

**Intercomparisons of Airborne Measurements of Aerosol Ionic
Chemical Composition during TRACE-P and ACE-Asia**

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ABSTRACT

As part of the two field studies, Transport and Chemical Evolution over the Pacific (TRACE-P), and the Asian Aerosol Characterization Experiment (ACE-Asia), the inorganic chemical composition of tropospheric aerosols was measured over the western Pacific from three separate aircraft using various methods. Comparisons are made between the rapid online techniques of the Particle Into Liquid Sampler (PILS) for measurement of a suite of fine particle ionic compounds and a mist chamber (MC/IC) measurement of fine sulfate, and the longer time-integrated filter and multi-orifice impactor (MOI) measurements. Comparisons between identical PILS on two separate aircraft flying in formation showed that they were highly correlated (e.g., sulfate r^2 of 0.95), but were systematically different by $10 \pm 5\%$ (linear regression slope and 95% confidence bounds), and had generally higher concentrations on the aircraft with a low turbulence inlet and shorter inlet-to-instrument transmission tubing. Comparisons of PILS and mist chamber measurements of fine sulfate on two different aircraft during formation flying had an r^2 of 0.78 and a relative difference of $39\% \pm 5\%$. MOI ionic data integrated to the PILS upper measurement size of $1.3 \mu\text{m}$ sampling from separate inlets on the same aircraft showed that for sulfate, PILS and MOI were within $14\% \pm 6\%$ and correlated with an r^2 of 0.87. Most ionic compounds were within $\pm 30\%$, which is in the range of differences reported between PILS and integrated samplers from ground-based comparisons. In many cases, direct intercomparison between the various instruments is difficult due to differences in upper-size detection limits. However, for this study, the results suggest that the fine particle mass composition measured from aircraft agree to within 30-40%.

1. INTRODUCTION

Particle chemical composition is useful for identifying aerosol sources and investigating atmospheric aerosol processing through links with gaseous species. A number of new techniques have recently been developed for quantitative and rapid online measurements of aerosol chemical composition (e.g., [Stolzenburg and Hering, 2000; Weber *et al.*, 2001; Boring *et al.*, 2002; Orsini *et al.*, 2003; Scheuer *et al.*, 2003]). These techniques are especially useful for airborne studies where rapid and continuous measurements are needed for resolving the highly variable ambient concentrations.

From February to April 2001, the NASA Global Tropospheric Experiment (GTE) mounted a two-aircraft (Wallops P3-B and Dryden DC-8) research campaign, called Transport and Chemical Evolution over the Pacific (TRACE-P) with the primary objective to study the pathways and chemical evolution of Asian outflow over the western Pacific. A concurrent mission, the Asian Aerosol Characterization Experiment (ACE-Asia), sponsored by the NSF, was also conducted in the region from late March to early May 2001, involving the NSF/NCAR C-130 as one of the major research aircraft. The ACE-Asia objectives were to investigate the physical, chemical, and radiative properties of Asian aerosols as they advected from the continent. All aircraft deployed a large suite of instruments for measurements of meteorological parameters, gaseous species, and a range of aerosol properties. The inorganic particle chemical composition measurements on the various aircraft included both integrated filter and impactor measurements, and two relatively new approaches for fast online measurements of particle composition. During the campaign, several close proximity formation flights among pairs of the various aircraft provided a unique opportunity for in situ

intercomparison of similar measurements and justify the merging of different data sets from multi-platform experiments. *Eisele et al. [2003]* compared a range of measurements between the two NASA aircraft, (DC-8 – P3-B), focusing primarily on gaseous species, and *Moore et al. [2003]* focused on aerosol physical properties. In this paper comparisons of instruments of various design for measuring particle inorganic composition are presented by both contrasting measurements on the same aircraft and comparing measurements from different aircraft.

2. EXPERIMENTAL

A total of six instruments for measuring particle ionic composition were flown on three aircraft; five of these are compared in this paper. The various methods are summarized in Table 1. Identical Georgia Tech PILS-ICs were installed on both the NASA P3-B and the NSF C-130 for TRACE-P and ACE-Asia, respectively. Although identical, the instruments were independently calibrated and employed different inlet designs and inlet-to-instrument sample tubing arrangements. During the TRACE-P campaign, aerosol chemical composition measurements were also conducted on the NASA DC-8 research aircraft. The University of New Hampshire deployed two measurement approaches on the DC-8: one instrument measured total aerosol chemical composition by filtration [*Dibb et al., 1996, 1997*], and the other measured fine sulfate aerosol (particles estimated to be smaller than $\sim 2.7 \mu\text{m}$ aerodynamic diameter) by mist chamber-ion chromatograph (MC/IC) [*Scheuer et al., 2003*]. For ACE-Asia, the University of Hawaii deployed a Multi-Orifice Impactor (MOI, MSP, Minneapolis MN) on the C-130, for size-resolved measurements, and a Total Aerosol Sampler (TAS) was

used in an attempt to measure the composition of all particles. The TAS sampling arrangement is designed to collect all particles by locating the filter and an extractable inlet cone outside the aircraft cabin. In this comparison the TAS data is not directly used, but it is indirectly involved since TAS data have been used to correct the MOI measurements. Although the sampling and collection techniques are different for these instruments, they all use Ion Chromatography as the analytical technique. A detailed description of the measurements is given in the following section.

***Georgia Institute of Technology, Particle Into Liquid Sampler-Ion Chromatograph:
NASA P3-B and NSF C-130***

The Particle-Into-Liquid Sampler continuously collects ambient particles into a small flow of purified water for online measurement of the liquid composition. Sample air is first drawn through denuders to remove interfering gases and is then mixed with saturated water vapor. The vapor condenses on the ambient particles to produce droplets that are easily collected by inertial techniques. The resulting liquid flow of approximately 0.1 ml min^{-1} is analyzed via Ion Chromatograph (IC) (two Metrohm, 761 compact ICs) for separation and quantification of soluble aerosol ionic chemical components. With appropriate columns, in a 4-minute duty cycle the following species are separated and quantified: Li^+ , Na^+ , NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-} . A more detailed instrument and method description is given in *Weber et al. [2001]* and *Orsini et al. [2003]*. PILS results from these studies are discussed elsewhere [*Lee et al., 2003; Ma et al., 2003*].

The size dependent sampling efficiency for the PILS-IC was determined experimentally by generating monodisperse calibration particles over a range of sizes

using a combination of nebulizer/Differential Mobility Analyzer, Vibrating Orifice Aerosol Generator (VOAG, TSI Inc, St. Paul MN) and quantifying the particle collection efficiency through a fluorimetric analysis. Figure 1 shows that for this study the PILS-IC has a cut size of approximately 1.3 μm aerodynamic diameter. In the following discussions, the PILS-IC measurements are referred to as fine aerosols. Also note that for fine particles the efficiency is 87%. This is accounted for by multiplying all PILS data by 1.15. The causes of the PILS upper size limit and sample losses is discussed in *Orsini et al.* [2003], and a modified instrument that samples particles at near 100% efficiency up to 10 μm aerodynamic diameter is also discussed.

The PILS-IC has been compared to other techniques at a number of ground-based sites for measurements of PM_{2.5} (particulate matter less than 2.5 μm aerodynamic diameter) [*Weber et al.*, 2003; *Drewnick et al.*, 2003; *Hogrefe et al.*, 2003; *Orsini et al.*, 2003].

Integrated filter measurements by Georgia Tech were also periodically conducted on the P3-B for some of the local missions during TRACE-P to provide an in-situ comparison of the PILS performance. This filter system shared the same sampling inlet and sampling line with the PILS-IC; the 30 l min⁻¹ sample flow was split evenly between filter and PILS. Only one filter measurement was made per flight on 6 out of 24 TRACE-P flights. The filters were extracted with DI-water following the flight and measured by the PILS- ICs mounted in the aircraft.

During sampling, ram air heating and heat transfer from the cabin to the sample during transport to the instrument will result in particle heating and possible loss of semi-volatile aerosol components. For the ionic compounds measured here, this will most

likely result in an under-measurement of nitrate and the ammonium associated with nitrate. Measurements show that the difference between sample and ambient temperatures were typically about 10°C at low altitudes and 35°C at higher altitudes making volatility losses most severe during higher altitude measurements.

To estimate how representative the measurements are of the ambient aerosol, inlet and sampling transmission efficiencies are estimated. The PILS measurements on the C-130 and P3-B were from different inlet designs, both sampled isokinetically. The P3-B used a solid diffuser cone to slow the flow, similar to the inlet described by *Porter et al.* [1992], but in this case the inlet tip was shrouded. The C-130 employed a low turbulence inlet (LTI) [Seebaugh and Lafleur, 1996] in which much of the flow is removed at the diffuser wall to reduce turbulence. For particles smaller than $\sim 1 \mu\text{m}$ diameter both inlets have near 100% transmission efficiencies, however, for larger particles the transmission efficiency of the solid diffuser inlet (P3-B) decreases below 100% and the C-130 LTI transmission increases to above 100%. The two inlets have been characterized and compared in a separate study and a report is available at http://saga.pmel.noaa.gov/aceasia/platforms/lt_inlet/report.html.

Particle losses during transmission from inlet to PILS are also estimated by considering losses due to gravitational settling, diffusion, inertial deposition in bends and flow splitters (various formulas can be found in *Willeke and Baron*, [1993]). For both the P3-B and C-130 PILS the $1 \mu\text{m}$ particle transmission efficiency is calculated to be better than 98%.

University of New Hampshire (UNH), Integrated Filter: NASA DC-8

A dual-inlet aerosol sampling system was used by the University of New Hampshire to measure particle chemical composition by filtration from the NASA DC-8 aircraft. One of the inlets was used to expose a 90mm-diameter, 2 μ m pore-size Teflon filter (Gelman Zefluor) for the determination of soluble ionic species concentrations. The other was used to sample radionuclides. The inlets were forward facing solid diffuser designs that sampled isokinetically at several hundred standard liters per minute, with no intentional upper size restriction. The filter was located in the sample line near the entrance into the aircraft cabin to minimize particle transmission losses, and the sample was not denuded of possible interfering gases. After sampling, the filters were placed in a clean bag and heat-sealed, and then placed in a cooler at -20°C for storage. The soluble aerosol ions were determined after aqueous extraction with subsequent ion chromatographic analysis. For a more detailed description, see *Dibb et al.* [1996, 1999].

University of New Hampshire (UNH), Mist Chamber – Ion Chromatograph (MC/IC): NASA DC-8

UNH also deployed a mist chamber coupled to dual anion ICs (MC/IC) to measure fine sulfate particles with median time resolution of 130 seconds. Particles and gases are collected in the mist chamber through scrubbing by a water droplet mist created by accelerating sample air to a high velocity through a nozzle that aspirates ultra pure water [Talbot et al., 1997]. A 25-ml reservoir of water is contained within the mist chamber vessel as the collection liquid, and a Teflon filter at the top of the mist chamber refluxes the mist back into the reservoir. Two mist chambers operate alternately between

collection and analysis cycles to ensure continuous sampling. Sample air is not denuded prior to the measurement since this would interfere with other gas measurement.

