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## AN ASSESSMENT OF ACID FOG

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## INTRODUCTION

Airborne particles have long been associated with adverse effects on public health, beginning with the notorious air pollution disasters of several decades ago.<sup>1</sup> Although H<sub>2</sub>SO<sub>4</sub> was identified early on as a potential causal factors during these episodes (in part because of fog),<sup>2</sup> concern for potential health effects of particle acidity per se has intensified only recently.<sup>3</sup> Most of the recent aerometric research in the U.S. on acid fog has focused on the ability of clouds and fog to deliver acidity to vegetation and ecosystems.

Strong acids are characterized chemically by their pH or H<sup>+</sup> concentration. For fog, concentrations are referred to the droplet liquid content; for other (i.e., "clear air") aerosols, to the volume of air sampled. A useful measure of the relationship between aerosol and fog is obtained by comparing their mass concentrations on the basis of the same volume of air, by multiplying fogwater concentrations by liquid water content (LWC). For fog, LWC ranges from about 0.01 to 1 g H<sub>2</sub>O per cubic meter of air (about four orders of magnitude higher than clear air aerosols, depending on the relative humidity). For this reason, the same mass concentrations of acid fog particles and acid aerosol particles represent greatly different ionic strengths and pH's. For example, a fog with LWC = 1 g/m<sup>3</sup> and pH = 3.7 corresponds to an air concentration of 10 µg/m<sup>3</sup> as sulfuric acid. That same concentration in a clear air aerosol could correspond to pH values less than 1. Inspired aerosols may be changed chemically and physically during breathing because of humidification and by neutralization from endogenous ammonia.

This paper reviews fog measurement capability, physical properties and chemistry, and presents a simple urban airshed model which is used to simulate the evolution of fog and aerosol concentrations under urban stagnation conditions. More detailed discussions of extant field measurements of fog chemistry may be found in the technical report<sup>4</sup> from which this paper was condensed.

## THE PHYSICS AND CHEMISTRY OF FOGS

## Types of Fog

The source of the cooling identifies the type of fog. Adiabatic expansion due to flow over a mountain creates lee clouds. Advection of cooler air can create fog. The situation of most interest with respect to air pollution is radiation fog, in which cooling is provided by means of radiative heat transfer from a more-or-less stagnant air mass. Radiation fog can occur due to trapping in valleys or because of thermal inversions. The major urban air pollution fog episodes were caused by inversions.

## Fog Measurements

The properties of fogs are largely deduced from analyses of collected liquids; number distributions may be estimated from particle counters. The methods used to accomplish this can be crucial. It is important to collect fog droplets of all sizes and to prevent their subsequent evaporation. Droplets are usually obtained by impaction against nylon or teflon surfaces. In order to estimate LWC, the amount of air processed and the efficiency of liquid collection must be known with precision.

A field intercomparison of five different fog water collectors was performed in June 1983 near Los Angeles.<sup>5</sup> The LWC "calibration" factors of each sampler ("true"

value/sampler value) varied from 1.25 to 3.50; it appears from these experiments that adjustments should be made to the LWC values obtained from specific types of fog collectors. Fogwater chemistry was found to be quite repeatable in blind split replicate analyses for the major ions; coefficients of variation were in the range 3-5%. The pooled standard deviation of pH was 0.6 pH units, with higher pH values in the laboratory than in the field. pH values appeared to be unbiased, but variable.

### Physical Considerations

Fog is often defined as a cloud in contact with the ground and consists of a suspension of condensed water droplets of the order of 5-50  $\mu\text{m}$  in diameter, with number concentrations from ten to hundreds per cc of air.<sup>3</sup> The distinction between a haze particle and a fog/cloud droplet is essentially one of size. As relative humidity (RH) increases, hygroscopic particles increase in diameter. Since the vapor pressure of water over a droplet's surface depends on the surface curvature, there is a critical diameter above which the droplet will grow by means of additional condensation of vapor. Particles or condensation nuclei which exceed this diameter are said to be "activated." Because of the abundance of condensation nuclei, fog may be more common in polluted atmospheres, such as British cities before smoke was controlled.

