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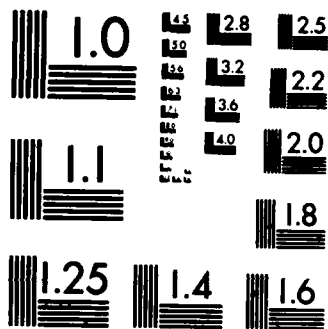
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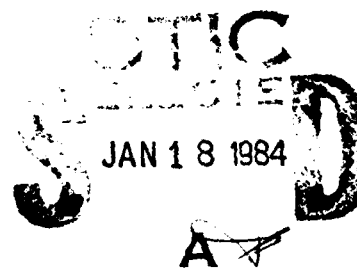
— **USAF OEHL REPORT** —

83-298EH374JGA



AD A 136935

**TEMPORAL AND SPATIAL GASEOUS HCl CONCENTRATIONS IN THE
NEAR FIELD STS POSTLAUNCH ENVIRONMENT
KENNEDY SPACE CENTER, FLORIDA
SEPTEMBER 1983**



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 83-298EH374JGA	2. GOVT ACCESSION NO. AD-A136935	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) TEMPORAL AND SPATIAL GASEOUS HCl CONCENTRATIONS IN THE NEAR FIELD STS POSTLAUNCH ENVIRONMENT		5. TYPE OF REPORT & PERIOD COVERED Final- Aug 83
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) WILLIAM D. CHRISTENSEN, Lt Colonel, USAF, BSC JIMMY D. LANGWELL EDWARD S. BARNES, Major, USAF, BSC		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS USAF Occupational and Environmental Health Laboratory, Brooks AFB TX 78235		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS USAF Occupational and Environmental Health Laboratory, Brooks AFB TX 78235		12. REPORT DATE September 1983
		13. NUMBER OF PAGES 17
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) <div style="border: 1px dashed black; padding: 5px; width: fit-content; margin: 0 auto;">This document has been approved for public release and sale; its distribution is unlimited.</div>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Approved for public release; distribution unlimited		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) STS Hydrogen chloride Space Shuttle Shuttle Launch Space Transportation System		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report presents the results of hydrochloric acid (HCl) measurements accomplished following the launch of Space Shuttles 5, 6 and 7 from launch complex 39, pad A, at the Kennedy Space Center (KSC). The objective of the sampling program was to evaluate the potential for revolatilization of HCl deposited in the vicinity of the launch complex and to determine the time history of the event if it occurred. The data collected during the program demonstrate that HCl can persist for several hours following Shuttle launch		

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and that there is potential for isolated higher levels of HCl to occur. The data also provide insight to the magnitude of HCl concentration variability which can be influenced by meteorological, topographical and operational parameters. The relative importance of these parameters can be shown to have a major influence on HCl concentrations and will likely be superimposed on any revolatilization or concentration decay curve. The importance of even low level HCl concentrations on pad reentry personnel is discussed, however, the potential effect on electronic equipment and circuitry remains to be addressed.

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TEMPORAL AND SPATIAL GASEOUS HCl CONCENTRATIONS IN THE
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SEPTEMBER 1983

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I. BACKGROUND

Following early Space Shuttle launches, crews that had a need to reenter the launch complex shortly after launch reported experiencing eye and skin irritation. Short duration air sampling was accomplished using a variety of direct and indirect sampling and analytical schemes to determine the source and significance of the irritating substances. In addition to the suspected presence of HCl, a variety of other combustion and decomposition products were identified as shown in Table 1.

Table 1. Typical GC/MS Analysis of Air Samples Collected at STS-5 Launch

<u>Compound</u>	<u>Analysis</u> <u>($\mu\text{g}/\text{m}^3$)</u>
Cyclobutane	.45
Aziridine	.02
Methane, Trichlorofluoro (R-11)	.40
Pentane	.48
Cyclopropane, 1,1-Dimethyl	.10
Methane, Dichloro	.03
Acetaldehyde	.20
Butane, 2,3-Dimethyl	.12
Pentane, 3-Methyl	.05
Hexane	.10
Cyclohexane	.04
Ethane, 1,1-Dichloro-1-Nitro	.03
Benzene	.34
1-Pentanol, 4-Methyl	.01
Hexane, 3-Methyl	.09
Heptane	.04
Cyclohexane, Methyl	.28
Benzene, Methyl	1.22
Hexane, 2,3,4-Trimethyl	.06
Benzene, 1,3-Dimethyl	.18
Unknown (4)	.31

Note: This sample was collected on a Tenax^R tube at the northwest elevated camera pad for L+0:10 to L+3:28 hours following the launch of STS-5 at KSC.

