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ASSESSMENT OF POSSIBLE ENVIRONMENTAL EFFECTS
OF SPACE SHUTTLE OPERATIONS

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16. ABSTRACT

The objectives of this study are to examine the potential of Shuttle operations to contribute to atmospheric pollution, bound the problems if any of significance are found, and provide a preliminary investigative report on the subject. Presented in this interim report are results of the study to date on rocket exhaust inventory, exhaust interactions, dispersion of the ground cloud, detection and measurement of hydrochloric acid and aluminum oxide, environmental effects of hydrochloric acid and aluminum oxide, stratospheric effects of Shuttle effluents, and mesospheric and ionospheric effects of orbiter reentry. The results indicate Space Shuttle operation will not result in adverse environmental effects if appropriate launch constraints are met. Several areas which require additional study and information are identified.

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1. EXHAUST AND GROUND CLOUD INVENTORY

1.1. INTRODUCTION

We have applied the equations of the conservation of mass on an element by element basis to the exhaust inventory, and to a preliminary ground cloud estimate. These estimates serve to highlight areas where data are lacking. The most serious were water input from the tower, the extent of afterburn of CO and H_2 in the exhaust, and the effect of adsorption or reactions between Al_2O_3 and gaseous HCl and H_2O.

1.2. GROUND CLOUD INVENTORY

We have established the effluents of the SRM and orbiter by altitude range to check the inputs of gases into various levels of the atmosphere. The flight profile is shown in Figure 1. The data presented in Tables 1 through 7 represent these tabulations, including an application of the law of conservation of matter to each element and a check that the total mass of effluent equals the total mass of fuel. The result of these checks generally confirmed the earlier NASA data except for a large quantity of hydrogen in excess over stoichiometric, carried by the orbiter.

The writing of these tables brought to focus two potentially important areas where data are lacking, a) we have no reliable estimates of the mass of tower material and cooling water that enters the ground cloud, and b) we have as yet no data on the afterburning of the very large quantities of H_2 and CO emitted at the exit plane of the rocket.

SHUTTLE FLIGHT PATH

o.ɪ. – Orbiter Ignition

s.ɪ. – Solid Rocket Ignition

Figure 1

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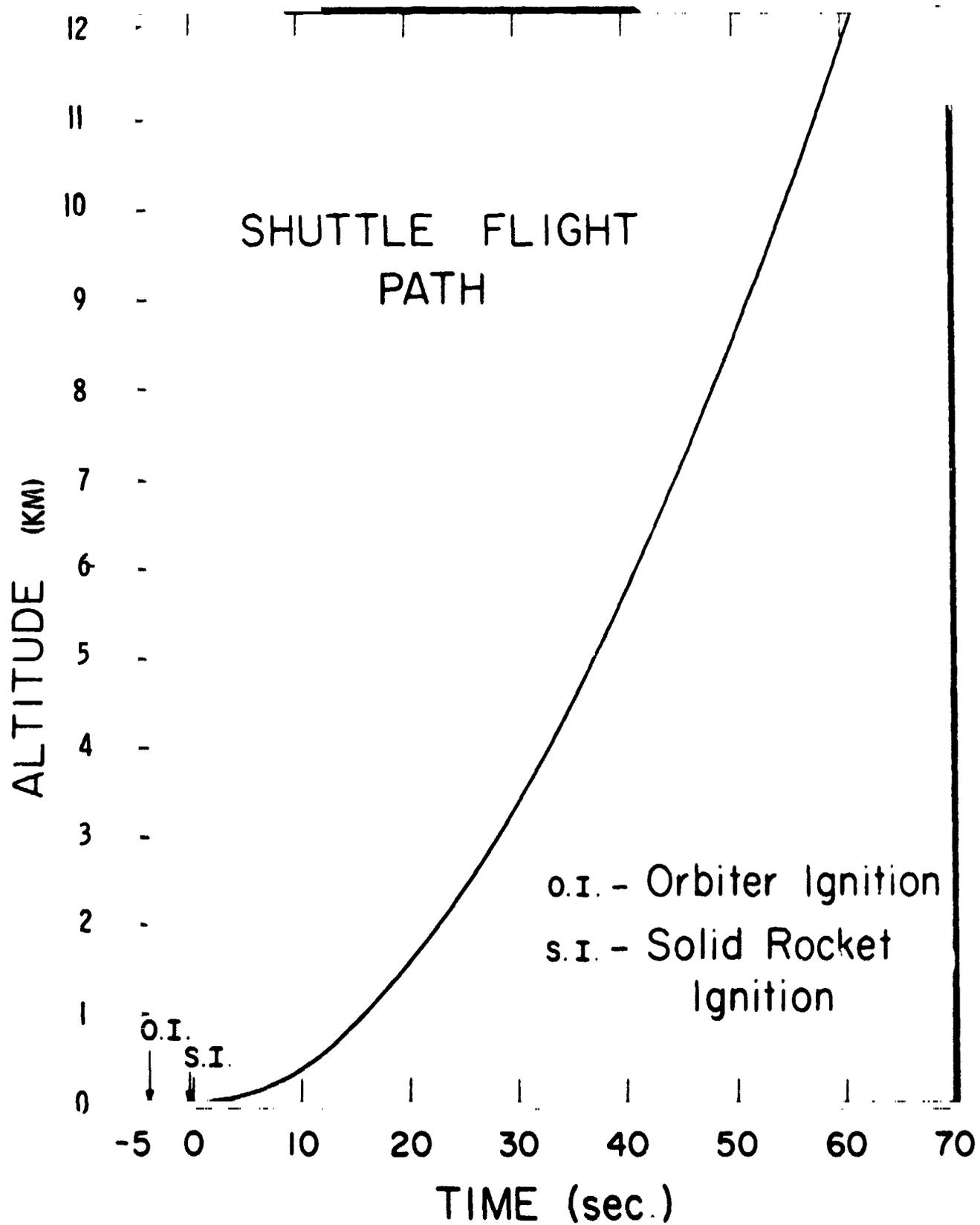
TABLE 1

SPACE SHUTTLE INVENTORY

COMBUSTION PRODUCTS EMITTED BY SRM AND ORBITER*

Combustion Product	ALTITUDE RANGE					TOTAL
	0-500 m	.5-10 km	10-50 km	50-67 km	67 + km	
	kg	kg	kg	kg	kg	kg
CO	37,200	113,100	115,100	--	--	265,400
CO_2	6,600	20,100	20,440	--	--	47,140
HCl	31,900	96,900	98,800	--	--	227,600
N_2	12,980	39,478	40,282	--	--	92,328
H_2O	34,638	107,905	164,357	47,111	387,004	741,015
H_2	3,974	12,195	13,520	1,889	15,496	47,074
Cl_2	92	278	284	--	--	654
H, OH	31	93	94	--	--	218
Aluminum Oxide	43,300	131,600	134,100	--	--	309,000
Iron Chloride	1,481	4,505	4,587	--	--	10,573
Aluminum Chloride	31	93	94	--	--	218

TOTAL ALL PRODUCTS EXPENDED: 1,741,220

PLUS: REMAINING IN BOOSTER: 2,080

LIFT-OFF FUEL WEIGHT : 1,743,300

*
a) Unknown H_2O input from cooling water is omitted.

b) Tabulated at exit plane. Reactions which occur during cooling have been neglected.

c) All entries checked for mass balance element by element shown on later tables.

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TABLE 2

SPACE SHUTTLE INVENTORY

COMBUSTION PRODUCTS EMITTED BY SRM AND ORBITER

Altitude Range	Combustion Product	Emissions (kg)		TOTAL
		SRM	ORBITER	
0-500m	CO	37,200	---	37,200
(14.01% of Total SRM)	CO_2	6,600	---	6,600
	HCl	31,900	---	31,900
	Cl_2	92	---	92
	Al_2O_3	43,300	---	43,300
	H_2O	15,870	18,768	34,638
	H_2	3,222	752	3,974
	$FeCl_3$	1,481	---	1,481
	N_2	12,980		
	$AlCl_3$	31		
	H,OH	31		
.5 - 10km	CO	113,100	---	113,100
(42.61% of Total SRM)	CO_2	20,100	---	20,100
	HCl	96,900	---	96,900
	Cl_2	278	---	278
	Al_2O_3	131,600	---	131,600
	H_2O	48,100	59,805	107,905
	H_2	9,800	2,395	12,195
	$FeCl_3$	4,505	---	4,505
	N_2	39,478		
	$AlCl_3$	93		
	H,OH	93		

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TABLE 2 (Concluded)

Altitude Range	Combustion Product	Emissions (kg)		
		SRM	ORBITER	TOTAL
10 - 50 km				
(43.38% of Total SRM)	CO	115,100	---	115,100
	CO_2	20,440	---	20,440
	HCl	98,800	---	98,800
	Cl_2	284	---	284
	Al_2O_3	134,100	---	134,100
	H_2O	49,900	114,457	164,357
	H_2	9,977	3,543	13,520
	$FeCl_3$	4,587	---	4,587
	N_2	40,282		
	$AlCl_3$	94		
	H,OH	94		
50 - 67 km	H_2O	---	47,111	47,111
	H_2	---	1,889	1,889
67 + km	H_2O	---	387,004	387,004
	H_2	---	15,496	15,496

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TABLE 3

SRM EXHAUST PRODUCTS PERCENT CONTRIBUTION BY WEIGHT

$\underline{\underline{C}}$

CO: $\frac{12}{28}$ x .2435 = .1043

CO_2: $\frac{12}{44}$ x .0432 = .0118

% C = .1161

$\underline{\underline{H}}$

HCl: $\frac{1}{36.5}$ x .2088 = .0057

H_2O: $\frac{2}{18}$ x .1041 = .0116

H_2: .0211 = .0211

OH&H: $\frac{2}{18}$ x .0002 = .0000

% H = .0384

$\underline{\underline{O}}$

AL_2O_3: $\frac{48}{102}$ x .2835 = .1332

CO: $\frac{16}{28}$ x .2435 = .1391

CO_2: $\frac{32}{44}$ x .0432 = .0314

H_2O: $\frac{16}{18}$ x .1044 = .0928

OH&H: $\frac{16}{18}$ x .0002 = .0002

% O = .3962

$\underline{\underline{N}}$

N_2: .0850 = .0850

$\underline{\underline{Fe}}$

$FeCl_2$: $\frac{56}{127}$ x .0097 = .0043

% F_e = .0043

$\underline{\underline{Al}}$

AL_2O_3: $\frac{54}{102}$ x .2835 = .1501

$AlCl_2$: $\frac{27}{98}$ x .0002 = .0001

% Al = .1502

$\underline{\underline{Cl}}$

HCl: $\frac{35.5}{36.5}$ x .2088 = .2031

Cl_2: $\frac{1}{1}$ x .0006 = .0006

$AlCl_2$: $\frac{71}{98}$ x .0002 = .0001

$FeCl_2$: $\frac{71}{127}$ x .0097 = .0054

% Cl = .2092

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TABLE 4

SRM MASS BALANCE CHECK FUEL INVENTORY*

Empirical Formula	(Moles)	M.W $\left[\frac{gm}{mole}\right]$	Gram Formula Weight	Percent Weight Contribution
Al	0.5930	26.98	15.99	.1600
C	0.9411	12.01	11.30	.1131
H	3.7087	1.00	3.71	.0372
N	0.6244	14.01	8.75	.0876
O	2.4330	15.99	38.90	.3892
Fe	0.0050	55.84	0.28	.0028
Cl	0.5924	35.45	21.00	.2101
TOTAL	8.8976		99.93	100.00

TOTAL MASS 1,090,000 kg

PERCENT CONTRIBUTION FROM EXHAUST PRODUCTS
(from Table 3)

Al	.1502	15.03
C	.1161	11.62
H	.384	03.84
N	.0850	08.50
O	.3962	39.64
Fe	.0043	00.43
Cl	.2092	20.94
	.9994	100.00%

TOTAL MASS 1,090,322 kg

*Data from NASA Huntsville. Small discrepancies represent differences in formulation of the solid rocket fuel. The entry under Fe and an extra impurity sulfur are particularly variable.

TABLE 5

TOTAL ORBITER OUTPUT*

Breakdown	kg	Percent
H_2O	627,145	96.3
H_2	24,075	3.7
Total	651,220	

* Exit plane composition stable molecules only does not include radical or atomic species. The amount of H_2 exhausted which burns in air before the plume cools is at present unknown.

TABLE 6

ORBITER MASS BALANCE CHECK

		kg		
		Less		
Element	Fuel Inventory	Fuel Remaining	Fuel Burned	Effluent
O	558,000	605	557,462	557,462
H	95,300	1542	93,758	93,758

TABLE 7

MOLE PERCENT OF GASEOUS EXHAUST PRODUCTS 0-500 m *

CO	19.7
CO_2	2.22
HCl	13
N_2	5.9
H_2O	28.6
H_2	29.4
Cl_2	0.019

* Exit plane composition neglecting free radicals and afterburn because of lack of data.

The next stage in the inventory is to transform the emissions inventory into a ground cloud composition. A preliminary attempt at that process is shown in Tables 8 and 9. The calculation uses the exhaust inventory of Table 1 and an estimate of the properties of an average ground cloud at T = 90 secs supplied by NASA (from Lockheed Environmental Impact Statement). This is a conservative calculation, probably representing a worst case, but again it serves to point out some problems: a) where is the cloud and what are its size, shape, and temperature parameters at T + 90 sec?, b) what fraction of the 0-500m emissions enters the cloud?, c) what is the size distribution and density of the Al_2O_3 particulate matter?, and d) what fraction of the HCl/H_2O is on the Al_2O_3?

1.3. FUTURE WORK

Several items are clear from the inventory of Table 8. The cloud is optically very thick with Al_2O_3 and contains toxic concentrations of both HCl, (301 ppm), and CO, (457 ppm) which greatly exceed allowable limits (see Section 4). We are presently conducting a study to determine to what degree HCl is bound to the Al_2O_3 particles. The inventory lacks clarity because we have no good data on cooling water input, ablated tower material or afterburn. The ground cloud composition we show contains a number of questionable assumptions, and lacks important data particularly in the size distribution of the Al_2O_3. Figure 2 shows a preliminary size distribution which will be refined by current studies at NASA Langley.

The CO/HCl ratio in ground cloud from the Final Impact Statement (1972) was the same as in the rocket effluent. Because of afterburn this is likely to be wrong (an initial guess

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TABLE 8

GROUND CLOUD CONCENTRATION INVENTORY *

Gas/Particle	Concentration
CO	457 ppm
HCl	301 ppm
H_2O	662 ppm
H_2	684 ppm
Al_2O_3	318 particles/cc 0.665 gm/m^3
$FeCl_2$	13.7 particles/cc

Dilution with ambient air 430:1

Ground Cloud Configuration: At T = 90 seconds
Altitude: 500 meters
Radius: 250 meters
Temperature: 85°F (120°F at T = 35 sec)
Ambient = 60°F

Assumptions:

1. All gases and particles are distributed evenly throughout the cloud.

2. All effluent below 500 meters is enveloped into the cloud.

3. Al_2O_3 and $FeCl_2$ particles assumed to be monodispersed at 5×10^{-6} radius.

4. The input from cooling water into the cloud has not been included for lack of data.

5. Cloud assumed to be centered at 500 meters and have a radius of 250 m at T = 90 sec (Ref: Lockheed Environmental Impact Statement).

6. Density Al_2O_3 = 3.965 gm/cc
          $FeCl_2$ = 3.160 gm/cc

7. Afterburn from exit plane neglected for lack of data.

* Details of the calculations are found in Table 9.

