

TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
10. ATMOSPHERIC CONSTITUENTS	10-1
10.1 Introduction	10-1
10.1.1 Sources of Particles	10-1
10.1.1.1 Primary Sources	10-1
10.1.1.2 Secondary Source	10-1
10.1.2 Distribution of Particles	10-1
10.1.3 Upper Atmospheric Aerosols	10-2
10.2 Threats Caused by Atmospheric Particles	10-4
10.2.1 Abrasion	10-4
10.2.2 Optical Hindrances	10-5
10.2.3 Corrosion	10-5
10.2.3.1 Rate of Atmospheric Corrosion	10-6
10.2.3.2 Protection From Atmospheric Corrosion	10-6
10.3 Characteristics of Specific Particles	10-6
10.3.1 Extraterrestrial Dust	10-8
10.3.2 Sea-Salt Particles	10-8
10.3.2.1 Salt Fog	10-9
10.3.3 Crustal Derived Aerosols	10-9
10.3.4 Volcanic Ash	10-9
10.3.5 Combustion and Other Man-Induced Aerosol	10-14
10.3.5.1 Acid Rain	10-16
10.4 Gaseous Constituents	10-16
10.4.1 Average Atmospheric Constituents	10-16
References	10-19

This Page Left Blank Intentionally

SECTION 10

ATMOSPHERIC CONSTITUENTS

10.1 Introduction. Gases and particles in the atmosphere must be considered during aerospace vehicle development in order to avoid detrimental effects to the vehicle on the ground or in flight. Some of these effects include corrosion, abrasion, and optical hindrances. These effects are explained later in this section. The intensity of damage depends on the source (type), location, and concentration of the particles. The particles together with the air that suspends them are termed aerosols.

10.1.1 Sources of Particles. Airborne particles develop from both primary (direct) and secondary (indirect) sources (ref 10.1).

10.1.1.1 Primary Sources.

- a. Meteorites - extraterrestrial or interplanetary dust
- b. World Oceans—sea-salt particles
- c. Arid and Semiarid Regions—soil dust, road dust, etc.
- d. Terrestrial Materials—volcanic debris
- e. Terrestrial Biota—biological material
- f. Combustion—carbonaceous materials, ash.

10.1.1.2 Secondary Source. The secondary source of atmospheric particles is gas to particle conversions (GPC) where chemical reactions convert natural and man-made atmospheric trace gases into liquid and solid particles.

10.1.2 Distribution of Particles. The distribution of aerosols is regionally dependent. Particles may have a “local” distribution as well as a “regional” distribution. The “local” aerosol takes place in the area surrounding factories, volcanoes, and other direct sources of aerosol. Since this aerosol can greatly affect an aerospace facility, the site should be surveyed for possible problems. Factors such as wind speed, distance from source, altitude, and particle size play an important part in determining the makeup and concentration of a “local” aerosol. These same factors also affect “regional” aerosol. On a regional scale, number concentrations of particles in the atmosphere increase rapidly with decreasing particle size, to sizes smaller than 0.1 μm radius. Work cited in references 10.2 and 10.3 shows that the concentrations and size distributions are highly variable with altitude. Some examples of these variations are given in subsection 10.3.

Natural aerosol size distribution is trimodal and dependent on number, surface, and volume. Aerosol particles ranging from 0.1 to 1.0 μm are in the “accumulation mode” because they tend to grow from smaller particles by coagulation or condensation. The “transient mode” consists of particles around 0.01 μm , usually resulting from combustion or anthropogenic nuclei sources. Dust, fly-ash, sea spray, and other particles that are larger than 1 μm make up the “coarse particle mode.” This mode is usually derived from mechanical processes (ref. 10.4).

10.1.3 Upper Atmospheric Aerosols. Atmospheric aerosols can exist at stratospheric levels (15- to 30-km altitude) as well as in the troposphere. The stratospheric aerosols, consisting mainly of liquid sulfuric acid droplets, are divided into three categories: (1) background aerosols, (2) volcanic aerosols, and (3) polar stratospheric cloud particles (PSC's) (ref. 10.5). Section 8.5.1.1 gives more information regarding PSC's. Table 10.1 presents the basic characteristics of stratospheric aerosols.

TABLE 10.1 Characteristics of Stratospheric Aerosols (ref. 10.6).

Particle Type	Sulfate Aerosol	Type-I PSC	Type-II PSC	Meteoric Dust	Rocket Exhaust
Physical State	Liquid or Slurry with Crystals	Solid Nitric Acid Trihydrate, Solid Solutions	Solid Crystal, Hexagonal or Cubic Basis	Solid Granular Irregular or Spherical	Solid Spheres or Irregular Surface Ablated Debris
Particle radius (μm , 10^{-6} m)	0.01 – 0.5, Amb. 0.01 – 10, Volc.	0.3 – 3	1 – 100	1 – 100, Micro-meteorites 0.01 – 0.1, smoke	0.1 – 10
Number (# cm^{-3})	~1 – 10	~0.1 – 10	<<1	10^{-6} , 100 μm 10^{-3} , 1 μm	10^{-4} , 10 μm 10^{-2} , 1 μm
Principal composition	$\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ~70%/30%	$\text{HNO}_3/\text{H}_2\text{O}$ ~50%/50%	H_2O	SiO_2 , Fe, Ni, Mg; C	Al_2O_3
Trace composition	NH_4^+ , NO_3	HCl SO_4^{2-}	HNO_3 , HCl	SO_4^{2-} (surface)	Cl^- , SO_4^{2-} (surface)
Physical characteristics	Dust inclusions, in solution	Equidimensional crystalline or droplets	Elongated crystals with polycrystalline structure	Irregular mineral grains, grain defects	Homogeneous composition; smooth spheres
Distribution	Global, Amb. Region, Volc, 12–35 km alt.	Polar winter 14–24 km alt.	Polar winter 14–24 km alt.	~Global >12 km alt.	Global >12 km alt.
Residence Time	~1–2 yr. Amb. ~1–3 yr. Volc.	~1 day to weeks	~ hours	<1 mo. (micro-meteorites) 1–10 yr. (meteoritic smoke)	<1 yr.

Background aerosols are those aerosols observed under normal stratospheric temperatures higher than 195 K (not volcanic) and are primarily supercooled H_2SO_4 (75 percent by weight) in H_2O solution. They are formed by heterogeneous nucleation on preexisting particles. Small amounts of ammonium ions or meteoritic material may also be present.

Large volcanic eruptions can inject both sulfurous gases and ash (radii <3 μm) into the stratosphere. These gases are responsible for the rapid generation (within a few weeks or months) of sulfuric acid aerosols which remain at stratospheric levels for several months or even years. The exponential 1/e decay time for the integrated aerosol backscattering was found to range between 12 and 18 months. Low levels of other species such as chlorine and NO_x can also be observed. Abundant halide particles (radii of 2 to 3 μm), probably derived from the chlorine-rich alkali magma, are also present (ref. 10.5).

The size distributions of volcanic aerosols (shown in figure 10.1 for an El Chichon simulation) exhibit a tri-modal structure that evolves with time. The principal size modes are: (1) a nucleation mode, which is most prominent at early times and at sizes near 0.01 μm ; (2) a sulfate accumulation mode, which evolves initially from the nucleation mode (by coagulation and condensation) and increases in size to about 0.3 μm after 1 year; and (3) a large-particle “ash” mode (of solid mineral and salt particles) that settles out of the layer in 1 or 2 months. A primary feature of the volcanic aerosol size distribution after several months is a greatly enhanced sulfate accumulation mode. The increased aerosol size is caused by accelerated growth in the presence of enhanced sulfuric acid vapor concentrations that are maintained by continuing SO_2 chemical conversion (ref. 10.6).