Potentially irritating substances, identified by coupled gas chromatograph/mass spectrometer analysis of samples collected during STS-5, were present in trace quantities only and were not believed to be significant in relation to the presence of HCl. On the basis of these findings, interest centered on the sampling and analysis of HCl in the postlaunch environment. The program's objective was to gain an understanding of HCl's persistence and to assess the health significance of that persistence as it might impact USAF Space Shuttle launches from Vandenberg AFB (VAFB). The importance of the program can best be understood when considering the close physical proximity

of launch support facilities and personnel at the VAFB launch site. In contrast to the remote setting of the KSC shuttle launch pad, the launch pad at VAFB will be surrounded by numerous shuttle support facilities and the occupied launch control center (LCC) within a 2000 foot radius.

II. GASEOUS HCl MEASUREMENT TECHNIQUES

Both direct and indirect methods were used at various times in an attempt to quantify the presence of gaseous HCl following Space Shuttle launches. Gas detector tubes which change color in the presence of nonaerosol forms of HCl were used because of their simplicity and quick response. The National Institute for Occupational Safety and Health (NIOSH) has certified the Draeger Company's HCl tube at a level of 2.5 ppm \pm 35%. The tube's response is based on the reaction of an acid with bromophenol blue producing a change in the length of color stain proportional to the acid's concentration.

Midget impingers or "bubblers" were used as an indirect method for HCl collection. In impinger sampling, a measured volume of air is passed through a liquid collecting media which is held for later analysis. Modifications which have been employed in the collecting system to improve collection efficiency include: lowering the airflow rate to lengthen contact time, using a micropore frit to improve contact surface area, and altering the collection media to improve retention of the contaminant. The major advantage of a midget impinger is its wide use and acceptance as a standard method for the collection of gaseous contaminants and it provides a sample for quantitative analysis by sensitive and specialized analytical techniques. Its major disadvantage is it does not provide immediate results.

Analysis for HCl in the collection media was accomplished by specific ion chromatography which allowed a sensitivity of 2.5 μ g/sample. The limit of detection in terms of airborne concentration is clearly a function of the amount of air sampled by the midget impinger. In a typical 30 minute sample at a flow of 1 Lpm, the limit of detection would be 0.08 mg/m³ or 0.06 ppm HCl. All sampling for HCl was corrected for background levels of the halogen present as sea spray at Kennedy Space Center and a reference temperature 77°F, barometric pressure at 760 mmHg.

III. SAMPLING PROTOCOL AND RESULTS

STS-5

Sampling accomplished in support of STS-5 involved the use of two standard midget impingers connected in series with a calibrated vacuum pump and using distilled deionized water as the collecting media. Sampling trains were positioned around the launch pad prior to launch as shown in Figure 1 and operated for various periods as reported in Table 2 with the results. The sampling stands were equipped with radio pagers provided by NASA to allow remote start and stop of all sampling. Upon reentering the launch pad area following launch, it was discovered that certain samplers which should have been operating were not. Analysis of the collecting media indicated that,

although the samplers were not running at reentry time, they had collected both HCl and other exhaust gas products. These data points are identified in the table by parentheses.

For data points where the sampling time was questionable, concentration estimates were based on the actual mass of HCl collected and the assumption that the samplers had operated until the reentry team arrived. Shorter sampling times would yield higher concentration estimates. Surface winds during the sampling period were from the east (090) at 9 knots.

STS-6

Sampling strategy for STS-6 was directed toward providing a basis for comparison with STS-5 but recognizing the fact that prevailing wind and operational parameters could influence the comparison. Samplers, as described for STS-5, were positioned at the locations shown in Figure 1 and Table 3. Poor pager response again contributed to sampling problems in STS-6. Sample results shown in parentheses in Table 3 indicate that the sampler was not operating when the reentry team gained access to the site. Estimated concentrations were again based on the actual mass of HCl found in collecting media and the assumption that the sampler had operated until the reentry team arrived. True concentrations higher than reported in Table 3 are, therefore, likely.

