Chapter II

Literature Review

2.1 Atmospheric Aerosol

An atmospheric aerosol is one type of particulates. In general, their characterization involves the specification not only of spatial and temporal distributions, but also of composition, particle size distribution, and physical properties such as morphology and indices of refraction. It refers to an assembly of liquid or solid particles suspended in a gaseous medium long enough to enable observation or measurement. The term originated as the gas phase equivalent of the term hydrosol, which refers to a suspension of particles in a liquid (from the Greek word combination "water particle"). The size of aerosol particles are in the range of 0.001 - 100 μm. If the particle concentration is high enough that the density of the aerosol is more than about 1% greater than the gas alone, the assembly is considered a cloud and has bulk properties that differ from a more diluted aerosol (US.EPA.,1989). Atmospheric aerosols can be broadly divided into two categories , primary particles that are injected into the atmosphere, and secondary particles that are formed in the atmosphere by chemical and microphysical processes.

a. Primary particles

Primary aerosols are those emitted directly into the atmosphere by natural and anthropogenic processes. These aerosols tend to have their greatest influence on local and regional energy balances and atmospheric chemistry.

The most common primary aerosols in the troposphere are sea salt, soil dust, and smoke or soot. Sea salt haze is created over the oceans by wind and wave action. The salt particles are generally large (greater than 1-10 μm radius) and typically do not travel more than ≈100 meters vertically into the atmosphere before falling back into the ocean. Sea haze (which should not be confused with the fog or stratus clouds that are common over oceans) is generally confined to windswept regions of the seas.
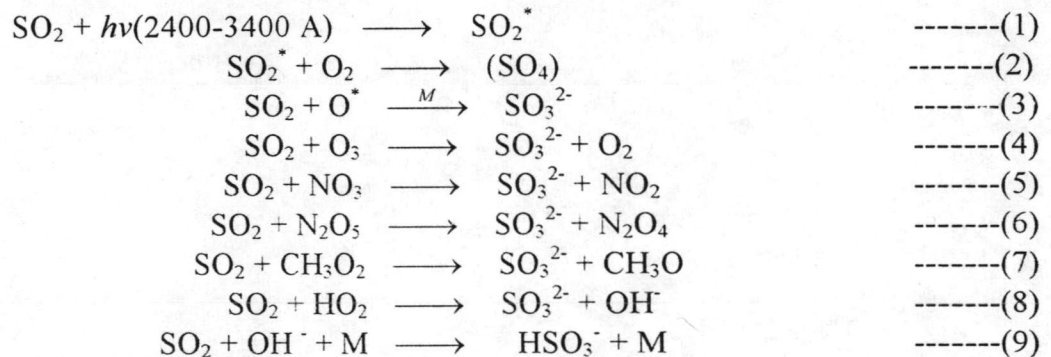
Soil dust in the atmosphere can be raised by winds moving across arid regions. Vehicles also raise large quantities of dust from arid lands. However, most of the dust mass consists of large particles (as the case of sea salt) with sizes typically exceeding 10 μm; these particles remain suspended for a few hours at most. A fraction of the dust mass consist of submicron particles. These smaller particles may remain in the atmosphere for days to weeks and travel thousands of kilometers (the aerolian dust). For example, the dust from the Gobi desert is occasionally detected over Mauna Loa in Hawaii. Ocean sediment cores also reveal patterns of continental dust fallout over the Western Pacific Ocean.(Trenberth,1992).

Smoke from biomass burning and soot from inefficient fossil fuel combustion are primary sources of aerosols over industrial region. Massive plumes associated with the combustion of agricultural and forest debris are clearly evident in satellite photographs. Smoke particles normally fall within the accumulation mode and, hence, are relatively long-lived and radiatived active.
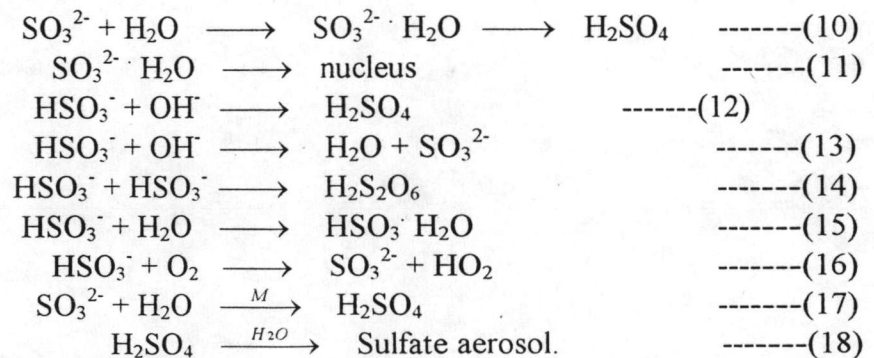
b. Secondary (photochemical and organic) aerosols

Secondary aerosols are composed primarily of sulfate, nitrate and organic compounds. The sources of sulfur for particles include natural emissions of reduced sulfur gases, amounting to as much as 70 Tg-S yr.$^{-1}$, and antropogenic sulfur emissions, mainly SO_2 totaling roughly 80 Tg-S yr.$^{-1}$. The production of sulfate aerosol is a complex function of gas phase photochemical oxidation reactions leading to condensable vapors, the conversion of these vapors into sulfate particles and the catalytic and non-catalytic oxidation of SO_2 on wetted aerosol surfaces. The sequence of sulfate aerosol formation is illustrated as below (Middleton et $al.$, 1980) (Trenberth, 1992):

Initial Steps

$$SO_2 + h\nu(2400\text{-}3400 \text{ A}) \longrightarrow SO_2^* \quad\quad\text{-------(1)}$$
$$SO_2^* + O_2 \longrightarrow (SO_4) \quad\quad\text{-------(2)}$$
$$SO_2 + O^* \xrightarrow{M} SO_3^{2-} \quad\quad\text{-------(3)}$$
$$SO_2 + O_3 \longrightarrow SO_3^{2-} + O_2 \quad\quad\text{-------(4)}$$
$$SO_2 + NO_3 \longrightarrow SO_3^{2-} + NO_2 \quad\quad\text{-------(5)}$$
$$SO_2 + N_2O_5 \longrightarrow SO_3^{2-} + N_2O_4 \quad\quad\text{-------(6)}$$
$$SO_2 + CH_3O_2 \longrightarrow SO_3^{2-} + CH_3O \quad\quad\text{-------(7)}$$
$$SO_2 + HO_2 \longrightarrow SO_3^{2-} + OH^- \quad\quad\text{-------(8)}$$
$$SO_2 + OH^- + M \longrightarrow HSO_3^- + M \quad\quad\text{-------(9)}$$

