Airborne Measurements of Space Shuttle Exhaust Constituents

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Airborne measurements of hydrogen chloride (HCl) and particulates made during penetrations into and flights under Space Shuttle exhaust clouds from launches STS-1,-2 and -5 are presented to permit comparision with dispersion model predictions for Space Shuttle exhaust clouds and with previous measurements made in Titan III exhaust clouds. Analytical techniques employed for the Shuttle measurements were developed and refined during earlier Titan III exhaust cloud measurements and include the measurements of particulate concentrations, size distributions, and the partitioning of HCl between the gaseous and aerosol phases. The results are useful in understanding the dynamics of ground cloud development, atmospheric dispersion, and potential environmental effects of Shuttle effluents.

Introduction

THE impact of launch vehicle emissions on the environment has been studied by NASA since the early 1970's. The exhaust effluents from large ammonium perchlorate/aluminum based solid-propellant rocket motors (SRM's) have been of particular interest since they release as exhaust large quantities of gaseous hydrogen chloride (HCl) and particulate aluminum oxide (Al_2O_3), and are used as boosters for the Space Shuttle.

Langley Research Center's involvement in the launch vehicle effluent (LVE) program has consisted predominantly of aircraft measurements of SRM effluents within Titan and Shuttle exhaust clouds. The chemical compositions of Titan and Shuttle exhaust are nearly identical. Aircraft characterizations of the concentrations of the major SRM effluents within rocket exhaust clouds as functions of time, meteorology, and dispersion are of great help in assessing the accuracy of analytical models, in predicting potentially adverse launch conditions, and/or in improving model evaluations of environmental impacts from launches.

This paper will focus on measurements made during penetrations into Shuttle exhaust clouds from launches STS-1, -2, and -5, and how these measurements relate to cloud chemistry and physics as well as dispersion predictions. Comparisons of the Shuttle data with the larger data base obtained in the Titan III exhaust clouds will be made where appropriate.

While this paper is intended to highlight the major results from the airborne measurements of STS-1,-2, and -5 exhaust clouds, more detailed discussion of the data can be found in the referenced work.

Exhaust Cloud Behavior

The hot plumes of rocket exhaust that result from launches of large rocket vehicles quickly rise and mix with the surrounding atmosphere. The initital heat content of the exhaust, the relative humidity of the encompassing air, the atmospheric temperature gradients, and the strengths and altitudes of the atmospheric inversion layers all play important roles in determining the eventual altitude at which the cloud stabilizes (reaches thermal equilibrium with the surrounding atmosphere), and hence the initial cloud structure. Typically, the exhaust cloud from a large launch vehicle will stabilize just below the surface mixing layer (500-3000 m) within 15 min after launch. Occasionally, segmentation into multiple exhaust clouds (as in STS-1) can result. This is thought to occur when several weak temperature inversions exist, with the individual segments stabilizing as they reach thermal equilibrium with the ambient air. After stabilization, the prevailing meteorology will dominate subsequent cloud movements and dispersion. Throughout the history of cloud development and existence in the boundary layer, deposition of exhaust effluent (HCl and Al_2O_3) on ground receivers has been a potential problem.

HCl and Al_2O_3

Our research has focused primarily on the behavior of HCl and Al_2O_3 in the exhaust clouds. For Space Shuttle launches, about 35,000 kg of HCl and 56,000 kg of Al_2O_3 are exhausted into the boundary layer and become part of the stabilized ground cloud.[1] The fate of these exhaust products is environmentally significant since precipitation scavenging and/or rainout of HCl from the exhaust cloud could lead to localized acidic rain desposition,[2-4] and the particulate Al_2O_3, partially chlorided from chemical reactions in the exhaust plume, 5-7 could potentially lead to short-term weather modifications.[8-11]

Instrumentation

A twin-engine light aircraft (Cessna 402) was used for exhaust cloud sampling. A complete description of the aircraft and its basic instrumentation can be found in Ref. [12] The aircraft was equipped with two different instruments for measuring HCl. Gaseous HCl was measured with a nondispersive infrared absorption technique[13,14] developed for these aircraft measurements that responded only to HCl in the gaseous state. Total HCl was measured with a chemiluminescent technique[14,15] that responded quantitatively to both gaseous HCl and HCl in the aqueous aerosol phase. Thus, the partitioning of HCl between gaseous and aqueous phases could be determined from the difference between the two measurements.

