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Martin G. Schultz
Harvard University

Daniel J. Jacob
Harvard University

J. D. Bradshaw
Georgia Institute of Technology - Main Campus

S. T. Sandholm
Georgia Institute of Technology

Jack E. Dibb
University of New Hampshire, jack.dibb@unh.edu

See next page for additional authors

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Authors

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Chemical NO_x budget in the upper troposphere over the tropical South Pacific

Martin G. Schultz,^{1,2} Daniel J. Jacob,¹ John D. Bradshaw,³ Scott T. Sandholm,⁴ Jack E. Dibb,⁵ Robert W. Talbot,⁵ and Hanwant B. Singh⁶

Abstract. The chemical NO_x budget in the upper troposphere over the tropical South Pacific is analyzed using aircraft measurements made at 6–12 km altitude in September 1996 during the Global Tropospheric Experiment (GTE) Pacific Exploratory Mission (PEM) Tropics A campaign. Chemical loss and production rates of NO_x along the aircraft flight tracks are calculated with a photochemical model constrained by observations. Calculations using a standard chemical mechanism show a large missing source for NO_x; chemical loss exceeds chemical production by a factor of 2.4 on average. Similar or greater NO_x budget imbalances have been reported in analyses of data from previous field studies. Ammonium aerosol concentrations in PEM-Tropics A generally exceeded sulfate on a charge equivalent basis, and relative humidities were low (median 25% relative to ice). This implies that the aerosol could be dry in which case N₂O₅ hydrolysis would be suppressed as a sink for NO_x. Suppression of N₂O₅ hydrolysis and adoption of new measurements of the reaction rate constants for NO₂ + OH + M and HNO₃ + OH reduces the median chemical imbalance in the NO_x budget for PEM-Tropics A from 2.4 to 1.9. The remaining imbalance cannot be easily explained from known chemistry or long-range transport of primary NO_x and may imply a major gap in our understanding of the chemical cycling of NO_x in the free troposphere.

1. Introduction

Reactive nitrogen oxides (NO_x = NO + NO₂ + NO₃ + 2 N₂O₅ + HNO₂ + HO₂NO₂) play a critical role in the photochemical production of ozone in the troposphere, and they have a major effect on the abundance and partitioning of HO_x radicals (= OH + peroxy species) which determine the oxidizing power of the troposphere. Sources of NO_x in the tropical upper troposphere include major contributions from convective input of NO_x emitted at the surface, chemical recycling from nitric acid (HNO₃) and peroxyacetyl nitrate (PAN) and production from N₂ and O₂ in lightning flashes. The residence time of air in the tropical upper troposphere is about 10 days [Prather and Jacob, 1997]. This is generally long compared to the lifetime of NO_x with re-

spect to oxidation to the reservoir species HNO₃ and PAN (2–10 days [Jacob *et al.*, 1996]). Therefore one would expect average NO_x concentrations in the upper troposphere to be near a chemical steady state between loss by oxidation and recycling from the reservoirs.

The most important NO_x reservoir in the upper troposphere according to current models is HNO₃. HNO₃ is formed during daytime through oxidation of NO₂ by OH and during nighttime by hydrolysis of N₂O₅ on aqueous aerosol surfaces (N₂O₅ itself is formed by reaction of NO₂ with NO₃, where NO₃ is produced by reaction of O₃ with NO₂). Regeneration of NO_x from HNO₃ takes place during daytime by photolysis and reaction with OH. Conversion of NO_x to PAN in the upper troposphere takes place by photochemical degradation of acetone and other carbonyls [Singh *et al.*, 1995]. PAN is photolyzed back to NO_x (thermal decomposition of PAN is very slow in the upper troposphere). The cycling between NO_x and PAN in the tropical upper troposphere is typically 10 times slower than the cycling between NO_x and HNO₃ [Jacob *et al.*, 1996].

Observed HNO₃/(NO + NO₂) concentration ratios (hereinafter denoted as R_N) in the free troposphere can be compared to chemical steady state model calculations as a test of the cycling between NO_x and HNO₃ [Chatfield, 1994]. Model ratios reported in a number of studies overestimate observed values by factors of 2–10 [Liu *et al.*, 1992; Chatfield, 1994; Davis *et al.*, 1996; Hauglustaine *et al.*, 1996; Jacob *et al.*, 1992, 1996; Jaeglé *et al.*, 1998] suggesting major flaws in our current understanding of the chemical budget of NO_x. Similar overestimates are found in global

¹Division of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts.

²Now at Max-Planck-Institut für Meteorologie, Hamburg, Germany.

³Deceased June 16, 1997.

⁴School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta.

⁵Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham.

⁶NASA Ames Research Center, Moffett Field, California.

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three-dimensional models [Brasseur *et al.*, 1996; Wang *et al.*, 1998a,b; Lawrence and Crutzen, 1998; Hauglustaine *et al.*, 1998]. Only a few studies find no discrepancy [Fan *et al.*, 1994; Singh *et al.*, 1998].

It has been proposed that the overestimate of R_N in chemical models is due to a perturbation of the chemical equilibrium by primary NO_x sources from lightning, aircraft, or deep convection [Singh *et al.*, 1996b; Liu *et al.*, 1996; Smyth *et al.*, 1996; Kawakami *et al.*, 1997; Prather and Jacob, 1997; Jaeglé *et al.*, 1998]. Prather and Jacob [1997] used a simple box model to determine the mean shift in upper tropospheric (above 12 km altitude) R_N due to tropical deep convection. With a dynamical turnover rate of 10%/day and a chemical lifetime of NO_x of 10 days, they find that injection of primary NO_x from convection and lightning would lower R_N by a factor of 2 from its chemical equilibrium value. The effect would be less at lower altitudes because of the shorter lifetime of NO_x. In an analysis of aircraft data (8–12 km) over the central United States, Jaeglé *et al.* [1998] found that the discrepancy between simulated and observed NO_y/(NO + NO₂) ratios (NO_y = NO_x + HNO₃ + organic nitrates) was anticorrelated with the number concentration of condensation nuclei. They concluded that convective injection of boundary layer NO_x plays an important role in lowering R_N .