A heated glass-coated manifold maintained at approximately 40°C was used to bring ambient air to the instruments. Volumetric airflow was maintained at a nearly constant flow through the manifold (1,500 l min⁻¹) leading to a residence time of about 0.2 seconds. The mist chambers sub sampled the ambient air coming from this manifold through a tube positioned 90° to the airflow. Outside the aircraft, the sample inlet consisted of a tube also positioned 90° to the aircraft. Diffuser and venturi pumps were also added to help maintain flows at various altitudes. This sampling arrangement was designed to exclude a majority of super-micron aerosols and the calculated median upper particle size cutoff is estimated to be 2.7 µm aerodynamic diameter [Scheuer *et al.*, 2003].

The aqueous samples collected by the mist chambers were removed by computer controlled syringe pumps (Kloehn 50300), and injected into custom fabricated ion chromatographs employing sample preconcentration (Dionex TAC-LP1). More details on the analytical method are given in Scheuer *et al.* [2003].

University of Hawaii, Multi-Orifice Impactor (MOI): NSF C-130

A Multi-Orifice Impactor (MSP, St Paul MN) deployed on the C-130 by the University of Hawaii collected particles for size-resolved measurements of aerosol chemical composition. Five stages with un-greased aluminum foil substrates and cut sizes of 5, 1.4, 0.77, 0.44, and 0.26 µm were followed by a 1 µm pore-size Gelman Zefluor after filter. The aluminum substrates were extracted with 10 ml of the weak acid solution with manual agitation, and the filter was placed in a micro clean polyethylene

bag and extracted using 1 ml of ethanol (to wet the filter) and 9 ml of weak acid solution (10^{-5} M trifluoroacetic acid) in an ultrasonic bath. All extracts were analyzed within 1-3 days after the research flight with Dionex ICs according to the procedures described by Huebert *et al.* [1998]. The MOI sampled from an LTI identical to that used by the PILS, but located on the other side of the aircraft.

The MOI data set used in this comparison has been corrected for sampling due to the following artifacts: 1) LTI large particle enhancements (this does not effect particles smaller than 1 μm diameter and do not affect this comparison), 2) losses in the MOI itself, and 3) the bounce of large particles (especially dry dust) from their intended stage to the backup filter. This corrected data set is constrained by the total aerosol sampler (TAS) data, and also involves a variety of assumptions.

3. SAMPLING SITES

TRACE-P and ACE-Asia both focused on the region of eastern Asia and the western Pacific. The two NASA TRACE-P aircraft operated out of Hong Kong, P.R. China (22.3°N, 113.92°E) and Yokota Air Force Base, Japan (35.76°N, 139.92°E) during February through April 2001, however they generally investigated different regions. These two operational bases were well situated to sample Asian outflow over the full range of latitudes from 10°N to 50°N. The intensive field study was mainly within the area of 5° -45°N, 110°-155°E. Three separate intercomparison flights between the NASA aircraft were conducted in three different locations: Guam, Japan, and Hawaii, resulting in a total of 2.5 hours of close-proximity measurements. The flight tracks for these flights are shown in Figure 2.

One of the major research aircraft involved in ACE-Asia was the NSF/NCAR C-130. The intensive field study portion of this experiment was based from Iwakuni Marine Core Air Station (MCAS), Japan (34.08°N, 132.14°E) from March 23, 2001 to May 9, 2001, with an operational range from 20° to 45°N, and 120° to 145°E. At the end of the TRACE-P and the beginning of the ACE-Asia campaign, two intercomparison flights were made between the P3-B and C-130 on March 31, 2001 and April 1, 2001. These flight tracks are also shown in Figure 2.

The most extensive set of comparisons can be made between the MOI and PILS-IC since both were located on the C-130, and both were operational for most of the ACE-Asia experiment. No intercomparison flights were conducted between the NASA DC-8 and the NSF C-130, thus these data are not compared.

4. RESULTS AND DISCUSSIONS

Comparison Between P3-B PILS-IC And Georgia Tech P3-B Filter

Filter measurements were made on the P3-B by Georgia Tech for some of the local missions during TRACE-P in order to test the PILS-IC's performance during the field study. Only sulfate is compared since it is the most straightforward ionic species to measure by filtration and it is less susceptible to sampling artifacts than other ionic components, including interferences from gases (sample air was not denuded), and sulfate is mainly associated with fine particles (PILS-IC only measures fine sulfate, whereas the filter measures total sulfate). The split between filter and PILS was made at the entrance to the PILS, and the PILS-IC's were used during aircraft downtimes between flights to analyze the extracts. From this comparison, shown in Figure 3, PILS-IC sulfate generally recorded about $96 \pm 11\%$ of the filter sulfate. Although this comparison can

test neither the IC calibration nor the inlet loss and sampling loss because the same IC was used for analysis and the air flow was only split at the instrument rack, it does provide some evidence of the airborne PILS's quantitative performance and precision for collecting particles into the liquid for analysis.

As seen on Figure 3, the above statistical calculation is based on a linear regression slope and 95% confidence bounds. In the discussion below, most of the statistical calculations are based on this method, unless specified. A Deming linear regression is used to perform a least-square fit by minimizing the distance of both x and y variables to the fit line [Deming, 1943]. For the P3-B PILS and DC-8 measurement intercomparison, the statistical calculation is based on the relative difference \pm standard error (standard deviation/square root of N) instead of the linear regression method due to the limited data points for intercomparison.

Comparison Between PILS-ICs On Two Separate Aircraft

Two coordinated flights were made between the C-130 and P3-B. During these formation flying events, the aircraft maintained similar altitudes but remained approximately 50 meters apart for horizontal legs. The C-130 PILS-IC system was operational only for one of the two intercomparison flights due to a delay in shipment of supplies to the base of operation. Figure 4 shows the temporal intercomparisons of the ionic species measured during intercomparison flight I on March 31, 2001, and Figure 5 shows the scatter plots. Similar to many of the flights in this region, interception of a polluted layer situated in the boundary layer below a temperature inversion near 2 km altitude accounts for much of the observed temporal variation.

These comparisons show that for sulfate, nitrate, ammonium, sodium and chloride, the two separate aircraft measurements track well and are highly correlated with an r^2 of 0.95 for sulfate and nitrate, 0.91 for ammonium, 0.84 for sodium, and 0.95 for chloride. Calcium, magnesium, and potassium are not compared since calcium and magnesium were near or below the Limits Of Detection (LOD) of approximately 20 ng sm^{-3} (standard m^{-3} , $T=20^\circ\text{C}$, $P=1$ atmosphere), and for this flight the C-130 PILS was not set up to measure potassium. Although highly correlated, for sulfate, nitrate and ammonium, the P3-B PILS is consistently lower. Based on linear regressions and 95% confident intervals, P3-B sulfate, ammonium, and nitrate were lower by $10\pm5\%$, $11\pm8\%$, and $18\pm5\%$, respectively (see Figure 5). As an alternative to a regression analysis, the calculated mean difference in these measurements relative to the C-130 PILS for sulfate, ammonium, and nitrate is $33.9\% \pm 3.3\%$ (mean difference \pm standard error), $31.9\% \pm 3.7\%$, and $24.9\% \pm 3.5\%$, respectively, which is an average difference of 1.45, 0.38, 0.18 $\mu\text{g sm}^{-3}$. The ammonium to sulfate molar ratio in the low-level runs are similar on both aircraft at approximately 1.7.

Sodium and chloride do not follow the systematic differences of sulfate, ammonium, and nitrate. Instead of being lower, the P3-B sodium is consistently higher by a factor of 2, and P3-B chloride is 1.3 times of that of the C-130. Both are based on linear regression slopes. The sodium and chloride trends are as expected; concentrations are highest at low altitudes near the ocean surface. Chloride to sodium molar ratios for the P3-B are on average 1.108 ± 0.038 , which is closer to Cl^-/Na^+ molar ratio in seawater (1.164) than that of C-130, which were 1.769 ± 0.11 . It is common to see Cl^- deficits due to H_2SO_4 and HNO_3 reactions with wet sea salt aerosol. Dust may also contribute to the

sodium concentration, which would also make the Cl^-/Na^+ ratio lower than the sea-water ratio. Thus, the P-3B Na^+ data appear more reasonable than that of the C-130 and the C-130 PILS either overestimated Cl^- or underestimated Na^+ during this flight.

Comparing C-130 PILS data with the MOI corrected data integrated up to 1.4 μm also suggests that the C-130 PILS under measured the Na^+ concentration (these types of comparisons are discussed in more detail in a following section). The C-130 PILS Cl^- is $102 \pm 15\%$ of that of MOI with r^2 of 0.67 while the C-130 PILS Na^+ is only $\sim 71 \pm 22\%$ of that of MOI and with a lower r^2 of 0.48 (see Table 2). Also, the MOI Cl^- to Na^+ molar concentrations are much better correlated than the PILS Cl^- to Na^+ . These comparisons are generally consistent with an under measurement of C-130 PILS Na^+ .

Although the difference between the PILS measurements on the two separate aircraft is within the combined experimental error, estimated at 30%, for sulfate, nitrate, and ammonium it is systematic. Furthermore, this is larger than estimates of PILS precision made through side-by-side measurements of identical PILS instruments sampling from the same inlet in urban Atlanta. For sulfate concentrations between 4 and 10 $\mu\text{g m}^{-3}$, with 99% confidence, the precision is expected to be within 0.4 $\mu\text{g m}^{-3}$ [Orsini *et al.*, 2003], significantly less than our observed difference. The systematic differences are likely due to issues relating to the ICs, or from losses during airborne sampling. Systematic IC errors include calibration errors or uncertainties in peak integration. Because both sodium and chloride are the first to elude from the columns, and these chromatograms have been compressed as much as possible to enable fast measurements, peak integration at low concentrations for sodium and chloride are the most uncertain of all species. This may be the dominant error for these ions. One systematic difference

between the two aircraft is the inlet sampling and particle transmission efficiencies from inlet to instrument. The systematically lower concentrations of sulfate, nitrate, and ammonium on the P3-B are consistent with less efficient particle sampling compared to the C-130; the C-130s low turbulence inlet (LTI) does have higher passing efficiencies than the P3-Bs solid diffuser inlet. Differences in sampling efficiencies are also consistent with the nonzero intercept on the scatter plots of Figure 5 which can be explained by the C-130 PILS recording measurable concentrations while the P3-B PILS measurement was below the detection limit.

