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Contribution of particulate nitrate to airborne measurements of total reactive nitrogen


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Simultaneous measurements of speciated, total reactive nitrogen (NOy) and particulate NO$_3^-$ (particle diameter <1.3 µm) were made on board the NASA P-3B aircraft over the western Pacific in February–April 2001 during the Transport and Chemical Evolution over the Pacific (TRACE-P) experiment. Gas-phase and particulate NO$_3^-$ was measured using a gold tube catalytic converter. For the interpretation of particulate NO$_3^-$, conversion efficiencies of particulate NH$_4$NO$_3$, KNO$_3$, NaNO$_3$, and Ca(NO$_3$)$_2$ were measured in the laboratory. Only NH$_4$NO$_3$ showed quantitative conversion, and its conversion efficiency was as high as that for HNO$_3$. NO$_3^-$ measured on board the aircraft was found to be systematically higher by 10–30% than the sum of the individual NO$_y$ gas components (\(\sum (NO_y)_i\)) at 0–4 km. Particulate NO$_3^-$ concentrations measured by a particle-into-liquid sampler (PILS) were nearly equal to NO$_3^-$ = \(\sum (NO_y)_i\) under low-dust-loading conditions. The PILS data showed that the majority of the particulate NO$_3^-$ was in the form of NH$_4$NO$_3$ under these conditions, suggesting that NH$_4$NO$_3$ particles were quantitatively converted to detectable NO by the NO$_3^-$ converter, consistent with the laboratory experiments. The contribution of particulate NO$_3^-$ to NO$_y$ was most important at 0–2 km, where NO$_3^-$ constituted 10–30% of NO$_y$ during TRACE-P. On average, the amounts of particulate NO$_3^-$ and gas-phase HNO$_3$ were comparable in this region.


1. Introduction

[2] Reactive nitrogen species play a central role in determining the levels of ozone and hydroxyl radicals in the troposphere [e.g., Crutzen, 1979; Liu et al., 1987; Chameides et al., 1992]. Total reactive nitrogen (NO$_y$) in the troposphere is generally composed of NO, NO$_2$, peroxycetyl nitrates (PANs), nitric acid (HNO$_3$), HONO, HO$_2$NO$_2$, NO$_3$, N$_2$O$_5$, organic nitrate, and particulate nitrate (NO$_x$). One of the major uncertainties in evaluating the budget of reactive nitrogen is due to a lack of fast response and accurate measurements of both gas-phase HNO$_3$ and particulate NO$_3^-$ by adsorption of HNO$_3$ on basic soil [Wolff, 1984] or sea-salt particles [Savoie and Prospero, 1982]. In the upper troposphere, HNO$_3$ uptake on cirrus ice cloud particles followed by gravitational settling may reduce the abundance of HNO$_3$ [Lawrence and Crutzen, 1998]. At high latitudes in the lower stratosphere, HNO$_3$ is irreversibly removed by sedimentation of large HNO$_3$-containing polar stratospheric cloud (PSC) particles (dentrification) formed at very low temperatures [Solomon et al., 1986]. Therefore it is important to assess the contribution of particulate NO$_3^-$ to NO$_y$ in order to understand distributions of reactive nitrogen.
2. Experiment

[8] During the TRACE-P experiment (February–April 2001), NO_3 and individual NO_y compounds were measured on board the P-3B aircraft over the Pacific at 0–7 km [Kondo et al., 2004]. We use the data obtained in the region of 10°–45°N, 110°–140°E, where most of the P-3B sampling was made (Figure 1). The data used in this study were obtained during flights 10–20 (9 March to 4 April 2001). Since details of each measurement technique are summarized elsewhere [see Miyazaki et al., 2003, Table 1], we describe here the NO_y and aerosol measurements.

2.1. Gas-Phase and Particulate NO_y

[9] NO_y was measured using an NO-O_3 chemiluminescence technique combined with a gold tube heated to 300°C with addition of CO, catalytically converting NO_y compounds into NO [Kondo et al., 1997a]. The NO_y converter unit was mounted on the side of the window plate inside the aircraft cabin to minimize the length of the inlet tubes. During in-flight calibrations, known concentrations of NO and NO_2 in N_2 were added into the sample air to calibrate the absolute sensitivity and conversion efficiency. The estimated uncertainty of the NO mixing ratios of the calibration gas was 2%, and the uncertainty of the flow rates was estimated to be ±2%. The error from the artifact for NO_y is estimated to be ±2% for NO_y mixing ratios of 500 parts per trillion by volume (pptv). The HNO_3 conversion efficiency was higher than 95%, which was determined by both laboratory tests and in-flight calibration during the previous aircraft missions [Kondo et al., 1997a; Koike et al., 2000]. It was measured to be stable over time within ±5% [Kondo et al., 1997a]. The conversion efficiencies of HCN and CH_3CN were 2% and 1–2%, respectively [Koike et al., 2000]. From the observed values of HCN (<220 pptv) and CH_3CN (<150 pptv) at 0–6 km during TRACE-P [Singh et al., 2003], the uncertainty associated with the conversion of these species is estimated to be less than 2%. Overall, the accuracy of the NO_y measurement was estimated to be ±13%.