### Droplet Size Considerations

Acid aerosols are conveniently classified according to the physical nature of the particles, which in turn relates to the way they are formed in the atmosphere. "Primary" sulfates are emitted from combustion of sulfur-bearing fuels, in various size ranges. "Secondary" aerosols are formed in the atmosphere from gas-phase precursors, involving some of the same chemical reactions that can acidify precipitation. These particles begin as very small condensation nuclei and grow over time, due to both agglomeration with other particles and by absorbing water vapor. The characteristically submicron size of acid aerosols (at RH < -85%) reduces their rates of atmospheric deposition, thus increasing atmospheric residence times and transport distances. Particles of this size can also penetrate deep into the lung. Thus, air concentrations rather than deposition rates are the preferred metric for acid aerosols (including fog) and the direct effects of inhalation are the main concern.

Particles smaller than the critical size (which depends on the amount of supersaturation present) decay, while those that are larger will grow. Hygroscopic particles such as sulfates lower the vapor pressure and the amount of supersaturation required and thus promote droplet growth. Cloud droplets do not grow substantially by collisions and coalescence; for diameters less than about 36  $\mu\text{m}$ , collisions by falling droplets are infrequent.<sup>6</sup> Droplet growth occurs by changes in the entire population, by diffusion of water vapor onto droplet surfaces. Larger drops lead to precipitation, and increases in droplet size increases settling velocities. Gravitational settling is an important pollutant removal mechanism in fog.

After fog droplets evaporate and the fog clears,  $\text{SO}_4^-$  particles may be left behind. These precipitated particles tend to be larger ( $\sim 0.7 \mu\text{m}$ ) than aerosol particles formed by condensing gas phase precursors.<sup>7</sup> Although data are sparse, there is evidence<sup>8,9</sup> that solute concentrations tend to increase with droplet size in general but that the smaller particles may be more acidic.

### Chemistry

Fog water may reflect either the composition of the atmosphere before the fog formed or the composition may be modified by chemical reactions that would have otherwise been much slower. There are two paths for acidification: absorption of previously-existing particles and gases, and chemical reactions among these species in the aqueous phase.

Among the latter, dissolution of  $\text{SO}_2$  followed by oxidation ( $\text{S}_{\text{IV}}$  to  $\text{S}_{\text{VI}}$ ) is probably the most important. Since photochemistry is less important during foggy conditions, models have been proposed featuring transition metal catalysis as an important oxidation pathway.

To the extent that additional sulfate is produced in the aqueous phase, becoming submicron aerosol as the fog evaporates, fog can add to the longer-term pollution of the

atmosphere. In a sense, fog represents a temporary storage medium for water-soluble air pollutants.<sup>10</sup>

**Scavenging of Aerosol Particles by Fog.** Since the common sulfate particles are quite hygroscopic, they are readily scavenged by the relatively large (ca. 5-50  $\mu\text{m}$ ) fog water droplets. There is also evidence that soot is scavenged by fog. In addition, if gaseous  $\text{SO}_2$  is absorbed into the droplets, it may be oxidized to form  $\text{H}_2\text{SO}_4$  by any of several chemical reactions involving either oxidants or catalysts within the droplet. These processes constitute one of the natural "sinks" for  $\text{SO}_2$ .

The interaction between aerosol and fog can be very important.<sup>11</sup> Aerosols provide condensation nuclei for fog; after the fog dissipates, those aerosol particles which have not been deposited on surfaces remain airborne. Pandis et al.<sup>11</sup> find that urban fogs may scavenge around 80% of the aerosol, with lower values for sulfate and higher values for nitrate. The lower  $\text{SO}_4^{=}$  values result from the typically smaller sulfate aerosol particles

**Absorption of Gases and Heterogeneous Chemistry.** Fog chemistry is also affected by scavenging water-soluble gases. Nitric acid is completely scavenged as is ammonia at  $\text{pH} < 5$ .<sup>12</sup> However,  $\text{NO}_x$  is nearly insoluble.<sup>13</sup> The solubility of  $\text{SO}_2$  is pH-dependent, decreasing with pH. This often limits the acidification process, depending on the rate at which the dissolved  $\text{SO}_2$  ( $S_{IV}$ ) is oxidized to  $\text{SO}_4^{=}$  ( $S_{VI}$ ). The oxidation of dissolved  $\text{SO}_2$  in fog droplets is potentially important, since the rates can be much faster than in gas phase. Lamb et al.<sup>14</sup> considered limitations in the availability of atmospheric water, concluding that such heterogeneous oxidation was not important in haze, but could be important in clouds. Fogs were intermediate, depending on the LWC. These observations are consistent with theory.<sup>11</sup>

Since fog droplets can readily scavenge soluble gases, they can change the locus of deposition of those species within the respiratory tract. These gases include  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{SO}_2$ , among others. As gases, these species may be efficiently scrubbed by the moist upper airways, but as particles, some of them will penetrate to the lung.<sup>15,16</sup> Fractional penetration was seen to vary substantially among individuals. Also, droplet sizes tend to increase with time during a fog event, so that the time of human exposure may be important.