Comparison Between P3-B PILS-IC And DC-8 Integrated Filter And DC-8 MC/IC

Comparison of the aerosol bulk chemical composition measurements on the P3-B and DC-8 by the PILS/IC, MC/IC and integrated filter is complicated mainly by differences in the range of particle sizes measured by each instrument, and also by differences in particle sampling and transmission efficiencies. An analysis of the aerosol number size distribution measurements in the regions where the P3-B and DC-8 performed the intercomparison flights, shows that the differing measurement ranges of these instruments is likely the main reason for the observed discrepancies [Moore *et al.*, 2003]. The PILS-IC's upper measurement size is $\sim 1.3 \mu\text{m}$ (see Figure 1), the DC-8 mist chamber/ion chromatograph (MC/IC) upper measurement size is theoretically estimated at $2.7 \mu\text{m}$, and the upper size range of DC-8 integrated filter is determined by the inlet and sample transmission efficiency and is not actually known, but likely approximately $3 \mu\text{m}$.

Before comparisons are made between P3-B PILS-IC, DC-8 MC/IC, and integrated filters for the three intercomparison flights between these aircraft, a broad

comparison is made by looking at the spatial distribution of sulfate, ammonium, nitrate, and calcium measured by each aircraft during the TRACE-P period of intensive measurements. Based on the P3-B and DC-8 flight tracks, the 120°-130° longitude and 0°-40° latitude region is selected for comparison since this area has the highest data density for both the P3-B and DC-8. The data in this longitude range are binned by 5°-latitude and by 0.5 km-altitude resolution. Since the P3-B has a ceiling of ~7 km, the DC-8 data which were obtained at altitudes higher than 7 km are not considered. The calculated median concentration is displayed for each bin. Because the integrated filter also measures coarse particles, we use Non Sea-Salt (NSS) -sulfate for filter sulfate based on the DC-8 integrated filter sodium data and an average sea water $\text{SO}_4^{2-}/\text{Na}^+$ molar ratio of 0.0603. Note that coarse sulfate and nitrate can also be associated with mineral dust as calcium sulfate and calcium nitrate, and will bias the comparisons of filter nss-sulfate and nitrate to higher concentrations compared to the fine measurements of the particle-into-liquid sampler (PILS) and mist chamber (MC). Based on the DC-8 integrated filter measurements, *Jordan et al. [2003]* report that significant levels of calcium were recorded throughout the region. Figure 6 shows the spatial distributions of selected particulate ionic compounds recorded by the different measurements for longitudes between 120°-130°.

For sulfate, the PILS, integrated filter, and MC/IC data, all three show a similar pattern. Highest concentrations are observed mainly near the surface and in the latitude range 25°-35°N. For ammonium there is no MC/IC measurement, however, both the PILS and filter show a similar trend of decreasing concentration with altitude, although there are clearly some differences in the measurements. For example, the PILS shows

higher concentrations at 2.5 to 3 km asl at 20 to 25°N latitude. This is due to the P3-B's encounter with a biomass-burning plume (discussed in *Ma et al.*, [2003]), which was not sampled by the DC-8.

Molar ratios of ammonium to sulfate are also compared in Figure 6. In order to study the distribution of $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios, only data with SO_4^{2-} higher than 200 pptv are included to limit extreme values when the sulfate concentrations are low. Clearly, the DC-8 integrated filter shows much lower molar ratios than the PILS, which generally records a more neutral aerosol. A number of factors may contribute to the discrepancy; one is from measurements in unique plumes not sampled by both aircraft. For example, in the P3-B biomass plume region, high concentrations of other acidic species with associated NH_4^+ , such as NO_3^- (also plotted in Figure 6), account for a $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio that is much higher than 2. Another cause may be explained by the presence of coarse mode CaSO_4 that is not detected by the PILS. Filter measurements of coarse sulfate associated with calcium will lower the $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios. Figure 6 suggests that both DC-8 calcium and nitrate have a similar pattern and are much higher than the PILS calcium and nitrate measurements (note differences in color scales between PILS and DC-8 filter) suggesting that a significant fraction of these compounds may be associated with coarse mode particles. These often are also regions of high sulfate and ammonium, (e.g., note a surface layer in the region of 25°-35°N latitude), resulting in an integrated filter $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio lower than neutral.

More direct comparisons are possible between the PILS, MC/IC, and integrated filter during periods of formation flying. On three occasions during the TRACE-P experiment, the NASA P3-B and DC-8 flew in formation. For the first two of the three

intercomparisons between the P3-B and DC-8, the instruments were operated in their normal mode, however, on the third intercomparison, a 1 μ m cut MOI plate was installed upstream of the PILS-IC to provide a sharp upper size limit. Since only sulfate was measured by all three techniques, only this species is compared. The filter data is converted to nss-sulfate based on measured Na⁺ concentrations to remove the contribution of coarse mode sea salt particles. Again interferences from coarse sulfate associated with calcium will bias the filter to higher measurements than the measurements of fine sulfate by the PILS and MC/IC. Figure 7 shows the sulfate measurements and the aircraft's altitude. Horizontal error bars on the plots show the integration period for each measurement, and vertical error bars represent estimates of each techniques measurement uncertainty.

For intercomparison I, Figure 7(a) shows that the DC-8 filter total-sulfate agrees with the PILS-IC sulfate at low altitude with a relative deviation of $13\% \pm 3\%$, whereas the MC/IC fine sulfate was more than 40% lower than PILS and Filter. At the higher altitude segment of this comparison, the PILS and MC fine sulfate measurements are in better agreement (in terms of the absolute concentration difference) than at the low altitudes. In this region the MC/IC was on average 41% lower than the PILS (ie. PILS was on average 68% higher than MC/IC), which could be due to the lower measurement accuracy when the concentrations are approaching the LOD or ~ 3 pptv for both the PILS and the Mist Chamber. Calculation of the DC-8 NSS-sulfate based on the filter Na⁺ predicts no nss-sulfate. This may indicate a problem with the DC-8 sodium measurements during this period, or that the DC-8 NSS sulfate was very low and below the filter detection limit.

Figure 7(b) shows the results of the second comparison flight. This flight was conducted at a constant altitude of approximately 5.2 km asl. As expected, at this altitude there is little Na^+ present and thus most filter sulfate is NSS (i.e., the DC-8 filter sulfate and DC-8 NSS sulfate are nearly identical). The DC-8 fine sulfate (MC/IC) generally agrees with the filter measurements with relative deviation of $30 \pm 8 \%$. PILS sulfate, however, has the same trend but was typically $\sim 45\%$ of the filter sulfate and $51 \pm 4\%$ of the DC-8 fine sulfate. Although little NaCl aerosol was detected at this altitude, there was dust. Calcium concentrations recorded by the DC-8 filter were as high as 1165 pptv, ($1.9 \mu\text{g sm}^{-3}$) and averaged PILS calcium was about 25% of that of the DC-8 filter. The discrepancy between the PILS and DC-8 during intercomparison II could be caused by the PILS-IC not function properly at high altitude, real difference in the sulfate measured by the two aircraft, or the PILS not measuring coarse sulfate. No consistent PILS under measurement at higher altitudes has been observed based on the comparison between the C-130 PILS and C-130 MOI (discussed later). For example, for PILS sulfate data higher than $0.2 \mu\text{g sm}^{-3}$, the averaged PILS/MOI mass ratio was 0.98 ± 0.04 (mean difference \pm standard error) for data collected lower than 2 km altitude, and was 0.99 ± 0.07 for data obtained higher than 2 km altitude. The spatial differences in sulfate sampled by the two aircraft are likely minimal since CO and ozone measured by the two aircraft were within 4 %. One plausible explanation is the presence of CaSO_4 . The mean Ca^{2+} concentration measured by the PILS for the leg was 220 pptv, and the filter mean Ca^{2+} was 810 pptv. The difference between integrated filter and PILS sulfate ranges between 117 and 324 pptv, which is less than the differences in Ca^{2+} concentrations of 580 pptv. Based on a mass estimate from optical particle counter (OPC) size distribution measurements, *Moore*

et al. [2003] suggests that the difference between the measurements in this case is due to the association of some of the ionic species (including sulfate) with particles larger than the PILS cut size. Because the mist chamber does not measure Ca^{2+} , the effect of calcium on its measurement cannot be determined..

For intercomparison III, shown in figure 7(c), MC/IC tracked with the integrated filter ($r^2 = 0.64$) with a relative difference of $30\% \pm 5\%$. PILS $1\mu\text{m}$ -sulfate tracked with DC-8 mist chamber sulfate fairly well at both high and low altitude with an r^2 of 0.78 and relative difference of $39\% \pm 6\%$. It also tracked with DC-8 filter NSS sulfate with a relative difference of $33\% \pm 7\%$. At the highest altitudes measured at the beginning of this intercomparison, the lower concentrations recorded by DC-8 filter could be from the combination of a short integration time within a pristine region, leading to sample concentrations near detection limits. There was apparently little interference from coarse CaSO_4 during period for this comparison since the average calcium concentration recorded by the DC-8 integrated filter is only approximately 123 pptv compared to 810 pptv measured during intercomparison II discussed above.

Comparison Between C-130 PILS-IC And C-130 MOI

As has been pointed out, differences in the size of particles measured by the various bulk sampling techniques makes the instrument comparison ambiguous. However, this can be accounted for when comparing the PILS and MOI since the MOI provides size-resolved measurements. In the following comparisons, the MOI is integrated for particle diameters up to $1.4\mu\text{m}$, the upper detection limit of the PILS (see Figure 1).

Results from the linear regression comparisons are summarized in Table 2 and scatter plots with linear regression fits are shown in Figure 8. Overall, throughout the ACE-Asia study, the mean of the total ionic mass measurements of these two methods were within 10%. These results tend to confirm that the PILS deployed in these studies had an upper size limit near 1.3 μm , as determined from laboratory calibrations, since integrating the MOI over different size ranges generally increases the discrepancies. It is noted that although the MOI measured oxalate while PILS-IC did not, this has little effect on the intercomparison since oxalate only comprised less than 1% of the total ionic mass measured by the MOI. The scatter plot of the sum of ionic masses shows that the measurements are correlated with an r^2 of 0.75, and PILS total ionic mass was about $90.6\% \pm 7.1\%$ (slope and 95% confidence interval) of that of MOI.

The PILS and MOI are also compared for individual ions. The overall PILS/MOI regression slopes for different ionic species ranges approximately between 0.66 and 1.44, with NH_4^+ the lowest at about $65.7 \pm 5.4\%$ and Ca^{2+} the highest at about $144.0 \pm 19.1\%$. The linear correlation coefficients (r^2) between PILS and MOI range between 0.48 and 0.87, with sulfate the highest at $r^2 = 0.87$ followed by calcium at 0.82. The least correlated was sodium at $r^2 = 0.48$.