[10] In this study, \( \Delta \text{NO}_y \) is defined as the difference between the measured NO_y and \( \sum \text{(NO}_y)_k \),

\[
\Delta \text{NO}_y = \text{NO}_y - \sum (\text{NO}_y)_k
\]
Table 1. Approximate Stokes Numbers Calculated for the P-3B NO$_3$ Inlet at a Pressure Altitude of 950 hPa

<table>
<thead>
<tr>
<th>$D_p$ (μm)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.01</td>
</tr>
<tr>
<td>0.5</td>
<td>0.03</td>
</tr>
<tr>
<td>1.0</td>
<td>0.09</td>
</tr>
<tr>
<td>1.5</td>
<td>0.19</td>
</tr>
</tbody>
</table>

where $\sum$(NO$_y$)$_i$ is defined as the sum of individually measured gas-phase NO$_y$ compounds.

$$\sum$(NO$_y$)$_i$ = NO + NO$_2$ + HNO$_3$ + PAN + PPN + C$_1$-C$_5$ alkyl nitrates

(2)

The uncertainties of $\sum$(NO$_y$)$_i$ and $\Delta$NO$_y$ were estimated to be ±14% and ±32%, respectively, by combining possible errors of the individual instruments.

[11] During TRACE-P, two NO$_y$ inlets were located on the right window plate of the cabin, one facing rearward and the other facing forward. The inlet of the NO$_y$ instrument was made of 3/8-inch outer diameter Teflon tubing heated to 50°C for rearward and 100°C for forward upstream of the NO$_y$ converter unit. The tubing from the inlet to the gold tube converter is not straight but is curved (angle 90 deg, radius 5 cm). In order to estimate the collection efficiency of particles for the rearward NO$_y$ inlet, we made a simple calculation based on the Stokes number, which is the ratio of a particle’s “persistence” to the size of the obstacle, often used to characterize inertial impaction. The rearward facing inlet allows the collection of particles with Stokes numbers less than about 0.2, which track streamlines of sample air because of their negligibly small inertia. At Stokes numbers greater than 0.2, particles do not follow the streamlines that curve into the rearward facing inlet. Approximate Stokes numbers were estimated for the P-3B NO$_y$ sampling inlet by a simple aerodynamical calculation (Table 1). On the basis of these calculations, we estimated that the NO$_y$ inlet discriminates against particles with $D_p$ larger than 1.5 and 1.1 μm at altitudes of 0.5 and 6 km, respectively. The collection efficiency of particles with $D_p > 1.5$ μm is estimated to be almost zero. It should be noted that effects of turbulence were not taken into account in the above estimate. Turbulence introduces uncertainties in the estimate of the cutoff size, although they are not quantified in this work.

[12] During TRACE-P, NO$_y$ was also sampled through a forward facing inlet using an independent detection channel. The forward facing inlet was subisokinetic and collected particles including those with $D_p > 1.5$ μm that were unlikely sampled by the rearward NO$_y$ inlet. The NO$_y$ measured through the forward facing inlet (NO$_y$ (f)) represents the sum of gas-phase NO$_y$ and amplified particulate NO$_y$. When particulate NO$_y$ is absent, NO$_y$ signals from NO$_y$ (f) and NO$_y$ are identical. When encountered, particulate NO$_y$ including larger particles ($D_p > 1.5$ μm), NO$_y$ (L), can be defined as follows:

$$\text{NO}_y(L) = \left(\text{NO}_y(f) - \sum \text{NO}_y_i\right)/\text{EF}$$

(3)

EF represents the enhancement factor for the forward facing inlet, which depends on the size of the particles due to subisokinetic sampling [Fahey et al., 1989].

2.2. Laboratory Experiments

[11] In order to estimate the conversion efficiency of particulate NO$_y$ in the gold tube converter, we conducted laboratory experiments using an aerosol generation system (Figure 2). Because particulate NO$_y$ is observed typically in the form of NH$_4$NO$_3$, KNO$_3$, NaNO$_3$, and Ca(NO$_3$)$_2$ in the troposphere, we measured the conversion efficiencies of the particles in these forms in the laboratory. Dry particles made of these chemical compositions were generated using an atomizer (TSI model 3076) and diffusion dryer. A differential mobility analyzer (DMA) (TSI model 3080) was used to produce monodisperse particles with a size range between 300 and 400 nm. The number concentrations were monitored by a condensation particle counter (CPC) (TSI model 3022A). Mass concentrations of nitrate particles were calculated using the density (ρ), diameter, number concentrations, and shape factor [Jayne et al., 2000; DeCarlo et al., 2004]. The results are summarized in Table 2. The conversion efficiency for NH$_4$NO$_3$ was 91 ± 9% at NO$_y$ mixing ratios of 2000–5000 pptv. The derived conversion efficiency for particulate NH$_4$NO$_3$ was as high as that for HNO$_3$. The difference between the two conversion efficiencies is to within the measurement uncertainties. Uncertainties of the
NH$_4$NO$_3$ conversion efficiency due to evaporation of NH$_4$NO$_3$ particles in the inlet system are small. The residence time of particulate NO$_3^-$ between the atomizer and NO$_3^-$ converter is about 1 s, which is much shorter than the typical timescale of a few minutes required for evaporation of particulate NO$_3^-$ [e.g., Neuman et al., 2003]. In fact, our recent ground-based measurements showed that the ambient HNO$_3$ concentrations were smaller than 8% of the particulate NO$_3^-$ levels (~1 ppbv) during nighttime, when the ambient temperature was about 15°C (K. Kita et al., A chemical ionization mass spectrometer for ground-based measurement of nitric acid, submitted to Journal of Atmospheric and Oceanic Technology, 2005), which is similar to the room air temperature during the laboratory experiments. By contrast, the conversion efficiencies for KNO$_3$, NaNO$_3$, and Ca(NO$_3$)$_2$ were as low as 1.2 ± 0.5%, 2.0 ± 0.3%, and 3.4 ± 0.8%, respectively.