TABLE 9

GROUND CLOUD CALCULATIONS

1. Volume of Cloud: $V = \frac{4}{3} \pi r^3 = \frac{4}{3} (3.16)(250m)^3$

$$= 65.05 \times 10^6 \ m^3$$

$$= 65.05 \times 10^{12} \ cc$$

2. Standard molecule density in cloud at S.T.P.

$$\frac{6.023 \times 10^{23} \text{ molecules/mole}}{22,400 \text{ cc/mole}} = 2.69 \times 10^{19} \text{ molecules/cc}$$

3. Effluent of concern contained in cloud at 500 M.:

Gas/Particle	Weight (kg)
CO	37,200
H Cl	31,900
H_2O	34,638
H_2	3,974
Al_2O_3	43,300
$FeCl_2$	1,481

4. Molecules per cc of Gases in Cloud

CO: Molecules per gram $= \dfrac{6.023 \times 10^{23} \text{ molecules/mole}}{28 \text{ grams/mole}}$

$$= 2.15 \times 10^{22}$$

Total Molecules in Cloud $= (2.15 \times 10^{22})(37,200 \times 10^3)$

$$= 80,019 \times 10^{25}$$

CO Molecules per cc in cloud $= \dfrac{80,019 \times 10^{25}}{65.05 \times 10^{12}} = 1230 \times 10^{13}$

HCl: Molecules per gram $= \dfrac{6.023 \times 10^{23}}{36.5} = 1.65 \times 10^{22}$

Total molecules in cloud $= (1.65 \times 10^{22})(31,900 \times 10^3)$

$$+ 52,639 \times 10^{25}$$

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HCl Molecules per cc in cloud $= \dfrac{52,639 \times 10^{25}}{65.05 \times 10^{12}} = 809 \times 10^{13}$

$\underline{H_2O}$: Molecules per gram $= \dfrac{6.023 \times 10^{23}}{18} = 3.35 \times 10^{22}$

Total molecules in cloud $= (3.35 \times 10^{22})(34,638 \times 10^3)$

$= 115,902 \times 10^{25}$

H_2O Molecules per cc in cloud $= \dfrac{115,902 \times 10^{25}}{65.05 \times 10^{12}} = 1782 \times 10^{13}$

$\underline{H_2}$: Molecules per gram $= \dfrac{6.023 \times 10^{23}}{2} = 3.012 \times 10^{23}$

Total molecules in cloud $= (3.012 \times 10^{23})(3,974 \times 10^3)$

$= 11,968 \times 10^{26}$

H_2 Molecules per cc in cloud $= \dfrac{11,968 \times 10^{26}}{65.05 \times 10^{12}} = 184 \times 10^{14}$

5. Total no. of solid particulates in cloud

$\underline{Al_2O_3}$: Volume of 1 particle $= \frac{4}{3} \pi r^3 = \frac{4}{3}(3.16)(5 \times 10^{-6})^3 \ m^3$

$= 526.7 \times 10^{-18} \ M^3$

$= 526.7 \times 10^{-12} \ cc$

Weight of 1 Al_2O_3 particle $=$ (density Al_2O_3)(Vol. 1 Particle

$= (3.965 \ \frac{gm}{cc})(5.26.7 \times 10^{-12} \ \frac{cc}{part})$

$= 2088.2 \times 10^{-12} \ grams$

Total no. of Al_2O_3 particles $=$

$\dfrac{\text{total wt. } Al_2O_3}{\text{weight 1 particle}} = \dfrac{43,300 \times 10^3 \ gms.}{2088.2 \times 10^{-12} \ gm/part}$

$= \underline{\underline{2.07 \times 10^{16}}}$

$FeCl_2$: Weight of 1 $FeCl_2$ particle $= (3.160 \ \frac{gm}{cc})(526.7 \times 10^{-12} \ \frac{cc}{part})$

$= 1664.2 \times 10^{-12} \ grams$

Total no. of $FeCl_2$ particles $= \dfrac{1,481 \times 10^3 \text{ gm}}{1,664.2 \times 10^{-12} \text{ gm}}$

$$= \underline{8.90 \times 10^{14}}$$

6. Calculation of Gas/Particle concentrations

CO: $\dfrac{\text{No. of Part./cc}}{\text{Normal Cloud density: molecules/cc}} = \dfrac{1230 \times 10^{13}}{2.69 \times 10^{19}} = 457 \times 10^{-6}$

HCl: $\dfrac{809 \times 10^{13}}{2.69 \times 10^{19}} = 301 \times 10^{-6}$

H_2O: $\dfrac{1781 \times 10^{13}}{2.69 \times 10^{19}} = 662 \times 10^{-6}$

H_2: $\dfrac{184 \times 10^{14}}{2.69 \times 10^{19}} = 684 \times 10^{-6}$

Al_2O_3: $\dfrac{\text{No. of Particulates in Cloud}}{\text{Cloud Volume: cc}} = \dfrac{2.07 \times 10^{16}}{65.05 \times 10^{12} \text{ cc}}$

$$= \underline{318 \text{ particles/cc}}$$

$FeCl_2$: $\dfrac{8.90 \times 10^{14}}{65.05 \times 10^{12}} = \underline{13.7 \text{ particles/cc}}$
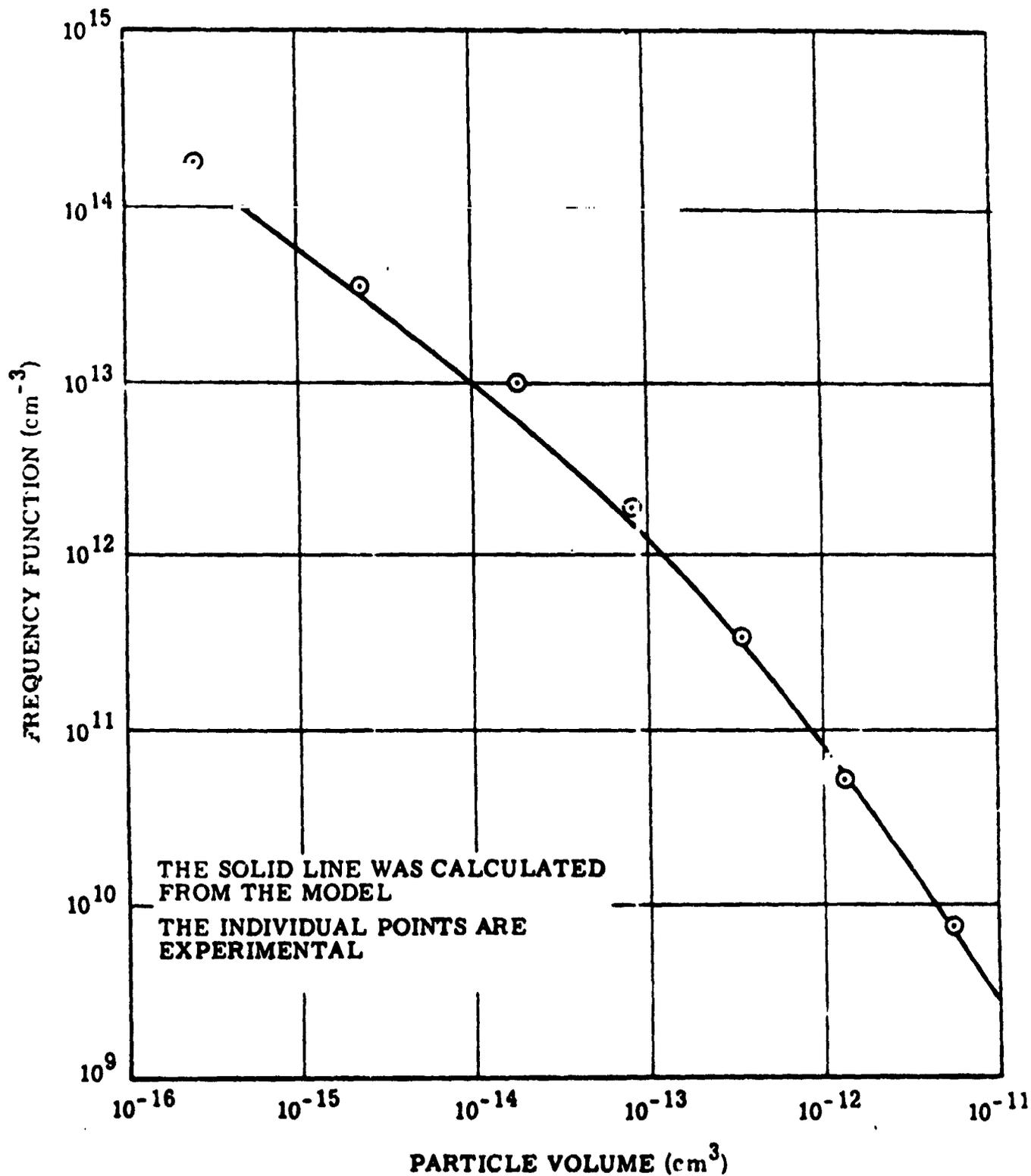
FIGURE 2. THEORETICAL AND EXPERIMENTAL FREQUENCY
FUNCTIONS AT A CHAMBER PRESSURE OF 500 PSI
(Fein, 1965).

would be an order of magnitude reduction in CO and H_2. We are currently working to improve on this guess by numerical modeling of the afterburn situation.

2. INTERACTIONS AND DISPERSION OF GROUND CLOUD

2.1. INTRODUCTION

A preliminary model of the interaction of Al_2O_3, HCl, and H_2O has shown that even for spherical, nonadsorptive, Al_2O_3 particles over one-half of the gas phase HCl concentration is removed, and the spheres are coated with 4.8 molal HCl.

2.2. GROUND CLOUD MODELING

Professor A. N. Dingle at The University of Michigan is currently active in theoretical studies of acidic rain, especially the rainout of H_2SO_4. He has developed a sophisticated computerized model (Storebö and Dingle, 1973) to simulate the transition from the gas phase chemistry through to the precipitation of H_2SO_4, including all the important meteorlogical variables. A recent article, "Acid Rain" in Environment, March, 1972, discusses how little is known. The computer simulation uses a microscopic model of cloud-droplet growth nucleation, rainout, and washout by superriding rainfall. His model is a dynamic one taking into account meteorological variables, and has been used successfully in studies relating to acid rainfall in Europe.

This modeling has been extended to treat HCl; the major problem is lack of knowledge on how gas phase HCl gets onto particles, e.g., alumina (Al_2O_3) particles. To our knowledge the only experimental setups available to study this phenomenon are at NASA Langley. We add simple diffusion of gaseous HCl into the particle phase (assumed spherical nonadsorptive), and

then calculate the rate of the ground cloud and the acidity of resulting mists of rain. It would be particularly valuable for this purpose if we could obtain some detailed meteorological and emissions information on the Dade County test which caused extensive crop damage. It would be a good test of the model if it could indeed predict (albeit after the event) such an occurrence.

Necessary parameters include chemical constants such as surface tensions, solution densities, molalities and accommodation coefficients, and particle size distributions. The sources of the values used are shown in Table 10.

The nonequilibrium droplet-nucleation model was thus used to study the processes of removal of HCl and H_2O vapor from the exhaust plume of the shuttle booster. Initial efforts were addressed to the problem of managing the bilateral (both physically inherent and numerical) instabilities of HCl and H_2O vapor concentrations in the presence of a log-normal size spectrum of Al_2O_3 particles.

By introducing an arbitrary limitation upon the change of molality of the condensed phase from one time step to the next, allowing this limitation to vary systematically with particle size, we were able to compute the initial cloud particle size distribution, temperature, and humidity for a nearly steady state condition after some 75 cycles of computation. The results for particle size are shown in Figure 3. The initial and final values of the important variables are given in Table 11.

Noteworthy is the fact that the smallest size class has acquired considerable acid and water, more than quadrupling its radius in this time period. This raises a question as to the relative importance of still smaller ($\gamma < .02\mu m$) size classes.

The rise of temperature of nearly 4°C indicates the release of both latent heat and heat of solution of HCl. Because this warming is great, the final relative humidity is surprisingly low (less than 75%). The final molality at this point is about 4.82.

TABLE 10

INPUT PARAMETERS FOR HCl SCAVENGING MODELS

Input Data Sources	References
Heat Capacities of Acid Solutions	Handbook of Chemistry and Physics D79
Heat of Dilution of Acids	Handbook of Chemistry and Physics D77
Densities of Acid Solutions	Handbook of Chemistry and Physics D189
Surface Tension of Solutions	International Critical Tables, Vol. 4, p. 464.
Vapor Pressure of Solutions	International Critical Tables, Vol. 3, p. 301.
H_2O Partial Pressures	Othmer and Naphtali (1956)

PARTICLE GROWTH DURING EQUILIBRATION PHASE

Figure 3

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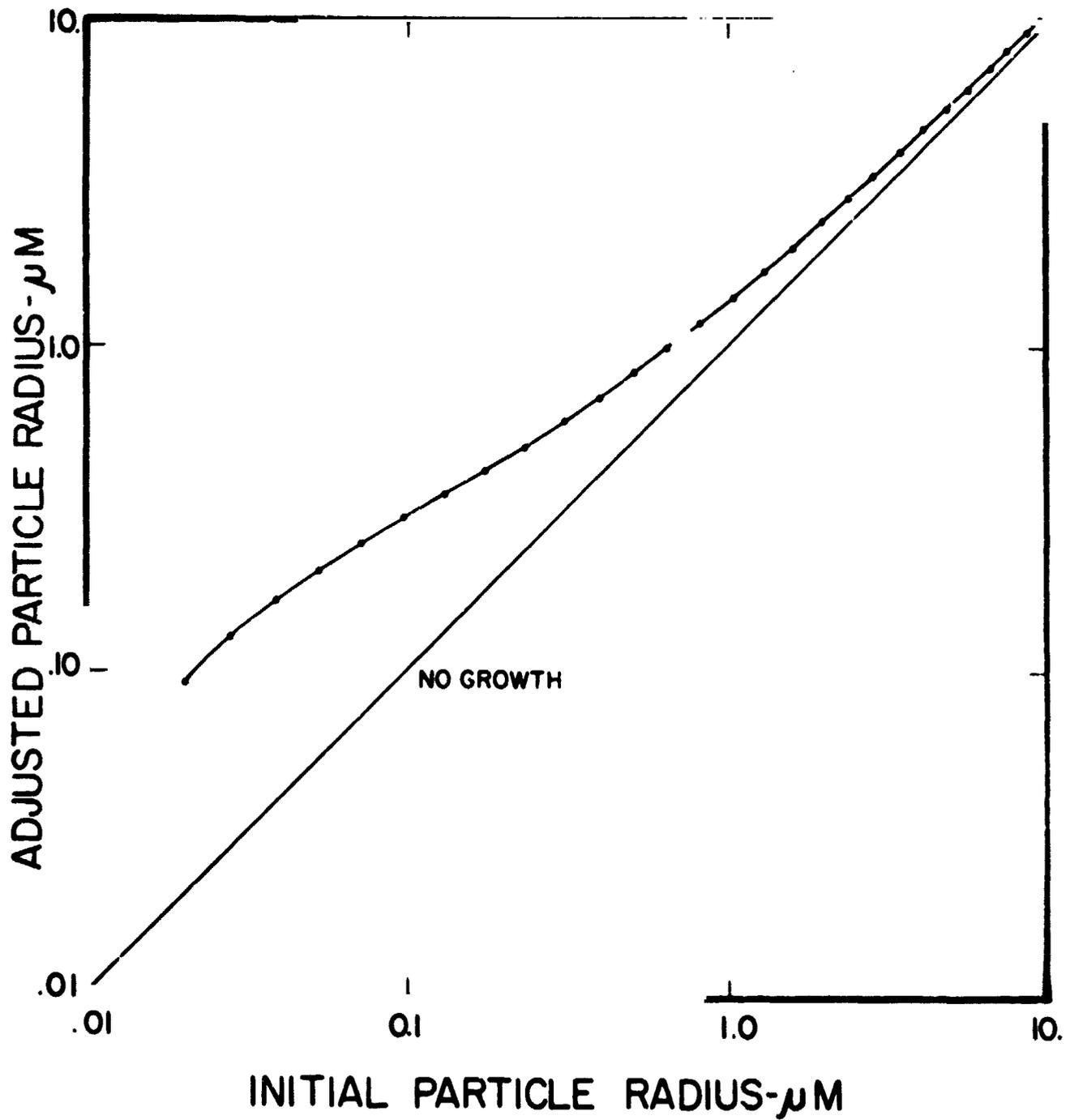
TABLE 11

SAMPLE RESULTS OF HCl SCAVENGING MODELS

	BEFORE	AFTER 75 CYCLES
Cloud Temperature-°K (85°F)	302.600	306.558
Mixing Ratio (H₂O)-g/kg	27.985	26.357
Relative Humidity-%	100.000	74.387 (94.183 without temp. change)
HCl Gas Concentration-ppm	352.2	134.7
Liquid H₂O per GM Air-g	0.0	1.628×10^{-3}
Dissolved HCl per GM Air-g	0.0	2.863×10^{-4}

Resultant mean molality = 4.823

After equilibration, particle molality ranges

from a minimum of 4.8148 for size class #1 (smallest)
to a maximum of 4.8255 for size class #20, then
decreases to 4.8238 for size class #30 (largest)

Further experimentation with molality limitation has led to negative results, i.e., a closer limitation on the molality change from one step to the next failed to produce an improved containment of the $HCl-H_2O$ oscillation.

Further cycling beyond 150 or so steps led to an increased oscillation of the large particles, alternately over-acquiring H_2O and HCl, evidently at the expense of the small particles.

To simplify, and possibly improve the computations, we adopted a new model on an experimental basis. In this model we have initially apportioned all the HCl among the Al_2O_3 particles in direct proportion to their spherical equivalent area. This HCl is then permanently attached to the respective particles, and the system is allowed to acquire H_2O from the environment (or evaporate it). This procedure is more arbitrary than the earlier one, but it is considerably simpler computationally, and we believe it will approach very closely to the same steady state molality as the earlier model.

The approach is designed to supplement the Marshall diffusion model (Dumbauld et al., 1973). This model explicitly takes account of particle nucleation, growth, and the effects of overriding rain. The Marshall model treats only atmospheric motion and diffusion with arbitrary loss terms. When this model is fully developed the ideal approach will be to fuse the capabilities of the two models.

3.   DETECTION AND MEASUREMENT

3.1.   INTRODUCTION

We have attempted to find the best method of determining
the low levels of H_2, CO, HCl, and Al_2O_3 in the ground cloud.
Unfortunately, an unknown amount of afterburn reduces H_2 and
CO, probably to levels too low to measure.   Therefore one must
look for HCl and Al_2O_3, however as we discussed in the previous
chapter, a large amount of the gaseous HCl may be removed by
the Al_2O_3 to the particle phase.   Thus very low concentrations
of gaseous HCl, and acid-coated $Al_2O_3/AlCl_3/H_2O/HCl$ particles
are to be sought.   These features render NASA Langley's mea-
surement task particularly difficult, since there is already
a large sea-sourced background component of NaCl in the wet
particulate phase.

It would be helpful to all concerned if the two classified
documents RADC-TR-67-667 "Particle Identification" and RADC-TR-
70-185 "Particle Sampling" could be declassified as soon as
possible.