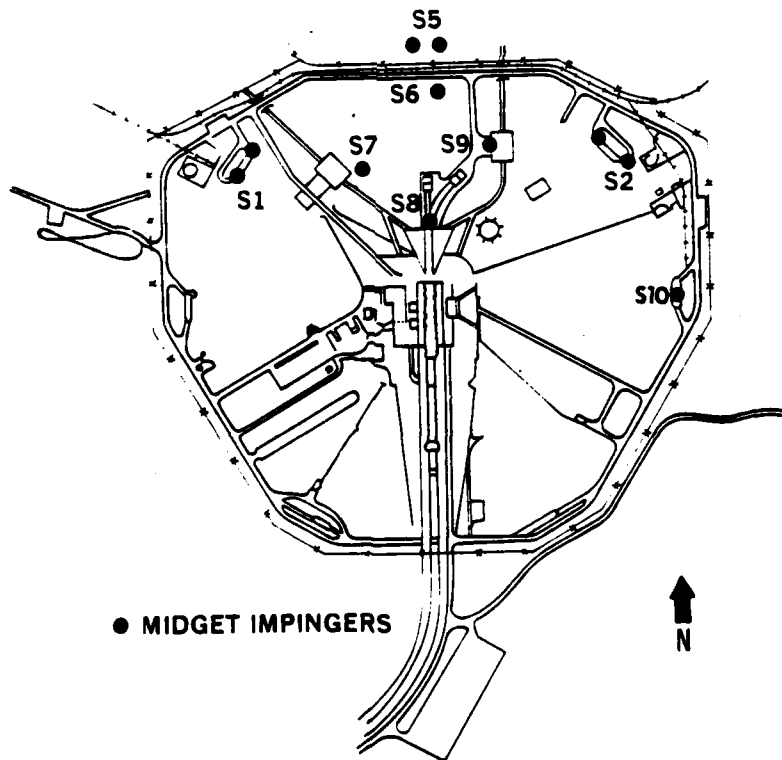


Figure 1. Sampling Site Identification, Pad 39A

Table 2. STS-5 HCl Sampling Results

<u>Location</u>	<u>Site</u>	<u>Start Time</u>	<u>Stop Time</u>	<u>Total HCl (ug/sample)</u>	<u>Concentration HCl (ppm)</u>
NW Pad	S1	L-0:05	L+0:10	315	23.8
	S1	L+0:10	L+3:28	2997	11.4
NE Pad	S2	L-0:05	L+0:10	39	2.9
	S2	L+0:10	(L+1:41)	305	(2.5) ¹
Knollenberg SRB	S5	L-0:05	(L+0:10)	372	(28.1) ²
	S5	L+0:10	(L+4:11)	12,437	(38.7) ²
SRB	S6	L+4:22	L+6:51	217	0
	S7	L+5:46	L+6:58	697	3
	S8	L+5:47	L+7:05	16	0
	S9	L+4:47	L+7:21	7	0

¹Concentration estimate based on an assumed sampling time. See text for details. Concentration could have been higher.

²This sampler sustained blast damage during launch. The reentry team noted that a vacuum line had been blown from the apparatus at some point during the launch.

Table 3. STS-6 HCl Sampling Results

<u>Location</u>	<u>Site</u>	<u>Start Time</u>	<u>Stop Time</u>	<u>Total HCl (ug/sample)</u>	<u>Concentration HCl (ppm)</u>
NW Pad	S1	L-0:05	L+0-10	17	1.3
	S1	L+0:10	(L+4:00)	37	(0.1) ¹
NE Pad	S2	L-0:05	L+0:10	15	1.1
	S2	L+0:10	(L+4:00)	12.5	(0.1) ¹
Knollenberg	S5	L-0:05	L+0:10	8086	610
	S5	L+0:10	(L+4:00)	13377	(46) ¹
SRB	S6	L+4:37	L+6:06	57	0.2
	S7	L+4:27	L+5:58	137	0.5
	S8	L+4:16	L+5:50	25.5	0.1
	S9	L+4:11	L+5:44	19.5	0.1

¹Concentration estimate based on an assumed sampling time. See text for details.

In addition to the single sample trains, sequential samplers were introduced at STS-6 to obtain more complete time history data for HCl concentrations at sites S1, S2, and S10 shown in Figure 1. Sequential sampling was accomplished by connecting several standard midget impinger trains to individual sampling ports on a timer-actuated vacuum manifold. The vacuum source as set to move from one impinger train to the next at 28 minute intervals with a 2 minute delay between samples. Sampling data obtained from sequential sampling during STS-6 are presented in Table 4. Surface winds following launch were from the east-northeast (050) at 8 knots.

