

## CHAPTER 6

THE RELATIONSHIP BETWEEN SULFATE AIR QUALITY  
AND VISIBILITY AT LOS ANGELES6.1 Introduction

The problem at hand is to determine the relationship between atmospheric sulfate concentrations and visibility reduction at downtown Los Angeles over the past decade. Severe visibility deterioration is one of the most readily apparent features of the Los Angeles smog syndrome. During the 25-year period since 1950, prevailing visibilities of less than three miles at relative humidities below 70 percent have been observed at downtown Los Angeles on an average of 100 days per year (Birakos, 1974). Recently completed short-term studies of particulate air quality in relation to visibility (Hidy, et al., 1975; White and Roberts, 1975) indicate that sulfates in the Los Angeles atmosphere are much more effective light scatterers per unit mass than other particulate components, and that sulfates may be responsible for over half of the light scattering at downtown Los Angeles.

The findings of White and Roberts have important implications for a strategy aimed at improving visibility in Los Angeles. A particulate control strategy for the Los Angeles basin proposed by Trijonis, et al. (1975), involving reduction of sulfates and nitrates from annual average levels of 14 micrograms per cubic meter  $\text{SO}_4^-$  and 12 micrograms per cubic meter  $\text{NO}_3^-$  to levels of 6.1 and 10 micrograms per cubic meter annual mean, respectively, was estimated to cost

approximately 156 million dollars annually. If such pollution control measures were to be proposed in part on the basis of visibility improvement, it is important to determine if the relationship observed by White and Roberts (1975) is persistent, and not simply an anomaly of the few days on which their samples were taken.

A brief discussion of the causes of light extinction in the atmosphere will serve as the basis for structuring a statistical model for visibility at Los Angeles. The model will then be applied to the routine air monitoring data base of the Los Angeles Air Pollution Control District over the historic period August 1965 through December 1974. Empirical results will be compared to theory and to the more detailed observations of others where possible. Then the model will be used to estimate the impact of reduced levels of particulate sulfates in the atmosphere on the cumulative distribution of daily visibilities at Los Angeles.

## 6.2 Visibility in Theory and by Observation

Attenuation of light intensity,  $I$ , by a column of air over distance,  $x$ , can be used to define an extinction coefficient,  $b$ , for that air parcel in accordance with the Beer-Lambert law:

$$\frac{dI}{I} = -b dx \quad (6.1)$$

In his classical visibility theory, Koschmieder (1924) proposed a relationship between this extinction coefficient  $b$  (which is a property measurable by instrumental methods) and the maximum distance at which an average individual could distinguish an ideal black object

silhouetted against the horizon sky. By assuming that a contrast level of 0.02 was the lower limit distinguishable to the human eye, Koschmieder was able to define a theoretical maximum visual distance, now known as "meteorological range",  $L_v$ , by:

$$L_v = \frac{-\ln 0.02}{b} = \frac{3.912}{b} \quad \text{in consistent units.} \quad (6.2)$$

Visibility apparent to an individual observer can differ from Koschmieder's theoretical result due to a number of factors including variation in the observer's visual acuteness and the inhomogeneous illumination of the atmosphere. Thus it is useful to consider a more personal measure of visibility, called "visual range", which is defined as the actual distance at which an ideal black object can just be seen against the horizon sky. To partially account for spatial variation in the optical properties of the atmosphere, daylight visual range observations made in accordance with National Weather Service standards are stated in terms of a "prevailing visibility". Prevailing visibility is defined as the greatest visibility which is attained or surpassed around at least half of the horizon circle, but not necessarily in continuous sectors (Williamson, 1973). A discussion of the possible errors involved in using Koschmieder's formula to estimate visibility apparent to a human observer is given by Horvath (1971). He suggests that by proper selection of visibility markers it should be possible to use the Koschmieder formula to calculate the extinction coefficient from observed visibilities with an error of less than about ten percent.

### 6.3 Relating Visibility to Atmospheric Composition

From expression (6.2), it is seen that the larger the extinction coefficient,  $b$ , the lower the expected visibility. This extinction coefficient is depicted by Charlson (1969) as the sum of several components:

$$b = b_{\text{scat}} + b_{\text{Rayleigh}} + b_{\text{abs-gas}} + b_{\text{abs-aerosol}} \quad (6.3)$$

where  $b_{\text{scat}}$  is the contribution due to light scattering by aerosol particles,  $b_{\text{Rayleigh}}$  is scattering due to air molecules,  $b_{\text{abs-gas}}$  is light absorption due to gases like  $\text{NO}_2$ , and  $b_{\text{abs-aerosol}}$  represents absorption due to particles such as carbon black. Charlson, et al. (1972) observed that scattering usually dominates light extinction in the Los Angeles area atmosphere, with wavelength-dependent absorption by  $\text{NO}_2$  being significant about 20 percent of the time.

While the theory of light scattering by aerosols is well advanced, there are practical difficulties in computing the effect of multi-component smog aerosols on visibility from first principles in an urban situation. Extensive information would be needed on the size distribution of the aerosol, its refractive index, particle shape, illumination, humidification of the atmosphere, and the spatial distribution of aerosol mass concentration. However, there is a growing body of empirical evidence suggesting that total suspended particulate mass concentration, TSP, alone is very highly correlated with scattering coefficient measurements and inversely correlated with prevailing visibility. From simultaneous measurements of light scattering and aerosol mass at a variety of locations, Charlson, Ahlquist and Horvath

(1968) reported that:

$$L_v \cdot TSP \cong \frac{3.9 TSP}{b} \cong 1.2 \frac{\text{gm}}{\text{m}^2} \quad (6.4)$$

or restated in units which we will use later:

$$b \cong 0.0325 \cdot (TSP) \quad (6.5)$$

where

$b$  is the atmospheric extinction coefficient in units of  $[10^4 \text{ m}]^{-1}$ .

$TSP$  is the total suspended particulate mass in  $\mu\text{gm}/\text{m}^3$ .

Visual range observations were correlated with aerosol mass loadings by Noll, Mueller and Imada (1968) and a similar proportionality was found.

Figure 6.1 shows a plot of the ratio of atmospheric light scattering coefficient to mass concentration for a monodisperse aerosol of unit density spherical particles of refractive index 1.5 and diameter  $D_p$  (White, Roberts and Friedlander, 1975). Much of the total suspended particulate mass in the atmosphere resides in a large particle mode ( $D_p > 1\mu$ ) whose contribution to light scattering per unit mass concentration is well below that typically observed for the atmosphere as a whole; smaller particles of diameter equal to that of the wavelength of incoming solar radiation in the visible spectrum are the most effective light scatterers. This relatively small fraction of the particulate mass residing in the region around  $D_p \cong 0.5$  microns is responsible for the bulk of the light scattering. *If these particles have an identifiable origin, then perhaps a relatively efficient strategy might be proposed for improving visibility in Los Angeles.*

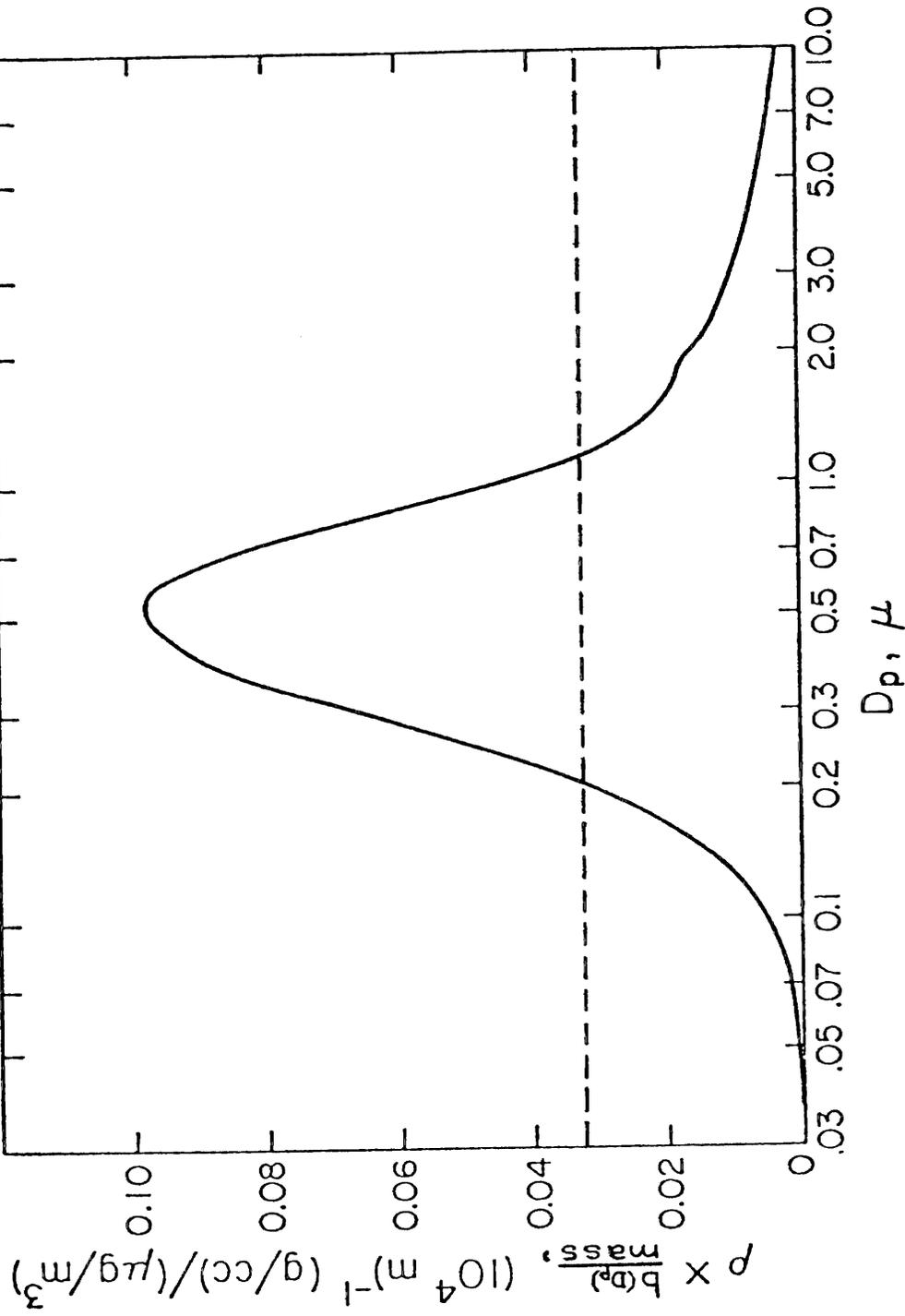


FIGURE 6.1

Normalized light scattering by aerosols as a function of particle diameter,  $D_p$ . Computed for unit density spherical particles of refractive index 1.5 (White, Roberts and Friedlander, 1975).

In a series of papers, Hidy and Friedlander and their co-workers (Hidy and Friedlander, 1971; Miller, Friedlander and Hidy, 1972; Heisler, Friedlander and Husar, 1973; Gartrell and Friedlander, 1975; Hidy et al., 1975) have examined the chemical composition of Los Angeles area atmospheric aerosols. These studies show that in Los Angeles the bulk of the particulate material in the effective light scattering size range (between one-tenth and one micron particle diameter) consists of sulfate, nitrate and ammonium ion, plus condensed organics. These portions of the atmospheric aerosol are known as secondary particulates because they originate predominantly from the conversion of pollutant gases to particulate matter in the atmosphere rather than from direct emission of dust or fume from natural or man-made sources.

The results of a variety of field investigations of visibility reduction support the proposition that such secondary particulates are largely responsible for atmospheric light extinction. Early studies of visibility reduction at Los Angeles, briefly outlined in Appendix D1, make it clear that such a relationship has been understood at least qualitatively for a long time. The importance of secondary particulates to light scattering is hardly unique to downtown Los Angeles. Eggleton (1969), for example, found a close inverse relationship between ammonium sulfate concentration and visibility in England. Investigations by Lundgren (1970) demonstrated a strong inverse correlation between atmospheric nitrates and visibility at Riverside, California.

In an attempt to isolate the relative importance of various particulate species to light extinction, White and Roberts (1975) examined nine days of simultaneous observations on light scattering in relation to aerosol chemical composition in the Los Angeles area. Their data consisted of 60 two-hour aerosol samples taken by the ACHEX II study (Hidy, et al., 1975) distributed among several locations in the Los Angeles basin along with nephelometer measurements of  $b_{\text{scat}}$ , plus relative humidity readings. They split the aerosol mass into four components: sulfates, nitrates, organics, and total mass less these three distinct chemical fractions. Postulating an additive relationship similar to expression (6.3), they were able to estimate the following dependence of  $b_{\text{scat}}$  on aerosol mass composition by linear regression techniques:

$$\frac{b_{\text{scat}}}{\text{TSP}} = 0.032 \pm 0.009 \quad (6.6)$$

and

$$\begin{aligned} b_{\text{scat}} &= 0.025 (\text{TSP-SULFATES-NITRATES}) \quad (6.7) \\ &+ 0.074 \text{ SULFATES} \\ &+ (0.025 + 0.049 \text{ RH}^2) \text{ NITRATES} - 1.1 \end{aligned}$$

$$R = 0.97 = \text{Multiple correlation coefficient}$$

where

$b_{\text{scat}}$  is in units of  $[10^4 \text{ m}]^{-1}$ .

RH is relative humidity in (%/100).

TSP is total suspended particulate matter in micrograms per cubic meter.

SULFATES and NITRATES are taken as  $1.3 \cdot \text{SO}_4^{=}$  and  $1.3 \cdot \text{NO}_3^{-}$  concentrations (in  $\mu\text{gm}/\text{m}^3$ ) in order to account for the mass of associated cations (thought to be ammonium ion).

(TSP-SULFATES-NITRATES) thus denotes the non-sulfate, non-nitrate fraction of the total suspended particulate matter.

White and Roberts (1975) concluded that sulfates in the Los Angeles atmosphere are more effective light scatterers per unit mass than other suspended particulate components. Changes in relative humidity seemed to affect only light scattering by nitrates to a statistically significant degree. Furthermore, light scattering by organics could not be distinguished statistically from the relatively ineffective scattering provided by the rest of the non-sulfate, non-nitrate, aerosol components, even though large amounts of organics were found to be present. The relative abundance of the various components of the atmospheric aerosols studied by White and Roberts is shown in Figure 6.2, while the estimated fraction of light scattering due to each component is shown in Figure 6.3 (White, Roberts and Friedlander, 1975).

From a knowledge of aerosol chemical composition, the emission source classes responsible for particulate concentrations at an air monitoring station may be inferred (Friedlander, 1973). Using trace metal concentrations at their monitoring sites as an indicator of pollutant origin, White, Roberts and Friedlander (1975) estimated that half of the light scattering at downtown Los Angeles was due to combustion of fuel oil and refining of crude oil. All but a few percent of the remaining light scattering at that location was attributed to pollutant emissions from automobiles.