3.2.   HCl DETECTOR

We wrote to every likely manufacturer of instrumental
analytical equipment concerning the detection of 1-10 ppm HCl.
The only instrument which was quoted as being available was an
adaptation of the Mine Safety Apparatus "Billionaire" device.
We have no practical experience with this equipment but have
heard from others that it has some instability problems.

We have followed the pertinent literature in this field
and note that two new detectors have been described in the
last six months.   Both are wet chemical, one is a modification

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of the coulometric Mast ozone detector (Miller et al., 1971) (and is automatic), the other is based in the $AgNO_3$ reaction and is similar to the specific chloride electrode process currently in use by Langley.

The Billionaire apparatus uses the reaction between HCl and ammonia to generate particles which cause an ionization response. We believe that the sensitivity and fast response of the chemiluminescent NO detector to NH_3 (Stedman et al., 1972) can be used to monitor the decrease in NH_3 signal. A proposal to NASA to develop such a detector is currently under review.

Solid state detectors of air pollutants have only recently appeared on the market. Thin film electrochemical devices offer some promise of response to low concentrations of HCl, which needs to be investigated.

3.3. Al_2O_3 DETECTION

Unambiguous sampling of airborne particles is an experimentally difficult matter. Direct measurement of light scattering can give a particle count, and an approximate size distribution down to 1.5μ, but can not give a chemical analysis. Filtration catches all particles larger than a given size. Impaction gives a size distribution. Unfortunately both processes pass large quantities of air over the collected particle. Thus before it can be examined the particle will have interacted to equilibrium with the ambient air, frequently gaining or losing water in the process.

Direct examination by light microscopy of the collected particles is the least destructive process, but the wavelength of light is around 5μ, so small particles cannot be discerned. Scanning electron microscopy (SEM) has resolution down to $100\overset{o}{A}$ (0.1μ) but the particle must be gold-coated and placed under high vacuum, thus frequently altering its nature.

Some SEM pictures which were taken by a NASA Langley study showed flattened spheres, less than 1μ in diamter. We have generated similar looking particles by controlled combustion of aluminum in oxygen. An electron micrograph of these particles is shown in Figure 4.

Nondestructive chemical analysis of the whole filtrate or imported sample for Al can be done to a very high sensitivity by Neutron Activation Analysis. The lower limit for detection is of the order of 1.0 ng. Chloride can be similarly determined down to 2.0 ng, but the confusion due to sea-salt cannot be overcome. Analysis of single particles by electron microprobe analysis can confirm the presence of Al, but it may not be possible to determine by this technique how much of the HCl originally was in the form of $AlCl_3$ or HCl solution on the Al_2O_3 particle.

The difficulties of these measurements constitute a strong reason for pushing the modeling of the ground cloud to as accurate a prediction as possible, and for pursuing the current studies of $HCl/H_2O/Al_2O_3$ interactions in the laboratory. All facets of the interaction may not prove amonable to direct experimental verification in a launch situation.

Figure . Scanning Electron . . . . . rap . . . . . . A
. art i c l e . . . 20 , .

4. ENVIRONMENTAL EFFECTS OF HCl

4.1. INTRODUCTION

One of the major effluents of the Solid Rocket Motors to be used on the Space Shuttle Boosters will be hydrogen chloride gas (HCl). In combination with water, HCl forms a strongly acidic solution, hydrochloric acid. The dangers of hydrochloric acid solutions to the student are often one of the first things one learns in elementary chemistry courses, and the basic toxicology is given in standard handbooks (for example, Industrial Hygiene and Technology 2nd Edition, Vols. 1 and 2, Interscience, 1958). Because HCl is used in, or a by-product of, certain industrial operations, it has been of some concern to those involved in environmental safety and with air pollution. Perhaps the most complete summary to be found is the "Preliminary Air Pollution Survey of Hydrochloric Acid, A Literature Review" (Stahl, 1969) published by the National Air Pollution Control Administration. Tables 13 through 15 are reproduced from this work.

Our literature survey has found one Soviet study suggesting genetic defects in flowers but little quantitative information on the direct effects of low level doses.

4.2. LITERATURE SURVEY

We have conducted an extensive survey of literature, seeking qualitative and quantitative information on this problem. Generally this work has been time-consuming and discouraging, revealing a dearth of information at least that is available from the open literature in English. Many hopeful-sounding titles have turned out to be "popular articles", abstracts, or in Russian. Others remain to be examined. From the various reports in

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"Hydrochloric Acid and Air Pollution: An Annotated Bibliography" (E.P.A.), from "Preliminary Air Pollution Survey of Hydrochloride Acid" (U.S.P.H.S. Air Pollution Control Administration), from the Science Citation Index and by examining recent issues of Chemical Titles we have identified several names and references on current work on plants. A couple of these articles (and a Ph.D. thesis) report substantive research but the level of research and the state of the art is much lower than we had hoped.

We performed a computer search for literature on toxic effects of the HCl in the University of Michigan Library and requested a similar, more extensive search by the National Library of Medicine, N.I.H. in Bethesda, Maryland. Again, many of the references are to obscure sources, are difficult to find, and often Japanese, German, etc. We have examined the lists we received, as well as the Toxicity Bibliography and recent Air Pollution Abstracts.

This survey has focused on toxic effects of HCl and the purposes of the contract for which this report is written, the survey of Stahl is incomplete. First, it only covers the literature to 1969, second it admittedly does not "attempt to interpret or reconcile conflicting data", and there are considerable discrepancies in the HCl literature and third, it does not point out where additional research is needed. This report attempts to correct these deficiencies (at least in part) in the case of the toxicological studies. Table 12 shows a summary of various standards set for human exposure.

4.3 ANNOTATED BIBLIOGRAPHY

Stahl, Quade R. Preliminary Air Pollution Survey of Hydrochloric Acid. A Literature Review. U. S. Department of Health, Education, and Welfare. National Air Pollution Control Administration, 1969.

TABLE 12

HUMAN EXPOSURE STANDARDS FOR HCl

Max. Allowed Concentration (ppm)	Time Period	Conditions	Country	Stahl Ref.
0.009	24 hr average	ambient air quality	USSR	86
0.02	24 hr average	ambient air quality	Czecnoslo-vakia	84
0.03	single exposure		USSR	86
0.07	single exposure		Czechoslo-vakia	84
0.5	30 min average	ambient air quality	West Germany	55
1.0	30 min average	max. allowable	West Germany	55
5.0		work station	West Germany	55
5.0	8 hr day/5 day week		U.S.	111

(above data from Stahl)

				Ref.
2	1 hr average	general public	U.S.	NAS/NRC 1971
2	30 min average	general public	U.S.	NAS/NRC 1971
4	10 min average	general public	U.S.	NAS/NRC 1971
3	1 hr average	general public-emergency limits	U.S.	NAS/NRC 1971
3	30 min average	general public-emergency limits	U.S.	NAS/NRC 1971
7	10 min average	general public-emergency limits	U.S.	NAS/NRC 1971
10	1 hr average	controlled (work Sta) pop. Short-term emergency limits	U.S.	NASA/1968
20	30 min	controlled (work Sta) pop. Short-term emergency limits	U.S.	NASA/1968

Refs.   NAS/NRC-1971 = "Guide for Short-term exposure of the Public to Air Pollutants. II. Guide for Hydrogen Chloride. (Nat. Advisory Center on Toxicology NAS, NRC Aug. 1971)

NASA/1968 = "Compendium of Human Responses to the Aerospace Environment" Vol III, NASA CR1205 (111), Nov. 1968

Probably most complete survey up to that time.
Tables 13, 14, and 15 (see attached) summarize results of various
studies in easily usable form. The report is not "a synthesis
of available information but rather a summary without an attempt
to interpret or reconcile conflicting data." There are major
conflicts though as can be seen from scanning the tables. Some
of them arise because the data are from experiments performed
many years ago when accurate measurements and control of HCl
concentrations may have been difficult. The present author
is unable to evaluate the problems in the studies in man and
other animals. In most cases of the studies on plants and
data in Table 14 are from abstracts or reports of field obser-
vations where the information for evaluating the accuracy are
either not given or were unavailable to the author.

Two things stand out from Table 14: (1) Different plants
have different susceptibilities to HCl. (2) Almost all ex-
periments are short term. There are virtually no studies
covering several generations (to consider effects on repro-
duction) or cumulative effects of low level repeated or con-
tinuous exposure.

TABLE 13

SUMMARY OF REPORTED EFFECTS OF INHALATION OF HYDROGEN CHLORIDE BY HUMANS

Concentration (ppm)*	Exposure Time	Effects or Comments
50-100		Work is impossible
10-50		Work is difficult but possible
10		Work is undisturbed
1,300-2,000	Few min	Lethal
1,000-1,300	30-60 min	Dangerous
50-100	60 min	Intolerable
35		Irritation of throat after short exposure
1,000-2,000		Brief exposures are dangerous
10		Irritation
5		No organic damage
10		Odor threshold value
0.067-0.134		Odor threshold value
0.402		Concentration for threshold reflex effect on optical chronaxic
0.134		Concentration for threshold reflex effect on eye sensitivity to light
0.335		Concentration for threshold effect on digito-vascular toxicity
0.067-0.134		Threshold concentrations of change in the rhythm and depth of respiratory movement
1-5		Odor threshold value

*1 ppm = 1,470 μg/m³ at 25°C.

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TABLE 14

SUMMARY OF REPORTED EFFECTS OF INHALATION
OF HYDROGEN CHLORIDE ON ANIMALS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments
Rabbits	4,300	30 min	Fatal in some cases, due to laryngeal spasm, laryngeal edema, or rapidly developing pulmonary edema
Guinea pigs	4,300	30 min	Fatal in some cases, due to laryngeal spasm, laryngeal edema, or rapidly developing pulmonary edema
Cats	3,400	90 min	Death after 2 to 6 days
Rabbits	3,400	90 min	Death after 2 to 6 days
Guinea pigs	3,400	90 min	Death after 2 to 6 days
Cats	1,350	90 min	Severe irritation, dyspnea, and clouding of the cornea
Rabbits	1,350	90 min	Severe irritation, dyspnea, and clouding of the cornea
Guinea pigs	1,350	90 min	Severe irritation, dyspnea, and clouding of the cornea
Rabbits	670	2 hr	Fatal in some cases
Guinea pigs	670	2 hr	Fatal in some cases
Rabbits	300	6 hr	Corrosion of the cornea and upper respiratory irritation
Guinea pigs	300	6 hr	Corrosion of the cornea and upper respiratory irritation
Rabbits	100-140	6 hr	Only slight corrosion of the cornea and upper respiratory irritation
Guinea pigs	100-140	6 hr	Only slight corrosion of the cornea and upper respiratory irritation

TABLE 14 (Concluded)

Species	Concentration (ppm)*	Exposure Time	Effects or Comments
Rabbits	100	6 hr/day for 50 days	Slight unrest and irritation of the eyes and nose
Guinea pigs	100	6 hr/day for 50 days	Slight unrest and irritation of the eyes and nose
Pigeons	100	6 hr/day for 50 days	Slight unrest and irritation of the eyes and nose
Monkey	33	6 hr/day 5 days/week for 4 weeks	No immediate toxic effects and no pathological changes
Rabbit	33	6 hr/day 5 days/week for 4 weeks	No immediate toxic effects and no pathological changes
Guinea pig	33	6/hr/day 5 days/week for 4 weeks	No immediate toxic effects and no pathological changes
Rabbits	60	5 min	Cessation of ciliary activity without recovery
Rabbits	30	10 min	Cessation of ciliary activity without recovery

*1 ppm = 1,470 μg/m³ at 25°C.

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TABLE 15

SUMMARY OF REPORTED TOXIC EFFECTS OF
HYDROGEN CHLORIDE EXPOSURE ON PLANTS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments
Plants	10-50		No leaf damage
Plants	100-1,000		Leaf damage
Sugar beets	10	Few hr	Threshold for marking
Viburnum seedlings	5-20	24 hr	Leaves rolled at the edges, withered, shrunk, faded, and necrotic
Beech	1,000	1 hr	Local lesions produced
Oak	1,000	1 hr	Local lesions produced
Maple	2,000		Marginal leaf scorch
Birch	2,000		Marginal leaf scorch
Pear	2,000		Marginal leaf scorch
Viburnum seedlings	5-20	48 hr	Plants died
Larch	5-20	48 hr	Plants died
Fir	1,000	1 hr	Local lesions formed
Spruce	2,000	1 hr/day for 80 days	No apparent injury
Tomato plants	5	2 hr	Developed interveinal bronzing followed by necrosis within 72 hours after exposure
Liriodendron tulipifera	3	4 hr	Threshold for visible injury
Alnus glutinosa	6	4 hr	Threshold for visible injury
Prunus serotina	6	4 hr	Threshold for visible injury

TABLE 15 (Concluded)

Species	Concentration (ppm)*	Exposure Time	Effects or Comments
Acer saccharus	7	4 hr	Threshold for visible injury
Acer platanoides	7	4 hr	Threshold for visible injury
Quercus rubus	13	4 hr	No visible injury
Pinus strobus	8	4 hr	Threshold for visible injury
Psaudotsuga mantissii	10	4 hr	Threshold for visible injury
Abies balsamca	10	4 hr	Threshold for visible damage
Pinus abies	19	4 hr	Threshold for visible damage
Pinus nigra	18	4 hr	No visible damage
Thuja occidentalis	43	4 hr	No visible damage
Spruce seedlings	<50	20 min	Plants died

*1 ppm = 1,470 $\mu g/m^3$ at 25°C.

Bibliographic Sources

*Air Pollution Abstracts - U.S. Environmental Protection
     (Monthly)   Agency Air Pollution Technical
                       Information Center (APTIC)
                       Research Triangle Park, N. C. 27711

Air Pollution Abstracts - Department of Trade and Industry
     (Monthly)   (Britain) Warren Spring Laboratory

*Toxicity Bibliography - U.S. Public Health Service -
     (Monthly)   Library of Medicine

Toxicity Information Program - National Library of Medicine
     will do literature search on request. (See example attached).

Air Pollution Technical Information Center - Research Triangle
                                  Park, N. C. 27711
     will do literature search on request (not used)

Hydrochloric Acid and Air Pollution: An Annotated Bibliography,
     U.S. Environmental Protection Agency, Research Triangle
     Park, N. C. (1971) pp. 51-64 deal with effect on humans
     (9p) and on plant and livestock (4p) (a one-shot thing,
     apparently).

*Best sources for continuing review of (relatively) current
literature.

NOTES: General Abstracting Journals such as Chem. Abstracts
         or Biographical Abstracts can be used but are generally
         inefficient. The toxicity information program search
         did give Chem. Abstract or Biol. Abstract references
         so that if nothing else, we have the abstracts. Another
         source, once one has several articles located is the
         Science Citation Index (which tells which other authors
         have referred to the paper of interest). This has not
         proved particularly rewarding either. Key word indexes
         in Chemical Titles and Biographical Abstracts are also
         useful for keeping up with current material.

4.4. SEMI-ANNOTATED LISTING OF OTHER ARTICLES OF INTEREST:

Arndt, V. "Konzentrations Anderungen ben Blettforbotoffen unter dem Einfluss von Luftverunreinigungen. Ein Diskussionalibeitrax Zun Pigment Analyse," Environmental Pollution 2, 37-48 (1971).

Reports that β-carotene is a better indicator of damage than chlorophylls are. Finds that 0.5 mg/m^3 HCl (ca. 0.34ppm) (exposure time not clear - could be several (6-10) months) results in 20% to 35% lower chlorophyll upon treatment with acid - in vitro.
[If the reading of the German is right, this could be one report of long-term, low-level exposure - and there is an effect, at least on pigment concentration.]

Baetjer, A. M. "Chronic Exposures to Air Pollutants and Acute Infectious Respiratory Diseases", Arch. Ind. Hyg. and Occupational Medicine 2, 400-406 (1950) [Source: Air Pollution Abst. (U.S.) Vol. 2 (6), 10857]

Quote from abstract: "data available at present are insufficient to draw conclusion".

Berge, H. Phytotoxische Immissionen (P. Parcy, Berlin, 1963) pp 51-53 (on HCl)

Description of properties of HCl, macroscopic and microscopic descriptions of damage, basis of effects, diagnosis of plant. References (few are given) are primarily in the 1930's.

Berry, C. R. "A Plant Fumigation Chamber Suitable for Forestry Studies," Phytopathology 60, 1613-1615 (1970).

[Article not read. Included in case someone wants to get into experimental work or wants to track somebody down who might do experimental work.]

Boray, E.   "The Effects of Air Pollution On Plants," (in
            French) in Probleme der luft verumreinigung
            durch die Industry (ed. (not recorded in my
            notes) (Vogt-Schild S. A., Switzerland, 1969)
            pp 1 - 19, 126 references.

        [Mostly on SO_2, may have some references on HCl -
        which is why it's mentioned here. Sources: Air
        Pollution Abstracts (U.S.) Vol. 2 (#6), 10994.]

[Cesta, R. P. and M. E. McLouth   "Launch Conditions Pro-
                                  duced By The Titan III-C
                                  Launch Vehicle", Amer.
                                  Inst. Indust. Hyg. J.
                                  30 635 - 639 (1969)]

        Included here because it contains actual measurements
        of HCl concentrations. Techniques and values - and
        their reliability - are worth looking at.

