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Citation

Published Version
doi:10.1029/98JD01891

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Latitudinal distribution of reactive nitrogen in the free troposphere over the Pacific Ocean in late winter/early spring

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Abstract. The late winter/early spring (February/March, 1994) measurements of Pacific Exploratory Mission-West (PEM-W) B have been analyzed to show latitudinal distributions (45°N to 10°S) of the mixing ratios of reactive nitrogen species (NO, peroxyacetylnitrate (PAN), HNO3, and NOy), ozone, and chemical tracers (CO, NMHCs, acetone, and C2Cl4) with a focus on the upper troposphere. Mixing ratios of all species are relatively low in the warm tropical and subtropical air south of the polar jetstream (≥28°N) but increase sharply with latitude in the cold polar air north of the jetstream. Noteworthy is the continuous increase in reservoir species (PAN and HNO3) and the simultaneous decrease in NOx toward the northern midlatitudes. The Harvard global three-dimensional model of tropospheric chemistry has been used to compare these observations with predictions. In the upper troposphere the magnitude and distribution of measured NO and PAN as a function of latitude is well represented by this model, while NOx (measured NO + model calculated NO2) is underpredicted, especially in the tropics. Unlike several previous studies, where model-predicted HNO3 exceeded observations by as much as a factor of 10, the present data/model comparison is improved to within a factor of 2. The predicted upper tropospheric HNO3 is generally below or near measured values, and there is little need to invoke particle reactions as a means of removing or recycling HNO3. Comparison between measured NOx and the sum of its three main constituents (PAN + NOx + HNO3) on average show a small mean shortfall (<15%). This shortfall could be attributed to the presence of known but unmeasured species (e.g., peroxyacetic acid and alkyl nitrates) as well as to instrument errors.

1. Introduction

Pacific Exploratory Mission-West (PEM-W) B was an airborne experiment designed to study the chemistry of the troposphere over the western Pacific Ocean during the winter and early spring season (February-March) of 1994. A total of 16 flights each averaging ~8 hours in duration focused on studying the impact of Asian outflow on the composition and chemistry of the Pacific troposphere. There were additional opportunities to study the troposphere and the stratosphere under largely unperturbed conditions. The airborne missions covered tropical, subtropical, and polar air masses and originated from Guam, Hong Kong, and Yokota, Japan. An overview of the PEM-W B instrumentation, experimental design, and meteorology have been provided by Hoell et al. [1997] and Merrill et al. [1997] as well as by individual investigators in the special PEM-W B issue of Journal of Geophysical Research (102(D23), 1997). This paper presents further analyses of data collected by the NASA DC-8 research aircraft during PEM-W B and compares measured and modeled latitudinal distributions of selected reactive nitrogen species (NO, HNO3, peroxyacetylnitrate (PAN), and NOx) and ozone (O3) in the upper troposphere (6–12 km). The present manuscript complements other aspects of atmospheric composition and chemistry based on the PEM-W B data that have recently been published [Kondo et al., 1997a; Koske et al., 1997; Thompson et al., 1997].

