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### Authors

Miyazaki, Y  
Kondo, Y  
Takegawa, N  
[et al.](#)

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## Contribution of particulate nitrate to airborne measurements of total reactive nitrogen

Y. Miyazaki,<sup>1</sup> Y. Kondo,<sup>1</sup> N. Takegawa,<sup>1</sup> R. J. Weber,<sup>2</sup> M. Koike,<sup>3</sup> K. Kita,<sup>4</sup> M. Fukuda,<sup>1</sup> Y. Ma,<sup>5</sup> A. D. Clarke,<sup>6</sup> V. N. Kapustin,<sup>6</sup> F. Flocke,<sup>7</sup> A. J. Weinheimer,<sup>7</sup> M. Zondlo,<sup>8</sup> F. L. Eisele,<sup>2,7</sup> D. R. Blake,<sup>9</sup> and B. Liley<sup>10</sup>

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

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### 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 ( $\text{NO}_y$ ) in the troposphere is generally composed of  $\text{NO}$ ,  $\text{NO}_2$ , peroxyacetyl nitrates (PANs), nitric acid ( $\text{HNO}_3$ ), HONO,

$\text{HO}_2\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ , organic nitrate, and particulate nitrate ( $\text{NO}_3^-$ ). 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  $\text{HNO}_3$  and particulate  $\text{NO}_3^-$ . This point is also important in evaluating loss rates of  $\text{NO}_y$ , because the deposition velocity for particulate  $\text{NO}_3^-$  with particle diameters ( $D_p$ )  $< 1 \mu\text{m}$  is 10 times smaller than that of gas-phase  $\text{HNO}_3$  [Warneck, 1988].

[3] Reaction of  $\text{NH}_3$  with  $\text{HNO}_3$  produces ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) particles generally with  $D_p < 1 \mu\text{m}$ . The thermodynamic equilibrium between  $\text{HNO}_3$  and  $\text{NH}_4\text{NO}_3$  shows a strong dependence on ambient temperature and relative humidity characteristic of the troposphere. Particulate  $\text{NO}_3^-$  with  $D_p > 1 \mu\text{m}$  can be produced by adsorption of  $\text{HNO}_3$  on basic soil [Wolff, 1984] or sea-salt particles [Savoie and Prospero, 1982]. In the upper troposphere,  $\text{HNO}_3$  uptake on cirrus ice cloud particles followed by gravitational settling may reduce the abundance of  $\text{HNO}_3$  [Lawrence and Crutzen, 1998]. At high latitudes in the lower stratosphere,  $\text{HNO}_3$  is irreversibly removed by sedimentation of large  $\text{HNO}_3$ -containing polar stratospheric cloud (PSC) particles (denitrification) formed at very low temperatures [Solomon *et al.*, 1986]. Therefore it is important to assess the contribution of particulate  $\text{NO}_3^-$  to  $\text{NO}_y$  in order to understand distributions of reactive nitrogen.

<sup>1</sup>Research Center for Advanced Science and Technology, University of Tokyo, Tokyo, Japan.

<sup>2</sup>School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.

<sup>3</sup>Earth and Planetary Science, Graduate School of Science, University of Tokyo, Tokyo, Japan.

<sup>4</sup>Department of Environmental Science, Ibaraki University, Mito, Ibaraki, Japan.

<sup>5</sup>Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina, USA.

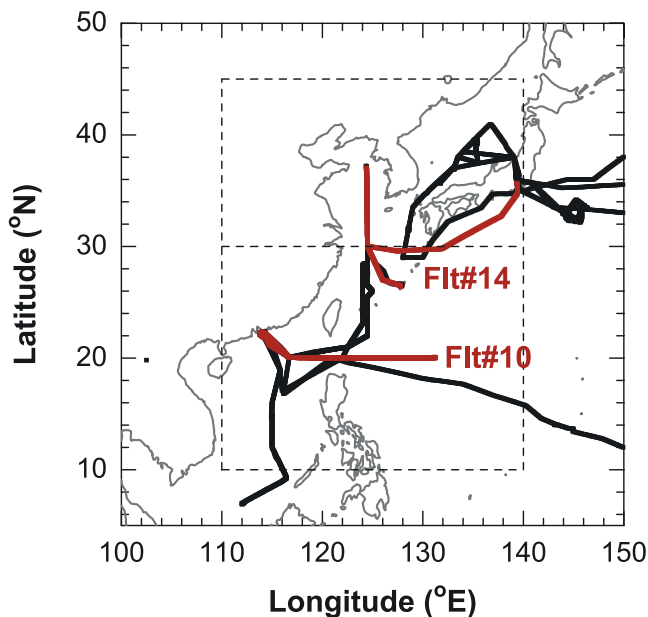
<sup>6</sup>School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honolulu, Hawaii, USA.

<sup>7</sup>National Center for Atmospheric Research, Boulder, Colorado, USA.

<sup>8</sup>Southwest Sciences, Inc., Santa Fe, New Mexico, USA.

<sup>9</sup>Department of Chemistry, University of California, Irvine, California, USA.

<sup>10</sup>National Institute of Water and Atmospheric Research, Lauder, New Zealand.



**Figure 1.** Flight tracks near the Asian continent during TRACE-P and regions where flights 10 and 14 were made (see text for details).

[4] To date, a number of attempts have been made to quantify the budget of NO<sub>y</sub> over a variety of regions. Catalytic conversion of NO<sub>y</sub> compounds on the surface of a heated gold tube, followed by chemiluminescence detection of NO [Fahey *et al.*, 1985] has been widely used for airborne measurements, because of its fast response and high sensitivity [e.g., Hübler *et al.*, 1992; Ridley *et al.*, 1994; Sandholm *et al.*, 1994; Kondo *et al.*, 1997a]. Over the western Pacific, NO<sub>x</sub>, PAN, and HNO<sub>3</sub> obtained by airborne measurements together accounted for 90% of concurrently measured NO<sub>y</sub> up to 7 km [Kondo *et al.*, 1997b]. Measurements of NO<sub>y</sub> and the sum of reactive nitrogen species in the upper troposphere over the North Atlantic [Talbot *et al.*, 1999] showed that 90% of the measured NO<sub>y</sub> was accounted for by measurements of the individual NO<sub>y</sub> species.

[5] Over the North American continent in summer, aircraft measurements showed that the individually measured species (NO<sub>x</sub> + HNO<sub>3</sub> + PANs + C<sub>1</sub>-C<sub>5</sub> alkyl nitrate) constituted more than 90% of the measured NO<sub>y</sub> on average at altitudes up to 7 km [Neuman *et al.*, 2002; Ryerson *et al.*, 2003; Parrish *et al.*, 2004]. They concluded that the sum of the individual NO<sub>y</sub> constituents agreed with the measured NO<sub>y</sub> within the instrument uncertainties over the region. Day *et al.* [2003] recently showed that the sum of total alkyl nitrates (RONO<sub>2</sub>) routinely accounted for 10–20% of NO<sub>y</sub>, using annual ground-based measurements at a rural site in California.

[6] In situ aircraft measurements of NO<sub>y</sub> have been made through forward and/or rearward facing inlets. NO<sub>y</sub> measured through forward facing inlets represents amplified particulate NO<sub>y</sub> plus gas-phase NO<sub>y</sub>. Fahey *et al.* [2001] observed large, HNO<sub>3</sub>-containing particles with D<sub>p</sub> = 10–20 μm in the winter Arctic lower stratosphere by in situ aircraft measurements of NO<sub>y</sub>. Similarly, NO<sub>y</sub> contained in cirrus cloud ice particles has been measured in the upper

troposphere [Weinheimer *et al.*, 1998; Kondo *et al.*, 2003] and in the lowermost stratosphere [Feigl *et al.*, 1999]. However, the response of NO<sub>y</sub> measurement techniques or their sampling systems to particulate NO<sub>3</sub><sup>-</sup> in the lower troposphere is not fully understood. In particular, a quantitative assessment of the contribution of particulate NO<sub>3</sub><sup>-</sup> to NO<sub>y</sub> sampled through rearward facing inlets has not been made on airborne platforms in the lower troposphere. The major uncertainties are (1) particle collection efficiency of the rearward facing inlet and (2) conversion efficiency of particulate NO<sub>3</sub><sup>-</sup> in the NO<sub>y</sub> converter.