Possible Subsequent Reactions

$$SO_3^{2-} + H_2O \longrightarrow SO_3^{2-} \cdot H_2O \longrightarrow H_2SO_4 \quad\text{-------(10)}$$
$$SO_3^{2-} \cdot H_2O \longrightarrow nucleus \quad\quad\text{-------(11)}$$
$$HSO_3^- + OH^- \longrightarrow H_2SO_4 \quad\quad\text{-------(12)}$$
$$HSO_3^- + OH^- \longrightarrow H_2O + SO_3^{2-} \quad\quad\text{-------(13)}$$
$$HSO_3^- + HSO_3^- \longrightarrow H_2S_2O_6 \quad\quad\text{-------(14)}$$
$$HSO_3^- + H_2O \longrightarrow HSO_3 \cdot H_2O \quad\quad\text{-------(15)}$$
$$HSO_3^- + O_2 \longrightarrow SO_3^{2-} + HO_2 \quad\quad\text{-------(16)}$$
$$SO_3^{2-} + H_2O \xrightarrow{M} H_2SO_4 \quad\quad\text{-------(17)}$$
$$H_2SO_4 \xrightarrow{H_2O} \text{Sulfate aerosol.} \quad\quad\text{-------(18)}$$

Remark : M = metal catalysts

The final process represents the condensation of sulfuric acid (and related sulfate compounds) onto existing particles, or the formation of new particles by

nucleation. Sulfate can also be produced by various catalytic and non-catalytic oxidation reactions in wetted aerosol. SO_2 conversion to sulfate in clean water is a slow process, but is known to be accelerated in the presence of ammonia (Middleton *et al.*, 1980), metallic contaminations such as iron (Fe) and manganese (Mn) ions, soot or strong oxidizing agents such as ozone and hydrogen peroxide. Nitrates follow a similar chemical pathway as sulfates. Both sulfates and nitrates are often found in the form of ammonium salts in the troposphere, owing to the fact that ammonium gas (NH_3) is generated in large quantities by biological processes and reacts vigorously with sulfuric and nitric acids.

The chemical and physical mechanisms of secondary aerosol formation are complicate. First, the photochemistry of precursor vapors leading to condensable species involve the chemistry of OH^- and troposphere ozone. Second, the microphysical processes that govern the evolution of the aerosols after formation must be considered. Chemical reactions involving aerosols can influence the concentrations and distributions of climatologically important gases, such as ozone. The chemical transformations of gases into particles (e.g., SO_2 into sulfate aerosols) has both direct and indirect climate implications: direct, because the buildup of aerosols affects the scattering of radiation in the atmosphere; indirect because aerosols are involved in the formation of clouds, which affect the planetary albedo.

Aerosols can also be categorized by size. Large particles are those with radii exceeding about 1 μm; these quickly fall out of the atmosphere or are efficiently scavenged by clouds and precipitation. Particles having radii in the range of $\approx 0.1\text{-}1$ μm are referred to as "accumulation mode" aerosols. These particles have relatively low fallspeeds, but are still efficiently scavenged by precipitation. The accumulation mode is formed by gas-to-particle conversion through chemical reactions and condensation as well as coagulation. The rate of particle growth from condensation slows down with increasing particle diameter. However, the growth of droplets in this mode continues until deposition occurs, usually within one day or two days, thus limiting the ultimate particle size. As a result, the accumulation mode does not extend much beyond a few micrometers in diameter, and remains distinct from the larger particles in the coarse mode. At radii much smaller than 0.1 μm, an aerosol "nucleation mode" is often found, consisting of new particles generated from vapors. These fine particles are generally depleted by coagulation. Aerosols are generated by the nucleation of vapors that are supersaturated. Homogeneous nucleation involves the condensation of a vapor into a pure aerosol of that material; heterogeneous nucleation involves the deposition of a vapor onto a substrate particle (for example, dust). Condensation or evaporation indicate to the deposition of a vapor onto, or evaporation from, a pre-existing aerosol containing similar material. The rate of condensation or evaporation is proportional to the difference between the vapor pressure and the partial (ambient) pressure of the condensing gas over the particle. Coagulation refers to a class of dynamical processes by which one aerosol particle dynamically encounters another and the two particles coalesce. This process is quantitatively represented by a coagulation (or collision or coalescence) kernel. Finally, the sedimentation of a macroscopic particle under the

influence of gravity is described by its terminal fallspeed, for which the gravitational force is balanced by the aerodynamic drag of the atmosphere.

2.2 Chemical and Physical Properties of Acid Aerosols

Atmospheric aerosol consists of two principle components: a gas phase (air) and a solid or liquid particle phase in suspension. The major strong acid species that contribute to aerosol acidity, primarily strong acid sulfates (particles at typical ambient conditions) and to, a lesser extent, nitric acid (a vapor at typical ambient conditions) and other acidic species.

Strong acid sulfate - sulfuric acid (H_2SO_4) and ammonium bisulfate (NH_4HSO_4) appear to be the main species of concern in ambient acid aerosols. Weak acid such as nitric acid may influence neutralization reactions and thus total aerosol acidity. Nitric acid is completely scavenged to droplets in fog. Weak acids may also be present in the atmosphere, but these have not been measured in conjunction with strong acid aerosol at ground base monitors.

2.2.1 Particle Size of SO_4^{2-} and H^+

Sulfate is in the fine particle size range (< 2.5 μm) and is in the acidic fraction of the atmosphere aerosol as shown in table 2-1. The aerosol and annual size segregation results from the nine class I Sulfate Regional Experiment (SURE) sites located in the Eastern U.S. from 1977 through 1987 show that 80 percent of the SO_4^{2-} is in the fine particle range (Mueller and Hidy,1983). The percentage varied from 50 to 100 percent, depending upon the site and the month of the year with the lowest percentage occurring in the fall and the winter.

Size distribution data have been acquired for sulfate and hydrogen ion by Pierson et al.(1980b) and Keeler (1987) in two separate investigations at Allegheny Mt., PA during July and August of 1977, and August in 1983. The mass median equivalent diameters were 0.84 μm and 0.7 μm for H^+ and SO_4^{2-}, respectively. Since these data were taken in the Eastern U.S., the potential for having high relative humidity in the summer would increase the particle size of the sulfate species above that found initially by gas-phase or liquid-phase reactions. In the 1977 study the average relative humidity was 79 percent and the average nighttime relative humidity was 91 percent. The presence of large particle acid in the size distribution suggests the formation of fog during the sampling periods, which would be consistent with the high relative humidity during the night.