2. Data Processing and Model Application

In this manuscript we will not provide details of measurement techniques as these have appeared in previous publications (Journal of Geophysical Research, 102(D23), 1997, and references therein). It is noted, however, that NO and NOx in PEM-W B were measured by two separate investigators (Nagoya University and Georgia Institute of Technology (GIT)) using independent techniques (chemiluminescence and laser-induced fluorescence (LIF)). In both cases, NOx was measured by catalytically converting it to NO on the surface of a heated gold tube with the addition of CO. While NO levels...
were in good agreement, NOy data disagreed substantially. The GIT group, using the LIF technique, concluded that their NOy data should not be used (J. Bradshaw, private communication, 1997). The NO and NOy data used in this study are from the 30 s measurements obtained by the chemiluminescence instrument from Nagoya University [Kondo et al., 1997b]. This instrument has been tested extensively and found to be minimally impacted by interferences from species such as HCN (2%-5%). Accuracies of the NO and NOy measurements have been estimated to be 12% and 13%, respectively. Similarly, PAN was measured by electron capture gas chromatography with an accuracy of ±20% [Singh et al., 1996]. HNO3 was measured using the mist chamber technique with an estimated overall uncertainty of ±35% [Talbot et al., 1997]. NOy was not directly measured during PEM-W B. It was calculated from NO using the photochemical model described by Crawford et al. [1996]. NOy is therefore the sum of measured NO and calculated NO2. Although measured and calculated NOy have differed substantially in the past [e.g., Crawford et al., 1996, and references therein], recent improved measurements made during PEM-Tropics A show good agreement between the measured and model-calculated NOy concentrations (e.g., J. Bradshaw et al., Photostationary state analysis of the NO2-NO system based on airborne observations during PEM-Tropics, submitted to Journal of Geophysical Research, 1998). We note that in the upper troposphere, only a small fraction (20%-30%) of daytime NOy is present as NO2; nevertheless, some uncertainty in the NOy data should be expected.

All PEM-W B data were archived in a central location, and a variety of merged data files (30-300 s time resolution) were created to provide the best time overlap among the many species that were measured. The most highly time-resolved merged files (i.e., 30 s) were used when possible. The atmosphere sampled during PEM-W B was divided into three regions representing the upper troposphere (UT; 6-12 km), the middle troposphere (MT; 3-6 km), and the lower troposphere (LT; 0-3 km). Latitudinal cross sections of trace species and relevant meteorological parameters were constructed by averaging all data within 5° latitude bins for these altitude regions. About 200 data points for UT and 100 points for MT were averaged per bin. Data strongly influenced by stratospheric air (O3 > 100 ppb and dew point < -60°C) were excluded to restrict this analysis to the troposphere. Stratospheric data collected during PEM-W B have been discussed elsewhere [Singh et al., 1997]. The latitudinal cross sections are based on airborne measurements performed over a wide area extending from 115° to 160°E over the Pacific. To assess better the nature of the partitioning and budget of reactive nitrogen, we have also evaluated aggregated data for UT, MT, and LT within two latitudinal bins of 30°-45°N (midlatitude) and 10°-30°N (subtropical) and for level legs of 20-40 min duration (Table 1). Measured latitudinal cross sections are compared with those available from the Harvard global three-dimensional (3-D) model of tropospheric chemistry for a northern hemispheric winter climatology (December/January/February). The Harvard model has a spatial resolution of 4° x 5° with nine vertical layers extending from the surface to 10 mbar and a temporal resolution of 4 hours. Meteorological fields are obtained from the NASA Goddard Institute for Space Studies (GISS) general circulation model (GCM) II. The present version of the model transports 15 reactive chemical tracers: odd oxygen, NOx, N2O5, HNO4, PANs, alkyl nitrates, HNOs, CO, ethane, higher alkanes, alkenes, isoprene, acetone, higher ketones, and H2O2. Hydrolysis of N2O5 to HNO3 on aerosol surfaces is included with a reaction probability of 0.1. Global sources of NOy (Tg N yr⁻¹) in the model include 21 from fossil fuel combustion, 0.46 from subsonic aircraft, 11.6 from biomass burning, and 6.6 from soils. A lightning source of 4 Tg N yr⁻¹ is apportioned over convective regions following Price and Rand [1994]. The amount of NOy transported from the stratosphere is 0.5 Tg N yr⁻¹. In sum, the total NOy source in the troposphere is 44 Tg N yr⁻¹. Details of this model, including its structure and validation, are presented by Wang et al. [1998a, b]. Latitudinal distributions of selected chemical species for the average winter season were retrieved from this model for the longitudinal band of 130°-150°E. This longitudinal band was considered most representative of the geographical area sampled in PEM-W B. The model output was used from levels that represented averages between 7.4-10.3 km (9 km run) and 2.8-7.3 km (5 km run) and are assumed to correspond to the PEM-W (B) UT and MT, respectively. The model output was also studied for the longitude 115°-130°E for exploratory purposes.