These results are consistent with the boiling or melting points of the particulate NO$_3^-$ species (Table 2). NH$_4$NO$_3$ (boiling point 210°C) should be vaporized at the temperature of the NO$_3^-$ converter (300°C). On the other hand, the melting or boiling points of KNO$_3$, NaNO$_3$, and (Ca(NO$_3$)$_2$) are higher than the temperature of the NO$_3^-$ converter, leading to significantly low conversion efficiencies.

### Table 2. Conversion Efficiencies of Particulate NO$_3^-$ Species Measured in the Laboratory

<table>
<thead>
<tr>
<th>Species</th>
<th>NH$_4$NO$_3$</th>
<th>KNO$_3$</th>
<th>NaNO$_3$</th>
<th>Ca(NO$_3$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$ Conversion Efficiency, %</td>
<td>1.2 ± 0.5</td>
<td>2.0 ± 0.3</td>
<td>3.4 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>Assumed Density, g/cm$^3$</td>
<td>1.72</td>
<td>2.11</td>
<td>2.66</td>
<td>2.36</td>
</tr>
<tr>
<td>Boiling point/Melting point, °C</td>
<td>210 (b) 334 (m)</td>
<td>380 (b) 561 (m)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The assumed density and boiling/melting points for different forms of particles are also shown. Here, “(b)” and “(m)” denote boiling point and melting point, respectively.*

Although the collection efficiency within this range is less than 50%. On the other hand, it is unlikely that particles with D$_p = 1.5 – 3$ μm were sampled by the NO$_3^-$ instrument. We discuss the difference in the threshold of particle size in section 4.

Ambient aerosol size distributions were measured by a laser optical counter (OPC, PMS LAS-X, Boulder, CO) [Clarke et al., 2004]. The OPC provided size distributions of “dry” (heated to 40°C) particles between 0.1 and 20.0 μm. The terms “fine particle” and “coarse particle” in this paper are defined as particles within size ranges of D$_p < 1$ μm and D$_p > 1$ μm, respectively. Ambient wet particle size distributions are estimated by assuming that particles with D$_p < 0.6$ μm absorb water as a typical marine boundary layer aerosol [Swietlicki et al., 2000], and particles with D$_p > 0.6$ μm are treated as dust and do not absorb water [Weber et al., 2003]. All of the P-3B data were merged into the time interval of aerosol sampling (~4 min).

### 3. Particulate NO$_3^-$ Detected by the NO$_3^-$ Instrument

Figure 4 shows time series plots of NO$_3^-$, ΔNO$_3$, NO$_3^-$, and K$^+$ obtained on 9 March (flight 10) and 18 March (flight 14) 2001. The flight tracks are also shown in Figure 1. A large enhancement of NO$_3^-$ up to 2500 pptv was observed at an altitude of 3 km during flight 10. The ΔNO$_3$ and NO$_3^-$ concentrations reached their maximum values in the same air masses. An interesting feature is that K$^+$ also showed its maximum (~900 pptv) in these plumes, which were identified as originating from biomass burning in southeast Asia by using back trajectories and satellite fire maps [Ma et al., 2003; Kondo et al., 2004]. Ma et al. [2003] used observed K$^+/$/sulfate ratios to infer that 30% of total aerosol mass in Asian pollution plumes sampled

Figure 3. Upper size limits of particle measurements for the NO$_3^-$ and PILS instruments. The NO$_3^-$ transmission curve was derived on the basis of the calculated Stokes number assuming no turbulence. Turbulence introduces uncertainties in the estimate of the cutoff size, although they are not quantified in this work. The transmission curve for the PILS was determined experimentally by generating monodisperse calibration particles using a nebulizer/DMA and vibrating-orifice aerosol generator in the laboratory [Ma et al., 2004].
during TRACE-P originated from biomass or biofuel burning. During flight 14, very distinct plumes were observed and all species reached their highest concentrations at 0–1 km over the Yellow Sea (34°–36°N, see Figure 1). Peak concentrations for NO$_y$, ΔNO$_y$, and NO$_3^-$ were 13,000, 6500, and 16,000 pptv, respectively. For both cases, fine-particle volumes were also enhanced (25–70 μm/cm$^3$) in these plumes.