In the Eastern United States, reactions involving dissolved  $\text{SO}_2$  are of primary interest. Current chemical models find that the most important reaction is that involving hydrogen peroxide, which is very fast even at low pH. The reaction is catalyzed by acid, with the rate increasing with decreasing pH (for  $\text{pH} > 2$ ). When coupled with the decrease in  $\text{SO}_2$  solubility with decreasing pH, the result is a rate expression for  $\text{SO}_2$  that is essentially independent of pH.<sup>17</sup> However, this reaction is effective only as long as  $\text{H}_2\text{O}_2$  is present, and cloud sampling has shown that  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  tend to be mutually exclusive.<sup>18</sup>  $\text{SO}_2$  levels in clouds aloft over nonurban areas tend to be of the order of a few ppb, as does  $\text{H}_2\text{O}_2$  in summer. For high  $\text{SO}_2$  concentrations and nonphotochemical situations, this reaction will be of less importance, because of insufficient  $\text{H}_2\text{O}_2$ . These situations include most urban fog events, and the major episodes of the 1960s and earlier should undoubtedly be characterized as nonphotochemical. The other aqueous phase reactions of interest for dissolved  $\text{SO}_2$  involve oxidation by  $\text{O}_2$ , catalyzed by transition metals such as  $\text{Fe}^+$  or  $\text{Mn}^+$  or by carbon. The rate for metal catalysis is positively dependent on pH, and thus cannot lead to very acidic fogs (especially when coupled with the rapid decrease in  $\text{SO}_2$  solubility as pH decreases). Current regional models do not consider carbon or soot catalysis, perhaps because elemental carbon is not expected to be very abundant in clouds over nonurban areas.

Hansen et al.<sup>19</sup> compared the rates of  $\text{SO}_2$  oxidation in a continuous flow cloud chamber with and without the presence of  $\text{NH}_3$ .  $\text{NaCl}$  and soot particles served as condensation nuclei. With an excess of ammonia, conversion of  $\text{SO}_2$  was rapid and 80% complete. Without  $\text{NH}_3$ , conversion was negligible. Conversion was also negligible in the absence of condensation. Comparison of soot and  $\text{NaCl}$  particle nuclei suggested a minor catalytic role (if any) for soot.

## Deposition Considerations

It appears that water cycles between ground and air during a fog event. Fog droplets containing impurities (often acids) deposit by gravity to surfaces, some of which may be warmer than the air. Evaporation prevents a continuous build-up on the surface. However, in many cases, the liquid water content of the fog decreases over time. If acids are present in the fog droplets, they may attack the ground surfaces and thus be effectively removed through neutralization, leaving the salts behind as particles. This mechanism explains the observed general tendency for the aerosol equivalent loadings (liquid concentration\*LWC) to decrease over time during a fog event. Such rates of change will also depend on the presence of emissions sources within the area impacted by fog, as well as by transport in or out of the area.

One of the favorable properties of fog from the standpoint of urban air quality is the resulting increase in particle size and hence rates of pollutant deposition. Sulfate aerosol particles tend to remain airborne for many days since their deposition rates are only around 0.1 cm/sec, due to their predominantly submicron particle size. However, when scavenged by 10-20  $\mu\text{m}$  fog droplets, the rates of deposition increase to 1-2 cm/s (Waldman, 1986). In addition, large amounts of water are deposited from fogs, and the resultant wetted surfaces become much more efficient sinks for gaseous  $\text{SO}_2$  (Lipfert, 1989).<sup>20</sup> Thus, a relevant question for a stagnating fog event may be whether the rates of pollutant removal exceed the rates of pollutant build-up. This has been considered in some detail for a case study in the San Joaquin Valley of California,<sup>21</sup> but was not considered in the early analyses of the major pollution episodes which predicted high rates of conversion of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$ .<sup>2</sup>