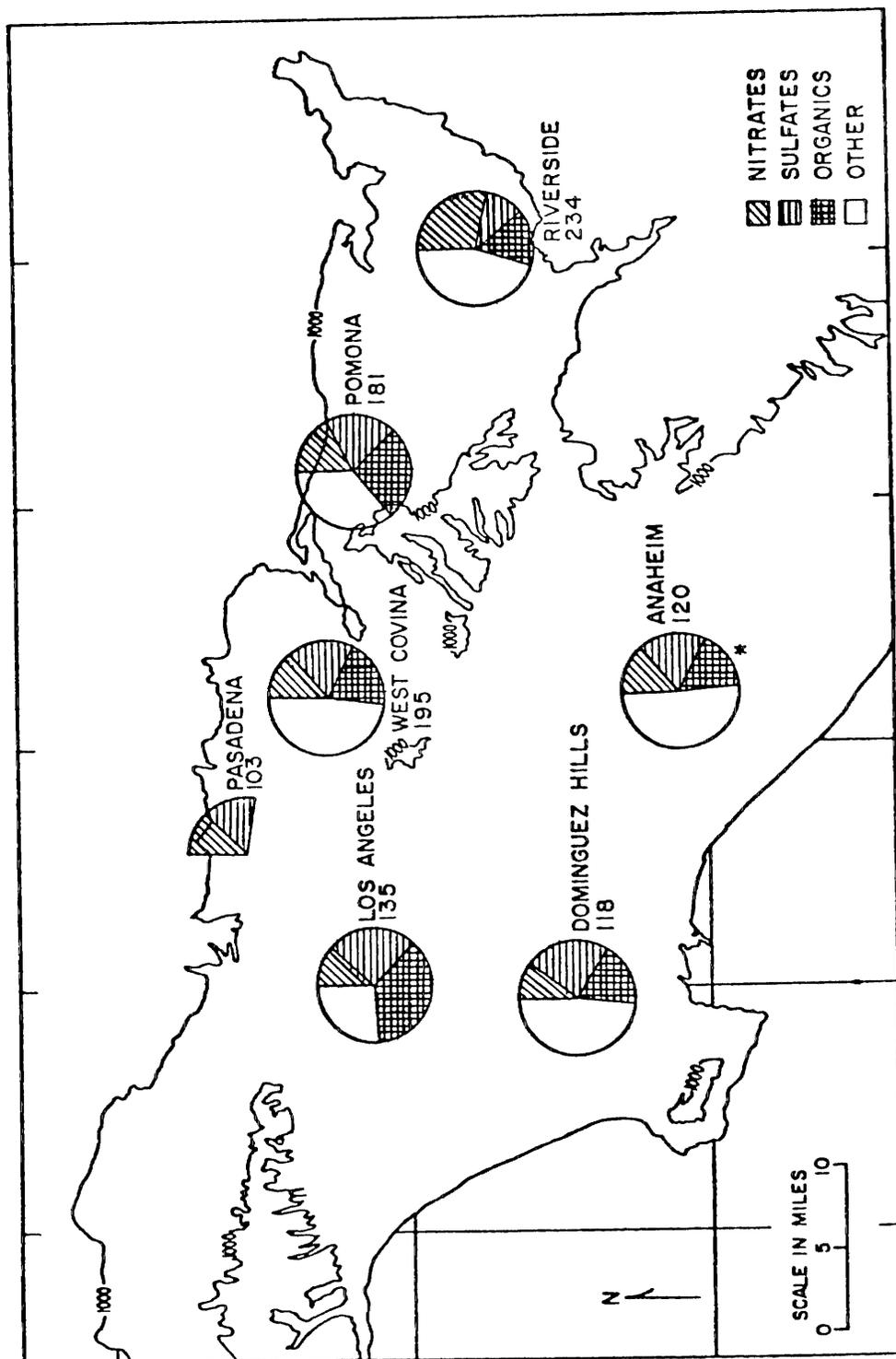


FIGURE 6.2

Division of total suspended particulate mass into its major chemical components on days and at locations covered by the ACHEX 1973 study. Numbers below locations give total suspended particulate mass in micrograms per cubic meter (from White, Roberts, and Friedlander, 1975).

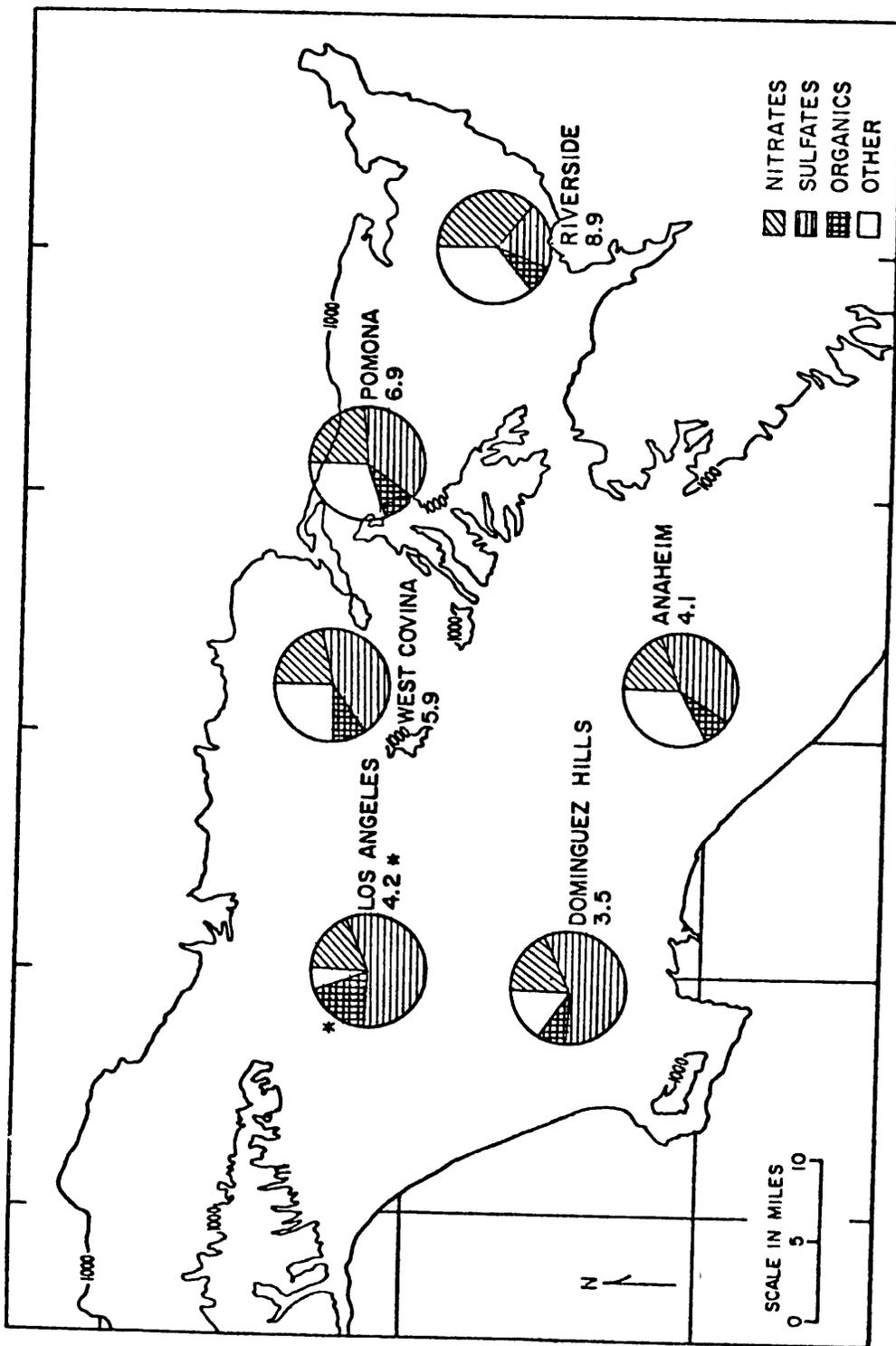


FIGURE 6.3

Attribution of bscat to major components of the atmospheric aerosol at locations covered by the ACHEX 1973 study. Numbers below locations give average bscat in units of  $[10^4 \text{ m}]^{-1}$ . Note the dominance of sulfates at downtown Los Angeles (from White, Roberts, and Friedlander, 1975).

#### 6.4 An Investigation of Visibility in Relation to Atmospheric Composition at Downtown Los Angeles: 1965 through 1974

Our first objective is to determine whether the findings of White, Roberts and Friedlander are supported by the long-term historical particulate data base accumulated by the Los Angeles Air Pollution Control District (LAAPCD). Ideally, one would like to be able to make comparisons between continuous records of particulate composition and visibility observations. A high degree of chemical and temporal resolution in the data base would be desired. The historical data base, however, was not designed with this particular experiment in mind. Total suspended particulate matter samples have been collected by the LAAPCD at downtown Los Angeles by high volume sampling on a regular basis since August 1965. The sampling period is 24 hours in duration. Duplicate samples are taken simultaneously on a pair of matched Staplex Hi Vols. Gravimetric determination of total suspended particulate matter collected is made after filter equilibration at low relative humidity. At least one sample taken from each pair of filters is analyzed for sulfates, nitrates, and seven metals. Sulfates are determined by the turbidimetric method and nitrates by the xylenol method. At various times during the history of the sampling program, sampling frequency has ranged from weekly, to twice weekly, to every fifth day. From August 1965 through August 1970, samples were taken from 8:00 am to 8:00 am. Since that time, all samples were taken from midnight to midnight. The Air Pollution Control District's particulate sampling program is more fully described in a series of papers by MacPhee and Wadley (1972 through 1975).

Since July 1964, prevailing visibility observations have been taken at the downtown headquarters of the LAAPCD. Observations are made from the roof of a building at 80 feet above ground level, at the same location and elevation as the high volume samplers. A typical daily record consists of nine consecutive hourly observations beginning at 8:00 am civil time and ending at 4:00 pm civil time. Weekend observations often are not taken. Relative humidity data are available, usually for 14 daylight hours. Hourly observations on  $\text{NO}_2$  concentrations (which could reduce visibility by absorption) have been taken at the same location by the automated continuous Saltzman method (Mills, Holland and Cherniack, 1974).

The temporal relationship between available useful observations is shown in Figure 6.4. There is clearly no way to adjust the historical data base to place 24-hour integrated particulate concentrations into exactly the same time frame as the daylight visibility observations. The best that can be done is to integrate the visibility observations for the longest period of time available within each particulate sampling event. Our mathematical treatment must take the available data into account. Suppose that we return to expression (6.3):

$$b = b_{\text{scat}} + b_{\text{Rayleigh}} + b_{\text{abs-gas}} + b_{\text{abs-aerosol}} \quad (6.8)$$

Making the assumption that  $L_v$  equals prevailing visibility,  $V$ , at any instant,  $i$ , observations on the left hand side of (6.8) can be obtained from existing data by use of Koschmieder's formula as follows:

$$b_i \cong \frac{24.31}{V_i} \quad \text{for conversion of } V_i \text{ in miles to } b_i \text{ in } [10^4 \text{ meters}]^{-1} \quad (6.9)$$

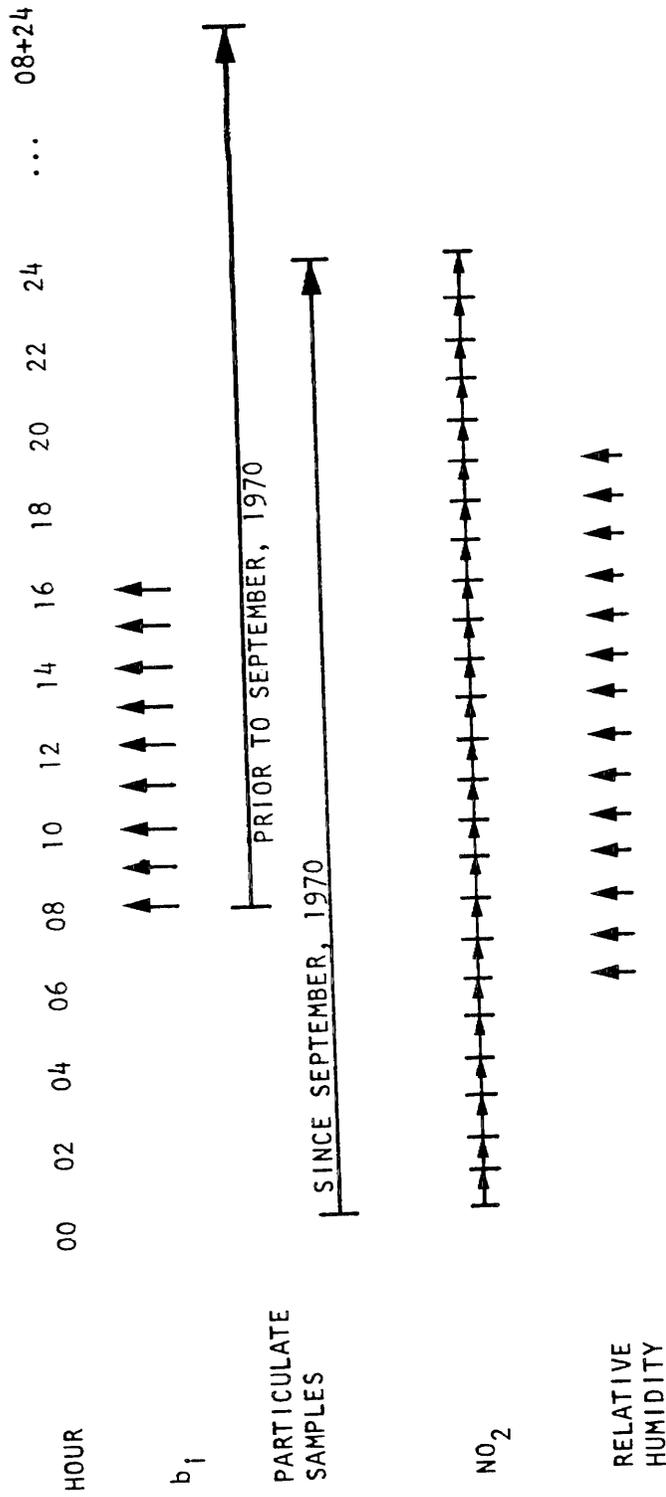


FIGURE 6.4

Temporal relationship between routine air monitoring observations. Averaging times indicated between arrows ( $\overline{\uparrow}$ ). Instantaneous readings indicated by ( $\uparrow$ ).

where  $i$  now refers to the  $i^{\text{th}}$  hour of the day. After White and Roberts, we further assume that  $b_{\text{scat}_i}$  can be represented as the sum of the extinction contributions of distinct chemical subfractions of the measured particulate, plus associated water. Since prevailing visibility takes into account aerosol light extinction due to both scattering and absorption, we assume:

$$b_{\text{scat}_i} + b_{\text{abs-aerosol}_i} = \sum_m \beta_{m_i} M_{m_i} \quad (6.10)$$

where

$\beta_{m_i}$  = the extinction coefficient per unit mass of the  $m^{\text{th}}$  particulate chemical species at time  $i$ .

$M_{m_i}$  = the mass concentration of the  $m^{\text{th}}$  particulate chemical species at time  $i$ .

And similarly for light absorption by gases

$$b_{\text{abs-gas}_i} = \sum_n \gamma_{n_i} C_{n_i} \quad (6.11)$$

where

$\gamma_{n_i}$  = the extinction coefficient per unit volumetric concentration of the  $n^{\text{th}}$  gaseous chemical species at time  $i$ .

$C_{n_i}$  = the volumetric concentration of the  $n^{\text{th}}$  gaseous chemical species at time  $i$ .