Other investigations have attempted to explain the model overestimates of R_N by invoking a fast chemical reaction to convert HNO₃ to NO_x in sulfate aerosols [Chatfield, 1994; Fan *et al.*, 1994] or on soot [Hauglustaine *et al.*, 1996; Lary *et al.*, 1997]. However, there is so far no laboratory evidence for fast conversion of HNO₃ to NO_x under conditions representative of the upper tropospheric aerosol [Jacob, 1999].

We present in this paper a chemical model analysis of airborne observations made up to 12 km altitude over the remote tropical and subtropical South Pacific in September 1996 (PEM-Tropics A [Hoell *et al.*, 1999]). This study extends the brief discussion of the chemical NO_x budget given by Schultz *et al.* [1999] in light of new kinetic data and information on aerosol composition. A review of previous studies is also presented.

2. Chemical NO_x Budget During PEM-Tropics A

The Global Tropospheric Experiment (GTE) Pacific Exploratory Mission (PEM) Tropics A campaign [Hoell *et al.*, 1999] surveyed the troposphere over the South Pacific in September and October 1996, during the peak of the burning season in the Southern Hemisphere. Two aircraft, a DC-8 and a P-3B, each spent more than 120 hours in flight conducting extensive trace gas measurements. In this paper we focus on data from the DC-8 aircraft because it had a higher ceiling (12 km compared to 8 km for the P-3B) and there were no HNO₃ measurements on board the P-3B. We restrict our analysis to the tropical and subtropical South Pacific (0–30°S, 165°E–105°W) and to altitudes above 6 km. The aircraft data are averaged over the HNO₃ measurement intervals (~3 min), which were the longest of all the gas-

phase species observed. This data set is then used to constrain the chemical model. For the discussion of the aerosol chemical composition in section 3, the temporal resolution of the aerosol measurements (~20 min) is retained.

Figure 1 shows vertical profiles for the mixing ratios of several NO_y species over the tropical South Pacific during PEM-Tropics A. NO_x was computed from the sum of observed NO (measured with two-photon laser induced fluorescence (TP-LIF) [Bradshaw *et al.*, 1985; Sandholm *et al.*, 1990, 1994, 1997]) and locally computed chemical model values for NO₂, HO₂NO₂, NO₃, and N₂O₅ [Schultz *et al.*, 1999]. Schultz *et al.* [1999] compared observed and modeled NO₂/NO ratios and found agreement to within 30% (interquartile range) at all altitudes above 2 km. We will use calculated NO₂ throughout the remainder of this paper because of the greater availability. HNO₃ was measured with the mist chamber technique [Talbot *et al.*, 1988, 1990, 1997], and PAN was measured with a gas chromatography electron capture detector (GC/ECD) system [Singh and Salas, 1983; Gregory *et al.*, 1990a]. Table 1 compiles the instrumental accuracies and limits of detection (LOD) for the key NO_y species during PEM-Tropics A.

Concentrations of PAN and HNO₃ show pronounced maxima in the lower and middle free troposphere (between 2 and 8 km), reflecting the extensive biomass burning influence during PEM-Tropics A [Schultz *et al.*, 1999; Talbot *et al.*, 1999a]. Concentrations of NO_x increase steadily with altitude, reaching typical values of 50 parts per trillion by volume (pptv) at 8–10 km (Figure 1b). The observed R_N is about 5 mol/mol in the lower and middle troposphere and decreases to 1 mol/mol at 8 km and to about 0.4 mol/mol at 11 km (Figure 1e). The median NO/NO_x ratio (not shown) above 6 km is 0.53 (interquartile range 0.47–0.58) for zenith angles < 60°. Figure 1f displays the concentration ratio of aerosol nitrate (NO₃⁻) to gas-phase HNO₃. Aerosol nitrate was measured from bulk filter samples [Dibb *et al.*, 1999]. The median NO₃⁻/HNO₃ ratio at 6–12 km is 0.29 mol/mol, and the interquartiles span the range from 0.15 to 0.91 mol/mol. Of the NO₃⁻ data above 6 km, 55% are below the limit of detection (10 pptv). In marine convective outflow, NO₃⁻ concentrations occasionally exceeded gas-phase HNO₃ concentrations by up to a factor of 4.

Table 2 gives medians and interquartile ranges for the air mass composition over the tropical and subtropical South Pacific at 6–12 km altitude. The subset of data with very low relative humidity (< 10%) exhibits significantly enhanced pollution presumably from biomass burning (compare concentrations of CO, C₂H₂, PAN, and organic acids of this subset with the overall data). While the lower R_N and higher C₂H₂/CO ratio indicate relatively fresh pollution in these air masses, the high concentrations of HNO₃ and organic acids suggest that they have not encountered scavenging in convection for at least a couple of days.

We calculated chemical production and loss rates of NO_x along the PEM-Tropics A DC-8 flight tracks with a chemical point model [Schultz *et al.*, 1999]. The model is constrained by concurrent observations of O₃, HNO₃, PAN, H₂O, CO, H₂O₂, CH₃OOH, hydrocarbons, temperature, and photol-