Daessler, H. G. and Ewart "Damage to Plants Caused by
                           Hydrogen Chloride", Biologische
                           Zentralblatt 88 209 - 213 (1969)

        [Chem. Abstracts 71 7367f: exposure of plants to
        0.05 - 2.0 mg/m^3 HCl (0.03-1.3ppm) resulted in a
        Cl^- ion content of up to 20 times that in the controls.
        (damage and [HCl] concentration were proportional at
        lower concentrations)].

European Congress on the Influence of Air Pollution on Plants
and Animals, First Proceedings. Air Pollution (Centre for
Agricultural Publishing and Documentation, Wageningen, The
Netherlands, 1969).

        [Included here primarily as information on it's exis-
        tence. It does not appear to have much, if any,
        discussion of HCl.]

Ewart, E. "Die Einwirkung von Chlorwasserstoff auf Plantzen
            in Experiment", Polsha Ahal Nauk...(See Air
            Pollution Abstracts, Vol. 2 (#11) 14624)-(for
            abstract's complete reference).

Under intermittent gassing (test periods between 50
and 470 hours) there was no damage when "maximum
permissible emission concentration of 0.05 mg/m^3
($\sim$0.03ppm) was not exceeded. At 2.0 mg/m^3 ($\sim$1.4ppm),
peas or beans showed "first symptoms of necrosis after
eight hours" (if plants were removed at this stage
some leaves died and fell off, but plant survived
and produced new, undamaged leaves). After 100
hours at the higher concentration all plants died.
[This may be the same Ewart working with Daessler,
above. If we continue to keep eye on literature,
his name may be one to look out for.]

Godish, T. J.   Effects of Hydrogen Chloride Gas on Photo-
synthesis, Respiration, Transpiration and
Photosynthetic Pigments of Tomato C.V.
Bonny Best Ph.D. Thesis Pennsylvania State
University, 1970.

Found effects on transpiration [water loss, important in cooling
the plant], respiration and photosynthesis at both high and low
exposure (8-10ppm for two hours = high 70pphm for ten hours per
day times two days or 40pphm for eight hours per day times seven
days = low). Effects were dependent on growing season and in
some cases on humidity. Depending on exposure he found increase
or decrease in respiration and photosynthesis, [making explana-
tion of response difficult]. In all cases, studies were made
within 24 hours of exposure [what happens in the long term? -
not answered.]

Abstract concludes: "The most significant findings of this study
were (1) changes in respiration and transpiration would be in-
duced in the absence of visible symptoms; (2) visible symptoms
in the form of chlorosis [loss of color] may have little to do
with plant debilitation, especially under saturating light in-
tensities; and (3) HCl gas, supposedly acidic does not convert
chlorophyll to pheophytin at low concentration exposures."
[(2) means that plants can still photosynthesize, at least

shortly after damage occurs, even though they show spotting,
etc. There are serious problems in accepting conclusion (3)
from a reading of the thesis. A great deal of experience in
chlorophyll measurements and the data presented in thesis indi-
cates that there were major deficiencies in the experimental
procedure so that the conclusion is not a reliable one. This
casts a bad light on the other conclusions although they may
be O.K. One point is clear: there are physiological effects on
plant processes which are not always immediately evident from
the external appearance of the plant. These physiological ef-
fects may be significant for the long term survival and growth
of the plant under low levels of exposure.]

Heck, W. W. "Symptomology of Injury to Vegetation By
Other Pollutants".
Section XI: 1-20, in Lacasse and Moroz, Editors, Handbook of
effects Assessment - Vegetation Damage (CAES, [CAES: Center Air
Environment Studies] The Pennsylvania State University, Univer-
sity Park, 1969).

Hindawi, I. J. "Injury by Sulfer Dioxide, Hydrogen Fluoride
and Chlorine As Observed and Reflected
On Vegetation In The Field." J. Air Pol-
lution Control Assn. 18, 307-312 (1968).

At one half maximum plant operations, smokestack
was emitting 119-473ppm HCl and 0.5-0.9ppm Cl_2.
Article has pictures of damaged plants. Residents
had complained of an acid mist smell and variety of
ornamental plants were damaged including necroting
spotting and decay of leaf margins. Early leaf ab-
scission (falling off of leaves) was also observed.

Hindawi, I. J. Air Pollution Injury to Vegetation (N. S.
Public Health Service, National Air Pol-
lution Control Administration, 1970) 44pp.
[not seen].

Il'kum, G. M. "Effect of Toxic Gases on Plants" (in Russian)
Fiziol. Biokhim, Kul't. Rost. 3, 87-92 (1971)

[in Chem. Abstract, Vol. 59] [Source: Air
Pollution Abstracts (British)]

K^+, Na^+, Ca^{2+} occur in greater amounts in trees living
near industrial plants giving off HCl. [This is con-
sistent with findings of Daessler and Ewart and of
Shriner and LaCasse (see these papers) which indicate
large increase of Cl^- in HCl treated plants. The
cations above would be picked up at the same time
to give total charge neutrality. H^+ is probably
neutralized by soil, or and the pH maintained (re-
latively) constant by uptake of plant roots].

Kisser, J. "Physiologische Probleme der Einwockung von
Luft verumreinigungn aufdie Vegetation."
Polsha Ahad Nauk...(See Air Pollution Abstracts,
Vol. 2, (#11) 14636 for abstract and complete
reference) "exposure of plants to hydrochloric
acid caused a depression of the water balance"
..."[see also Godish. This could also be
due to increased salt content; see Daessler
and Ewart, Il'kum, and Shriner and LaCasse].

Konstantinov, A. V. "Disturbances of Meiosis In Some
Plants Under the Effects of Hydro-
chloric Acid". Genet. Tsitol. 191-
199 (1970)(in Russian) see Chem.
Abst. 76, 54771g.

Treatment of flowers of variety of plants with 0.047 HCl
solution before meiosis in the anthers [process of cell
division during pollen formation] caused severe aberra-
tions in cells and chromosomes. A pH decrease of 0.8
was observed in some cell nuclei.
[This paper is known only from Chem. Abstracts. De-
spite the fact the work was done with HCl solutions
it has profound implications regarding the effect of
HCl in the reproduction of plants.]

Lind, C. T. and S. A. London "Exposure of Marigold (Tagetes

To Gaseous Hydrogen Chloride",
(U.S. Nat. Tech. Inform.
Service AO Report #732195
(18pp)(1971). See also
Chem. Abstracts 76, 76073r
and government reports an-
nouncement 71(24)31

From Chem. Abstracts: all plants died after five
minutes exposure to 2071ppm HCl. At 95ppm no
effect was noted.

Means, W. E., Jr. and M. C. Lacasse "Relative Sensitivity
of 12 Tree Species
TO HCl Gas". Phyto-
pathology, 59, 401,
(1959) Abstract.

[While only an abstract it does summarize data: e.g.
Liriodendron tulipifera had visible injury after
four hours exposure to 3ppm HCl. Others were more
tolerant Message Sensitivity is species specific,
at least.]

Ryabuskina, Zh. P. "Eye Lesions in the Hydrochloric Acid
Industry" Vestn. Oftamol. 3, 76-77
(1970) (in Russian?) c.f. Biol. Abst.
5258106

Shriner, D. S. and N. L. LaCasse "Rapid Determination of
Chloride Content of
Vegetation for Assessment
of Air Pollution Injury
From Hydrogen Chloride",
Phytopathology 62, 412-
429 (1972).

Exposure to tomato and chrysanthemum to 2-18ppm HCl
for one to three hours resulted in large amounts of
CL^- in leaves. "The procedure has potential useful-
ness as a diagnostic tool in assessment of air pollu-
tion injury from HCl gas."

Thomas, M. D. "Effects of Air Pollution on Plants" in
           Air Pollution (WHO Monograph Series, #46)
           Columbia Univ. Press, N. Y., 1961, pp 233-
           278.

Thomas, M. D. "Gas Damage to Plants", Ann. Rev. Plant
           Physiology, 2, 293 (1951)

Has two paragraphs on HCl. According to Thomas, older
literature implies that threshold concentration for
visible marking was 50-100ppm. Thomas and coworkers
found threshold for sugar beets is 10ppm for several
hours.

Tolo, K. J., et al. "Acidified Drinking Water and Dental
           Enamel In Rats", Z. Versuchsterk, 11:
           229-233 (1969).

This reference was run across a couple of times but
could never be tracked down. It is intriguing in the
same way that the Ryabuskina reference is - except
more so.

The following technical articles have also been studied
in more detail as follows:

Machle, W., et al. "The Effect Of The Inhalation of Hydro-
           gen Chloride", J. Ind. Hyg. Toxicol.,
           24: 222, 1942.

Because of its corrosive action the gas primarily
affects the respiratory tract. Damage in the form
of edema, necrosis, and hemorrhaging occurs to tracheal,
bronchial, and alveolar epithelium as well as pulmonary
blood vessels, interstitial tissues and pulmonary
alveoli. Damage can also occur to liver and kidneys
in severe cases where death results. In addition,
hearts in dead animals occasionally showed massive
myocardial infarctions.

Daessler, H. G. and E. Ewart   "Damage to Plants Caused
                               by Hydrogen Chloride",
                               Biologische Zentralblatt,
                               88, 209-213, 1969.
"Damage to plants in the emissions areas of chemicals
and potash may be diagnosed, not only by air analysis,
but by determination of chloride in damaged plants.
In various plants experimentally exposed to HCl gas
chloride levels up to 20 times critical values were
found, which persisted long after exposure was ended.
At lower concentrations, damage and HCl concentration
were proportional."

Heck, W. W.   "Symptomology of Injury to Vegetation by
              Other Pollutants", Sec. IX: 1-20, Handbook
              of Effects Assessment-Vegetation Damage CAES,
              Lacasse and Moroz, Editors, Pennsylvania
              State University.
A separate letter has been written requesting this
document.

Thomas, M. D.   "Effects of Air Pollution in Plants", Air
                Pollution WHO Monograph series 46, Columbia
                University Press, New York, 233-278, 1961.
"Hydrogen Chloride, of which about 10ppm for a few
hours is required to cause incipient plant damage,
was an important pollutant a century ago... (London-
Manchester area of England)."

"Guide to Short Term Exposure of the Public to Air
Pollutants II. Guide for Hydrogen Chloride", NAS/
NRC-1971, National Advisory Center on Toxicology,
August 1971.

This is a well documented short critique of HCl ex-
posure. Based on relatively little evidence they suggest
tentative short term public limits of 4ppm (6 mg/m^3) for
ten minutes with a public emergency limit of 7ppm for ten
minutes, with suitable caveats regarding the need for more
research.

4.5.   COMMENTS ON LITERATURE SEARCH

Search of literature to date reveals a common pattern.
HCl contamination has not been generally regarded as a health
problem for plants or animals, consequently data and research
on the problem is limited.

Research on plants to date indicates almost any detectable
amount of HCl is potentially harmful, if not immediately, then
eventually through damage of the reproductive process. Work
done on animals has been in the laboratory, and primarily on
rabbits and guinea pigs, and only occasionally chimpanzees, as
the effects of the gas are so severe as to rule out the use of
human subjects. The work done concerns the effects of exposure
to high concentrations of the gas for short periods of time
(a few days), the results of which are usually devastating.

Data are lacking on the effects of lower concentrations and
intermittent exposure over a longer period of time. Another
problem is the lack of quantitative data on the extent of
damage done by variable exposures, data usually taking the form
of statements like "more damage generally occurs with greater
exposure." The only pathological data concerns animals that
were injured so severely that they died and were subsequently
autopsied.

4.6   CONCLUSIONS

1)   Direct effects of HCl on humans have been studied rela-
     tively extensively, mostly concerned with either ac-
     cidents (e.g. swallowing concentrated HCl) or industrial
     exposure. These have resulted in setting of standards
     which interestingly enough, are different in different
     countries. This difference is due either (1) to differ-
     ences in the value of human life or human health or (2)
     different experimental techniques and results.

2) There appears to be no information on long term cummulative effects of continuous or frequent low level exposures on people. This is an area where some research could be useful. Of particular concern might be the effect on people of older ages of exposure that might be insignificant or minor for the general population. (There are frequent references to the increased death rate during air pollution alerts, etc.) This point is raised in view of the geographical location of the launch facility for the Space Shuttle.

3) The literature on plants raises two points. First low level exposures have physiological manifestations even when there is no visible, morphological effect. The experiments were usually terminated before the effects on the growth and long-term vitality of the planet could be evaluated. Also related is the question of continued low level exposures. The possible effect on flowering and reproduction, suggested by the work of Konstantinov deserves serious consideration and further experimental work. These experiments should be carried out on plants of the type surrounding the launch site at different HCl concentrations and should be done and evaluated before extensive launches are carried out. The second point is the fact that not all plants are equally sensitive to HCl. Thus experiments should be done on the plants in the vicinity of the launch sites.

As to whether shuttle represents a major source of atmospheric HCl on a nationwide basis, the total shuttle effluent from 50 launches per year is 1.1×10^6 kg. An estimate of total annual industrial U.S. HCl emission of 4.3×10^9 kg. can be made from data in Stahl (1969).

5. ENVIRONMENTAL EFFECTS OF Al_2O_3

5.1. INTRODUCTION

Our studies of the effects of Al_2O_3 have centered around the potentially harmful effects of inhalation by animals and man. None of our studies to date indicates there is any known or potentially harmful effect on plants from exposure to clean Al_2O_3 particles. But the effects of $AlCl_3$, or HCl-coated, wet $AlCl_3/Al_2O_3$ particles is unknown. An effect of Al_2O_3 particles causing lung damage (Shaver's Disease) is well known among public health personnel, but seems ill-documented in the literature. A preliminary consensus of medical opinion is that such occasional exposure as may arise from Shuttle launch is unlikely to show identifiable medical effects

5.2. SHAVER'S DISEASE

The effects of Al_2O_3 on the lung depend on a combination of particle size, dosage rate and length of exposure. Precise data on the effects of alumina particle inhalation is not available but enough is known to docume t the effects as potentially harmful. This phenomenon was first recognized in 1942 in workmen at bauxite plants and has been given the name Shaver's Disease.

Human lungs act as very efficient size-selective dust samplers (Figure 5). Airborne dust, when inspired into the lung, undergoes a process of separation based on size and falling rate. About 80% of larger particles (6μ or over) impact on the mucus lining of the larger passageways and are usually removed quite rapidly by ciliary escalation. Smaller dust partici
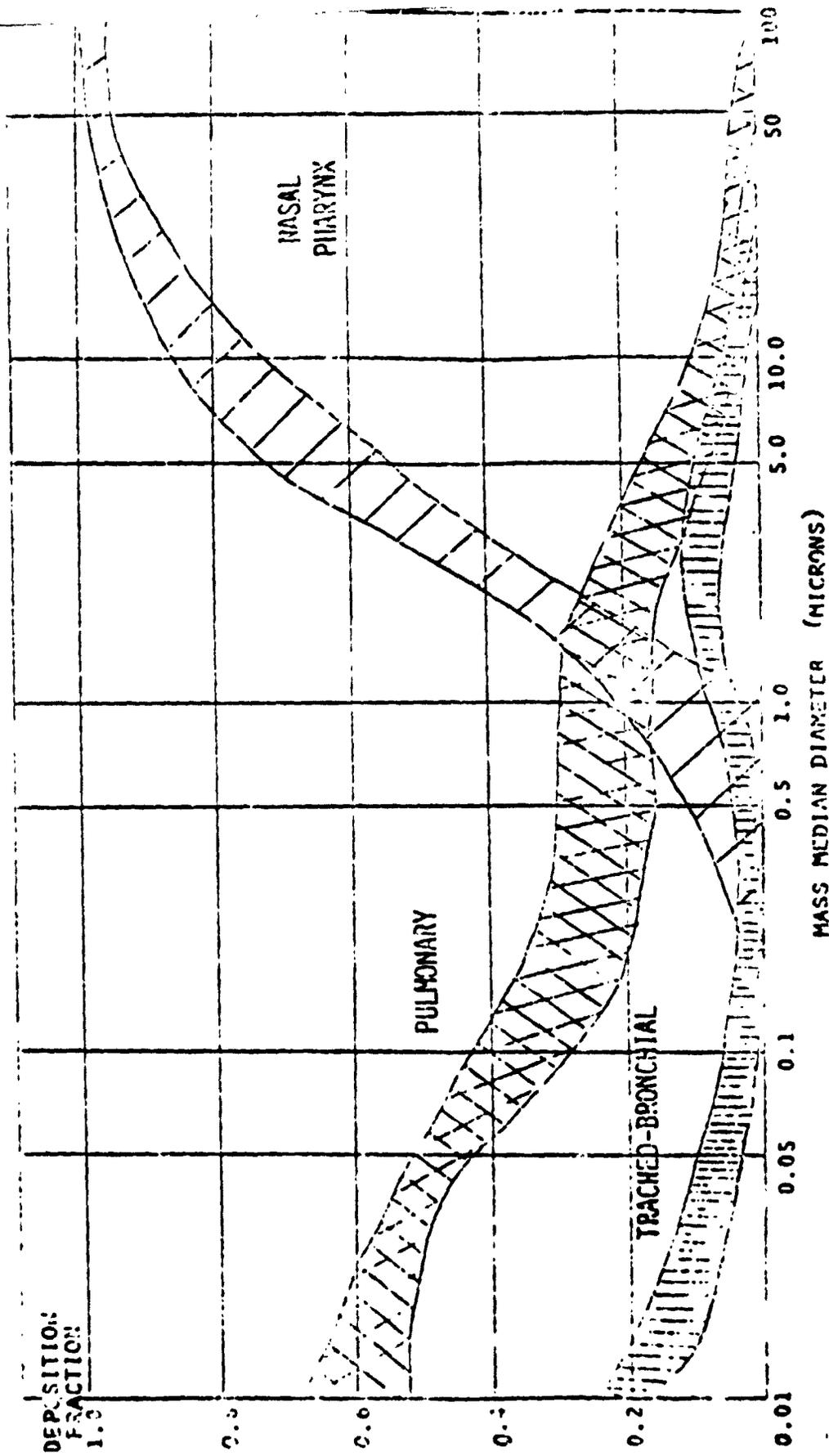
DEPOSITION OF DUST IN THE LUNG

FIGURE 5

penetrate more deeply and very fine particles on the order of
2μ or less penetrate the alveolar spaces. Here, the retention
rate is thought to be high (about 60%) in the 1 to 2μ size,
probably even higher in those below 0.2μ, and moderately severe
in the 0.2 to 0.5μ range. (The literature is unclear as to
whether the above mentioned sizes are radii or diameter; for
sizes below 2μ the answer is probably unimportant.)