Averaging over the  $t$  hours of visibility observations in a day, we obtain:

$$\frac{1}{t} \sum_{i=1}^t b_i = \frac{1}{t} \sum_{i=1}^t \sum_m \beta_{m_i} M_{m_i} + \frac{1}{t} \sum_{i=1}^t \sum_n \gamma_{n_i} C_{n_i} + b_{\text{Rayleigh}} \quad (6.12)$$

where  $b_{\text{Rayleigh}}$  is taken as constant. Let  $\bar{M}_m$  be the available 24-hour average concentration of particulate species  $m$ . Let  $M_{m_i}$  be decomposed into the sum of a 24-hour mean value plus a fluctuating component:

$$\beta_{m_i} M_{m_i} = \beta_{m_i} (\bar{M}_m + M'_{m_i}) \quad (6.13)$$

Forming a t hour daylight average corresponding to our period of visibility observations, and rearranging:

$$\frac{1}{t} \sum_{i=1}^t \beta_{m_i} M_{m_i} = \frac{1}{t} \sum_{i=1}^t \beta_{m_i} \bar{M}_m + \frac{1}{t} \sum_{i=1}^t \beta_{m_i} M'_{m_i} \quad (6.14)$$

For ease of notation, the last term on the right side of expression (6.14) will be referred to as  $\delta_m$ , the daily residual difference between the average of  $\beta_{m_i} M_{m_i}$  and the product of the separate averages of  $\beta_m$  and  $M_m$ . Summing (6.14) over the particulate species and assuming that light absorption per unit concentration by pollutant gases is unchanging over time, we may substitute into (6.12) and rearrange to get

$$\bar{b} = \frac{1}{t} \sum_{i=1}^t b_i = \sum_m \frac{1}{t} \sum_{i=1}^t \beta_{m_i} \bar{M}_m + \sum_n \gamma_n \frac{1}{t} \sum_{i=1}^t C_{n_i} + b_{\text{Rayleigh}} + \sum_m \delta_m \quad (6.15)$$

### 6.5 The Models Estimated

Following the practice of previous investigators, and as a rough check on the visibility and total suspended particulate data (TSP), a purely linear relationship will be fit between undifferentiated aerosol mass and light extinction similar to equation (6.6):

$$\bar{b}_j = \beta_{\text{TSP}} \cdot \text{TSP}_j + \alpha \cdot \text{DUMMY}_j + A + \epsilon_j \quad (6.16)$$

As used above,  $\bar{b}_j$  is the average extinction coefficient for t hours of visibility data (nominally t = 9) on any day, j, as estimated from prevailing visibility by Koschmieder's formula. Only a single particulate species is considered, and light extinction per unit particulate

concentration,  $\beta_{TSP}$ , is taken as an undetermined constant. Light absorption by gases is neglected. In this model and those that follow, a dummy variable,  $DUMMY_j$ , has been introduced to capture any effect on equation fit due to the change in particulate sampling schedule previously noted to have occurred beginning in September 1970.  $DUMMY_j$  will be taken as unity for all samples prior to September 1970, and zero for all samples taken thereafter. The term  $b_{Rayleigh}$  is absorbed into the regression constant,  $A$ , in equation (6.16). For the time being we will assume that the residual difference term  $\sum_m \delta_m$  from equation (6.15) has mean zero and random fluctuation about its mean, and thus will be absorbed into the daily residual,  $\epsilon_j$ . This assumption is not likely to be strictly correct, as will be discussed later.

Results of the regression of extinction coefficient on total suspended particulate concentration alone are shown in Table 6.1.<sup>1</sup> Referring to the second entry of Table 6.1, we see that the estimated light scattering coefficient per unit total suspended particulate concentration is virtually identical to that found by the short-term study of White and Roberts (1975), as shown in equation (6.6). The coefficient  $\beta_{TSP}$  is significantly different from zero with greater than 99 percent confidence, while the constant term,  $A$ , was not significantly different from zero at any reasonable confidence level. However, the

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<sup>1</sup>All computations shown in Tables 6.1 and 6.2 were performed using the double precision ordinary test squares stepwise regression package of the MAGIC data handling program maintained on the Caltech IBM 370/158 computer by R. C. Y. Koh. Data base preparation is detailed in Appendix D2 along with a statistical description of the data used.

TABLE 6.1  
 Linear Regression Model Used to Test the Relationship Between Total Suspended Particulate  
 Matter Concentrations and Light Extinction in the Los Angeles Atmosphere

Model Estimated:  $\bar{b}_j = \beta_{TSP} \cdot TSP_j + \alpha \cdot DUMMY_j + A + \epsilon_j$

Entry Number	Time Period	Number of Observations	$\bar{b}_j$ Average ( $b_j$ Variance)	$\beta_{TSP}$	Coefficients (Standard Error) $\alpha$	A	Correlation Coefficient (Variance of Residual)
1.	8/65 thru 12/74	413	6.62 (30.52)	0.037 (0.0043)	1.023 (0.498)	0.154 NS	0.40 (25.53)
2.	9/70 thru 12/74	199	6.01 (18.19)	0.032 (0.0044)	N/A	1.034 NS	0.45 (14.41)

Legend: N/A means that the dummy variable is not applicable in a regression involving only data taken after the change in particulate sampling schedule.

NS means not significantly different from zero at a 95% confidence level.

total fit of the model, as judged by the reduction in residual variance, is unimpressive. Twenty-four hour total suspended particulate concentration values alone are not a very precise estimator of daylight visibility reduction in the Los Angeles area.

Next, by analogy to equation (6.15), a series of regression models are proposed to explain the average light extinction coefficient,  $\bar{b}_j$ , on any day  $j$  at downtown Los Angeles as a detailed function of atmospheric composition. These models differ only in the means of incorporating relative humidity effects into the structure of the model.

Of necessity, in light of the available data, it is assumed that division of the particulate samples into SULFATES, NITRATES, and (TSP-SULFATES-NITRATES) is sufficient to capture the major light scattering differences among these particulate components which can be resolved on the basis of chemical analysis. It is further assumed that  $\text{NO}_2$  is the only light absorbing gas of major significance to light extinction in the Los Angeles Basin.

Incorporation of relative humidity into our model poses several potentially serious problems. As relative humidity rises, hygroscopic and deliquescent particles pick up associated water and grow in size. Usually, this humidity-induced growth of an atmospheric aerosol is accompanied by an increase in light scattering which is not necessarily linear in relative humidity.<sup>2</sup> Three different approaches will be tried in an attempt to deal with the relative humidity effect.

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<sup>2</sup>Growth associated with increased humidification may also affect atmospheric chemistry, for example, by providing a larger volume of the solution phase as a site for liquid phase reactions.

In the first case, a baseline for comparison of relative humidity-dependent models is established. The suspected non-linearity is disregarded, and a purely linear model is proposed:

$$\begin{aligned} \bar{b}_j = & \beta_{\text{SULFATES}} \cdot \text{SULFATES}_j + \beta_{\text{NITRATES}} \cdot \text{NITRATES}_j \\ & + \beta_{(\text{TSP-SULFATES-NITRATES})} \cdot (\text{TSP-SULFATES-NITRATES})_j \\ & + \gamma_{\text{NO}_2} \cdot \overline{\text{NO}_2}_j + \Delta_{\text{RH}} \cdot \overline{\text{RH}}_j + \alpha \cdot \text{DUMMY}_j + A + \varepsilon_j. \end{aligned} \quad (6.17)$$

In this simple model, the light scattering coefficients per unit concentration,  $\beta_m$  and  $\gamma_{\text{NO}_2}$ , are taken to be undetermined constants, and the difference between light extinction on a high vs. low humidity day is captured by the undetermined coefficient,  $\Delta_{\text{RH}}$ , applied to the day-time average relative humidity.

When the chemically resolved linear model of equation (6.17) is estimated for the entire range of available average relative humidities (Table 6.2, entries 1 and 2), a substantial improvement in explanatory power is achieved over the total suspended particulate model of equation (6.16). Sulfates and  $\text{NO}_2$  are implicated as major contributors to visibility reduction at downtown Los Angeles. As expected, increasing relative humidity is related to increasing light extinction, as shown by the significant t test on the coefficient  $\Delta_{\text{RH}}$ . The estimated light extinction coefficients per unit concentration for NITRATES and (TSP-SULFATES-NITRATES) are at least an order of magnitude lower than that for SULFATES. In the case of NITRATES, the coefficient is not significantly different from zero at any reasonable confidence level for either time grouping tested. The constant term, A, is significantly

TABLE 6.2

Chemically Resolved Linear Regression Model  
 Relating Pollutant Concentrations to Light Extinction in the Los Angeles Atmosphere

MODEL ESTIMATED:

$$\bar{b}_j = \beta \text{SULFATES}_j + \beta \text{NITRATES}_j + \beta \text{(TSP-SULFATES-NITRATES)}_j + \gamma \text{NO}_2 + \Delta \text{RH}_j + \alpha \text{DUMMY}_j + A + \epsilon_j$$

ENTRY NO.	TIME PERIOD	NUMBER OF USABLE OBSERVATIONS (Comments)	$\bar{b}_j$ Average ( $\bar{b}_j$ Variance)	COEFFICIENTS (Standard Error)				Correlation Coef. (Variance of Residual)			
				$\beta$ SULFATES	$\beta$ NITRATES	$\beta$ (TSP-SULFATES-NITRATES)	$\gamma$ NO <sub>2</sub>		$\Delta$ RH	$\alpha$ A	
1.	8/65 thru 12/74	413	6.62 (30.52)	0.173 (0.015)	0.014 (0.019) NS	0.0080 (0.0043) S <sub>90</sub>	38.30 (4.42)	8.30 (1.27)	2.89 (0.38)	-7.37 (0.93)	0.76 (12.70)
2.	9/70 thru 12/74	199	6.01 (18.19)	0.161 (0.012)	-0.016 (0.013) NS	0.0080 (0.0034)	29.79 (3.69)	4.33 (1.22)	N/A	-3.53 (0.84)	0.86 (4.62)
3.	8/65 thru 12/74	406 (seven observations with $b_j > 20$ removed)	6.20 (15.84)	0.157 (0.009)	-0.017 (0.011) NS	0.0152 (0.0026)	24.99 (2.66)	6.36 (0.76)	1.85 (0.23)	-4.98 (0.56)	0.85 (4.35)
4.	8/65 thru 12/74	390 (visibility data used only when RH not > 70%)	5.65 (14.68)	0.134 (0.0096)	-0.0063 (0.0116) NS	0.013 (0.0026)	28.57 (2.63)	6.14 (0.95)	1.79 (0.24)	-4.84 (0.61)	0.82 (4.63)
5.	9/70 thru 12/74	192 (visibility data used only when RH not > 70%)	5.18 (13.08)	0.139 (0.011)	-0.0098 (0.0115) NS	0.0040 (0.0030) NS	29.17 (3.05)	2.78 (1.28)	N/A	-2.13 (0.76)	0.86 (3.39)

Legend: All coefficients are significantly different from zero with greater than 95% confidence unless otherwise indicated.  
 NS means not significantly different from zero at a 95% confidence level.  
 S<sub>90</sub> means significantly different from zero with greater than 90% confidence.  
 N/A means that the dummy variable is not applicable in a regression involving only data taken after the change in particulate sampling schedule.

less than zero in all years tested. This is not too surprising since an attempt to fit a linear function to a non-linear phenomenon will likely result in the numerous days of high light extinction at higher relative humidities dominating the location of the intercept, rather than the few days of extremely good visibility which should fall close to the origin of our coordinate system.

Upon examination of the extinction coefficient data, it was observed that roughly half of the variance of  $\bar{b}_j$  was contributed by a few very high values from among the 413 available samples. For example, on January 21, 1970, prevailing visibility ranged from 0.2 miles to 0.8 miles during the day, while relative humidity for the daylight hours averaged 87 percent, indicating a high likelihood of stabilized fog. The effect of deleting such observations from the data base was investigated. Discarding the data for all seven days over the nine-year period for which  $\bar{b}_j$  exceeded  $20 \times [10^4 \text{ m}]^{-1}$ , then re-estimating the previous model, the results shown in entry 3 of Table 6.2 are obtained. The coefficients in this model are similar to those of entry 2 of Table 6.2 which employed all of the data available since the change in sampling schedule in August of 1970. All coefficients except  $\beta_{\text{NITRATES}}$  are significantly different from zero with greater than 99 percent confidence. The t statistic on  $\beta_{\text{SULFATES}}$  is very large.

The second approach taken to dealing with the relative humidity effect is to attempt to remove the non-linearity by selecting only those observations which occur at low relative humidity. Equation (6.17) will again be the basis for the model, but this time daily

visibility, humidity, and  $\text{NO}_2$  averages will be computed only for those hours in the day for which relative humidity was not greater than 70 percent. Data for days of persistent high humidity will be discarded.

When the chemically resolved linear model of equation (6.17) is applied to the low humidity data base, the relationships outlined in Table 6.2 entries 4 and 5 are found. The size of the relative humidity effect has been reduced, but not eliminated, as shown by comparison of  $\Delta_{\text{RH}}$  between corresponding entries 1 and 4, as well as between entries 2 and 5 of Table 6.2. The size of the coefficient  $\beta_{\text{SULFATES}}$  has been reduced to a lower value of between 0.139 and 0.134  $[10^4 \text{ m}]^{-1}$  per  $\mu\text{gm}/\text{m}^3$  when the higher humidity observations are eliminated, a trend which was not unexpected. The fit of the low humidity model is comparable to that obtained in the regressions of entries 2 and 3 of Table 6.2.

A third model which attempts to deal directly with the physical basis of the relative humidity effect is proposed as follows. The radius of a hygroscopic particle in equilibrium with a surrounding humid atmosphere is determined by a competition between the vapor pressure raising effects of particle surface curvature and the vapor pressure lowering effect of dissolved substances in the particle. Neiburger and Wurtele (1949) used this fact to develop a model for correlating light scattering with relative humidity over a broad range of relative humidities. Their analysis shows that particle radius,  $r_p$ , should as a rough approximation be dependent on solute mass,  $m_s$ , and relative humidity as follows:

$$r_p = K[m_s / (1-RH)]^{1/3} \quad (6.18)$$

where K is a parameter of the dissolved substance which is approximately constant over a broad range of temperature and solute concentration. Approximation of changes in particle size by a hyperbolic function of relative humidity, though not strictly correct, provides a practical basis for non-linear regression analysis without introducing an excessive number of degrees of freedom into the curve-fitting processes. A brief summary of Neiburger and Wurtele's derivation is contained in Appendix D3.

Neiburger and Wurtele were concerned with large sea salt particles of several microns in diameter. They noted that for a given particle number concentration and solute mass per particle, light scattering by large particles should increase as the cross-sectional area of the aerosol, and thus light scattering should be correlated with relative humidity as  $(1-RH)^{-2/3}$ . Our case of interest is considerably more complicated than Neiburger and Wurtele's hypothetical behavior of uniform sea salt solution droplets. As previously mentioned, the bulk of the soluble salts in the atmosphere at downtown Los Angeles is thought to consist of sulfate and nitrate compounds. These particles are found predominantly in submicron size ranges where the Mie theory of light scattering would not predict a simple dependence of light scattering on particle cross-sectional area as was the case with Neiburger and Wurtele's larger sea salt nuclei. However, Hidy, et al. (1975) have shown empirically that light scattering by submicron aerosols is well correlated with total submicron aerosol volume. Thus

it is expected that light scattering by a hygroscopic submicron aerosol will correlate well with changes in particle radius cubed. If it is assumed that total suspended solute mass concentration changes from day to day are proportional to changes in total particle number concentration, with the relative shape of the size distribution of dry solute nuclei remaining unchanged from day to day, then light scattering by SULFATES and NITRATES might be fit by a regression model containing the terms  $\beta_{\text{SO}_4} \cdot (1-\text{RH})^{-1} \cdot \text{SULFATES}$  and  $\beta_{\text{NO}_3} \cdot (1-\text{RH})^{-1} \cdot \text{NITRATES}$ .