Table 1. Reactive Nitrogen Budgets and Partitioning Based on Pacific Exploratory Mission-West (PEM-W) B Measurements at Midlatitudes (30°-45°N) and the Subtropics (10°-30°N)

<table>
<thead>
<tr>
<th>Latitude, °N</th>
<th>Altitude, km</th>
<th>PAN/NOy,*</th>
<th>HNO3/NOy,*</th>
<th>NO2/NOy,*</th>
<th>NOy/NOy,</th>
<th>NOy, NOy,</th>
<th>NOy, NOy,*</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-45</td>
<td>6-12 (UT)</td>
<td>0.43 ± 0.19</td>
<td>0.34 ± 0.20</td>
<td>0.08 ± 0.08</td>
<td>0.86 ± 0.21</td>
<td>106.1 ± 133.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-6 (MT)</td>
<td>0.56 ± 0.13</td>
<td>0.22 ± 0.09</td>
<td>0.04 ± 0.02</td>
<td>0.83 ± 0.17</td>
<td>126.5 ± 135.4</td>
<td></td>
</tr>
<tr>
<td>30-45</td>
<td>0-3 (LT)</td>
<td>0.65 ± 0.18</td>
<td>0.21 ± 0.06</td>
<td>0.08 ± 0.05</td>
<td>0.98 ± 0.17</td>
<td>26.1 ± 182.4</td>
<td></td>
</tr>
<tr>
<td>10-30</td>
<td>6-12 (UT)</td>
<td>0.26 ± 0.14</td>
<td>0.44 ± 0.22</td>
<td>0.22 ± 0.09</td>
<td>0.89 ± 0.22</td>
<td>59.2 ± 80.2</td>
<td></td>
</tr>
<tr>
<td>10-30</td>
<td>3-6 (MT)</td>
<td>0.30 ± 0.19</td>
<td>0.44 ± 0.31</td>
<td>0.13 ± 0.04</td>
<td>0.84 ± 0.27</td>
<td>95.3 ± 138.6</td>
<td></td>
</tr>
<tr>
<td>10-30</td>
<td>0-3 (LT)</td>
<td>0.32 ± 0.23</td>
<td>0.45 ± 0.34</td>
<td>0.27 ± 0.41</td>
<td>0.94 ± 0.22</td>
<td>95.2 ± 136.7</td>
<td></td>
</tr>
</tbody>
</table>

*Mean ± 1σ. The numbers in parentheses are the median and the number of data points.
3. Results and Discussion

3.1. Transport

Figure 1 shows the cross section for the aircraft-measured wind speed and static air temperature (SAT) for the UT. To show standard deviations as clearly as possible in Figure 1 (and elsewhere in this paper), data points of the two distribution curves have been shifted by 1° with respect to latitude. The polar jetstream separating the relatively cold polar air to the north and the warm subtropical and tropical air to the south is clearly outlined. The jetstream coincides with the area of large temperature gradient (baroclinic zone) between 25° and 40°N. This baroclinic zone was also present at the same location in the middle troposphere from 700 to 500 mbar. It generally identifies the latitude region where strong 3-D tropospheric circulations associated with extratropical cyclones are present. The heavy arrow in Figure 1 indicates the average position (29°N) of the jetstream obtained from the PEM-W B meteorological analyses. The core of the jetstream was at ~200 mbar (~12 km). Isentropic trajectories computed by Merrill et al. [1997] indicated that UT air parcels from 25°N to 45°N were associated with westerly (270°) wind directions with transport from the Asian continent across Japan ("continental north"). At latitudes below 25°N, UT air parcels generally originated from the southeast Asian continent ("continental south"). These trajectories also showed that at 45°N, air parcels originated from a location north of the Arctic circle over the Arctic Ocean near the island of Nova Sembla (75°N, 80°E) 5 days earlier.

