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Author
Talbot, R

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Reactive nitrogen in Asian continental outflow over the western Pacific: Results from the NASA Transport and Chemical Evolution over the Pacific (TRACE-P) airborne mission


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[1] We present here results for reactive nitrogen species measured aboard the NASA DC-8 aircraft during the Transport and Chemical Evolution over the Pacific (TRACE-P) mission. The large-scale distributions total reactive nitrogen (NO$_{y,sum}$ = NO + NO$_2$ + HNO$_3$ + PAN + C$_1$–C$_5$ alkyl nitrates) and O$_3$ and CO were better defined in the boundary layer with significant degradation of the relationships as altitude increased. Typically, NO$_{y,sum}$ was enhanced over background levels of ~260 pptv by 20-to-30-fold. The ratio C$_2$H$_2$/CO had values of 1–4 at altitudes up to 10 km and as far eastward as 150°E, implying significant vertical mixing of air parcels followed by rapid advection across the Pacific. Analysis air parcels originating from five principal Asian source regions showed that HNO$_3$ and PAN dominated NO$_{y,sum}$. Correlations of NO$_{y,sum}$ with C$_2$Cl$_4$ (urban tracer) were not well defined in any of the source regions, and they were only slightly better with CH$_3$Cl (biomass tracer). Air parcels over the western Pacific contained a complex mixture of emission sources that are not easily resolvable as shown by analysis of the Shanghai mega-city plume. It contained an intricate mixture of pollution emissions and exhibited the highest mixing ratios of NO$_{y,sum}$ species observed during TRACE-P. Comparison of tropospheric chemistry between the earlier PEM-West B mission and the recent TRACE-P data showed that in the boundary layer significant increases in the mixing ratios of NO$_{y,sum}$ species have occurred, but the middle and upper troposphere seems to have been affected minimally by increasing emissions on the Asian continent over the last 7 years. INDEX TERMS: 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks


1. Introduction

[2] The Transport and Chemical Evolution over the Pacific (TRACE-P) airborne mission was conducted by the National Aeronautics and Space Administration to better understand how outflow of anthropogenic emissions and crustal dust from the Asian continent affects the composition of the global atmosphere. The TRACE-P flights were designed to determine the pathways and chemical evolution of trace gases and aerosols transported to and across the north Pacific troposphere. TRACE-P built upon the results and experience from previous NASA missions conducted in this region in 1991 and 1994, the Pacific Exploratory Missions-West A and B, respectively [Hoell et al., 1996, 1997]. Owing to the rapid industrialization on the Asian continent during the 1990s [Streets et al., 2003], TRACE-P was conducted to quantify the corresponding increase in emissions and their impact on tropospheric chemistry over the Pacific basin. The airborne mission was conducted in February–April 2001, the time period of the year characterized by the most significant outflow of pollutants and crustal dust from the Asian continent [Jacob et al., 2003]. The timing of this expedition compared to PEM-West presented an ideal situation to assess decadal changes in Asian inter-continental transport.

[3] PEM-West A was conducted in the September–October 1991 time frame and demonstrated the complex nature of emissions over the western Pacific. For example, in the lower troposphere continental outflow was enhanced in numerous combustion and industrial tracers but at higher
altitudes the ratio C2H2/CO was <1.5 indicating much older inputs, possibly from European origin [Talbot et al., 1996]. In the upper troposphere air parcels were enhanced in CH4 but depleted in CO2 and COS, indicating potential biogenic emissions of CH4 and vegetative uptake of CO2 and COS.

[4] A much more comprehensive sampling and analysis of Asian outflow was conducted during PEM-West B (1994) which revealed important subtle details. Backward 5-day isentropic trajectories and atmospheric chemistry together indicated that there was extensive rapid outflow from Asian continental areas below 5 km altitude [Talbot et al., 1997a, 1997b]. Aged marine air was rarely encountered over the western Pacific due to the strong late winter/springtime continental outflow, and then it was only sampled at latitudes <20°N. The outflow at low altitude had significant enhancements of industrial tracers such as C2Cl4, CH3CCl3, and C6H6 intermixed with the combustion products C2H2, C2H6, CO, and NO. In the middle-to-upper troposphere, Middle Eastern and European source regions were implicated as possible contributors to the outflow. The importance of vertical convective transport was apparent, with subsequent removal of water-soluble species like HNO3, SO2, and H2O2. The long-range transport of PAN in the midtroposphere with subsequent downward mixing and conversion to NOX was postulated to be an important source of reactive nitrogen to the remote Pacific boundary layer [Dibb et al., 1997].

[5] The rapid industrialization on the Asian continent is of compelling interest to atmospheric chemistry and climate change. Energy use in eastern Asia has increased by 5% yr−1 over the past decade and is expected to continue at this rate for several more decades [U.S. Department of Energy, 1997]. Combustion of fossil fuels is the main source of energy, with emissions of NOX predicted to increase nearly five-fold by 2020 [Van Aardenne et al., 1999].