[7] In this paper, we present evidence of the detection of particulate NO<sub>3</sub><sup>-</sup> by an airborne NO<sub>y</sub> instrument during the NASA Transport and Chemical Evolution over the Pacific (TRACE-P) experiment. We focus on evaluating the contribution of NO<sub>3</sub><sup>-</sup> to NO<sub>y</sub> measurements over the western Pacific.

## 2. Experiment

[8] During the TRACE-P experiment (February–April 2001), NO<sub>y</sub> and individual NO<sub>y</sub> 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<sub>y</sub> and aerosol measurements.

### 2.1. Gas-Phase and Particulate NO<sub>y</sub>

[9] NO<sub>y</sub> was measured using an NO-O<sub>3</sub> chemiluminescence technique combined with a gold tube heated to 300°C with addition of CO, catalytically converting NO<sub>y</sub> compounds into NO [Kondo *et al.*, 1997a]. The NO<sub>y</sub> 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<sub>2</sub> in N<sub>2</sub> 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<sub>y</sub> is estimated to be ±2% for NO<sub>y</sub> mixing ratios of 500 parts per trillion by volume (pptv). The HNO<sub>3</sub> 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<sub>3</sub>CN were 2% and 1–2%, respectively [Koike *et al.*, 2000]. From the observed values of HCN (<220 pptv) and CH<sub>3</sub>CN (<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<sub>y</sub> measurement was estimated to be ±13%.

[10] In this study, ΔNO<sub>y</sub> is defined as the difference between the measured NO<sub>y</sub> and ∑(NO<sub>y</sub>)<sub>i</sub>,

$$\Delta\text{NO}_y = \text{NO}_y - \sum(\text{NO}_y)_i \quad (1)$$

**Table 1.** Approximate Stokes Numbers Calculated for the P-3B NO<sub>y</sub> Inlet at a Pressure Altitude of 950 hPa

	Value
D <sub>p</sub> = 0.3 μm	0.01
D <sub>p</sub> = 0.5 μm	0.03
D <sub>p</sub> = 1.0 μm	0.09
D <sub>p</sub> = 1.5 μm	0.19

where  $\sum(\text{NO}_y)_i$  is defined as the sum of individually measured gas-phase NO<sub>y</sub> compounds.

$$\sum(\text{NO}_y)_i = \text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{PAN} + \text{PPN} + \text{C}_1\text{-C}_5 \text{ alkyl nitrates} \quad (2)$$

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

[11] During TRACE-P, two NO<sub>y</sub> inlets were located on the right window plate of the cabin, one facing rearward and the other facing forward. The inlet of the NO<sub>y</sub> 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<sub>y</sub> 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<sub>y</sub> 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<sub>y</sub> sampling inlet by a simple aerodynamical calculation (Table 1). On the basis of these calculations, we estimated that the NO<sub>y</sub> inlet discriminates against particles with D<sub>p</sub> larger than 1.5 and 1.1 μm at altitudes of 0.5 and 6 km, respectively. The collection efficiency of particles with D<sub>p</sub> > 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.

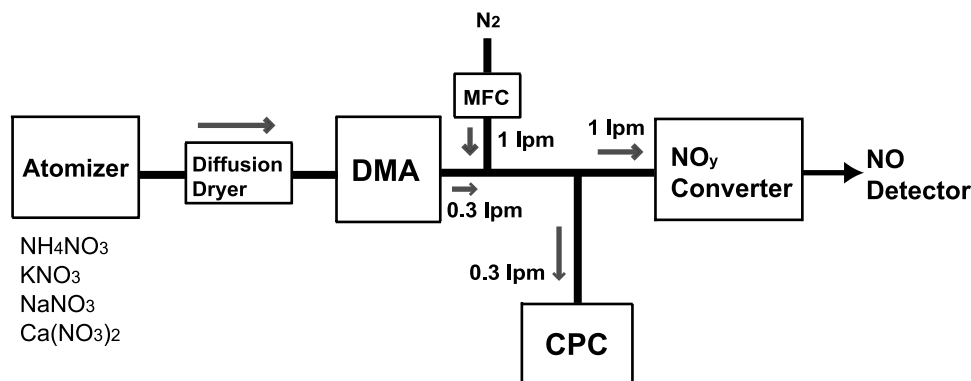
[12] During TRACE-P, NO<sub>y</sub> was also sampled through a forward facing inlet using an independent detection channel. The forward facing inlet was subsokinetic and collected particles including those with D<sub>p</sub> > 1.5 μm that were unlikely sampled by the rearward NO<sub>y</sub> inlet. The NO<sub>y</sub> measured through the forward facing inlet (NO<sub>y</sub>(f)) represents the sum of gas-phase NO<sub>y</sub> and amplified particulate NO<sub>3</sub><sup>-</sup>. When particulate NO<sub>3</sub><sup>-</sup> is absent, NO<sub>y</sub> signals from NO<sub>y</sub>(f) and NO<sub>y</sub> are identical. When encountered, particulate NO<sub>3</sub><sup>-</sup> including larger particles (D<sub>p</sub> > 1.5 μm), NO<sub>3</sub><sup>-</sup>(L), can be defined as follows:

$$\text{NO}_3^-(\text{L}) = (\text{NO}_y(\text{f}) - \sum(\text{NO}_y)_i) / \text{EF} \quad (3)$$

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

## 2.2. Laboratory Experiments

[13] In order to estimate the conversion efficiency of particulate NO<sub>3</sub><sup>-</sup> in the gold tube converter, we conducted laboratory experiments using an aerosol generation system (Figure 2). Because particulate NO<sub>3</sub><sup>-</sup> is observed typically in the form of NH<sub>4</sub>NO<sub>3</sub>, KNO<sub>3</sub>, NaNO<sub>3</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub> 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<sub>4</sub>NO<sub>3</sub> was 91 ± 9% at NO<sub>3</sub><sup>-</sup> mixing ratios of 2000–5000 pptv. The derived conversion efficiency for particulate NH<sub>4</sub>NO<sub>3</sub> was as high as that for HNO<sub>3</sub>. The difference between the two conversion efficiencies is within the measurement uncertainties. Uncertainties of the

**Figure 2.** Schematic of the laboratory setup to generate and measure particulate NO<sub>3</sub><sup>-</sup>. The number concentration of generated aerosol was measured by a condensation particle counter (CPC).

**Table 2.** Conversion Efficiencies of Particulate NO<sub>3</sub><sup>-</sup> Species Measured in the Laboratory<sup>a</sup>

	NH <sub>4</sub> NO <sub>3</sub>	KNO <sub>3</sub>	NaNO <sub>3</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>
NO <sub>3</sub> <sup>-</sup> Conversion Efficiency, %	90.7 ± 9.0	1.2 ± 0.5	2.0 ± 0.3	3.4 ± 0.8
Assumed Density ρ, g/cm <sup>3</sup>	1.72	2.11	2.66	2.36
Boiling point/Melting point, °C	210 (b)	334 (m)	380 (b)	561 (m)

<sup>a</sup>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.

NH<sub>4</sub>NO<sub>3</sub> conversion efficiency due to evaporation of NH<sub>4</sub>NO<sub>3</sub> particles in the inlet system are small. The residence time of particulate NO<sub>3</sub><sup>-</sup> between the atomizer and NO<sub>y</sub> converter is about 1 s, which is much shorter than the typical timescale of a few minutes required for evaporation of particulate NO<sub>3</sub><sup>-</sup> [e.g., Neuman *et al.*, 2003]. In fact, our recent ground-based measurements showed that the ambient HNO<sub>3</sub> concentrations were smaller than 8% of the particulate NO<sub>3</sub><sup>-</sup> 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<sub>3</sub>, NaNO<sub>3</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub> were as low as 1.2 ± 0.5%, 2.0 ± 0.3%, and 3.4 ± 0.8%, respectively.