In California, two types of sulfur particle mass size distributions have been noted (Friendlander,1980). The Pasadena, CA sulfate distribution appears to be similar to that observed by Pierson et al. (1980b) and Keeler (1987) with most of the mass found centered around 0.5 μm. Friedlander has classified this as a coastal sulfur aerosol (multiple by 3 to approximate sulfate mass). The distribution shows the sulfur mass having a mode which is shifted down to between 0.1 and 0.2 μm. This was

classified as desert type aerosol that appeared to be formed from homogeneous reaction mechanisms but did not grow appreciably in the arid atmosphere. The concentration of the desert sulfate aerosol was less than 2.0 $\mu g/m^3$. This could have contributed to the smaller sizes since there would have been less coagulation of particles in dispersed conditions.

Table 2-1   Classification of Major Chemical Species Associated with Atmospheric Particles

Fine Fraction	Coarse Fraction	Both Fine and Coarse Fractions	Variable
SO_4^{2-} , C (soot) Organic (condensed vapors) Pb , NH_4^+ , As Se , H^+ , acids	Fe , Ca , Ti , Mg K , PO_4^{3-} , Si , Al , Organic (pollen , spores , plant parts) Bases	NO_3^- , Cl^-	Zn , Cu , Ni ,Mn Sn , Cd , V , Sb

Source: Air Quality Criteria for Particulate Matter and Sulfur Oxides (U.S. Environmental Protection Agency,1982a.).

2.2.2 Formation of acid sulfates

The formation of acid sulfates mechanisms involve in the rate of transformation reaction of SO_2 and the heterogeneous reactions which produce H_2SO_4 in the gas phase or within the aqueous phase (table 2-2). In addition, an important mechanism involves in metal catalysts, carbon, and surface reactions. The reaction rates in the atmosphere range from <0.5 to >100 percent per hour. Some of the values have a greater degree of confidence associated with them than others. Although it is not readily apparent from the table, all these reactions will not occur at the same time. Rather each will be associated with particular environmental condition either near a source, in a plume, or in the general atmosphere. The importance of a particular reaction scheme will depend on the season, geographic location, time of day (nighttime or daytime) and local or prevailing meteorology (US.EPA,1989).

An important conclusion that can be drawn from table 2-2 is that there are two types of possible conversion processes. In the presence of catalysts (Mn, Fe and C) in liquid water droplets, conversion can be very fast. These are local reactions. These reactions do not require sunlight nor warm temperatures.

Table 2-2 Important Reaction Rates for Oxidation of Sulfur Dioxide

Reaction	Rate, Percent h⁻¹			Comments*
I. Gas Phase				
HO radical	0.3-1.3			a
HO$_2$ radical	0.4-2.0			a,b
CH$_3$O$_2$ radical	0.3-1.5			a,b
II. Aqueous Phase	**pH 1**	**pH 3**	**pH 5**	
Mn (II) catalysis	0.1	10	1×10^3	b,c,d,i
Fe (III) catalysis	5×10^{-5}	0.5	5×10^3	c,e,i
C (soot) catalysis	30	30	30	f,i
O$_3$ (40 ppb)	2×10^{-8}	2×10^{-6}	2×10^{-4}	c,g
O$_3$ (120 ppb)	6×10^{-8}	6×10^{-6}	6×10^{-4}	c,g
H$_2$O$_2$ (1 ppb)	0.02	0.03	0.03	c,h
H$_2$O$_2$ (10 ppb)	0.2	0.2	0.3	c , h

Source: An Acid Aerosols Issue Paper: Health Effects and Aerometrics (U.S. Environmental Protection Agency,1989)

Comments*:

a.   Typical range for daytime at northern midlatitudes during the summer.

b.   This reaction rate is not well established.

c.   Assumed that liquid water volume of aerosol = 50 x 10^{-12} m^3/m^3, (SO$_2$) = 10 ppb.

d.   Assumed that Mn (II) mass concentration = 20 ng/m^3; also, the Mn (II) is assumed to be uniformly dissolved in the liquid water of the aerosol ([Mn (II)] = 8.9 x 10^{-3} M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958).

e.   Assumed that Fe(III) mass concentration = 2 μg/m^3; also, the Fe (III) is assumed to be uniformly dissolved in the liquid water of the aerosol([Fe (III)] = 0.9 M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958).

f.   Assumed that C mass concentration = 10 μg/m^3 and behaves as the soots studied by Chang *et al.* (1979), whose expression was used for this calculation.

g.   Rate calculation was based on equation 2-39, in criteria document (U.S. Environmental Protection Agency,1982a).

h.   Rate calculation was based on equation 2-43, in criteria document (U.S. Environmental Protection Agency,1982a).

I.   Influence of inhibitors has been ignored, but they are likely to suppress the rate by orders of magnitude.

In the absence of catalysts, and in the presence of various photochemically produced radicals, with or without liquid water, the maximum reactions rates are 2 percent per hour or less. This implies long reaction times and therefore long distance transport before substantial amounts of acid sulfate are formed. This is clearly the

pathway for most of the summer, and is associated with long distance transport acid events (US.EPA.,1989). This distinction is important in evaluating the epidemiology studies, as the presence of acid aerosols must be imputed in these studied based upon the meteorology and assumed pollution mix.

Middleton *et al.* (1980) estimated theoretical of various urban sulfate aerosol production mechanisms by calculation. The purpose of this investigation was to study the relative importance of various possible pathways for sulfate aerosol production under different atmospheric conditions. The calculation scheme developed to determine the rates of sulfate production and corresponding gas depletion was based on the concept that vapor transfer to the aerosols and conversion within the aerosols were coupled kinetic processes, and the rates were calculated in a sequence of kinetic and equilibrium steps. The relative importance of sulfate production mechanisms in different urban environments was studied by varying the initial gas concentrations, temperature and particle composition with respect to particle size. The initial particle composition with respect to particle size is illustrated in table 2-3.

Table 2-3 Initial Particle Concentrations: for Daytime Conditions[#]

Diameter (μm)	Mixing ratio	Concentration (μg/m³)			
		Total	Soot	Fe	Mn
0.1	2.1×10^{-12}	2.1	0.2	2×10^{-3}	2×10^{-4}
0.2	2.4×10^{-11}	23.7	2.4	2×10^{-2}	2×10^{-3}
0.3	4.3×10^{-11}	42.8	4.3	4×10^{-2}	4×10^{-3}
0.4	5.0×10^{-11}	49.5	5.0	5×10^{-2}	5×10^{-3}
0.5	3.3×10^{-11}	33.0	3.3	3×10^{-2}	3×10^{-3}
0.7	5.7×10^{-12}	5.7	0.6	6×10^{-3}	6×10^{-4}
1.0	1.3×10^{-11}	13.1	1.3	1×10^{-2}	1×10^{-3}
2.0	4.2×10^{-11}	42.4	8.5	8×10^{-2}	8×10^{-3}
3.0	5.9×10^{-12}	5.9	1.2	1×10^{-2}	1×10^{-3}
4.0	6.3×10^{-13}	0.6	0.1	1×10^{-3}	1×10^{-4}

Remark: # For nighttime conditions, the values are 3/4 of the daytime conditions.