[6] The suite of NASA western Pacific missions has observed the time-dependent impact on the Northern Hemisphere tropospheric chemistry of a major industrial revolution on the Asian continent. Long-term observations from ground sites provide a continuous framework, but aircraft and satellite observations significantly augment our understanding of dynamical and chemical processes affecting atmospheric composition over a large remote geographic region like the Pacific basin. TRACE-P is the most recent NASA mission in the Pacific Rim region, and it provided a detailed chemical characterization of Asian continental outflow and emissions. In this paper we focus specifically on the suite of reactive nitrogen species, which are critical in determining the overall photochemical mixture of chemical species in continental outflow over the north Pacific. This outflow is expected to begin to influence atmospheric chemistry over North America within the current decadal time frame [Bernsten and Karlssott, 1999; Jacob et al., 1999].

2. Airborne Mission

[7] The airborne component discussed in this paper was conducted aboard the NASA Dryden DC-8 research aircraft. Transit and intensive science missions comprised 20 flights, with each one averaging ~8 hours in duration and covering an altitude range of 0.3–12.5 km. The flights over the western Pacific, from which the data for this paper are drawn, were centered in the region west of 150°E longitude. The base of operations for these flights was from Hong Kong (seven missions) and Yokota, Japan (five missions).

[8] The overall scientific rationale and description of the individual aircraft missions are described in the TRACE-P overview paper [Jacob et al., 2003]. The features of the large-scale meteorological regime and associated air parcel backward trajectory analyses for the February–March 2001 time frame are presented by Fuelberg et al. [2003]. A general description of the chemical composition of the Asian continental outflow is in a companion paper [Russo et al., 2003]. The focus of that paper is primarily CO, O3, and hydrocarbons, with minimal discussion of the NOX family. The purpose of this paper is to fill that gap and provide more detail that can be addressed in a general discussion of continental outflow.

[9] We present here a broad description of the outflow chemistry focused on the reactive nitrogen family and refer to the overview paper [Jacob et al., 2003] and companion papers for descriptions of the various measurements. Additionally, more specific information is included below for measurement details of the reactive nitrogen species. Since total reactive nitrogen (NOy) was not measured on the DC-8, we use the sum of NO, NO2, PAN, HNO3, and C1−C5 alkyl nitrates to represent NOy (NOy,sun). Aerosol nitrate and PPN were not included in NOy,sun since their contribution to NOy,sun rarely exceeded 5% and 1%, respectively, and because in the case of nitrate its measurement time base (~10 min) was substantially longer than that for gas phase species. In general, the agreement between NOy,sum and NOy measured with a gold catalytic converter is ~20% for the suite of TRACE-P instruments and NOy mixing ratios in the range 100–3000 pptv [Talbot et al., 1999].

[10] NO and NO2 were measured by the Georgia Institute of Technology using photofragmentation two-photon laser-induced fluorescence (TP-LIF) [Sandholm et al., 1990]. The method spectroscopically detects NO, with UV laser photolysis of NO2 and subsequent detection of NO. The optical detection scheme involves sequentially exciting rotationally resolved transitions in the X′1Σ+ − A′2Σ+ and the A′2Σ+ − D′2Σ+ bands of NO using laser wavelengths centered at 226 nm and 1.1 μm, respectively. The resulting blue shift in fluorescence is monitored near 190 nm. Calibration utilized a NIST certified NO standard (±1–2%). Additional NOy measurement details of the reactive nitrogen species. Since total reactive nitrogen (NOy) was not measured on the DC-8, we use the sum of NO, NO2, PAN, HNO3, and C1−C5 alkyl nitrates to represent NOy (NOy,sun). Aerosol nitrate and PPN were not included in NOy,sun since their contribution to NOy,sun rarely exceeded 5% and 1%, respectively, and because in the case of nitrate its measurement time base (~10 min) was substantially longer than that for gas phase species. In general, the agreement between NOy,sum and NOy measured with a gold catalytic converter is ~20% for the suite of TRACE-P instruments and NOy mixing ratios in the range 100–3000 pptv [Talbot et al., 1999].

[11] PAN was measured by NASA Ames Research Center using cryogenic preconcentration of ambient air and analysis of it using gas chromatography with electron capture detection. PAN was measured every 5 min aboard the DC-8 by an electron-capture gas-chromatographic technique [Singh et al., 2001]. Typically, 160 ml of ambient air was preconcentrated at −140°C over a 2-min period. PAN calibrations were performed by using a 2-ml diffusion tube filled with pure liquid PAN in an n-tridecane matrix. A dynamic dilution system was used to generate low-pptv mixing ratios of PAN. The technique has a measurement
sensitivity of better than 1 pptv PAN. Instrument precision and accuracy are estimated to be ±10% and ±25%, respectively. Intercomparison studies performed during TRACE-P further confirmed that the reliability of the PAN measurements was within these specifications [Eisele et al., 2003].

[12] Nitric acid was measured by the University of New Hampshire using the mist chamber/ion chromatography technique [Talbot et al., 2000]. Sampling was conducted using a high-flow manifold (3000 liters per min) that was glass-coated (vapor-deposited) and heated to 50°C. The manifold was 8 cm ID and had a diffuser configuration over the entrance to boost the flow/pressure and facilitate sampling at the high velocities (Mach 0.88) of the DC-8. The inlet design was nearly identical to that used for NO/NO₂ [Brdshaw et al., 1999] and OH/HO₂ [Brune et al., 1998]. The inlet was equipped with the capability to conduct standard additions of HNO₃ into the manifold and quantify its passing efficiency frequently during flight. A permeation source was used for HNO₃ from which the output was tracked using Nylon filters and a NOx chemiluminescence instrument equipped with a molybdenum NOy converter heated to 350°C. The output of the permeation source was about 200 ppbv of HNO₃ that could be readily diluted to pptv levels and quantified in our manifold. Thus standard additions were conducted at approximately twice ambient HNO₃ mixing ratios. The precision and accuracy of the HNO₃ measurements are both in the range of 10–20% depending on the ambient mixing ratio. The time resolution of the ambient measurements was two minutes. Inter-comparisons with a chemical ionization mass spectrometer instrument aboard the NASA P-3 aircraft during TRACE-P showed good agreement (±20%) under most atmospheric conditions [Eisele et al., 2003].