[14] These results are consistent with the boiling or melting points of the particulate NO<sub>3</sub><sup>-</sup> species (Table 2). NH<sub>4</sub>NO<sub>3</sub> (boiling point 210°C) should be vaporized at the temperature of the NO<sub>y</sub> converter (300°C). On the other hand, the melting or boiling points of KNO<sub>3</sub>, NaNO<sub>3</sub>, and (Ca(NO<sub>3</sub>)<sub>2</sub>) are higher than the temperature of the NO<sub>y</sub> converter, leading to significantly low conversion efficiencies.

### 2.3. Aerosol Measurements

[15] Aerosol chemical composition (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>) was measured every 4 min, using a particle-into-liquid sampler coupled with ion chromatography analysis (PILS-IC) [Weber *et al.*, 2001; Orsini *et al.*, 2003]. The PILS employs a steam saturator to grow the aerosol to sizes that result in liquid impaction followed by measurement of the major ions using IC. For the PILS, the collection efficiency for D<sub>p</sub> < 0.7 μm was estimated to be 90%, decreasing to ~50% for D<sub>p</sub> = 1.3 μm (upper size cut), which was determined by laboratory calibration [Ma *et al.*, 2004]. The efficiency for D<sub>p</sub> > 3 μm was nearly zero. The uncertainty of the NO<sub>3</sub><sup>-</sup> measurement was estimated to be ±15%. The P-3B used a shrouded inlet for the aerosol measurements, which maintained an attack angle independent of turbulence characteristics in the diffuser cone [Clarke *et al.*, 2004]. The aerosol inlet was kept isokinetic during flight by adjusting flow rates as flight parameters changed.

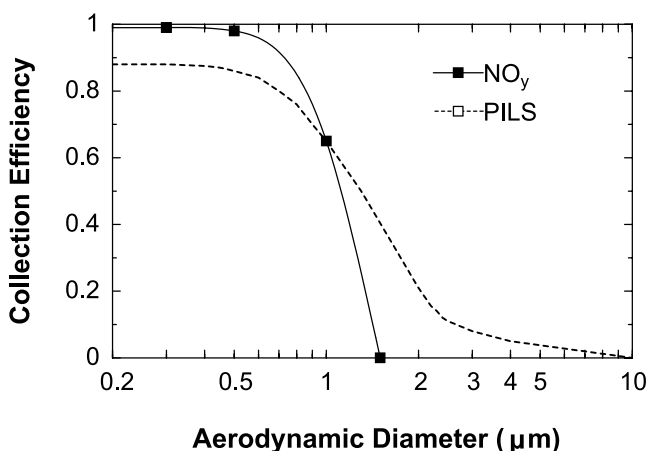
[16] Upper size cuts of the NO<sub>y</sub> and PILS systems are shown in Figure 3. Basically, the size cutoff of the PILS is similar to that of the NO<sub>y</sub> instrument. However, the PILS measures particles within a size range of D<sub>p</sub> = 1.5–3 μm,

although the collection efficiency within this range is less than 50%. On the other hand, it is unlikely that particles with D<sub>p</sub> = 1.5–3 μm were sampled by the NO<sub>y</sub> instrument. We discuss the difference in the threshold of particle size in section 4.

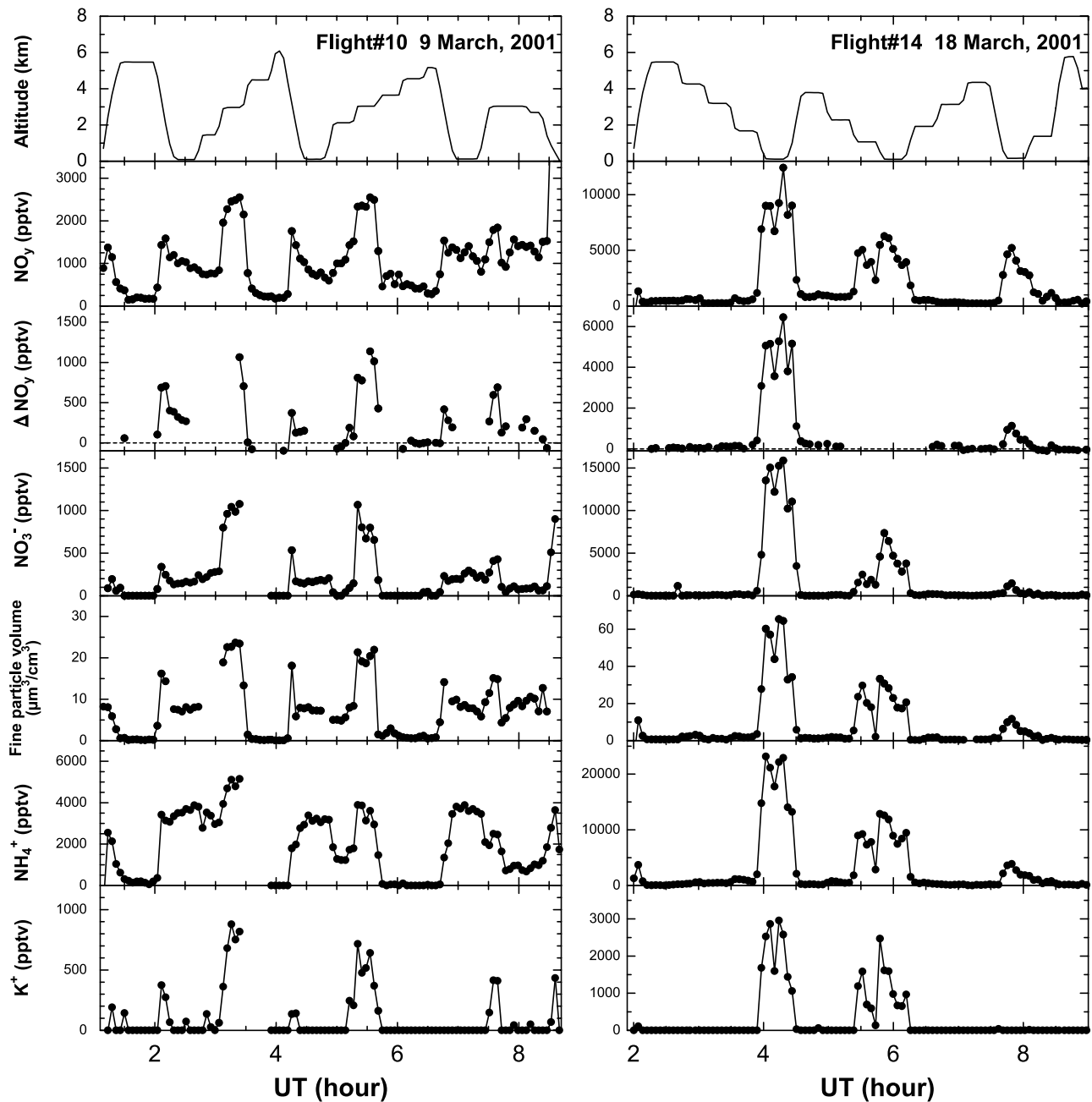
[17] Ambient aerosol size distributions were measured by a laser optical counter (OPC, PMS LAS-X, Boulder, CO) [Clarke *et al.*, 2004]. The OPC provided size distributions of “dry” (heated to 40°C) particles between 0.1 and 20.0 μm. The terms “fine particle” and “coarse particle” in this paper are defined as particles within size ranges of D<sub>p</sub> < 1 μm and D<sub>p</sub> > 1 μm, respectively. Ambient wet particle size distributions are estimated by assuming that particles with D<sub>p</sub> < 0.6 μm absorb water as a typical marine boundary layer aerosol [Swietlicki *et al.*, 2000], and particles with D<sub>p</sub> > 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<sub>3</sub><sup>-</sup> Detected by the NO<sub>y</sub> Instrument

[18] Figure 4 shows time series plots of NO<sub>y</sub>, ΔNO<sub>y</sub>, NO<sub>3</sub><sup>-</sup>, fine-particle volume, NH<sub>4</sub><sup>+</sup>, and K<sup>+</sup> 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<sub>y</sub> up to 2500 pptv was observed at an altitude of 3 km during flight 10. The ΔNO<sub>y</sub> and NO<sub>3</sub><sup>-</sup> concentrations reached their maximum values in the same air masses. An interesting feature is that K<sup>+</sup> 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<sup>+</sup>/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<sub>y</sub> and PILS instruments. The NO<sub>y</sub> 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].