The differences appear not to be systematically related to the chemical size distributions of the various ionic components. The MOI data show that nitrate and calcium are mostly found on large particles, and sulfate, ammonium, and potassium on fine particles. PILS nitrate and calcium are higher than the MOI, however, PILS potassium is also higher. PILS sulfate is roughly 10% lower than and ammonium is consistently lower than that of MOI.

Assuming that most of the ammonium is associated with sulfate [Lee *et al.*, 2003], one would expect the sampling efficiency of sulfate and ammonium to agree, but in this case the PILS ammonium measurement was consistently lower than sulfate by 20%. The overall PILS $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio is 1.75, which is lower than that of MOI at about 2.01 for particles integrated up to 1.4 μm . A possible explanation is under-measurement of ammonium by the PILS due to volatility loss in the hot drops formed in the instrument, or losses in the liquid phase during transport to the ICs. Alternatively, the result could reflect a MOI over-measurement, possibly from ammonium contamination during manual filter handling within the aircraft and during filter extractions.

4. CONCLUSIONS

Five instruments for measuring fine particle ionic compounds on three separate aircraft are compared to assess the accuracy of airborne measurements of particle chemical composition. The measurements were made as part of the ACE-Asia and TRACE-P experiments conducted in the spring of 2001 to investigate the outflow of Asian pollutants into the Western Pacific. The techniques compared are an integrated filter, a 5-stage Multi-Orifice-Impactor (MOI), an online Mist Chamber (MS) measurement of fine sulfate (diameters less than nominally 2.7 μm), and a Particle-Into-Liquid Sampler (PILS) which measures bulk composition for particles smaller than nominally 1.3 μm .

A comparison between identical PILS operating on two separate aircraft during formation flying for a period of 3 hours were highly correlated with r^2 of 0.95 for sulfate and nitrate, but were systematically different by $10 \pm 5\%$ (95% confidence bounds) for a comparison of 44 measurements. Laboratory side-by-side comparisons of identical PILS

are found to be within 5% [Orsini *et al.*, 2003]. The observed airborne measurement difference may be due to systematic differences in calibrations, or differences in particle sampling efficiencies. Higher concentrations were observed from the PILS sampling from a low turbulence inlet compared to a shrouded solid diffuser inlet. Intercomparisons of these inlets show that for particles increasing in size above 1 μm diameter, there is an increasing enhancement of particles in the low turbulence inlet, whereas the solid diffuser has an increasing loss with size, consistent with the differences observed between the PILS. IC peak integration errors may also be the cause for discrepancies observed between sodium and chloride concentrations.

A comparison is also made between two different instruments sampling from the same aircraft (NSF C-130), but from separate inlets. Comparing a PILS to the MOI integrated over the PILS sampling size range resulted in an r^2 in the range of 0.48 to 0.87 based on approximately 50 comparisons for each of the various ionic compounds. For sulfate, the PILS and MOI were within $14\% \pm 6\%$ and correlated with an r^2 of 0.87. Overall, for the various ionic species measured, the PILS and MOI were within $\pm 44\%$, and the sum of all ionic species measured by each technique was within $\pm 9\%$. These differences between PILS and integrated measurement techniques are similar in magnitude to those observed in ground-based intercomparison studies and thus apparently are mostly due to difficulties inherent with measurements of particle chemical composition.

Comparisons are also made between different measurement techniques on different aircraft. During three separate flights of formation flying between the NASA DC-8 and NASA P3-B for a total of 2.5 hours and over an altitude range of 5 km, the

mist chamber and PILS sulfate concentrations were correlated with r^2 of 0.78, and had an average relative difference of $39\% \pm 6\%$. However, differences were as high as 68% on specific flights. PILS also tracked with integrated filter non-sea salt sulfate with a relative deviation $33\% \pm 7\%$, when there was little influence from coarse mode particles. In these cases, measurement discrepancies are thought to be mainly due to differences in the upper particle-size measurement efficiencies between the various instruments. MC/IC, co-located with the integrated filter on the NASA DC-8, was generally within 30% of the integrated filter. When coarse particles were present (e.g. Intercomparison flight II), the MC/IC tracked the integrated filter better than PILS, which is consistent with a higher cutoff size of the MC/IC ($\sim 2.7 \mu\text{m}$) versus PILS ($1.3 \mu\text{m}$).

These results are consistent with the idea that inlet and transmission issues limit the accuracy of aerosol composition measurements. This is less of a problem when the ambient aerosol is mostly submicron, since those particles are generally sampled and transmitted with near-unit efficiency. However, aerosol components that have significant concentrations of supermicron particles generally exhibited higher levels of disagreement emphasizing the difficulty of making these measurements without artifact. While inlets and transmission lines are also problematic for surface sampling, the difficulties are magnified when sampling from airborne platforms.

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FIGURE CAPTIONS

Figure 1. Laboratory calibration of the PILS sampling efficiency deployed during TRACE-P and ACE-Asia.

Figure 2. Flight tracks for the intercomparison flights during the TRACE-P and ACE-Asia field campaign, February-May 2001.

Figure 3. Comparison between the sulfate mass concentration measurements of the PILS-IC and Georgia Tech integrated filters for TRACE-P local flights. The vertical and horizontal error bars are the estimated measurement uncertainties for PILS and filter respectively.

Figure 4. Intercomparisons of ionic species measured by identical PILS on two separate aircraft during formation flying in the Sea of Japan on 31 March 2001 (a) sulfate; (b) nitrate; (c) ammonium; (d) sodium; (e) chloride.

Figure 5. Linear regressions for (a) sulfate, (b) ammonium, and (c) nitrate, plotted in Figure 4.

Figure 6. Spatial distribution of sulfate, ammonium, $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratio, calcium, and nitrate measured by the P3-B PILS-IC and DC-8 MC/IC and DC-8 integrated filter during TRACE-P, 2001 for the western Pacific region.

Figure 7. Sulfate intercomparisons between the P3-B PILS-IC and DC-8 integrated filter and DC-8 MC/IC during TRACE-P, the horizontal error bar shows the integration time

for each sample, and vertical error bar indicate the estimated measurement uncertainties

(a) Intercomparison I; (b) Intercomparison II; (c) Intercomparison III.

Figure 8. Linear regressions for various ionic species measured on the C-130 PILS-IC and MOI corrected data integrated up to 1.4 μm throughout the ACE-Asia experiment.

Table 1. Summary of aerosol inorganic ionic chemical composition measurement methods and relative parameters during TRACE-P and ACE-Asia campaign, 2001

Aircraft Instrument	Institution	Species measured	Measurement cycle	Inlet	Particle size range
P3-B PILS- IC	Georgia Institute of Technology	SO_4^{2-} , NO_3^- , Cl^- , Na^+ , NH_4^+ , Ca^{2+} , K^+ , Mg^{2+}	4 minutes, continuously sampling	Standard diffuser inlet	Smaller than $1.3\mu\text{m}$
DC-8 Integrated filter	University of New Hampshire	SO_4^{2-} , NO_3^- , Cl^- , Na^+ , NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , $\text{C}_2\text{O}_4^{2-}$	10-20 minutes, only sample at constant altitude	Isokinetic inlet	No intentional restriction
DC-8 MC/IC	University of New Hampshire	SO_4^{2-}	2-4 minutes, continuously sampling	Diffuser inlet	Smaller than $2.7\mu\text{m}$
C-130 PILS-IC	Georgia Institute of Technology	SO_4^{2-} , NO_3^- , Cl^- , Na^+ , NH_4^+ , Ca^{2+} , K^+ , Mg^{2+}	4 minutes, continuously sampling	Low turbulence inlet	Smaller than $1.3\mu\text{m}$
C-130 MOI	University of Hawaii	SO_4^{2-} , NO_3^- , Cl^- , Na^+ , NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , $\text{C}_2\text{O}_4^{2-}$	20 minutes to hours, only sample at constant altitude	Low turbulence inlet	No intentional restriction

Table 2. Summary of the ratios between C-130 PILS-IC and MOI mass concentration integrated up to 1.4 μm for different ionic species measured during ACE-Asia.

Species	PILS/MOI _{corrected} (Dp < 1.4 μm)	
	Ratio	r ²
Total ionic mass	90.6%	0.75
Sulfate	85.7%	0.87
Ammonium	65.7%	0.80
Potassium	138%	0.63
Nitrate	119%	0.71
Calcium	144%	0.82
Chloride	102%	0.67
Sodium	71.0%	0.48

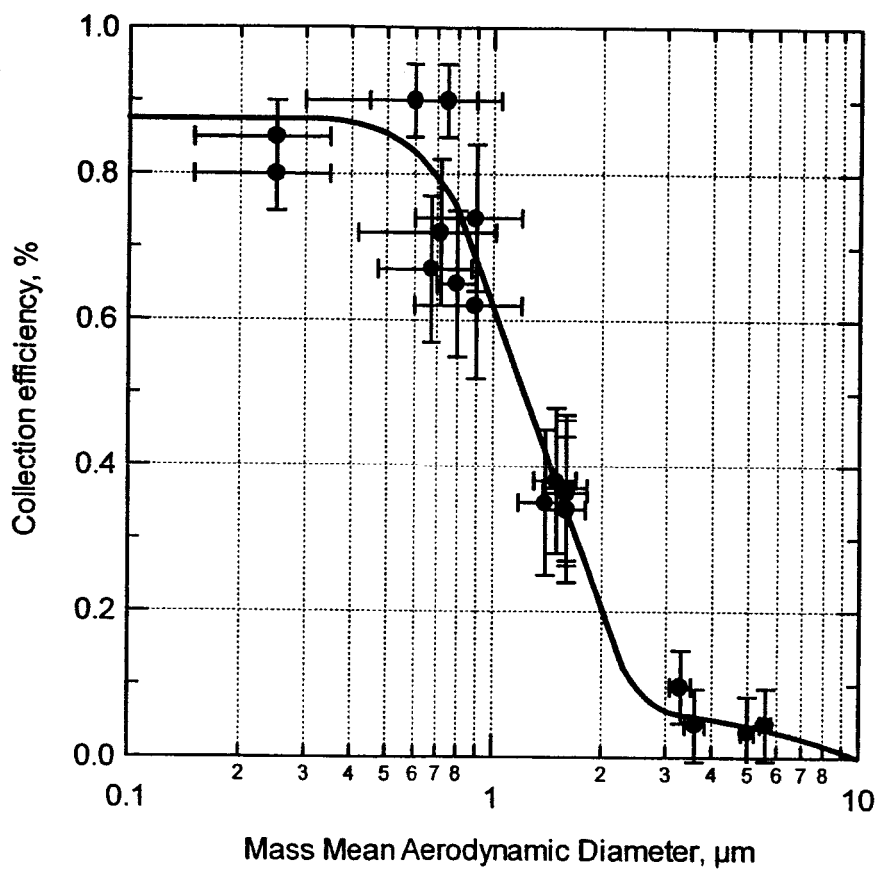


Figure 1. Laboratory calibration of the PILS sampling efficiency deployed during TRACE-P and ACE-Asia.