3.2. Reactive Nitrogen Species

Figure 2 presents the average (±1σ) UT and MT latitude distributions of NO, NOx, PAN, HNO3, and NOy. NO data presented here were restricted to solar zenith angles <70° to minimize the effects of diurnal variations. In general, variabilities in Figure 2 are largest in the latitude region of 20°-35°N which represents the core region of the jetstream (Figure 1). These reflect the large variations in atmospheric circulations in this region caused by the migratory midlatitude synoptic-scale storm systems that are closely tied to the polar jetstream. NO makes up a high fraction of NOx in the low-temperature environment of UT (NO/NOx = 0.75 ± 0.09) but decreases rapidly with decreasing altitude (NO/NOx = 0.42 ± 0.10 in MT). In the UT region (Figure 2a), high average NOx concentrations (75-100 ppt) are present between 20° and 50°N near the center of the jetstream. Individual (30 s average) NO measurements as high as 300-350 ppt were recorded, and significant variability was observed. Koike et al. [1997] have suggested that this sampling area is downwind of a busy commercial air corridor between Japan and southeast Asia, and aircraft emissions may have affected the NO measurements. The indicated high NOx could also be associated with processes involving wet continental convection with associated lightning and long-range transport. Lack of a coincident HNO3 signature in the UT (Figure 2b) suggests that either HNO3 was washed out during convection or NOx was too fresh to have undergone oxidation to HNO3. The relatively high UT NO (also NOx) concentrations south of the equator are attributed to lightning. Weather satellites observed large clusters of cumulonimbus clouds south of the equator, and lightning data from satellites showed a maximum frequency during February 1994. Individual NO peaks of 800-900 ppt (10 s data) were often observed [Kawakami et al., 1997]. A coincident HNO3 and NOx increase (Figure 2b) was evident in this instance. A similar lightning NO signature was not observed in the MT
Figure 2. Mean latitudinal distribution of NO, NOx, peroxyacetyl nitrate (PAN), HNO3, and NOy in the (a) and (b) UT and (c) and (d) MT. For clarity, data points of the heavy dashed distribution curves (PAN and NOx) have been shifted by 1° in latitude with respect to the NOx, NO, and HNO3 curves.

Figure 3. Mean latitudinal distribution of NOx, PAN, HNO3, and NOy in the LT.

region (Figure 2c). The MT NOx peak around 20°N was generally associated with significant continental pollution signatures that included high HNO3 and NOy (Figure 2d). On the polar side of the jetstream, average NOx concentrations decreased rapidly at all altitude regions. Coincident with this decline were increases in reservoir species as indicated by high PAN and NOy mixing ratios. Figure 3 shows the mean distribution of these reactive nitrogen species for the LT. The strongest features associated with Asian continental outflow around 20°-25°N are evident. Under these conditions, nearly half of the NOy was present as HNO3. Even in the UT, PAN was strongly correlated (R 2 = 0.7-0.8) with tracers of anthropogenic origin (e.g., CO and C2H2). Maxim et al. [1996] show that midlatitude storm systems can transport PAN (and supposedly other pollutants) poleward and upward from the surface combustion emission regions into the upper tropospheric westerlies.

3.3. Chemical Tracers

To facilitate further data interpretation, we show the mean latitudinal distribution of a number of anthropogenic tracer species for the UT, MT, and LT in Figure 4. These tracer profiles clearly show that most of the sources of these pollutants are located in the industrial northern hemisphere (NH), and their concentrations decline rapidly toward the tropics. The two ratios of C2H2/CO and ln (C3H8/C2H6), independently proposed by Smyth et al. [1996] and Koike et al. [1997] as indicators of air mass processing and age, further suggest that in the NH, even UT air masses are processed to a much lesser
extent than in the tropics and southern hemisphere (SH) (Figure 5). For nearly all cases in Figure 4 a strong gradient of concentrations from the LT to UT, indicative of anthropogenic pollutants with surface level sources, was present. The Asian continental outflow impact near 20°N is clearly evident in the LT-MT measurements (e.g., Figure 4a and 4b) but is greatly moderated in the UT. Trajectory analysis [Merrill et al., 1997] shows that the double maxima in CO and C$_2$H$_2$ (tracers of combustion) are associated with Asian outflow at the latitudes of Japan (continental north) and China/southeast Asia (continental south), the latter showing little enhancement in C$_2$Cl$_4$ (Figure 4e), a synthetic organic chemical commonly used in highly industrialized nations. The Asian outflow characteristics for continental north and continental south regimes have been discussed in more detail by Gregory et al. [1997] and Talbot et al. [1997]. Because of excessive moisture interference in the LT, acetone (CH$_3$COCH$_3$) was measured only in the UT/MT regions (Figure 4c). The latitudinal distribution of acetone is different from other anthropogenic tracer species, in part because of its diverse but poorly characterized sources. Acetone has been proposed as a major source of PAN and HOx in the UT [Singh et al., 1995; Arnold et al., 1997; Wennberg et al., 1998].