Since the respiratory bronchioles and alveoli are lined
with surfactant, not mucus, dust particles settling here are
attacked by the surfactant (alveolar photocytosis). A large
proportion of these fine particles find their way to, and
penetrate, the lung interstitions and lymphatic tissues. It is
at this level that damage can occur and fibrosis result. Further-
more, the lungs natural clearance mechanisms can be overworked,
(mucus and surfactant production, ciliary activity and endocytosis
all increase) expecially if exposure is intermittent.

The first symptoms of Shaver's Disease are difficult or
labored breathing, brought on at first by considerable exertion
and later by less effort, until it is eventually present at rest.
In some people, an irritating dry cough precedes the awareness
of shortness of breath. These symptoms can develop to a dis-
abling degree in a remarkably short time, even within a few
months of first exposure. In advanced cases weakness and weight
loss result. Respiratory failure appears late in the course of
the disease, along with pulmonary hypertension, right heart strain
and subsequent right heart failure.

The response of the tissues of the lung to inorganic dusts
such as Al_2O_3 has been compared to the color spectrum to emphasize
the variety and type of response and its activity. One parameter
is certainly dose-related, a function of cumulative exposure over
time, less the "clearance" time over the years. It is also thought
to depend on the quantity and particle size of the dust, as well
as the absence or presence of infection, and the possible effects
of other synergistic or antigenic respirable materials in the
environment.

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In summary, we do not know as much about the effects of Al_2O_3 on the human lung as we would like. There is the question of what dosage is harmful and for how long a period. Is the alumina itself harmful or must we also consider its effects along with other particles, such as silica? Then there is the question of particle size, with that of 1μ or less thought to be of most concern.

5.3. INTERVIEW WITH PUBLIC HEALTH PROFESSOR I. HIGGINS

On February 21, 1973 an interview was conducted with Dr. Ian Higgins of the University of Michigan School of Public Health. Dr. Higgins specializes in the effects of the inhalation of organic and inorganic dusts on the human lung and is a lecturer to the University of Michigan Medical School.

Dr. Higgins pointed out that not much is known about the effects of the inhalation of Al_2O_3, as the disease is extremely rare and where it has occurred, documentation and the application of the "scientific method" has been marginal.

Research on the subject must also make the distinction between Shaver's Disease (the inhalation of Al_2O_3 dust) and Aluminosis (inhalation of aluminum dust). How little work has been done in the area is illustrated by the fact that some reputable sources make no distinction between the effects of the two, while other sources clearly indicate there is a difference. A further confusion seems to arise from occasional common usage in the grinder trade of "aluminum" when they should say "aluminum oxide" or "alumina". Our concern is, of course, with Shaver's Disease, Al_2O_3 inhalation, not aluminum dust inhalation.

There is also agreement that, if there is a potential concern with Al_2O_3 inhalation, it is due to particle sizes on the order of 1μ or less, due to the selective size dust sampling

characteristics of the human lung. (As pointed out in Figure 5, Source: "Deposition and Retension Models for Internal Dosimetry of the Human Respiratory Tract", Health Physics, Vol. 12, 1966). As shown in the figure, pulmonary retention, our area of concern, dramatically increases for all dusts as particle size decreases below 1μ.

After a description of the ground cloud, Dr. Higgins felt we would be "hard pressed" to show a cause-effect relationship between the operations of the space shuttle and the disease (although he agreed the cloud was dirty). He felt that the chances for exposure to the cloud being severe enough to cause problems was extremely remote. All information on hand lists exposures on the order of "8 hours per day; five days per week, for months" required to cause even the first symptoms of the disease. The space shuttle cloud cannot produce these levels of exposures, in even the worst situations.

5.4.   UP-TO-DATE LITERATURE SEARCH

As part of our continuing study on Shaver's Disease a Med-Line Search was conducted through the University of Michigan Medical School. The Med-Line is a computer-assisted search of medically-related sources conducted in conjunction with the Library of Congress. As a result of this search several new sources of information have been uncovered and subsequently researched.

Although these additional sources have been studied, they have yielded no significantly new information on the disease. It has been interesting to note, however, the continuing lack of distinction between the effects of aluminum dust and aluminum oxide dust inhalation. For example, recently, in an issue devoted to occupational lung diseases, Disease-a-Month, March 1972, aluminum oxide and aluminum are treated almost interchangeably.

One possible explanation for this can be traced back to the original work by Shaver and Riddell (1947). In this work, which is on aluminum oxide pneumoconiosis Shaver also mentions cases reported in Germany (about the same time, post war) on aluminum dust pneumoconiosis. Shaver speculates on the commonality of cause and effect to the cases he studied in Ontario. Arriving at no conclusions, but raising the question, he says, "The process concerned evidently differs considerably from that in Germany. The exposures are therefore probably dissimilar. There may be, however, a significant common factor".

Another side of the problem is that the term aluminosis seems to be used interchangeably in referring to either aluminum oxide or aluminum dust inhalation. Compounding the problems of recognition of cause and effect, of course, are the long delay times involved, problems in measuring dosage, and uncertainty in particle size distribution. Abstracts relating to this lung disease are attached in Section 5.5.

5.5. ABSTRACTS

appearing in the NEW ENGLAND JOURNAL OF MEDICINE

March 26, 1970

in the letters to the editor section:

SHAVER'S DISEASE

To the Editor: I refer to the editorial of February 12 justifying the publication of reports by unknown authors and particularly that of Dr. Tullis appearing in the same issue of the *Journal.* Dr. Tullis may be an "unestablished" author but is certainly not "sans patron." In his report Dr. Tullis acknowledged his indebtedness to Dr. C. G. Shaver for encouragement and permission to publish the cases of the patients admitted to the Niagara Peninsula Sanatorium. It was in 1947, while working at the same institution, that Dr. Shaver, with Dr. AR Riddell (J Indust Hyg Toxic 29:145, 1947), reported a series of cases of a hitherto unrecognized disease associated with the manufacture of the artificial abrasive corundum (Al_2O_3), a process considered for many years to be harmless. Shaver's disease has become a well recognized entity characterized by interstitial, non-nodular lung fibrosis, profound emphysema, pneumothorax and even death.

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University of Western Ontario

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THE PROBLEMS in the recognition of lung disease due to occupational exposure are numerous. A wide variety of pulmonary diseases unassociated with occupational exposure remain of undetermined etiology. The industrial hazards frequently are established by the observation that certain lung diseases are seen with exceptional frequency in some occupational groups. The long delay from exposure to the onset of symptoms adds to the difficulty in recognition. The average physician, even though his primary interest may be in pulmonary disease, generally has little opportunity to study problems arising in industrial groups.

With expanding technology, new types of potentially hazardous exposures are continuing to be created. The physician frequently has difficulty in obtaining information concerning possible harmful materials in the worker's environment. Much of the confusion results from a lack of understanding of the exact nature of possible toxic agents that may be created in various manufacturing processes. The worker frequently has little idea of the nature of the materials with which he works. Management officials frequently share the worker's lack of knowledge, although at times their reluctance to furnish the physician precise information must be recognized as an evasion in an attempt to avoid legal and labor union action. This inability of the physician to ferret out potentially harmful agents in the patient's occupation places him in a poor position in the recognition of an industrially related illness. Unfortunately, some physicians, who are too readily convinced that all respiratory illnesses in their patients are due to occupational exposure, are responsible for some of the failure of communication between industry and the medical profession.

Any physician who expects to recognize occupational hazards must take a complete history, including a chronologic listing of the work history of the individual, or important occupational exposure will go unrecognized. The exact type of work must be understood. To know that a patient works in a foundry does not help a great deal unless the physician understands the variety of exposure in various jobs, as well as the size and age of the plant and the types of safety measures used to control potential hazards. The possibility of exposure to toxic materials from another operation in the work area must be considered. Physicians can obtain information on potential hazards from departments of occupational and industrial hygiene in most states and some cities. Insurance companies that write workmen's compensation policies frequently can furnish helpful information. The industrial hygiene groups at the Massachusetts Institute of Technology, Harvard University and The University of Michigan are valuable sources of information. Also, any physician who undertakes the diagnosis of occupational lung diseases should have a few books on occupational diseases for reference.

Use of the chest roentgenogram in the recognition of occupational pulmonary disease has been valuable. However, this examination only reveals evidences of changes within the lung that may not be very diagnostic and certainly rarely are pathognomonic. In addition to the diagnostic difficulties there has been a tendency to assess the degree of disability by the extent of the roentgenographic abnormality. Although there is some degree of correlation, it is far from infallible. Extensive, fine, interstitial changes may be impossible to recognize in the chest roentgenogram when the patient's symptoms and pulmonary function tests clearly indicate a profound pulmonary dysfunction. In the larger and more readily seen densities, the amount of lung involved frequently is small enough that the patient's symptoms are minimal and the function tests remain quite normal. The classification of various dust diseases of the lung by roentgenographic evidence is complicated by the many dusts and mixtures of dusts, including the relatively inert ones of iron, carbon, tin and barium.

The occupational hazards of infectious nature, such as tuberculosis, coccidioidomycosis, histoplasmosis and anthrax do exist. The frequency of tuberculosis in the general population makes the proof of an occupational hazard difficult to establish. The special problem of tuberculosis in the individual exposed to silica will be discussed with the problem of silicosis. Otherwise, the development of tuberculosis as an occupational hazard must be considered carefully. In general, the proof is difficult, but the most helpful evidence for establishing an occupational origin is to demonstrate a tuberculin reaction in a previously nonreacting individual who has a reasonable occupational exposure to tuberculosis and whose family is free from tuberculosis. These criteria frequently are impossible to meet and without them the breakdown of a previously acquired tuberculous infection is impossible to eliminate. In both coccidioidomycosis and histoplasmosis, the exposure to soil where the spore forms exist can result in infection. If fellow workers are similarly involved, the occupational hazard will be much more clearly identified, as many individuals are infected in casual contacts with the spores in a nonoccupational exposure. Anthrax is a rare infection usually resulting in a skin infection. Occasionally, the anthrax organism can be inhaled and can produce a severe disease.

Classification of diseases of the respiratory tract due to dusts is difficult, but the one presented by Hardy and Leahy will be modified here.

Causes of Respiratory Disease — Pneumoconiosis

1. Inorganic dusts.
   A. Dusts capable of producing fibrosis, such as silica, silicates and diatomaceous earth.

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BAUXITE FUME FIBROSIS

Bauxite fume fibrosis (Shaver's disease) is a well-recognized industrial hazard among the workers manufacturing abrasive wheels of corundum. Bauxite is mixed with iron and coke and then fused by electric current, using carbon electrodes, at a temperature of approximately 2000 C. A dense white fume is produced. This contains considerable amounts of aluminum oxide and some amorphous silica along with small amounts of other substances, all in a finely divided state. The men exposed to these fumes developed symptoms of rapidly progressive shortness of breath, cough, chest tightness, substernal pain, weakness, fatigue and cyanosis. Chest roentgenograms revealed an extensive fibrosis with large blebs. Spontaneous pneumothorax was a frequent complication. Histologic examination of the lung revealed extensive fibrosis accompanied by blebs. The fibrosis lacked the characteristic whorling fibrotic pattern of a silicotic nodule. Chemical and spectrographic analysis showed all the constituents of the bauxite fumes. Although aluminum has not been clearly established as the cause of bauxite fume fibrosis, aluminum in a finely divided state has been implicated in a generalized fibrosis of the lung. The patient was employed in the production of a fine aluminum powder. At post mortem, aluminum was found in large amounts in the very fibrotic lung

6. STRATOSPHERIC EFFECTS OF SHUTTLE EFFLUENTS

6.1. INTRODUCTION

The possible stratospheric effects of two Shuttle exhaust products, gaseous hydrogen chloride (HCl), and aluminum oxide (Al_2O_3) particles are being examined. Particular attention is being given to a potential stratospheric ozone depletion mechanism due to a catalytic cycle involving Cl and ozone.

6.2. HCl IN THE STRATOSPHERE

The shuttle booster will deposit 10^5 kilograms of HCl per flight in the stratosphere. Although there are Cl^- ions in the troposphere from sea-salt spray, transport upward through the tropopause is slow and present knowledge indicates little or none present in the stratosphere, but we are also looking into the possibility of chlorine-containing compounds from other sources such as volcanoes. Thus we are examining the possible effects of chemicals never before considered in stratospheric matters. The first analysis of HCl in the stratosphere described below, indicates the possibility of ozone depletion through a catalytic cycle similar to that involving the nitrogen oxygen compounds, NO_x.

We have carried out some preliminary studies of a globally averaged steady state model of HCl chemistry. For this purpose the production rate of HCl was assumed constant with altitude at a value given by the total number of HCl molecules per launch divided by the volume of the stratosphere divided by the time between launches. This gives a steady production rate (molecules cm^{-3} sec^{-1}) averaged over time and the entire stratosphere. Any possible effects seen in such a model are global in nature. Local effects would be much larger. The globally averaged production rate for 100 launches per year was calculated

to be 0.3 cm^{-3} sec^{-1}. Any changes in the launch frequency would be reflected by a linear change in the production rate and corresponding changes in the results. Although this production rate of HCl is quite small, relatively large densities can be built up because of the slowness of chemical destruction and eddy transport.

The model we have used is one-dimensional with vertical eddy transport and the chemistry summarized in Figure 6. HCl can be photodissociated by radiation of wavelength less than ~2770Å with a peak in the photodissociation cross section occurring at about 1550Å. The resulting Cl atom reacts rapidly with ozone to either go back to Cl or to form ClOO. The ClOO either reacts with ozone to reform ClO or is dissociated by solar radiation back to Cl. Thus, the following reactions briefly summarize the likely chemistry.

(1) $h\nu + HCl \rightarrow H + Cl$
(2) $Cl + O_3 \rightarrow ClO + O_2$
(3) $ClO + O_3 \rightarrow Cl + 2O_2$
(4) $ClO + O_3 \rightarrow ClOO + O_2$
(5) $ClOO + O_3 \rightarrow ClO + 2O_2$
(6) $ClOO + h\nu \rightarrow Cl + O_2$
(7) $Cl + O_2 + M \rightarrow ClOO + M$

The significant point to be made is that once HCl has been deposited in the stratosphere, the chlorine atom may be in the form of HCl, Cl, ClO, or ClOO but it cannot be chemically removed. Thus, the problem divides itself into two tasks. First determine the total chlorine atom distribution which depends only on the source strength and transport rates, then determine the fraction of the chlorine atoms in each type of molecule, which depends upon reaction rates and dissociation coefficients.

In practice for our global average model we have determined the HCl density by solving a one-dimensional diffusion equation with the shuttle as a source and photodissociation as a sink.