Because of the large range of particle sizes and the varying amounts of liquid water associated with the particulates, aerosols could not be adequately measured with any one technique. Therefore, three particle measuring systems were employed for the in-cloud measurements: 1) an integrating nephelometer, 2) a 10-stage quartz crystal microbalance (QCM), and 3) a Knollenberg particle measuring system. Both the nephelometer and the QCM were equipped with heated (130°C) inlets to volatilize aqueous phase before particle measurements were made.

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The nephelometer operates on light scattering principles and is sensitive to particles in the 0.2-5.0 μm range. Nephelometer measurements have been discussed by Charlson.[16] The QCM operates on a piezoelectric principle and measures the accumulation of mass on 10 individual quartz crystals. A 10-stage cascade impactor was used in conjunction with these crystals to differentiate particle sizes from about 0.1 to 5μm in diameter.

Size spectra of predominantly aqueous aerosol particulates were measured external to the aircraft with a Knollenberg particle system using the OAP-200X probe, preset to measure aerosols in the 20-400 μm diam range. The Knollenberg probe utilizes a laser beam occultation principle, and aerosols were counted in 15 equally spaced size intervals.

In addition, temperatures were measured within the exhaust clouds with platinum resistance probes, and cloud water content with a dew point hygrometer system. The aircraft was equipped with nose probes that provided uncontaminated freestream air for sampling. Isokinetic sampling inlets were attached to these probes and directed to the individual instruments. Aircraft sampling passes were executed through the visual center of the exhaust cloud after stabilization. The aircraft traverses generally began within several minutes after launch and continued as long as the cloud remained visible, usually about 1-2 hours.

Results and Discussion

The influence of the attending meterology on all aspects of exhaust cloud behavior cannot be overstated. The stabilized cloud geometry and dispersion of each launch cloud can vary substantially. The aircraft data presented in this report, however, have primarily been chosen to permit comparisons with dispersion model predictions and to emphasize HCl and Al_2O_3 behavior considered representative of Space Shuttle exhaust clouds.

Peak total HCl concentrations measured during multiple aircraft penetrations of stabilized exhaust clouds from launches STS-1, STS-2, and STS-5 are presented in Fig. 1 as a function of time after launch. Two HCl data sets are shown in Fig. 1 for STS-1. Segmentation and subsequent stabilization into several distinct exhaust clouds were observed with this first Shuttle launch. The two most prominent clouds were sampled. The first (low-altitude cloud ~900 m) drifted northward and was sampled during the initital 40 mins after launch. The second cloud (high-altitude ~1500 ms) drifted westward and was sampled from about 50 to 120 min after launch. The launches of STS-2 and STS-5 produced single clouds stabilized at about 1100 and 1200 m altitude, respectively.

Concentrations of HCl as high as 40 ppmv were observed during the earliest aircraft penetrations of the exhaust clouds and generally decreased by about an order of magnitude within an hour of the initial measurements (see Fig. 1). The concentration/time behavior of HCl in the Shuttle exhaust clouds sampled appear to be reasonably well characterized over the measurement interval of 10-200 min by the empirical power-law expression for decay

$$C = C_0 t^a$$

where C is the mixing ratio (ppmv) for HCl in the cloud at a nondimensionalized time t, C_0 represents the intercept at $t=1$, and a a nondimensionalized empirical constant. The constant a, based on dispersion considerations, should vary from -1.0 for an exhaust cloud vertically constrained to -1.5 for an unbounded cloud (K-theory, Smith[17]). An average a of -1.3 was obtained from the HCl data plotted in Fig. 1. Individual values of a for each of the Shuttle exhaust clouds sampled can be found in Sebacher et al.[18]

The use of HCl measurements as a basis for modeling exhaust cloud dispersion, however, can potentially lead to overpredictions, since HCl mixing ratios are subject to significant loss through aqueous aerosol fallout. This can result in lowered in-cloud HCl mixing ratios that could be misinterpreted as cloud dispersion. Radke et al.[19] applied K-theory dispersion based on cloud volume measurements (rather than HCl concentrations) to stabilized Atlas and Titan launch clouds and obtained a's of -0.98 and -0.94, respectively.