PSC’s form when aerosol particles encounter cold temperatures ($<195\text{ K}$) in wintertime polar regions and are formed by excess condensation of water vapor on background stratospheric sulfate particles. Nitric and hydrochloric acids may also be impinging onto the PSC particles. Section 8 provides a more in-depth study of PSC’s.

Aerosol particles with a radius greater than 0.1 μm typically obey a size distribution of the form (ref. 10.4);

$$n(r) = dN/d(\log r), \quad (10.1)$$

where

r = radius of particle

dN = number of particles in the radius interval $d(\log r)$.

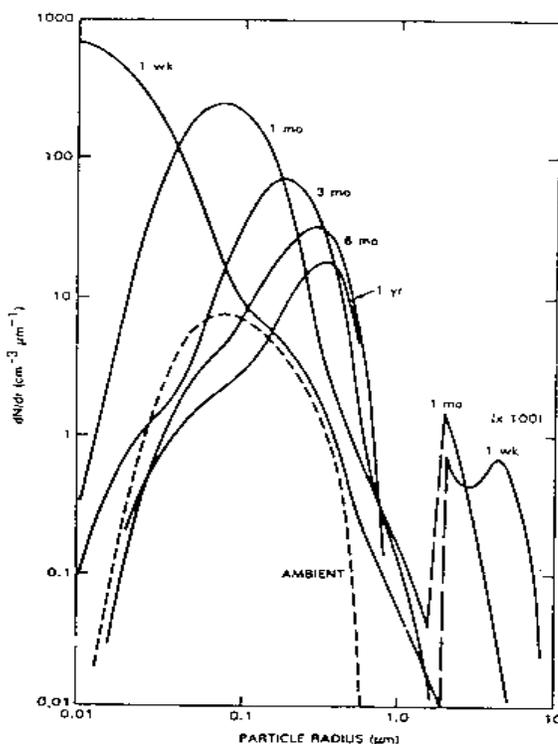


FIGURE 10-1. Evolution of the Volcanic Aerosol Size Distribution at 20 Km in the Simulated El Chichon Eruption Cloud. Size Distributions are Shown at Various Times, and are Compared to the Ambient Size Distribution (Ref. 10.6).

10.2 Threats Caused by Atmospheric Particles. Abrasion, optical hindrances, and corrosion are the main problems caused by gases and airborne particles that must be considered during aerospace vehicle development. For an example of specific launch related threats, refer to subsection 10.3.5.

10.2.1 Abrasion. When an aerosol exists around an object, the particles usually follow the airflow around the object. However, if the momentum of the particles is sufficiently great, they will deviate from the flow path to impact the surface. Whether or not impaction occurs depends on the particle size, shape, and density and on air density; the relative speed of the aerosol and object; and the size and shape of the object. Impaction theory is reviewed in reference 10.7. The greater the size and density of the particles and the greater the relative aerosol velocity, the greater is the likelihood of impact.

The effect of the impact depends on the physical characteristics of the particle, and the impact surface, the velocity of the particle, and the angle of impact. Direct impact of dry particles on a surface may cause abrasion, and, when voids are filled with dry particles, they may interfere with or cause wear on moving parts. Particles may also clog various mechanisms or produce electrical shorts.

The degree of hardness, i.e. the resistance offered by a mineral to abrasion or scratching, is often compared using the Mohs' scale of hardness. This scale of mineral hardness was devised in 1822 by a German mineralogist, Fredrich Mohs, and has been used since because of its simplicity and usefulness. This scale is made up of a number of minerals of increasing hardness, as given in table 10.2 with a comparison of other materials given in table 10.3 (ref. 10.8). A complete listing as well as mineral breaking or cleaving shapes can be found in reference 10.9.

The Mohs' scale of hardness is used as a guide to determine which materials will abrade or scratch other materials. A material can be scratched by another material of the same hardness or a higher hardness number.

Two minerals included in table 10.3 are halite (NaCl) and kaolinite ($H_4Al_2Si_2O_9$). Halite, a naturally occurring salt, indicates the general hardness of sea-salt particles. Although NaCl is usually cube-shaped, it may be an irregular shape if broken. Kaolinite, an aluminum silicate, is a common clay mineral (usually a crystal plate) which makes up many of the fine particles in the air from sandy soils.

TABLE 10.2. Mohs' Scale-of-Hardness for Minerals.

Moh's Relative Hardness	Mineral
1	Talc
2	Gypsum
3	Calcite
4	Fluorite
5	Apatite
6	Orthoclase
7	Quartz
8	Topaz
9	Carborundum
10	Diamond

TABLE 10.3. Mohs' Hardness Values for Some Other Materials

MATERIAL	HARDNESS
Lead	1.5
Aluminum	2-2.5
Halite (sea-salt)	2-2.5
Kaolinite	2-2.5
Zinc	2.5
Copper	2.5-3
Gold	2.5-3
Brass	3-4
Iron	4-5
Platinum	4.3
Glass	4.5-6.5
Steel	5-8.5
Volcanic Ash	6-7

The larger and harder sand particles, primarily quartz (SiO_2), are usually rounded but may be jagged. Volcanic ash particles, consisting of SiO_2 , orthoclase (KAlSi_3O_8) and various other minerals, are usually jagged. Gypsum particles, ($\text{CaSO}_4, 2\text{H}_2\text{O}$), are at times raised by winds over arid areas, especially in the White Sands, New Mexico, area which is almost entirely gypsum. Most smog particles are droplets of soft organic particles or salts, although some harder particles such as fly ash from power plants may be present.

A discussion of rain erosion is covered in section 7.

10.2.2 Optical Hindrances. Atmospheric aerosols affect optical properties in a variety of ways. The optical effects of an aerosol depend on the sizes, optical constants, and shapes of the aerosol (ref. 10.10). One of the most evident manifestations of air pollution is the production of haze which causes a reduction in visibility or visual range. Other particles may coat optical and transparent surfaces to affect visibility. The effect of aerosols on optical and infrared transmission can be assessed using the LOWTRAN 7 computer code.

10.2.3 Corrosion. Certain atmospheric gases may cause engineering metals to react chemically and cause atmospheric corrosion. Atmospheric corrosion is the degradation of a material exposed to the air and its pollutants and is the cause of more failures in terms of cost and tonnage than any other single environment. The basic types of atmospheric corrosion are often classified and defined as follows (ref. 10.11):

- a. Dry corrosion - Corrosion which occurs in the absence of moisture. Usually, this corrosion occurs very slowly unless elevated temperatures exist.
- b. Damp corrosion - Corrosion occurring when there is some moisture in the air. When the relative humidity reaches a specific critical value, around 70 percent, a thin layer of moisture on the metal surface provides an electrolyte for current transfer, and consequently increases the rate of corrosion.
- c. Wet corrosion - Visible water layers caused by sea spray, dew, or rain cause wet corrosion. Wet corrosion usually occurs most rapidly due to the high conductivity.

10.2.3.1 Rate of Atmospheric Corrosion. The rate of atmospheric corrosion depends on many different atmospheric variables. Some of these variables are temperature, humidity, and other climatic conditions, as well as surface shape and properties. Table 10.4 provides average corrosion rates over 10- and 20-year intervals for certain surface metals (ref. 10.11).

TABLE 10.4 Average Atmospheric-Corrosion Rates of Various Metals for 10- and 20-Year Exposure Times (Ref. 10.11)

Corrosion rates are given in mils/yr (1 mil/yr = 0.025 mm/yr). Values cited are one-half reduction of specimen thickness.

