm54$	$64 \pm 33$	
	69	$191 \pm 182 \ (153, 109)$	$92 \pm 54$	$65 \pm 30$		$134 \pm 108 \ (84, \ 62)$	$122\pm50$	$103 \pm 33$	
	9–12	$147 \pm 139$ (99, 143)	$110 \pm 83$	$92 \pm 33$		$57 \pm 47 \ (38, \ 27)$	$191 \pm 108$	$157\pm65$	
NO,	0.5 - 3	$662 \pm 854 \ (335, \ 105)$	$117 \pm 102$	$55\pm 63$	$64 \pm 41$	$735 \pm 624 \ (519,82)$	$116\pm122$	$73 \pm 60$	$48 \pm 34$
	3–6	$771 \pm 753$ (544,179)	$82 \pm 32$	$42 \pm 22$	$47\pm12$	$558 \pm 527$ (418, 103)	$92\pm 64$	$71 \pm 35$	$66 \pm 28$
	6-9	$567 \pm 406 \ (441, \ 114)$	$95\pm41$	$65 \pm 30$	$77 \pm 28$	$769 \pm 1376 \ (450, 164)$	$53\pm18$	$68 \pm 25$	$70 \pm 27$
	9–12	$778 \pm 526 \ (619, \ 148)$	$63 \pm 34$	$71 \pm 27$	$58 \pm 29$	1270 ±807 (1372, 345)	$32 \pm 9$	$78 \pm 32$	$74 \pm 36$
O <sub>3</sub>	0.5 - 3	$41 \pm 16 \ (42, 136)$	$104\pm19$	$79 \pm 26$	$92 \pm 26$	$36 \pm 50 \ (16,94)$	$105\pm12$	$107 \pm 33$	$79 \pm 26$
	3–6	$55 \pm 20$ (54, 212)	$90\pm13$	$82\pm18$	$90 \pm 24$	$26 \pm 35 \ (16, \ 127)$	$111 \pm 11$	$135\pm33$	$108\pm33$
	69	$56 \pm 23$ (54, 125)	$93 \pm 19$	$95 \pm 29$	$114\pm 67$	$45 \pm 52 \ (34,  125)$	$86 \pm 9$	$135 \pm 30$	$136\pm74$
	9–12	$72 \pm 55 \ (62,  150)$	$74 \pm 19$	$106 \pm 38$	$102 \pm 102$	$68 \pm 89 \ (55, 107)$	$23 \pm 4$	$65 \pm 24$	$100 \pm 61$

Table 4 A comparison of global observational data with predictions from three selected models

<sup>a</sup>Mean  $\pm 1$  sigma (median, N). Mixing ratios of nitrogen containing species are in parts per trillion (pptv); O<sub>3</sub> is in parts per billion (ppbv). <sup>b</sup>Model-H (Harvard-model), Model-I (IMAGES-model), Model-M (MATCH-model). The value is % of observed mean. See text for detail. Peroxyacetyl nitrate (PAN) is a major contributor to the odd nitrogen budget in the troposphere and serves as an important reservoir for NO<sub>x</sub> (Singh et al., 1996, 1998). As stated earlier, the MATCH model lacks NMHC chemistry in its present state of development and cannot simulate PAN. Both IMAGES and Harvard models seem to generally catch the main features of PAN distribution but substantial disagreements with observations are evident (Fig. 8). In general, the Harvard model predicts substantially more PAN than IMAGES (Fig. 8). The over-prediction of PAN is most severe in the upper troposphere and in winter (Table 4).

#### 4.4. NO<sub>y</sub>

The chemical family  $NO_v$  (sum of  $NO_x$  and its oxidation products) is computed by adding all individual reactive nitrogen species in the model output and compared with a direct measurement of NO<sub>v</sub>. We note that NO<sub>v</sub> detectors can also detect interfering species such as HCN leading to an artificially high measured value although in most cases this effect should be small (Kondo et al., 1997). As can be seen from Fig. 9,  $NO_{\nu}$ levels of about 300–1000 ppt are typically present in the troposphere (stratosphere has much higher levels of  $NO_{\nu}$ ). Overall, there is a tendency among models to underpredict  $NO_{y}$  in the troposphere irrespective of season (Table 4). The ability of a model to predict  $NO_{y}$ correctly greatly hinges on its ability to simulate individual species (e.g. PAN, NO<sub>x</sub>, and HNO<sub>3</sub>) because of the presence of substantially different removal mechanisms.

#### 4.5. O3

The  $O_3$  concentration ranged from 20 ppbv in the free troposphere to 700 ppbv in the lower stratosphere. As is evident from Fig. 10 and Table 4, the models do a better job of predicting  $O_3$  than reactive nitrogen species. The underestimation of  $NO_x$  in the upper troposphere does not lead to an underprediction of  $O_3$  in this region. This could in part be due to the fact that stratospheric transport contributes strongly to  $O_3$  in this region. We recognize that a more extensive database for  $O_3$  is available from the ozonesonde network (Logan, 1994) while in the present study only aircraft data are considered.