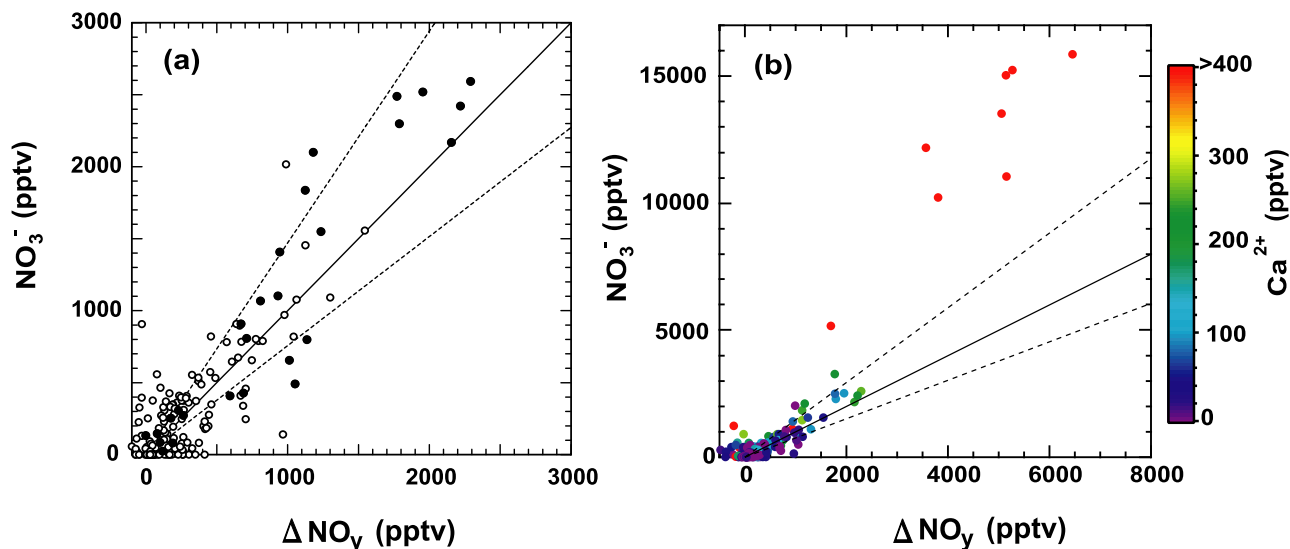
**Figure 4.** Time series plots for flight 10 and flight 14 with altitude,  $\text{NO}_y$ ,  $\Delta\text{NO}_y$ ,  $\text{NO}_3^-$ , fine-particle volume,  $\text{NH}_4^+$ , and  $\text{K}^+$ .

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 ( $34^\circ$ – $36^\circ\text{N}$ , see Figure 1). Peak concentrations for  $\text{NO}_y$ ,  $\Delta\text{NO}_y$ , and  $\text{NO}_3^-$  were 13,000, 6500, and 16,000 pptv, respectively. For both cases, fine-particle volumes were also enhanced ( $25$ – $70 \mu\text{m}^3/\text{cm}^3$ ) in these plumes.

[19] In order to evaluate the contribution of  $\text{NO}_3^-$  to  $\Delta\text{NO}_y$ , their correlations at 0–4 km are shown in Figure 5. A majority of the  $\text{NO}_3^-$  and  $\Delta\text{NO}_y$  ( $<2500$  pptv) data points in Figure 5a lie along the 1:1 line, within the error bars, indicating that  $\text{NO}_3^-$  measured by the PILS-IC can account for the  $\Delta\text{NO}_y$ . In Figure 5b, data points with  $\Delta\text{NO}_y >$

2500 pptv are also shown according to  $\text{Ca}^{2+}$  concentration.  $\text{Ca}^{2+}$  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  $\Delta\text{NO}_y < 2500$  pptv, which accounted for 97% of all the data points, dust loadings were low ( $[\text{Ca}^{2+}] < 200$  pptv). On the other hand,  $\text{NO}_3^-$  with  $\Delta\text{NO}_y > 2500$  pptv far exceeded  $\Delta\text{NO}_y$ , where dust loadings were high ( $[\text{Ca}^{2+}] > 400$  pptv). These data with  $\Delta\text{NO}_y > 2500$  pptv were all obtained over the Yellow Sea during flight 14 (Figure 4). A possible explanation of the excess  $\text{NO}_3^-$  relative to  $\Delta\text{NO}_y$  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,



**Figure 5.** Linear relationship between particulate  $\text{NO}_3^-$  and  $\Delta\text{NO}_y$  observed at 0–4 km for all flights during the TRACE-P period. Solid and dashed lines indicate the 1:1 line and the uncertainty of  $\Delta\text{NO}_y$ , respectively. (a) Solid circles indicate the data in which  $\text{NO}_3^- + \text{SO}_4^{2-}$  and  $\text{NH}_4^+$  in equivalence balanced to within  $\pm 30\%$ . (b) The data points are color-coded according to the concentration of  $\text{nss-Ca}^{2+}$ . Note that Figure 5a is a subset of the data points in Figure 5b and that the scales of the x and y axes in both figures are different.

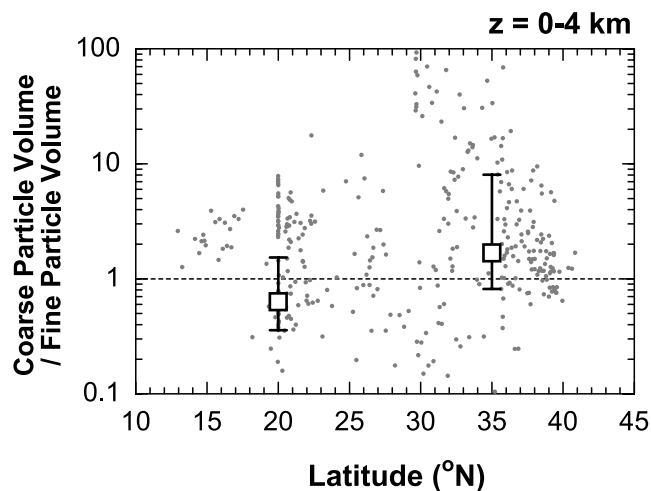
the median ratio at  $10^\circ$ – $30^\circ\text{N}$  was lower than 1, suggesting that a majority of particles was in the fine mode ( $D_p < 1 \mu\text{m}$ ), likely in biomass burning plumes [Kondo *et al.*, 2004]. A dominance of fine particles in biomass burning plumes was previously observed, for instance, in Brazil [Reid and Hobbs, 1998]. By contrast, at  $30^\circ$ – $45^\circ\text{N}$ , 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  $30^\circ$ – $45^\circ\text{N}$  during TRACE-P. Figure 7 presents a plot of the  $\text{NO}_3^-/\Delta\text{NO}_y$  ratio versus the (coarse-particle volume)/(fine-particle volume) ratio. At the  $\text{NO}_3^-/\Delta\text{NO}_y$  ratio close to 1, fine-particle volume was generally larger than coarse-particle volume and dust loadings were low with  $[\text{Ca}^{2+}] < 200$  pptv. These results suggest that a majority of  $\Delta\text{NO}_y$  can be attributed to fine particles.

[21] Contributions of  $\text{NO}_y$  species not measured in this study to  $\Delta\text{NO}_y$  are not significant in this study. Model calculations [Brasseur *et al.*, 1999; Talbot *et al.*, 1999] indicate that  $\text{HO}_2\text{NO}_2$  is the most abundant unmeasured  $\text{NO}_y$  species. However, it is thermally stable only at the cold temperatures of the upper troposphere, and the  $\text{HO}_2\text{NO}_2/\text{NO}_y$  ratio is estimated to be lower than 0.01 below 4 km [Brasseur *et al.*, 1999]. On the other hand,  $\Delta\text{NO}_y$  is significantly large in the lower troposphere (0–4 km) in this case. Consequently, the contribution of  $\text{HO}_2\text{NO}_2$  to  $\Delta\text{NO}_y$  can be negligible in this study.