These depositional aspects of fog seem to have been largely overlooked in considering fog effects upon health, although they are central to concerns about ecological impacts and were the main topic of Waldman's dissertation.<sup>22</sup>

## Typical Fog Concentration Data

The time-course of concentrations in fog can be quite variable, depending on circumstances. Figure 1 presents two contrasting examples. Figure 1(a) shows a fog event in the San Joaquin Valley (CA);<sup>22</sup> LWC,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  drop with time, as does dissolved  $\text{SO}_2$  ( $\text{S}_{\text{IV}}$ ). However, after about 7 hr  $\text{SO}_4^{2-}$  begins to increase, apparently due to aqueous phase oxidation. This fog was not very acidic ( $\text{NH}_4^+$  was the most abundant ions as is commonly the case in this area). However, Figure 1b shows a highly fog event at Del Mar<sup>23</sup> in SCAB, where  $\text{NO}_3^-$  and  $\text{H}^+$  are the most abundant ions, and no  $\text{SO}_4^{2-}$  oxidation is seen. In both cases, we interpret the drop in equivalent aerosol concentrations over time as evidence of deposition.

The relative contributions of the major ions are compared for Whiteface Mountain (NY) and a group of California sites in Figure 2. At the coastal California sites (north of the South Coast Air Basin [SCAB]), ammonium is less abundant than the other alkaline species, nitrate levels are low, and acidity is moderate (pH=4.05). In the Bakersfield area, where  $\text{SO}_2$  (gas) levels are the highest in California,  $\text{SO}_4^{2-}$  is more important but, since  $\text{NH}_4^+$  is quite abundant, average net acidity is also moderate (pH=3.9). In SCAB, nitrate is the major factor and ammonium levels are higher than near Bakersfield but not high enough to neutralize the fog. The average fog pH is 3.1. Ionic strengths are lower at Whiteface Mountain (part of this apparent difference may be due to differences in the reported LWC values from different fogwater collector designs).  $\text{SO}_4^{2-}$  is about the same at Whiteface in the summer as in California, but  $\text{NO}_3^-$  is much lower. In general, fog  $\text{SO}_4^{2-}$  levels are about the same as typically found in aerosol, but  $\text{NO}_3^-$  levels are much higher.

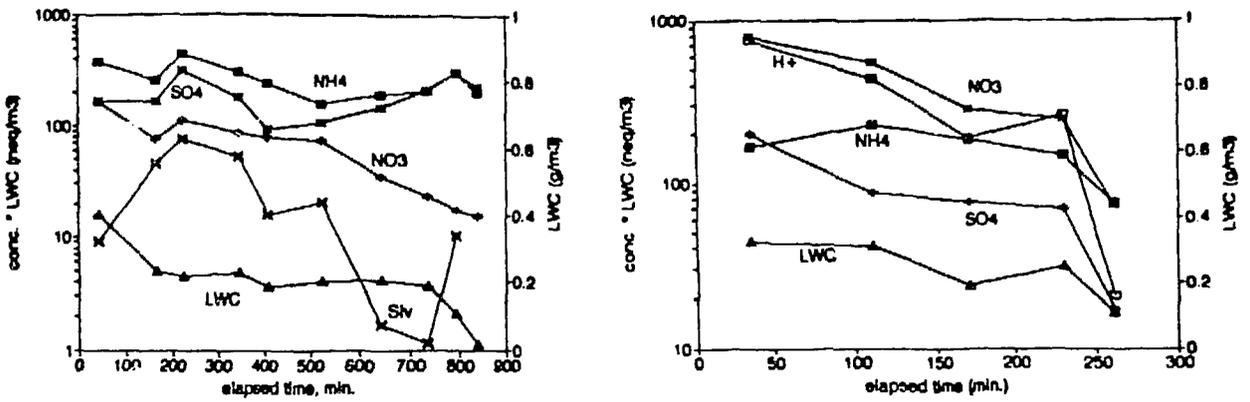


Figure 1. Example time histories of aerosol equivalent fog concentrations. (a) Bakersfield (CA) Airport, Jan. 2-3, 1985. Data from Waldman.<sup>22</sup> (b) Del Mar, CA, Jan. 1983. Data from Jacob et al.<sup>23</sup>