### 3.4. Data-Model Comparisons

Figures 6 and 7 present measured and modeled mean latitudinal distributions of NO, NO$_x$, PAN, HNO$_3$, and O$_3$ for the UT and MT. Similar results for NO$_2$ are presented in Figure 8. While such comparisons are instructive, perfect agreement should not be expected as measurements were often geographically selective and affected by specific weather conditions that prevailed during the late winter/early spring of 1994.
Figure 6. Mean measured and modeled latitudinal distributions of NO, NOx, and PAN for the UT and MT. The model results in this and subsequent figures are computed for the longitudinal area of 130°–150°E and for a northern hemispheric winter season (December/January/February). The model levels are averaged for 7.4–10.3 km (9 km run) and 2.8–7.3 km (5 km run) and are assumed to correspond to the UT and MT measurements, respectively.

Figure 7. Mean measured and modeled latitudinal distributions of HNO$_3$ and O$_3$ for the UT and MT.
was largely due to sampling of polluted air parcels (high CO and NMHCs) from high latitudes was sampled. It is also evident that the model captures the source from the Asian continent is underestimated in this model, on the other hand, reflects conditions of atmospheric circulation and chemistry during a typical northern hemispheric winter season. In general, the UT environment should be better represented in the model because it is less impacted by episodic events and more by relatively long-term mixing and transport. For the UT region, there, indeed, is good general agreement between PEM-W B measured and model-predicted PAN, NOx, and O3 but less so for HNO3 and NO (or NO2). NOx in the subtropics is significantly underestimated by the model, most likely because the convective outflow/lightning source from the Asian continent is underestimated in this climatology. Trajectory analysis indicated that the deviation (increase) at ~45°–50°N observed in PAN, HNO3, NOy, and O3 was largely due to sampling of polluted air parcels (high CO and NMHCs) that originated from a location north of the Arctic circle. It is also evident that the model captures the south of the equator UT NO (also NOy) lightning increase well (Figure 6a).

An important feature in Figure 7a is the comparison between measured and model-predicted UT HNO3. In previous studies, UT model-predicted HNO3 have exceeded measurements by as much as factors of 10 [Singh et al., 1996; Jacob et al., 1996; A. N. Thakur et al., Distribution of reactive nitrogen species in the remote free troposphere: Data and model comparisons, submitted to Atmospheric Environment, 1997, hereinafter referred to as Thakur et al., submitted manuscript, 1997]. Such large disagreements have been used as an argument for the presence of mechanisms to rapidly recycle or remove HNO3 via heterogeneous chemical mechanisms [Fan et al., 1994; Chatfield, 1994; Hauglustaine et al., 1996; Dentner et al., 1996; Larry et al., 1997; A. Tabazadeh et al., HNO3 scavenging by mineral and biomass aerosols, submitted to Nature, 1998, hereinafter referred to as Tabazadeh et al., submitted manuscript, 1998]. The UT comparison between measured and calculated HNO3 here is within a factor of 2 with no systematic hemispheric asymmetry. Here the predicted HNO3 is generally below measured values, and there is little obvious need to invoke particle reactions as a means of removing HNO3. The notion that models significantly overpredict the UT HNO3, where heterogeneous chemistry may be most effective because of low temperatures and high aerosol acidity, needs to be reassessed. It is noted that gas/particle reactions may be minimized in the UT during winter/early spring because of reduced deep convection resulting in fewer particles. A possible interpretation of these results is that HNO3 removal by particles is highly seasonal with potentially significant impact only during summer months when particle concentrations may be high (Thakur et al., submitted manuscript, 1997; Tabazadeh et al., submitted manuscript, 1998).