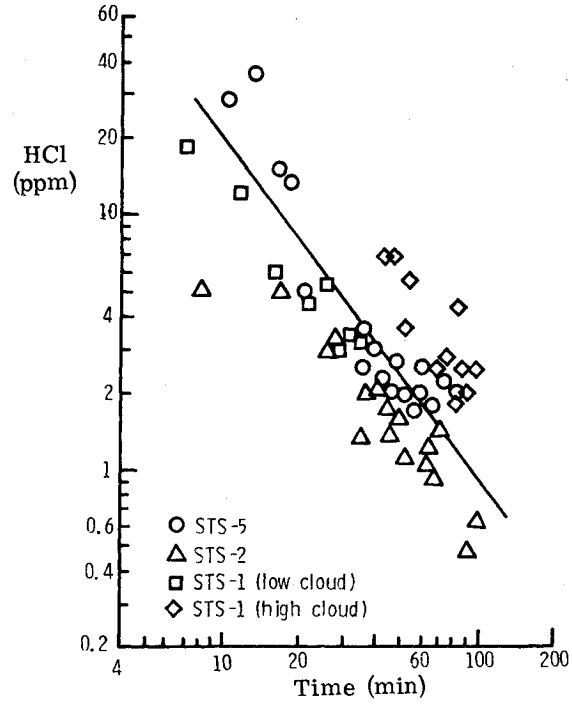

Fig. 1 Peak HCl concentrations measured from aircraft penetrations of Shuttle exhaust clouds.

The HCl within a Shuttle exhaust cloud can exist as a gas, be absorbed by aqueous droplets, or be absorbed on the surface of Al_2O_3 particles. Laboratory investigations[5] and analyses[7] of Shuttle exhaust Al_2O_3 suggest that less than 5% of the exhaust HCl should be scavenged through reactions with Al_2O_3 particulates. The partitioning of HCl between the gaseous state and aqueous aerosol, however, can vary extensively. Initially, the Shuttle exhaust cloud is water-rich. Large quantities of H_2O are generated during rocket motor combustion, and a significant amount of the deluge water used for acoustic baffling and launch pad cooling is entrained into the exhaust.[20] Calculations based on vapor/liquid equilibrium by Rhein[21] and Pellett et al.[4] indicated that most of the HCl in the Shuttle exhaust cloud should be in the aqueous phase early in the cloud history. Relative humidity and temperature of cloud dilution air will largely determine the subsequent partitioning. Subsequent dispersion and deposition of the HCl will be strongly influenced by the phase that the HCl is in. Thus it is clear that an understanding of HCl partitioning in the exhaust cloud, and the chemical and physical parameters that influence it, is not trivial.

HCl partitioning data from launches STS-1, -2, and -5, are shown as a function of time after launch in Fig. 2. Liquid aerosol phase HCl was determined by subtracting the concentrations of HCl measured in the gas phase from the total HCl measurement. No attempt was made to reconcile the slightly different time constants of the two HCl techniques. Aircraft measurements of HCl made early in the history of the exhaust clouds indicated that the HCl was largely in the aqueous aerosol phase. Within 40 to 60 min, however (see Fig. 2), the amounts of gaseous HCl measured equaled or exceeded that in the liquid phase. The decrease in the ratio of aqueous/gaseous HCl observed in the aging Shuttle exhaust

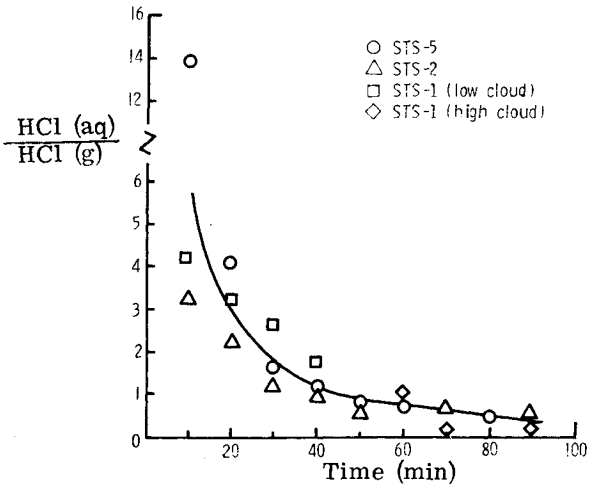

Fig. 2 Ratios of aqueous to gaseous HCl as a function of time after launch.