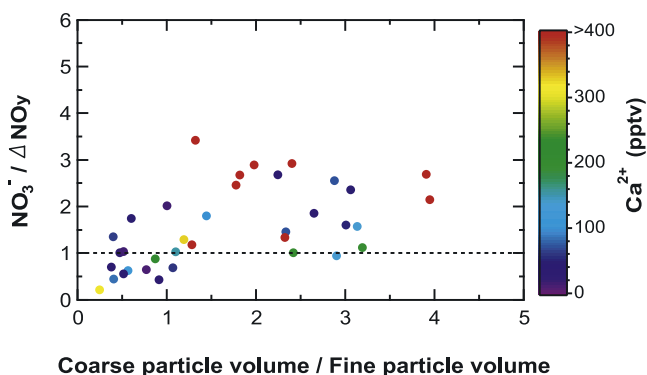
#### 4. Chemical Form of Particulate $\text{NO}_3^-$

[22] In this section, we infer the chemical form of particulate  $\text{NO}_3^-$  detected by the  $\text{NO}_y$  instrument. Figure 8

shows average ionic composition at 0–4 km with  $\Delta\text{NO}_y$  both less than and greater than 2500 pptv, where dust loadings were low with  $[\text{Ca}^{2+}] < 200$  pptv and high with  $[\text{Ca}^{2+}] > 400$  pptv, respectively.  $\text{NH}_4^+$  was the main neutralizing agent of the acidic aerosol species, which accounted for 82 and 73% of the total cations with  $\Delta\text{NO}_y < 2500$  pptv and  $\Delta\text{NO}_y > 2500$  pptv, respectively.  $\text{NH}_4\text{NO}_3$  forms by condensation of gas-phase  $\text{HNO}_3$  with available  $\text{NH}_3$  once all  $\text{SO}_4^{2-}$  is neutralized [Seinfeld and Pandis, 1998]. In order to examine this, the relationship between  $\text{NO}_3^-$  and  $\text{NH}_4^+$  minus  $\text{SO}_4^{2-}$  in equivalence is shown in Figure 9. Overall, a



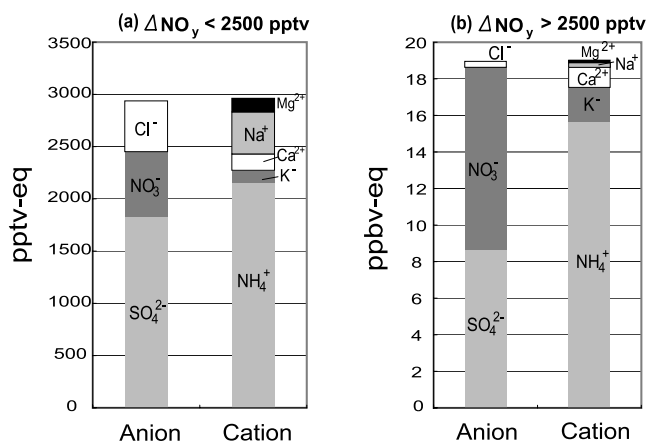
**Figure 6.** Latitudinal distributions of coarse ( $D_p = 1$ – $20 \mu\text{m}$ )/fine ( $D_p = 0.1$ – $1 \mu\text{m}$ ) particle volume observed at 0–4 km. Median values are shown for  $10^\circ$ – $30^\circ\text{N}$  and  $30^\circ$ – $45^\circ\text{N}$ . The data points with fine-particle volume  $< 0.2 \mu\text{m}^3/\text{cm}^3$  are not used.



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

positive correlation ( $r^2 = 0.77$ ) with a slope of 1.10 shows that ion balance between  $\text{NH}_4^+$  minus  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in equivalence is nearly complete, within 10% on average, suggesting available  $\text{NH}_3$  to form  $\text{NH}_4\text{NO}_3$ . For  $\Delta\text{NO}_y < 2500\ \text{pptv}$ , the slope was 0.97 with  $r^2 = 0.66$  and 1.34 with  $r^2 = 0.74$  for  $\Delta\text{NO}_y > 2500\ \text{pptv}$ . The data for which  $\text{NO}_3^- + \text{SO}_4^{2-}$  and  $\text{NH}_4^+$  in equivalence balanced within  $\pm 30\%$  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  $\text{NH}_4\text{NO}_3$  was detected by the  $\text{NO}_y$  instrument.

[23] In order to estimate the relative contribution of cations other than  $\text{NH}_4^+$  associated with  $\text{NO}_3^-$ , we consider the relative amounts of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  by using PLS chemical composition data. If we assume that all of the  $\text{Ca}^{2+}$  and  $\text{K}^+$  take up  $\text{SO}_4^{2-}$ , measured  $\text{NO}_3^-$  is considered to be in the form of  $\text{NH}_4\text{NO}_3$ , that is,  $\text{NO}_3^-$  as  $\text{NH}_4\text{NO}_3 = \text{NH}_4^+ - \text{SO}_4^{2-}$  in equivalence (upper limit). By contrast, when all  $\text{Ca}^{2+}$  and  $\text{K}^+$  are assumed to take up the measured  $\text{NO}_3^-$ , the



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

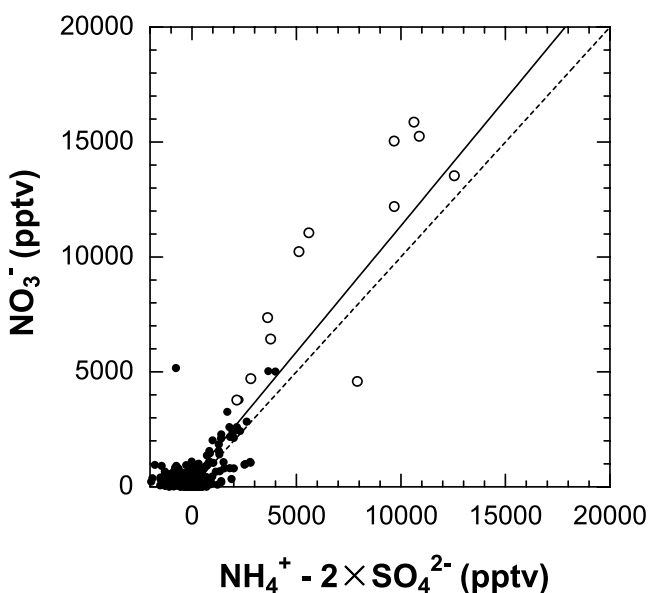
amount of  $\text{NO}_3^-$  as  $\text{NH}_4\text{NO}_3$  can be derived from  $\text{NO}_3^- - (\text{Ca}^{2+} + \text{K}^+)$  in equivalence (lower limit). Considering these two limiting cases for  $\text{NH}_4\text{NO}_3$ , the amount of  $\text{Ca}^{2+}$  plus  $\text{K}^+$  in equivalence is 44% of  $\text{NO}_3^-$  for the data points with  $\Delta\text{NO}_y < 2500\ \text{pptv}$ . Thus, when  $\text{Ca}^{2+}$  and  $\text{K}^+$  are taken into account, the lower limit of  $\text{NH}_4\text{NO}_3$  was estimated to be 56% of the total  $\text{NO}_3^-$ .

[24] For  $\Delta\text{NO}_y < 2500\ \text{pptv}$ , the correlation between  $\text{Cl}^-$  and  $\text{Na}^+$  showed a slope of 1.35 with  $r^2 = 0.78$  (not shown), close to the seawater ratio of 1.16. Moreover,  $\text{Mg}^{2+}$  showed a correlation with  $\text{Na}^+$  ( $r^2 = 0.64$ ) 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  $\text{Cl}^-/\text{Na}^+$  ratio lower than the seawater ratio indicates acidification of particles by  $\text{HNO}_3$ , resulting in a  $\text{Cl}^-$  deficit to form  $\text{NaNO}_3$ . By using these data points,  $\text{NaNO}_3$  was estimated to contribute  $< 12\%$  of  $\text{NO}_3^-$  for  $\Delta\text{NO}_y < 2500\ \text{pptv}$ . Overall, more than 44% of particulate  $\text{NO}_3^-$  ( $\Delta\text{NO}_y < 2500\ \text{pptv}$ ) was estimated to be in the form of  $\text{NH}_4\text{NO}_3$ .