[19] In order to evaluate the contribution of NO$_3^-$ to ΔNO$_y$, their correlations at 0–4 km are shown in Figure 5. A majority of the NO$_3^-$ and ΔNO$_y$ (<2500 pptv) data points in Figure 5a lie along the 1:1 line, within the error bars, indicating that NO$_3^-$ measured by the PILS-IC can account for the ΔNO$_y$. In Figure 5b, data points with ΔNO$_y$ > 2500 pptv are also shown according to Ca$^{2+}$ concentration. Ca$^{2+}$ is generally considered to be derived from soil and crustal material and thus can be used as a tracer for dust. For the data with ΔNO$_y$ < 2500 pptv, which accounted for 97% of all the data points, dust loadings were low ([Ca$^{2+}$] < 200 pptv). On the other hand, NO$_3^-$ with ΔNO$_y$ > 2500 pptv far exceeded ΔNO$_y$ where dust loadings were high ([Ca$^{2+}$] > 400 pptv). These data with ΔNO$_y$ > 2500 pptv were all obtained over the Yellow Sea during flight 14 (Figure 4). A possible explanation of the excess NO$_3^-$ relative to ΔNO$_y$ is discussed in section 4.

[20] Figure 6 shows latitudinal distributions of (coarse-particle volume)/(fine-particle volume) ratios observed at 0–4 km during TRACE-P. Although variability was large,
the median ratio at 10°–30°N was lower than 1, suggesting that a majority of particles was in the fine mode (Dp < 1 μm), likely in biomass burning plumes [Kondo et al., 2004]. A dominance of fine particles in biomass burning plumes was previously observed, for instance, in Brazil [Reid and Hobbs, 1998]. By contrast, at 30°–45°N, coarse-particle volume was larger than fine-particle volume. Air masses with a large abundance of coarse particles observed in this region were heavily influenced by dust [Jordan et al., 2003a]. In fact, Jordan et al. [2003a] found that dust particles accounted for 77% of the total aerosol mass in the Chinese low-altitude outflow, typically observed at 30°–45°N during TRACE-P. Figure 7 presents a plot of the NO3/ΔNOy ratio versus the (coarse-particle volume)/ (fine-particle volume) ratio. At the NO3/ΔNOy ratio close to 1, fine-particle volume was generally larger than coarse-particle volume and dust loadings were low with [Ca2+] < 200 pptv. These results suggest that a majority of ΔNOy can be attributed to fine particles.

[21] Contributions of NOy species not measured in this study to ΔNOy are not significant in this study. Model calculations [Brasseur et al., 1999; Talbot et al., 1999] indicate that HO2NO2 is the most abundant unmeasured NOy species. However, it is thermally stable only at the cold temperatures of the upper troposphere, and the HO2NO2/NOy ratio is estimated to be lower than 0.01 below 4 km [Brasseur et al., 1999]. On the other hand, ΔNOy is significantly large in the lower troposphere (0–4 km) in this case. Consequently, the contribution of HO2NO2 to ΔNOy can be negligible in this study.

4. Chemical Form of Particulate NO3–

[22] In this section, we infer the chemical form of particulate NO3– detected by the NOy instrument. Figure 8 shows average ionic composition at 0–4 km with ΔNOy both less than and greater than 2500 pptv, where dust loadings were low with [Ca2+] < 200 pptv and high with [Ca2+] > 400 pptv, respectively. NH4 was the main neutralizing agent of the acidic aerosol species, which accounted for 82 and 73% of the total cations with ΔNOy < 2500 pptv and ΔNOy > 2500 pptv, respectively. NH4NO3 forms by condensation of gas-phase HNO3 with available NH3 once all SO42− is neutrized [Seinfeld and Pandis, 1998]. In order to examine this, the relationship between NO3− and NH4+ minus SO42− in equivalence is shown in Figure 9. Overall, a...
positive correlation ($r^2 = 0.77$) with a slope of 1.10 shows that ion balance between NH$_4^+$ minus SO$_4^{2-}$ and NO$_3^-$ in equivalence is nearly complete, within 10% on average, suggesting available NH$_3$ to form NH$_4$NO$_3$. For $\Delta$NO$_3$ < 2500 pptv, the slope was 0.97 with $r^2 = 0.66$ and 1.34 with $r^2 = 0.74$ for $\Delta$NO$_3$ > 2500 pptv. The data for which NO$_3^-$ + SO$_4^{2-}$ and NH$_4^+$ in equivalence balanced within ±30% are plotted in Figure 5a (solid circles). The slope for the data points was 1.16 ($r^2 = 0.87$), lying close to the 1:1 line within the error bars, indicating that NH$_4$NO$_3$ was detected by the NO$_y$ instrument.