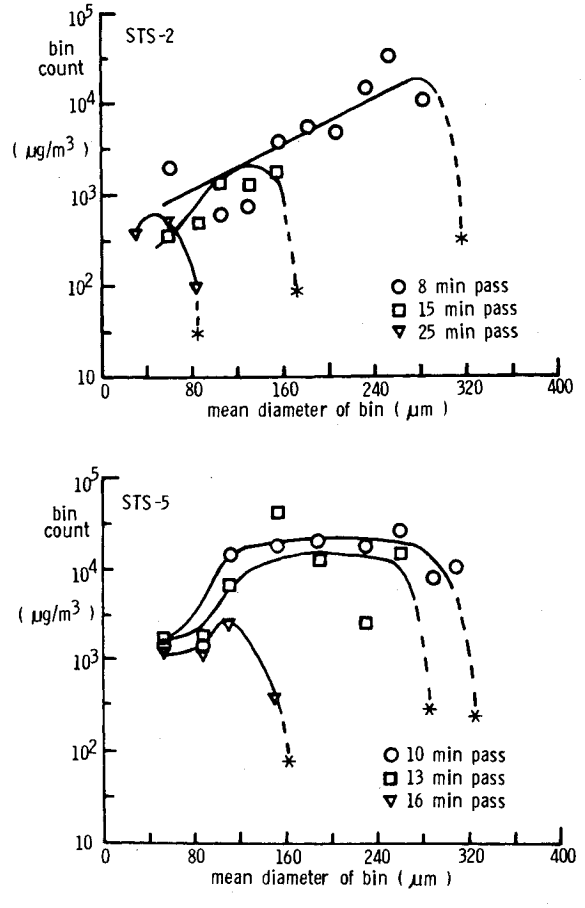

Fig. 3 In-cloud large particle measurements from STS-2 and STS-3.

clouds can be postulated to be the result of predominantly two major processes – evaporation and aerosol fallout. Both processes are strongly influenced by humidity. Low ambient humidities lead to droplet evaporation and optimum HCl dispersion, while high humidities may allow droplets to grow to the point that fallout (rainout) of hydrochloric acid aerosol occurs. Obviously, the later case is less desirable.

Aqueous acid aerosol fallout from Space Shuttle exhaust clouds is suggested by the large particle measurements shown in Figs. 3 and 4. Large particle data were counted in 15 equally spaced (25 μm width) sizing bins over a 20 - 400 μm

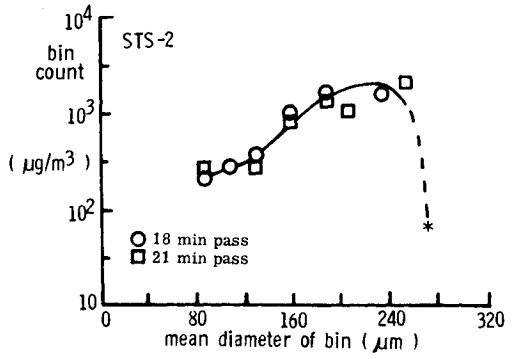

Fig. 4 Beneath cloud large particle measurements form STS-2.

diam range. Particle density was assumed to be that of water, 1.0 g/cm^3 for mass calculatons. Data displayed in Figs. 3 and 4 represent the calculated mass/volume count for each bin vs the mean particle diameter of the bin. Curves marked with an asterisk indicate larger diameter particle masses were below our detection and/or measurement capability.