REACTION SCHEME FOR HCl CHEMISTRY

SOLID BOOSTER EFFLUENT

$$h\nu + HCl \longrightarrow H + Cl$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O_3 \longrightarrow Cl + 2O_2$$
$$ClO + O_3 \longrightarrow ClOO + O_2$$
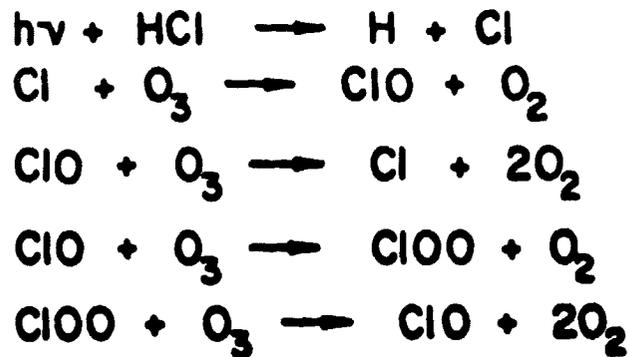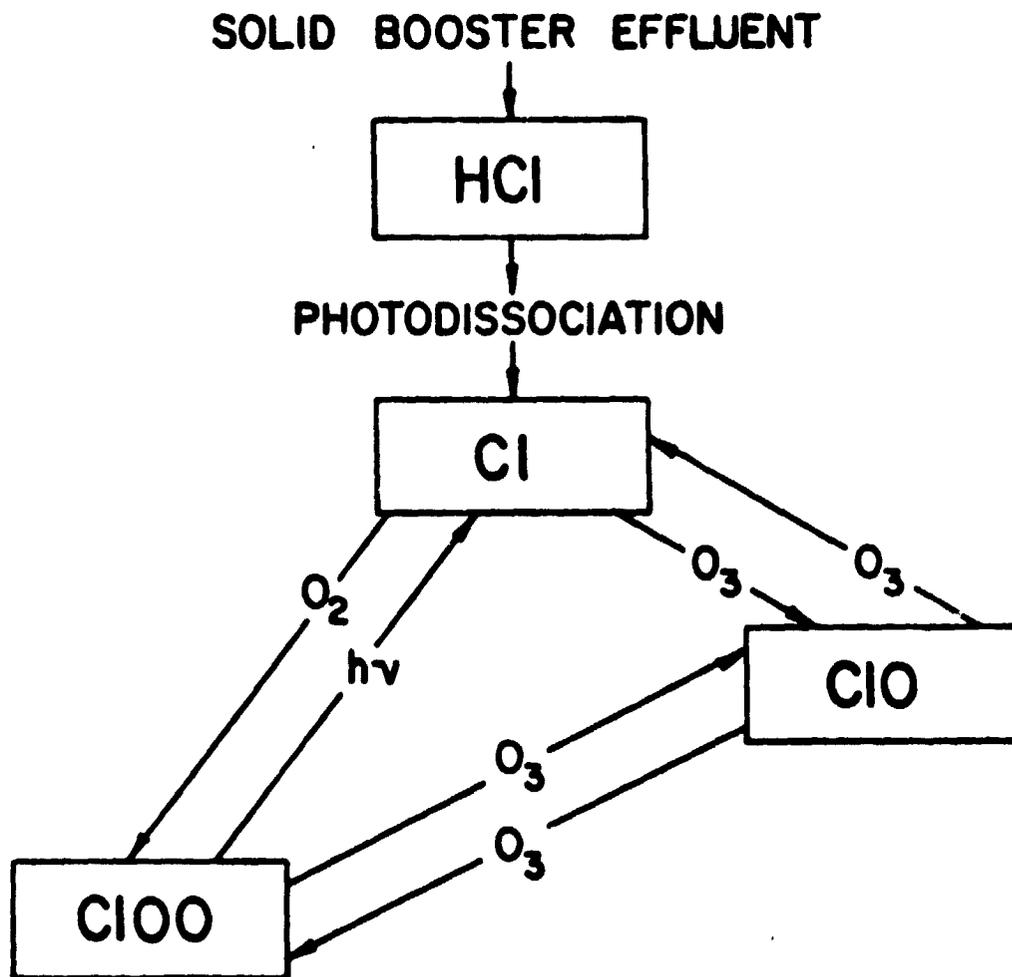$$ClOO + O_3 \longrightarrow ClO + 2O_2$$

Figure 6

The photodissociation coefficient has been calculated using the UV solar spectrum of Brinkman et al. (1966) and Hinteregger et al. (1965) and the HCl photodissociation cross section measured by Romand (1949). Figure 7 shows the calculated photodissociation coefficient. Diurnal averaging was obtained by taking 1/4 of the overhead sun value. Resulting HCl profiles are shown in Figure 8. Figure 9 shows the eddy diffusion coefficient which is a global mean value taken from Hays and Olivero (1970). The HCl density is then multiplied by the photodissociation coefficient to obtain the production rate of Cl atoms. The species Cl, ClO, and ClOO are treated as a single constituent, ClO_x. ClO_x is produced from HCl but not destroyed until it reaches the ground. Thus its concentration can be calculated without knowing the reaction rates involved in the exchange between different forms of ClO_x. A one-dimensional diffusion equation is solved for ClO_x in which the source is HCl destruction and there is no sink except the ground (or the top of the troposphere). The resulting profile is also shown in Figure 8.

The critical parameter in the chemistry of the perturbed stratosphere is the effect of the perturbation on the ozone layer. Johnston (1972) has shown for a pure oxygen atmosphere (O, O_2, O_3) and observed O_3 densities that the production rate of odd-oxygen (O, O_3) is a factor of four larger than the destruction rate. He has further shown that NO_x (NO, NO_2 NO_3) in quantities about 10 ppb can account for the missing destruction rate via catalytic chains of the type

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

in which there is no net loss of NO or NO_2. The ClO_x chain shown in Figure 6 is just such a catalytic chain. It is poten-

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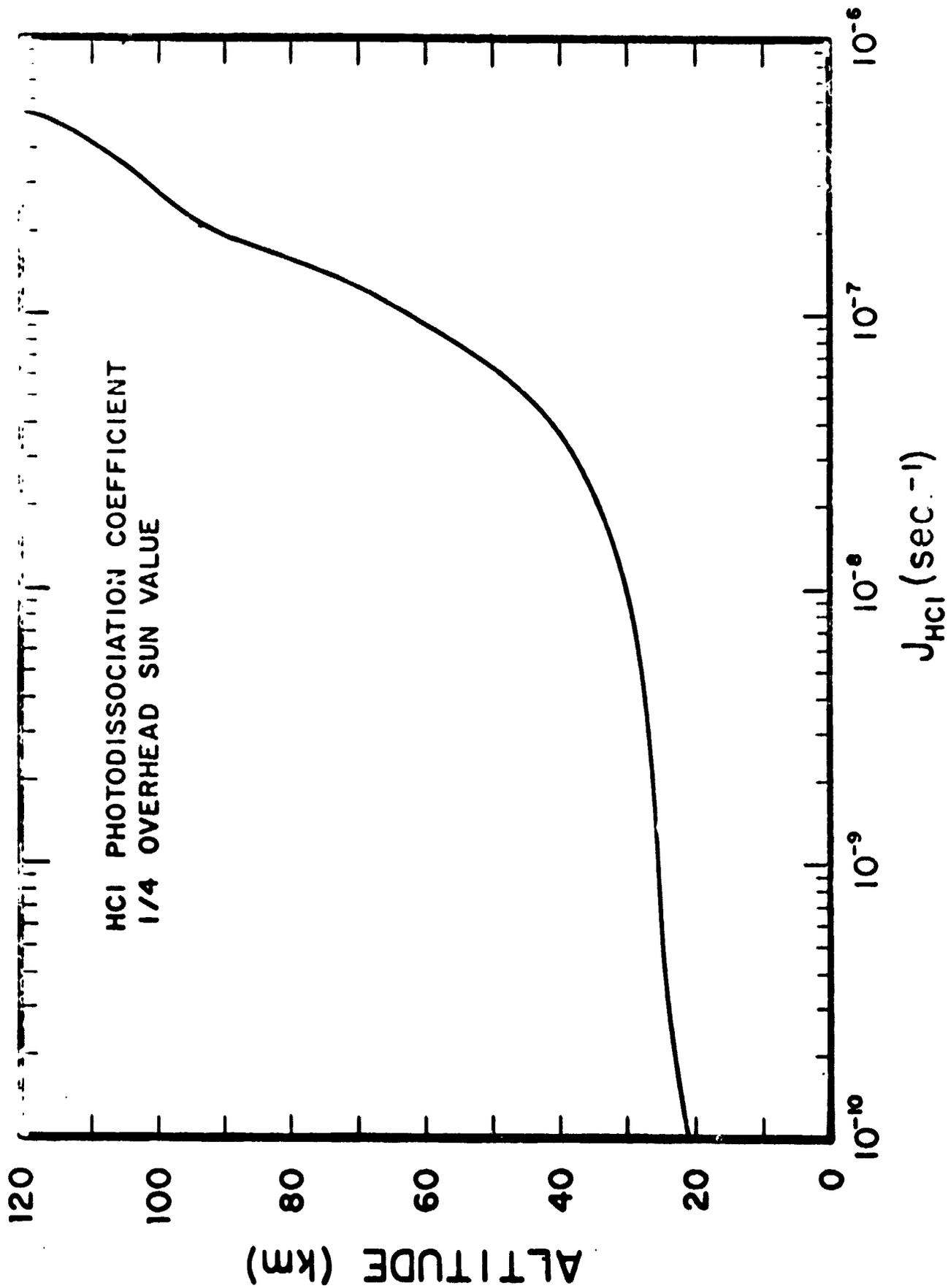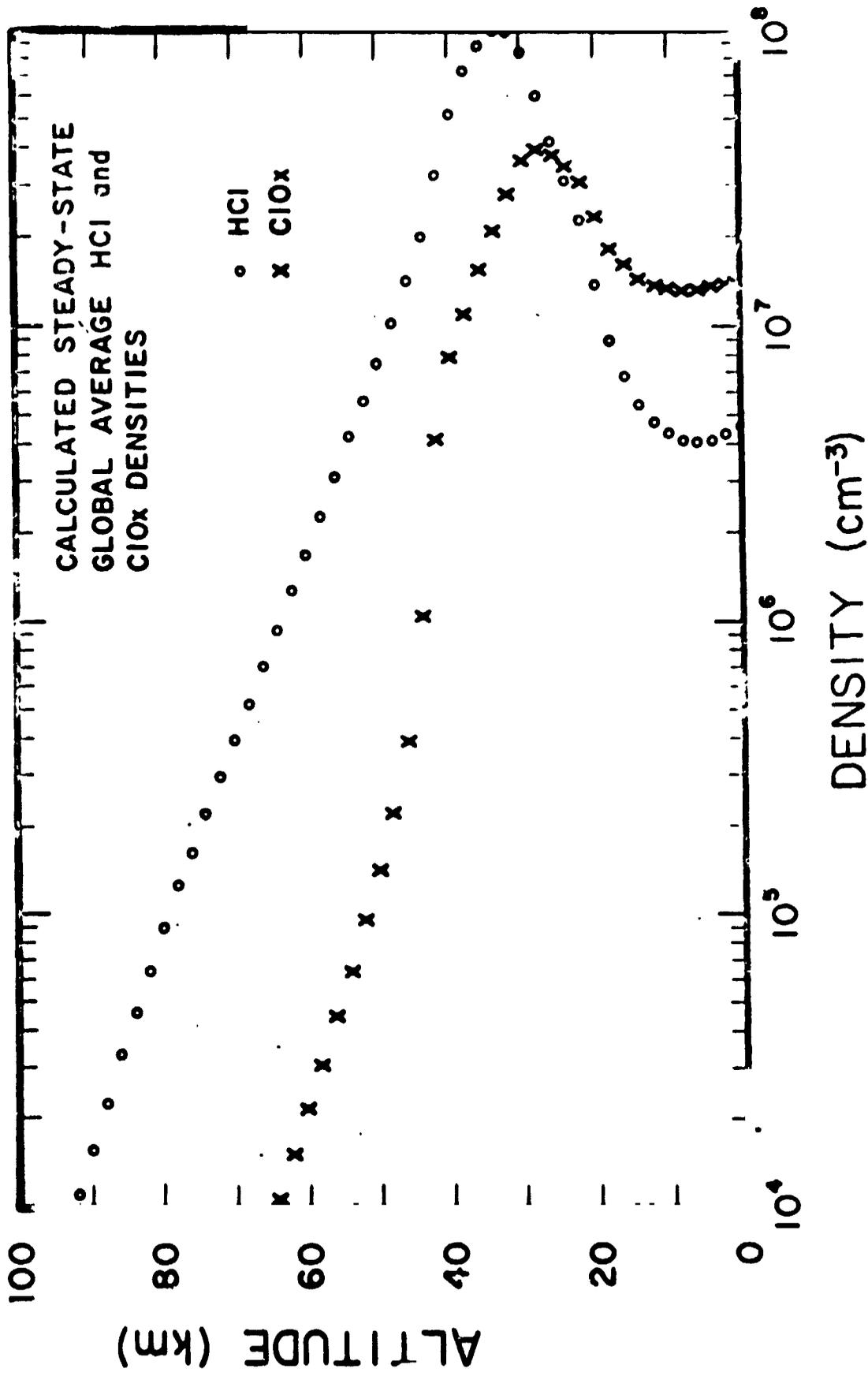HCl PHOTODISSOCIATION COEFFICIENT
1/4 OVERHEAD SUN VALUE

ALTITUDE (km)

J_{HCl} (sec.$^{-1}$)

Figure 7

CALCULATED STEADY-STATE
GLOBAL AVERAGE HCl and
ClOx DENSITIES

o HCl
x ClOx

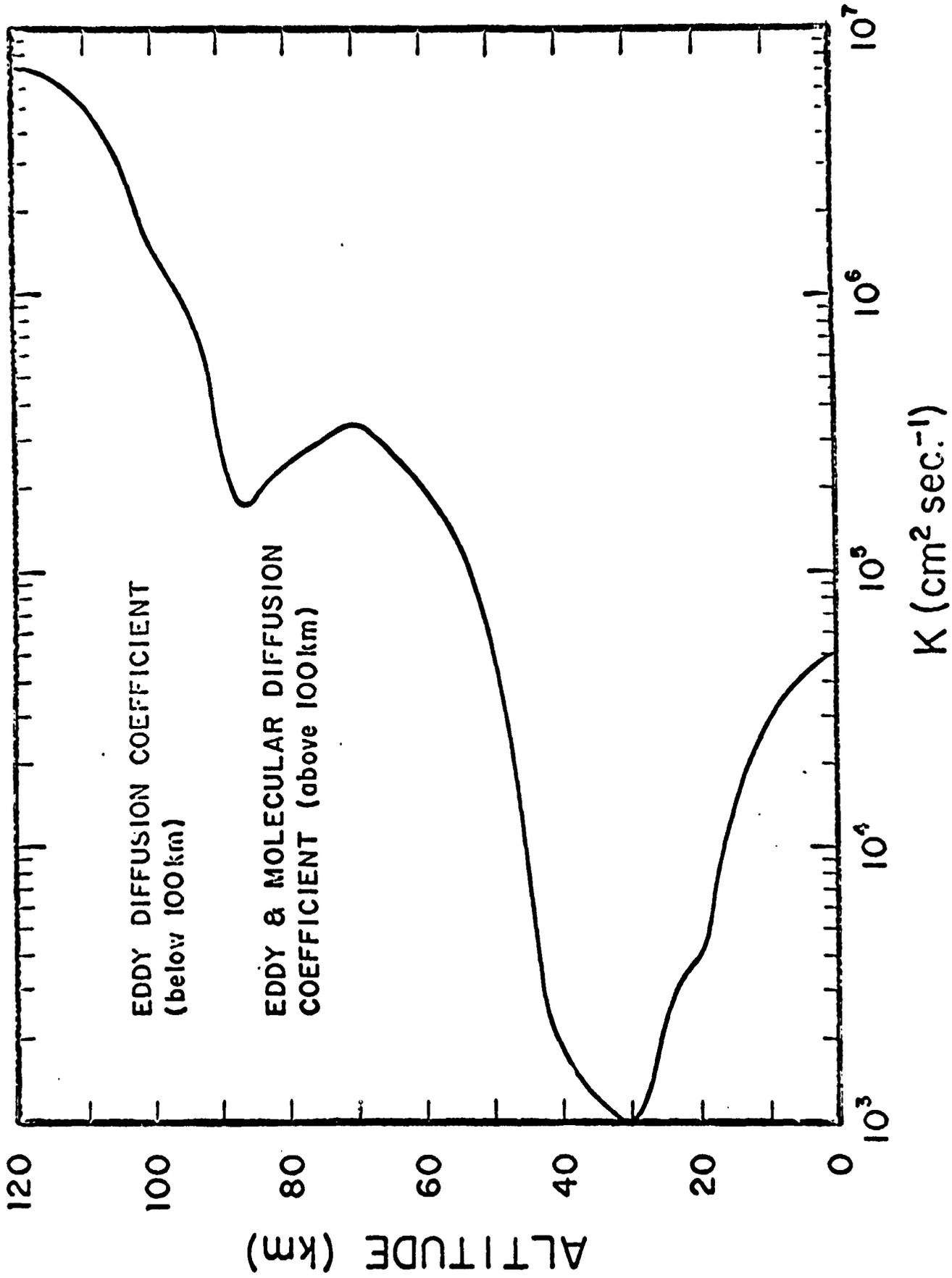DENSITY (cm⁻³)

ALTITUDE (km)

Figure 8

FIGURE 9

tially a much faster chain because it does not require atomic oxygen (which has very low densities at stratospheric altitudes).

Assuming that Cl is converted to ClO by O_3 faster than it is converted to ClOO by O_2, the rate-limiting process in the chain depends upon what happens to the ClO. If it is converted back to Cl then that process determines the rate of cycling through the simple two-constituent chain. If, however ClO is more rapidly converted to ClOO then we have a three-constituent chain which is controlled by the slower of the rate of formation of ClOO and its destruction. In either case we can get an estimate of the rate-determining reaction rate necessary for ozone destruction to become significant. This is done by comparing the destruction rate by the ClO_x chain to the odd-oxygen production rate, both integrated over altitude. The production rate of odd-oxygen is just the rate of photodissociation of O_2 usually denoted by J_{O_2} [O_2] where J_{O_2} is the photodissociation coefficient (sec^{-1}), and [O_2] is the density of O_2(cm^{-3}). The destruction rate by the ClO_x chain is given by k_{eff}[O_3] [ClO_x] where k_{eff} is the effective reaction rate for the chain (i.e., the rate-determining step). If we arbitrarily set the significance level at the point where the integrated destruction rate is 1% of the integrated odd-oxygen production rate we obtain a condition on the effective reaction rate, i.e., we set

$$\int_{\text{stratosphere}} k_{eff}[ClO_x] \ [O_3]dz = .01 \ x \int_{\text{stratosphere}} J_{O_2} \ [O_2]dz$$

and obtain

$$k_{eff} \cong 3 \ x \ 10^{-16} \ cm^3 \ sec^{-1} \ .$$

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The reaction rate of ClO and O_3 has been estimated to be $k < 10^{-15}$ cm^3 sec^{-1} (Coxon, 1967). Thus, on the global scale the ClO_x compounds may be significant destroyers of ozone depending upon the values of the reaction rates in the chain and upon the uncertainties in the above calculation (for instance, the eddy diffusion coefficient may vary by as much as a factor of 5 in either direction).