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

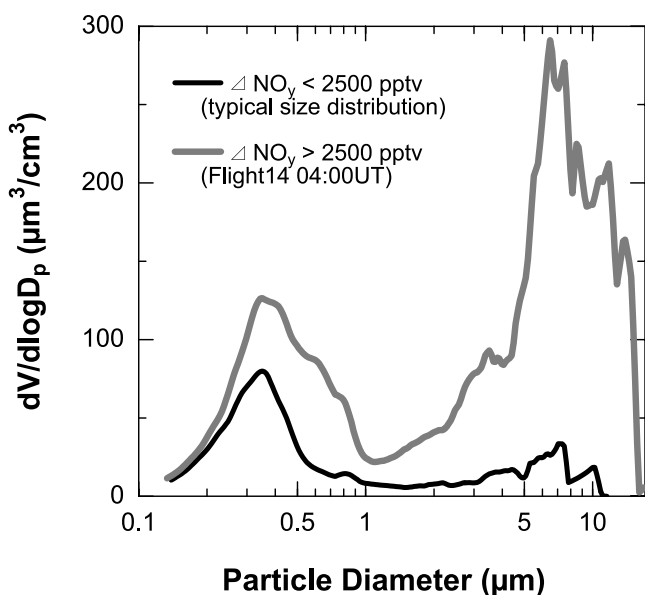
[26] For the data points with  $\Delta\text{NO}_y > 2500\ \text{pptv}$  ( $< 3\%$  of the total), however,  $\text{NO}_3^-$  (7500–12,000 pptv) far exceeded the 1:1 line relative to  $\Delta\text{NO}_y$  (Figure 5b). As stated in section 2, there are two possible explanations for the excess  $\text{NO}_3^-$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

$$\delta\text{NO}_3^- = \text{NO}_3^- - \Delta\text{NO}_y \quad (4)$$



**Figure 9.** Relationship between  $\text{NO}_3^-$  and  $\text{NH}_4^+$  minus  $\text{SO}_4^{2-}$  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  $\text{Ca}^{2+}$  ( $> 400\ \text{pptv}$ ) obtained at 0–2 km over the Yellow Sea during flight 14.





**Figure 10.** Typical size distributions representative of particles with  $\Delta\text{NO}_y < 2500$  pptv (black line) and within the plumes with  $\Delta\text{NO}_y > 2500$  pptv at 0400 UTC during flight 14 (gray line) measured by the OPC. The size distributions are calculated from number distributions for particles grown at ambient relative humidity, assuming that uptake is by dust particles.

(1) particles were not sampled by the NO<sub>y</sub> instrument but were by the PILS-IC, because of their sizes, with  $D_p = 1.5\text{--}3$   $\mu\text{m}$  in the different inlet systems, and (2) particles were measured as water-soluble ions by the PILS-IC but not converted to measurable NO in the NO<sub>y</sub> instrument (i.e., Ca(NO<sub>3</sub>)<sub>2</sub> and KNO<sub>3</sub>). We explore these two possibilities in detecting particulate NO<sub>3</sub><sup>-</sup> by the NO<sub>y</sub> instrument and the PILS-IC system.

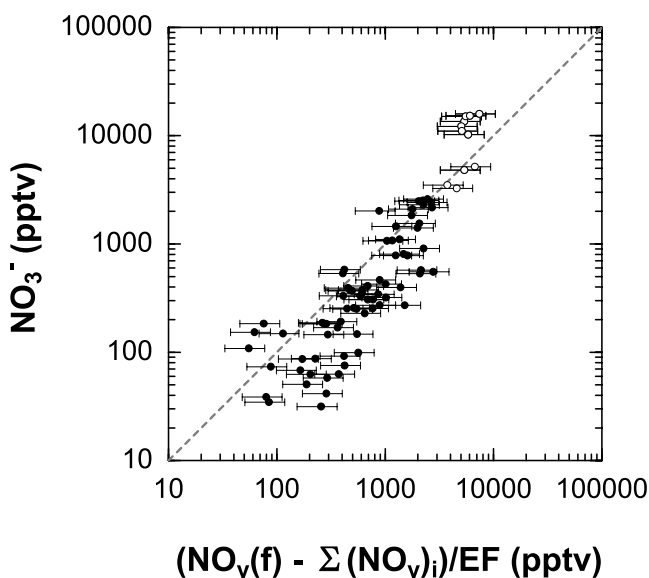
[27] Regarding particle size, the data points where NO<sub>3</sub><sup>-</sup>/ΔNO<sub>y</sub> ratios exceed 1 (Figure 7), where coarse-particle volume tends to be larger relative to fine-particle volume under the high concentrations of Ca<sup>2+</sup> (>400 pptv), are indicative of dust loading. Jordan *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  $\Delta\text{NO}_y > 2500$  pptv and typical distributions representative of particles for  $\Delta\text{NO}_y < 2500$  pptv. The size distributions of particles with  $\Delta\text{NO}_y < 2500$  pptv show that particles reside mostly in the fine mode ( $D_p < 1$   $\mu\text{m}$ ), while the abundance in the coarse mode ( $D_p > 1$   $\mu\text{m}$ ) is minimal. On the other hand, the distributions of particles with  $\Delta\text{NO}_y > 2500$  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  $D_p = 1.5\text{--}3$   $\mu\text{m}$  could contribute to about 10% of the total volume of particles collected by the PILS for  $\Delta\text{NO}_y > 2500$  pptv.

[28] We further examined particulate NO<sub>3</sub><sup>-</sup> containing the 1.5–3- $\mu\text{m}$  range by using the NO<sub>y</sub>(f) data. Figure 11 shows

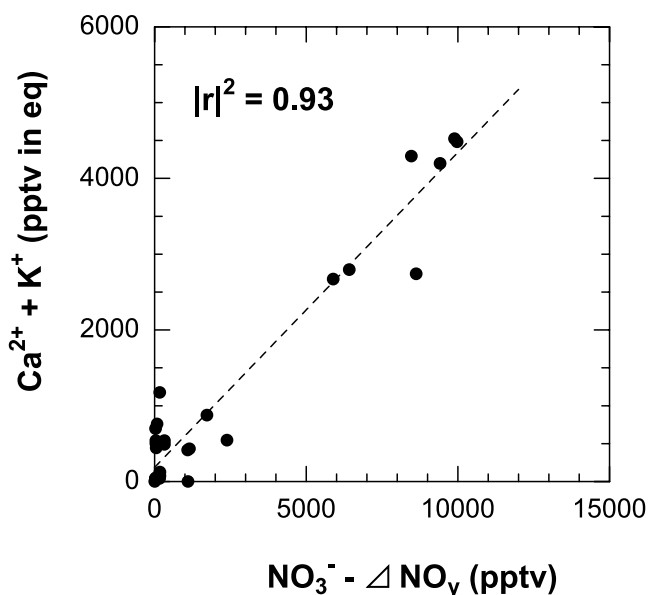
the relationship between NO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>(L) (equation 3). Using the empirical expression given by Durham and Lundgren [1980], EF was estimated to be 2 for  $D_p = 1.5$   $\mu\text{m}$ , by assuming a particle density of 1.8 g cm<sup>-3</sup> estimated from the OPC data. As stated in section 2, NO<sub>3</sub><sup>-</sup>(L) represents particulate NO<sub>3</sub><sup>-</sup> including larger particles ( $D_p > 1.5$   $\mu\text{m}$ ), mainly as NH<sub>4</sub>NO<sub>3</sub>, which can be detected by the NO<sub>y</sub> instrument. Considering that the EF range is  $2 \pm 0.5$  for particles with  $D_p = 0.5\text{--}3$   $\mu\text{m}$ , the estimated uncertainty of NO<sub>3</sub><sup>-</sup>(L) is given as +40%/–30%. For  $\Delta\text{NO}_y < 2500$  pptv, NO<sub>3</sub><sup>-</sup> showed agreement with NO<sub>3</sub><sup>-</sup>(L), including particles that were not efficiently detected by the rearward NO<sub>y</sub> system, indicating that almost all of  $\delta\text{NO}_3^-$  can be explained by NO<sub>3</sub><sup>-</sup>(L). For  $\Delta\text{NO}_y > 2500$  pptv, although it is difficult to evaluate the contribution of NO<sub>3</sub><sup>-</sup>(L) to  $\delta\text{NO}_3^-$  because of the uncertainty of the EF, we estimate that approximately  $20 \pm 10\%$  of  $\delta\text{NO}_3^-$  can be explained by NO<sub>3</sub><sup>-</sup>(L). The amount of NO<sub>3</sub><sup>-</sup>(L) in this case corresponds to 10% of the PILS NO<sub>3</sub><sup>-</sup> 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.