METAL	ATMOSPHERE					
	New York, NY (Urban-Industrial)		La Jolla, CA (Marine)		State College, PA (Rural)	
	10	20	10	20	10	20
Aluminum	0.032	0.029	0.028	0.025	0.001	0.003
Copper	0.047	0.054	0.052	0.050	0.023	0.017
Lead	0.017	0.015	0.016	0.021	0.019	0.013
Tin	0.047	0.052	0.091	0.112	0.018	...
Nickel	0.128	0.144	0.004	0.006	0.006	0.009
65% Ni, 32% Cu, 2% Fe, 1% Mn (Monel)	0.053	0.062	0.007	0.006	0.005	0.007
Zinc (99.9%)	0.202	0.226	0.063	0.069	0.034	0.044
Zinc (99.0%)	0.193	0.218	0.069	0.068	0.042	0.043
0.2% C Steel(a) (0.02% P, 0.05% S, 0.05% Cu, 0.02% Ni, 0.02% Cr)	0.48
Low-Alloy Steel(a) (0.1% C, 0.2% P, 0.04% S, 0.03% Ni, 1.1% Cr, 0.4% Cu)	0.09

10.2.3.2 Protection From Atmospheric Corrosion. Prevention from atmospheric corrosion can be temporary or permanent. During transport or storage, lowering the atmospheric humidity by artificial methods may temporarily prevent corrosion. Changing the surface material or applying a coating can provide a longer term solution. In determining the materials, the type of environment must be considered. Table 10.5 and table 10.6 list the corrosivities for iron, steel, and zinc for various environments (ref 10.12).

10.3 Characteristics of Specific Particles. Included in this section are characteristics of some particles that should be considered in aerospace vehicle design. Table 10.7 gives estimates of the sizes of various particles (refs. 10.1 and 10.13), but the actual sizes may vary greatly depending on the specific atmospheric conditions. Typical sizes for suspended water droplets (fog) can be found in section 7.

TABLE 10.5 Relative Corrosivity of Atmospheres at Different Locations (Ref. 10.12).

LOCATION	Type of Atmosphere	Average Weight Loss of Iron Specimens in 1 Year: mg/cm ²	Relative Corrosivity
Khartoum, Sudan	Dry island (arid)	0.08	1
Singapore	Tropical/marine	0.69	9
State College, PA	Rural	1.90	25
Panama Canal Zone	Tropical/marine	2.28	31
Kure Beach, NC (250-m, or 800-ft, lot)	Marine	2.93	38
Kearny, NJ	Industrial	3.92	52
Pittsburgh, PA	Industrial	4.88	65
Frodingham, UK	Industrial	7.50	100
Daytona Beach, FL	Marine	10.34	138
Kure Beach, NC (25-m, or 80-ft, lot)	Marine	35.68	475

TABLE 10.6 Measured Atmospheric-Corrosion Rates for Steel and Zinc (Ref. 10.12).

Site	LOCATION	Type of Atmosphere	Relative Corrosivity	
			Steel	Zinc
1	Normal Wells, Northwest Territory	Rural	0.02	0.2
2	Saskatoon, Saskatchewan	Rural	0.2	0.2
9	State College, PA(a)	Rural	1.0	1.0
17	Pittsburgh, PA (roof)	Industrial	1.8	1.5
18	London (Battersea), UK	Industrial	2.0	1.2
27	Bayonne, NJ	Industrial	3.4	3.1
28	Kure Beach, NC (250-m, or 800-ft, site)	Marine	3.6	1.9
31	London (Stratford), UK	Industrial	6.5	4.8
33	Point Reyes, CA	Marine	9.5	2.0
37	Kure Beach, NC (25-m, or 80-ft, site)	Marine	33.0	6.4

(a) The average weight losses on two 100- by 150-mm (4- by 6-in) specimens after 1 year of exposure at the indicated site were used to calculate the relative corrosivity of the site. The losses in the rural atmosphere at State College, PA, were taken as unity and the relative corrosiveness at each of the other sites is given in this table as a fraction or a multiple of unity.

TABLE 10.7 Estimated Size Ranges of Natural Occurring Atmospheric Particles.

Particle Type	Radii Size (µm)
Extraterrestrial	0.1–1,000
Sea-Salt	0.02–60
Crustal Aerosol	0.02–100
Volcanic Ash ¹	0.1–10
Combustion and Secondary Particles (average)	<1.0
Indirect Sources	under 0.1

¹Directly after the eruption particles as large as 5 mm can be found (ref. 10.13).

10.3.1 Extraterrestrial Dust. Extraterrestrial dust is usually formed by the breakup of meteoroids and orbital debris. It reaches the troposphere through processes such as gradual sedimentation, stratospheric subsidence, followed by a rapid pulsing from the stratosphere into the troposphere in the “stratospheric folds.” Within the troposphere, the extraterrestrial dust is concentrated around the polar regions. The larger dust particles are “fluffy and compacted aggregates” while the smaller particles (submicrometer) are more dense (ref. 10.1). The residence time for these particles in the stratosphere and troposphere ranges from months to years.

10.3.2 Sea-Salt Particles. Sea-salt particles are the most common aerosol component (ref. 10.1). Most airborne sea-salt droplets are formed by the breaking of myriads of air bubbles at the surface of the sea. The bubbles are produced by the breaking of small waves or the larger surf, and, to a lesser extent, by rain or snow falling on the water. The droplets, thus formed, evaporate when the humidity falls below 75 percent. If humidities above 75 percent are encountered, the sea-salt particles become droplets again (ref. 10.14).

Atmospheric temperature inversions over the oceans, such as the tropical inversion, tend to keep sea-salt particles below a few kilometers in altitude. Above such inversions the particles are largely of continental origin, except near clouds or near the residues from dissipated clouds. Table 10.8 lists a few average concentrations of sea-salt with respect to altitude (ref. 10.14).

TABLE 10.8 Mean Sea-Salt Particle Concentrations in Maritime Air Masses and Corresponding Altitudes.

Altitude (m)	Concentration (cm ⁻³)
Sea level	200–300
600–800	10–20
1,200	2–4

Sea-salt particle concentrations also depend on the wind speed. In figure 10.2, the concentrations at two altitudes are shown as a function of wind speed (ref. 10.13).

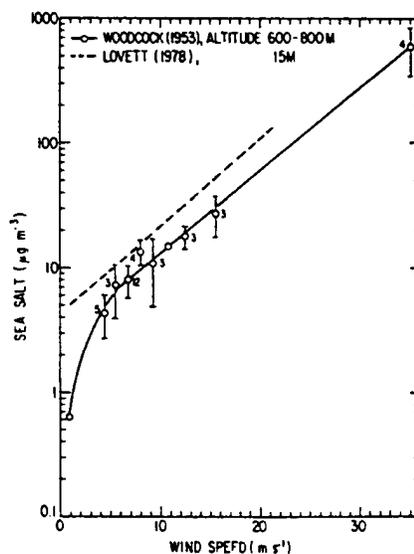


FIGURE 10.2. Sea-Salt Concentration at Two Altitudes as a Function of Wind Speed Near the Surface of the Sea. The Number Of Observations Averaged for Each Data Point is Given, as Well as Standard Deviation (Ref. 10.13).

Salt (sodium chloride (NaCl)) particles, whether from the ocean or areas where salt occurs in nature on the continents, may be detrimental to space vehicles and associated systems because of their corrosive actions and their ability to coat transparent areas until they become opaque. Salt attacks many metals, and the corrosion is especially rapid at high humidities and high temperatures. Salt solutions also provide a conductive path that can alter or short electrical circuits.