What should be done to refine and verify the predictions? Obviously, careful laboratory measurement of the relevant reaction rates is necessary, particularly the reaction of ClO with O_3. Not only should the rate be determined, but the reaction products are also of prime importance in determining which path the chain takes. In addition the modeling needs considerable refining. We plan to improve our model by considering the local perturbation of stratospheric chemistry caused by the line source from a single shuttle launch. This should allow prediction of the perturbation as a function of time and thus indicate possible measurements which can be made after a solid-fuel rocket launch in an attempt to verify model predictions.

6.3. Al_2O_3 IN THE STRATOSPHERE

The analytical modeling technique used to study HCl in the stratosphere can also be applied to Al_2O_3 but we are first examining some qualitative aspects of the problem. We would like to obtain additional detailed chemical and physical information before proceeding, for example, the size distribution of the emitted Al_2O_3 particles. The size distribution is important because of the effect of the gravity term on the vertical diffusion. Larger particles will fall out rapidly and the smaller ones will remain longer. In the limit the smallest particles will behave similarly to molecules. The two-dimensional model can be applied to the diffusion of Al_2O_3 particles by

considering size ranges separately.

Once the model has established profiles of particles of various sizes the effect of these on ozone chemistry can be investigated. The catalysis of the reaction depends upon the efficiency of the surface in adsorbing O_3, the amount of surface available, the capacity of the surface for adsorbed O_3, the efficiency of the reaction of two adsorbed O_3 molecules, and the interference of the O_3 adsorbing process by the adsorption of other molecules such as HCl and H_2O. H_2O may be particularly important in reducing the catalytic effect on ozone. The hygroscopic properties of Al_2O_3 may cause most available reaction sites to be occupied by water vapor fairly rapidly. The possibility of adsorption of HCl could drastically change any conclusions made on the basis of gas chemistry.

7. MESOSPHERIC AND IONOSPHERIC EFFECTS OF ORBITER REENTRY

7.1. INTRODUCTION

We have modeled the localized effect of a single Shuttle Orbiter reentry on mesospheric odd nitrogen. The perturbations of the odd nitrogen species last for a time of the order of hours depending critically upon the value used for the horizontal diffusion coefficient. The processes included in the calculation are the perturbation of NO, photochemical reactions, and horizontal and vertical eddy diffusion. Effects not modeled but which may be important are the initial excesses of H and O, wind shear, diurnal variations and the influence of heat shield ablation products or water vapor. We have not considered specifically the problem of buildup from repeated orbiter reentries at the same place. However, the results indicate that even in the worst case the disturbance lifetime is less than five days. This combined with the fact that winds will move the disturbance fairly rapidly indicate that there is little possibility of buildup for predicted launch frequencies.

7.2. QUALITATIVE DESCRIPTION OF THE POTENTIAL PROBLEM AND OUR MODEL

Each Shuttle Orbiter reentry will produce a shock wave disturbance in the atmosphere at mesospheric altitudes, say 65 to 80 km. The disturbance, energized by the slowing of the Orbiter vehicle, will extend approximatley one quarter of the way around the earth, and will be characterized by altered atmospheric composition. In particular, large amounts of nitric oxide (NO), atomic oxygen (O) and atomic nitrogen (N) will be produced through conversion of molecular oxygen and nitrogen. Quantitative estimates have been made of the degree of this conversion by Park at NASA/Ames (Park, 1972).

Such calculations depend on details of the trajectory, aircraft materials and several aerodynamic considerations, but it seems reasonable to conclude for NO, for example, that each reentry will produce an amount equal to five or ten percent of the Orbiter mass. This means that perhaps 10,000 kg of NO will be distributed along a 10^4 km segment of the reentry trajectory.

Initially this enhancement of NO will be localized in a trail of small radius, say 10 to 100 meters, wherein the NO concentrations would be 10^{13} - 10^{14} cm^{-3}, which is perhaps six orders of magnitude above normal undisturbed values in the middle mesosphere. The subsequent dispersion and depletion of this NO enhancement is described below. An excess of NO in the atmosphere has several potential effects: it can alter the ambient atmospheric composition through chemical reactions, notably the destruction of ozone which is an atmospheric constituent critical to biological processes. Excess NO can also enhance the local ionosphere. The latter effect is likely because NO has a lower ionization potential than other atmospheric gases and is of interest because of the ionosphere's role in radio communications.

As stated previously the air which is directly altered by the passage of the Orbiter is severely disturbed but it is also highly localized. The severity of the disturbance is expected to diminish by dilution as its size increases through atmospheric mixing and transport processes. The nature of the disturbance also is expected to change as chemical reactions occur.

To model these phenomena quantitatively one must perform time-dependent calculations based on a particle-conservation equation which includes the effects of transport and of chemistry. Transport mechanisms include eddy and molecular diffusion in both the horizontal and vertical directions, wind effects and flows driven by gravity and thermal gradients. The relevant chemical reactions include those with major and minor atmospheric gases, including electrons and solar photons. A model including the most important of these effects can be used to estimate the

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time history of each reentry disturbance and to determine if
cumulative effects are likely locally. In other words, will
there be enough time between successive Orbiter reentries for
the previous disturbance to dissipate before the onset of the
next one?

We have concentrated only on possible local effects be-
cause global problems seem unlikely. This lack of concern for
global effects is based on a comparison of the amount of NO
the Shuttle will add to the mesosphere and that thought to flow
in from the higher atmosphere. The former should be about 10^6 kg
per year, using Park's (1972) computations, while the latter
should be at least 10^8 kg per year if one assumes fluxes computed
by Strobel (1971b). Also we have treated only the NO enhancement
but intend to include the N and O enhancements in future work.

7.3. DETAILED EXPLANATION OF THE MODEL

The model we have developed uses the odd-nitrogen concept
set forth by Strobel (1971a, 1971b) and a set of photochemi-
cal reactions similar to his but more general. Table 16 shows
the reactions we include to evaluate the behavior of the NO
enhancement in the mesosphere, along with the respective reac-
tion rates. We have used these chemical reactions in a time-
dependent continuity equation written for ON (odd nitrogen)
following Strobel's method. The idea is to lump all the nitro-
gen constituents except N_2 into one fictitious component called
ON then solve the continuity equation for ON, then to use algebra
on the resultant profile to solve for all the separate consti-
tuent concentrations, like $N(^4S)$, $N(^2D)$, NO, NO_2, and NO^+. This
procedure is justified by the fact that chemical lifetimes for
these constituents are less than transport times in the meso-
sphere as Strobel has shown. Thus, the algebraic equations we
solve for the separate constituent concentrations are relation-
ships based on photochemical equilibrium. The ON continuity

PHOTOCHEMICAL REACTIONS INVOLVING N, NO, AND NO^+
below 90 km but above 50 km

(1)	$h\nu + N_2 \rightarrow N(^4S) + N(^4S)$	J_1
(2)	$N(^4S) + NO \rightarrow N_2 + O$	2.2×10^{-11}
(3)	$N(^4S) + O_2 \rightarrow NO + O$	$2.4 \times 10^{-11} \exp(-3975/T)$
(4)	$N(^4S) + O_2(^1\Delta) \rightarrow NO + O$	3.0×10^{-15}
(5)	$N(^4S) + O_3 \rightarrow NO + O_2$	$3.0 \times 10^{-11} \exp(-1200/T)$
(6)	$N(^4S) + O + M \rightarrow NO + M$	$1.0 \times 10^{-32} \, n(M)$
(7)	$h\nu + NO \rightarrow N(^4S) + O$	J_7
(8)	$h\nu + NO \rightarrow NO^+ + e$	I_8
(9)	$NO^+ + e \rightarrow N(^4S) + O$	$2.5 \times 10^{-8} \, (T/1000)^{-1.5}$
(10)	$NO^+ + e \rightarrow N(^2D) + O$	$7.5 \times 10^{-8} \, (T/1000)^{-1.5}$
(11)	$N(^2D) + O_2 \rightarrow NO + O$	6.0×10^{-12}
(12)	$N(^2D) + NO \rightarrow N_2 + O$	2.2×10^{-11}
(13)	$O_3 + NO \rightarrow NO_2 + O_2$	$9.5 \times 10^{-13} \exp(-1240/T)$
(14)	$O + NO + M \rightarrow NO_2 + M$	$6.8 \times 10^{-32} \, n(M)$
(15)	$O + NO \rightarrow NO_2 + h\nu$	6.4×10^{-17}
(16)	$N(^2D) + O \rightarrow N(^4S) + O$	2.0×10^{-13}
(17)	$N(^4S) + OH \rightarrow NO + H$	6.8×10^{-11}
(18)	$NO_2 + O \rightarrow NO + O_2$	$3.2 \times 10^{-11} \exp(-300/T)$
(19)	$NO_2 + h\nu \rightarrow NO + O$	8.0×10^{-3}
(20)	$NO_2 + N(^4S) \rightarrow N_2O + O$	
(21)	$NO_2 + N(^4S) \rightarrow N_2 + O + O$	1.2×10^{-11}
(22)	$NO_2 + N(^4S) \rightarrow N_2 + O_2$	
(23)	$NO_2 + N(^4S) \rightarrow NO + NO$	0.6×10^{-11}

equation itself includes the important transport terms and is written for the range 50 to 90 km. Specifically, the flux continuity equation for ON is:

$$\frac{\partial [ON]}{\partial t} = \frac{\partial \phi_{ON}}{\partial z} + P_{ON}(z,t) - L_{ON}(z,t) \qquad (1)$$

where [ON] is the concentration of odd nitrogen, ϕ is its vertical flux, z is altitude, and P and L are chemical production and loss terms, respectively which result from the reactions of Table 16. Following Strobel (1971b)

$$\phi_{ON} = -K\left[\frac{\partial [ON]}{\partial z} + \left(\frac{1}{T}\frac{\partial T}{\partial z} + \frac{1}{H_{AV}}\right)[ON]\right] \qquad (2)$$

where K is the eddy diffusion coefficient, T is temperature, H_{AV} is the scale height of the mixed atmosphere, and molecular diffusion has been neglected in comparison to eddy diffusion. Further, it can be shown that

$$\frac{1}{T}\frac{\partial T}{\partial z} << \frac{1}{H_{AV}} \qquad (3)$$

in the mesosphere, which allows neglect of the thermal diffusion term in Equation (2).

When Equations (2) and (3) are substituted into Equation (1) a linear second order partial differential equation results. Again following Strobel's method we have employed flux boundary conditions, one at the upper boundary (90 km) and one at the lower boundary (50 km). Numerical solution proceeds by converting the differential equation to a finite difference equation, then employing a standard implicit scheme. The upper boundary condition is a downward flux from the thermosphere and represents the NO produced by ion-neutral reactions discussed by Strobel

(1971a). The use of such a boundary condition enables us to omit a great number of reactions in our photochemical scheme, leaving only photoionization and recombination processes for NO^+, as shown in Table 16. Furthermore, by parametering this upper boundary condition (see section 7.7.) the strength of this thermospheric source of NO can be varied.

The model described up to this point includes all the important chemistry and physics needed to compute the steady state vertical distribution of all the odd-nitrogen constituents. This one-dimensional model was applied to the natural, undisturbed mesosphere; results are shown in Section 7.4. Before attempting to model the time history of the Orbiter-induced disturbance, however, it is necessary to include <u>horizontal</u> transport in the computations. We have included the effects of horizontal diffusive transport by employing the one-dimensional diffusion equation to describe the horizontal dispersion of the disturbance. If x is horizontal distance measured from an initial line source the concentration $N(x,t)$ at all points in space and later time, t, given by

$$N(x,t) = \frac{N_o}{(4\pi Dt)^{\frac{1}{2}}} \exp(-x^2/4Dt) \tag{4}$$

where N_o is the line source strength, and D is any diffusion coefficient. In the actual numerical solution Equation (4) was used to evaluate the amount of excess NO remaining in a box 1 km square (x = 500m) centered on the reentry trajectory. Specifically, the spatial field of Equation (1) was first swept for vertical transport and chemical terms in a given time step. Then it was swept for horizontal depletion due to eddy diffusion in the same step by using the proper form of Equation (4) with an initially homogeneous (rectangular) pulse disturbance spread over a box 1 km wide horizontally.

7.4. RESULTS OF COMPUTATIONS AND DISCUSSION

Figure 10 shows the calculated steady state concentrations of the odd nitrogen species NO^+, $N(^4S)$ and NO_2 in the mesosphere for the flux boundary conditions $\phi_{NO}(90 \text{ km}) = -10^8$ $cm^{-2}sec^{-1}$ (downward flow) and $\phi_{ON}(50 \text{ km}) = 10^6 cm^{-2}sec^{-1}$ (upward flow). The NO concentration is much greater and appears in the next figure. $N(^2D)$ is vanishly small and is not shown. In all the results to follow the vertical eddy diffusion coefficient, K in Equation (2) was taken to be $5 \times 10^4 cm^2sec^{-1}$ at 50 km, increasing exponentially to $5 \times 10^6 cm^2sec^{-1}$ at 90 km similar to Strobel's (1971b). The profiles of Figure 10 and the NO profile of Figure 11 constitute the ambient mesosphere into which we introduced the Orbiter-produced excess NO.

Figure 11 also shows the computed time history of the mesospheric NO concentration following Orbiter reentry. The concentrations shown are those averaged over a 1 km square box perpendicular to the reentry trajectory, as discussed in Section 7.3. The times shown in Figure 11, thus are one, three and eight hours after the disturbance had already dispersed 1 km horizontally. The coefficient, K, for horizontal eddy diffusion was taken to be $10^3 cm^2sec^{-1}$ at 50 km varying exponentially with altitude to $10^5 cm^2sec^{-1}$ at 90 km. Relaxation to the undisturbed NO profile was nearly complete after 110 hours for this case (one of slow eddy transport). Figure 12 shows the time history of the D-region NO^+. The Orbiter-produced NO^+ disturbance would be easily detectable and is long lasting like the NO concentrations of Figure 11, but is not large in absolute magnitude.