Treatment of the effect of relative humidity on the non-SULFATE, non-NITRATE portion of the total suspended particulate matter is complicated by lack of detailed information on its chemical composition. Much of the remaining particulate mass is thought to reside in larger size ranges where light scattering per particle should be proportional to particle cross-sectional area. If the particles were hygroscopic, then a dependence of light scattering on relative humidity of  $(1-\text{RH})^{-2/3}$  would be indicated, similar to Neiburger and Wurtele's sea salt droplets. If the particles are hydrophobic, then no dependence on relative humidity is expected, and the term  $(1-\text{RH})$  would be raised to the zero power. In all likelihood, the atmospheric aerosol contains a mix of both types of large particles, and thus some intermediate behavior would be found to represent the relative humidity dependence of best fit. Therefore, our third regression model will be formulated as:

$$\begin{aligned}
\bar{b}_j = & \beta_{\text{SO}_4} \cdot \left\{ \frac{1}{t} \sum_{i=1}^t (1-\text{RH}_i)^{\Delta_{\text{SO}_4}} \right\}_j \cdot \text{SULFATES}_j + \beta_{\text{NO}_3} \cdot \left\{ \frac{1}{t} \sum_{i=1}^t (1-\text{RH}_i)^{\Delta_{\text{NO}_3}} \right\}_j \cdot \text{NITRATES}_j \\
& + \beta_{(\text{TSP-SULFATES-NITRATES})} \cdot \left\{ \frac{1}{t} \sum_{i=1}^t (1-\text{RH}_i)^{\Delta_{\text{P}}} \right\}_j \cdot (\text{TSP-SULFATES-NITRATES})_j \\
& + \gamma_{\text{NO}_2} \cdot \overline{\text{NO}_2}_j + \alpha \cdot \text{DUMMY}_j + A + \epsilon_j
\end{aligned} \tag{6.19}$$

where each symbol is as previously defined, except that the  $\Delta_m$  are now undetermined exponents applied to the relative humidity dependence of light scattering by aerosol species  $m$ .

The non-linear model of equation (6.19) is not suitable to fitting by ordinary least squares regression procedures. Therefore the results of Table 6.3 were obtained by minimizing the sum of the squared residuals by the algorithm suggested by Marquardt (1963) as implemented by the Caltech computing center subroutine LSQENP.

Entry 1 of Table 6.3 begins with a test of our prior beliefs about the relative humidity dependence of light scattering by various types of aerosol species. The exponents  $\Delta_{\text{SO}_4}$  and  $\Delta_{\text{NO}_3}$  are initially set equal to -1.0 reflecting the expected correlation between submicron aerosol volume and light scattering. The exponent  $\Delta_{\text{P}}$  is first set equal to -0.667 as would be the case if total suspended particulate matter resided in large particles which could grow in size with increasing humidification. The fit achieved is comparable to that of the linear model of entry 1, Table 6.2 fitted to the same data base. The only coefficient which is not of the expected sign appears to be

TABLE 6.3

Non-linear Regression Model Incorporating the Relative Humidity Effect on Light Scattering by Hygroscopic Particulate Matter in the Los Angeles Atmosphere

MODEL ESTIMATED:

$$\bar{b}_j \cdot SO_4 \cdot \left( \frac{1}{t} \sum_{i=1}^t (1-RH_i) \right) \cdot \Delta SO_4 \cdot \left( \frac{1}{t} \sum_{i=1}^t (1-RH_i) \right) \cdot \Delta NO_3 \cdot \text{NITRATES} + \beta \cdot \left( \frac{1}{t} \sum_{i=1}^t (1-RH_i) \right) \cdot \Delta NO_3 \cdot \text{NITRATES} + \beta \cdot \left( \frac{1}{t} \sum_{i=1}^t (1-RH_i) \right) \cdot \Delta NO_3 \cdot \text{NITRATES} + \alpha \cdot \overline{NO_2} + \epsilon \cdot \Delta \epsilon_j$$

TIME PERIOD: August 1965 through December 1974  
 NUMBER OF USABLE OBSERVATIONS = 413

ENTRY NO.	COMMENTS	$\bar{b}_j$ Average ( $\bar{b}_j$ Variance)	$\beta_{SO_4}$	$\Delta_{SO_4}$	$\beta_{NO_3}$	$\Delta_{NO_3}$	COEFFICIENTS (Standard Error) $\beta$ (TSP-SULFATES-NITRATES) -NITRATES)	$\Delta_p$	$\gamma_{NO_2}$	$\alpha$	A	CORRELATION COEF. (Variance of Residual)
1.	$\Delta_{SO_4}$ and $\Delta_{NO_3}$ forced to equal -1.0 $\Delta_p$ forced to equal -0.667	6.62 (30.53)	0.041 (0.003)	-1.0 Fixed	0.025 (0.005)	-1.0 Fixed	-0.002 NS	-0.667 Fixed	41.80 (3.86)	2.54 (0.38)	-1.76 (0.51)	0.76 (13.03)
2.	$\Delta_{SO_4}$ and $\Delta_{NO_3}$ forced to equal -1.0	6.62 (30.53)	0.039 (0.004)	-1.0 Fixed	0.022 (0.005)	-1.0 Fixed	0.004 NS	-0.24 (0.96)	38.57 (4.43)	2.31 (0.38)	-2.23 (0.56)	0.76 (13.02)
3.	$\Delta_{SO_4}$ forced to equal $\Delta_{NO_3}$	6.62 (30.53)	0.089 (0.010)	-0.67 (0.077)	0.040 (0.0095)	-0.67 (0.077)	0.0038 NS	-0.35 (0.92)	33.81 (4.14)	2.87 (0.36)	-3.28 (0.54)	0.80 (11.13)
4.	All parameters free to seek local minimum	6.62 (30.53)	0.107 (0.015)	-0.53 (0.10)	0.024 (0.008)	-1.09 (0.13)	0.0033 NS	-0.28 (1.07)	33.86 (4.07)	2.82 (0.35)	-3.14 (0.53)	0.81 (10.68)

Legend: NS means not significantly different from zero at a 95% confidence level.

insignificantly different from zero. The principal species responsible for explaining visibility reduction are again SULFATES and  $\text{NO}_2$ . The light extinction coefficient estimated for  $\text{NO}_2$  is similar to that of entry 1, Table 6.2, indicating that our change in humidity treatment has left estimated light attenuation by this gas phase component largely unaffected, as expected. Finally, we note that the change in relative humidity treatment has brought the intercept, A, closer to zero, and for the period prior to September 1970 the coefficient on the dummy variable,  $\alpha$ , almost cancels A, leaving a net intercept value which is indistinguishable from zero. In short, our model based on simple assumptions about the light scattering behavior of a hygroscopic aerosol as a function of relative humidity displays many nice properties.

In an attempt to improve model fit, constraints placed on the exponents describing the relative humidity dependence of light scattering by various aerosol components will be relaxed one at a time. Perturbation of the parameter values shows that there is roughly a one-to-one trade-off possible between the values of the coefficients  $\beta_{\text{SO}_4}$  and  $\Delta_{\text{SO}_4}$  without disturbing model fit very much. Similar compensating adjustments could be made between  $\beta_{\text{NO}_3}$  and  $\Delta_{\text{NO}_3}$  and between  $\beta_{(\text{TSP-SULFATES-NITRATES})}$  and  $\Delta_p$ . Total model fit continues to improve until all parameters  $\Delta_m$  are freed to seek a local minimum in entry 4 of Table 6.3. In that case, the function of relative humidity associated with NITRATES almost exactly matches our prior expectation that  $\Delta_{\text{NO}_3}$  would equal -1.0. Light scattering by SULFATES is also a fairly strong function of relative humidity. Coefficients estimating the

light scattering by non-sulfate non-nitrate particulates are now of the expected sign, but are still not known with great accuracy.

Figure 6.5 shows the historical cumulative distribution of visibilities at downtown Los Angeles as compared to model output of entry 4, Table 6.3. The comparison is quite close.

Theoretical calculations have been performed by Garland (1969) to determine the extinction coefficient per unit concentration for liquid phase atmospheric ammonium sulfate aerosols as a function of relative humidity. Garland's example calculation for light scattering by a monodisperse ammonium sulfate aerosol of dry particle diameter equal to  $0.42\mu$  is plotted in Figure 6.6 along with the values of the function  $\beta_{\text{SULFATES}} = \beta_{\text{SO}_4} (1-\text{RH})^{\Delta \text{SO}_4}$  from entry 4 of Table 6.3. The regression results are of similar shape, but somewhat higher than Garland's extinction coefficient calculations. If the assumption were made that the sulfate aerosols in Los Angeles over the period 1965 through 1974 on days of high relative humidity were predominantly ammonium sulfate, then the comparison would be somewhat closer. That is because the molecular weight of ammonium sulfate is 1.38 times that of the  $\text{SO}_4^{=}$  ion, instead of the 1.3 times greater proportionality assumed at our data preparation step.

The model of equation (6.19) has the great advantage that it is close to being physically realizable for a hygroscopic aerosol. However, many sulfate and nitrate species exhibit a pronounced deliquescence. For example, light scattering by ammonium sulfate particles is not a smooth, slowly increasing function of relative humidity over a

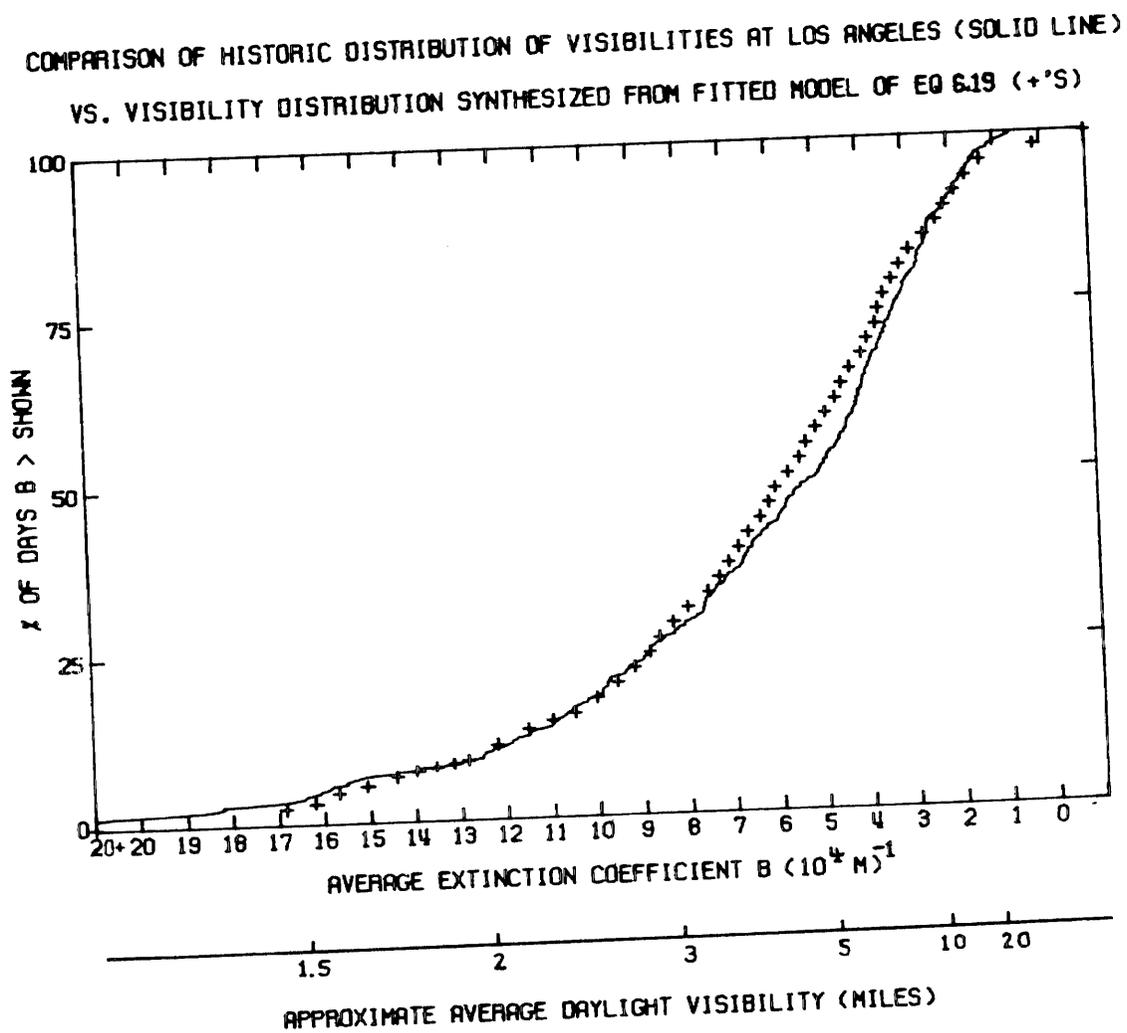


FIGURE 6.5

Results of model of entry 4, Table 6.3. Cumulative distribution of days on which the average extinction coefficient,  $\bar{b}_j$ , exceeded the stated values during the period August 1965 to December 1974 (413 days considered). Solid curve is historic data from LAAPCD visibility measurements. Broken curve is synthesized from regression model shown in entry 4 of Table 6.3.