The MT comparisons (Figures 6c, 6d, 7c, and 7d) show larger differences than the UT, most likely because the MT (and even more the LT) begins to reflect the effects of deviations from the model wintertime climatology, i.e., the absence of episodes and weather conditions relevant to the 1994 late winter/early spring. In fact, the HNO3 and O3 measurements start to show the significant impact from Asian outflow near 20°N.

### 3.5. Ratios of Reactive Nitrogen Species

Figure 9 shows modeled and data-derived latitudinal distributions for NOy/NOx, HNO3/NOy, PAN/NOx, and NOy/O3 ratios for the UT. The observed tendencies of latitudinal behavior of these ratios is generally captured by the model except at 40°–50°N where trajectory analysis showed that polluted air (high CO and NMHCs) from high latitudes was sampled. There is no consistent hemispheric asymmetry in the data versus the modeled HNO3/NOy ratio (Figure 9b). The agreement between data and model is substantially better than has been reported in the past [Liu et al., 1992; Chatfield, 1994]. The deviations at 10°–30°N are largely attributable to the under-prediction of NOy, The NOy/O3 ratio reported by Murphy et al. [1993] and by Folkins et al. [1995] during two January DC-8 flights from California to Tahiti are in good agreement with Figure 9d. However, the level of agreement between data and modeled NOy/NOx ratios seen in Figure 9 is significantly better than that achieved by Folkins et al. [1995]. It is also evident that most of the NOy at northern latitudes resides in reservoir species such as PAN and HNO3. The presence of chemicals such as acetone in the UT and hydrocarbons in the lower troposphere allows the conversion of NOy to PAN at all altitudes. Singh et al. [1995] use a 3-D model to calculate that 35–45 ppt of PAN in the UT (30°–50°N) could have come from acetone alone. Even higher PAN/NOy ratios have been reported from northerly latitudes of Alaska and Greenland [Singh et al., 1992]. Once formed, PAN acts as a stable reservoir of NOy in the UT. Reservoir species such as PAN also

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**Figure 8.** Latitudinal distributions of mean measured NOy and NOx and modeled NOy for the UT and MT. NOy is directly measured and represents total available reactive nitrogen. NOx is the sum of NOx + PAN + HNO3. Modeled NOy (dashed lines) is computed from the sum of all reactive nitrogen species included in the model.

**Figure 9.** Model: 9 km

- (a) UT NOy, NOx, and NOy versus NOx latitudinal distributions for NOy/NOx, HNO3/NOy, PAN/NOx, and NOy/O3 ratios for the UT. The observed tendencies of latitudinal behavior of these ratios is generally captured by the model except at 40°–50°N where trajectory analysis showed that polluted air (high CO and NMHCs) from high latitudes was sampled. There is no consistent hemispheric asymmetry in the data versus the modeled HNO3/NOy ratio (Figure 9b). The agreement between data and model is substantially better than has been reported in the past [Liu et al., 1992; Chatfield, 1994]. The deviations at 10°–30°N are largely attributable to the under-prediction of NOy, The NOy/O3 ratio reported by Murphy et al. [1993] and by Folkins et al. [1995] during two January DC-8 flights from California to Tahiti are in good agreement with Figure 9d. However, the level of agreement between data and modeled NOy/NOx ratios seen in Figure 9 is significantly better than that achieved by Folkins et al. [1995]. It is also evident that most of the NOy at northern latitudes resides in reservoir species such as PAN and HNO3. The presence of chemicals such as acetone in the UT and hydrocarbons in the lower troposphere allows the conversion of NOy to PAN at all altitudes. Singh et al. [1995] use a 3-D model to calculate that 35–45 ppt of PAN in the UT (30°–50°N) could have come from acetone alone. Even higher PAN/NOy ratios have been reported from northerly latitudes of Alaska and Greenland [Singh et al., 1992]. Once formed, PAN acts as a stable reservoir of NOy in the UT. Reservoir species such as PAN also...
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Figure 9. Mean latitudinal distributions of NOy/NOx, HNO3/NOx, PAN/NOx and NOy/O3 ratios for the UT based on measurements and model predictions. All ratios are expressed as ppt ppt⁻¹.