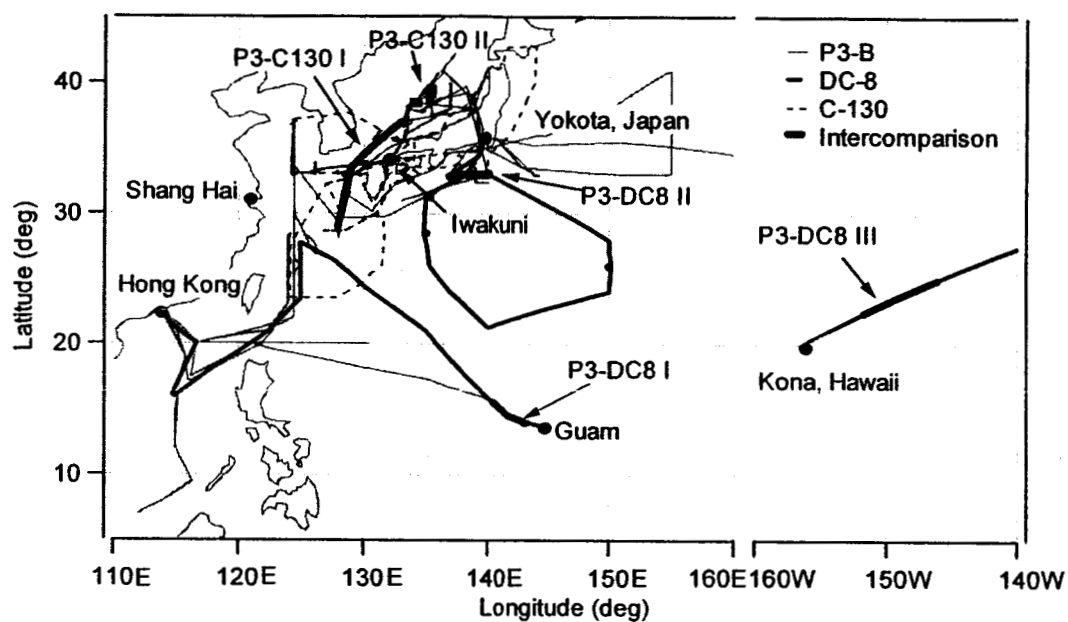


Figure 2. Flight tracks for the intercomparison flights during the TRACE-P and ACE-Asia field campaign, February-May 2001.

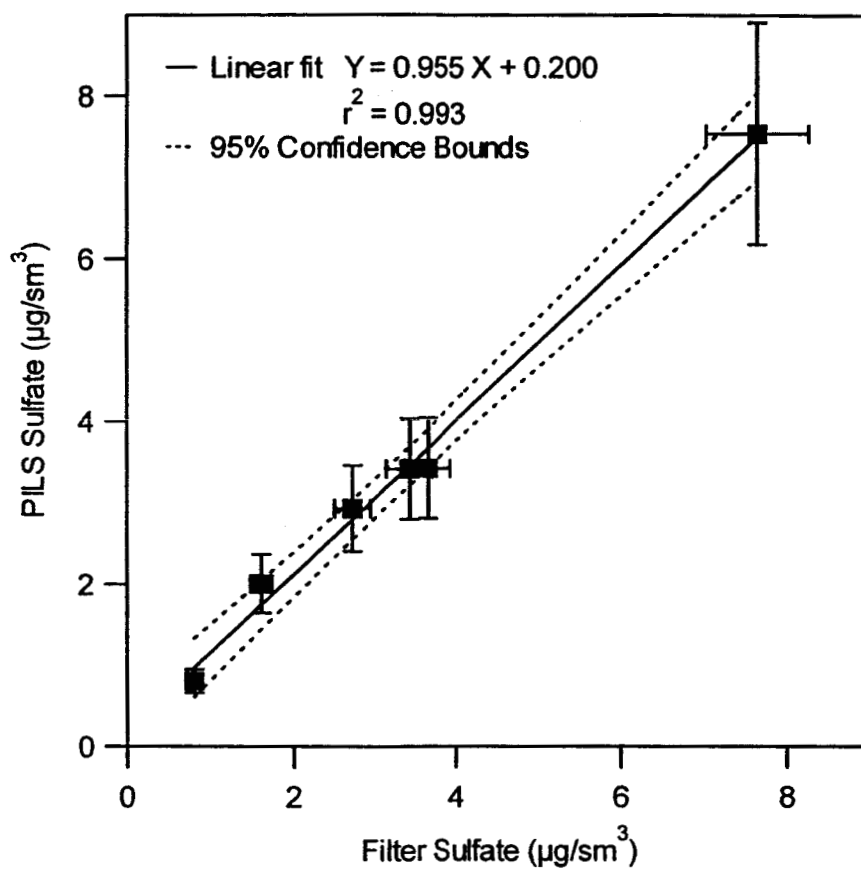
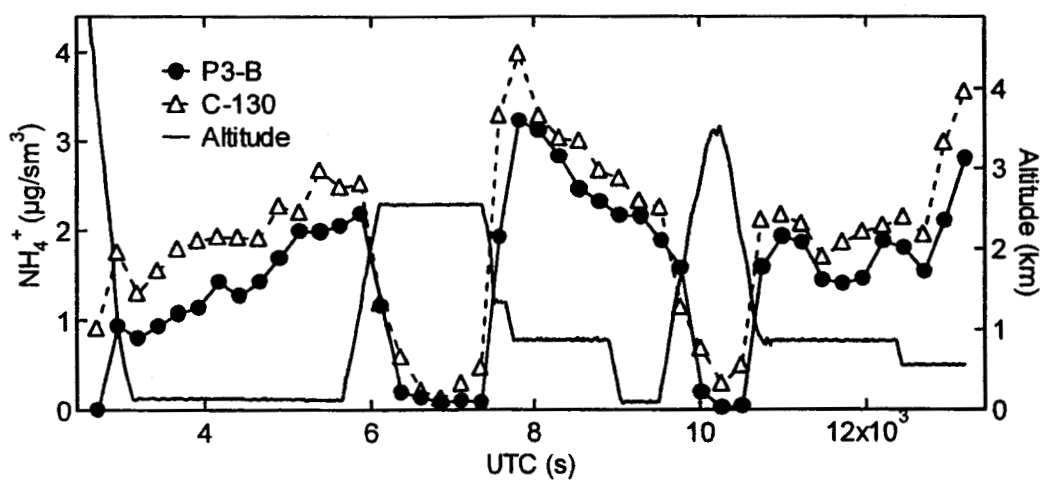
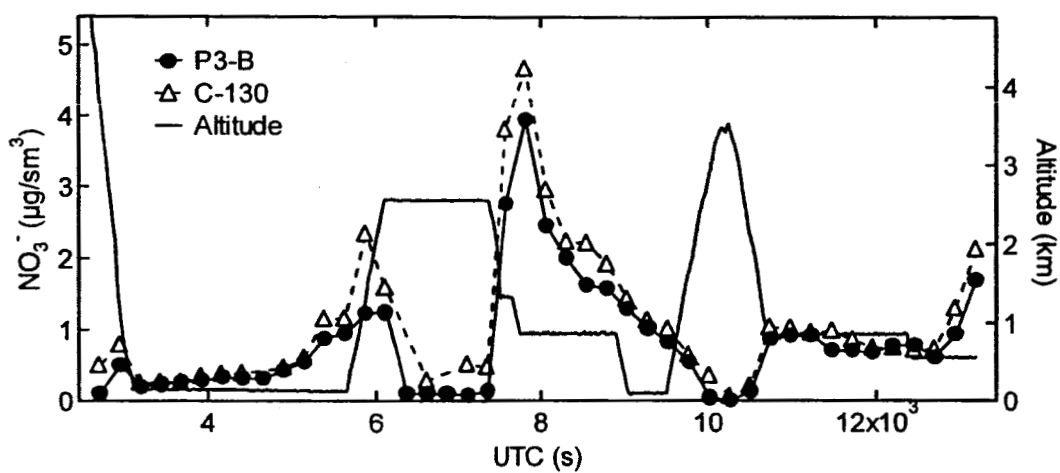
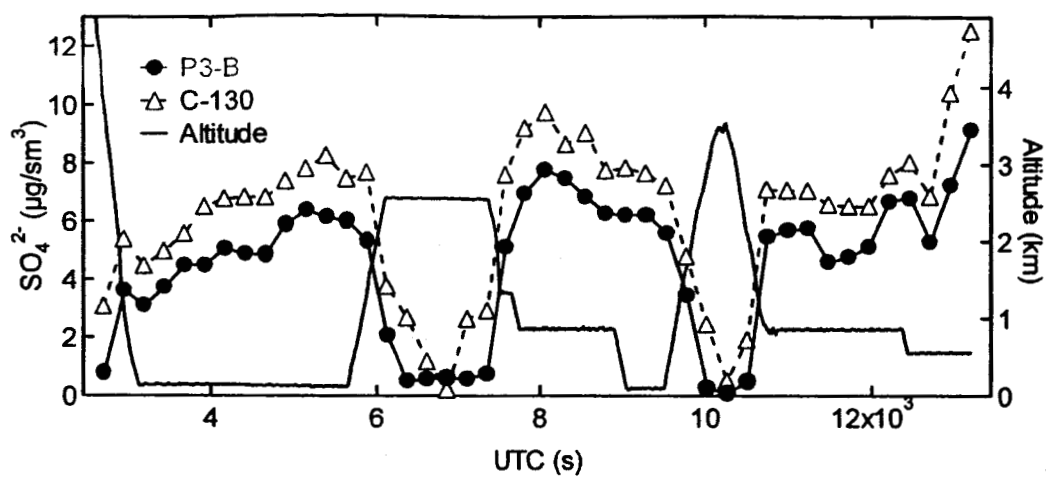


Figure 3. Comparison between the sulfate mass concentration measurements of the PILS-IC and Georgia Tech integrated filters for TRACE-P local flights. The vertical and horizontal error bars are the estimated measurement uncertainties for PILS and filter respectively.