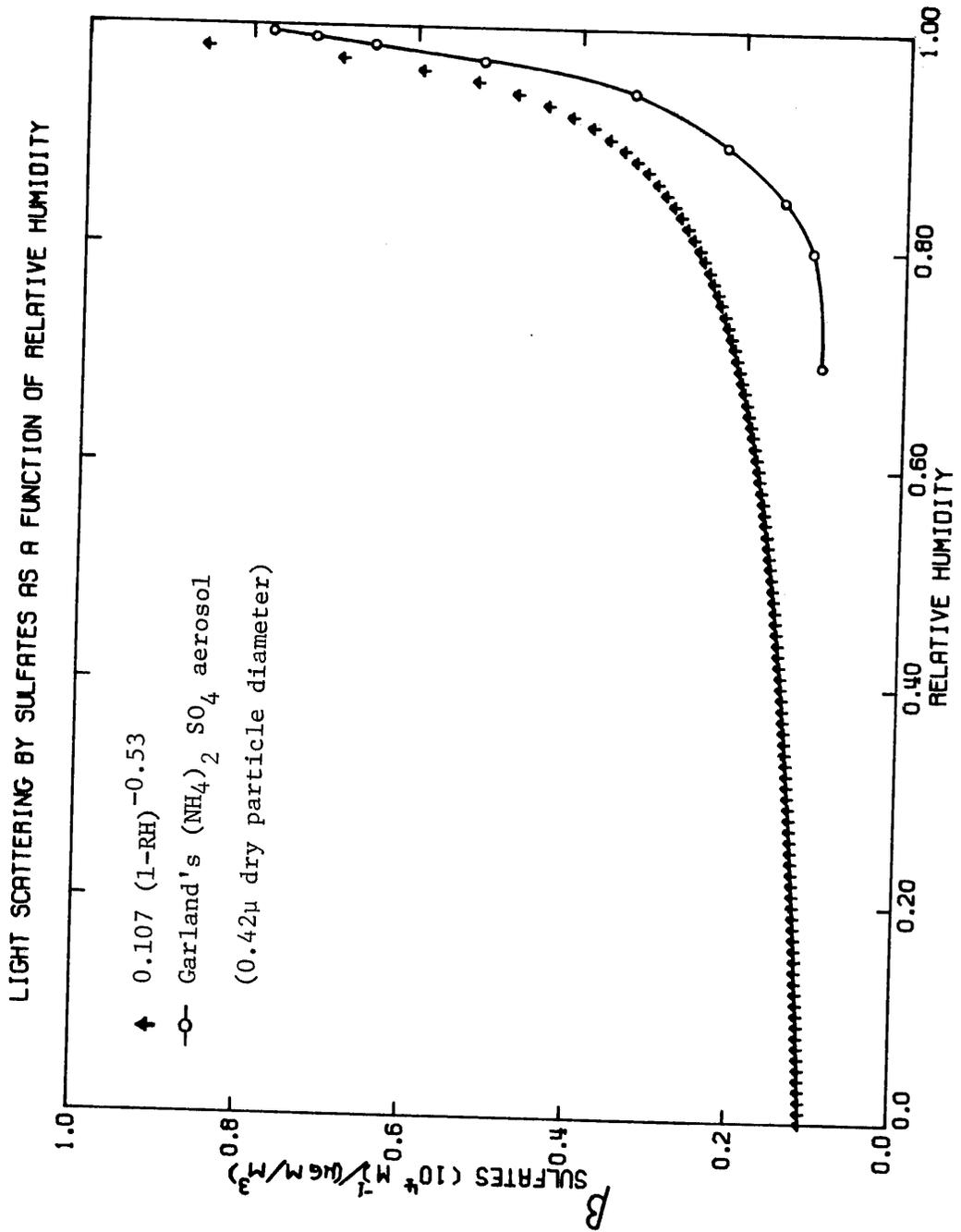


FIGURE 6.6

broad range of humidification. Instead, light scattering per unit mass for an ammonium sulfate aerosol remains fairly constant up to a relative humidity of ca. 80 percent, at which point the particle goes rapidly into solution with an attendant sharp rise in light scattering (Charlson, et al., 1974). Such complicated behavior would be difficult to incorporate theoretically into a simple regression model. Instead, an approach similar to that adopted by White and Roberts (1975) was tested in which an arbitrary relative humidity effect was to be approximated by fitting coefficients to series constructed from polynomials in relative humidity, pre-multiplying each aerosol mass concentration term. That approach was abandoned after discovering that only a slight improvement in model fit was achieved at the expense of creating estimated light scattering functions for each aerosol species which were ill-behaved at either the highest or lowest ends of the possible relative humidity range.

The function  $\beta_{\text{NITRATES}} = \beta_{\text{NO}_3} (1-\text{RH})^{\Delta_{\text{NO}_3}}$  describing light scattering by NITRATES as a function of relative humidity from entry 4 of Table 6.3 is plotted in Figure 6.7. Also plotted is the function  $(0.025 + 0.049 \text{ RH}^2)$  from equation (6.7) describing White and Roberts' result for light scattering by NITRATES. At relative humidities below 60 percent, our estimate matches that of White and Roberts almost exactly.

In the regression models tested, the estimated light extinction coefficient per ppm for  $\text{NO}_2$  has ranged between  $41.80 [10^4 \text{ m}]^{-1}$  and  $24.99 [10^4 \text{ m}]^{-1}$ . In all but one case, the estimate of  $\gamma_{\text{NO}_2}$  is within

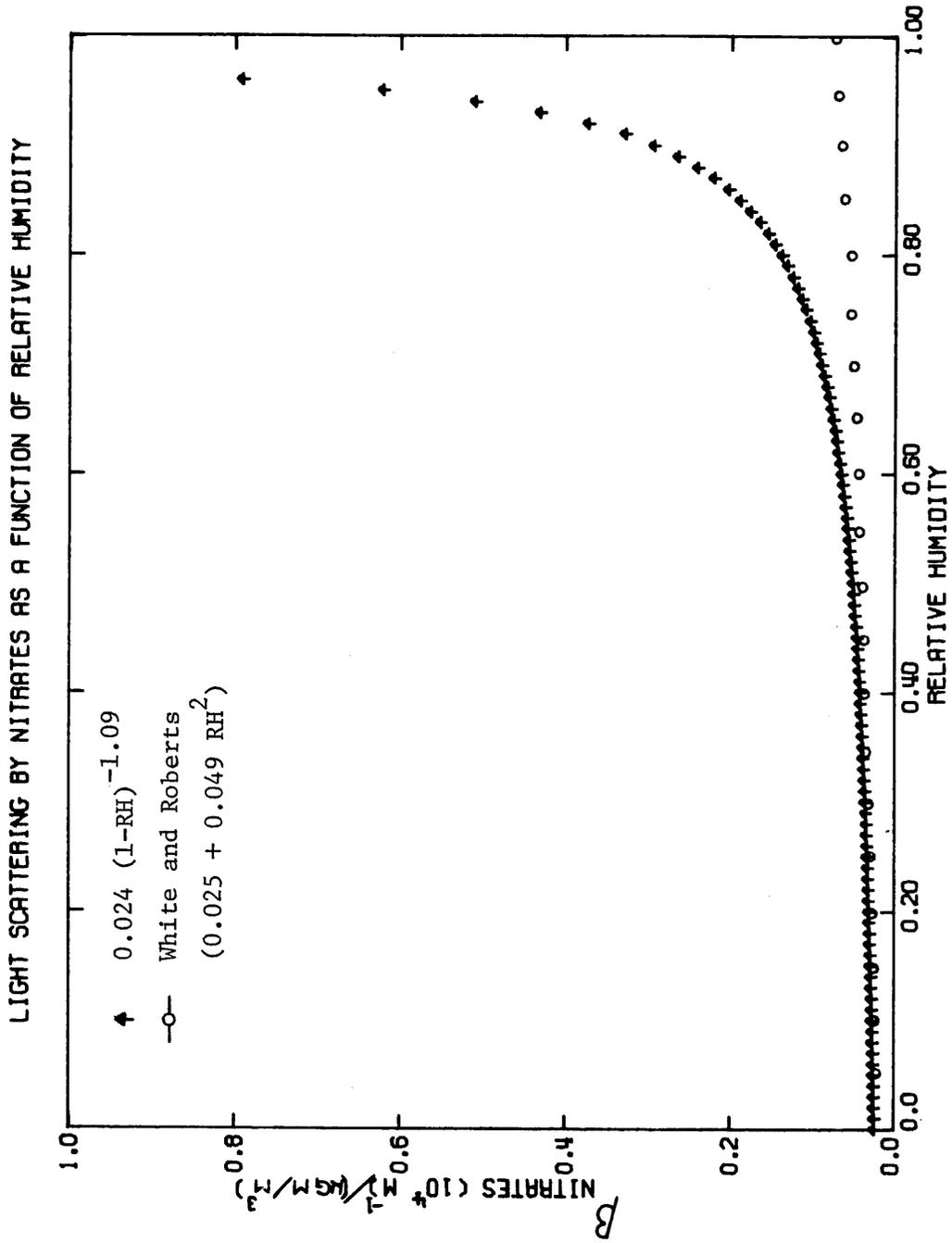


FIGURE 6.7

two standard errors of  $30 [10^4 \text{ m}]^{-1}$  per ppm. That value exceeds the literature estimates for light absorption by  $\text{NO}_2$  as cited by Charlson and Ahlquist (1969) by roughly a factor of two to four, depending on the wavelength of light of interest. The discrepancy could be due in part to systematic underestimation of either  $\text{NO}_2$  concentration or overestimation of the total atmospheric extinction coefficient. From the comments of previous investigators, it is not at all unlikely that less than ideal availability of visibility markers, plus the requirement that the markers be clearly recognized and not just seen could lead to a minimum contrast level for prevailing visibility observations in Los Angeles of 0.05 instead of Koschmieder's value of 0.02. Estimation of  $\bar{b}_j$  from Koschmieder's formula would then be systematically high by about 25 percent, as would be the values of the coefficients estimated in our regression models. Experimental verification of the relationship between LAAPCD routine prevailing visibility observations and the atmospheric extinction coefficient,  $b$ , would be desirable. That still is unlikely to be a large enough source of error to account for the consistently high coefficient estimates for  $\text{NO}_2$ .

The coefficient on  $\text{NO}_2$  might well be picking up some of the effects actually due to light scattering by its decay product, NITRATES. This seems quite likely in view of the difficulty in obtaining a significant contribution to light scattering by NITRATES in some of the linear regression models tested, even though most previous investigators have found a strong consistent NITRATE effect. The simple correlation between extinction coefficient and NITRATES is nearly zero, as shown

in Appendix D2. If light scattering were taken as an independent in situ check on the behavior of the nitrate air monitoring data, then the APCD might be well advised to check their nitrate collection and analysis techniques for possible interferences.

An additional interesting possibility is that  $\text{NO}_2$  might be highly correlated with an important aerosol subfraction, perhaps submicron organics, for which explicit data were unavailable for inclusion in the model. The LAAPCD's historical tape sampler particulate data have been displayed by Phadke, et al. (1975). Their study notes that the diurnal variation of that particulate index is similar to the observed diurnal pattern for carbon monoxide at downtown Los Angeles, and they suggest that the automobile is a major source of particulate matter at that location. If particulate loadings closely follow automotive pollutant levels in general, then the coefficient on  $\text{NO}_2$  in our regression models might be expected to be artificially high. If daylight  $\text{NO}_2$  values are a better estimator of daylight particulate loadings than are our 24-hour average (TSP-SULFATES-NITRATES) values, then the difficulty in obtaining a significant estimate of light scattering by non-sulfate non-nitrate particulates in Table 6.3 may be explained.

The existence of a persistent daylight peak in Los Angeles particulate concentration would have other implications for this study. If there is a persistent daytime peak in particulate loading of the Los Angeles atmosphere, then the residual difference term  $\sum_m \delta_m$  in equation (6.15), which we neglected, will not have mean zero and random fluctuation about that mean. Rather the 24-hour average particulate

measurements will be systematically lower than their 9-hour daytime counterpart corresponding to the period of visibility observations. The result will be that the extinction coefficients per unit concentration estimated from 24-hour averages of the particulate species exhibiting such a daytime peak will be artificially elevated in order to capture this discrepancy. Since aerosol sulfur (and for that matter its precursor,  $\text{SO}_2$ ) is typically seen to exhibit a daytime peak at downtown Los Angeles (Hidy, et al., 1975; Phadke, et al., 1975; Thomas, 1962), the reason for the modest elevation of the estimated sulfate scattering coefficient per unit mass in the models estimated in this paper above those predicted by Garland (1969) and by White and Roberts (1975) may have been identified. In such a circumstance, the qualitative finding of an important sulfate effect on visibility shown by the regressions of Tables 6.2 and 6.3 would remain valid, while the use of numerical values from Tables 6.2 and 6.3 for correlation of light scattering with hourly average sulfate concentrations would not be recommended. Our regression equations would remain an unbiased predictor of the likely daylight visibility impact of a strategy aimed at control of 24-hour average particulate levels as long as the relative diurnal variation of pollutant concentrations remained unchanged. Since current State and Federal particulate standards and most historical particulate sampling data are stated in terms of 24-hour and longer concentration averages, the analysis contained in this study provides useful results in spite of the above potential problems.

## 6.6 Exploring the Visibility Impact of Reduced Sulfate Concentrations

We have seen that our statistical models are probably best behaved with respect to predicting the marginal impact of SULFATES on visibility. The test statistics on the  $\beta_{\text{SULFATES}}$  coefficients are consistently significant, confidence intervals on these parameters are narrow, and the shape of the predicted non-linear humidity effect on light scattering by SULFATES is reasonable. The magnitude of the light scattering per unit mass predicted for SULFATES, while perhaps somewhat high, is still understood in relation to theory, the empirical findings of others, and several of the potential sources for error. Whatever problems may exist with estimating the light extinction behavior of other pollutant species, the behavior of light scattering by SULFATES is strong enough to stand out clearly from the background noise in the system. This is fortunate, because the motivation behind this study was to explore the impact of altered sulfate concentrations on the long-run distribution of prevailing visibilities at Los Angeles.

With this discussion in mind, the regression model of Table 6.3, entry 4, is used to "backcast" the impact on visibility of decreased sulfates levels at downtown Los Angeles. The sampling period of interest is again our data base of 413 rainless days distributed from August 1965 through December 1974.

Two cases will be considered. In the first instance, the daily average extinction coefficients,  $b_j$ , will be synthesized from the regression model using our historic air quality data after having reduced each day's SULFATES value by 50 percent. In the second case,

daily SULFATES values will be taken as 25 percent of their actual measured concentrations. This latter case approximates removal of virtually all of the non-background SULFATES in the Los Angeles atmosphere over the time period considered.<sup>3</sup> This is, of course, not to say that one knows how to achieve such a uniform proportionate reduction, but merely to estimate the visibility resulting should such an event have come to pass.

A comparison between the historic cumulative distribution of extinction coefficients and the distributions implied by the SULFATES reduction calculations is presented in Figures 6.8 and 6.9. The effect of sulfate reduction in those years is not uniform across the entire distribution of prevailing visibilities. Rather, as is most clearly shown in Figure 6.9, a 75 percent reduction in SULFATES levels on a daily basis would have reduced the number of days with worse than three-mile visibility by about two thirds, while improvement in the number of days of average visibility greater than ten miles (the California Air Resources Board's visibility target) would be much smaller, about 10 percent.

One likely explanation for this disproportionate SULFATES impact on the days of the very worst visibility is found in Table D2.1 of Appendix D2. As can be readily seen, suspended sulfate mass loadings are positively correlated with relative humidity. Thus days of high sulfate concentration often coincide with days of high light scattering

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<sup>3</sup> Estimation of average  $\text{SO}_4^{=}$  background concentrations in the Los Angeles basin is discussed by Trijonis, et al. (1975) and by Hidy, et al. (1975), and in Chapters 2 and 5 of this study.