[13] Alkyl nitrate species were measured by the University of California, Irvine and the National Center for Atmospheric Research (NCAR) after collection of ambient air samples in 2-liter electropolished stainless steel canisters. A two-stage metal bellows pump was used to pressurize the canisters to 3.8 hPa. Samples were obtained every 3–7 min during horizontal flight legs with a collection interval of 8 s at 150 m to 90 s at 12 km. The following alkyl nitrate were measured in each sample: methyl nitrate (CH₃ONO₂), ethyl nitrate (C₂H₅ONO₂), n-propyl nitrate (n-C₃H₇ONO₂), i-propyl nitrate (i-C₃H₇ONO₂), 2-butyl nitrate (2-C₄H₉ONO₂), 2-penty nitrate (2-C₅H₁₁ONO₂), and 3-pentyl nitrate (3-C₅H₁₁ONO₂). The analytical procedures are detailed by Colman et al. [2001]. The C₁–C₂ alkyl nitrate were separated using three of the five column-detector combinations in the UC-Irvine laboratory. The limit of detection for alkyl nitrates was typically 0.02 pptv with a precision of ±5% at mixing ratio > 5 pptv and ±10% below 5 pptv. Calibration for alkyl nitrites used regular analysis of whole air standards which were intercalibrated with synthetic air standards prepared at NCAR. Analysis of duplicate samples and standards by both laboratories agreed within ±2%.

3. General Trends Over the Western Pacific

[14] To present the overall distribution of reactive nitrogen over the western Pacific, the entire 1 min data set for flights 6–17 was utilized. For species with a time response greater than 1 min, duplicated values generated by the merging process were removed from the database. Data collected above 7 km altitude was filtered additionally to remove stratospheric air influences using O₃ (>120 ppbv), CO (<70 ppbv), and dew point temperature (<−50°C) values indicative of stratospheric influence. However, the air parcels in this region often had both combustion and stratospheric influences superimposed, so it was impossible to completely remove the stratospheric component. The data set we used has some higher values of O₃ while the mixing ratios of other species such as CO were quite elevated. We only removed the most strongly influenced stratospheric cases.

[15] The latitudinal distributions of NOy,∑ and CO are presented in Figure 1, and they illustrate the widespread influence of combustion emissions on atmospheric chemistry over the western Pacific. The close correspondence in the distribution of mixing ratios of CO and NOy,∑ in the heavily polluted plumes suggests a direct source relationship between combustion and reactive nitrogen species. Indeed, at all altitudes in the latitudinal band of 20–40° N well-defined plumes contained NOy,∑ in excess of 1000 pptv. However, as shown later in this paper, outside the few large plumes the general correspondence between CO and NOy,∑ is not readily apparent (they are largely uncorrelated).

[16] The relationship between NOy,∑ and CO is shown in Figure 2. The correspondence in NOy,∑ and CO was most apparent in the boundary layer and was not well defined at altitudes above it. Presumably this reflects sampling of less processed air parcels down low and the close proximity of major emission sources on the Asian continent. Even in the boundary layer the relationship between NOy,∑ and CO was strongly driven by sampling of heavily polluted plumes advected over the Pacific Rim region from concentrated urban centers such as Shanghai. At higher altitudes the air parcels had undergone more processing, and they are also likely impacted by both Asian and other more distant sources. For example, a European influence was hypothesized for altitudes >7 km over the western Pacific during the PEM-West B time frame [Talbot et al., 1997a]. However, for TRACE-P the European influence above 7 km appears to have been minimal based on three-dimensional (3-D) model results [Liu et al., 2003].

[17] Photochemical processing of air parcels that have NOx-rich hydrocarbon mixtures leads to production of a suite of reactive nitrogen compounds and O₃. Thus the correspondence between NOy,∑ and O₃ is of interest. In general, the correlations between NOy,∑ and O₃ were poorly defined in the Asian outflow over the western Pacific (Figure 2). As in the case of CO, the tightest relationship was found in the boundary layer, where it was again determined largely by the most heavily polluted plumes. In the midtroposphere the values were centered on an O₃ mixing ratio of 60 ppbv, with NOy,∑ being as high as 2500 pptv. Observations very similar to these reported here were obtained during PEM-West B, except that it was centered on O₃ mixing ratios in the 40–50 ppbv range [Koike et al., 1997]. Above 7 km altitude there was a weak linear trend in NOy,∑ and O₃ that may be related to the strong linear correspondence between these species (i.e., HNO₃ and O₃) in stratospheric air [e.g., Talbot et al., 1997b]. As stated earlier, air parcels in this region were
Figure 1. Latitudinal distribution of mixing ratios of NO$_y$ and CO over the western Pacific west of 150°E longitude. Data is shown for three altitude bins of 0–2, 2–7, and >7 km.