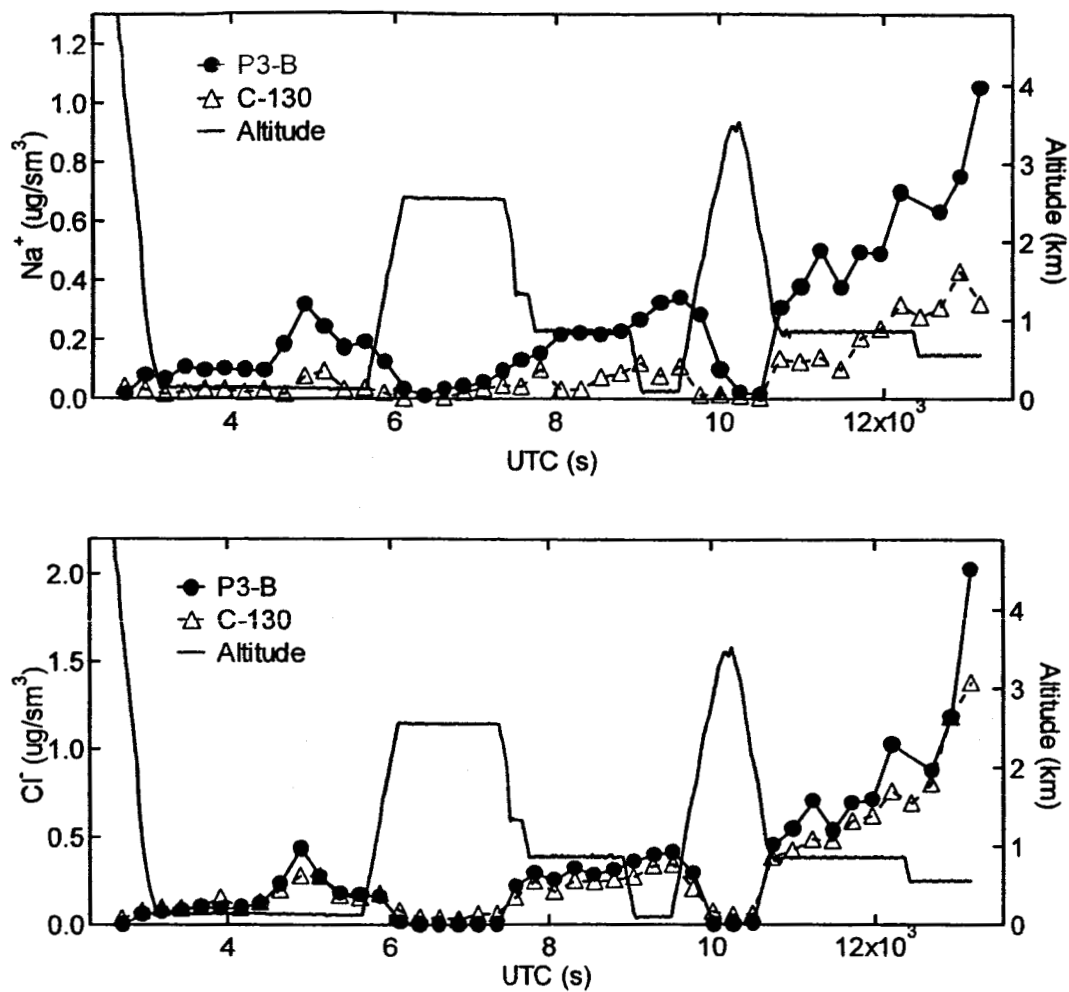
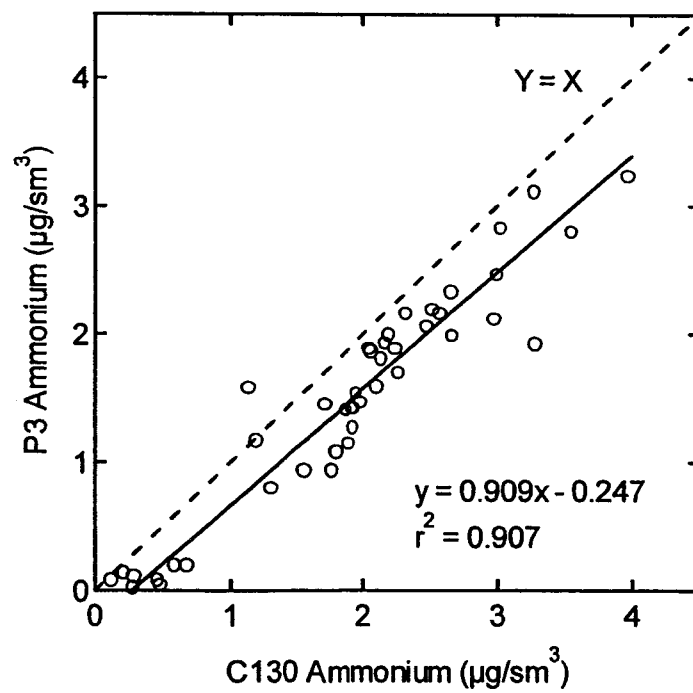
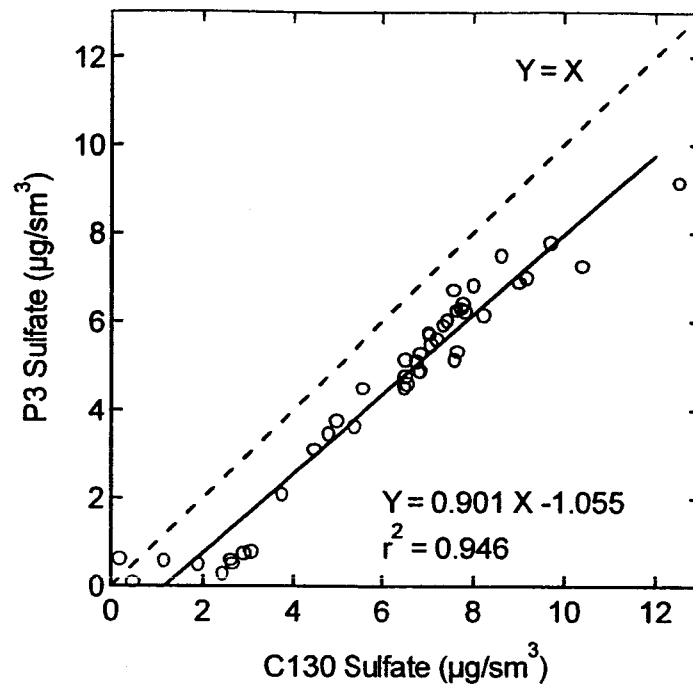


Figure 4 Intercomparisons of ionic species measured by identical PILS on two separate aircraft during formation flying in the Sea of Japan on 31 March 2001 (a) sulfate; (b) nitrate; (c) ammonium; (d) sodium; (e) chloride.



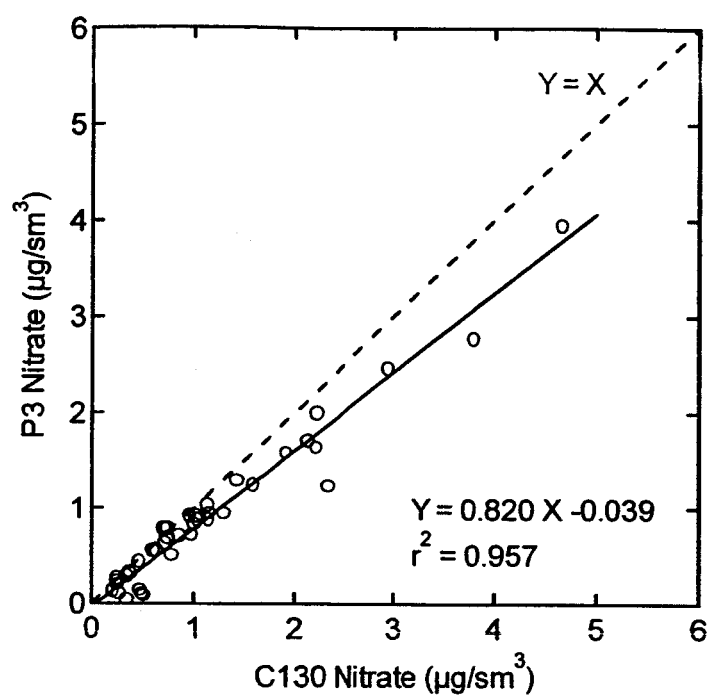
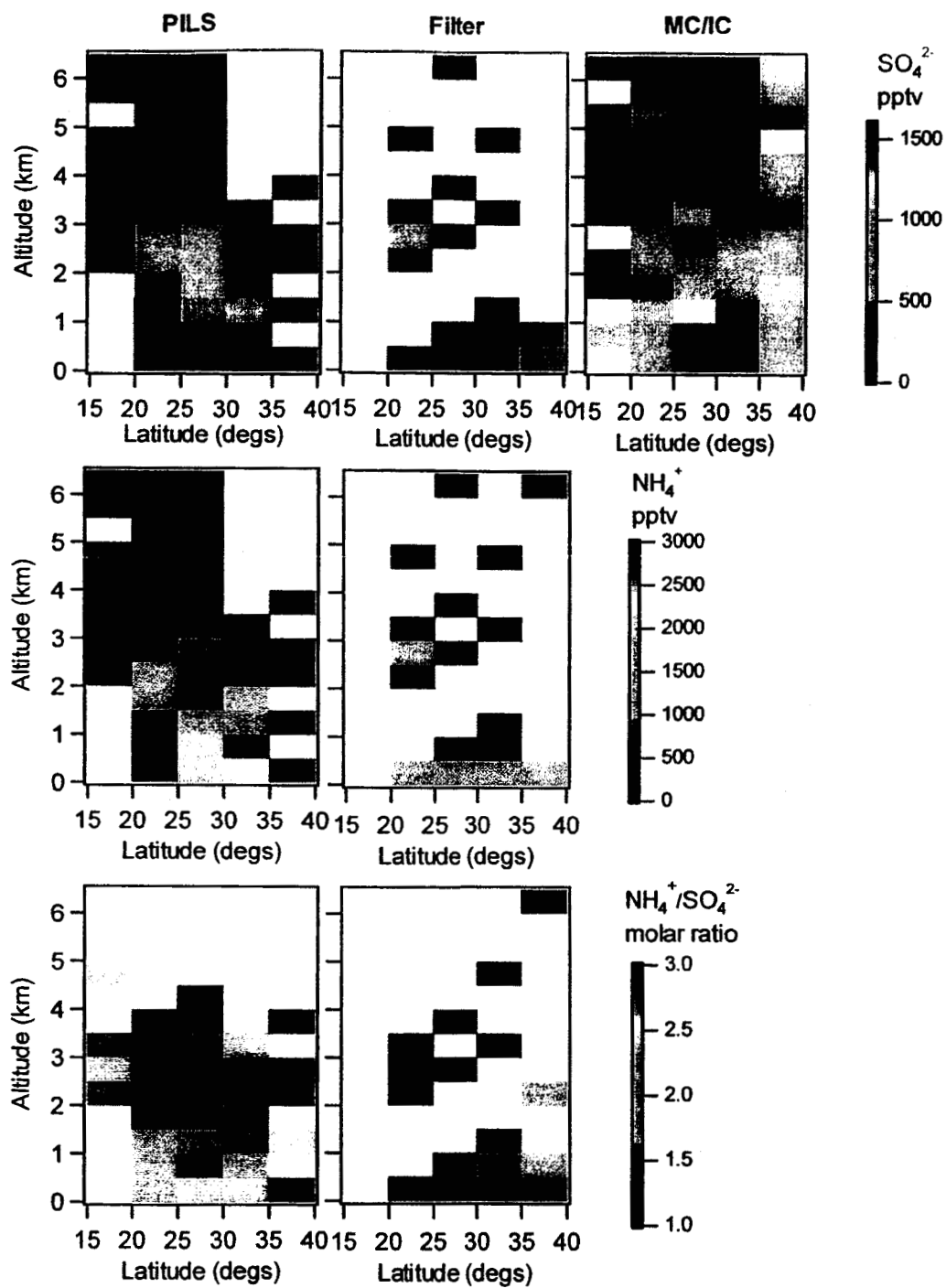


Figure 5. Linear regressions for (a) sulfate, (b) ammonium, and (c) nitrate, plotted in Figure 4.