In order to estimate the relative contribution of cations other than NH$_4^+$ associated with NO$_3^-$, we consider the relative amounts of Ca$^{2+}$, K$^+$, and Na$^+$ by using PILS chemical composition data. If we assume that all of the Ca$^{2+}$ and K$^+$ take up SO$_4^{2-}$, measured NO$_3^-$ is considered to be in the form of NH$_4$NO$_3$, that is, NO$_3^-$ as NH$_4$NO$_3$ = NH$_4^+$ − SO$_4^{2-}$ in equivalence (upper limit). By contrast, when all Ca$^{2+}$ and K$^+$ are assumed to take up the measured NO$_3^-$, the amount of NO$_3^-$ as NH$_4$NO$_3$ can be derived from NO$_3^-$ − (Ca$^{2+}$ + K$^+$) in equivalence (lower limit). Considering these two limiting cases for NH$_4$NO$_3$, the amount of Ca$^{2+}$ + K$^+$ in equivalence is 44% of NO$_3^-$ for the data points with $\Delta$NO$_3$ < 2500 pptv. Thus, when Ca$^{2+}$ and K$^+$ are taken into account, the lower limit of NH$_4$NO$_3$ was estimated to be 56% of the total NO$_3^-$. For $\Delta$NO$_3$ < 2500 pptv, the correlation between Cl$^-$ and Na$^+$ showed a slope of 1.35 with $r^2 = 0.78$ (not shown), close to the seawater ratio of 1.16. Moreover, Mg$^{2+}$ showed a correlation with Na$^+$ ($r^2 = 0.64$) with a slope of 0.13, very close to their seawater ratio of 0.11, suggesting that sea-salt particles partly contributed to these species. A Cl$^-$/Na$^+$ ratio lower than the seawater ratio indicates acidification of particles by HNO$_3$, resulting in a Cl$^-$ deficit to form NaNO$_3$. By using these data points, NaNO$_3$ was estimated to contribute <12% of NO$_3^-$ for $\Delta$NO$_3$ < 2500 pptv. Overall, more than 44% of particulate NO$_3^-$ ($\Delta$NO$_3$ < 2500 pptv) was estimated to be in the form of NH$_4$NO$_3$.

On the other hand, for $\Delta$NO$_3$ > 2500 pptv, the ion balance between NO$_3^-$ and NH$_4^+$ minus SO$_4^{2-}$ (open circles in Figure 9) and the relative abundance of Ca$^{2+}$ + K$^+$ compared to NO$_3^-$ (Figure 8) suggest that more than 70% of the observed NO$_3^-$ was in the form of NH$_4$NO$_3$. In this case, the contribution of NaNO$_3$ was negligible (<1%).

For the data points with $\Delta$NO$_3$ > 2500 pptv (<3% of the total), however, NO$_3^-$ (7500–12,000 pptv) far exceeded the 1:1 line relative to NO$_y$ (Figure 5b). As stated in section 2, there are two possible explanations for the excess NO$_3^-$, defined as $\delta$NO$_3$:

$$\delta$$NO$_3^- = NO_3^- - \Delta$NO$_3$  

Figure 7. Relationship between NO$_3^-$/$\Delta$NO$_3$ and coarse (D$_p$ = 1–20 μm)/fine (D$_p$ = 0.1–1 μm) particle volume observed at 0–4 km. The data points are color-coded according to the concentration of nss-Ca$^{2+}$. Dashed lines indicate that the NO$_3^-$/$\Delta$NO$_3$ ratio is 1. The data points with $\Delta$NO$_3$ < 100 pptv and fine-particle volume <0.2 μm$^3$/cm$^3$ are not used.

Figure 8. Ionic composition in pptv-equivalent with $\Delta$NO$_3$ (a) <2500 pptv and (b) >2500 pptv at 0–4 km. Note that the full scales of the y axes are different in Figures 8a and 8b.

Figure 9. Relationship between NO$_3^-$ and NH$_4^+$ minus SO$_4^{2-}$ in equivalence. The solid line represents the least squares best fit, with a slope of 1.10. The dashed line indicates the 1:1 line. Open circles correspond to the data with high concentrations of Ca$^{2+}$ (>400 pptv) obtained at 0–2 km over the Yellow Sea during flight 14.
On the other hand, the distributions of particles with Dp < 1 μm were by the PILS-IC, because of their sizes, with Dp = 1.5–3 μm, mainly as NH4NO3, which can be detected by the NOy instrument. Considering that the EF range is 2 ± 0.5 for particles with Dp = 0.5–3 μm, the estimated uncertainty of NOy(L) is given as ±40%–30%. For ΔNOy < 2500 pptv, NO3 showed agreement with NOy(L), including particles that were not efficiently detected by the rearward NOy system, indicating that almost all of eNO3 can be explained by NO3(L). For ΔNOy > 2500 pptv, although it is difficult to evaluate the contribution of NO3 in mass, which agrees well with the estimate from the particle volume by OPC (Figure 10), if the particle density is assumed to be constant.

One of the possible reasons for the NH4NO3 particle size to reside in larger sizes (Dp = 1.5–3 μm) is that the relative humidity of the ambient air was relatively high, causing particles to absorb water before sampling. However, there is no clear relationship between the NOy(NOy) ratios and ambient relative humidity (not shown). Moreover, whether these particles were internally or externally mixed in the dust particles cannot be identified from these data alone.