Figure 2. Relationships between mixing ratios of NO$_y$ and CO or O$_3$ in three altitude bins of 0–2, 2–7, and >7 km.
influenced coincidently by combustion and stratospheric sources which could not be separated adequately. Alternatively, the positive correlation could have been the result of biomass burning emissions occurring in southeastern Asia. This point is addressed further in this paper when we examine specific characteristics of various Asian source regions based on analysis of air parcel backward trajectories.

The latitudinal pattern of individual reactive nitrogen species over the western Pacific is presented in Figure 3. For the most part, mixing ratios of NO\textsubscript{x} were <100 pptv, suggesting that the sampled air parcels were aged at least 1–2 days which allowed for transformations of it to HNO\textsubscript{3}, PAN, and other NO\textsubscript{y, sum} species. The largest enhancements in all species occurred at 30\textdegreeN when the DC-8 sampled the Shanghai mega-city urban plume during a boundary layer leg over the Yellow Sea. This plume contained mixing ratios of NO\textsubscript{x}, HNO\textsubscript{3}, PAN, and alkyl nitrates of up to 3,000, 8,000, 4,300, and 225 pptv, respectively. In a later section of this paper we discuss the chemical composition of this plume in detail.

The vertical distribution of reactive nitrogen species provides insight to the nature of their sources, and in particular the association of origin either on the Asian continent or from long-range transport into the western Pacific region. These distributions are summarized in Figure 4, where the alkyl nitrate species are represented as the sum of the individual species (i.e., sum Alkyl-ONO\textsubscript{2}). Shown also is aerosol nitrate based on Teflon filter measurements with approximately 10 min time resolution as described by Dibb et al. [2003].

All the gas phase reactive nitrogen species showed significant deviations and enhancements well above their background values, defined as the median of the lowest 15% of the observed mixing ratios at a given altitude. The background mixing ratios exhibited little altitude dependence, and representative values were as follows: NO\textsubscript{x} (25 pptv), HNO\textsubscript{3} (125 pptv), PAN (100 pptv), alkyl nitrates (7 pptv), aerosol nitrate (25 pptv), and NO\textsubscript{y, sum} (257 pptv). The enhancements occurred at all altitudes up to the 12 km ceiling of the DC-8 aircraft. It was not uncommon for the enhanced mixing ratios to be 10-to-20-fold larger than their corresponding background value. The greatest enhancement generally occurred in the boundary layer indicating the predominance of surface sources in Asia on regional tropospheric chemistry. Particularly noteworthy were the alkyl nitrate species which exhibited combined increases of up to 50 pptv at altitudes up to 8 km. The alkyl nitrate distribution was dominated by 2-butyl nitrate which comprised on average 30% of the sum depicted in Figure 4. In general, the vertical distributions indicate a strong surface source for NO\textsubscript{y, sum} species with a strong influence up to 10 km altitude. We argue later in this paper that based on C\textsubscript{2}H\textsubscript{2}/CO ratios of 1–4 these enhancements reflect fairly recent Asian emissions rather than influence from long-range transport.

Figure 3. Latitudinal distribution of individual NO\textsubscript{y} species in three altitude bins of 0–2, 2–7, and >7 km.
The largest mixing ratios of aerosol nitrate were observed in the Asian coastal marine boundary layer. On some occasions ppbv values of aerosol nitrate were measured that far exceeded attendant mixing ratios of HNO₃. Undoubtedly, the high levels of nitrate reflected uptake of HNO₃ by sea salt aerosols, as evidenced by coincidently large mixing ratios of sodium and chloride [Dibb et al., 2003; Jordan et al., 2003].

An important consideration for interpretation of the TRACE-P observations is the relative processing of air parcels over various spatial and temporal scales. Here we use the ratio C₂H₂/CO as a scaling factor in this regard since it is unaffected by physical removal processes. The ratio is decreased over time by chemical attack by OH (i.e., C₂H₂ lifetime about 2 weeks compared with CO of several months) and physical mixing processes. The distribution

**Figure 4.** Vertical distribution of individual NOₓ species over the western Pacific west of 150°E longitude. The open circles represent the mean value with one standard deviation indicated by the horizontal bar for two km thick altitude bins.
of the values of this ratio over the western Pacific provides key insight into transport and mixing processes on various time scales. Values $>1$ indicate fairly recent emissions (<5 days) while ratios $<1$ indicate extensively processed air by mixing and chemical decomposition.