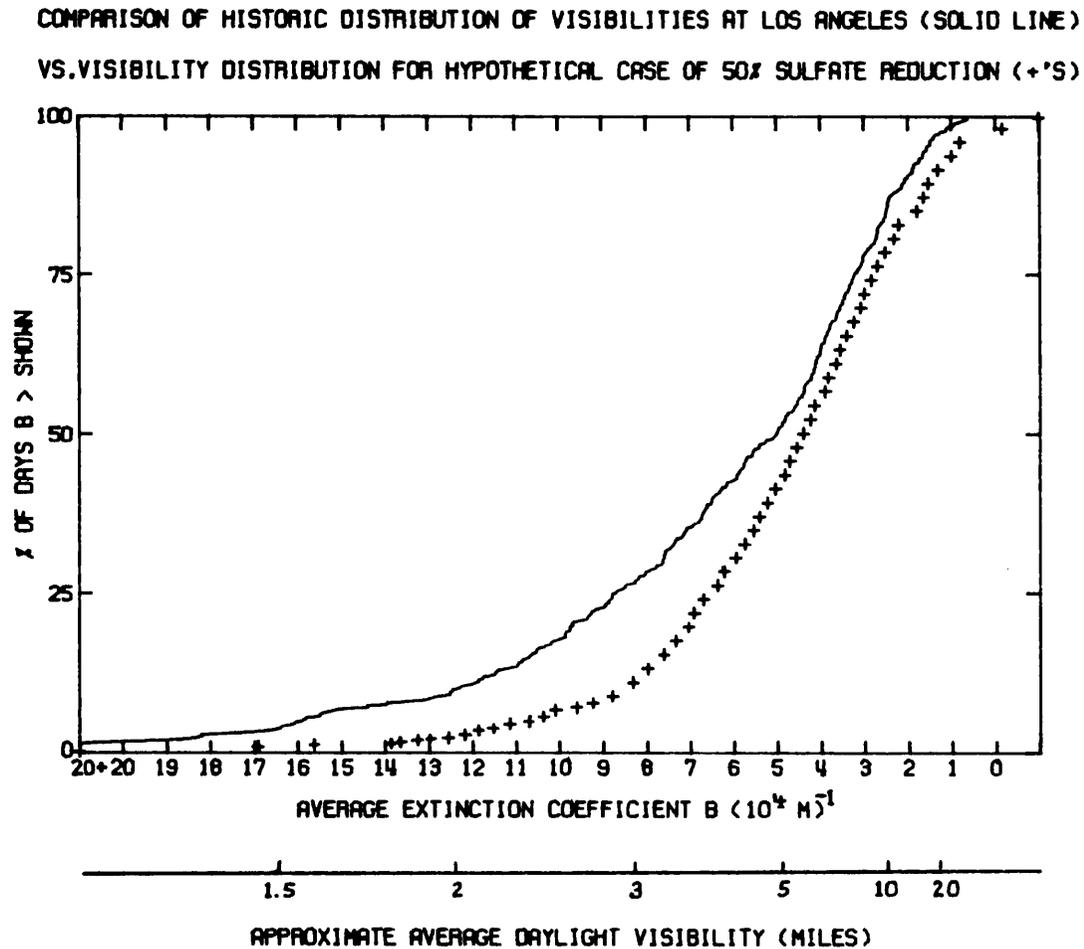


FIGURE 6.8

Impact of SULFATES reduction, Case I. Cumulative distribution of days on which the average extinction coefficient,  $\bar{B}_j$ , exceeded the stated values during the period August 1965 to December 1974 (413 days considered). Solid curve is historic data from LAAPCD visibility measurements. Broken curve is synthesized from regression model shown in entry 4, Table 6.3 after having reduced historic SULFATES levels by 50 percent on each day of observation.

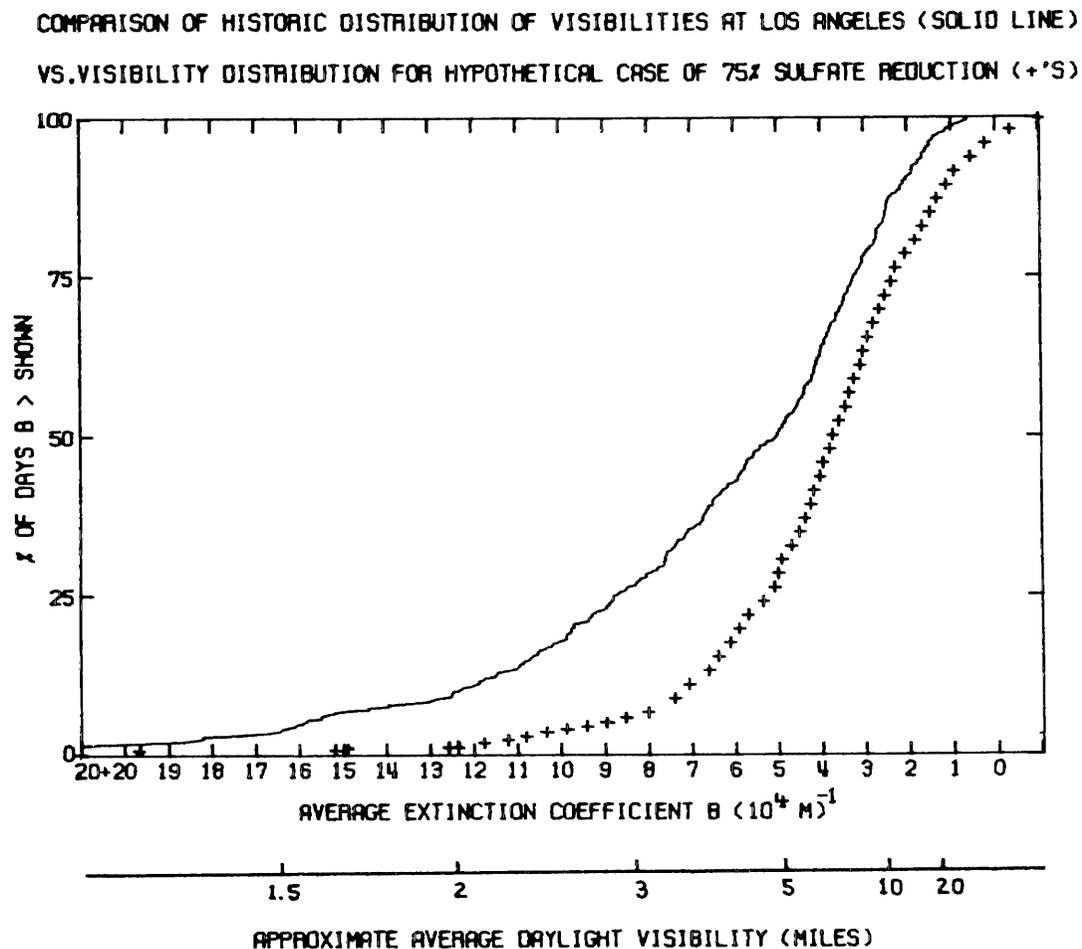


FIGURE 6.9

Impact of SULFATES reduction, Case II. Cumulative distribution of days on which the average extinction coefficient,  $\bar{B}_j$ , exceeded the stated values during the period August 1965 to December 1974 (413 days considered). Solid curve is historic data from LAAPCD visibility measurements. Broken curve is synthesized from regression model shown in entry 4, Table 6.3 after having reduced historic SULFATES levels by 75 percent on each day of observation.

per unit sulfate mass concentration. Conversely, fairly dry days on which visibility is relatively good were comparatively sulfate free.

#### 6.7 In Conclusion

Techniques have been developed for relating air pollution control agency routine air monitoring data to prevailing visibility at downtown Los Angeles over the decade 1965 through 1974. It was shown that the apparent relationship between light extinction and total suspended particulate mass implied by the long-term historical data base is consistent with the findings of previous short-term special studies. However, total suspended particulate mass was found to be an imprecise estimator of daylight visibility reduction in the Los Angeles area.

When total suspended particulate samples are subdivided chemically, it becomes possible to more closely assess the effect of water-soluble submicron aerosol species, particularly sulfates, on light scattering at Los Angeles. A non-linear regression model for light extinction at Los Angeles was constructed which combines available aerosol chemical information with relative humidity and  $\text{NO}_2$  data. Coefficients fitted to that model indicate that there is a pronounced increase in light scattering per unit sulfate mass on days of high relative humidity, as would be expected for a hygroscopic or deliquescent substance.

Having developed and fitted a model representing a decade of atmospheric events, it becomes possible to examine the likely long-run response of visibility in the Los Angeles basin to altered levels of particulate sulfates. It is estimated that the visibility impact of

reducing sulfates to a half or to a quarter of their measured historic values on each past day of record would be manifested most clearly in a reduction of the number of days per year of worse than three-mile visibility. The number of days of average visibility less than ten miles would be little affected. One reason for the disproportionate impact of the light scattering by sulfates on the days of the worst visibility is thought to result from a high positive correlation between sulfate mass loading and relative humidity. High values of light scattering per unit sulfate mass thus occur on days of high sulfate mass concentration.

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Postscript. This chapter was previously distributed as:

Cass, G. R. (1976), The Relationship Between Sulfate Air Quality and Visibility at Los Angeles, Pasadena, California, California Institute of Technology, Environmental Quality Laboratory Memorandum Number 18, August 1976.

Since that time, excerpts from the working papers referenced to White and Roberts (1975), and White, Roberts, and Friedlander (1975) have been published as:

White, W. H. and P. T. Roberts (1977), "On the Nature and Origins of Visibility-Reducing Aerosols in the Los Angeles Air Basin," Atmospheric Environment, Vol. 11, pp. 803-812.

Some of the results shown in that journal article differ from the results attributed to White and Roberts (1975) in this chapter because only the subset of their previous work was reprinted in which the intercept ( $\alpha$  in our regression equations) was suppressed. Either set of results may be referred to without material change in one's conclusions.

## CHAPTER 7

## PATHS TOWARD FUTURE RESEARCH

7.1 Introduction

Extensions of this research project can proceed along two general paths. First, tools developed in this study can be used to complete a public policy analysis of emission control strategy options. Secondly, the techniques developed for describing and modeling urban air quality problems may be further refined and improved. Points of departure along each of these paths will be suggested in turn.

7.2 Toward Improved Understanding of Airshed Physical Processes

Extension of the physical description of sulfate air quality problems developed in this study should proceed simultaneously by two mutually reinforcing routes. Physical measurement programs should be developed to relieve critical data deficiencies uncovered by this study. Development and testing of theoretical concepts also should be pursued in a way which makes further use of those data which already do exist.

Some of the most important data deficiencies facing a long-term average air quality study result from the short term nature of most special field measurement projects. Data on seasonal trends in sulfate background concentrations,  $\text{SO}_2$  oxidation rates in the atmosphere, and  $\text{SO}_2$  deposition velocity are virtually unavailable. Investigators with the skill to make such measurements should insist on obtaining a set of data which represents a year-round cycle. Sampling schedules should be sufficiently dense that narrow confidence

intervals will be obtained on such important statistics as the annual mean value of the phenomenon of interest.

Certain aspects of the routine monitoring networks which do supply year-round data also would benefit from systematic research. It should be clear by now that the attempt to use data obtained by three competitive air monitoring networks in the same locality within the same control strategy analysis has uncovered some serious problems with monitoring network design. While no one of these networks examined was without certain unique positive aspects, the sulfate and sulfur dioxide information system formed by the three networks operating concurrently could be improved greatly, possibly with a cost savings. Research into methods for coordinated design and operation of multiple air monitoring networks is needed.

Certain measurement technologies present prime candidates for further research. Since  $\text{SO}_2$  has been measurable for many years by many methods, one would possibly assume that  $\text{SO}_2$  concentration determination should be a dead issue. However, the analysis performed in this study shows that  $\text{SO}_2$  monitoring instruments as they are currently operated suffer large *percentage* errors in their results, that different monitoring techniques are in conflict as to ambient concentrations, and that the inability to closely specify  $\text{SO}_2$  concentrations is a serious handicap to control strategy formulation for sulfates. From the apparent erratic performance of the West-Gaeke  $\text{SO}_2$  method when placed in the field in Los Angeles, one suspects that the Federal reference method for  $\text{SO}_2$  will have to be revised.

If that is done, a researcher with a better method for  $\text{SO}_2$  determination would be in a position to make a substantial contribution to national air pollution control efforts.

Additional suggestions for research projects which would improve the ability of routine air monitoring networks to support visibility control strategy studies are given in Appendix D4 to this thesis.

In addition to improvement of current field measurement practices, there is room for a number of pioneering approaches to unsolved measurement problems. Important questions for chemical research include: What is the relative abundance of the individual chemical species which make up the complex that we have referred to as particulate sulfur oxides or sulfates? How can one measure the relative rates of heterogeneous versus homogeneous phase  $\text{SO}_2$  oxidation processes in an *open atmosphere*? Can those measurements lead to conclusions as to exactly which mechanisms are responsible for the bulk of the chemical conversion of  $\text{SO}_2$  in the atmosphere (as opposed to smog chambers)? Does that answer vary from place to place and from time to time? Coastal fogs have been shown to co-occur with serious Los Angeles sulfate episodes. Can the role of these fogs in the Los Angeles sulfate problem be placed on a quantitative rather than phenomenological basis through a clever experimental program?

Opportunities exist for valuable contributions by persons interested in field measurements of transport and dispersion.

Extension of puff and plume dispersion measurements over long downwind travel times is important if  $\sigma_y(t)$  is to be represented with reasonable accuracy over multi-day periods. It may even turn out that the concept of a Gaussian distribution of material about its centroid breaks down over very long travel times. Experimental determination of the distribution of air parcel retention times in the Los Angeles Basin would be of value. Validation of trajectory integration techniques used in air quality models could proceed if well defined data on instantaneous puff releases were available. Even more intriguing is the possibility that a long-term average physical (not mathematical) model for the airshed could be constructed based on the air quality simulation model derivation of Chapter 3. Sequential instantaneous SF<sub>6</sub> puff releases made at well-spaced periodic intervals from critical source locations, followed by automated integrated sampling at a grid-like network of receptor points could result in a direct estimate of source to receptor transport probabilities. Since the releases would be intermittent, the amount of SF<sub>6</sub> needed for a long-term study might be within the realm of economic reality when compared to the rather high cost of validating a mathematical air quality model applicable to very rough terrain. Assessment of especially complex transport situations, like the long-run impact of the Ormond Beach power plant located in Ventura County on Los Angeles air quality might well proceed by that means.

Statistical analysis of historic air quality data was shown to be a valuable technique for deducing the important physical

processes which must be incorporated within a successful sulfate air quality model for Los Angeles. Similar analyses should be performed in other geographic locations and for other pollutants. Great potential exists to expand the type and capability of data survey and screening techniques. Valuable contributions should be sought through the use of physical reasoning to improve the specification and structure of statistical models for air quality phenomena. An example of physical reasoning incorporated within the structure of a statistical model is found in the means for incorporating relative humidity effects within the non-linear visibility model of Chapter 6 to this study.

The air quality modeling approach of Chapter 3 of this study has considerable potential for improvement and adaptation to other problems. The dimensionality of that model can easily be increased to handle wind shear, trajectories computed from highly accurate wind fields, different averaging times, spatially inhomogeneous mixing depths over the airshed, changing atmospheric stability over time, finite vertical diffusion rates, and additional pollutant removal processes. A number of methods were identified in Chapter 5 for superimposing analytical solutions for the diffusion equation onto the simulation model in order to improve model accuracy within the first time step downwind of a source. The main barrier to these improvements is not technical knowledge, but rather the decision to pay for the added computing costs of a more realistic simulation. Therefore, research into the costs and benefits of increasing model capabilities should be pursued. A sensitivity study of model response

to simplifying assumptions would form a key part of that cost-benefit study.

The concept of computing long-term average source to receptor probabilities from Lagrangian marked particle statistics possesses great flexibility. In our application, each particle was tagged with magnitudes reflecting source emission strength, height of insertion into the atmosphere and chemical composition. There is no reason why the model could not be adapted to advecting marker particles labeled with certain moments of the aerosol size distribution function, or other pollutant properties of interest.