10.3.2.1 Salt Fog. Fog developing over a coastal area can be influenced by the marine environment and can contain sea salt (NaCl) which can degrade equipment and materials. The salt fog test (method 509.3) as outlined in MIL-STD-810E (ref. 10.15) should be followed to determine the resistance of equipment to the effects of an aqueous salt atmosphere. This type of atmosphere could impose three degradation effects on materials and equipment, i.e., corrosion, electrical, and physical effects.

The characteristics of marine fog droplets and salt nuclei are presented in references 10.16 and 10.17. Subsections 7.8 and 7.9 present a general and a location-specific discussion of fog.

10.3.3 Crustal Derived Aerosols. Dust and sand are transported through the air by wind blowing across a disturbed soil area. Strong winds are required to uplift the submicron sand and dust particles, because strong adhesive forces exist between the particles and the ground (ref. 10.18). Dense vegetation and ground cover also provide considerable protection from strong winds (ref. 10.19). The concentration of these particles is highly dependent on wind speed (the higher the speed, the greater the volume of sand and dust), the nature of the soil, and the amount of moisture in the soil and in the air (refs. 10.20 and 10.21). Threshold air velocities for the input of soil particles into the air increase with different types of soil surfaces in the following order: disturbed soils (except disturbed heavy clay soils), sand dunes, alluvial and aeolian sand deposits, disturbed playa (dry lake) soils, skirts of playa centers, and desert pavements (alluvial deposits) (ref. 10.22).

The larger, more abrasive particles in dust and sand storms are mostly in the lower 2 km of the atmosphere, although fine dust can reach great heights and travel great distances, e.g., approximately 10 million tons of red dust from northwest Africa was deposited on England in 1903. California experiences dust in two general regions. One region extends into southwestern Arizona and covers all the southeastern California with a maxima north of the Salton Sea and the western Mojave Desert. The second region is situated in central California. Figures 10.3 through 10.7 give maps on the characteristics of dust storms in the Southwest United States. In urban areas, the resuspension of dust by traffic or other methods must also be considered (ref. 10.10).

10.3.4 Volcanic Ash. Volcanic eruptions are normally followed by an emission of dust or ash and release of significant quantities of reactive gases. The emission rate, occurrence, and size distribution of the ash cannot be predicted by common meteorological methods because of the unpredictable timing and the different levels of intensity of volcanoes.

During the few days following an eruption, the distribution of the ash and gases is concentrated around the volcanic site, but over the following few months, a 2- to 4-km layer is formed above the troposphere over much of the world (ref. 10.14). Although most volcanic aerosol is found in the stratosphere, some of the aerosol is transported to high tropospheric layers and polar regions (ref. 10.1).

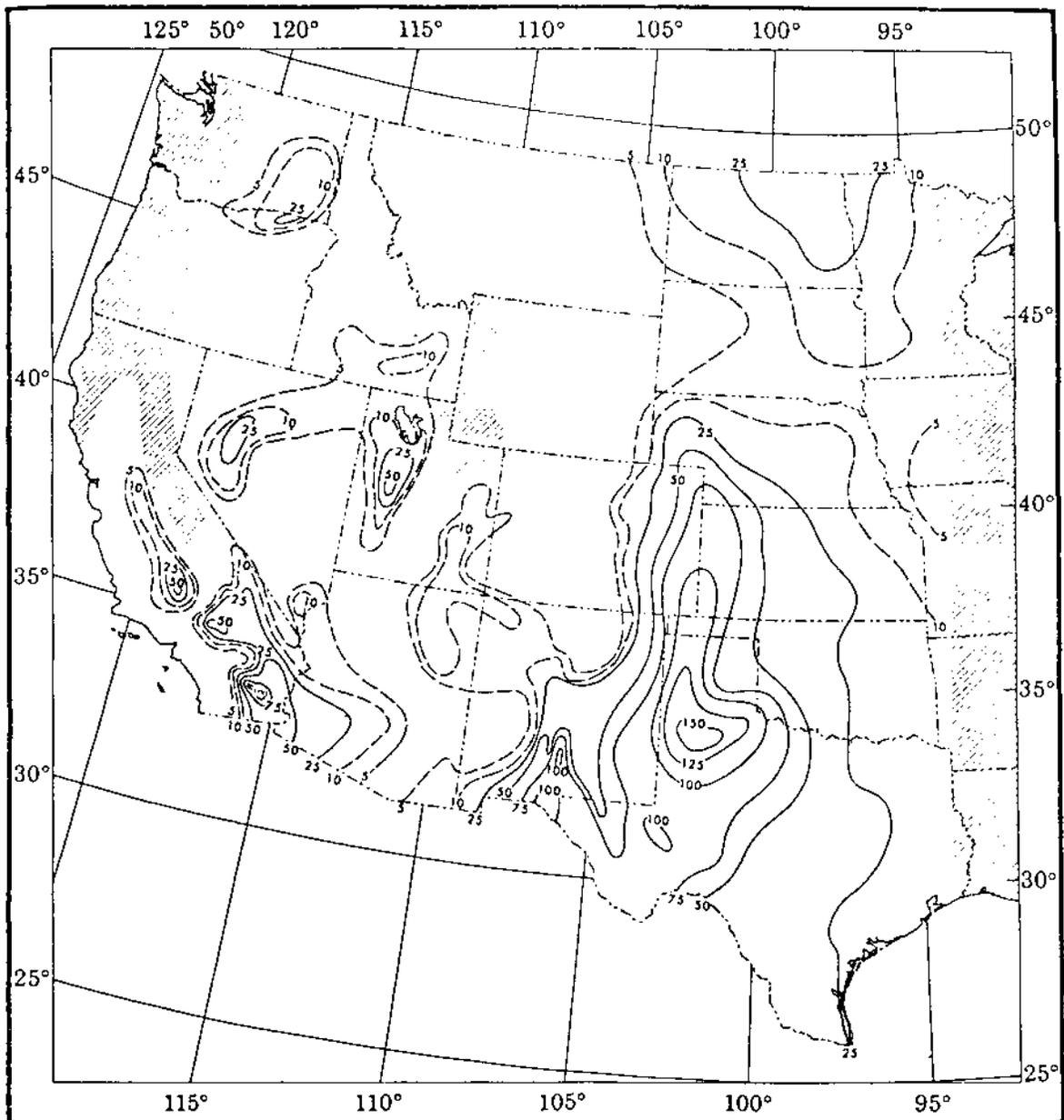


FIGURE 10.3. Annual Average Number of Hours of Dust Episode
Visibility Less Than 7 Miles (Ref. 10.19).

