10.13 AEROSOL CHEMICAL CHARACTERIZATION ON BOARD THE DOE G1 AIRCRAFT USING A PARTICLE-INTO-LIQUID-SAMPLER DURING THE TEXAQS 2000 EXPERIMENT

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1. INTRODUCTION

Knowledge of aerosol chemical composition is key to understanding a number of properties of ambient aerosol particles including sources, size/number distribution, chemical evolution, optical properties and human health effects. Although filter based techniques have been widely used to determine aerosol chemical constituents, they generally cannot provide sufficiently fast time resolution needed to investigate sources and chemical evolution that effect aerosol chemical, size and number changes. In order to gain an ability to describe and predict the life cycles of ambient aerosols as a basis for ambient air quality control, fast and sensitive determination of the aerosol chemical composition must be made available. To help to achieve this goal, we deployed a newly developed technique, referred to as PILS (particle-into-liquid-sampler), on the DOE G1 aircraft during the 2000 Texas Air Quality Study (TexAQS 2000) to characterize the major ionic species of aerosol particles with aerodynamic size smaller than 2.5 µm (PM 2.5). The results obtained are examined in the context of other simultaneously collected data for insights into the measurement capability of the PILS system.

2. EXPERIMENTAL SECTION

TexAQS 2000 was a major field experiment conducted to investigate photochemical O_3 production in the greater Houston region where frequent O_3 exceedance over the 1 hr-120 ppbv NAAQS was observed. Because the Houston area has a highly concentrated petroleum and chemical industry, investigating the role industrial emissions play, in addition to that of urban emission, in O_3 production was a major focus of TexAQS 2000. This field program was led principally by the Texas Natural Resources Conservation Commission, and a large number of research groups from universities, government and the private sector had participated. Both ground measurement sites and instrumented aircraft were used to characterize the air chemistry.

A PILS coupled to ion chromatography (IC) analysis was deployed on board the DOE-G1 aircraft during TexAQS 2000 to determine the ionic components of aerosol particles. The PILS was constructed based on the design that was used at the 1999 Atlanta EPA Supersite Experiment (Weber et al., 2001), and was deployed on an aircraft for the first time during TexAQS 2000. A schematic diagram of the aircraft system is shown in Figure 1. The principle of the PILS technique involves activating the particles under supersaturated conditions achieved by mixing steam with the sample air and collecting the resulting droplets using an impactor with a 50% cutoff at ~1 µm. The liquid sample collected on the impactor surface is washed off with a steady stream of carrier flow and delivered to two sample loops (150 µL each) for separate anion and cation analysis using two IC's. The samples were injected to the IC for analysis every 3 min and each sample represented a time average of ~2 min. The following species were quantified: Na^+, NH_4^+, K^+, Ca^{2+}, NO_3^-, and SO_4^{2-}. The limit of detection was ~0.1 ug m^{-3} for all the species at a limit of detection of ~0.1 µM of the IC and a sample air flow rate of 5.0 L min^{-1}.

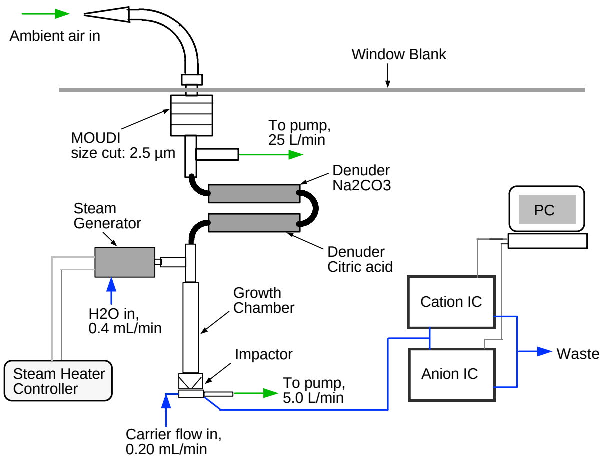

Figure 1. Schematic diagram of the PILS-IC system deployed on the G1 aircraft.

The inlet to the PILS system consisted of a diffusor cone (7 degree taper) with a 2.5 mm diameter nozzle for near isokinetic sampling at the G1 cruising speed (~200 k hr^{-1}), a MOUDI impactor for a 2.5 µm size cut, and two glass annular denuders in series to remove gaseous HNO_3 and NH_3. While the total flow into the system was 30 L min^{-1} appropriate for the inlet and the MOUDI impactor, 25 L min^{-1} was dumped after the MOUDI and 5 L min^{-1} was sampled by the PILS (Fig. 1).