Several research questions are posed for those who seek to improve emissions inventory techniques. First, what battery of tests is appropriate for validating an emissions inventory? Can additional types of simulation models be developed, similar to our natural gas curtailment model of Appendix A2, Section A2.2.3, that will faithfully reproduce the behavior of area source classes whose members are too small to be inventoried individually (e.g., off-highway diesel vehicles)? Adaptation of energy and material balance techniques to support inventory estimates for pollutants other than  $SO_x$  would be valuable.

Emissions inventory compilation requires enormous expenditure of time and effort. Means should be found to streamline the process without sacrificing accuracy. Extremely valuable uses for emissions inventory by-product data bases also can be identified. For example, our emission inventory is accompanied by a parallel energy dissipation

inventory which is spatially and temporally resolved over the Los Angeles Basin. Such a data base could be used in thermal modeling studies. Traffic count data can be used to validate transportation models.

### 7.3 Toward Emission Control Strategy Analysis

One intended use of this research is to advance the public policy analysis of sulfate air quality control strategy options. A procedure for emission control strategy analysis was briefly outlined at the bottom of Figure 1.2. Emissions forecasts first would be made. The air quality simulation model results then could be used to specify likely pollutant concentrations in the absence of further emissions controls. A wide variety of possible emission control techniques next should be identified. The air quality model would be used to project the air quality improvement likely to result from application of each control strategy option. At the same time, both the cost of the control technique and any quantifiable benefits (e.g., increased visibility) resulting from the air quality improvement would be estimated. Then control strategy options, their costs and some benefits could be arrayed in a manner that permits decision-makers to choose an economically attractive path toward any desired level of air quality improvement. Information on likely benefits is made available at that time in order to assist selection of an appropriate air quality goal if no firm prior objective exists.

Development of methods for performing each of these necessary steps toward a completed set of emission control strategies presents opportunities for advances in both decision theory and current engineering practice. In order to pose research questions for control strategy synthesis in concrete terms, a hypothetical example will be worked which illustrates the procedure, the data requirements, and some key dilemmas facing the control strategy designer.

For the moment, we will by-pass the question of making emissions and air quality forecasts. Attention is turned to the problems associated with identifying control options and choosing among them. Assume that the future status of some airshed of interest has been characterized and found to resemble the South Coast Air Basin as it existed in 1973. We wish to define attractive control strategy paths based on then-current knowledge. To confine the example to manageable proportions, we will further limit ourselves to those stationary source emissions control strategy options previously identified by Hunter and Helgeson (1976). Following Hunter and Helgeson, it is assumed that each control measure listed provides proportionately the same removal efficiency for both  $\text{SO}_2$  and primary  $\text{SO}_4^-$  emissions as is expected for total  $\text{SO}_x$  (probably a poor assumption). It is further assumed that each emission control technique listed will be applied equally to all members of the source class for which it is specified. Each emission control option will be used continuously if adopted (i.e., we are not interested in emergency episode abatement but rather a proportionate reduction in  $\text{SO}_x$  emissions on each day of record).

Technological emission control options identified by Hunter and Helgeson (1976) are listed in Table 7.1. Annual average  $SO_x$  emissions for the year 1973 to which each control measure would apply were estimated from the on-grid plus off-grid portions of the emission inventory of Appendix A2 to this study. Emissions control removal efficiencies and control costs per ton of  $SO_x$  emissions are as calculated from Hunter and Helgeson's examples.<sup>1,2</sup> The incremental sulfate air quality improvement at downtown Los Angeles shown in Table 7.1 is that which would have been realized in 1973 if each candidate control strategy option had been installed and in operation in that

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<sup>1</sup>Costs given are for both recovery of capital investment and operation on an annual basis, stated in 1975-76 dollars. Control cost estimates given by Hunter and Helgeson (1976) were intended to represent actual "manufacturing costs" for each control technology in those cases where market price data were unavailable. These cost data are limited to Hunter and Helgeson's work because that study forms a single consistent set of cost estimates across a variety of South Coast Air Basin emission sources. They should not be interpreted as the only control measures available, nor are they necessarily the least costly.

<sup>2</sup>Fuel burning emissions sources have been observed to operate with a margin of safety below the maximum permissible level of emissions under past 0.5% sulfur in fuel regulations. When limited to 0.5% sulfur, utilities burned 0.45% sulfur residual oil while industry burned about 0.40% sulfur residual oil. Further tightening of fuel sulfur content limits will be viewed as generating similar percentage safety factor choices by fuel customers and fuel vendors. In constructing Table 7.1, each tightening of sulfur content in fuel regulations was assumed to generate a nominal percentage reduction in historic emissions levels in proportion to the nominal change in the maximum fuel sulfur content permitted, rather than strict conformance to the maximum permitted sulfur level. Hunter and Helgeson's cost estimation method per ton of  $SO_x$  emissions reduced was not similarly adjusted, which results in a slight distortion of control cost effectiveness estimates (within the error bounds on their data).

TABLE 7.1

Annual Cost and Sulfate Air Quality Impact of Stationary Source SO<sub>x</sub> Emissions Control Technologies if Applied to SO<sub>x</sub> Emissions in the South Coast Air Basin as They Existed in 1973  
(Control Techniques and Costs Identified by Hunter and Helgeson (1976);  
Air Quality Impact Estimated From Model Validation in Chapter 5 of This Report.)

Emission Control Strategy Option	SO <sub>x</sub> Emissions Control Effectiveness When Applied to 1973 Emissions Inventory			Incremental Cost of Emission Control Option (1975-76 Cost Basis)		Annual Mean Sulfate Air Quality Improvement at Downtown Los Angeles		Cost Effectiveness Index	
	Degree of Control	Emissions from Source Class to Which Control Measure Would Apply (tons/day)	Emissions from Source Class After Application of that Control Measure (tons/day)	Total Reduction in Annual Average Emissions (tons/day)	Dollars Per Ton SO <sub>x</sub> Removed (10 <sup>6</sup> Dollars)	Total Annual Cost (10 <sup>6</sup> Dollars)	µgm/m <sup>3</sup> SO <sub>4</sub> <sup>-2</sup> per ton/day Emission Reduction		Total Incremental Sulfate Reduction (µgm/m <sup>3</sup> )
<b>Electric Utility Residual Fuel Oil Desulfurization (a)</b>									
(a) Reduction in fuel sulfur limit from 0.5% S to 0.4% S	-20%	239.9	191.9	48.0	377 <sup>(b)</sup>	6.60	0.0138 <sup>(e,f)</sup>	0.662	100.3
(b) Further reduction from 0.4% S to 0.3% S	-25%	191.9	143.9	48.0	471 <sup>(b)</sup>	8.25	0.0138 <sup>(e,f)</sup>	0.662	80.2
(c) Further reduction from 0.3% S to 0.2% S	-33%	143.9	95.9	48.0	942 <sup>(b)</sup>	16.50	0.0138 <sup>(e,f)</sup>	0.662	40.1
(d) Further reduction from 0.2% S to 0.1% S	-50%	95.9	47.9	48.0	1695 <sup>(b)</sup>	29.70	0.0138 <sup>(e,f)</sup>	0.662	22.3
<b>Industrial Residual Fuel Oil Desulfurization (a)</b>									
(a) Reduction in fuel sulfur limit from 0.5% S to 0.4% S	-20%	8.3	6.6	1.7	377 <sup>(b)</sup>	0.23	0.0158 <sup>(f)</sup>	0.027	117.4
(b) Further reduction from 0.4% S to 0.3% S	-25%	6.6	5.0	1.6	471 <sup>(b)</sup>	0.28	0.0158 <sup>(f)</sup>	0.025	89.3
(c) Further reduction from 0.3% S to 0.2% S	-33%	5.0	3.3	1.7	942 <sup>(b)</sup>	0.58	0.0158 <sup>(f)</sup>	0.027	46.6
(d) Further reduction from 0.2% S to 0.1% S	-50%	3.3	1.7	1.6	1695 <sup>(b)</sup>	0.99	0.0158 <sup>(f)</sup>	0.025	25.2
Chemical Plant Emission Limit Met at 500 ppm SO <sub>2</sub> (or less) in exhaust (Rule 53.3)	-93%	80.0	5.5	74.5	235 <sup>(c)</sup>	6.39	0.0217 <sup>(f)</sup>	1.617	253.0
(a) Claus tail gas clean-up units applied to sulfur plants									
(b) Additional absorption units, demisters, or plant derating applied to H <sub>2</sub> SO <sub>4</sub> plants									
<b>Petroleum Refining and Production</b>									
(a) Caustic scrubber applied to refinery fluid catalytic crackers (FCC)	-95%	52.1	2.6	49.5	1144	20.67	0.0257 <sup>(d)</sup>	1.272	61.5
(b) Claus plant applied to oil field fire flooding operation exhaust	-90%	4.5	0.5	4.0	312	0.46	0.0257 <sup>(d)</sup>	0.103	223.9
Petroleum Coke Calcining Kiln Emissions Reduction Obtained From Scrubbing Coke Dust Prior to Combustion (g)	-80%	25.5	5.1	20.4	600	4.47	0.0165	0.337	75.4
<b>Steel Mill</b>									
(a) Desulfurization of coke oven gas	-90%	21.2	2.1	19.1	122	0.85	0.0024	0.046	54.1
(b) Scrubber applied to mill sinter plants	-80%	4.8	1.0	3.8	470	0.65	0.0024	0.009	13.8

## Notes

- (a) Middle distillate fuel oil desulfurization was not addressed by Hunter and Helgeson (1976) and thus will be excluded from this example.
- (b) The additional cost beyond 0.5% sulfur fuel was estimated by Hunter and Helgeson (1976) as \$0.12, \$0.27, \$0.57, and \$1.11 per barrel for fuel meeting 0.4% sulfur, 0.3% sulfur, 0.2% sulfur, and 0.1% sulfur rules respectively. Thus 0.3% sulfur fuel would cost (\$0.27 - \$0.12) = \$0.15 more per barrel than 0.4% sulfur fuel. See Chapter 7 footnotes 1 and 2 for additional information and assumptions.
- (c) No specific cost data for sulfuric acid plant control were given, but rules affecting both sulfur recovery and acid plants were adopted simultaneously and are assumed to be equally cost-effective.
- (d) The air quality impact shown is proportional to the petroleum processing source class as a whole. This source is physically distant from downtown Los Angeles and this may not have an impact at downtown Los Angeles which is proportionately as large as from the FCC units which dominate that source class. However, the cost effectiveness of controlling that source is so high that control strategy conclusions would be distorted little even if the air quality impact estimate were reduced several fold.
- (e) Based on emissions from both on-grid plus off-grid power plants located within the 1973 boundaries of the South Coast Air Basin. If only a subset of those power plants were to be considered for control, the impact per ton of SO<sub>x</sub> emissions reduced would be expected to vary depending on the group of generating stations chosen.
- (f) Annual mean air quality impacts are sensitive to the seasonal variation in SO<sub>x</sub> emissions. Thus these values are specific to years with a seasonal emissions pattern like that of 1973.
- (g) SO<sub>2</sub> reduction attributed to this technology seems to us to be a bit speculative. Other more costly alternatives, however, do exist with reasonable certainty.

year. That air quality impact estimate for each source class was obtained from the 1973 air quality model validation effort of Chapter 5, evaluated at downtown Los Angeles.<sup>3</sup>

The last column of Table 7.1 contains a measure of source emission control option effectiveness, in terms of sulfate concentration reduction at Los Angeles per dollar spent on  $SO_x$  control. If these control measures were to have been implemented in 1973 in order of declining cost effectiveness index, the progression of air quality improvement versus cumulative control cost would have been as shown by the upper curve of Figure 7.1.

The points along the upper curve of Figure 7.1 form one possible emission control strategy. Up to 97 million dollars per year could have been spent in 1973 on these control measures, with up to 43% improvement expected in average sulfate air quality at downtown Los Angeles. Maximum obtainable visibility improvement would have been somewhat less than that illustrated in Figure 6.8. A decision could have been made to operate at any point along the upper control strategy curve of Figure 7.1 with fairly predictable results.

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<sup>3</sup>The relative effectiveness of emissions controls applied to particular source classes would be somewhat different at different locations in the airshed. The relatively high impact of refinery FCC units per ton of  $SO_x$  emitted when compared to the steel mill is due mainly to the distant siting of the steel mill versus downtown Los Angeles rather than to any design attribute of either source type. The fact that a source contributes weakly to sulfate levels at downtown Los Angeles of course says nothing about its influence elsewhere in the airshed.

STATIONARY SOURCE EMISSION CONTROLS  
 IDENTIFIED BY HUNTER AND HELGESON (1976)  
 APPLIED TO SO<sub>x</sub> EMISSIONS SOURCES LOCATED  
 IN THE SOUTH COAST AIR BASIN  
 AS THEY EXISTED IN 1973

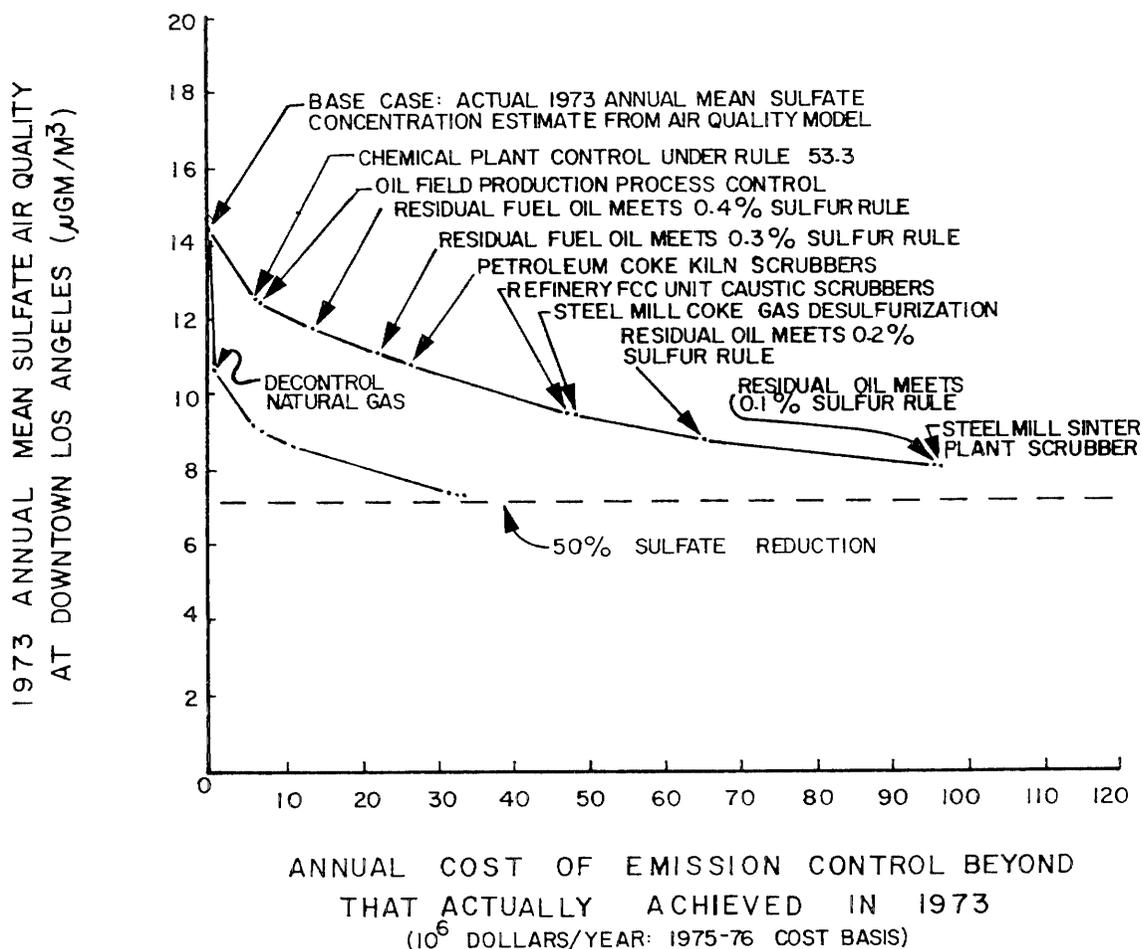


FIGURE 7.1

NOTE: This figure accompanies a sulfate air quality control strategy example calculation. It applies to conditions in that airshed as they existed in 1973. Further reductions in natural gas supply beyond the levels of service observed in 1973 will greatly increase the annual cost of the emissions control strategy pictured in the upper curve of this graph. Changes in assumptions about emissions control technology or clean fuel availability and price could significantly alter the cost effectiveness shown. This figure was constructed to illustrate the means by which the description of airshed physical processes developed in this study can be used almost immediately to formulate emission control strategies for sulfates in the South Coast Air Basin. It should not be interpreted as containing a control strategy recommendation. (Reproduction of this figure without this caption will not be authorized.)