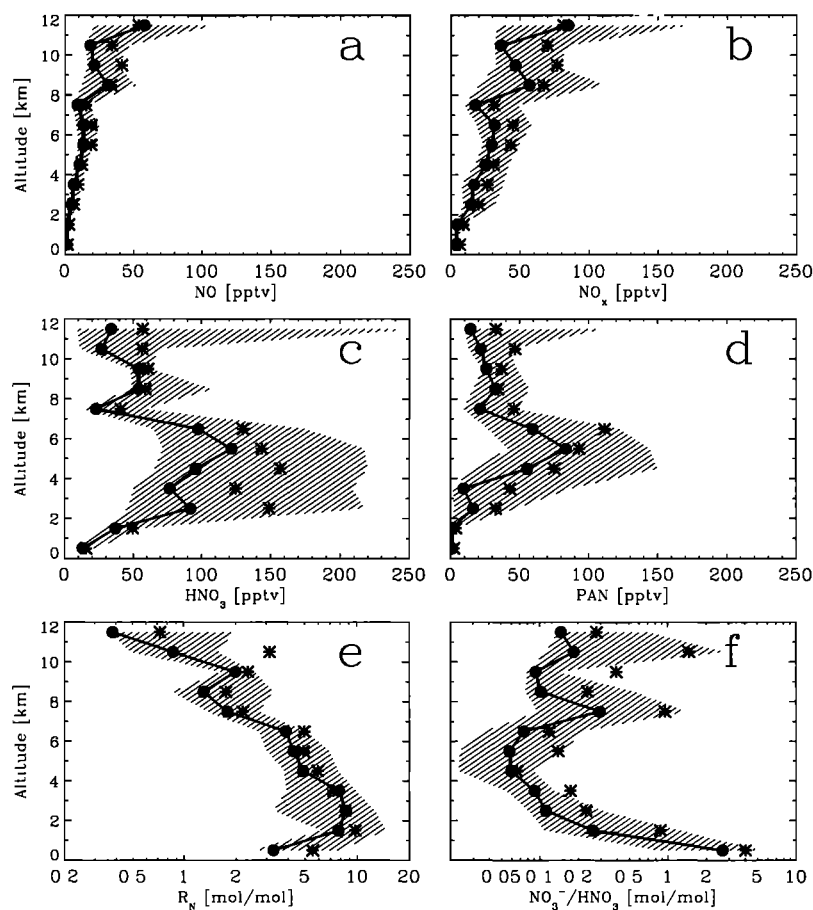


Figure 1. Vertical profiles of (a) NO, (b) NO_x (= NO + NO₂ + NO₃ + 2 N₂O₅ + HNO₂ + HO₂NO₂), (c) gas-phase HNO₃, and (d) PAN concentrations as well as (e) the HNO₃/(NO + NO₂) ratio (R_N) and (f) the ratio of aerosol NO₃⁻ to gas-phase HNO₃ concentrations. Concentrations of NO, PAN, HNO₃ and NO₃⁻ are aircraft measurements from PEM-Tropics A (0–30°S, 165°E–105°W). Concentrations of NO_x species other than NO are photochemical model values. NO data are displayed for zenith angles < 60° only. Circles are median values over 1 km altitude bands, stars denote means, and the shaded areas span the interquartile ranges. NO₃⁻ values below the limit of detection (LOD) are set to 1/2 × LOD for Figure 1f.

ysis frequencies for NO₂ and for O₃ to O(¹D). The NO_x concentration is chosen so that the model NO reproduces the observed NO within 1% at the solar time of measurement. The model computes local HO_x concentrations and chemical rates in diurnal steady state, defined by repeatability of model results over a 24 hour solar cycle. Acetone was not measured, and a typical concentration of 400 pptv was assumed [Singh *et al.*, 1995; McKeen *et al.*, 1997]. Our results are only modestly sensitive to this assumption (a 30% decrease in the acetone concentration leads to a 10% improvement in the chemical NO_x budget imbalance). The standard gas-phase chemical mechanism of the model follows the recommendations of JPL-97 [DeMore *et al.*, 1997], completed for volatile organic compound chemistry by Atkinson *et al.* [1997]. Absorption cross sections and quantum yields for photolysis of acetone are from Gierczak *et al.* [1998].

Heterogeneous oxidation of NO_x to HNO₃ is described as first-order losses of N₂O₅ and NO₃ on aerosol surfaces. Reaction probabilities follow the recommendations of Jacob

[1999], i.e. $\gamma = 0.1$ for N₂O₅ and $\gamma = 0.01$ (upper limit) for NO₃. Uptake of NO₃ was generally negligible. The aerosol surface area could not be reliably computed from measurements aboard the DC-8 and was specified with the median value of 3 $\mu\text{m}^2 \text{cm}^{-3}$ obtained from the companion P-3B aircraft at tropical latitudes above 6 km [Clarke *et al.*, 1999]. (Schultz *et al.* [1999] tried to estimate the aerosol surface area by correlating condensation nuclei counter measurements aboard the DC-8 with size-resolved measurements made aboard the P-3B aircraft. This approach yielded average aerosol surface areas of $\sim 24 \mu\text{m}^2 \text{cm}^{-3}$ above 6 km over the tropical and subtropical South Pacific which is about a factor of 10 higher than typical surface areas measured in the free troposphere (A. Clarke, personal communication, 1998). The difference could not be fully resolved.)

Table 3 gives the mean and median rates of individual reactions important in the model NO_x budget at 6–12 km altitude. There is a large budget imbalance throughout the upper troposphere, similar to previous studies. The loss rate

Table 1. Instrument Parameters for Key Measurements During PEM-Tropics A

Species	Technique	Limit of Detection	Accuracy, %	PI ^a
NO	TP-LIF	< 0.4 pptv	13	J. Bradshaw
NO ₂	photolysis, TP-LIF	0.5 – 11 pptv	25 – 40	J. Bradshaw
HNO ₃	mist chamber	< 20 pptv	15 – 20 (> 25 pptv)	R. Talbot
particulate NO ₃ ⁻	filter sampling/ion chromatography	10 pmol/mol	20	R. Talbot
PAN	GC/ECD	1 pptv	20	H. Singh
J(NO ₂) ^b	4π spectrometer	4 · 10 ⁻⁷ s ⁻¹	12	R. Shetter

TP-LIF, two photon-laser induced fluorescence; GC/ECD, gas chromatography with electron capture detector; pptv, parts per trillion by volume.

^aPrincipal Investigator.

^bPhotolysis frequency for NO₂.

of NO_x between 6 and 12 km surpasses the production rate by a factor of 2-3 on average. This imbalance exceeds the combined uncertainties in the measurements of NO_y species (Table 1). In the lower tropical troposphere, by contrast, thermal decomposition of PAN from biomass burning sources acts as a dominant source of NO_x and the NO_x budget is balanced [Schultz *et al.*, 1999].

Figure 2 displays the model-calculated diurnally averaged ratio of chemical loss to chemical production of NO_x (L_{NO_x}/P_{NO_x}) and the NO_x lifetime versus altitude. The median L_{NO_x}/P_{NO_x} ratio is fairly constant with altitude

(median 2.4, interquartile range typically 1.5–3). The NO_x lifetime increases with altitude from 2 days at 6 km to 10 days at 12 km.