In addition, initial SO_2, NH_3 and O_3 concentrations were obtained from measurements representative of urban environments (Appel *et al.*, 1978; Spicer, 1977). The ranges of gas concentrations and temperatures obtained from the study are listed in table 2-4.

From the investigation by Middleton *et al.* (1980), it was found that the total sulfate aerosol production changes noticeably under different atmospheric conditions. These changes were the result of variations in the relative importance or the different sulfate production mechanisms. Factors influencing that changes were the concentration of photochemically produced gaseous species, temperature and aerosol acidity and size distribution. It was also found that the rate of sulfate aerosol formation was higher under summer daytime conditions than under winter daytime or nighttime

conditions. The variation of total sulfate aerosol production was found to be the result of changes in the individual sulfate aerosol formation reaction rates under different atmospheric conditions. The range of contributions of each reaction rate reflected the ranges of gas concentrations used, the amount of effective catalysts in solution and the variation in different rate expressions for the uncatalyzed oxidation and the iron and manganese catalyzed oxidations. It was found that, in general, H_2SO_4 condensation and H_2O_2 oxidation on the wetted aerosol could be dominant pathways to sulfate aerosol formation under daytime conditions. Under summer daytime conditions sulfate formation was higher and H_2SO_4 condensation could be more the important mechanism while under winter daytime conditions the formation was lower and H_2O_2 oxidation could be the more important mechanism. Under nighttime conditions, the rate of formation was lower and catalytic and non catalytic oxidation mechanisms on the wetted aerosol surface became the major sulfate formation mechanisms. In particular, catalytic oxidation by soot, Fe and Mn appear to be the most important pathways under nighttime conditions (Middleton *et al.*,1980).

Table 2-4 Atmospheric Conditions and Initial Gas Concentrations

| Gas concentration (ppm)	Case		
	Summer day	Winter day	Summer day
SO_2	0.01	0.01	0.01
NH_3	0.001-0.01	0.001-0.01	0.0005-0.005
O_3	0.01-0.1	0.005-0.05	0.001-0.01
H_2O_2	0.001-0.01	0.0001-0.001	10^{-5}-10^{-4}
H_2SO_4	10^{-8}-10^{-7}	10^{-9}-10^{-8}	10^{-12}-10^{-11}
Temperature (^0C)	25	5	15

2.2.3 Phase Equilibrium

The particles with diameters less than approximately 2.5 μm contain most of the SO_4^{2-}, H^+ and NH_4^+, and these particles will interact more strongly with H_2O vapor. The most important sulfate components are those of H_2SO_4 , NH_4HSO_4 and $(NH_4)_2SO_4$. Most aqueous systems contain H^+, NH_4^+, SO_4^{2-}, NO_3^- and Cl^- and these species are usually present in sufficient mass to influence the liquid water concentration and the phase transition points of particles as a function of relative humidity. Some of these examples are the various interactions of fogwater, gases and aerosol. Fogwater acts as a transient sink of soluble gases and aerosols, in which they may react and from which they are released after fog dissipation. The aqueous phase during fog events represents a reactive medium, especially for oxidation processes of SO_2. Due to the pH dependence of the solubility of SO_2 and of its reaction rate with O_3 , the oxidation rate of SO_2 to SO_4^{2-} in the aqueous phase is strongly increased at high pH. In extreme conditions at high pH level (pH >6), mass-transport limitations of the oxidation of SO_2 by O_3 may occur; this effect may cause differences in the SO_4^{2-} concentrations in different droplet sizes and an accumulation of SO_4^{2-} in the small droplets (Ruprecht and Sigg,1990). Fog events may be important in enhancing the oxidation reaction of SO_2 to

SO_4^{2-} and in producing strong acidity. Such effects are possibly of importance in causing ecological damages in regions of frequent fog occurrence. Presently, phase diagrams for this multicomponent system are not available for conditions relevant for troposphere particles. However, from the Criteria Document (U.S. Environmental Protection Agency, 1982a) the phase diagram for the H^+-NH_4^+-SO_4^{2-}-H_2O system at equilibrium is shown in figure 2-1. In this diagram, the dry pure crystals of $(NH_4)_2SO_4$, letovicite $(NH_4)_3H(SO_4)_2$ and $(NH_4)HSO_4$ are indicated as points A, B, and C, respectively. If $(NH_4)_3H(SO_4)_2$ is exposed tö relative humidities starting at 0 and increasing to 100 percent, its behavior can be described in terms of the locus BO in figure 2-1. From 0 percent relative humidity the salt immediately enters the 3-phase zone consisting of $(NH_4)_3H(SO_4)_2$, $(NH_4)_2SO_4$ and some liquid solution of H^+, NH_4^+ and SO_4^{2-}. At point D, the locus intersects a phase boundary for $(NH_4)_3H(SO_4)_2$ and a partial deliquescence occurs. Between point D and the intersection with curve EE_1, solid $(NH_4)_2SO_4$ remains; however, at the intersection of EE_1, a second and complete deliquescence occurs. From EE_1 to point 0, only the solution phase is present. In similar fashion, equilibrium paths for salts subjected to various compositions and relative humidities can be traced. The locus EE_2 demonstrates the dependence of the complete deliquescence point relative humidity on the weight percent of H_2SO_4. As the acid compositions change from 0 to 35 percent, the complete deliquescence point relative humidity will decrease from 80 to 39 percent. Thus, NH_3 plays a key role in governing the phase transition points.