[23] The vertical altitudinal ensemble of values in C$_2$H$_2$/CO is presented in Figure 5 along with the longitudinal variation. The distributions are striking; ratio values in the middle-to-upper troposphere mimic the boundary layer and also indicate transport of continent emissions across the Pacific. Further, the data suggest that frontal uplifting and vertical transport must be rapid and operating continuously over the Asian continent in combination with extensive westerly transport of pollutants at all altitudes. The travel distances and timing implied by the backward trajectories suggest the uplifting and vertical transport must be occurring on the time scale of hours. A more detailed analysis is needed to better constrain these various transport rates. These results explain the blurred correlations between NO$_y$$_x$$_{sum}$ and CO or O$_3$. The continuous intermixing of air parcels of various ages and processing would lead directly to very complex distributions and relationships of NO$_y$$_x$$_{sum}$, CO, and O$_3$ over the western Pacific, which is exactly what we observed. This same picture was captured by the observation-based climatologies developed by Emmons et al. [2000]. For the western Pacific the model simulations for the PEM-West field campaigns showed the same vertical patterns and mixing ratios observed during TRACE-P for O$_3$, CO, and NO$_x$, but deviations were up to two-fold for HNO$_3$ and PAN. The model predicted ratios of PAN/NO$_x$ and HNO$_3$/NO$_x$ were 2–3 times higher than observations in the 2–8 km altitude range, indicating the difficulty in

Figure 5. Vertical and longitudinal distributions of the C$_2$H$_2$/CO ratio over the western Pacific west of 150°E longitude.
estimating the degree of air mass processing and interconversion of NOx species.

An important transport pattern over Asia during winter is bifurcation of westerly flow when it passes over the Tibetan Plateau. Here the northern branch forms many blocked anticyclones while the southern one forms many troughs or cut-off lows, such as the Bangladesh trough and other troughs in southern China. The two branches merge at the eastern edge of the Plateau, resulting in strong winds over the southern Sea of Japan, where the maximum wind speed can reach over 70 m s⁻¹ at 500 mb [Zhang, 1992]. Such a dynamic system is conducive to the occurrence of unstable weather systems in southern China in winter. The associated dynamical processes help explain why the TRACE-P data show pollutants mixed to high altitudes and transported eastward rapidly to 150°E.

4. Relationships Based on Source Region Apportionments

To examine the detailed relationships of NOy,Σ species with source tracer species and their spatial variability, air parcel backward trajectories were used to establish the principal source region locations on the Asian continent. Isentropic backward trajectories were provided by Florida State University for TRACE-P, and a description of the method is provided in Fuelberg et al. [2003]. For consistency with other TRACE-P analyses, we adopted the source region designations in this paper determined by Russo et al. [2003] and Jordan et al. [2003]. Five regions were identified in their analyses as depicted in Figure 6. These were classified as follows: (1) north-northwest (NNW), (2) west-southwest (WSW), (3) southeast Asia (SE Asia), (4) coastal and, (5) central. The major urban/industrial centers in China are located within the coastal and central source regions.

Since we have introduced the general latitudinal and vertical distributions of reactive nitrogen species for the western Pacific region, more specific source region relationships are presented here. We begin with the altitudinal budget of NOy,Σ species in air masses with backward trajectories from the various source regions (Figure 7). In the southeast and coastal groups, HNO₃ dominated NOy,Σ in the boundary layer and midtroposphere. This was especially true for the coastal group where HNO₃ comprised nearly 80% of NOy,Σ. There were nearly equal contributions from HNO₃ and PAN in the other three source regions, with PAN favored in the NNW and WSW groups at all altitudes. These distributions are consistent with expectations of less PAN in warmer locations due to its thermal instability and more PAN at higher altitudes where it is more stable. The predominance of HNO₃ and PAN in the NOy,Σ budget indicates that the majority of sampled air parcels were aged several days with significant photochemical processing over that time interval. It is not clear why NOₓ comprised 20–25% of NOy,Σ in the middle to upper troposphere in the WSW group. This finding was quite different than in the other four groups where its contribution was <10%. Possibilities include recent inputs from sources such as biomass burning, lightning, and stratospheric inputs or decreased photochemical activity (i.e., less efficient conversion to other NOy,Σ species).

Together these data indicate that significant outflow of reactive nitrogen occurs at all altitudes from the Asian continent with much of it residing in the reservoir species PAN. Owing to its long lifetime in the middle and upper troposphere, it can subsequently carry reactive nitrogen over long distances and be a source of NOₓ to various areas of the Northern Hemisphere troposphere. During PEM-West B strong outflow in the mid-troposphere contained high levels of PAN, and Dibb et al. [1997] hypothesized that it was a significant source of NOₓ and subsequently aerosol nitrate to the remote marine boundary layer over the central Pacific.
between C$_2$H$_2$ and NO$_y$_sum were examined for the five primary Asian source areas defined in Figure 6. These relationships are illustrated in Figure 8. To the best of our understanding, the only source of C$_2$H$_2$ to the atmosphere is combustion [Singh and Zimmerman, 1992]. NO$_y$_sum and C$_2$H$_2$ were highly correlated in the SE Asia region, and to a lesser extent in the central and coastal groups. The central group exhibited the best correspondence between NO$_y$_sum and C$_2$H$_2$, but this was largely driven by the highly polluted nature of the Shanghai plume. There was little or no correlation between these species in the NNW and WSW regions. These two regions are the farthest from the western Pacific, and as such have likely undergone more atmospheric processing than the other groups. The source relationships are consequently more blurred in these datasets. As presented previously, the WSW group also showed the largest mixing ratios of NO$_x$ above 7 km of all five source regions. The apparent low correlation with combustion suggests that the NO$_x$ may be related to stratospheric inputs or be from recycled reactive nitrogen in the upper troposphere. However, why these NO$_x$ sources would affect only this region is unclear.