The large particles (40 - 360 μm) shown in Fig. 3 are presumed to consist mainly of condensed water. The earliest aircraft passes through the exhaust clouds from STS-2 and STS-5 indicated significant mass loadings of particulates with diameters >120 μm. The large particle concentrations in the clouds can be seen to decrease progressively with sampling time. While a significant part of the measured decrease in particles of large diameter may be the result of evaporation, it seems reasonable to suggest that the indicated progression to particles of smaller diameter over the 20 - 360 μm interval was more strongly influenced by fallout. Evidence to support this is presented in Fig. 4.

Figure 4 shows significant concentrations of particulates in the 120 - 240 μm interval measured during aircraft traverses (~100 m below cloud base) beneath the STS-2 exhaust cloud at 18 and 21 min after launch. When these data are compared with the data from the 15 and 25 min traverses through the center of the STS-2 exhaust cloud (Fig. 3), it becomes apparent that higher concentrations of large aerosol particulates exist beneath the cloud and strongly suggest extensive aerosol fallout. As a result of HCl measurements beneath Shuttle exhaust clouds, Sebacher et al.[18] have not only suggested substantial aqueous aerosol fallout, but that the fallout aerosols are continuously degassing HCl. The fraction of aqueous acid aerosol that degasses before deposition is unknown, but most certainly will be strongly influenced by the existing meteorology.

Nephelometer data are shown in Fig. 5 for the 15, 18, 21, and 25 min after launch traverses of the STS-2 exhaust cloud. Time was selected as the abscissa (rather than particle diameter) in this figure in order to illustrate spatial variations in the clouds. Nephelometer measurements primarily respond to a particle size range, 0.2 - 2 μm in this case. While the quantitative aspects of nephelometer measurements are difficult to interpret, we feel that nephelometer data have substantial value when used for qualitative comparsions.

Peak in-cloud small particle mass loadings of over 225 μg/m^3 were observed for both the 15 and 25 min exhaust cloud traverses. Small particle mass loadings of about 40 μg/m^3 (approximately background) were measured during the 18 and 21 min traverses beneath the cloud. As expected, no significant fallout of small particles was observed during the underflights since 2 μm diam particles would have an undisturbed free-fall velocity of only about 0.007 m/min. Small particle concentrations, however, could result as the product of fallout of larger particles coupled with rapid evaporation.

Small particle (0.11 - 5.4 μm) data collected on separate stages (fractionation by geometric mean diameter) of a quartz crystal microbalance (QCM) during traverses through the low

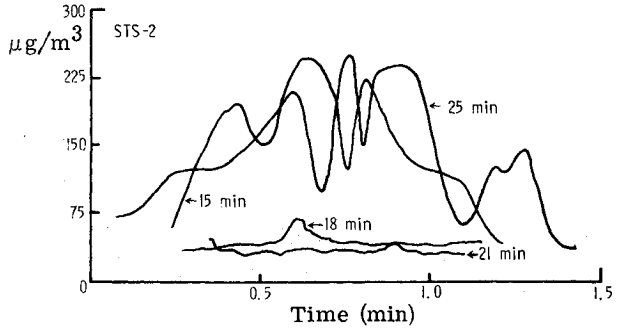

Fig. 5 Nephelometer Traces from STS-2 exhaust cloud.

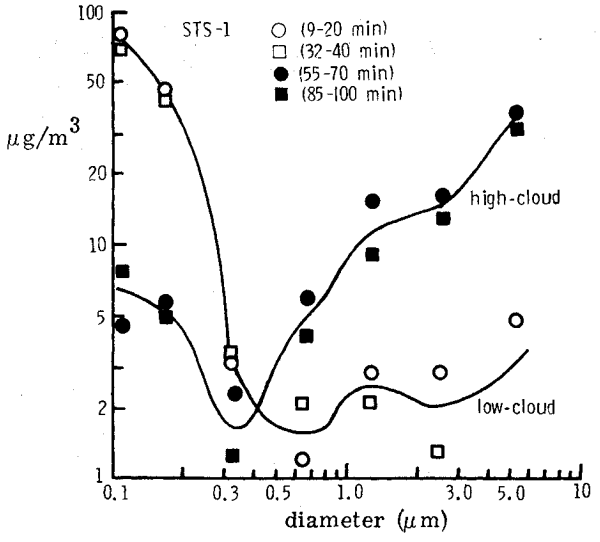

Fig. 6 Quartz crystal microbalance particle data from STS-1 exhaust cloud.

and high altitude exhaust clouds produced by STS-1 are shown in Fig. 6. These data represent the averaged mass loadings on individually sized QCM stages that were obtained from at least three separate in-cloud traverses over the specified time intervals after launch. Data from the low cloud traverses indicate substantial particle loadings in the 0.1 - 0.2 μm diam region. Particles in this size range can persist in the lower troposphere for weeks.