prevent the accumulation of large quantities of NOx. Kanakidou et al. [1991] calculated that PAN formation from C2H6 and C3H8 chemistry alone reduces NOx mixing ratios by nearly 30% during winter in the middle and upper troposphere of the NH. Atmospheric circulations known to be present on the anticyclonic windshear side of the jetstream can carry the reservoir PAN downward and southward to the warm lower troposphere where it can be thermally converted to NOx to influence regional O3 photochemistry [Moxim et al., 1996]. In general, the results from Figures 6-9 demonstrate that the latitude distributions observed during PEM-W B reflect to a large extent our present understanding of reactive nitrogen transport and chemistry.

3.6. Partitioning and Budget of Reactive Nitrogen

Figure 8a shows the mean UT latitudinal distribution of measured NOy. NOy increases from ~100-200 ppt in the tropics to nearly 700 ppt at northern midlatitudes. The high linear correlation that was found between NOy and O3 (R² = 0.82) and other tracers reflects the fact that NOy includes the precursors (e.g., NOx) and products (HNO3 and PAN) of O3 photochemistry. Also shown in Figure 8a is the latitudinal distribution of NOy (NOx + HNO3 + PAN). It is evident that both NOy and NOx have similar tendencies as a function of latitude, and their abundances are in reasonable agreement even though NOy is composed of three independent measurements. Further, the model-predicted UT NOy shows remarkably consistent behavior across all latitudes. The distribution of NOx and NOy in the MT (Figure 8b) is more complex, perhaps because of greater continental influences during the PEM-W B measurement period, but once again, there is excellent internal consistency in these observations. As discussed earlier, the model is unable to fully capture the complex observed structure in the MT in part because of the episodic nature of outflow events, limited sampling, and winter average conditions for the model.

In order to capture the nature of the partitioning and budget of reactive nitrogen in a more quantitative fashion we evaluated aggregated data for UT, MT, and LT within two latitudinal bands of 30°-45°N (midlatitude) and 10°-30°N (subtropical) and only for level legs of 20-40 min duration. Even though this restricted the available data, it provided a robust approach to studying this budget and partitioning involving multiple measurements on different timescales. A strong linear correlation between NOy and NOx (NOx + PAN + HNO3) that is independent of latitude can be seen in Figure 10. These partitioning results are further summarized in Table 1. Some 85% of the reactive nitrogen in the UT/MT region is accounted for by NOy, PAN, and HNO3. Thompson et al. [1997] have used a model to estimate that 10%-20% of reactive nitrogen in the UT may exist in the form of species that were not measured (e.g., alkyl nitrates and HNO4). The budget of reactive nitrogen thus appears to be reasonably balanced. It is further evident from Table 1 that PAN and HNO3 dominate the NOy reservoir while NOx makes a smaller contribution. These partitioning results are in general agreement with those reported earlier on the basis of an analysis of these data for the troposphere and the stratosphere [Kondo et al., 1997a; Singh et al., 1997]. The reasons for the overall improvement in the reactive nitrogen budget in PEM-W B, compared with previous experiments [Sandholm et al., 1994; Singh et al., 1996], are not ob-
knowledge support from the NASA Atmospheric Chemistry and Modeling Program.

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(Received April 22, 1997; revised May 21, 1998; accepted May 29, 1998.)