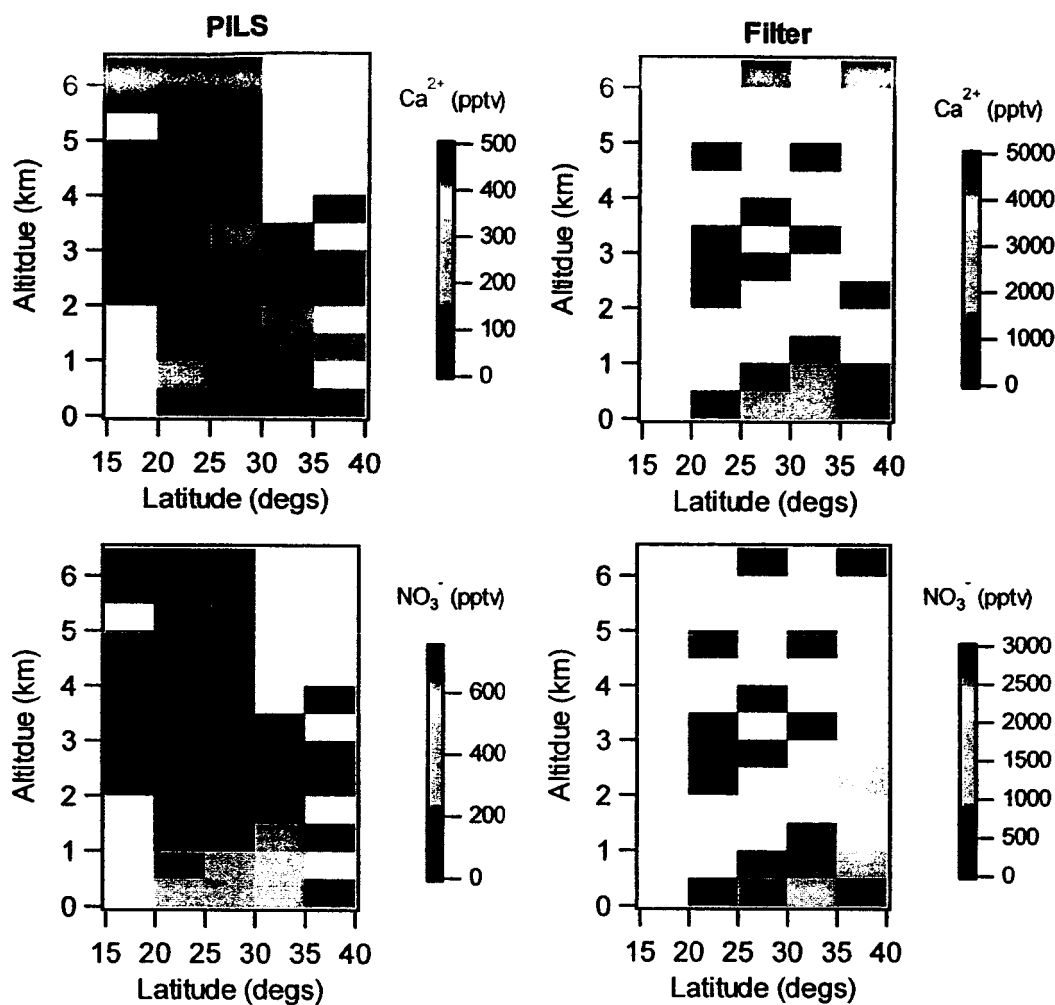
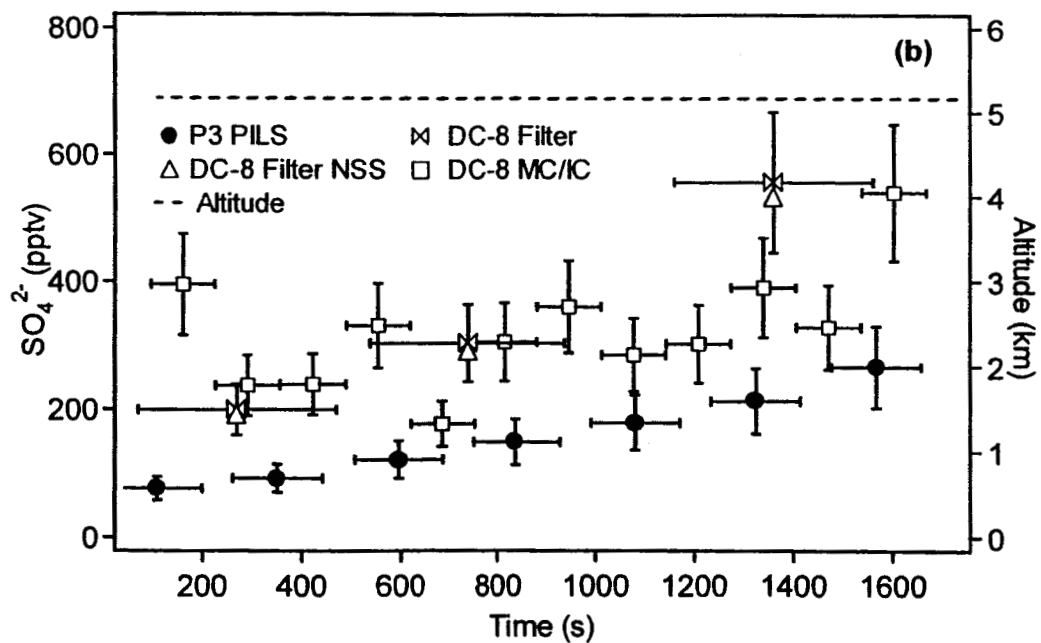
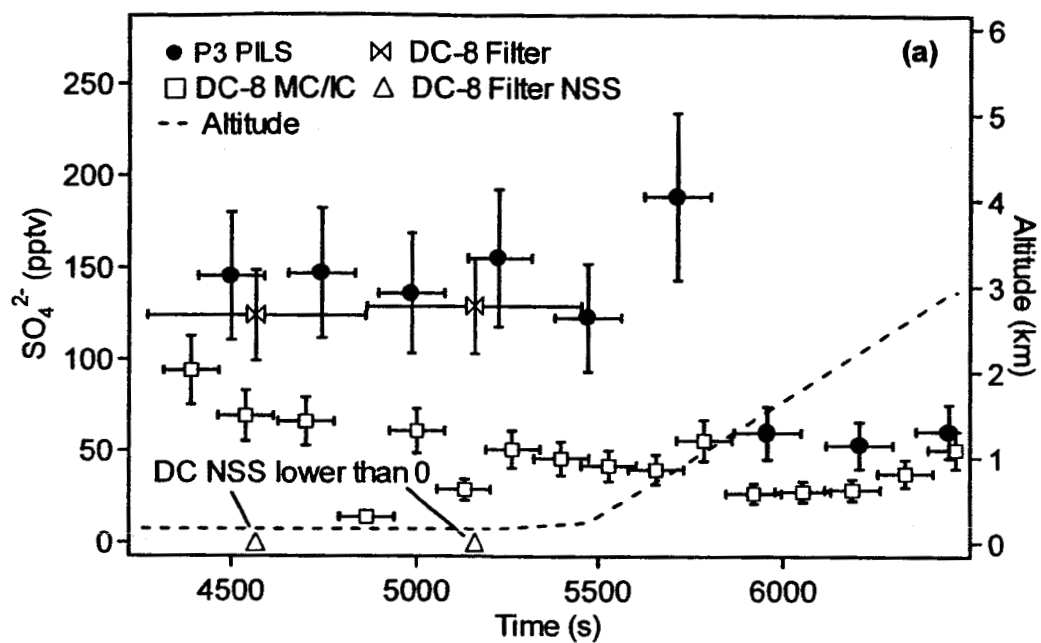