If recent injection of primary NO_x in convective outflow were the major cause of the imbalance of the chemical NO_x budget, then we would expect the imbalances to be greater under conditions of high relative humidity. However, as shown in Figure 3, the L_{NO_x}/P_{NO_x} ratio tends to be largest at low relative humidity. One could invoke a scenario where injection of lightning NO_x in convective downdrafts would provide a primary source of NO_x associated with low rela-

Table 2. Median Airmass Composition Over the Tropical South Pacific (0-30°S, 165°E-90°W, 6-12 km)

Species	All Data (<i>N</i> = 158)	Relative Humidity ^a < 10% (<i>N</i> = 33)
Temperature, K	249 (234-256)	252 (244-260)
Potential temperature, K	336 (331-342)	335 (331-339)
relative humidity, %	25 (13-46)	5 (3-7)
NO, pptv	16 (9-31)	36 (12-60)
NO _x , pptv ^b	35 (18-63)	77 (22-141)
HNO ₃ , pptv	48 (23-82)	87 (41-183)
<i>R_N</i> , mol/mol ^c	1.9 (1.2-3.2)	1.6 (0.8-3.5)
PAN, pptv	27 (15-64)	47 (15-121)
O ₃ , ppbv	33 (28-49)	48 (29-80)
CO, ppbv	58 (54-65)	69 (54-85)
C ₂ H ₂ , pptv	36 (27-58)	68 (29-94)
C ₂ H ₂ /CO, pptv/ppbv	0.6 (0.5-0.8)	1.0 (0.6-1.1)
H ₂ O ₂ , pptv	372 (269-592)	322 (209-446)
CH ₃ OOH, pptv	212 (116-340)	114 (75-199)
HCOOH, pptv	36 (27-58)	72 (41-133)
CH ₃ COOH, pptv	34 (24-68)	54 (24-114)
CH ₃ I, pptv	0.07 (0.05-0.11)	0.05 (0.04-0.07)
NH ₄ ⁺ , pmol/mol ^d	LOD (LOD-46)	27 (LOD-46)
SO ₄ ²⁻ , pmol/mol ^d	13 (LOD-22)	16 (LOD-21)
NO ₃ ⁻ , pmol/mol ^d	LOD (LOD-26)	LOD (LOD-26)

PEM-Tropics A DC-8 data. Values in parentheses are interquartile ranges.

^aWith respect to ice.

^bNO_x = NO + NO₂ + NO₃ + 2 N₂O₅ + HNO₂ + HO₂NO₂; concentrations of species other than NO are calculated from the photochemical model (standard simulation).

^c*R_N* = HNO₃/(NO + NO₂). NO₂ from photochemical model.

^dLimit of detection (LOD) = 25 pmol/mol for NH₄⁺ and 10 pmol/mol for SO₄²⁻ and NO₃⁻.

Table 3. Mean (Median) 24-Hour Average Chemical NO_x Budget in the Upper Troposphere Over the Tropical South Pacific

Reaction	Mean (Median)
<i>NO_x Production, pptv d⁻¹</i>	
HNO ₃ + OH	1.9 (1.2)
HNO ₃ + hν	2.0 (1.5)
PAN+ hν	1.1 (0.7)
PAN thermolysis	0.4 (< 0.1)
total production	5.4 (3.6)
<i>NO_x Loss, pptv d⁻¹</i>	
NO ₂ + OH+ M	11.6 (5.5)
N ₂ O ₅ + H ₂ O (aerosol)	3.4 (1.2)
NO ₂ + CH ₃ COO ₂ + M	2.6 (2.1)
total loss	17.6 (9.3)
<i>NO_x Budget, ratio</i>	
L _{NO_x} /P _{NO_x}	2.5 (2.1)

Model results for PEM-Tropics A (run 0, base case), 0-30° S, 165° E-105° W, 6-12 km altitude, with NO_x defined as NO + NO₂+ NO₃+ 2 N₂O₅+ HNO₂+ HO₂NO₂; PAN formation and loss rates are corrected for internal cycling within the [PAN+ CH₃COO₂] family [Jacob *et al.*, 1996].

tive humidity. Such a scenario would imply the sampling of recent outflow from very deep convection (cloud top > 12 km), but kinematic back-trajectories together with infrared satellite images from PEM-Tropics A found only few occurrences of these conditions. The lack of an evident dynamical explanation for the NO_x budget imbalance prompts an examination of possible chemical factors contributing to the imbalance.

3. Chemical Contributions to the NO_x Budget Imbalance

Recent laboratory measurements of the temperature-dependent rate constants for the NO₂+OH+M reaction [Brown *et al.*, 1999; Dransfield *et al.*, 1999] and the HNO₃+OH reaction [Brown *et al.*, 1999] indicate values lower

(NO₂+OH+M) and higher (HNO₃+OH) than the standard recommendations of DeMore *et al.* [1997]. A recent study of the NO_x/NO_y ratio in the lower stratosphere during polar summer [Gao *et al.*, 1999] found that using these new rate constants improves the simulated NO_x/NO_y ratio from 0.6 (with JPL-97 rates) to 0.9 times the observed ratio. For the PEM-Tropics A conditions at 6-12 km altitude, the rate constant for NO₂+OH+M is reduced by 20%, while the rate constant for HNO₃+OH is increased by 50-100% on average. The median L_{NO_x}/P_{NO_x} ratio decreases from 2.4 in the base case scenario to 2.2 using the new rate coefficients (Table 4).

Table 3 shows that hydrolysis of N₂O₅ in aerosols accounts on average for 20% of the total NO_x loss. Following the assumption commonly made in models, we assumed that the aerosol is aqueous so that N₂O₅ hydrolysis takes place [Dentener and Crutzen, 1993; Lamarque *et al.*, 1996; Wang *et al.*, 1998b]. McKeen *et al.* [1997] pointed out that this assumption is not necessarily correct, which has significant implications for the NO_x budget. The chemical composition of the aerosol measured during PEM-Tropics A (Figure 4) indicates full neutralization of SO₄²⁻ by NH₄⁺ in 70% of all tropical samples above 6 km (Figure 5a). Laboratory studies by Cziczo and Abbatt [1999] for (NH₄)₂SO₄ and Li-Jones *et al.* [1999] for mineral dust indicate that neutral aerosols would be dry under the upper tropospheric conditions found in PEM-Tropics A (median relative humidity 25%, Table 2). Cziczo and Abbatt [1999] find that (NH₄)₂SO₄ aerosols at temperatures typical of the middle and upper troposphere (below 240 K) are dry for relative humidities below 65%, even when the energy barrier for efflorescence is taken into account. Mozurkevich and Calvert [1988] measured the uptake of N₂O₅ on dry (NH₄)₂SO₄ aerosols at 25% relative humidity and found it to be negligible (γ < 0.003).