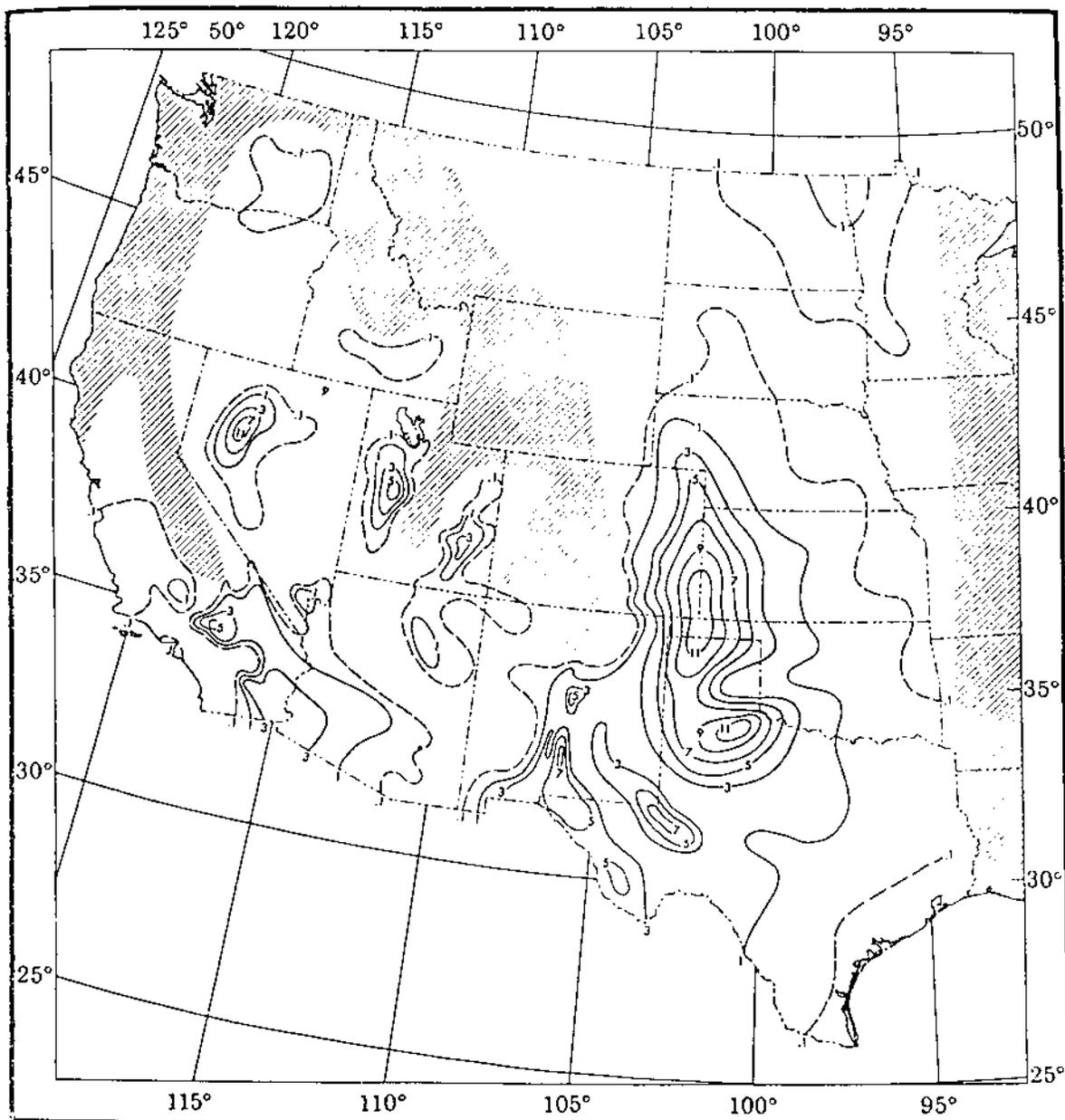


FIGURE 10.4. Annual Average Number of Hours of Dust Episode
Visibility Less Than $\frac{5}{8}$ Mile (Ref. 10.19).

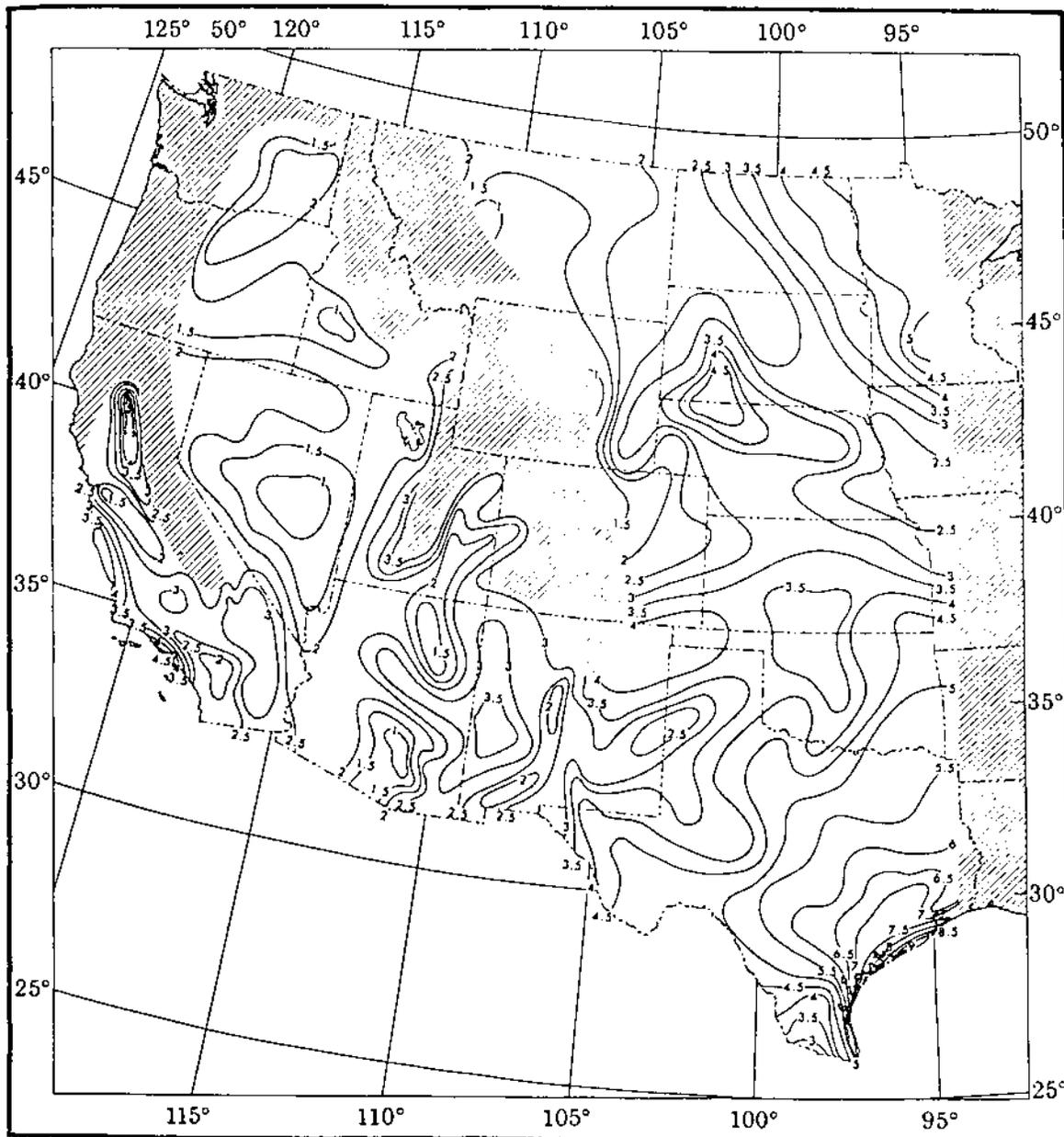


FIGURE 10.5. Average Duration (Hours) of Dust Episodes
With Visibility Less Than 7 Miles (Ref. 10.19).