Figures 13 and 14 show similar results in which the horizontal diffusion coefficients were taken to be $10^5 cm^2sec^{-1}$ independent of altitude. In this case relaxation to ambient took place in approximately five hours. If the horizontal diffusion coefficient were larger yet, there would be a corresponding decrease in the lifetime of the disturbance according to our model.
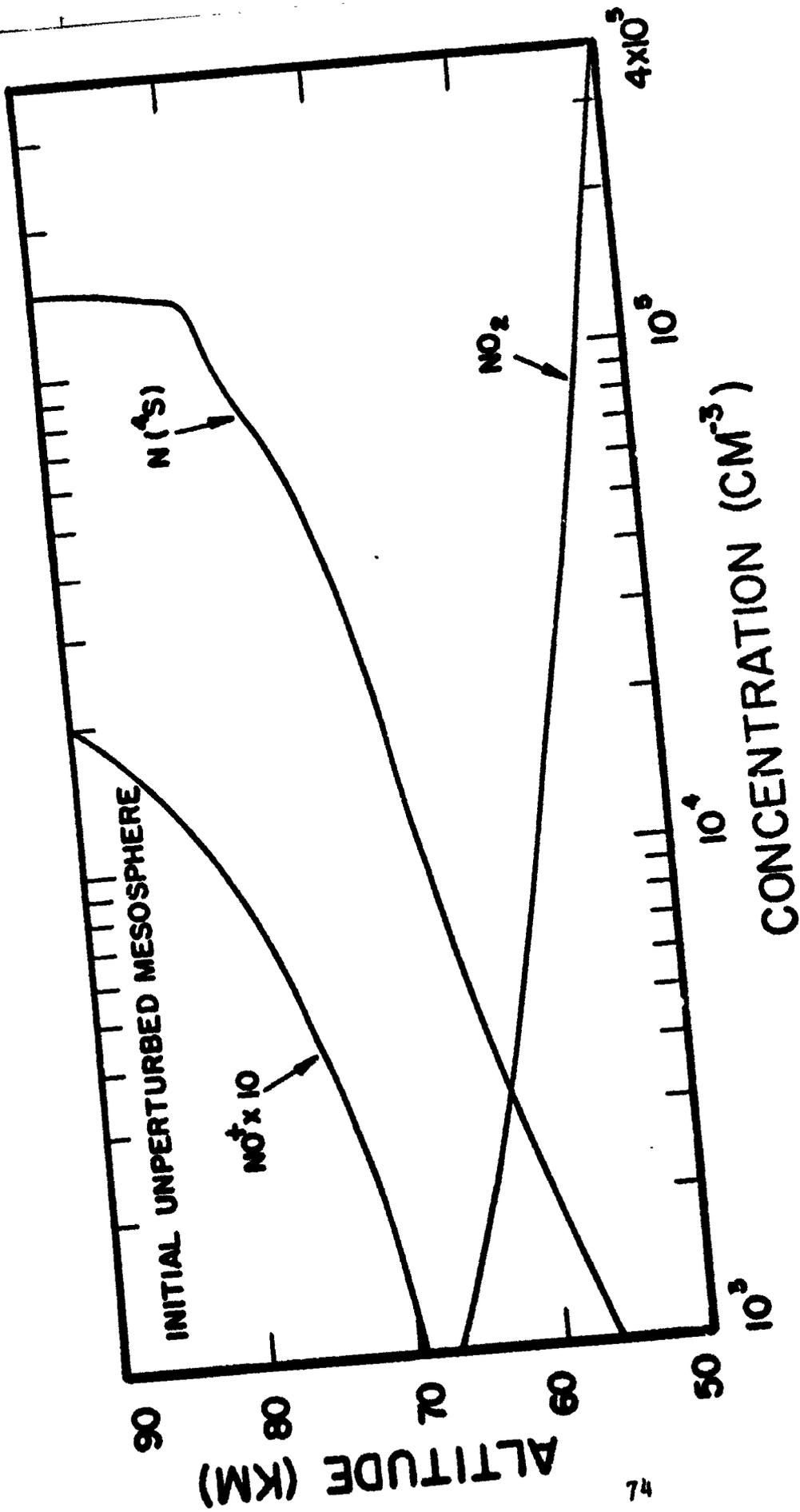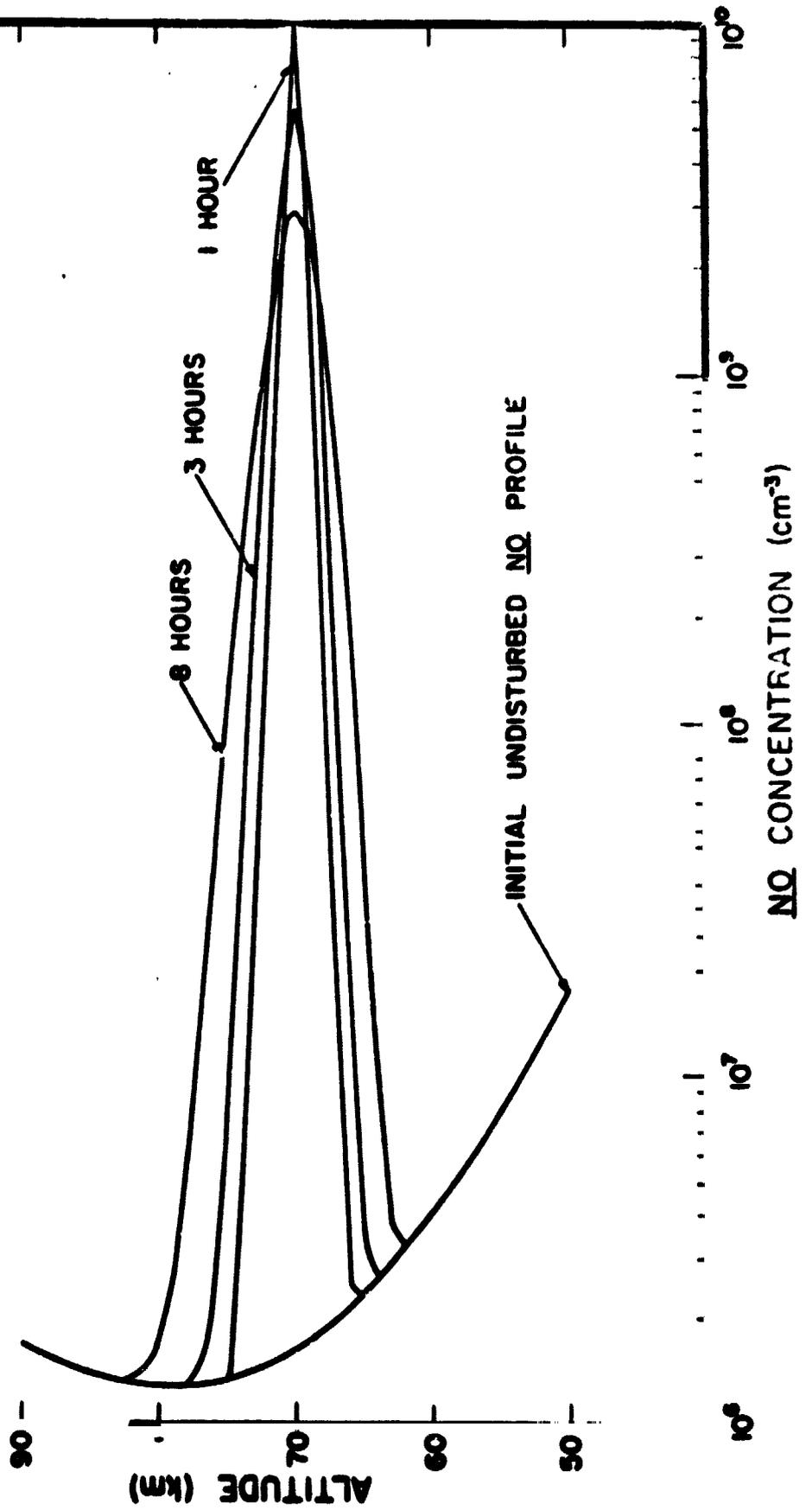
Figure 10. Undisturbed Mesospheric N. NO_2, and NO^+ Profiles.

FIGURE 11

Undisturbed NO Profile with Shuttle Perturbation for Low Horizontal Diffusion Coefficient.

75
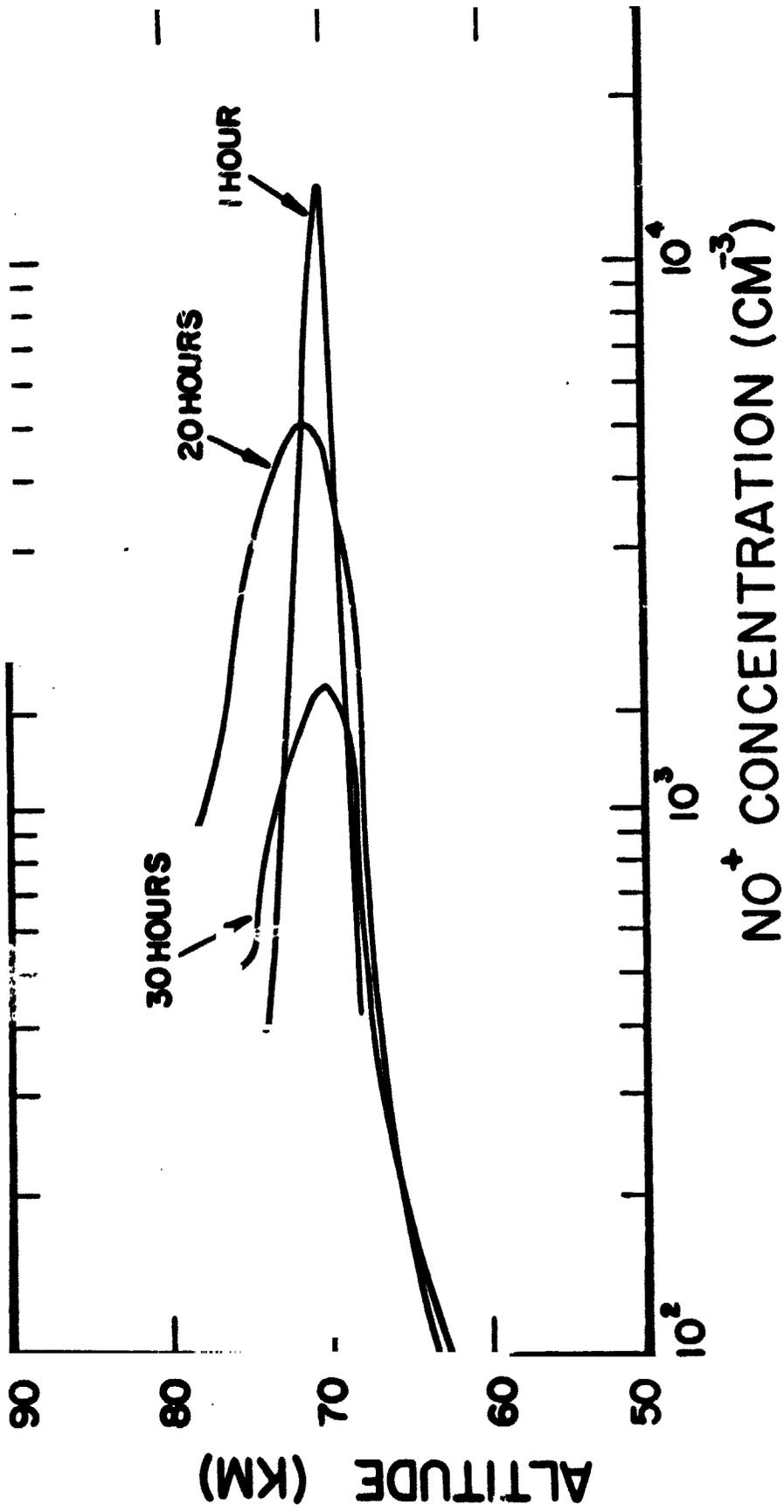
Figure 12. NO+ Perturbation for Low Horizontal Diffusion Coefficient.

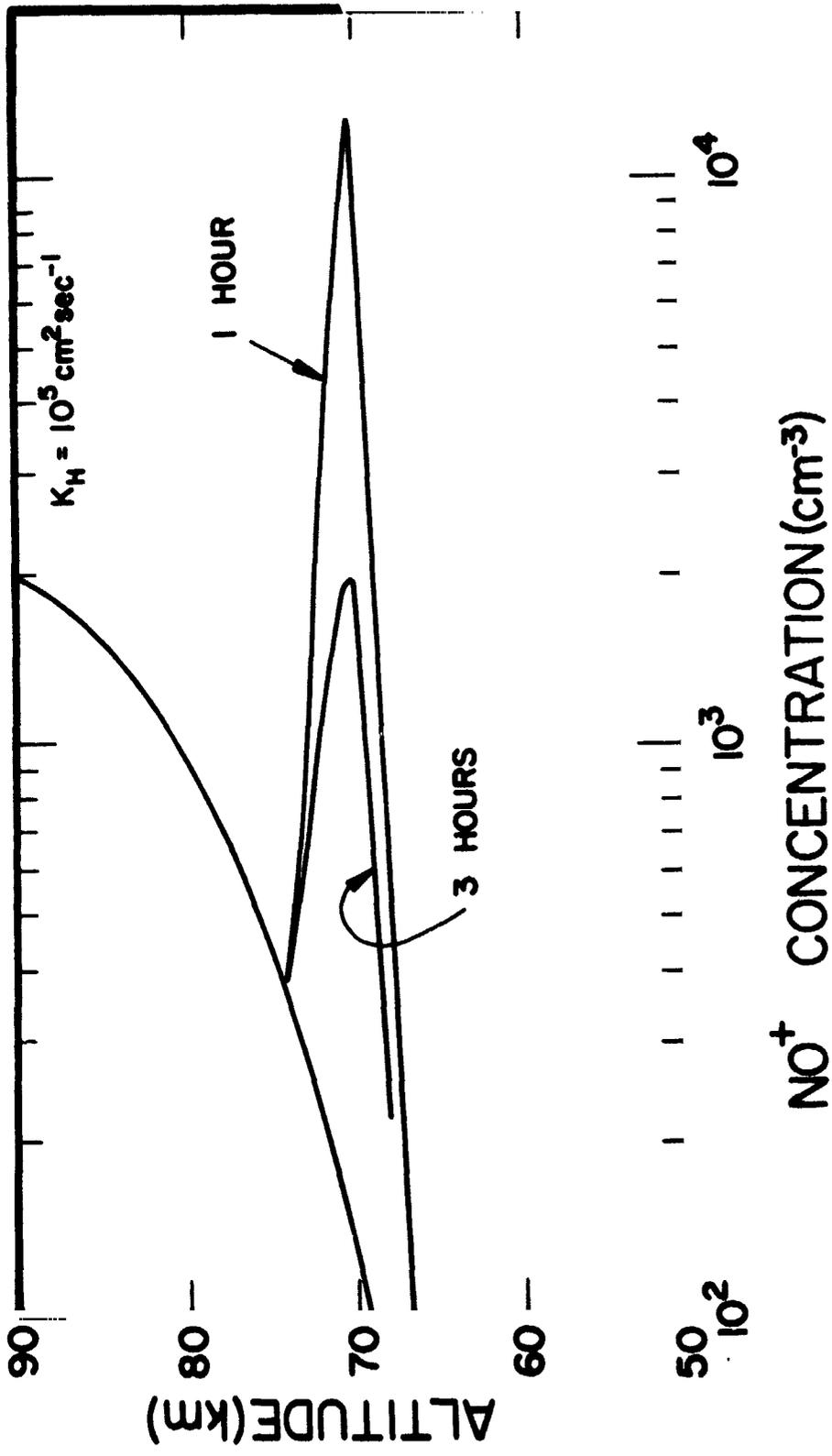Figure 13. ... temperature for NO, showing effect on coefficient = 10^5 cm^5 sec^{-1}.
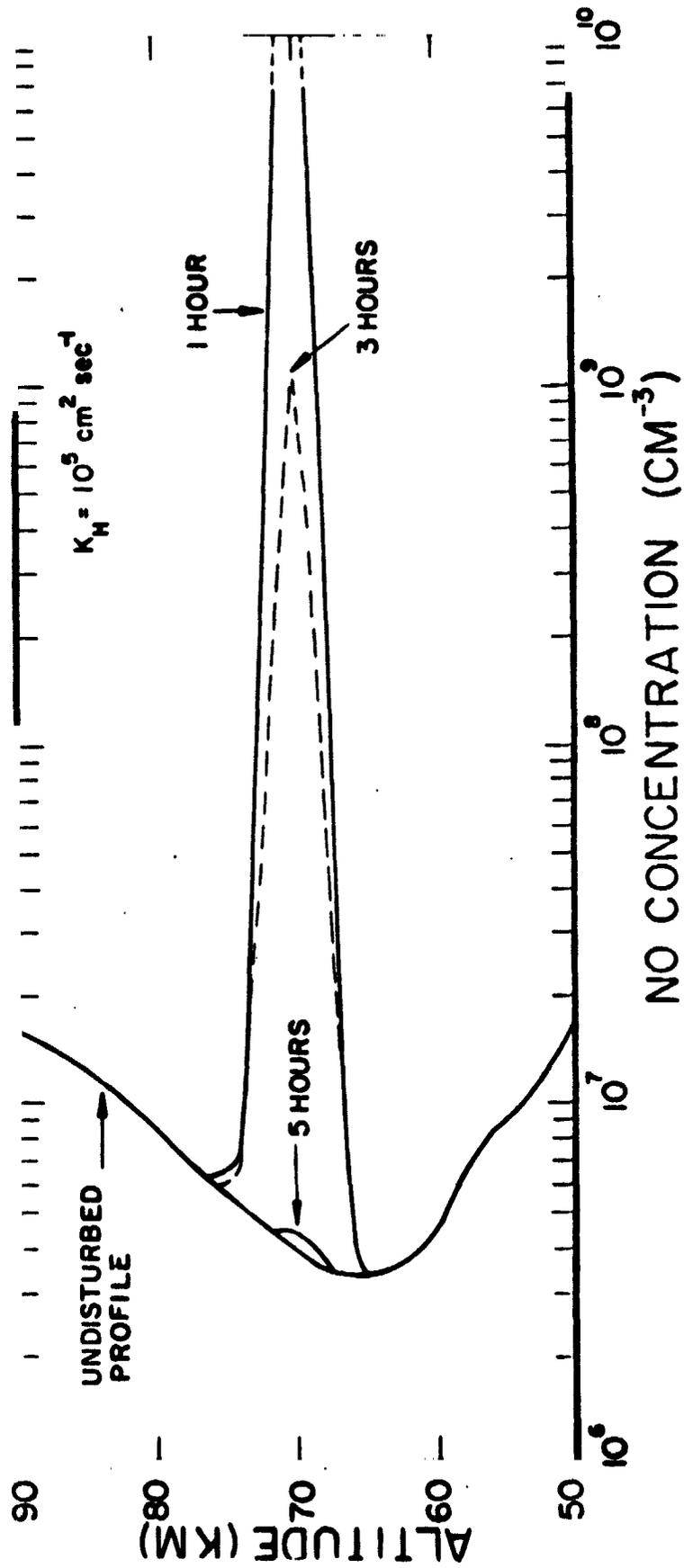
Figure 14. NO+ Perturbation for Horizontal Diffusion Coefficient = 10^5 cm²sec⁻¹

Taken altogether, the results of Figures 11 through 14 indicate that the duration of the Orbiter-produced disturbance depends critically on the effectiveness of horizontal diffusion. If the coefficient for horizontal eddy diffusion is 10^5 or more our model makes it difficult to conceive of cumulative effects of this localized disturbance. Our current model has the following limitations which should be removed before the reentry problem can be dismissed completely:

1) basic physical parameters used in mesospheric calculations, such as photoabsorption cross sections, solar fluxes, and molecular branching ratios, should be verified and the calculations checked for sensitivity to these parameters;

2) for calculations over time periods longer than a few hours diurnal variations in solar input, background concentrations and temperatures should be used;

3) So far we have identified the reentry disturbance with the initial excess of NO. We should also include the initially large excesses of N and O due to reentry as part of the disturbance, a task which should not be difficult.

4) To more accurately model the ionospheric enhancement we should treat other more realistic positive ions, such as hydrated NO^+.

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