The finding that aerosols in the upper troposphere over the South Pacific are frequently neutralized runs counter to the standard view of a background acid sulfate aerosol in the remote free troposphere [Gillette and Blifford, 1971; Huebert and Lazrus, 1980; Whelpdale *et al.*, 1987; Dentener and Crutzen, 1993]. Aerosol nitrate concentrations during PEM-

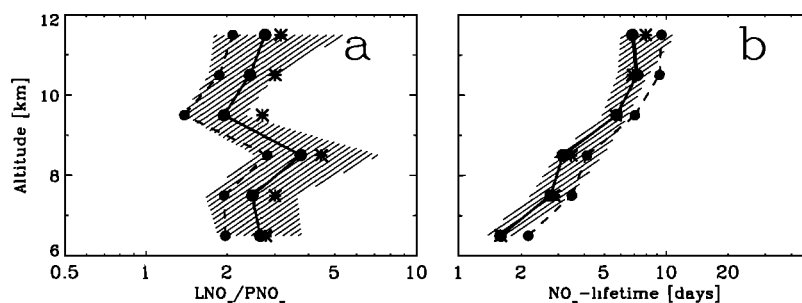


Figure 2. Vertical profiles of (a) the ratio of 24-hour averaged rates of chemical loss to chemical production of NO_x and (b) the chemical lifetime of NO_x. Values are results from standard steady state point model calculations for the ensemble of data summarized in Figure 1. Circles are medians over 1 km altitude bands, stars are means, and the shaded areas span the interquartile ranges from the standard simulation. The dashed line shows results for a simulation with new rate constants for NO₂+ OH+ M [Brown *et al.*, 1999; Dransfield *et al.*, 1999] and HNO₃+ OH [Brown *et al.*, 1999] and without N₂O₅ hydrolysis.

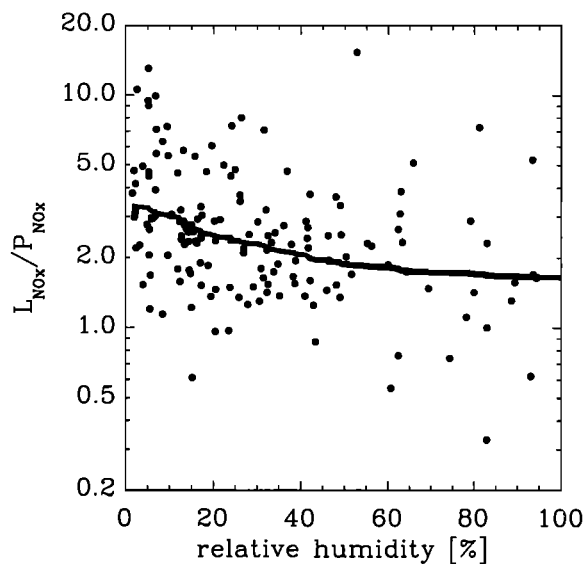


Figure 3. Ratio of chemical loss to production of NO_x for the data in Figure 1, plotted versus relative humidity with respect to ice. Loss and production rates of NO_x are from the standard simulation. Dots represent the individual calculations; the line is a smoothed running geometric average.

Tropics A (Figure 4c) occasionally exceeded the ammonium present in excess of H₂SO₄ neutralization (Figure 5b), although one would not expect significant HNO₃ dissolution in acid aerosol [Carslaw *et al.*, 1995]. In these cases, neutralization of nitrate could possibly be achieved by mineral ions (e.g., Ca₂⁺ or K⁺) as suggested by Tabazadeh *et al.* [1998] for aerosol over the central United States. In PEM-Tropics A, mineral ion concentrations were often below the detection limit (typically 15 pmol/mol), but if we assume concentrations just below the detection limit, they would always suffice to neutralize the aerosol. Independent support for a fully neutralized aerosol over the South Pacific is offered by airborne measurements from the Aerosol Charac-

terization Experiment (ACE-1) which indicated 50-100 pptv of gaseous NH₃ throughout the free troposphere (D. Davis, manuscript in preparation, 1999). Gaseous ammonia would be titrated if the aerosol were acidic. A neutral aerosol would exclude the possibility of fast heterogeneous chemical conversion from HNO₃ to NO_x involving formaldehyde on acidic aerosol as proposed by Chatfield [1994] and Fan *et al.* [1994]. A sensitivity run without N₂O₅ (and NO₃) hydrolysis reduces median L_{NO_x}/P_{NO_x} from 2.2 (run with new rate constants) to 1.9 (Table 4).

The availability of NH₄⁺ in amounts sufficient to neutralize the aerosol (Figure 4a) implies the possible presence of significant amounts of gas-phase NH₃, which could provide an additional source of NO_x via oxidation by OH [e.g., Logan, 1983]. According to DeMore *et al.* [1997], up to 80% of the NH₂ formed in the oxidation of NH₃ by OH would react with O₃ to form NO_x. Thus 100 pptv of NH₃ could provide a NO_x source of about 0.75 pptv day⁻¹, which is 15% of the median chemical NO_x source calculated for the PEM-Tropics A conditions (Table 3). There is a need for more observations of gas-phase NH₃ and for better understanding of the mechanism of NH₃ oxidation.

While the use of new rate constants for the reactions of NO₂ and HNO₃ with OH and the possible suppression of N₂O₅ hydrolysis significantly improve the NO_x budget for PEM-Tropics A (Table 4), a median L_{NO_x}/P_{NO_x} imbalance of 1.9 persists, corresponding to a missing NO_x source of 4.3 pptv day⁻¹ on average. Since the two factors discussed here increase the NO_x lifetime at 6–12 km by 30% (from 3.2 to 4.3 days; Figure 2), there is more potential for the missing source to be provided by long-range transport of primary NO_x. However, a gap in our understanding of NO_x chemistry in the free troposphere cannot be ruled out.