Traverses through the high altitude exhaust cloud from STS-1 revealed that concentrations of $\sim$0.1 μm particles were about an order of magnitude less than in the low cloud. Concentrations of particles of diameter $>$1.0 μm, however, were generally about a factor of 5 to 6 higher in the high altitude cloud. Since these size distributions were measured in different clouds with potentially different dispersion rates and at different times and relative humidities, too many variables exist to offer any explanation. Nevertheless, significant amounts of small particles ($<$1.0 μm) were always observed in the Shuttle exhaust clouds.

The fact that significant concentrations of small particles were always measured deserves comment. Small particles can reside (and interact) in the lower troposphere for days before sedimentation processes affect removal. This, coupled with the likelihood that the Shuttle Al_2O_3 particles will be hydrophilic[7,22] and thus good cloud condensation nuclei (CCN), has led to concern about potential inadvertent weather modification resulting from Shuttle launches. SRM production of large quantities of hydrophilic CCN has already been observed by Radke et al.[19] and Hindman et al.[11] in Titan exhaust clouds. Potential long-term effects (more than a few hours) such as these that would normally not result in near field (local) deposition will not be treated in this text.

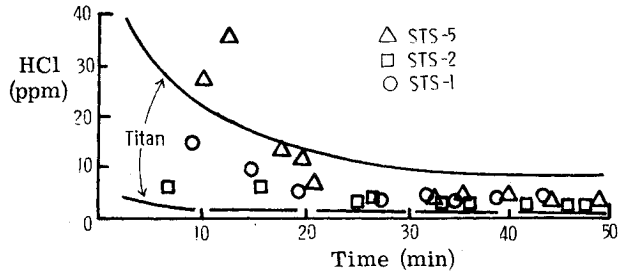

Fig. 7 Comparison of Shuttle and Titan HCl data.

The concentrations of exhaust effluents measured in Shuttle exhaust clouds were found to be very representative of those measured earlier in Tital III clouds. Evidence of this is shown in Fig. 7, where total HCl concentrations measured for STS-1, -2, and -5 can be compared with Titan measurements. Titan III data from 15 launches are shown as an envelope bounding maximum and minimum peak HCl concentrations measured time. The Titan and Shuttle data can be seen in Fig. 7 to compare favorably.

Conclusions

Concentrations of HCl in stabilized, boundary-layer Space Shuttle exhaust clouds willl generally decrease (disperse) in a systematic and predictable fashion for the first few hours after launch. The decrease in HCl concentration with time was adequately characterized for the three Shuttle clouds sampled by a simple empirical power-law expression. While the power-law characterization proved sufficient for the launches monitored, many potential meterological conditions were not observed.

Aircraft measurements of HCl made early (within the first half hour) in the histories of the Shuttle exhaust clouds indicated that most of the HCl existed as aqueous hydrochloric acid drolets. As the respective exhaust clouds aged, however, the ratio of aqueous/gaseous HCl rapidly decreased. After about an hour, most of the HCl was in the gaseous phase. While a substantial part of the decrease in aqueous hydrochloric acid aerosol undoubtably resulted from droplet evaporation during dispersion/dilution in atmospheric air, the indications that aqueous aerosol fallout was occurring were of some concern. The fraction of aqueous acid aerosol fallout that evaporated before deposition is unknown, but most certainly would have been largely determined by the existing humidities, winds, and temperatures.

Significant concentrations of small particulates were always measured in the Shuttle exhaust clouds. These particles may correspond to the cloud condensation nuclei measured by others.

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