2.2.4 Neutralization

A key factor in determining the persistence of atmosphere acid sulfate species is the potential for ammonia neutralization, which is controlled by the reaction of ammonia with sulfuric acid, and the formation of ammonium salts (NH_4HSO_4 and $(NH_4)_2SO_4$). The principle sources of environmental ammonia appear to be animals and humans, although there can also be significant contributions from fertilizer manufacturing. Animals are probably a much larger source due to the sewage treatment of human excrement. Over 99% of the earth's atmospheric ammonia is produced by biogenic sources, the main source being the decomposition of organic waste. However, in urban areas, anthropogenic sources may locally increase gaseous ammonia levels. Anthropogenic sources of NH_3 include anaerobic decay (in landfill, ponds,etc.), combustion processes (such a municipal incineration and automotive emissions), and industrial sources (such as fertilizer factories and petroleum refineries). Atmospheric losses of anhydrous ammonia fertilizers and ammonia from poultry houses and cattle feedlots are also sources of ammonia. Aside from reaction with atmospheric acids, major sinks of ammonia include plant absorption and absorption by bodies of water. In general, ambient measurements of ammonia gas suggest that the highest ammonia gas concentrations are recorded in major urban areas, the lowest over large water bodies, and intermediate levels in rural areas (Thurston et al.,1994). For these reasons, it has been commonly thought that sulfates are most likely to be almost exclusively in their most neutralized state in major urban areas (i.e., as $(NH_4)_2SO_4$) (Tanner et al.,1981). In the urban areas studied by Thurston et al.,(1994), it shown that after the air mass enters to urban areas, these acidic aerosols are apparently
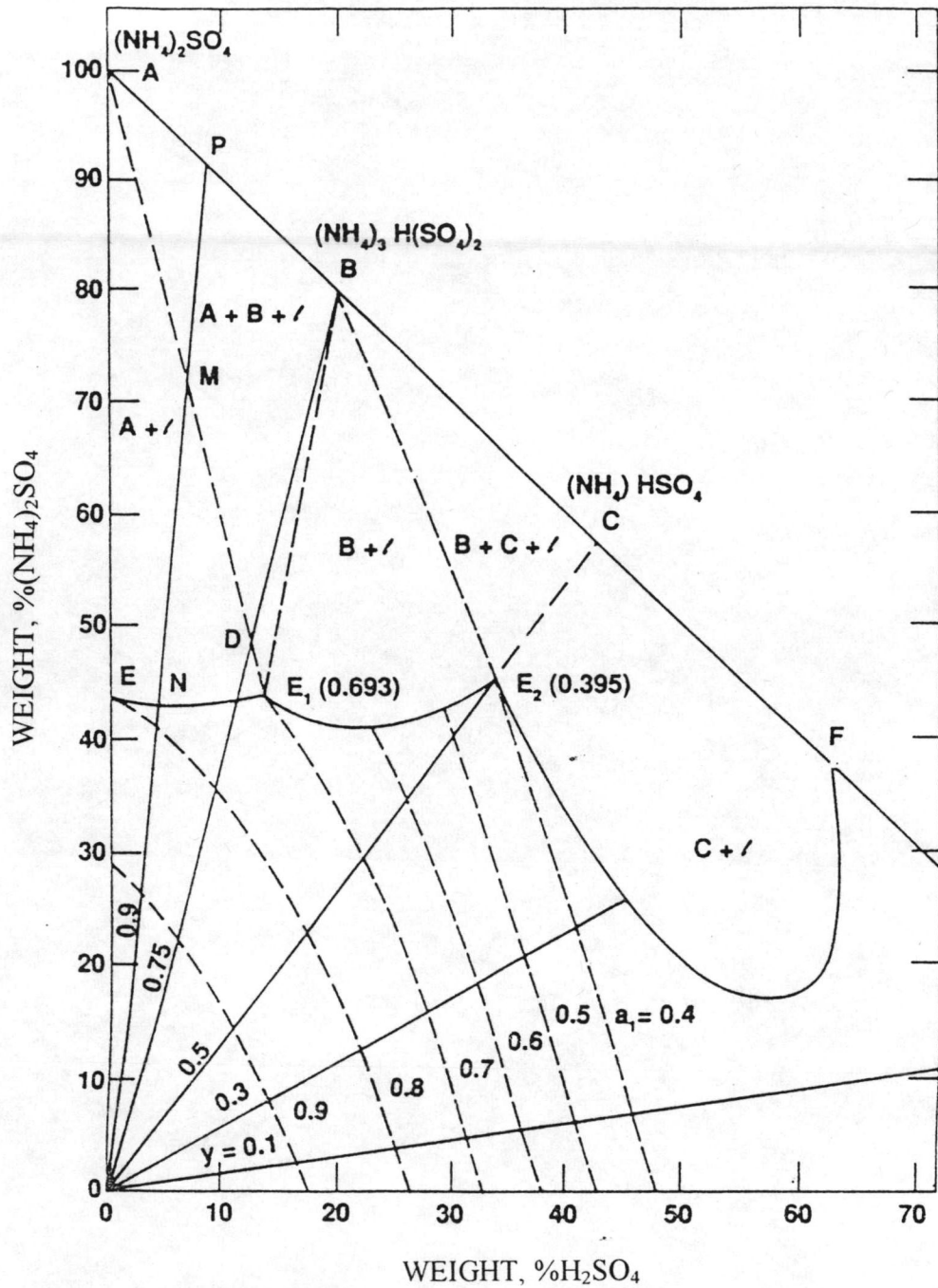
Figure 2-1 Solubility diagram for the H^+-NH_4^+-SO_4^{2-}-H_2O system at equilibrium (30^0C).

A = solid phase of $(NH_4)_2SO_4$
B = solid phase of $(NH_4)_3H(SO_4)_2$
C = solid phase of $(NH_4)HSO_4$
l = liquid solution phase
a_1 = fractional relative humidity
y = mole fraction of $(NH_4)_2SO_4$

The number in parentheses are the fractional relative humidities for the complete deliquescence points that are indicated.

Source: Tang (1980)

modified by neutralization, with the greatest neutralization occurring in the most urbanized areas. Waldman *et al.*,(1990) studies the spatial and temporal patterns in summertime the sulfate aerosol acidity and neutralization within Toronto metropolitan area, which indicated that the downtown area was somewhat protective against aerosol acidity.

There are very few measurements of ammonia, but there are data on the NH_4^+ ion which usually relate to the sulfate ion measurement. One comprehensive study of SO_4^{2-} was the Sulfate Regional Experiment (SURE) (Mueller and Hidy,1983) which included measurements of these two ions for nine site in the eastern U.S. over a two-year period. The mass ratio of SO_4^{2-}/NH_4^+ was calculated for all sites, and the frequency of occurrence suggested that 40 percent of the samples were a mixture of ammonium salts and 60 percent could have contained free sulfuric acid. The distribution of the data from a scatter diagram from the SURE of the Hi-Vol mass ratio of SO_4^{2-}/NH_4^+ versus sulfate concentration suggests that the highest percentages of acids are probably associated with relatively low sulfate concentrations (5-10 $\mu g/m^3$) and not with the extremely high sulfate concentrations that are usually measured during the intense portions of a photochemical smog episode. There are exceptions since acid concentrations can reach in excess of 20 $\mu g/m^3$ (Mueller and Hidy, 1983).