4. Previous Studies

A substantial body of observations for analyzing the chemical NO_x budget in the free troposphere has been presented

Table 4. Model Sensitivity of L_{NO_x}/P_{NO_x} and NO_x Lifetime in PEM-Tropics A

Model Run	L_{NO_x}/P_{NO_x}	NO _x Lifetime, days
Results from Schultz <i>et al.</i> [1999] ^a	2.6 (1.7-3.8)	2.8 (1.7-5.6)
Standard simulation with JPL-97 rates ^b	2.4 (1.4-3.5)	3.2 (2.1-5.8)
New rate constants ^c	2.2 (1.4-3.0)	3.4 (2.2-6.5)
New rate constants and no heterogeneous NO _x loss	1.9 (1.2-2.5)	4.1 (2.5-7.7)

L_{NO_x}/P_{NO_x} is the ratio of the 24-hour averaged chemical loss rate of NO_x (L_{NO_x}) to the chemical production rate of NO_x (P_{NO_x}) calculated with a chemical point model constrained by PEM-Tropics A aircraft observations over the tropical and subtropical South Pacific (0-30°S, 165°E-105°W, 6-12 km altitude). Values are medians, values in parentheses give the interquartile range.

^aAerosol surface area estimated from condensation nuclei counts. Median surface area too large (24 μm² cm⁻³).

^bN₂O₅ hydrolysis with $\gamma = 0.1$; water vapor and peroxide concentrations as observed. Aerosol surface area = 3 μm² cm⁻³.

^cRevised temperature dependent rate constants for NO₂ + OH + M [Dransfield *et al.*, 1999] and HNO₃ + OH [Brown *et al.*, 1999]. All other parameters as in standard simulation.

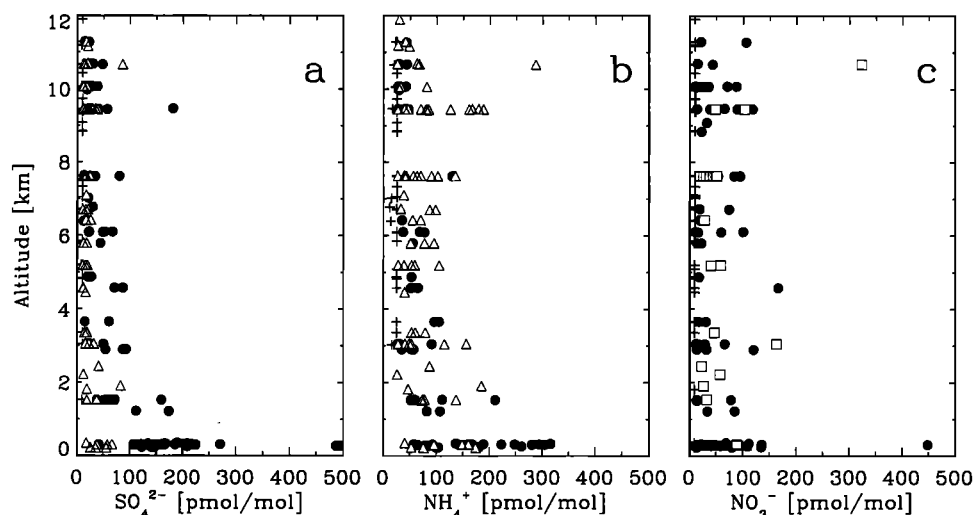


Figure 4. Vertical profiles of aerosol composition during PEM-Tropics A (0–30°S, 165°E–105°W, 6–12 km): (a) sulfate, (b) ammonium, (c) nitrate. Open triangles in Figures 4a and 4b denote samples where H₂SO₄ is fully neutralized by NH₃ ($[\text{NH}_4^+] > 2[\text{SO}_4^{2-}]$). Open squares in Figure 4c denote samples where HNO₃ titrates the excess NH₄⁺ ($[\text{NH}_4^+] > 2[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-] > [\text{NH}_4^+] - 2[\text{SO}_4^{2-}]$). Pluses show data below detection limit (LOD) (set to 1 × LOD for display). Closed symbols represent all other points, including those where diagnosis of the NH₄⁺–SO₄²⁻–NO₃⁻ balance could not be conducted due to concentrations below the detection limit.

in the literature (Table 5). Most studies report large imbalances in the NO_x budget. The reliability of the NO measurements in the experiments listed in Table 5 has been established in formal intercomparisons [Gregory *et al.*, 1990b; Crosley, 1996]. Aircraft measurements of NO₂ in missions prior to PEM-Tropics A had large positive biases [Crawford *et al.*, 1996]. However, most model studies in Table 5 did not use measured NO₂ but instead assumed NO₂ to be in photochemical equilibrium with NO, an assumption supported by the NO₂ measurements in PEM-Tropics A [Schultz *et al.*, 1999]. The measurement of HNO₃ appears reliable based on a recent measurement intercomparison and observed closure of the NO_y budget [Talbot *et al.*, 1999b].

The only previous studies listing average rates of individual reactions contributing to their model NO_x budget are Fan *et al.* [1994] for ABLE-3B and Jacob *et al.* [1996] for TRACE-A. The NO_x budget imbalance during ABLE-3B was small (Table 5). That study extended only to 6 km altitude; thermal decomposition of PAN was the dominant chemical source of NO_x, and N₂O₅ hydrolysis was ignored because the aerosol was fully neutralized. Therefore the effects that we investigated in section 3 would not alter the computed NO_x budget. In TRACE-A the NO_x budget imbalance at 4–12 km altitude was large (Table 5). If we suppress N₂O₅ hydrolysis and use the revised rate constants for NO₂ + OH + M and OH + HNO₃, we find a reduction in