In summary, each of the three chemical transport models tested here has varying degree of difficulty in representing the limited observational data available for reactive nitrogen species in the troposphere. The model results differ from each other in the comparisons discussed above and archived at the WWW site. The differences are not systematic and are a function of both location as well as season. It is likely that the causes of discrepancies are multiple and include both shortcomings in models as well as deficiencies in the observational data set. It is further evident from Figs. 1-3, that the current set of measurements of reactive nitrogen species do not provide a geographically complete data set. The shortcomings are even greater when seasonal variations and vertical structures are considered. No reliable trend information for any of the reactive nitrogen species is possible based on the present data set. To a large degree this is a result of the inherent weakness of the airborne platform which is much more useful in establishing detailed processes than in providing long-term data coverage. The only answer for global coverage can eventually come from satellite observations which are envisioned for the coming years (Jacob and Connors, 1995).

In addition to the paucity of data, a number of concerns have been raised about the quality of reactive nitrogen measurements (Crosley, 1994). There is good evidence that NO is reasonably well measured in the free troposphere to low parts per trillion levels. Nitrogen dioxide (NO<sub>2</sub>) also can be detected to about 10 ppt but the possibility that unknown interferences exist cannot be ruled out. This concern is largely based on the fact that NO<sub>2</sub> calculated from photostationary state assumptions is often much lower than actually measured (Crawford et al., 1996). However, recent improvements in measured  $NO_2$  (Bradshaw et al., 1998) show that photostationary state provides a valid means of estimating NO<sub>2</sub> and theory and observations are in good agreement when NO<sub>2</sub> is accurately measured. There are also perceived disagreements in HNO<sub>3</sub> measurements in the free troposphere but few intercomparisons are available. Some  $NO_{v}$  converters are problematic because they are able to convert significant fractions of species such as HCN to NO (S. Sandholm, private communication), while others report a very small conversion rate (Kondo et al., 1997). Other species such as the pernitrates (ROONO<sub>2</sub>) have yet to be measured. Typical accuracy of presently available measurements at the 100 ppt level is in the range of 20-50%. At present measurement techniques have several shortcomings and continued improvements are necessary.

Models also reflect the shortcomings in the fundamental understanding of chemical and transport processes. Reactive nitrogen chemistry is both highly nonlinear and incompletely understood. It is only now becoming evident that some oxygenated species (e.g. acetone) can be important sources of free radicals and are linked to the fate of atmospheric HO<sub>x</sub>, PAN and NO<sub>x</sub> (Singh et al., 1995). A better understanding of recycling processes possibly involving particle reactions is also necessary. In addition to chemical processes, transport schemes remain poorly validated in global models. The tracer test studies ( $^{222}$ Rn and NO<sub>y</sub> model calculations) show that dispersion among models is up to a factor of 5 in the upper tropospheric/lower stratospheric region (Friedl et al., 1997; Jacob et al, 1997). There is a critical need for a global data set made up of select tracers particularly designed to focus on the accurate simulation of transport processes. Sources of upper tropospheric  $NO_x$  are not well known and currently it cannot be reliably said how much  $NO_x$  is contributed by various individual sources (e.g. lightning, stratosphere, subsonic aircraft, surface sources).

#### 5. Conclusions

Available free tropospheric observational data on reactive nitrogen species and ozone have been collected and processed. Although the coverage of data is sparse both in space and time, this compilation shows our present state of the global distributions of these species and provides a beginning for testing and evaluating global models of atmospheric chemistry and transport. Comparisons with three chemical transport models point out that there are instances of significant differences among the models as well as between models and observations. Further studies are required to understand the cause of such differences. There is a critical need for a long-term strategy of atmospheric observations to fill the current gaps in our knowledge.

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#### Appendix A

#### A.1. Data archiving

All data described in this work have been archived and are accessible through the World Wide Web. The address is 'http://george.arc.nasa.gov/ ~athakur'. In addition to the information presented here, this site contains detailed tables, maps, plots and profiles. The searches can be done in several different ways. For example one can first look at the global maps and then go to detailed vertical profile or tables. The pages are continually updated as new data becomes available. This site can be best accessed by a frame capable browser. It is planned to incorporate JAVA Applets and dynamic programming capabilities. This will enable the user to interactively obtain information on global reactive nitrogen species.

#### A.2. Acronyms

AASE	Airborne Arctic Stratospheric Expedi-
AFRONOX	The impact of NO emissions from air-
MERONOX	craft upon the Atmosphere at Flight
	Altitudes
ABLE-2	Amazon Boundary Layer Expedition
ABLE-3	Arctic Boundary Layer Expedition
ССМ	Community Climate Model
CITE	Chemical Instrumentation Test and Eva-
	luation
ECHAM	ECMWF Model, Hamburg version
ECMWF	European Center for Medium Range
	Weather Forecast – UK
GCM	General Circulation Model
GISS	Goddard Institute for Space Studies
GTE	Global Tropospheric Experiment
IMAGES	Intermediate Model of Global Evalu-
	ation of Species
ISCCP	International Satellite Cloud Climatol-
	ogy Project
MATCH	Model of Atmospheric Transport and
	Chemistry
MLOPEX	Mauna Loa Observatory Photochemis-
	try Experiment
MPI-Ch	Max Planck Institute for Chemistry
NCAR	National Center for Atmospheric Re-
	search
NCEP	National Center for Environmental Pre-
	diction
NMHC	Non-methane Hydrocarbon
PAN	Peroxyacetyl Nitrate
PEM	Pacific Exploratory Mission
SASS	Subsonic Assessment
SPADE	Stratospheric Photochemistry Aerosol
	and Dynamics Expedition
STRATOZ	Stratospheric Ozone
TROPOZ	Tropospheric Ozone
TRACE-A	Transport and Atmospheric Chemistry
	near the Equator Atlantic

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