The sum of Ca2+ and K+ in equivalence is plotted against eNOy for ΔNOy > 2500 pptv in Figure 12. They are tightly correlated (r2 = 0.93), indicating that eNO3 is partly associated with dust particles. In the current analysis, we further examined particulate NO3 containing the 1.5–3-μm range by using the NOy(f) data. Figure 11 shows the relationship between NOy and NO3(L) (equation 3). Using the empirical expression given by Durham and Lundgren [1980], EF was estimated to be 2 for Dp = 1.5 μm, by assuming a particle density of 1.8 g cm−3 estimated from the OPC data. As stated in section 2, NO3(L) represents particulate NO3 including larger particles (Dp > 1.5 μm), mainly as NH4NO3, which can be detected by the NOy instrument. Considering that the EF range is 2 ± 0.5 for particles with Dp = 0.5–3 μm, the estimated uncertainty of NO3(L) is given as ±40%–30%. For ΔNOy < 2500 pptv, NOy showed agreement with NO3(L), including particles that were not efficiently detected by the rearward NOy system, indicating that almost all of eNO3 can be explained by NO3(L). For ΔNOy > 2500 pptv, although it is difficult to evaluate the contribution of NO3(L) to eNO3 because of the uncertainty of the EF, we estimate that approximately 20 ± 10% of eNO3 can be explained by NO3(L). The amount of NO3(L) in this case corresponds to 10% of the PILS NO3 in mass, which agrees well with the estimate from the particle volume by OPC (Figure 10), if the particle density is assumed to be constant.

Regarding particle size, the data points where NO3/ΔNOy ratios exceed 1 (Figure 7), where coarse-particle volume tends to be larger relative to fine-particle volume under the high concentrations of Ca2+ (>400 pptv), are indicative of dust loading. Jordan et al. [2003b] used the DC-8 aircraft data for TRACE-P and showed that the dust was generally mixed with pollution and that a large fraction of nitrate was taken up by dust particles in the coarse mode, presumably through displacement of carbonate. Figure 10 shows OPC size distributions at ambient relative humidity with ΔNOy > 2500 pptv and typical distributions representative of particles for ΔNOy < 2500 pptv. The size distributions of particles with ΔNOy < 2500 pptv show that particles reside mostly in the fine mode (Dp < 1 μm), while the abundance in the coarse mode (Dp > 1 μm) is minimal. On the other hand, the distributions of particles with ΔNOy > 2500 pptv were characterized by the bimodal peaks within fine and coarse modes. On the basis of the size distributions and the PILS correction efficiency, we can roughly estimate that particles with Dp = 1.5–3 μm could contribute to about 10% of the total volume of particles collected by the PILS for ΔNOy > 2500 pptv.

We further examined particulate NO3 containing the 1.5–3-μm range by using the NOy(f) data. Figure 11 shows the relationship between NOy and NO3(L) (equation 3). Using the empirical expression given by Durham and Lundgren [1980], EF was estimated to be 2 for Dp = 1.5 μm, by assuming a particle density of 1.8 g cm−3 estimated from the OPC data. As stated in section 2, NO3(L) represents particulate NO3 including larger particles (Dp > 1.5 μm), mainly as NH4NO3, which can be detected by the NOy instrument. Considering that the EF range is 2 ± 0.5 for particles with Dp = 0.5–3 μm, the estimated uncertainty of NO3(L) is given as ±40%–30%. For ΔNOy < 2500 pptv, NO3 showed agreement with NO3(L), including particles that were not efficiently detected by the rearward NOy system, indicating that almost all of eNO3 can be explained by NO3(L). For ΔNOy > 2500 pptv, although it is difficult to evaluate the contribution of NO3(L) to eNO3 because of the uncertainty of the EF, we estimate that approximately 20 ± 10% of eNO3 can be explained by NO3(L). The amount of NO3(L) in this case corresponds to 10% of the PILS NO3 in mass, which agrees well with the estimate from the particle volume by OPC (Figure 10), if the particle density is assumed to be constant.

[28] The sum of Ca2+ and K+ in equivalence is plotted against eNOy for ΔNOy > 2500 pptv in Figure 12. They are tightly correlated (r2 = 0.93), indicating that eNO3 is partly associated with dust particles. In the current analysis,
5. Contribution of Particulate NO$_3^-$ to the NO$_y$ Budget Over the Western Pacific

[31] Finally, we investigated the partitioning between particulate NO$_3^-$ and gas-phase NO$_y$. Figure 13 shows vertical profiles of NO$_3$, $\sum$(NO$_3$)$_i$, and $\sum$(NO$_3$)$_i$ + NO$_3$ to NO$_y$ ratios at 10°–30°N and 30°–45°N. The partitioning of individual NO$_3$ compounds is summarized in Table 3. The NO$_y$ mixing ratios were systematically higher by 10–30% than the sum of individual gas-phase NO$_y$ compounds at 0–4 km. An important feature is that particulate NO$_3^-$ contributed 10–30% of the measured NO$_3$ at 0–4 km. On average, the particulate NO$_3^-$ fraction of NO$_3$ was largest (26–37%) at 0–2 km, which was comparable to that of gas-phase HNO$_3$ (24–32%) at the same altitude. The result indicates that the active conversion of HNO$_3$ to NO$_3^-$ is important, and particulate NO$_3^-$ may thus contribute a significant fraction (~50%) to total nitrate, especially at 0–2 km during the TRACE-P period. Although the data for ΔNO$_3$ > 2500 pptv observed at 0–2 km are included in Figure 13, the fraction of these data was only <3% of the total. Therefore a majority of NO$_3^-$ shown in the figure are particles detected by the NO$_3$ instrument.