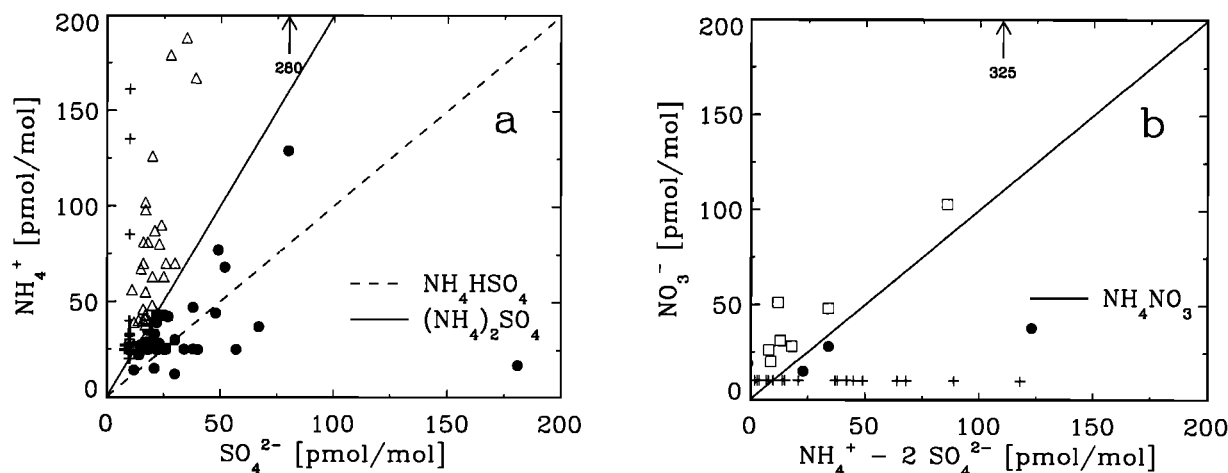


Figure 5. Relationships at 6–12 km between (a) aerosol sulfate and ammonium and (b) aerosol nitrate and ammonium in excess of sulfate. The dashed line in Figure 5a is the 1:1 line; the solid line is the 2:1 line. The solid line in Figure 5b is the 1:1 line. Symbols are the same as in Figure 4.

Table 5. Chemical NO_x Budget in the Free Troposphere: Observations and Models

Field Experiment	NO + NO ₂	HNO ₃	PAN	NO _x Budget	Notes	Reference
<i>Aircraft Studies</i>						
ABLE 3A, July/Aug. 1988 50°-75°N, 150°-170°W, 5-6.2 km	20	100	320	$((P - L)_{\text{HNO}_3} / (L - P)_{\text{PAN}} = 5.2)$	1, 10, 11, 12	Jacob et al. [1992]
ABLE 3B, July/Aug. 1990 45°-57°N, 65°-90°W, 2.5-6.2 km	33	50	240	$(L_{\text{NO}_2} / P_{\text{NO}_2} = 0.95)$	2, 10, 11, 12	Fan et al. [1994]
TRACE-A, Oct. 1992 40°S-20°N, 60°W-40°E, 4-8 km ibid., 8-12 km	57	130	294	$(L_{\text{NO}_2} / P_{\text{NO}_2} = 3.6)$	3, 10, 11, 13	Jacob et al. [1996]
PEM-West A, Oct. 1991 0-25°N, 100°E-140°W, 7-13 km	145 ~27	59 12	223 16	$(L_{\text{NO}_2} / P_{\text{NO}_2} = 5.6)$ $R_N < 0.7$ (3-5)	3, 10, 11, 13 4, 13	ibid. Singh et al. [1996a]
PEM-West B, Feb/Mar. 1994 110°E-180°, 5°S-25°N, 7-12 km	84	54	39	$R_N = 0.64$ (~2)	5, 10, 11, 13	Kondo et al. [1997]
PEM-West B, Feb/Mar. 1994 110°E-180°, 5°S-10°N, 6-12 km	70 (45)	160 (95)	25 (40)	$R_N \sim 2.9$ (2.8)	6, 12	Singh et al. [1998]
PEM-Tropics A, Sep/Oct. 1996 0-30°S, 160°E-90°W, 6-12 km	21	48	27	$(L_{\text{NO}_2} / P_{\text{NO}_2} = 1.9)$	10, 11, 13	this study
<i>Mountain Site Measurements</i>						
MLOPEX I, spring 1988 18°N, 156°W, 3.4 km	32 (20)	116 (184)	17 (15)	$R_N = 3.5$ (~17, 9.4)	7, 12	Liu et al. [1992], Brasseur et al. [1996]
MLOPEX IIa, fall 1991	26 (23)	76 (232)	12 (13)	$R_N = 2.0$ (10, 21)	8, 12	Brasseur et al. [1996], Hauglustaine et al. [1996]
MLOPEX IIb, winter 1992	33 (29)	78 (155)	29 (28)	$R_N = 1.4$ (5.9, 21)	8, 12	ibid.
MLOPEX IIc, spring 1992	41 (19)	140 (170)	36 (17)	$R_N = 3.2$ (8.8, 24)	8, 12	ibid.
MLOPEX IId, summer 1992	30 (25)	84 (351)	9 (11)	$R_N = 2.4$ (14, 24)	8, 12	ibid.
Tenerife, summer 1993 28°N, 16°W, 2.4 km	70 (49)	410 (380)	10 (14)	$R_N = 5.9$ (7.8)	9	Schultz et al. [1998]