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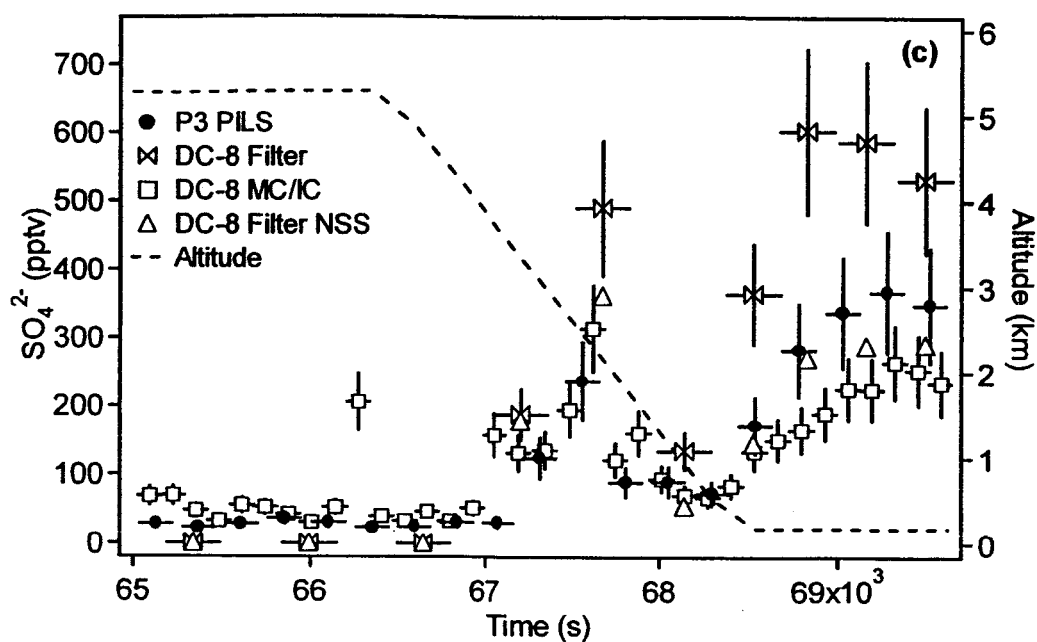
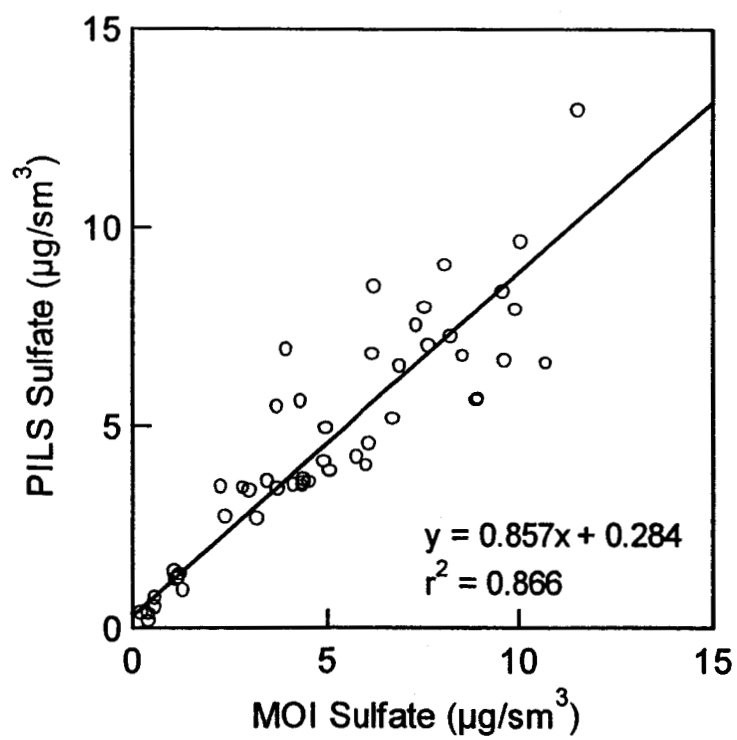
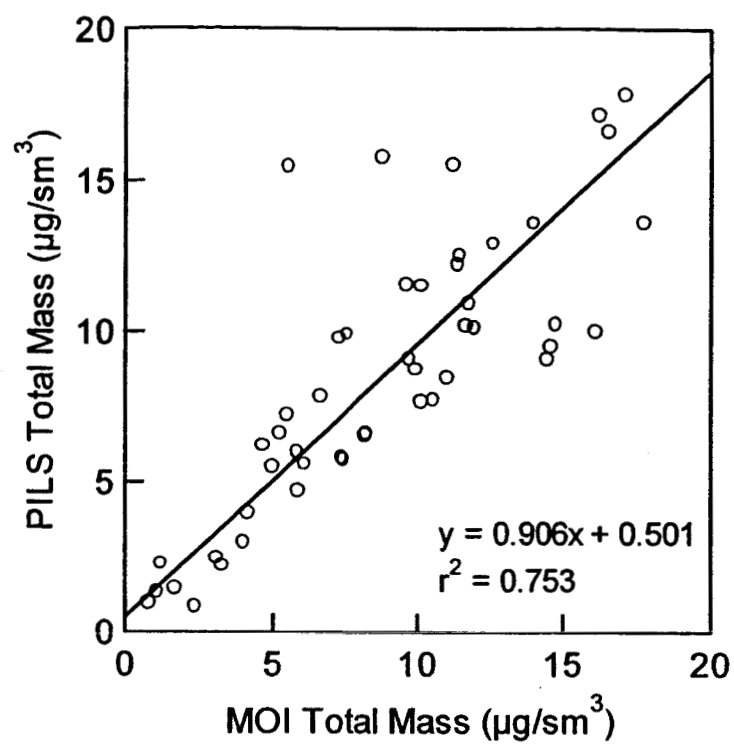
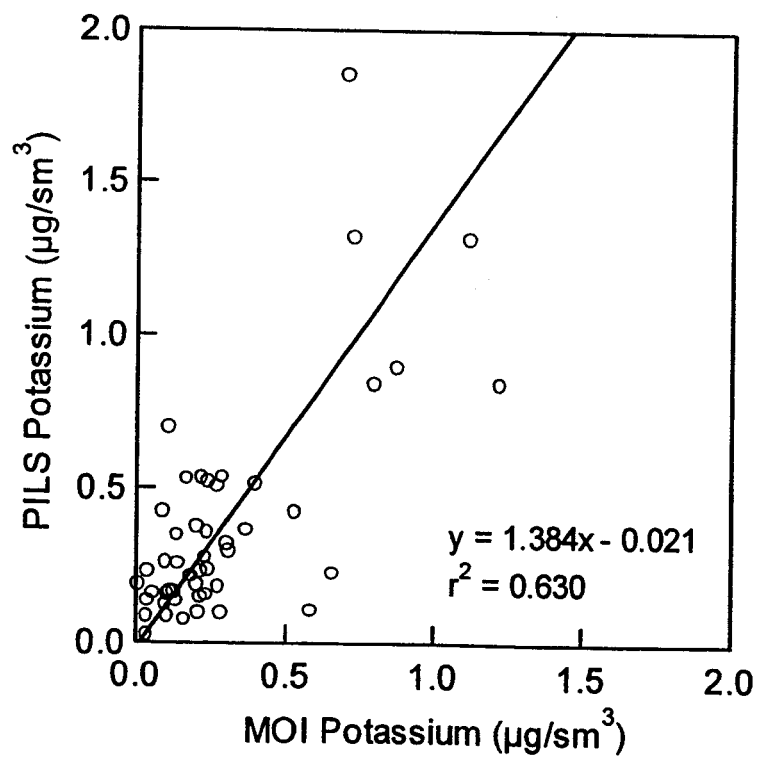
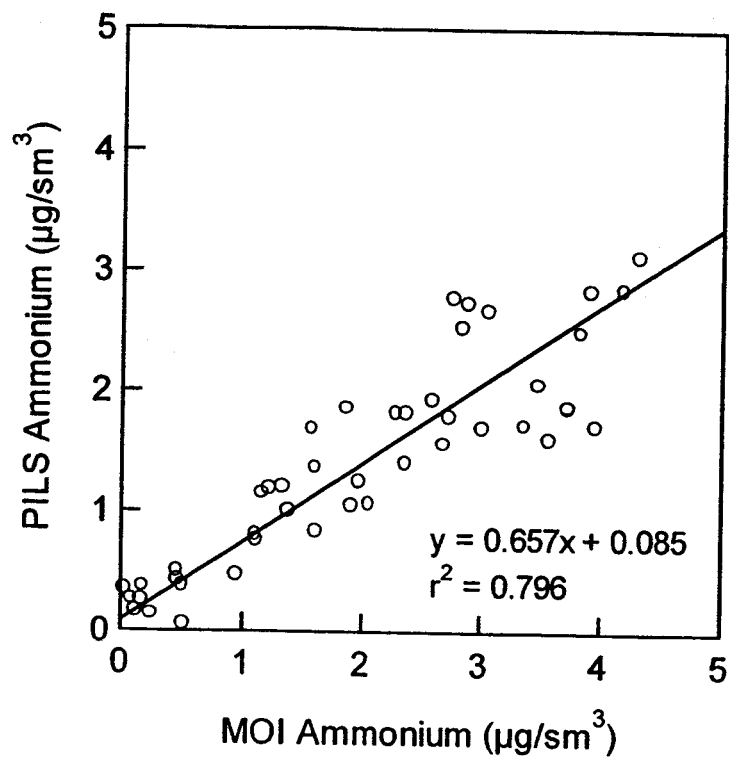


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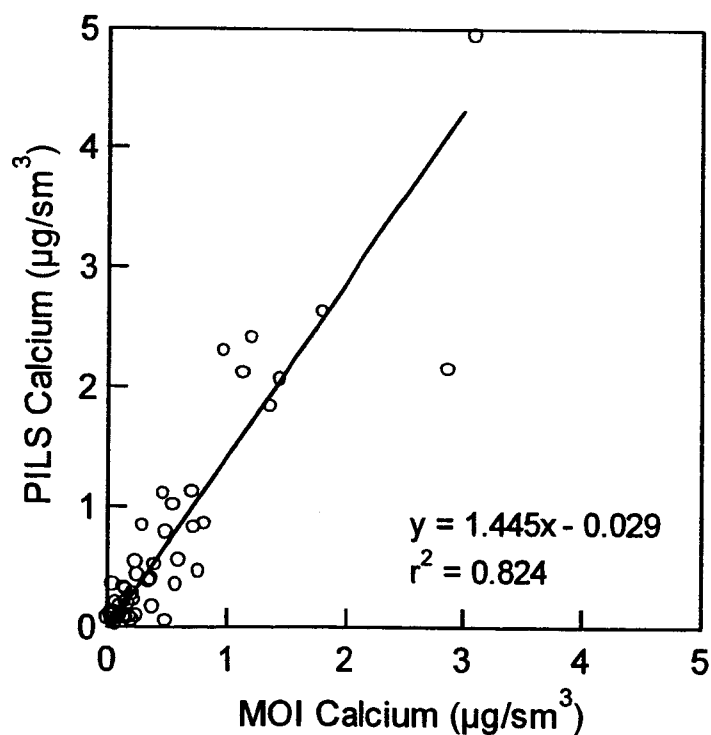
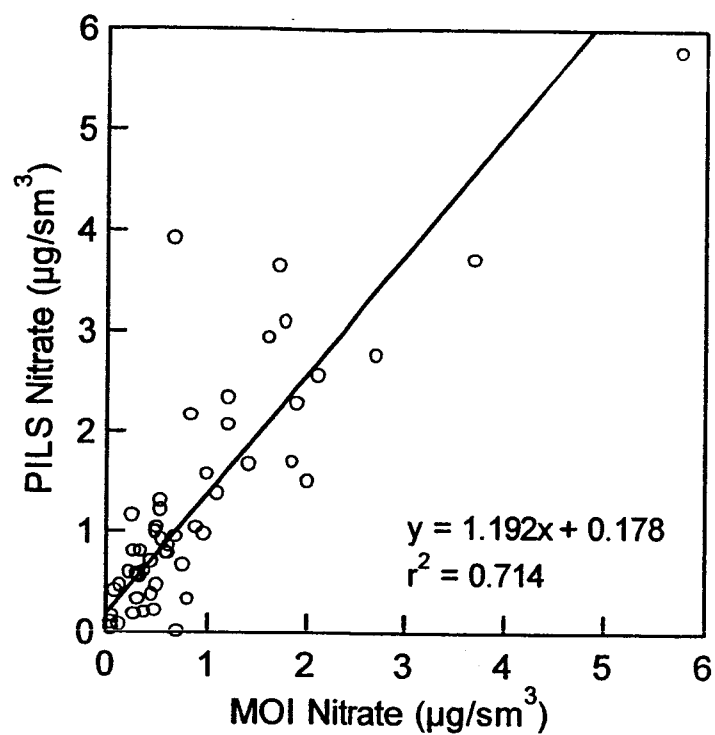


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