[29] One of the possible reasons for the NH<sub>4</sub>NO<sub>3</sub> particle size to reside in larger sizes ( $D_p = 1.5\text{--}3$   $\mu\text{m}$ ) 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 NO<sub>3</sub><sup>-</sup>/ΔNO<sub>y</sub> 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.

[30] The sum of Ca<sup>2+</sup> and K<sup>+</sup> in equivalence is plotted against  $\delta\text{NO}_3^-$  for  $\Delta\text{NO}_y > 2500$  pptv in Figure 12. They are tightly correlated ( $|r|^2 = 0.93$ ), indicating that  $\delta\text{NO}_3^-$  is partly associated with dust particles. In the current analysis,



**Figure 11.** Scatterplot between NO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>(L) = (NO<sub>y</sub>(f) –  $\sum(\text{NO}_y)_i$ )/EF, where the EF (enhancement factor) is assumed to be 2. Open circles correspond to the data with  $\Delta\text{NO}_y > 2500$  pptv, while solid circles correspond to  $\Delta\text{NO}_y < 2500$  pptv. Error bars indicate the uncertainty in EF. The dashed line indicates the 1:1 line.



**Figure 12.** Scatterplot of the sum of Ca<sup>2+</sup> and K<sup>+</sup> in equivalence and  $\delta\text{NO}_3^-$ . The dashed line represents the least squares best fit.

Ca<sup>2+</sup> and K<sup>+</sup> in equivalence accounted for 20% and 25% of  $\delta\text{NO}_3^-$  on average, respectively, for  $\Delta\text{NO}_y > 2500$  pptv. Namely, Ca(NO<sub>3</sub>)<sub>2</sub> and KNO<sub>3</sub>, which are not measured as NO<sub>y</sub>, can explain a maximum of 45% of the  $\delta\text{NO}_3^-$ . The remaining  $\delta\text{NO}_3^-$  (~35%), which cannot be explained by either larger NH<sub>4</sub>NO<sub>3</sub> ( $D_p = 1.5\text{--}3\ \mu\text{m}$ ) or Ca<sup>2+</sup> plus K<sup>+</sup> particles, is within the combined uncertainties of the measurements and EF.

### 5. Contribution of Particulate NO<sub>3</sub><sup>-</sup> to the NO<sub>y</sub> Budget Over the Western Pacific

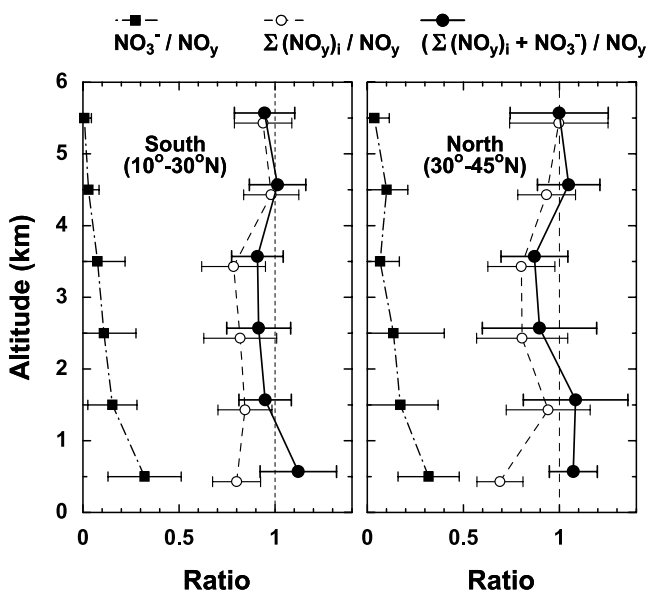
[31] Finally, we investigated the partitioning between particulate NO<sub>3</sub><sup>-</sup> and gas-phase NO<sub>y</sub>. Figure 13 shows vertical profiles of NO<sub>3</sub><sup>-</sup>,  $\sum(\text{NO}_y)_i$ , and  $\sum(\text{NO}_y)_i + \text{NO}_3^-$  to NO<sub>y</sub> ratios at 10°–30°N and 30°–45°N.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

[32] At altitudes of 2–6 km, very low values of NO<sub>3</sub><sup>-</sup>/NO<sub>y</sub> (0.02–0.10) indicate that a large fraction of the NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> concentrations discussed here are fine-mode fractions of the total particulate NO<sub>3</sub><sup>-</sup>, which were obtained by the PILS having a 50% size cut of 1.3 μm. When we use the NO<sub>3</sub><sup>-</sup> data obtained by the DC-8 filter samples, which measured particles with  $D_p$  up to 6 μm [Dibb et al., 2002], particulate NO<sub>3</sub><sup>-</sup> 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<sub>y</sub>, 80–90% of the measured NO<sub>y</sub> at 0–6 km is accounted for by NO<sub>x</sub> (= NO + NO<sub>2</sub>), PAN, and HNO<sub>3</sub>. 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<sub>3</sub> 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<sub>3</sub> 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 inter-comparison 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<sub>3</sub> relative to the true amount. Thus much more accurate evaluations of the NO<sub>y</sub> budget are enabled in this study by highly selective and sensitive measurements of gas-phase HNO<sub>3</sub> by the CIMS instrument and of particulate NO<sub>3</sub><sup>-</sup> 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<sub>y</sub> budget during TRACE-P. The



**Figure 13.** Vertical profiles of the mean values of NO<sub>3</sub><sup>-</sup>/NO<sub>y</sub> (solid squares),  $\sum(\text{NO}_y)_i/\text{NO}_y$  (open circles), and  $(\sum(\text{NO}_y)_i + \text{NO}_3^-)/\text{NO}_y$  (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-P<sup>a</sup>