The G1 aircraft had a wide range of instrumentation for gas and aerosol characterization. With regard to aerosols the most relevant instruments included a pcasp

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(passive cavity aerosol spectrometer, Particle Measurement System, Boulder, CO) which determines the size/number distribution of particles in 15 size bins within the range 0.1 to ~3 μm, and a PSAP (particle soot absorption photometer, Radiance Research, Seattle, WA) which measures aerosol optical absorption due primarily to black carbon.

A total of 18 research flights were conducted between 8/19/00 and 9/12/00, of which PILS data were collected on 16. On flight days, typically two flights were conducted, taking off at ~9:30 am and ~2:00 pm CDT, each lasting for ~2 hr. Although the flight tracks were slightly different between the AM and PM flights, they cover the greater Houston region over the perimeter, as well as the downtown area and the ship channel area where the petrochemical industry facilities are concentrated. The only flight that deviated from this pattern was the 0910a flight for a power plant plume study northeast of the Houston area (Springston et al., 2002). The altitude was maintained between 400 to 600 m except during spirals to determine the boundary layer height.

3. RESULTS AND DISCUSSION

The PILS-IC system measured the inorganic aerosol ionic components, namely, Na^+, NH_4^+, K^+, Ca^{2+}, NO_3^- , and SO_4^{2-}. Although Na^+, NH_4^+ and SO_4^{2-} were present in all samples, Na^+ was present at a much lower level (< 0.3 μg m^{-3}) than the other two. The median and maximum concentrations of NH_4^+ and SO_4^{2-} were 1.6 and 5.0, and 1.8 and 9.4 μg m^{-3}, respectively. NO_3^- was mostly <0.2 μg m^{-3}, but with occasional excursion reaching as high as half of SO_4^{2-}. K^+ and Ca^{2+} were seen in only ~15% of the samples, but K^+ reached as high as 6 μg m^{-3}. The distributions of these species are shown as frequency plots in Figure 2. In addition, the distribution of the total mass of the ionic species are shown as box plots for each of the flights (Figure 3). Note that the flights are labeled as dates with a and b denoting morning and afternoon flights, respectively.

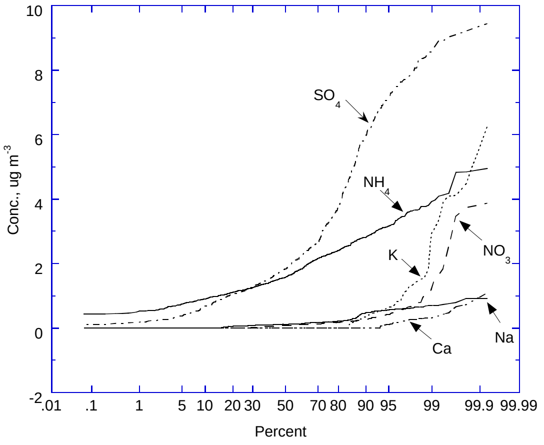

Figure 2. Probability distribution of the aerosol ionic species.

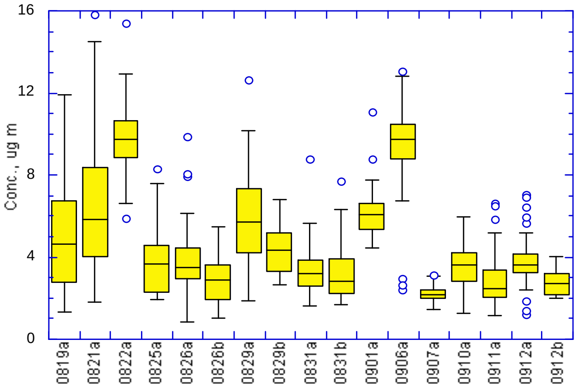

Figure 3. Box plots of total aerosol ion mass concentrations determined on each flight.

An important aerosol property is its acidity, or the extent of neutralization of sulfuric acid present in the aerosol. One measure used to gauge this property is the examination of the ratio (φ) of the principal neutralizing agent, NH_4^+, to the sum of $2xSO_4^{2-}$ and NO_3^-. A value of unity indicates complete neutralization of nitric and sulfuric acids by ammonia. Departure from unity suggests the presence of other acids, e.g., organic acids, if φ>1 or the presence of free strong acids if φ<1. The observed φ showed a fairly wide distribution, with the mode being between 1 and 2, suggesting additional anions to associate the excess NH_4^+. In Figure 4 we show box plots of the φ values as a function of $[SO_4^{2-}]$ in 4 quartiles. Not surprisingly, φ exhibited the highest values at the lowest SO_4^{2-} concentration and decreased with increasing SO_4^{2-} mass loading. However, even for the 4th $[SO_4^{2-}]$ quartile, φ ranged between 0.5 and 2 with a median value of 1.2, strongly suggests the presence of other anions, presumably organic in nature. One of