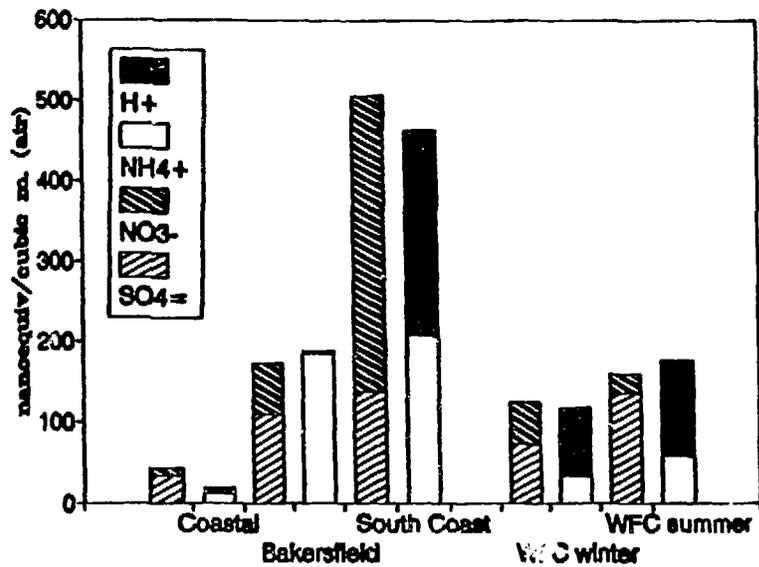


Figure 2. Comparison of average fogwater anions and cations, as equivalent aerosol loadings, for California sites and Whiteface Mtn., NY.

## SYNTHESIS

### Relevance to Urban Areas

Fog has been shown to have important air pollution consequences, especially for radiation fogs in urban areas. These events are more likely to occur under quiescent air conditions, and the higher air pollution loadings found in urban areas can increase the numbers of condensation nuclei. However, the heat retention capacity of urban agglomerations can act to decrease the relative humidity<sup>24</sup> and thus the frequency of fog formation. Fogs may thus be more common downwind of major urban areas.

Fogs often form at night when fewer people are likely to be exposed. Although penetration of fog into indoor environments was reported during the major fog episodes in London during the 1950s,<sup>1</sup> this is unlikely in the United States, in part because of typically higher indoor air temperatures resulting from our near universal use of central heating

### A Simple Urban Stagnation Model, Applied to London

The tendency for fog to oxidize dissolved  $\text{SO}_2$  to  $\text{SO}_4^-$  (which may be acidic, depending on the  $\text{NH}_3$  level) runs counter to the trend of increased deposition; a simple model was devised to compare rates of formation and removal. A reasonable upper limit for oxidation (in winter, with an abundance of  $\text{SO}_2$ ) may be about 3% per hour.<sup>21</sup> Neglecting advection, the rate of removal depends on the deposition velocity ( $V_d$ ) and the volume of the urban "reservoir" compared to the surface area available for deposition. For a heavy fog event, it is reasonable to assume that all of this surface area will be wetted by deposition of water, through gravitational settling, condensation, and impaction of droplets. In dense urban areas, the total structural surface area ( $A_s$ ) exceeds the ground plane area ( $A$ ), by as much as a factor of three.<sup>25</sup> The depositional flux is thus given by the product of  $A_s$ , the concentration ( $C$ ), and  $V_d$ . The mass stored in the atmospheric reservoir is given by  $C \cdot A \cdot h$  where  $h$  is the mixing height. Under the stagnant conditions typical of urban fog and ignoring any mass transfer limitations (the so-called well-stirred reactor model), the  $\text{SO}_2$  content of the atmospheric reservoir at time  $t$  may be obtained from a mass balance:

$$C(t) = C(t-1) + (E/h)dt - C(A_s/A)(V_d/h)dt - rCdt \quad [1]$$

where  $E$  is the emission rate per unit area,  $r$  is the fractional oxidation rate, and  $dt$  is the time increment.