Values in parentheses are model results. The table compiles mean or median concentrations of NO_x, HNO₃, and PAN observed in previous field studies of the remote troposphere, together with summary results of chemical NO_x budget analyses conducted using photochemical point models or in some cases global three-dimensional models. Some models use the HNO₃/(NO + NO₂) concentration ratio (R_N) as diagnostic of the NO_x budget while others use the ratio of chemical loss of NO_x (L_{NO_2}) to chemical production (P_{NO_2}) when the model is constrained with local observations. Notes are as follows: (1) No heterogeneous NO_x loss. The ratio of net loss of PAN to net production of HNO₃ exaggerates the NO_x budget imbalance. (2) Value for background conditions. Concentrations are weighted averages over three altitude bands. $L_{\text{NO}_2}/P_{\text{NO}_2}$ is read from figure and corresponds to $\text{mean}(L_{\text{NO}_2})/\text{mean}(P_{\text{NO}_2})$. (3) N₂O₅ hydrolysis in aerosols included. (4) The sum of mean NO and mean NO₂ given by Singh et al. [1996a] is ~58 pptv, but Crawford et al. [1996] conclude that observed NO₂ is high by a factor of 3-4. The values in this table include mean NO₂ reduced by a factor of 3. Observed R_N taken from Singh et al. [1996b, Figure 5]. Modeled R_N from the MOGUNTIA global three-dimensional model which includes N₂O₅ hydrolysis in aerosols. (5) Entry for air masses that were classified as "maritime tropical". Crawford et al. [1997] state that recycling from HNO₃ contributes 32% of the required NO_x source for the complete upper tropospheric PEM West B data. (6) Average of observations and model results binned in 5° latitude intervals, taken from Singh et al. [1998, Figures 6 and 9]. Global three-dimensional model from Wang et al. [1998]. (7) Model concentrations from MOZART global three-dimensional model [Brasseur et al., 1996]. First modeled R_N from Liu et al. [1992]; photochemical steady state box model with no heterogeneous NO_x loss. Second modeled R_N from the MOZART model including N₂O₅ hydrolysis in aerosols. In a third analysis of MLOPEX I data, Chatfield [1994] gives a range from 14-25 for simulated R_N from a Lagrangian box model with N₂O₅ hydrolysis. (8) Model concentrations and first modeled R_N values are from Brasseur et al. [1996] who report results from the MOZART global three-dimensional model which includes N₂O₅ hydrolysis. (9) Second modeled R_N from Hauglustaine et al. [1996]; Lagrangian box model with heterogeneous N₂O₅ hydrolysis ($\gamma = 0.1$) and aerosol surface areas estimated from local aerosol scattering coefficient measurements. (10) HNO₃ estimated as NO_y - NO_x - PAN. Case study with Lagrangian box model along descending trajectory. No heterogeneous NO_x loss. (11) NO₂ from photochemical steady state. (12) Photochemical box model in diurnal steady state constrained by observed NO, HNO₃, and PAN. (13) Mean values. (14) Median values.

$L_{\text{NO}_x}/P_{\text{NO}_x}$ from 3.6 to 2.1 (4–8 km) and from 5.6 to 3.1 (8–12 km). The large effect is mainly caused by the importance of N₂O₅ hydrolysis in the Jacob *et al.* [1996] model budget which in turn is due to the high ozone concentrations observed in TRACE-A.

Global three-dimensional (3-D) models which account for long-range transport of NO_x from primary sources such as lightning and combustion also experience difficulties in simulating R_N in the upper troposphere [Brasseur *et al.*, 1996; Wang *et al.*, 1998a,b; Lawrence and Crutzen, 1998; Hauglustaine *et al.*, 1998; Thakur *et al.*, 1999]. These models generally achieve a good simulation of NO_x (reflecting, however, in part an adjustment of the source from lightning) but overestimate HNO₃ concentrations by a factor of 2–10 in the upper troposphere, similar to the chemical equilibrium model studies in Table 5. Aside from possible gaps in our understanding of the chemical budget of NO_x, other factors could contribute to the overestimates of HNO₃ in the 3-D models. One factor would be the fractionation of HNO₃ into aerosol nitrate (NO₃⁻), which is not resolved by the models [Wang *et al.*, 1998b; Tabazadeh *et al.*, 1998]. However, during PEM-Tropics A, the NO₃⁻/HNO₃ concentration ratio was usually < 0.2 (Figure 1f). Another factor would be insufficient precipitation scavenging in the free troposphere [Wang *et al.*, 1998b]. Lawrence and Crutzen [1998] proposed that gravitational settling of cirrus ice crystals, not accounted for in global models, can reduce HNO₃ by a factor of 10 in the tropical upper troposphere while the impact on zonally averaged NO_x concentrations typically remains < 20%.

5. Summary and Conclusions

The chemical NO_x budget in the middle and upper troposphere over the remote tropical South Pacific during PEM-Tropics A was examined with model calculations using concurrent measurements of NO, HNO₃, and PAN as constraints. A standard calculation yields a median factor of 2.4 excess of chemical loss of NO_x (conversion to HNO₃ and PAN) relative to chemical production (recycling from HNO₃ and PAN), corresponding to a missing NO_x source of about 12 pptv day⁻¹. This imbalance is reduced by 10% when the recently remeasured temperature- and pressure-dependent reaction rate constants for OH + NO₂ + M [Brown *et al.*, 1999; Dransfield *et al.*, 1999] and OH + HNO₃ [Brown *et al.*, 1999] are incorporated in the chemical mechanism.

The bulk aerosol chemical composition measured in PEM-Tropics A at 6–12 km altitude indicates in most cases total H₂SO₄ neutralization by NH₃. This observation, combined with the low relative humidities measured in PEM-Tropics A (median 25% relative to ice), suggests that the aerosol should be present in the solid phase. Suppression of N₂O₅ hydrolysis in the model improves the chemical NO_x budget imbalance in PEM-Tropics A by another 15%. Further study of the composition and phase of free tropospheric aerosols is evidently needed.

The observation of 50–100 pptv of gas-phase NH₃ in the free troposphere over the Pacific (D. Davis *et al.*, manuscript in preparation, 1999) is inconsistent with global models [e.g., Dentener and Crutzen, 1994] and invites speculation about a potential NO_x source from NH₃ oxidation. For PEM-Tropics A, we derive an upper limit of 15% of the total NO_x source from this process.

If the results from this paper are applied to previous studies, reductions of the chemical NO_x budget imbalance of up to 40% are expected. The new rate constants and the possibly suppressed nighttime sink of NO_x would bring most studies into a $L_{\text{NO}_x}/P_{\text{NO}_x}$ range of 2–3.

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- J. E. Dibb and R. W. Talbot, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH 03824.
- D. J. Jacob, Division of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02139. (djj@io.harvard.edu)
- S. T. Sandholm, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332.
- M. G. Schultz, Max-Planck-Institut für Meteorologie, Bundesstr. 55, 20146 Hamburg, Germany. (martin.schultz@dkrz.de)
- H. B. Singh, NASA Ames Research Center, Moffett Field, CA 94035.

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