Table 4. Sequential Sampling Data, STS-6

Approximate Times (L+)		HCl Concentration (ppm)		
<u>Start</u>	<u>Stop</u>	<u>S1</u>	<u>S2</u>	<u>S10</u>
0:00	0:30	0.24	1:11	0.71
0:30	1:00	0.19	1.11	<0.13
1:00	1:30	0.68	1.07	<0.13
1:30	2:00	0.19	1.31	<0.13
2:00	2:30	0.24	1.36	<0.13
2:30	3:00	0.19	1.11	0.19
3:00	3:30	0.19	2.17	<0.13
3:30	4:00	0.19	0.68	<0.13
4:00	4:30	2.11	1.14	0.19
4:30	5:00		1.79	0.37
5:00	5:30		1.75	0.24
***	***		-	-
10:30	11:00	0.82	-	-
11:00	11:30	0.82	-	-
11:30	12:00	0.48	-	-
12:00	12:30	0.48	-	-
12:30	13:00	0.24	-	-
13:00	13:30	0.35	-	-

STS-7

Based on examination of STS-5 and 6 results, the sampling program for STS-7 centered on the need to carefully evaluate the validity of the revolatilization hypothesis. The standard midget impinger trains used in previous surveys were modified by the introduction of a micropore frit into the impingers to improve collection efficiency and reduce breakthrough to the second impinger. The sample collection flow rate was lowered to less than 1 Lpm to permit longer residence time with the collecting media. Sequential samplers were positioned at locations S1 and S6 following the launch (approximately L+2:00) to avoid blast damage during launch and possible contamination of equipment from the initial cloud of exhaust products. Site selection was made on the assumption that both areas would receive considerable acid deposition and provide the best opportunity to observe the time change in HCl concentration

resulting from evaporation of the deposited acid. Sequential sampling data are presented in Table 5. Surface winds at the sampling sites were determined to be from the north-northeast (040) at 3 knots.

Table 5. Sequential Sampling Data, STS-7

Approximate Times (+)		HCl Concentration (ppm)	
<u>Start</u>	<u>Stop</u>	<u>S1</u>	<u>S6</u>
2:45	3:15	-	0.94
3:15	3:45	0.48	(1)
3:45	4:15	0.15	0.73
4:15	4:45	0.56	0.47
4:45	5:15	1.78	0.50
5:15	5:45	1.17	0.62
5:45	6:15	0.97	0.31
6:15	6:45	1.22	0.27
6:45	7:15	3.77	0.17
7:15	7:45	0.81	0.32
7:45	8:15	2.82	(2)
8:15	8:45	0.66	0.21
8:45	9:15	1.17	0.07
9:15	9:45	1.86	0.16
9:45	10:15	0.41	0.13
10:15	10:45	-	0.20
10:45	11:15	-	0.19

(1) Impinger leaked

(2) Flow blocked

Measurements made using the Draeger HCl tubes at a small culvert 50 meters east of site S6 at L+2:30 indicated a level of 8 ppm HCl, while measurements at site S6 in the same time period indicated a level of 2 ppm. There was no measurable concentration of HCl at site S1 using the Draeger HCl tubes at L+3:00.

IV. DISCUSSION OF RESULTS

The objective of this sampling program has been to examine the near field spatial distribution of gaseous HCl concentrations and the potential for revolatilization of deposited HCl. It is necessary to recognize that impingers collect both aerosol and gaseous forms of contaminants and, therefore, when both are likely to be present, they cannot be differentiated. This is an important consideration when evaluating the data reported in Tables 2 and 3 for the periods L-0:05 to L+0:10. In the early postlaunch environment, both aerosol and gaseous forms of HCl are present.² The data in Table 3 suggest that the aerosol form played a significant role in impinger loading at site S5

but not at sites S1 or S2 which are outside the direct influence of the solid rocket booster (SRB) exhaust trench. This observation is supported by a qualitative evaluation of vegetation damage on the launch pad following launch. A clear line of acid deposition damage has been observed following each launch which did not extend to sites S1 and S2. It is reasonable to believe that HCl concentrations in the early postlaunch period measured at site S5 are the result of both aerosol and gaseous loading integrated over the sampling time whereas concentrations at S1 and S2 are principally the result of gaseous loading.

The elevated time-weighted average (TWA) concentrations estimated to exist at site S5 during the period L+0:10 to L+4:00 (see Tables 2 and 3) can be attributed to the possible revolatilization of deposited HCl from the area near the sampling site. Since the active sampling did not begin until L+0:10, aerosol produced by the launch would have been transported away from the site by prevailing winds. The inadvertent entry of a sufficient number of HCl droplets into the sampler inlet prior to active sampling is considered remote. This analysis suggests that the measured loading of HCl in the time frame of L+0:10 to L+4:00 at site S5 following both STS-5 and STS-6 was the result of gaseous HCl. The issue of the timing of the presence of gaseous HCl can be refined by an examination of the sequential sampling data in Table 5.