To check for stratospheric inputs, correlations were examined between NO$_x$, and H$_2$O vapor, dew point, O$_3$, CO, and HNO$_3$ in upper troposphere for the WSW group. There was a trend of higher mixing ratios of NO$_x$ occurring coincidently with low mixing ratios of H$_2$O vapor, dew point temperature, and CO (Figure 9). The highest mixing ratios of NO occurred simultaneously with the lowest dew point temperature and CO values near 50 ppbv, clearly indicative of stratospheric air. Mixing ratios of HNO$_3$ sporadically reached 300–800 pptv in these same air parcels (not shown). Although these trends lean toward a stratospheric source for the enhanced upper tropospheric NO$_x$ in the WSW group, other sources such as lightning and combustion cannot be ruled out. Furthermore, it is clear that the air parcels in this upper tropospheric region were influenced by multiple sources, as the relative proportions of HNO$_3$ and PAN to NO$_y$_sum are not consistent with a purely stratospheric source and the intermittent presence of CO mixing ratios in the 100–300 ppbv range.

C$_2$Cl$_4$ is released exclusively by urban/industrial processes [Blake et al., 1996], and as such is a good tracer of air parcels influenced by metropolitan areas. In the central and coastal groups there were very general linear relationships between NO$_y$_sum and C$_2$Cl$_4$, but they were uncorrelated in the other groups (Figure 10). We examined correlations between individual NO$_y$_sum component species and they too showed no clear correspondence with C$_2$Cl$_4$. However, it appears that the use or release of C$_2$Cl$_4$ has decreased since the PEM-West B mission. Russo et al. [2003] found that median values of C$_2$Cl$_4$ were about two-fold less than those observed in the PEM-West B study. This reduced urban/industrial signal probably contributed to the weak correlations between NO$_y$_sum, and C$_2$Cl$_4$ during TRACE-P. As indicated by the central group, concentrated urban sources of C$_2$Cl$_4$ still do exist on the Asian continent. Mixing ratios of C$_2$Cl$_4$ peaked near 125 pptv when the Shanghai urban plume was sampled over the Yellow Sea.

Biomass burning on the Asian continent is expected to be a large source of NO$_y$_sum [Streets et al., 2003]. These emissions originate from fossil fuel combustion, bio-fuels for space heating and cooking, and agricultural practices. Good tracers of biomass burning emissions include soot carbon, fine aerosol potassium and ammonium, HCN, and CH$_3$Cl [Crutzen et al., 1979; Crutzen and Andreae, 1990]. Here we have chosen to use CH$_3$Cl due to its availability on a 1-min time basis. The NO$_y$_sum correlations with CH$_3$Cl over the western Pacific are depicted in Figure 11. The tightest correspondence was observed for the central source region, but it is entirely driven by sampling of the Shanghai plume. There were weak linear correlations in the SE Asia and coastal groups, and none in the NNW and WSW areas. Correlations very similar to those shown in Figure 11 were found using HCN instead of CH$_3$Cl (not shown). This is a bit unexpected, especially for the SE Asian region where extensive biomass burning was indicated by satellite surveying during the TRACE-P time period (available at http://www.people.fas.harvard.edu/~heald/fires.html). Both the

Figure 7. NO$_y$ budget comparison for the five Asian source regions as a function of altitude (0–2, 2–7, and >7 km). Median values were used for to construct these budgets.

Figure 8. Relationships between NO$_x$ and NO$_y$ for the five Asian source regions.
Heald et al. [2003] and Singh et al. [2003] companion papers indicate that HCN is a better tracer of biomass burning than CH₃Cl in the free troposphere, but this does not appear to hold up for clearly identifying a biomass burning source for NOₓ, sum. For species with simpler chemical transformations such as CO or C₂H₂, good correlations were found with HCN in a few limited cases [Russo et al., 2003].

Figure 8. Relationships between NOₓ and C₂H₂ for each of the five Asian source regions. C₂H₂ is a unique indicator of combustion emissions.
Overall, it appears that a unique source signal rarely remained in air parcels advected from over the Asian continent to the western Pacific after extensive processing during transport at the spatial resolution of the present analysis. Both C2Cl4 and CH3Cl, which are fairly specific tracers of urban and biomass burning emissions respectively, provided minimal insight to the relative importance of these sources. This may be related to removal of NOy during transport eroding the original source signatures and correlations. For urban/industrial tracers we expanded our efforts to include CH3CCl, Halon-1211, and CH3Br (enhanced greatly in Japanese urban areas). None of these improved the source recognition issues. Most distributions were centered commonly around the median mixing ratio of the tracer species employed in the analysis. This result implies that we must rely more than ever on mesoscale modeling results and associated emission inventories to facilitate our understanding of continental scale atmospheric chemistry and intercontinental transport.

5. Characterization of the Shanghai Plume

The Shanghai urban plume was sampled during flight 13 at 0.34 km altitude over the Yellow Sea. The plume was encountered ~100 km north of Shanghai and sampled along a 300 km transect over a 38-min period around midday. The wind speed in the plume averaged 7 m s⁻¹, yielding a travel time of 4 hours at the south end to 16 hours at the northernmost point sampled. Thus the plume seemingly sampled air originating in the Shanghai urban center in the late night hours (northern point) and midmorning at the southern end of the transect. Thus it is possible that the peak mixing ratios represent the morning rush hour time period. However, this is pure speculation and we do not know the three-dimensional positioning of the plume and how the DC-8 transected it. This plume contained the largest mixing ratios of most species, with O₃ being one exception, observed during the TRACE-P mission. The plume was a combination of various age air parcels, with the freshest components exhibiting a C₂H₂/CO ratio of 9.3 and the rest in the 4–6 range (Figure 5). These values suggest a well-defined plume with emissions less than 1 day old.