2.3 Atmospheric Concentration

2.3.1 Atmospheric Acidic Sulfate Studies

The ranges of SO_4^{2-}, H^+ (as H_2SO_4) and /or H_2SO_4 concentrations recorded in some atmospheric acidic sulfate studies in the United States are shown in table 2-5. It was apparent that a wide range of SO_4^{2-} values were encountered in acid aerosol studies with the peak concentration being 75 $\mu g/m^3$ for an 8 hr period in Toronto, Canada (Waldman *et al.*, 1988). At other times, each study recorded SO_4^{2-} decreases to as low as 0-2 $\mu g/m^3$. The peak H_2SO_4 value, measured with a flame photometry detector (FPD), was 41 $\mu g/m^3$ (1 hr average) in 1984 at a site in St. Louis, MO (Ferris and Spengler, 1985).

H^+ concentration (as equivalent H_2SO_4) of 39 $\mu g/m^3$ was observed in 1975 just northeast of St. Louis in Glasgow, IL (Tanner and Marlow, 1977). The features of the Glasgow data were: (1) the H^+ was measured in the fine particle size range; (2) the measurements were 12 hour duration samples, and (3) the visibility maps indicate the development of an urban plume from St. Louis. A comparison of the $(H^+)/\{(H^+) + (NH_4^+)\}$ ratio on July 29, 1975 indicated that the aerosol in Glasgow, IL contained both NH_4HSO_4 and H_2SO_4.

Table 2-5 Concentration Ranges of SO_4^{2-}, H^+ (as H_2SO_4) and H_2SO_4 (in $\mu g/m^3$)

Study	Sample Duration Hours	Concentration Range ($\mu g/m^3$)		References
		SO_4^{2-}	H_2SO_4	
Glasgow, IL	12	7-48	0-39	Tanner and Marlow (1977)
St. Louis, MO				
1977 Summer	1	5-60	0-28	Cobourn (1979)
1978 Winter	1	3-24	0-12	Coubourn and Husar (1982)
Lennox, CA	2-8	1.2-18	0-11	Apple *et al.* (1982)
Allegheny Mt.,PA	12	1-32.5	0-20	Pierson *et al.* (1980b)
Tuxedo, NY	1-12	1-41	1-8.7	Morandi *et al.* (1983)
St. Louis, MO	QC	3-25	0-7	Huntzicker et al. (1984)
St. Louis, MO	QC	<5-43	0-34	Ferris and Spengler(1985)
Los Angeles, CA	12	3-10	0.6-3.2	John *et al.* (1985)
Fairview Lake, NJ	QC,4	13-27	0-12	Lioy and Lippman (1986)
Toronto, Canada	8,16	0-75	0-19.4	Waldman *et al.* (1988)
Allegheny Mt.,PA	7,10	1.7-45.4	0.4-30.5	Pierson *et al.* (1989)
Laurel Mt., PA	7,10	2.2-55.5	0.5-42.0	Pierson *et al.* (1989)

Remark: QC = quasi-continuous

There have been a number of studies which indicated the presence of both H_2SO_4 and NH_4HSO_4 species (Tanner and Marlow, 1977; Morandi *et al.*, 1983; Huntzicker *et al.*, 1984; Lioy and Lippman, 1986). Pierson *et al.* (1989) completed a study at both Allegheny Mountain and Laurel Mountain in 1983 with observed peak H^+ (as apparent H_2SO_4) concentrations of 30.4 and 42.0 $\mu g/m^3$ at the respective sites.

As stated previously, work by Morandi *et al.* (1983) included an attempt to infer the distribution of acidic species from coincident instrumental FPD measurements of H_2SO_4 and filter analyses for H^+. The results of that study indicated there was no evidence of the presence of any strong acids (pKa < 2) other than NH_4HSO_4 or H_2SO_4. On the basis of this observation, and using data from the FPD and filter samples, the SO_4^{2-} associated with H_2SO_4 and NH_4HSO_4 was inferred from the molar differences between the H^+ and the simultaneously measured H_2SO_4 by the FPD (i.e., using equivalent average time periods for the latter data). The results of the analysis showed:

1) The species H_2SO_4 , NH_4HSO_4 and $(NH_4)_2SO_4$ can occur simultaneously in a present-day polluted atmosphere.
2) On occasion, SO_4^{2-} will be associated only with H_2SO_4 and NH_4HSO_4.
3) During a period of sustained sulfate concentrations (2 to 3 days) the sulfates change in composition from acid to basic species.

For each of the summertime studies, peaks of H_2SO_4 and/or H^+ were observed sporadically, and based upon the meteorological data, were associated with the presence of a slow moving hazy summertime high pressure system. A major acid sulfate event occurred over the period from August 1 through August 12, 1977 (Lioy et al., 1980). The daily variation of the six hour particulate sulfate, hydrogen ion samples, and the daily maximum ozone concentrations are shown in figure 2-2.

A study by Appel et al. (1982) at Lennox in the Los Angeles basin was conducted for the period July 10 to July 17, 1979. A four hour maximum of 11 $\mu g/m^3$ of H_2SO_4 was observed on July 16 apparently associated with the daytime oxidation of local SO_2 emissions. Three other acid events were measured during this interval, although SO_4^{2-} was above 10 $\mu g/m^3$ throughout the interval of sampling. Recently, John et al. (1985) conducted a study in Los Angeles where the apparent H_2SO_4 was lower during this week-long study. They used two sites, and the downwind location, east of LA, recorded acid concentrations above 2 $\mu g/m^3$

There have been a couple of studies in which the acid sulfate species were measured at two or more sites located <45 km apart (Waldman et al., 1988; Pierson et al., 1989). One study was conducted in Toronto, Canada during the summer of 1986 and on July 25th, H^+ (as H_2SO_4) was observed at all three sites (one in downtown Toronto and another in the suburban areas). The 8 h average peaks at each site were 8.3, 14.4, and 19.4 $\mu g/m^3$. On the same day H^+ measurements of 28 $\mu g/m^3$ (as H_2SO_4) were made at Dunnville, Ontario, which is approximately 30 km south of Toronto. The other study, the 1983 Allegheny-Laurel Experiment, was conducted at sites 36 km apart. Nine-hour average H^+ (as H_2SO_4) concentrations of 30 and 42 $\mu g/m^3$ were observed at these Pennsylvania sites on August 17, 1983 (Pierson et al., 1989).