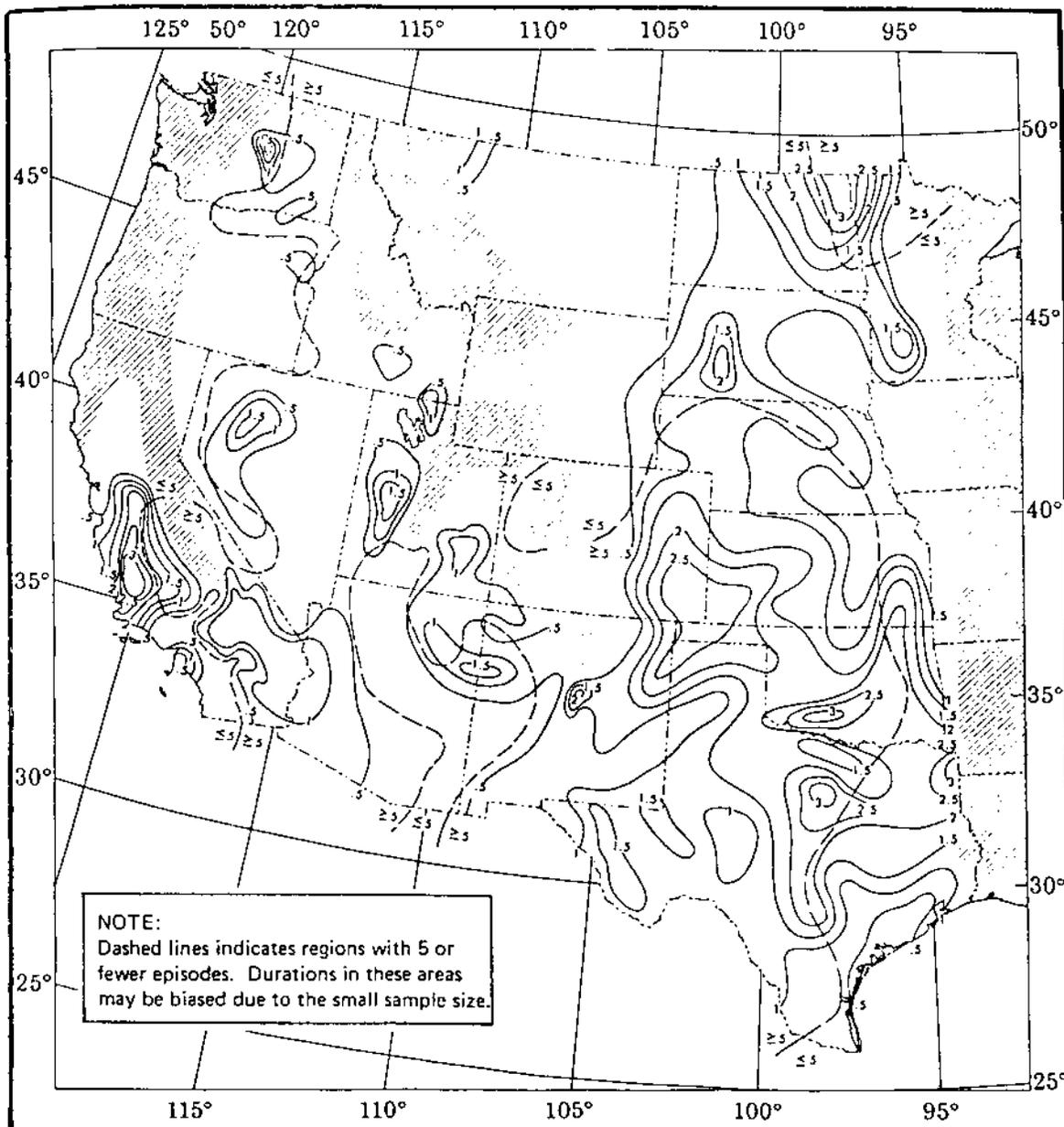


FIGURE 10-6. Average Duration (Hours) of Dust Episodes with Visibility Less Than $\frac{5}{8}$ Mile (Ref. 10.19).

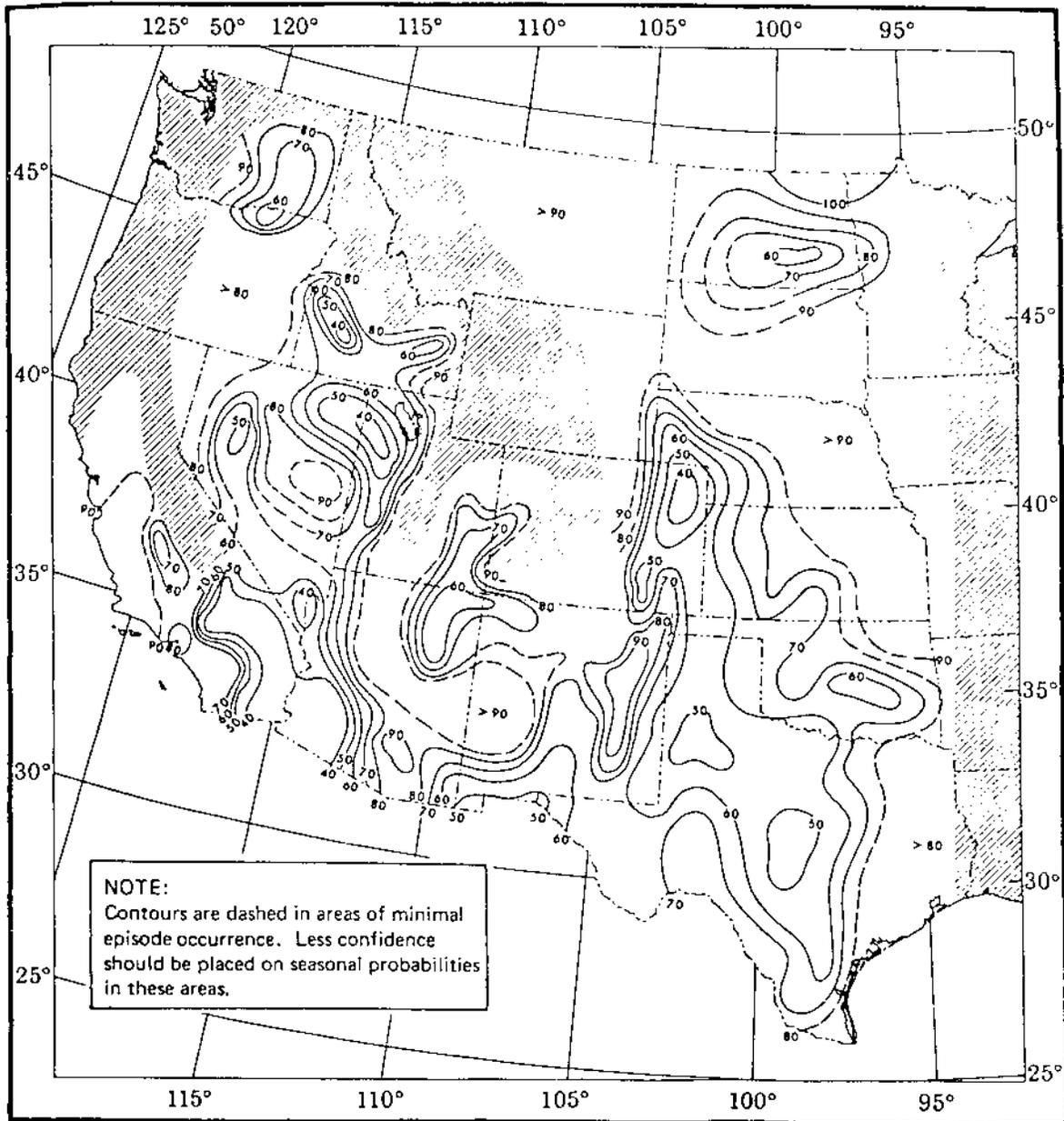


FIGURE 10-7. Probability (Percent) of Dust Episodes with Visibility Less Than $\frac{5}{8}$ Mile Occurring During Primary Season (Ref. 10.19).