The large mixing ratios of highly reactive species such as C₂H₄ are evidence of the very recent emissions associated with the Shanghai plume (Figure 12). The combustion nature of the plume was captured by the very high levels (~10,000 pptv) of C₂H₂. Mixing ratios of CO peaked at 1100 ppbv and 392 ppmv for CO₂ (not shown). The urban/industrial signature of the plume contained a large ensemble of enhanced volatile organic compounds, including C₂Cl₄ and CH₃Br (Figure 12). Mixing ratios of CH₃Cl and HCN exceeded 1600 pptv (3 times background levels), indicating that a strong biomass burning/biofuel component also influenced the chemical composition of the plume (not shown). Li et al. [2003] hypothesized a possible source from residential coal combustion for both CH₃Cl and for HCN in this plume.

Since the Shanghai plume appears to represent a large source of reactive nitrogen to the marine boundary layer over the Yellow Sea, we examined its NOy,∑ budget in detail. This included examination of the distribution of individual NOy,∑ species, plus a breakdown of the seven alkyl nitrate compounds measured by the UCI-NCAR
groups. These data show that i-propyl and 2-butyl nitrate were the most abundant alkyl nitrate species in this urban/industrial plume. Their peak mixing ratios were \( \approx 70 \) pptv, followed by the pentyl nitrates at \( 20–25 \) pptv. Methyl and ethyl nitrate were among the least abundant, opposite to their distribution over the tropical Pacific where they appear to be released from the surface ocean contributing to the \( 30–50 \) pptv levels typical of the remote marine boundary.

**Figure 10.** Relationships between NO\(_3\) and C\(_2\)Cl\(_4\) for each of the five Asian source regions. C\(_2\)Cl\(_4\) is an indicator of urban/industrial emissions.
layer [Talbot et al., 2000; Blake et al., 2003]. Together the alkyl nitrate sum exceeded 200 pptv in the heart of the plume, a very significant amount but still less than 2% of total NO$_{y,\text{sum}}$.

The distribution of individual NO$_{y,\text{sum}}$ species showed the following approximate contributions: NO$_x$ (15%), HNO$_3$ (53%), PAN (30%), and alkyl-ONO$_2$ (2%). At one point in the marine boundary layer aerosol nitrate

Figure 11. Relationships between NO$_{y}$ and CH$_3$Cl for each of the five Asian source regions. CH$_3$Cl is an indicator of biomass burning emissions.
reached 13,500 pptv in the plume [Dibb et al., 2003]. Thus it was equal to or greater than total gas phase NO$_{y,\text{sum}}$. This finding suggests that the Shanghai plume contains very large mixing ratios of HNO$_3$ over the Asian continent, but that it is rapidly lost to sea salt aerosols over the ocean. Together the HNO$_3$ and aerosol nitrate must exceed 20,000 pptv over the Asian continent, with HNO$_3$ likely dominating the phase partitioning. These data indicate that OH levels in the plume are probably controlled to a large extent by reaction with NO$_2$ to form HNO$_3$. However, detailed measurements are

Figure 12. Chemical relationships and breakdown of individual NO$_x$ species in the Shanghai mega-city plume. The DC-8 flight track was located along a 300 km north-south longitudinal transect at 125°E.
6. Comparison of TRACE-P With PEM-West B Results

[37] Owing to rapid industrialization on the Asian continent, it is of great interest to examine changes in tropospheric chemistry over the western Pacific during the past decade. Since PEM-West B was conducted during the same monthly time frame in 1994 that TRACE-P covered in 2001, direct meaningful comparisons are possible. In addition, many of the species were measured by the same investigator groups during both missions, minimizing measurement biases.

[38] Russo et al. [2003] found few changes in the distributions and mixing ratios of a large suite of trace gases. One exception to this was O₃, which appears to have increased by 10–20 ppbv throughout the western Pacific. There was a very significant increase in the mixing ratios of water-soluble aerosol species during TRACE-P compared to PEM-West B [Dibb et al., 2003]. It is difficult to access how much of the 2–5 fold increases were due to emissions compared to other confounding factors such as variations in the degree of precipitation scavenging.

[39] For the comparisons we used summary statistics for the PEM-West B period reported by Talbot et al. [1997a]. The PEM-West B data were broken into two groups, continental north and south, divided by a geographic separation at 20°N. We thus compared the continental north group with the TRACE-P coastal, central, and NNW groups and the continental south region with the SE Asia group. The WSW group was not used in these comparisons since it overlaps significantly with both PEM-West B source regions. The values of NOₓ,sum for PEM-West B were taken from Talbot et al. [1997a, 1997b].

[40] Tables 1 and 2 contain a summary of NOₓ,sum species comparisons for the two western Pacific missions. In the boundary layer for the northern groupings median mixing ratios of HNO₃ and PAN were 2–5 times higher during TRACE-P compared to PEM-West B. An exception was for PAN in the coastal group. Although most of the differences in mean values are statistically significant (t-test, P = 0.05), the maximum values are relatively similar. The comparisons for NOₓ,sum are not significantly different except for the central group at 0–2 km altitude where they were much greater than the PEM-West B results (P = 0.05). Comparisons for the middle and upper troposphere revealed a remarkable similarity over the 7 year period between the missions. The only significant difference was for HNO₃ in the coastal group where the mean values for TRACE-P were a factor of 2 higher than in PEM-West B (P = 0.05).