Altitude, km	Latitude <sup>b</sup>	NO <sub>3</sub> <sup>-</sup> , pptv	NO <sub>y</sub> , pptv	HNO <sub>3</sub> , pptv	PAN, pptv	PPN, pptv	Alkyl Nitrate, pptv	NO <sub>y</sub> , pptv	Σ(NO <sub>y</sub> ) <sub>i</sub> + NO <sub>3</sub> <sup>-</sup> , pptv
4–6	N	25 ± 42	34 ± 37	115 ± 81	174 ± 122	21 ± 19	15 ± 7	388 ± 238	359 ± 203
		(0.06 ± 0.12)	(0.08 ± 0.08)	(0.34 ± 0.20)	(0.47 ± 0.11)	(0.05 ± 0.02)	(0.05 ± 0.02)	(–)	(1.05 ± 0.23)
4–6	S	18 ± 18	30 ± 15	156 ± 70	143 ± 104	14 ± 10	9 ± 4	368 ± 174	437 ± 229
		(0.02 ± 0.04)	(0.08 ± 0.03)	(0.44 ± 0.16)	(0.35 ± 0.13)	(0.03 ± 0.01)	(0.03 ± 0.01)	(–)	(0.98 ± 0.16)
2–4	N	103 ± 408	70 ± 91	221 ± 139	438 ± 258	61 ± 38	30 ± 11	997 ± 628	883 ± 747
		(0.10 ± 0.21)	(0.07 ± 0.05)	(0.23 ± 0.14)	(0.46 ± 0.13)	(0.06 ± 0.02)	(0.04 ± 0.01)	(–)	(0.91 ± 0.29)
2–4	S	110 ± 237	63 ± 47	289 ± 308	160 ± 142	24 ± 13	15 ± 7	713 ± 655	889 ± 628
		(0.09 ± 0.16)	(0.10 ± 0.05)	(0.39 ± 0.17)	(0.21 ± 0.14)	(0.03 ± 0.02)	(0.04 ± 0.03)	(–)	(0.91 ± 0.15)
0–2	N	1761 ± 3199	1142 ± 4948	430 ± 316	928 ± 542	155 ± 91	63 ± 24	3836 ± 5865	3943 ± 4749
		(0.37 ± 0.39)	(0.16 ± 0.15)	(0.24 ± 0.20)	(0.33 ± 0.10)	(0.05 ± 0.02)	(0.03 ± 0.01)	(–)	(1.18 ± 0.34)
0–2	S	230 ± 432	146 ± 200	209 ± 222	189 ± 184	47 ± 34	34 ± 18	776 ± 624	1011 ± 556
		(0.26 ± 0.19)	(0.16 ± 0.10)	(0.32 ± 0.17)	(0.20 ± 0.12)	(0.05 ± 0.03)	(0.05 ± 0.03)	(–)	(1.06 ± 0.19)

<sup>a</sup>Values are mean ± 1 σ. The numbers in parentheses are the ratios to the measured NO<sub>y</sub>. The numbers of data points are within a range of 40–120 in each column.

<sup>b</sup>Latitudes 10°–30°N are denoted as S, and latitudes 30°–45°N are denoted as N.

present results emphasize that the contribution of particulate NO<sub>3</sub><sup>-</sup> to NO<sub>y</sub> should be taken into account when evaluating NO<sub>y</sub> speciation and budget closure using an NO<sub>y</sub> instrument with a catalytic converter, especially when near a large source region of particulate NO<sub>3</sub><sup>-</sup>.

## 6. Conclusions

[35] The sum of individual NO<sub>y</sub> gas components (Σ(NO<sub>y</sub>)<sub>i</sub>), NO<sub>y</sub>, and particulate NO<sub>3</sub><sup>-</sup> (D<sub>p</sub> < 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 NO<sub>3</sub><sup>-</sup>, was measured by the PILS-IC technique. In addition to the field measurements, conversion efficiencies of particulate NH<sub>4</sub>NO<sub>3</sub>, KNO<sub>3</sub>, NaNO<sub>3</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub> by the gold tube catalytic converter were measured in the laboratory. NH<sub>4</sub>NO<sub>3</sub> was converted to NO with an efficiency of 91 ± 9%, which was as high as that for HNO<sub>3</sub>. Meanwhile, the conversion efficiencies of the aerosols in the other forms were as low as 1–3%. These results are consistent with the particulate NO<sub>3</sub><sup>-</sup> measurements made on board the aircraft.

[36] Elevated NO<sub>3</sub><sup>-</sup> was typically observed within biomass/biofuel burning plumes at 0–4 km. The measured NO<sub>y</sub> was systematically higher by 10–30% than the Σ(NO<sub>y</sub>)<sub>i</sub> at 0–4 km. Under low dust loadings with [Ca<sup>2+</sup>] < 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 ([Ca<sup>2+</sup>] > 400 pptv). The ΔNO<sub>y</sub> = NO<sub>y</sub> – Σ(NO<sub>y</sub>)<sub>i</sub> values were approximately equal to NO<sub>3</sub><sup>-</sup> concentrations under low dust loadings, suggesting that the NO<sub>y</sub> instrument quantitatively converted NO<sub>3</sub><sup>-</sup> to NO. More than 44% of the NO<sub>3</sub><sup>-</sup> detected by the NO<sub>y</sub> instrument was estimated to be in the form of NH<sub>4</sub>NO<sub>3</sub>, which was identified from the measured ionic composition of the aerosols.

[37] NO<sub>3</sub><sup>-</sup> far exceeded ΔNO<sub>y</sub> 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 NO<sub>y</sub> inlet, 20% of the excess NO<sub>3</sub><sup>-</sup> (δNO<sub>3</sub><sup>-</sup> = NO<sub>3</sub><sup>-</sup> – ΔNO<sub>y</sub>) was estimated to be mainly in the form of NH<sub>4</sub>NO<sub>3</sub>, suggesting that the size of this NO<sub>3</sub><sup>-</sup> particle species detected by PILS-IC was in the range of D<sub>p</sub> = 1.5–3 μm, which was larger than the size cutoff of the rearward facing NO<sub>y</sub> instrument. Some of the

other δNO<sub>3</sub><sup>-</sup> can be in the form of Ca(NO<sub>3</sub>)<sub>2</sub> (<20%) and KNO<sub>3</sub> (<25%) under high dust loading with a mixture of anthropogenic pollution, considering the measured aerosol ion composition. Particulate NO<sub>3</sub><sup>-</sup> in these forms can partly explain the large δNO<sub>3</sub><sup>-</sup>, because their conversion in the NO<sub>y</sub> instrument is negligible. The remaining δNO<sub>3</sub><sup>-</sup> (~35%), which cannot be explained either by larger NH<sub>4</sub>NO<sub>3</sub> (D<sub>p</sub> = 1.5–3 μm) or Ca<sup>2+</sup> + K<sup>+</sup> particles, is within the combined uncertainties of the measurements and the enhancement factor for the forward facing NO<sub>y</sub> inlet.

[38] Generally, the contribution of particulate NO<sub>3</sub><sup>-</sup> to NO<sub>y</sub> was most important at 0–2 km, where the NO<sub>3</sub><sup>-</sup> concentrations constituted 10–30% of NO<sub>y</sub>. On average, the concentrations of NO<sub>3</sub><sup>-</sup> and gas-phase HNO<sub>3</sub> were comparable in this region. These results indicate the importance of properly including particulate NO<sub>3</sub><sup>-</sup> in assessing the budget of reactive nitrogen using measurements of NO<sub>y</sub> by the catalytic conversion technique, especially when near a large source region of particulate NO<sub>3</sub><sup>-</sup>.

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D. R. Blake, Department of Chemistry, University of California, Irvine, Irvine, CA 92697, USA. (drblake@uci.edu)

A. D. Clarke and V. N. Kapustin, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honolulu, HI 96822, USA. (tclarke@soest.hawaii.edu; kapustin@soest.hawaii.edu)

F. L. Eisele, F. Flocke, and A. J. Weinheimer, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80303, USA. (eisele@ucar.edu; ffl@ucar.edu; wein@ucar.edu)

M. Fukuda, Y. Kondo, Y. Miyazaki, and N. Takegawa, Research Center for Advanced Science and Technology, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan. (fukuda@atmos.rcast.u-tokyo.ac.jp; kondo@atmos.rcast.u-tokyo.ac.jp; yuzom@atmos.rcast.u-tokyo.ac.jp; takegawa@atmos.rcast.u-tokyo.ac.jp)

K. Kita, Department of Environmental Science, Ibaraki University, Bunkyo 2-1-1, Mito, Ibaraki 310-8512, Japan. (kita@env.sci.ibaraki.ac.jp)

M. Koike, Earth and Planetary Science, Graduate School of Science, University of Tokyo, Tokyo 113-0033, Japan. (koike@eps.s.u-tokyo.ac.jp)

B. Liley, National Institute of Water and Atmospheric Research, Lauder, PB 50061 Omakau, Central Otago 9182, New Zealand. (b.liley@niwa.co.nz)

Y. Ma, Department of Civil and Environmental Engineering, Duke University, Durham, NC 27708-0287, USA. (yilinma@duke.edu)

R. J. Weber, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332-0340, USA. (rweber@eas.gatech.edu)

M. A. Zondlo, Southwest Sciences, Inc., 1570 Pacheco Street, Suite E-11, Santa Fe, NM 87505, USA. (mzondlo@swsciences.com)