10.3.5 Combustion and Other Man-Induced Aerosol. Secondary and combustion aerosols are formed by three major processes: gas-to-particle conversion resulting from physical or chemical changes; condensation of a supersaturated gas; and direct emissions of solids or liquids from the combustion sources (ref. 10.10). The particles resulting from primary combustion are carbonaceous (soots) or noncarbonaceous (fly-ash). The inorganic ionic aerosols, which include sulfate and nitrate aerosol particles are produced by secondary processes through condensation. These aerosols are usually submicron size unless further aggregation of the particles occurs. The number and mass concentrations are highly dependent on location and time (ref. 10.23).

The industrial and anthropogenic activities in eastern North America provide a major source of secondary and combustion aerosol. Atmospheric pollutants tend to be trapped beneath atmospheric temperature inversions. Incidents of severe smog usually are associated with such inversions. In the Los Angeles Basin, the pollutants are frequently trapped and cannot disperse because the basin is surrounded on the north, east, and south by mountain ranges higher than the inversions, with frequent prevailing easterly winds.

The firing of solid rocket motors (SRM's) during a rocket launch or static test is an example of an emission source which is of particular importance for aerospace activities. The byproducts of the SRM's include a significant amount of gaseous hydrogen chloride (HCl) and particulate aluminum oxide (Al_2O_3). The mass fractions of HCl and Al_2O_3 in SRM exhaust are 0.21 and 0.30, respectively. In test and launch configurations which utilize substantial amounts of cooling or sound suppression water, or when rain, fog, or other natural sources of water are present, the HCl gas and Al_2O_3 particulates will combine with the water yielding an acidic deposition which will be dispersed by the exhaust plume over the facility and may be carried downwind as well. The amounts and location of deposition are strongly influenced by the configuration of the water spray, as well as by wind and other meteorological factors. Concentrations of a few deposition spots per square centimeter are typical within a few kilometers of a Shuttle launch. In one extremely windy case (STS-2), trace amounts of deposition were found up to 22 km downwind from the launch site. (See section 11 for additional discussion.)

For the aerospace design engineer, the most serious issue is usually the heavy deposition which occurs (for systems like Shuttle which use large quantities of sound suppression water) within 1 km of the firing location. For the Shuttle, the initial deposition is usually about one-third Al_2O_3 solids by volume in a moderately acidic (~2N) solution. Once dispersed over the facility the solution generally evaporates quite rapidly. However, the water vaporizes more rapidly than the acid, resulting in a highly concentrated acidic solution for a short time—typically a few minutes on an open surface. The rate of evaporation depends on wind speed, ambient humidity, air temperature, and surface temperature. For the shuttle launch system, there are sufficient quantities of deposition to impact both vegetation and animal life within 1 km of the launch facility, as well as to be corrosive to manmade structures. When the evaporation potential of the HCl is high (warm temperatures, low humidity, and moderate to high wind speeds), the immediate corrosion damage is typically not evident except on the most sensitive surfaces. However, even in this situation the acid greatly increases the bonding between the aluminum oxide particulates and the exposed surface. The surface may be coated with particulates which will not come off without direct scrubbing. This material is hygroscopic and will enhance corrosion over long periods of time. The addition of chemical additives to the water source is an option for reducing the bonding potential.

Gaseous HCl, which is either released during a firing or is the result of evaporation of this deposition, can also be a corrosion hazard at or near the facility, especially for sensitive electronic systems. Concentrations in the 5 to 10 ppm range have been measured at the Shuttle launch site in the hours following a launch. As one would expect, the most severe cases tend to correlate with times when the ground was wet from rain prior to the launch. Special precautions should be taken whenever extensive electronic equipment is to be located close to the launch pad or test site. Computer or other electronic equipment is usually very sensitive to HCl gas; an 8- to 10-h exposure may render a system inoperable. Electronics are often sensitive to gas concentrations of 10 to 100 ppb, and concentrations above this level may be encountered intermittently for at least 2 days following a SRM firing. The threshold limit value for HCl exposure for workers is 5 ppm, and the exposure limit for the public is 1 ppm (ref. 10.24). (See section 11 for a discussion of far field effects.)

10.3.5.1 Acid Rain. Acid rain is rain with a pH in the range of 4 to 5 and is common in the northeastern United States, southeastern Canada, and in Europe. This rain is a result of the HNO₃ vapor, H₂SO₄ vapor, and HCl vapor being dissolved in rain drops. A pH of 5.6 has been selected to be the neutral point below which precipitation is said to be acidified (ref. 10.26). Acid rain can occur anywhere in the United States. The maximum concentrations occur in the northeastern United States over the Ohio River Valley, southern Ontario, Canada, and western New York State. The lowest (highest acidity) observed values of annual pH are between 4.0 and 4.2 and are centered in this area. Table 10.9 gives mean annual values of ion concentrations, deposition, and pH for this area in 1982 (ref. 10.26).

Acidic deposition can also occur in dry (in gaseous or particulate form) as well as in the wet form with precipitation. Acid rain measurements are generally expressed in terms of constituent concentration (mg/l) and deposition (g/m²) of sulfate (SO₄²⁻), or nitrate (NO₃⁻), and hydrogen ions (H⁺) in precipitation or in terms of pH.

The availability of the hydrogen ion allows acid rain to react with materials (including minerals and plants) that it contacts. The other sulfate, nitrate, chloride, ammonium, and calcium ions are also more abundant in acid rain and contribute to its detrimental effects (ref. 10.26).

Increases in the acidity of precipitation are caused by the many industrial, energy producing, and transportation-related activities which release acidic wastes into the atmosphere. At the present time, between 75 and 100 million metric tons of anthropogenic, or man-made, sulfur emissions are released into the atmosphere yearly (ref. 10.27).

At the Eastern Range, annual average pH values of 4.58 are observed (ref. 10.25).

TABLE 10.9. Mean, Annual Concentration, and Deposition in 1982 of Hydrogen, Sulfate, and Nitrate Ion in Wet Deposition for Sites in the Precipitation Chemistry Data Base, When pH < 4.2 (Ref. 10.26).

	Concentration (mg/L)	Deposition (g/m ²)
H ⁺	0.073	0.065
SO ₄ ²⁻	3.497	3.079
NO ₃ ⁻	2.240	1.984

10.4 Gaseous Constituents. Gaseous as well as particulate matter can cause detrimental effects on aerospace vehicles and ground equipment due to various chemical reactions/processes. Nitrogen (N₂) and oxygen (O₂) make up approximately 99.0 percent by volume (98.6 percent by weight) of the lower atmosphere. These two atmospheric constituents along with carbon dioxide, water vapor, and ozone are the gases of primary concern. Water vapor (H₂O) is discussed in section 6 of this document. Stratospheric ozone depletion is discussed in section 8.5.1.1.