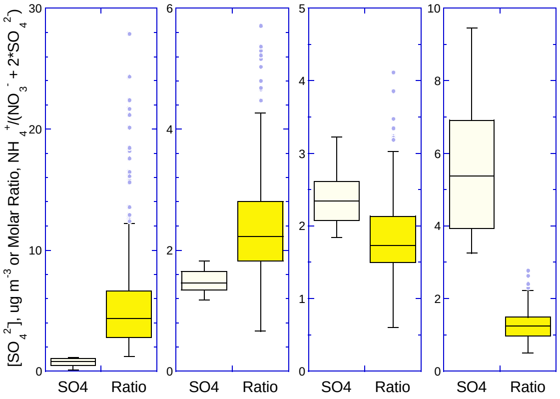

Figure 4. Box plots of the ratio of $[NH_4^+]$ to the sum of $[NO_3^-]$ + $2*[SO_4^{2-}]$ for each quartile of SO_4^{2-} mass concentration.

the possible artificial causes of an elevation of NH_4^+ concentrations, and therefore φ, is an depleted denuder that allowed gaseous NH_3 to be collected and counted as aerosol NH_4^+. To examine this possibility, we eliminated the data between 8/26 and 9/1 during which φ was in general the highest. In this subset of data, the φ values ranged between 0.5 and 6 with a median value of 1.7. Consequently the overall picture concerning the excess NH_4^+ comparing to NO_3^- and SO_4^{2-} is not changed.

The activation and collection efficiency of the PILS has been characterized in the laboratory using $(NH_4)_2SO_4$ and tested in the field during the 1999 EPA Atlanta Supersite Experiment (Weber et al., 2001). The laboratory results showed that particles with a diameter greater than 100 nm are quantitatively collected. In addition, the field results showed that aerosol mass was nearly quantitatively captured based on TEOM (Tapered Element Oscillation Microbalance, Rupprecht and Patashnick, Albany, NY) measurement.

For the current aircraft study, it is also desirable to compare the PILS-IC data with the total aerosol mass for the purpose of examining the mass contributions of the inorganic ionic species. In the absence of a direct aerosol mass measurement on the G1, we estimated the total aerosol mass using the number/size distribution of the accumulation mode particles determined using the pcasp with an assumed density. It should be noted that the raw pcasp data were determined with the instrument calibrated using polystyrene latex spheres that have a refractive index (RI) of ~1.58. Because this RI value is not representative of ambient aerosols (Liu and Daum, 2000), we have corrected the pcasp data using a RI of 1.40.

The total aerosol mass was estimated with an initial assumption of a density of 1.7 g cm^{-3} appropriate for $(NH_4)_2SO_4^{2-}$. However, if the ion mass fraction was found to account for ≤70 % of the initial estimated total mass, then a reduced density was applied which assumed a linear combination of 1.7 for the inorganic fraction and 1.0 for the rest which conceivably is due to organic components. Although an iterative process can be taken to reach a final total mass, the fact that the total aerosol volume also has a sizable uncertainty owing to the assumed RI makes it unwarranted to adjust the density beyond the second step. We surmise that the estimated aerosol mass has a 15% uncertainty. The total aerosol mass estimated based on this procedure is referred to as pcasp mass.

The pcasp mass in general correlated well with the total ion mass and the correlation coefficients ranged between 0.4 to 0.8, except for flights 0831a, 0831b, 0907a, and 0910b. Additional effort will be applied to these data to understand the sources of the poor correlation. For those that exhibit a good correlation, we display as examples two flights, 0906b and 0912a, where, respectively, nearly the highest and lowest aerosol mass loadings were observed during the mission (Fig. 5). In these analyses, the pcasp mass were estimated using 1.25 and 1.7 as density for 0906p and 0911a, respectively.

The relatively strong correlation between the pcasp mass and the total ion mass, especially for those flights where a low aerosol mass loading was found (and the