The parameters of the rate of  $\text{SO}_2$  build-up in a stagnant situation are thus seen to be the emission rate, the mixing height, the effective deposition velocity  $V_d A_s/A$ , and the oxidation rate. When the last three terms of Eq. 1 are balanced, an equilibrium situation with constant air concentration will be attained. However, as a practical matter, all of the controlling parameters are likely to vary diurnally, so that such an equilibrium state may never be reached in practice. With  $E$  set to zero, the half lives of  $\text{SO}_2$  under specified conditions may readily be determined (by numerical integration). Under fog conditions, the half life could be as short as 1 h; under the lower deposition conditions typical of haze, it was several hours. A similar approach was taken in tracking the build-up of  $\text{SO}_4^-$  under stagnant conditions:

$$C(t) = C(t-1) + (E/h)dt - C(V_d/h)dt + rC(\text{SO}_2)dt \quad [2]$$

In this case, the emission term refers to primary emissions of  $\text{SO}_4^-$  and the conversion rate  $r$  operates on the  $\text{SO}_2$  remaining in the reservoir at time  $t$ . For fog droplet deposition, we assume that only the horizontal surfaces are active (gravitational settling). The enhanced sinks which characterize foggy conditions can act to limit the build-up of pollutants which would have occurred under the same stagnation conditions in the absence of fog. However,  $\text{SO}_4^-$  will continue to form as long as  $\text{SO}_2$  remains in the air, so that its concentration does not reach equilibrium. Also, insoluble and chemically unreactive pollutants such as CO will continue to accumulate in a stagnation situation as long as emissions continue.

When sulfur-bearing fuels are used, the rate of emission of  $\text{SO}_2$  in winter in a residential area is controlled mainly by the demand for space heating. In the U.S., for single-family homes, the demand may be represented by about  $160 \text{ Btu/m}^2$  per degree day.<sup>26</sup> For an average heated floor space of, say  $150 \text{ m}^2$ , in the mid-Atlantic region, this figure corresponds to a maximum rate of about  $50,000 \text{ Btu/h}$  and a seasonal consumption of about  $1000 \text{ gal}$  of fuel oil. If a fuel producing  $4 \text{ lb SO}_2/10^6 \text{ Btu}$  (coal) were used (as was the case during the severe air pollution episodes), the maximum  $\text{SO}_2$  emission rate would be  $0.09 \text{ g/hm}^2$ . The average emission rate in 1952 in London was only about  $0.015 \text{ g/hm}^2$ ; the maximum may have been twice that.<sup>2</sup> The London figures are lower because central heating was not in widespread use and because single-family homes were less prevalent.

### Estimates of $\text{SO}_2$ and $\text{H}_2\text{SO}_4$ Under Fog and Haze Conditions

Assuming a stagnant situation in which the stirred reactor model is appropriate, the hourly rate of increase of  $\text{SO}_2$  is given by the emissions relative to the content of the reactor and the rates of deposition and oxidation, as shown above. The average winter  $\text{SO}_2$  concentration in London was about  $200 \mu\text{g/m}^3$ ; we assume that under conditions of good ventilation, a typical value might have been  $100 \mu\text{g/m}^3$ . Thus the content of the reservoir at the beginning of an episode would be given by  $0.1 \text{ hA}$ . With a mixing height of  $100 \text{ m}$ , the initial  $\text{SO}_2$  content would be  $0.01 \text{ g/m}^2$ , so that cessation of ventilation would act to increase  $\text{SO}_2$  concentrations quite rapidly. Under non-foggy (haze) conditions, with primarily gas-phase reactions, both oxidation and deposition rates will be substantially lower. By way of comparison, an annual average emission rate of about  $0.015 \text{ g/hm}^2$  would yield an annual average  $\text{SO}_2$  concentration of about  $80 \mu\text{g/m}^3$  under normal ventilation conditions.<sup>27</sup>