[41] Comparisons of the continental south group with the TRACE-P SE Asia group showed that differences existed but they did not vary in a systematic manner. In the boundary layer median mixing ratios of HNO₃ and NOₓ,sum were eight-fold and six-fold lower during TRACE-P, respectively. This may be due to the fact that during PEM-West B relatively few data were obtained in the continental south region [Talbot et al., 1997b]. We clearly did not get a good statistical sampling of air parcels in 1994, so the results are

Table 1. TRACE-P Nitrogen Budget Summary Statistics

<table>
<thead>
<tr>
<th>Source Region</th>
<th>NOₓ</th>
<th>PAN</th>
<th>HNO₃</th>
<th>ΣAlkyl-ONO₂</th>
<th>NOₓ,sum*</th>
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<tr>
<td>0–2 km mean</td>
<td>351</td>
<td>505</td>
<td>447</td>
<td>56</td>
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<tr>
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<td>424</td>
<td>54</td>
<td>597</td>
</tr>
<tr>
<td>min.</td>
<td>0.79</td>
<td>1.3</td>
<td>62</td>
<td>12</td>
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<tr>
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<td>3507</td>
<td>1422</td>
<td>1198</td>
<td>89</td>
<td>5115</td>
</tr>
<tr>
<td>2–7 km mean</td>
<td>68</td>
<td>292</td>
<td>197</td>
<td>25</td>
<td>388</td>
</tr>
<tr>
<td>stdev</td>
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<td>244</td>
<td>243</td>
<td>15</td>
<td>413</td>
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<tr>
<td>median</td>
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<td>189</td>
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<td>21</td>
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<tr>
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<td>322</td>
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<td>222</td>
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<tr>
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<tr>
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<td>157</td>
<td>191</td>
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<tr>
<td>median</td>
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<td>86</td>
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<td>295</td>
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<td>3.6</td>
<td>60</td>
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<tr>
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<td>557</td>
<td>550</td>
<td>1030</td>
<td>50</td>
<td>1123</td>
</tr>
</tbody>
</table>

*Sum of the individual species (see text).
likely to be representative of that region. It may be fortuitous for the previous reason that the middle and upper tropospheric data are similar for both missions. Nevertheless, it appears that in general the NOy,sum loading above the boundary layer has been affected minimally by increasing emissions on the Asian continent over the last 7 years. The data show that the biggest changes and influences were in the boundary layer. Liu et al. [2003] hypothesize that the higher mixing ratios of water-soluble aerosol in TRACE-P relative to PEM-West B [Dibb et al., 2003] together with higher NOy,sum in the boundary layer, may reflect stronger boundary layer outflow during TRACE-P because of more frequent frontal passages. Such interannual variability in the western Pacific region requires careful documentation to distinguish it from response to changes in emission sources.

7. Summary

[42] We presented the general distributions of NOy,sum and individual NOy,sum species over the western Pacific during the TRACE-P study period of February–March 2001. In general, NOy,sum was dominated by HNO3 and PAN, while NOx mixing ratios were commonly <100 pptv except in plumes where they exceeded 1000 pptv on a few occasions. There was a significant combustion influence over the western Pacific, as evidenced by the distributions of CO and C2H2. Correlations of NOy,sum with an urban tracer such as C2Cl4 and CH3Cl for biomass burning were not well defined in most cases.

[43] The distribution of the ratio C2H2/CO was striking, showing values in the middle to upper troposphere that mimicked the boundary layer and ones that support a scenario of rapid advective transport of continent emissions across the Pacific to at least 150°E. These findings suggest that extensive and rapid frontal uplifting and vertical transport is operating continuously over the Asian continent combined with extensive westerly transport of pollutants at all altitudes. This result helps explain the blurred correlations observed between NOy,sum and CO or O3. Such continuous intermingling of air parcels of various ages and processing would lead directly to the very complex distributions and relationships that we observed for NOy,sum, CO, and O3. In addition, removal of NOy during transport would further distort source signatures and species intercorrelations.

[44] On one occasion the Shanghai mega-city plume was characterized during a flight over the Yellow Sea. The plume was intercepted at 0.34 km altitude and exhibited peak mixing ratios of more than 10,000 pptv C2H2, 3,000 pptv C2H4, 12,000 NOy,sum, 8,000 pptv HNO3, and 30 pptv CH3Br. C1–C5 alkyl nitrates totaled 100–200 pptv, being dominated by 2-BuONO2 and i-PrONO2. Our results suggest that the Shanghai plume represents a large source of reactive nitrogen to the marine boundary layer over the Yellow Sea.

[45] Comparison of results between the earlier PEM-West B mission and the recent TRACE-P campaign show remarkable similarities in tropospheric chemistry. This was most evident in the middle and upper troposphere where NOy,sum loadings appear to have been affected minimally by increasing emissions on the Asian continent over the last 7 years. However, significant increases in the mixing ratios of NOy,sum species were readily apparent in the boundary layer.

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References