10.4.1 Average Atmospheric Constituents. The variability (range) of many atmospheric trace gases is quite large. However, given in table 10.10 are the average or typical gas concentration values expected at both ground level and with altitude. Seasonal, diurnal, locational, and other changes can all add to the variability of various atmospheric constituents. The mean values presented in table 10.10 are based on model information taken from references 10.27 and 10.28

TABLE 10.10 Average Concentrations (Standard Atmosphere Values) of Various Gaseous Constituents from the Earth's Surface Up to 900-Km Altitude.^a (Refs. 10.27, 10.28)

Constituent	Typical Concentration (ppbv*)	
	Altitude (km)	ppbv
N ₂	0 and above	7.81x10 ⁸
O ₂	0 and above	2.09x10 ⁸
Rare Gases	0	very small
O ₃	0	27
	7	50
	22	3,650
	40	7,300
	75	250
	90	700
N ₂ O	0	320
	9	320
	32	117
	49	5
	90	0.5
NO ^b	0	0.3
	12	0.3
	18	0.2
	40	11
	70	11
	90	213
NO ₂ ^b	0	0.02
	10	0.02
	18	0.8
	35	7.3
	50	0.4
	90	0.2
H ₂ S ^b	0	0.1
	2	0.03
	10	0.01
	26 and above	10 ⁻¹⁵
CS ₂ ^b	0	0.07
	14	0.03
	32 and above	10 ⁻¹⁵
COS	0	<0.05
NH ₃ ^b	0	0.5
	12 and above	<0.01
H ₂	0 to 90	560
CH ₄	0	1,700
	10	1,700
	40	564
	50	210
	90	140
SO ₂ ^b	0	0.3
	30	0.01
	70	0.04
	90	0.002
CO	0	150
	10	100
	21	12
	50	46
	90	5,840
CO ₂	0	330,000
	75	330,000
	90	310,000
HNO ₃ (vapor) ^b	0	0.05
	15	0.45
	22	5.5
	50	0.06
	90	0.03
H ₂ SO ₄ (vapor)	0 to 90	small except in localized areas

a. This table gives average values such that a constituent value at altitude can be obtained by linear interpolation between the listed altitude/concentration values. See references 10.27 and 10.28 for more exact curves.

b. These gases have a very large latitudinal and longitudinal gradient, due to short lifetimes, causing a large range

of local concentrations with altitude to exist.
* ppbv = parts per billion volume.

This Page Left Blank Intentionally

REFERENCES

SECTION 10

- 10.1 d'Almeida, G.A., Koepke, P., and Shettle, E.P.: "Atmospheric Aerosols Global Climatology and Radiative Characteristics." 1991, pp. 11–24.
- 10.2 "U.S. Standard Atmosphere." United States Government Printing Office No. 003-017-00323-0, Washington, DC, October 1976.
- 10.3 Blifford, I.H. and Ringer, L.D.: "The Size and Number Distribution of Aerosols in the Continental Atmosphere." *Journal of Atmospheric Sciences*, vol. 26. 1969, pp. 716–726.
- 10.4 Jennings, S.G.: "Physical Characteristics of the Natural Atmospheric Aerosol." TSLP: Final Technical Report, March 1975–September 1976, p. 2.
- 10.5 Kent, G.S., and Yue, G.K.: "The Modeling of CO₂ Lidar Backscatter From Stratospheric Aerosols." *Journal of Geophy. Res.*, vol. 96, No. D3, March 20, 1991, pp. 5279–5292.
- 10.6 Turco, R.: "Upper-Atmosphere Aerosols: Properties and Natural Cycles." Chapter 3B of "The Atmospheric Effects of Stratospheric Aircraft: A First Program Report," NASA RP-1272, January 1992, pp. 63–91.
- 10.7 Cadle, R.D.: "The Measurement of Airborne Particles." Wiley-Interscience, New York, 1975, p. 342.
- 10.8 "CRC Handbook of Chemistry and Physics." 73rd Edition, CRC Press, Inc., Boca Raton, Florida, 1992.
- 10.9 Ford, W.E.: "Dana's Manual of Meteorology." John Wiley & Sons, Inc., New York and Chapman & Hall, London, 13th Edition, 1912.
- 10.10 Patterson, E.M.: "Size Distributions, Concentrations, and Composition of Continental and Marine Aerosols." *Atmospheric Aerosols: Their Formation, Optical Properties, and Effects*. Spectrum Press, Hampton, Virginia, 1982.
- 10.11 Pohlman, S.L.: "General Corrosion." *Metals Handbook, Ninth Edition, Volume 13–Corrosion*. ASM International, United States, 1987, pp. 80–83.
- 10.12 Money, K.L.: "Corrosion Testing in the Atmosphere." *Metals Handbook, Ninth Edition, Volume 13–Corrosion*. ASM International, United States, 1987, pp. 204–206.
- 10.13 Prata, A.J.: "Observations of Volcanic Ash Clouds in the 10–12 μm Window Using AVHRR/2 Data." *International Journal of Remote Sensing*, vol. 10, Nos. 4 and 5, 1989, pp. 751–761.
- 10.14 Blanchard, Duncan C.: "The Production, Distribution, and Bacterial Enrichment of Sea-Salt Aerosol." *Air-Sea Exchange of Gases and Particles*, D. Reidel Publishing Company, 1983, pp. 407–454.

- 10.15 Military Standard: Environmental Test Methods and Engineering Guidelines, MIL-STD-810E, AMSC F4766, 14 July 1989.
- 10.16 Woodcock, A.H.: "Marine Fog Droplets and Salt Nuclei—Part I." *J. of the Atmos. Sci.*, vol. 35, April 1978, pp. 657–664.
- 10.17 Woodcock, A.H.: "Marine Fog Droplets and Salt Nuclei—Part II." *J. of the Atmos. Sci.*, vol. 38, January 1981, pp. 129–140.
- 10.18 Twomey, S.: "Atmospheric Aerosols." Elsevier Scientific Publishing Company, New York, 1977, p. 27.
- 10.19 Changery, M.J.: "A Dust Climatology of the Western United States." NUREG/CR-3211. National Oceanic and Atmospheric Administration, prepared for U.S. Nuclear Regulatory Commission. National Climatic Data Center, Asheville, NC 28801-2696, April 1983.
- 10.20 Gillette, D.A., Clayton, R.N., Mayeda, T.K., Jackson, M.L., and Sridhag, K.: "Tropospheric Aerosols From Some Major Dust Storms of the Southwestern United States." *Journal of Applied Meteorology*, vol. 17, 1978, pp. 832–845.
- 10.21 Gillette, D.A.: "Fine Particulate Emissions Due to Wind Erosion." *Transactions of American Society of Agricultural Engineers*, vol. 20, 1977, pp. 890–897.
- 10.22 Gillette, D.A., Adams, J., Endo, A., and Smith, D.: "Threshold Velocities for Input of Soil Particles Into the Air of Desert Soils." *Journal of Geophysical Research*, vol. 85, 1980, pp. 5621–5630.
- 10.23 Cadle, R.D., Kiang, C.S., and Louis, J.F.: "The Global Scale Dispersion of the Eruption Clouds From Major Volcanic Eruptions." *Journal of Geophysical Research*, vol. 81, 1976, pp. 3125–3132.
- 10.24 Anderson, B.J. and Keller, V.W.: "A Field Study of Solid Rocket Exhaust Impacts on Near-Field Environment." NASA TM 4172, MSFC, Alabama, January 1990.
- 10.25 Madsen, B.C., et al.: "Characterization and Evaluation of Acid Rain in Central Florida From 1978 to 1987—Ten Year Summary Report." NASA TM-102149, January 1989.
- 10.26 Barchet, W.R.: "Acid Rain: A Primer on What, Where, and How Much." Pacific Northwest Laboratory Report PNL-SA-13199, April 1985.
- 10.27 Anderson, G.P., et al.: "AFGL Atmospheric Constituent Profiles (0–120 km)." AFGL-TR-86-0110, Environmental Research Papers, No. 954, Air Force Geophysics Laboratory, Hanscom AFB, MA 01731, May 15, 1986.
- 10.28 Smith, M.A.H.: "Compilation of Atmospheric Gas Concentration Profiles From 0 to 50 km." NASA TM-83289, March 1982.