These relationships are displayed parametrically in Figures 3 and 4 according to Eqs. 2 and 3, based on arbitrary conditions in the "reactor" which are held fixed over time and neglecting mass transport limitations. In reality, these conditions tend to change diurnally, so that Figures 3 and 4 should be used only to display the interactions among variables, not as a prediction of actual environmental conditions. Figure 3(a) plots the evolution of  $\text{SO}_2$  and  $\text{SO}_4^{=}$  emitted into a stagnant air mass with heavy fog present. The oxidation rate is  $3\%/h$  (independent of pH), the effective "dry" deposition velocity of  $\text{SO}_2$  is  $1 \text{ cm/s}$  (including the enhanced surface area); of fog,  $2 \text{ cm/s}$  (high LWC and large droplets are assumed). Eq. 2 shows that under these somewhat artificial conditions, the equilibrium concentration reached (when losses = emissions) depends mainly on the emission rate, and the mixing height controls the time to reach equilibrium, as seen in Figure 3(a). The evolution of  $\text{SO}_4^{=}$  (which may or may not be acidic, depending on the level of ammonia present, depends on the fraction of  $\text{SO}_x$  emitted as  $\text{SO}_4^{=}$ , the oxidation rate, and the deposition velocity, as well as the volume/surface ratio of the reactor. With low mixing heights and no primary emissions (Figure 3b), only small amounts of  $\text{SO}_4^{=}$  accumulate. However, as seen by comparing  $\text{SO}_4^{=}$  levels in Figures 3(a) and (b), even a small fractional primary emission can make a substantial difference in  $\text{SO}_4^{=}$  under stagnant conditions.  $\text{SO}_2$  concentrations scale roughly with emission rate

Under haze conditions, we assume an oxidation rate of  $1\%/h$ , a dry deposition velocity of  $0.25 \text{ cm/s}$  for  $\text{SO}_2$  and  $0.1 \text{ cm/s}$  for  $\text{SO}_4^{=}$ . As expected, with the reduced rates of loss, air concentrations reach much higher levels and depend on both the emission rate and the mixing height (Figure 4). Note that the assumed emission rate in Figure 4 is  $1/3$  of that in Figure 3(a). Since the deposition of  $\text{SO}_4^{=}$  is so much slower under haze conditions, as compared to fog, concentrations are much higher with low mixing heights (Figure 5). At more moderate mixing heights, the two rates are comparable and under large mixing heights (which are incompatible with the presence of fog), aerosol  $\text{SO}_4^{=}$  concentrations would be expected to be lower than equivalent fog concentrations. Note that emissions from space heating are incompatible with high levels of photochemistry and thus the oxidation rate assumed may be unrealistically high. However, this might not be the case in summer. Also, Chang and Novakov<sup>28</sup> report that  $\text{SO}_2$  oxidation products act to "poison" the catalytic activity of soot in

the absence of liquid water surrounding the particles, which would limit the extent of oxidation under haze conditions.

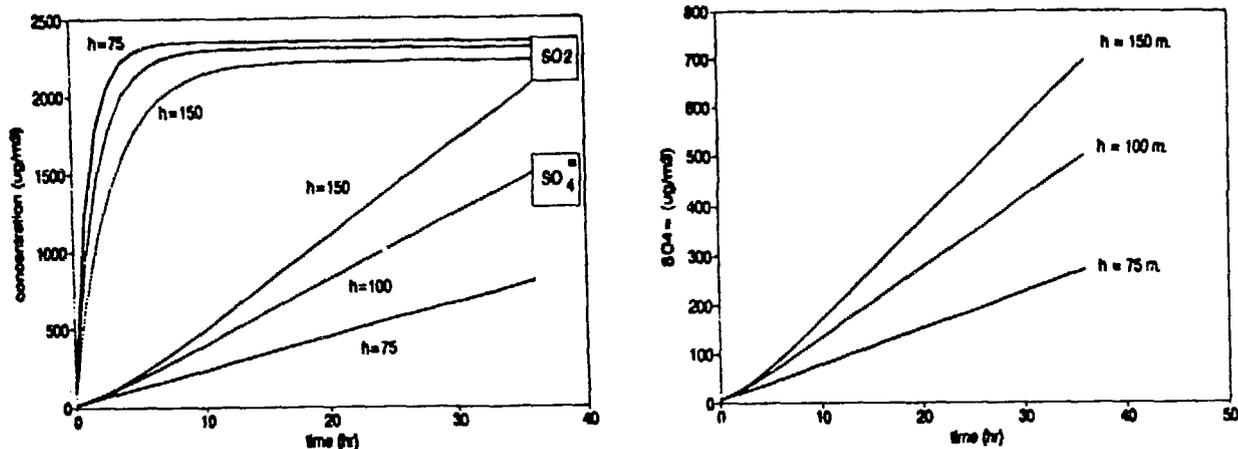


Figure 3. Simulation of the evolution of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> under foggy stagnant urban conditions. Oxidation rate = 3%/h, equivalent SO<sub>2</sub> dry deposition velocity = 1 cm/s, fog deposition velocity = 2 cm/s. (a) SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> with SO<sub>2</sub> emissions of 0.09g/hm<sup>2</sup> and primary SO<sub>4</sub><sup>2-</sup> emission = 1% of SO<sub>2</sub> emission. (b) SO<sub>4</sub><sup>2-</sup> with SO<sub>2</sub> emissions of 0.03g/hm<sup>2</sup> and no primary SO<sub>4</sub><sup>2-</sup> emissions.