[32] At altitudes of 2–6 km, very low values of NO$_3$ / NO$_y$ (0.02–0.10) indicate that a large fraction of the NO$_3^-$ was scavenged by cloud droplets during the vertical transport from lower altitudes (0–2 km) [Koike et al., 2003; Kondo et al., 2004]. Note that the NO$_3^-$ concentrations discussed here are fine-mode fractions of the total particulate NO$_3^-$, which were obtained by the PILS having a 50% size cut of 1.3 μm. When we use the NO$_3$ data obtained by the DC-8 filter samples, which measured particles with $D_p$ up to 6 μm [Dibb et al., 2002], particulate NO$_3^-$ constituted 54% of the total nitrate on average, reaching a maximum of 72% at 0–2 km where observed particles were heavily influenced by dust during TRACE-P [Jordan et al., 2003b].

[33] For gas-phase NO$_y$, 80–90% of the measured NO$_y$ at 0–6 km is accounted for by NO$_x$ (= NO + NO$_2$), PAN, and HNO$_3$. These values are similar to those in air masses influenced by continental surface emissions previously observed at 0–5 km over the western Pacific during the Pacific Exploratory Mission (PEM) West B in 1994 [Kondo et al., 1997b]. It is noted that gas-phase HNO$_3$ was measured using a chemical ionization mass spectrometer (CIMS) onboard the P-3B during TRACE-P. During PEM-West B and TRACE-P, on the other hand, HNO$_3$ was measured by the University of New Hampshire’s (UNH) mist chamber/ion chromatography (MC-IC) instrument onboard the DC-8 research aircraft. The UNH/MC-IC could sample nitrate-containing particles, as indicated by intercomparison between the two instruments during TRACE-P [Zondlo et al., 2003]. Accordingly, the sampling by the UNH/MC-IC would result in higher measurements of gas-phase HNO$_3$ relative to the true amount. Thus much more accurate evaluations of the NO$_y$ budget are enabled in this study by highly selective and sensitive measurements of gas-phase HNO$_3$ by the CIMS instrument and of particulate NO$_3^-$ by the PILS-IC.

[34] PAN was systematically higher at 30°–45°N (175–930 pptv) than at 10°–30°N (140–190 pptv), consistent with its chemical stability at lower temperatures. Meanwhile, PPN (<6%) and alkyl nitrate (<5%) were minor compounds in the NO$_y$ budget during TRACE-P. The

![Figure 12](image-url)  
**Figure 12.** Scatterplot of the sum of Ca$^{2+}$ and K$^+$ in equivalence and δNO$_3^-$. The dashed line represents the least squares best fit.

![Figure 13](image-url)  
**Figure 13.** Vertical profiles of the mean values of NO$_3$ / NO$_y$ (solid squares), $\sum$(NO$_3$)$_i$ / NO$_y$ (open circles), and ($\sum$(NO$_3$)$_i$ + NO$_3$) / NO$_y$ (solid circles) at (left) 10°–30°N and (right) 30°–45°N.
Table 3. Reactive Nitrogen Budgets and Partitioning at 10°–30°N and 30°–45°N on Board P-3B During TRACE-Pa

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>Latitude</th>
<th>NO3, pptv</th>
<th>NOx, pptv</th>
<th>HNO3, pptv</th>
<th>PAN, pptv</th>
<th>PPN, pptv</th>
<th>Alkyl Nitrate, pptv</th>
<th>NOy, pptv</th>
<th>2(NOy)2 + NO3, pptv</th>
</tr>
</thead>
<tbody>
<tr>
<td>4–6</td>
<td>N</td>
<td>25 ± 42</td>
<td>34 ± 37</td>
<td>115 ± 81</td>
<td>174 ± 122</td>
<td>21 ± 19</td>
<td>15 ± 7</td>
<td>388 ± 238</td>
<td>359 ± 203</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.06 ± 0.12)</td>
<td>(0.08 ± 0.08)</td>
<td>(0.34 ± 0.20)</td>
<td>(0.47 ± 0.11)</td>
<td>(0.05 ± 0.02)</td>
<td>(0.05 ± 0.02)</td>
<td>(-)</td>
<td>(1.05 ± 0.23)</td>
</tr>
<tr>
<td>4–6</td>
<td>S</td>
<td>18 ± 18</td>
<td>30 ± 15</td>
<td>156 ± 70</td>
<td>143 ± 104</td>
<td>14 ± 10</td>
<td>9 ± 4</td>
<td>368 ± 174</td>
<td>437 ± 229</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.02 ± 0.04)</td>
<td>(0.08 ± 0.03)</td>
<td>(0.44 ± 0.16)</td>
<td>(0.35 ± 0.13)</td>
<td>(0.03 ± 0.01)</td>
<td>(0.03 ± 0.01)</td>
<td>(-)</td>
<td>(0.98 ± 0.16)</td>
</tr>
<tr>
<td>2–4</td>
<td>N</td>
<td>103 ± 408</td>
<td>70 ± 91</td>
<td>221 ± 139</td>
<td>438 ± 258</td>
<td>61 ± 38</td>
<td>30 ± 11</td>
<td>997 ± 628</td>
<td>883 ± 747</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.10 ± 0.21)</td>
<td>(0.07 ± 0.05)</td>
<td>(0.23 ± 0.14)</td>
<td>(0.46 ± 0.13)</td>
<td>(0.06 ± 0.02)</td>
<td>(0.04 ± 0.01)</td>
<td>(-)</td>
<td>(0.91 ± 0.29)</td>
</tr>
<tr>
<td>2–4</td>
<td>S</td>
<td>110 ± 237</td>
<td>63 ± 47</td>
<td>289 ± 308</td>
<td>160 ± 142</td>
<td>24 ± 13</td>
<td>15 ± 7</td>
<td>713 ± 655</td>
<td>889 ± 628</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.09 ± 0.16)</td>
<td>(0.10 ± 0.05)</td>
<td>(0.39 ± 0.17)</td>
<td>(0.21 ± 0.14)</td>
<td>(0.03 ± 0.02)</td>
<td>(0.04 ± 0.03)</td>
<td>(-)</td>
<td>(0.91 ± 0.15)</td>
</tr>
<tr>
<td>0–2</td>
<td>N</td>
<td>1761 ± 3109</td>
<td>1142 ± 4948</td>
<td>430 ± 316</td>
<td>928 ± 542</td>
<td>63 ± 24</td>
<td>3830 ± 5865</td>
<td>3943 ± 4749</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.37 ± 0.39)</td>
<td>(0.16 ± 0.15)</td>
<td>(0.24 ± 0.20)</td>
<td>(0.33 ± 0.10)</td>
<td>(0.05 ± 0.02)</td>
<td>(0.03 ± 0.01)</td>
<td>(-)</td>
<td>(1.18 ± 0.34)</td>
</tr>
<tr>
<td>0–2</td>
<td>S</td>
<td>230 ± 432</td>
<td>146 ± 200</td>
<td>209 ± 222</td>
<td>189 ± 184</td>
<td>47 ± 34</td>
<td>34 ± 18</td>
<td>776 ± 624</td>
<td>1011 ± 556</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.26 ± 0.19)</td>
<td>(0.16 ± 0.10)</td>
<td>(0.32 ± 0.17)</td>
<td>(0.20 ± 0.12)</td>
<td>(0.05 ± 0.03)</td>
<td>(0.05 ± 0.03)</td>
<td>(-)</td>
<td>(1.06 ± 0.19)</td>
</tr>
</tbody>
</table>