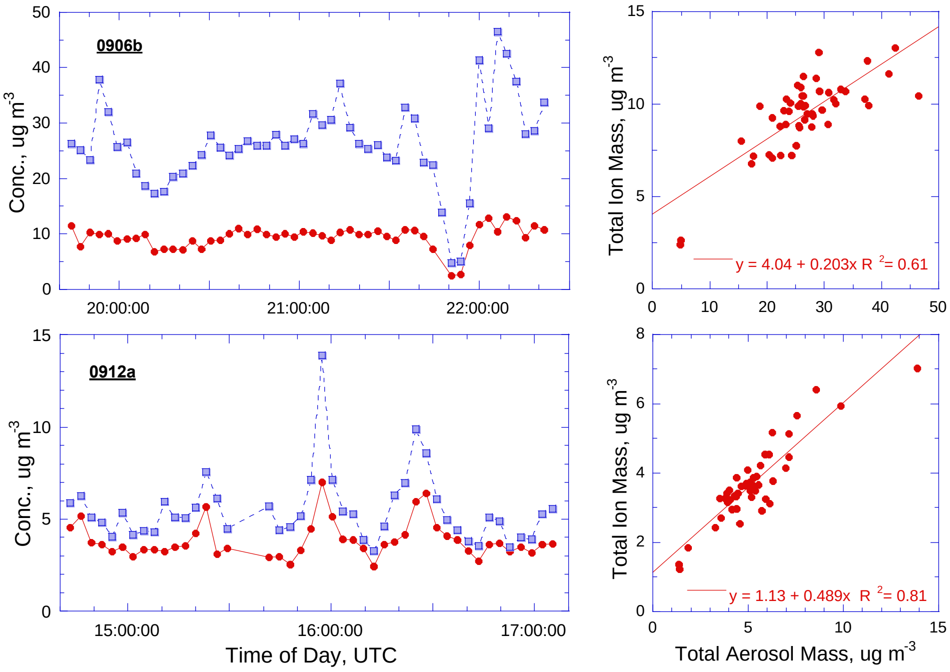

Figure 5. Left column: time series plots of the pcasp mass and the total ion mass on 9/6/00 and 9/12/00, when the highest and the lowest aerosol mass loading, respectively, were observed. Right column: correlation between the pcasp and total ion mass.

ionic components accounted for a major portion of the total aerosol mass), suggests that the PILS measurements are indeed reasonable. The difference between the pcasp mass and the total ion mass may therefore be attributed to organic constituents of the aerosol particles. This approach of inference will be useful to complement (and setting an upper bound limit) the existing techniques (e.g., the EC/OC technique by Chow et al., 1993) to gain an improved understanding of the contribution of organics to aerosol mass loading which is critically needed (Huebert and Charlson, 2000).

In this connection, we examine the relationship between the black carbon and the difference between the pcasp mass and the total ion mass, which we tentatively term as the organic fraction, shown for the two flights, 0906b and 0912a (Figure 6). Good correlation has been observed between organic carbon and elemental carbon when primary emission was important (e.g., Turpin and Huntzicker, 1995), The black carbon mass loading was derived from the PSAP data using a specific absorption coefficient of 10 m^2 g^{-1}, albeit it was well recognized this coefficient is variable depending on the environment (Liousse et al, 1993). Figure 6 shows a fairly strong correlation between the mass difference between pcasp and total ion and the black carbon mass, supporting that the mass difference is at least dominated by organic components. However, it is interesting to note that the slopes are significantly different between 0906b and 0912a, the latter being fairly close to that observed by Turpin and Huntzicker (1995) for a primary emission dominated situation. The much higher slope of 0906b may strongly suggest a case of secondary organic aerosol formation.

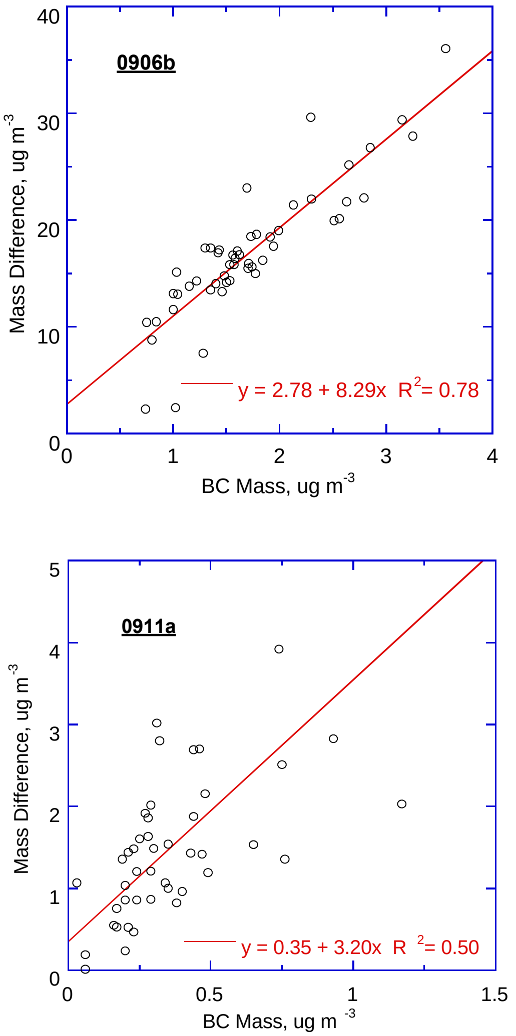

Figure 6. Correlation between the organic fraction (see text) and the black carbon mass concentration.

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