## CONCLUSIONS

Scavenged pre-fog aerosols and certain gases are the main contaminants in fog; heterogeneous reactions were found to usually play a minor role. Even though liquid concentrations can be quite high in fogs, the equivalent aerosol loadings (obtained by multiplying by LWC) are comparable to aerosol levels. The most acidic fogs were found in the South Coast Air Basin of California, where scavenged nitric acid contributes much of the acidity. Equivalent aerosol loadings may decrease over time because of droplet deposition to the ground. Although this mechanism appears to constitute a "cleansing" of the atmosphere, very few data are available comparing air quality before and after fog events. Determination of fogwater liquid chemistry is a straightforward matter, but there are large uncertainties associated with most of the extant liquid water content measurements. One of the most pressing research needs is time-resolved experimental data on fog chemistry and LWC by droplet size, since deposition within the human airways and to surfaces is size-dependent. With respect to the major air pollution episodes of the past, SO<sub>4</sub><sup>2-</sup> production was undoubtedly accelerated during fog, but SO<sub>2</sub> and particles were removed from the atmosphere much more rapidly by deposition on surfaces. In addition, few of the larger particles characteristic of fog would have reached the deep lung. In terms of today's urban air pollution, fogs are relatively infrequent in most locations and tend to occur at night when fewer people are likely to be exposed.

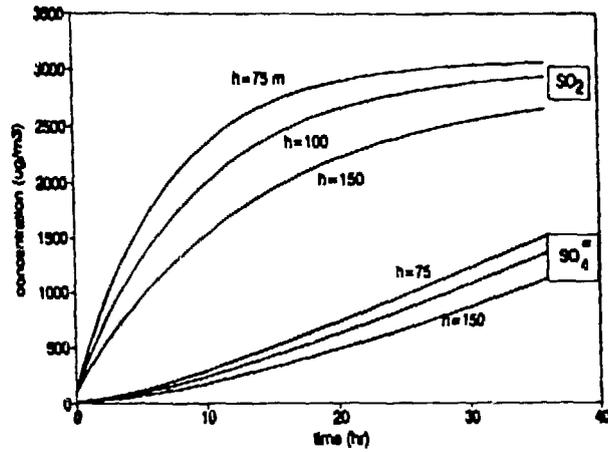


Figure 4. Simulation of the evolution of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  under hazy stagnant urban conditions. Oxidation rate = 1%/h, equivalent  $\text{SO}_2$  dry deposition velocity = 0.25 cm/s, fog deposition velocity = 0.1 cm/s, primary  $\text{SO}_4^{2-}$  emission = 1% of  $\text{SO}_2$  emission.

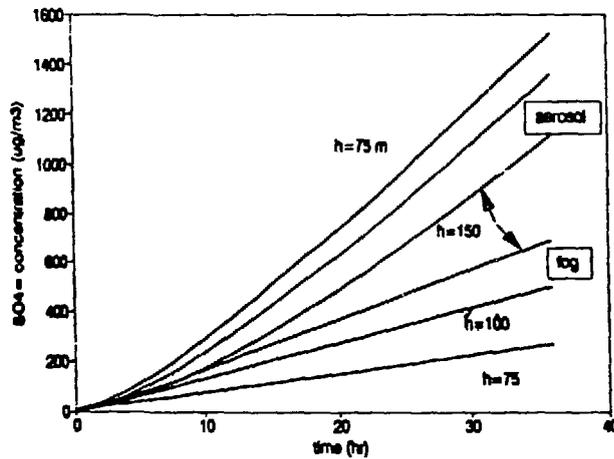


Figure 5. Comparison of  $\text{SO}_4^{2-}$  production under fog and haze conditions.  $\text{SO}_2$  emission rate = 0.03 g/hm<sup>2</sup>, other conditions as in Figures 3b and 4.

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