Values are mean ±1 σ. The numbers in parentheses are the ratios to the measured NOy. The numbers of data points are within a range of 40–120 in each column.

6. Conclusions

[35] The sum of individual NOx gas components (∑(NOx)i), NO3, and particulate NO3 (Dp < 1.3 μm) were measured simultaneously on board the P-3B aircraft at 10°–45°N over the western Pacific during TRACE-P. The inorganic chemical composition of aerosols, including NO3, was measured by the PILS-IC technique. In addition to the field measurements, conversion efficiencies of particulate NH4NO3, KNO3, NaNO3, and Ca(NO3)2 by the gold tube catalytic converter were measured in the laboratory. NH4NO3 was converted to NO with an efficiency of 91 ± 9%, which was as high as that for HNO3. Meanwhile, the conversion efficiencies of the aerosols in the other forms were as low as 1–3%. These results are consistent with the particulate NO3 measurements made on board the aircraft.

[36] Elevated NO3 was typically observed within biomass/biofuel burning plumes at 0–4 km. The measured NOx was systematically higher by 10–30% than the ∑(NOx)i at 0–4 km. Under low dust loadings with [Ca2+] < 200 pptv, the observed particles reside mostly in the fine mode, while the size distributions showed bimodal distribution within the fine and coarse modes under high dust loadings ([Ca2+] > 400 pptv). The ∆NO3 = NO3 - ∑(NOx)i values were approximately equal to NOx concentrations under low dust loadings, suggesting that the NOx instrument quantitatively converted NO3 to NO. More than 44% of the NO3 detected by the NO3 instrument was estimated to be in the form of NH4NO3, which was identified from the measured ion composition of the aerosols.

[37] NO3 far exceeded ∆NO3 only in polluted air masses with high dust loadings at 0–2 km over the Yellow Sea (30°–45°N). By using the forward facing NOx inlet, 20% of the excess NO3 (∆NO3 = NO3 - ∆NO3) was estimated to be mainly in the form of NH4NO3, suggesting that the size of this NO3 particle species detected by PILS-IC was in the range of Dp = 1.5–3 μm, which was larger than the size cutoff of the rearward facing NOx instrument. Some of the other ∆NO3 can be in the form of Ca(NO3)2 (<20%) and KNO3 (<25%) under high dust loading with a mixture of anthropogenic pollution, considering the measured aerosol ion composition. Particulate NO3 in these forms can partly explain the large ∆NO3, because their conversion in the NO3 instrument is negligible. The remaining ∆NO3 (~35%), which cannot be explained either by larger NH4NO3 (Dp = 1.5–3 μm) or Ca2+ + K+ particles, is within the combined uncertainties of the measurements and the enhancement factor for the forward facing NOx inlet.

[38] Generally, the contribution of particulate NO3 to NOx was most important at 0–2 km, where the NO3 concentrations constituted 10–30% of NOy. On average, the concentrations of NO3 and gas-phase HNO3 were comparable in this region. These results indicate the importance of properly including particulate NO3 in assessing the budget of reactive nitrogen using measurements of NOy by the catalytic conversion technique, especially when near a large source region of particulate NO3.

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