Site S6 was in close proximity to S5 and will be assumed to represent a common location. The earliest sampling at site S6 began at L+2:45 and was accomplished using equipment which could not have been contaminated by the launch. Given the time at which measurements began and the prevailing temperature and humidity conditions, the presence of aerosol HCl would have been unlikely.³ These data suggest that a level of approximately 1 ppm HCl would exist at site S6 at the time L+3:00. This information in conjunction with the data in Tables 2 and 3 for site S5 in the time period L+0:10 to L+4:00 supports the belief that elevated TWA levels of gaseous HCl can exist following launch of the Space Shuttle and that those levels decay with time to a value of approximately 1 to 4 ppm at L+3:00.

Although revolatilization may be a rapid postlaunch phenomenon, it also persists at a lower rate as evidenced by the elevated HCl levels for several hours postlaunch shown in Table 4 and 5. The prevailing wind direction and region of HCl deposition play a key role in determining the magnitude of HCl concentration at the two sites shown in Table 5. Although site S6 was in a region of high HCl deposition, the prevailing winds from the north-northeast carried more evaporating HCl to site S1 which resulted in a general trend towards higher HCl concentrations at that site. This observation is best understood from the concept of a pathlength leading to each site. Although site S6 was in a region of higher deposition, the prevailing winds and physical geometry of the deposition region combined to make the pathlength for evaporation leading to site S6 less than that for S1.

V. CONCLUSIONS

Generalizations regarding the data gathered during the three Space Shuttle launches must be viewed with skepticism given the numerous uncontrolled

variables that existed for every launch. These variables, such as wind speed and direction/air temperature and humidity, have been shown to exert a significant influence on the partitioning of total HCl between aerosol and gaseous phases and the distribution of HCl deposition around the launch pad following launch. Although the data from the three launches have been grouped as though from a common population, it is important to recognize the limits of that analysis. Given the influence of the uncontrolled variables, it is not reasonable to believe that the concentration of HCl in time or space will be the same from one launch to the next. It is reasonable to believe that certain physical and chemical processes will influence the HCl deposited by any launch and it is on that basis that the data have been grouped.

The survey data show that the HCl deposited on the launch pad produces a persistent contamination which can exist for several hours following launch. Integrated 30 minute samples beginning at approximately 3 hours postlaunch (L+3:00) show that average levels of less than 1 ppm to approximately 4 ppm exist depending on both location and local meteorological conditions. The small size of the data base and the apparent influence of local meteorology prevents confident extrapolation of results. It is, however, reasonable to believe that adverse weather conditions would result in higher concentrations. Current Occupational Safety and Health Administration (OSHA) criterion limits occupational exposure to HCl at a level of 5 ppm that is not to be exceeded even instantaneously. This is the same level recognized by the American Conference of Governmental Industrial Hygienists (ACGIH) and in use by the USAF.

A second but earlier phase of revolatilization is suggested by sampling performed at the SRB trench centerline following launches 5 and 6. Integrated samples collected in the period $L+0:10 < t < L+4:00$ were estimated to have contained at least 39 to 46 ppm HCl. A short sample collected just prior to L+0:10 showed a level of several hundred ppm and a sample collected as part of the sequential sampling program during the period $L+2:45 < t < L+3:15$ showed a level of approximately 1 ppm. Observation of the launches and a review of the videotapes have shown that the majority of the exhaust cloud would have been transported away from the pad area prior to the L+0:10 time. The exact distribution of HCl concentration with time cannot be derived from the available integrated concentration data; however, these results suggest that high levels can persist in the wetted SRB trench area which are not explained solely on the basis of the launch generated cloud alone. It is reasonable to believe that deposited HCl may undergo rapid evaporation from the wetted pad surfaces contributing to levels in excess of the USAF and OSHA standards for occupational exposure to HCl. Under the meteorological and launch parameters at the three launches, these high levels decayed to the 1 to 4 ppm level by L+3:00.

Translating the measurements from KSC to confident prediction of levels at VAFB is complicated by the many differences in launch pad geometry, surfaces available for deposition, and the amount of deluge water to be used during launch. Regardless of those differences, the implications for HCl revolatilization cannot be ignored. The potential for rapid evaporation of HCl from the wetted pad surfaces at KSC and the more persistent revolatilization over a period of hours will occur at VAFB to a greater or lesser extent depending on

the relative importance of the variables just mentioned and the meteorological conditions at the time of launch. Personnel reentering the pad area within three hours following a launch will need respiratory protection available for use in the event that HCl levels are found to be in excess of 5 ppm.

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