A distinct diurnal pattern of acidity was shown in studies which reported 6 hour or finer time resolution over a 24-hr period. These studies provide information on the diurnal cycle. Cobourn and Husar (1982) reported semi-continuous measurements of H_2SO_4 in St. Louis with a peak in H_2SO_4 clearly occurring between noon and 6 p.m. Inspection of a four-day period suggested that the diurnal pattern was more pronounced during periods of high acidity. Tanner et al. (1981) report 6-hour measurements of strong acidity by titration at three sites near New York City. The acidity peaks in the noon to 6 p.m. quarter at all three sites. Waggoner et al. (1983) report summertime measurements of H_2SO_4, HSO_4^- and SO_4^{2-}, and the sulfate concentrations showed distinct diurnal patterns with acidity and sulfate concentration peaking between noon and 6 p.m. (figure 2-3).

Morandi et al. (1983) examined the local character of the distribution of acid species for a regional smog episode from 27 to 29 August, 1980. It can be seen that the most acidic portion of this photochemical episode occurred at the beginning and that with time the acidity decreased. In a follow-up study at Fairview Lake, NJ. it was observed by Lioy et al.(1987) that in the period from July 31 through August 3, 1984 the acid aerosol was composed primarily of apparent NH_4HSO_4 (based on calculations
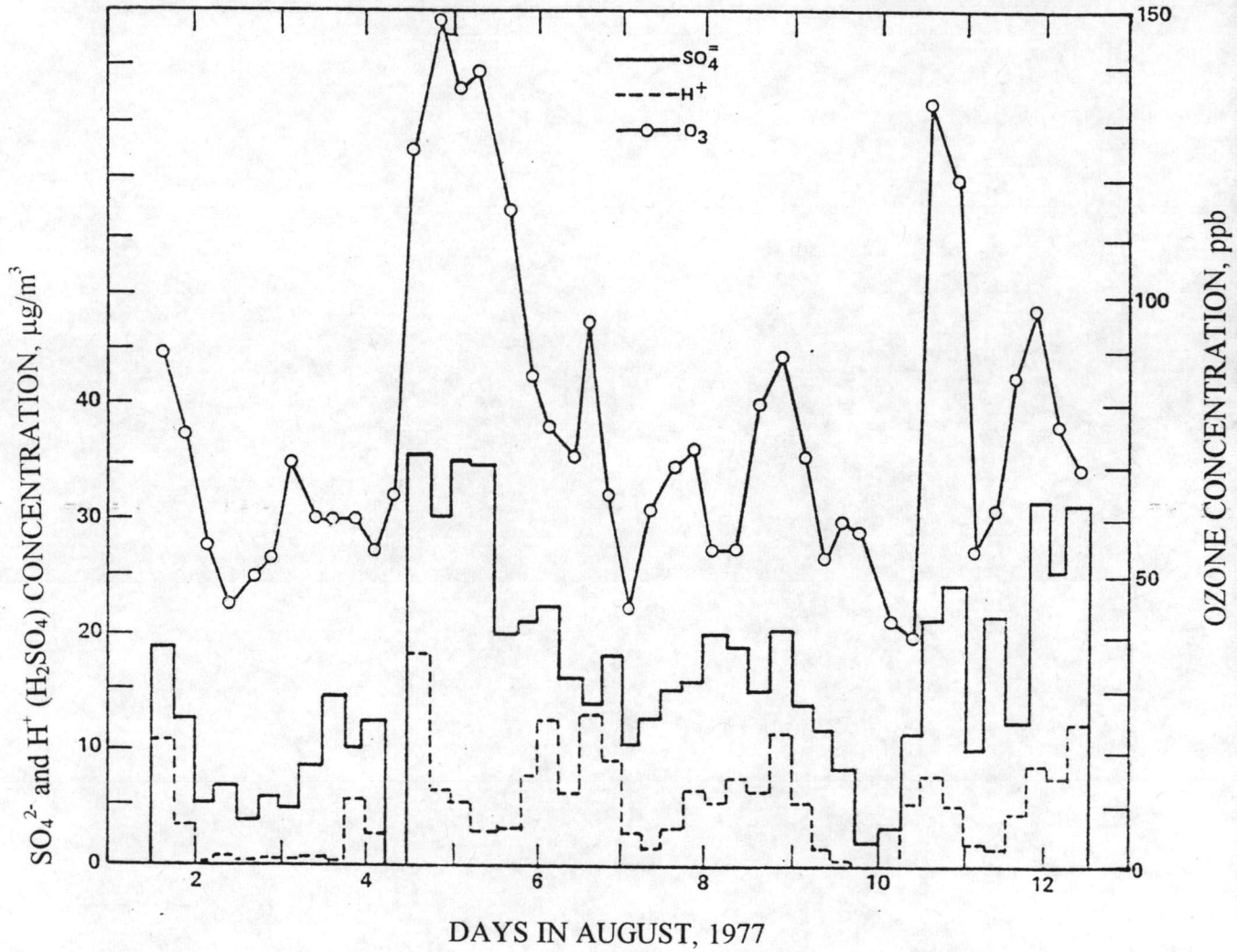
Figure 2-2 6-hour SO_4^{2-} and H^+, and 6-hour max, O_3 samples collected during August, 1977 at High Point, NJ., USA.

Source: Lioy and Waldman (1989)
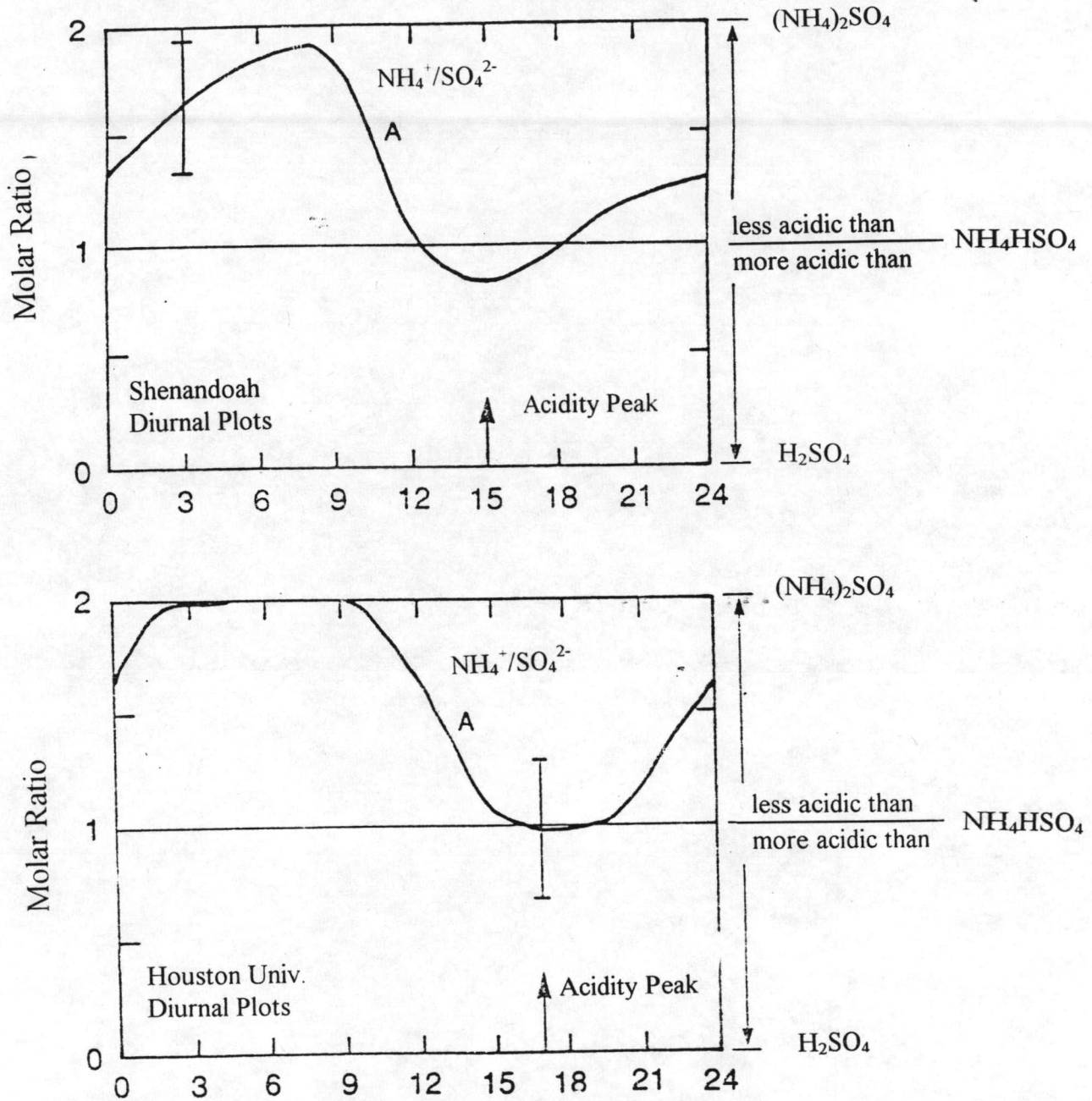
Figure 2-3 Diurnal variation, The molar ratio of ammonium to sulfate ion shows an acidity peak between noon and 6 p.m.

Source: Waggoner *et al.* (1983)

not measurements). During the last day of this period, however, the levels of H_2SO_4 increased from approximately zero to 4 $\mu g/m^3$ for 4 hours in the afternoon.

Waldman *et al.*, 1991 studied sulfate aerosol and its acidity in the SO_2 source region of Chestnut Ridge, PA during November 1987. The 3 x daily data suggest that higher acidity occurred in the overnight period (midnight to 8 a.m.), while sulfate had its highest levels in the morning to afternoon period. From the study, the slightly higher acidity in the overnight period, despite higher sulfate in the morning-afternoon periods, suggests the influence of a nocturnal inversion. Lower ammonia emissions at night would reduce the extent of acid neutralization of aerosol downwashing from aloft in the morning.

This diurnal pattern is important. If measurement techniques do not have at least a 6-hour resolution the peak acid concentrations will be averaged out to lower values. The reason for this pattern probably has to do with conversion of SO_2 to H_2SO_4 during the peak photochemical activity, and/or with processes involving (a) neutralization of H_2SO_4 by NH_3 from ground level sources and removal of H_2SO_4 by dry deposition during the night and (b) mixing downward of unneutralized H_2SO_4 from the upper part of the well-mixed layer as the height of the mixed layer goes up during the day. Both exposure models and air quality models will need to account for this diurnal variation. This may be especially important for exposure estimates since children tend to be outdoors during the peak concentration periods. There may be instances however, when peaks occur at night. This was seen by Pierson et al. (1980b) and Keeler (1987) for two elevated sites (>1000 ft) in Western, PA. Such situations will require further research concerning nighttime or nonphotochemical smog processes.

2.3.2 Acid Sulfate Exposure

The field studies described in the previous section measured a wide range of acid sulfate concentrations in the atmosphere. Most of the H_2SO_4 or H^+ (as H_2SO_4) values were below 5 $\mu g/m^3$, although events above 5 $\mu g/m^3$ occurred at least once over the course of each study. At present, there is no way to define an acid event systematically as an episode, since, as previously noted, periods of high acid sulfate do not necessarily coincide with periods of the highest SO_4^{2-} concentrations; e.g., photochemical haze or smog. Therefore, the definition of acid sulfate episode would be quite arbitrary.

In the context of the following exposure assessment, a significant pollution excursion for acid sulfate will be defined as an event in which the measurement of free sulfuric acid or H^+ (as H_2SO_4) reaches levels above 5 $\mu g/m^3$ for at least 1 hr. No relationship to possible health effects is intended or implied in using the words significant, episode, or event and in some cases the exposure may be overestimated, e.g., 24 hrs, because the actual amount of time spent outdoors and the penetration of acid indoors were not quantified in each study (U.S.EPA., 1989).

Research conducted at Camp Kiawa in Southern Ontario, USA by Spengler *et al.* (1989) considered exposure to acids on a 12-hr basis for H^+ and as 1-hr average for H_2SO_4. For the same event described by Waldman *et al.* (1988), a 1-hr maximum sulfuric acid concentration of 50 $\mu g/m^3$ was measured at the camp. The entire 36-hr event had measured 12-h sequential H^+ (as H_2SO_4) of 120, 336, and 150 ($\mu g/m^3$) x hr. This is within the range of exposures that evoked responses in controlled human studies by Koenig *et al.* (1983) and Utell *et al.* (1983), and supports the development of exposure estimates for individual acid sulfate episodes.

It must be emphasized that the exposure (concentration x time) calculation will only be applied for determination of exposures that can occur during an event. At the present time annual average calculations of exposure are inappropriate. Event exposure calculations may be of some biological significance since it has been shown in a controlled human study that exposures to 100 $\mu g/m^3$ for more than one hour will yield greater effects on mucocilliary clearance than a one hour exposure (Spektor *et al.*, 1989; Schlesinger, 1989). For the purposes of the following discussion, however, the exposure values ($\mu g/m^3$) x hr should be interpreted as the maximum potential exposure during an event, and not the biologically effective dose to an individual.