A control strategy designer who identified the upper curve of Figure 7.1 as the least-cost means of obtaining a particular sulfate air quality improvement could have made a serious omission. An alternative emission control strategy could have been predicated upon releasing the institutional constraints which impede the free market allocation of clean fuels to those parts of the country with serious air quality problems.

For the past two decades, the Federal Power Commission (or its successor) has regulated the wellhead price of natural gas sold in interstate commerce. Natural gas sold within the state in which it was produced has remained free of Federal price controls. As prices for substitute fuels, such as residual oil, rose over the years, a two-tier pricing system developed. Controlled interstate gas sales were constrained to a price which was a small fraction of the energy content equivalent price of fuel oil, while intrastate gas prices followed oil prices upward.

The results of this two-tier price system were multi-fold. Many persons able to obtain price-controlled gas sought it solely because it was cheaper than oil. Demand was artificially stimulated. On the supply side, gas producers ceased to commit new gas reserves to the interstate market. The conflict between excess demand and decreased interstate supply lead to natural gas curtailments similar to those pictured in Figure 1.3 as old interstate supply contracts failed to be renewed or were otherwise voided. In areas like Los Angeles with serious air pollution problems, emission source

owners paid high prices for unusually high quality fuel oil to replace lost interstate natural gas supplies, and at the same time local pollutant emissions increased because no oil available today burns as cleanly as natural gas. Meanwhile, vast amounts of natural gas were committed to the intrastate markets in Texas and Louisiana at prices lower than oil but higher than the price ceiling on interstate natural gas sales. For a detailed account of the history and economic effects of FPC natural gas regulation efforts, see Breyer and Macavoy (1974).

If governmental policy makers were to rely on market forces to set the price of new natural gas sales to interruptible gas customers, an  $SO_x$  emissions control strategy for Los Angeles like that of the lower curve of Figure 7.1 might well be achievable. Natural gas substitution at a small cost<sup>4</sup> over that of existing fuel oil prices would

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<sup>4</sup>The actual free market price obtained as a result of deregulation of new gas sales to interruptible gas customers is, of course, uncertain. However, a large number of analysts, including the FPC's own staff (Seidel and Bryan, 1975) have contended that deregulated natural gas prices will not rise above the price currently paid for premium quality imported fuel oils. Considerable evidence lies behind that prediction. Free market natural gas sales in all available intrastate and international markets supplying the United States have consistently cleared at prices lower than that paid for 0.5% sulfur fuel oil on the West Coast (see Federal Energy Administration, 1973-1977). Even if natural gas prices rose above the intrastate market price in a fully competitive bidding environment, the group with the highest cost for substitutes other than natural gas still will be in a position to bid the most for gas supplies without experiencing a total cost increase. Los Angeles utilities currently pay among the nation's highest prices for fuel oil, and thus would be expected to fare well in an auction market for gas if motivated to do so. During the period of time around the year (continued)

eliminate the emissions from residual oil combustion. Then the remaining technological emissions controls of Table 7.1 directed at sources other than residual fuel oil combustion could be applied in sequence to achieve a 49% sulfate reduction at an annual cost of about 33.5 million dollars per year, with visibility benefits like those of Figure 6.8. This combination of technological controls and institutional changes is superior to a purely technological solution to the problem in two respects. It achieves a greater local air quality benefit at a far lower cost.<sup>5</sup>

By reference to the above example, many quite complex research needs can be identified.

It is clear that as the number of emissions control strategy options are expanded, the chance for an attractive combination of control measures can improve greatly. First, what methods can be devised for identifying greater numbers of existing control strategy options in a systematic manner? Technically, how does one cope with the flood of alternatives which must then be compared to one another? Some of these control options may be sufficiently complex that they

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<sup>4</sup> (continued)

1970, before price control induced shortages led to natural gas rationing, Los Angeles did choose to bid for natural gas instead of further desulfurizing fuel oil. They succeeded in that attempt while other regions of the country facing less dramatic pollution control problems chose less drastic approaches to emissions control.

<sup>5</sup> That strategy calculation also comes close to defining a possible future case since emissions forecasts for fuel oil are unnecessary if natural gas restoration occurs.

can only be understood if the control technology or approach is itself made the subject of a simulation model. Development of models for emission source modification should be pursued.

The control strategy design process should be adopted to assess apparent inefficiencies within the air basin that are prime candidates for innovative solutions which do not yet exist. Referring to Chapter 4, one can identify large numbers of source types for which no control measures have been found so far. From the control strategy example, several situations can be isolated in which control measures are available, but their cost-effectiveness is relatively unattractive. By quantifying the shape of the present least-cost paths to air quality improvement, one can identify those points along each curve where the law of diminishing returns begins to set in. At those points, a technological breakthrough should be sought which will cause one to transfer to another control strategy path. While no one could guarantee that such a breakthrough could be achieved, at least the search would focus on a place where the breakthrough would be adopted quickly if found.

The control strategy example given in Figure 7.1 was purely hypothetical. This is because it was constructed without reference to expected future conditions in the air basin. It would have been desirable to pursue the expected future case at that point, but technical advances in emissions forecasting should be developed first in order to support such an effort.

The track record with regard to forecasting  $SO_x$  emissions levels several years in advance in the Los Angeles Basin is not very impressive (for example, see Cass, 1976). APCD ten-year emissions forecasts presented in Figures 1.4 through 1.7 of this thesis were rendered obsolete within three years (even before this thesis could reach publication). Similar surprises have befallen every other previous local  $SO_x$  forecast known to this author. That situation results not from carelessness, but rather from the highly volatile nature of both emissions control policy and clean-fuel availability in the South Coast Air Basin. Development of techniques for making better emissions forecasts is needed if deliberate analysis is to contribute to public policy formation. That is because lead times for a deliberate solution are longer than the apparent half-life of most forecasts. By "better" forecasting techniques, one does not necessarily mean more "accurate" forecasts in the sense of being able to predict the unforeseeable, but rather forecasts which explicitly acknowledge and search for a range of likely outcomes. An energy and sulfur balance approach to making  $SO_x$  emissions projections benefits from many built-in physical checks and balances. Potentially large perturbations in emissions behavior may be explored in that manner without creating a physically impossible forecast. Techniques for making energy and sulfur balance style  $SO_x$  emissions forecasts should be developed and demonstrated. An empirical parameterization of the relationship between past emissions forecasts and eventual outcomes also might be useful in evaluating the confidence interval on a state of the art forecast system.

In Chapter 5, the sulfate air quality simulation model was validated against three years of historic sulfate air quality data. The measured meteorological and other input parameters used in that simulation exercise were appropriate to those validation years. When faced with making air quality forecasts, how does one choose an appropriate set of meteorological and other input data? One promising technique could result from the development of synthetic meteorological data which statistically resembled measurements made in the airshed of interest without representing any particular year. This would be particularly useful in airsheds where the measured record is too short to locate even the expected worst year in a decade. The meteorological data synthesizer could be used to generate many decades of sequences of probable weather patterns. Then the air quality model, operating on a selection of that data, could be used to assess both the most likely results of an emission control strategy option, and the frequency of control strategy failure to deliver expected results within some tolerance limit.

The natural gas deregulation example illustrates that a mix of institutional changes and technological control measures may be more effective than either approach pursued independently. What are the technical, economic and political properties of such mixed strategies? What other mixed strategies could be defined which incorporate taxation as an incentive to induce desired emissions reductions?

The control strategy design example given above illustrated two alternate paths to a roughly equal emissions reduction. In

principle, many such alternate paths should be defined. History shows that no single path will be adhered to over great lengths of time. How can an air quality strategist systematically identify combinations of technologies which preserve the flexibility of decision-makers to alter their course without rendering large prior capital investments prematurely obsolete?

The existence of a large number of potentially attractive, but possibly mutually exclusive, approaches to emissions control raises serious questions about the methods available to assist choices among those alternatives. A cost-minimizing decision-maker might well feel comfortable with one of the two strategies defined in our example. But as the possible objectives of the emission control program expand beyond the question of least total cost for an air quality improvement, the entire picture can become quite muddled. The simultaneous existence of important questions concerning who pays the related control costs, combined with a variety of pollutant reduction benefits which are not reducible to a common measure (e.g., improved visibility, and reduced materials damage and reduced health effects) leads quickly to two questions. How can one better define the nature of those cost distributions and benefits, and what methods can be used to sharpen choices between increased costs accompanied by packages of incommensurable benefits? Additional health and welfare effect studies are clearly useful if that information can be obtained at an acceptable cost. Demonstration of multi-objective mathematical programming techniques applied to air quality problems

should be attempted. A fully deterministic means for resolving the final choice between control strategy alternatives does not exist. But practical methods may be developed to isolate those options which are Pareto-superior.

In conclusion, it can be seen that the ability to characterize an air pollution problem as was done in this study will probably lead to questions which are made more difficult (in the short run) in the presence of good physical information than would seem to be the case without it. Conventional approaches taken in the past may seem ill-advised in the presence of the ability to generate many good answers to previously intractable problems. Air pollution control strategy development is truly a design process with an open-ended rather than unique outcome. The objective of the design process is to generate many new opportunities while at the same time advancing and testing the state of the description of physical principles. As the multiplicity of possible control strategy options increases, the chances for an acceptable outcome to the design process increases, but the decision as to which option to select may become more difficult.

## CHAPTER 8

## SUMMARY AND CONCLUSIONS

8.1 Overview

The objective of this study has been to develop the technical understanding needed for sulfate air quality control strategy design. A general approach to air pollution control strategy design was described in which mathematical models verified against historical environmental data are used to define the likely costs and effects of sulfur oxides emission control alternatives.

A new type of long-run average emissions to air quality model was derived which computes pollutant concentrations from Lagrangian marked particle statistics based on the time sequence of measured wind speed, wind direction, and inversion base motion. Physical assumptions drawn from analysis of existing air quality and meteorological data were used to adapt this model to a specific application -- sulfate air quality prediction in Los Angeles. An energy and sulfur balance on the fate of energy resources containing sulfur was developed to test the consistency of a sulfur oxides emissions inventory for that air basin. Then material balance arguments were used to trace sulfur flows within that regional energy economy through the air quality model which also conserves sulfur mass. Sulfate air quality model predictions were compared to historical observations over the years 1972 through 1974. The sulfate air quality impact of individual emission source classes was estimated at a large number of air monitoring sites.

A hybrid theoretical-empirical model was constructed which explains the relationship between sulfate air quality and prevailing visibility

at Los Angeles. An estimate was made of the visibility improvement which would have accrued if Los Angeles sulfate concentrations were reduced by 50 percent on each past day of record. Then two emissions control strategy example calculations were performed to illustrate the means by which the air quality model results could be used to evaluate the cost of attaining such an air quality improvement.

One self-imposed constraint on this project was that the data employed be of the type available from air pollution control agency historical data banks and other public records. The result is that while the procedures developed were tested in Los Angeles, the data base required is available in kind (if not in such quantity) throughout the United States. With relatively minor modifications, analytical techniques developed in this study could have general application to a wide variety of air pollution control strategy studies, both for sulfates and for other selected contaminants.

## 8.2 Conclusions

### 8.2.1 Characterization of Los Angeles Sulfate Air Quality

Los Angeles forms an ideal location for sulfate air quality model development.

- It possesses a long term historic sulfate air quality data base.
- From those data it can be shown that the Los Angeles atmosphere is enriched in sulfates due to local emission sources. Annual mean sulfate concentrations above  $14 \mu\text{g}/\text{m}^3$  were measured over central Los Angeles County at a time when background concentrations in incoming marine or desert air averaged 3 to  $4 \mu\text{g}/\text{m}^3$ .

In contrast to the problems arising from long distance transport of sulfates in the eastern United States, a sulfate air quality model employing only local  $\text{SO}_x$  emissions data could be validated in the Los Angeles Basin.

Seasonal trends in sulfate air quality are similar throughout the South Coast Air Basin which surrounds Los Angeles.

- A broad summer seasonal peak in sulfate concentration occurs in all years of record, with clusters of high values in only two of nine winters examined.
- Long-term average spatial gradients in Los Angeles sulfate air quality are small.
- Simultaneous 24-hour average sulfate concentration measurements taken at widely separated monitoring sites are highly correlated.

In the Los Angeles area, temporal trends in sulfate air quality are far more pronounced than average spatial gradients. When constructing an air quality model which must explain the dynamic nature of Los Angeles sulfate air quality, concentration predictions made in time series should be emphasized.

The ability of available field data to verify time series air quality predictions was investigated statistically. From analysis of measurement errors and sampling frequency it was found that sulfate air quality predictions made over monthly and longer averaging times could be closely verified. Therefore, an air quality model for monthly average sulfate concentrations was sought.

Sulfate concentration changes from day to day are driven mainly by factors affecting the rate of  $\text{SO}_2$  oxidation to form sulfates, and by

changes in the effective mixing volume of the air basin. From analysis of pollutant concentration data and meteorological variables it was found that:

- Afternoon inversion base height determines the extent of vertical dilution for sulfates within this airshed.
- Changes in scalar average wind speed are uncorrelated with changes in sulfate concentrations, indicating that a successful air quality model should employ vector-valued wind data.
- Air parcel retention time within the air basin seems to be more important to explaining sulfate concentrations than is initial dilution at the source
- An air parcel trajectory integration time of two days would be needed to insure that 95 percent of the air parcels of that age are advected to beyond the borders of a 50 by 50 mile square modeling area laid over central Los Angeles and Orange Counties.

An air quality model is needed which can compute long term average sulfate concentrations from the time series of wind vectors and inversion base motion. Special attention must be paid to integrating the transport equations long enough that pollutants held over from the previous day are entered into the concentration predictions.

A mass balance on the fate of sulfur oxides emissions in Los Angeles conducted by Roberts (1975) shows that:

- Emissions of both primary sulfates and  $\text{SO}_2$  must be considered.
- Ground level deposition of sulfur oxides is a significant removal mechanism.
- The atmospheric oxidation of  $\text{SO}_2$  to form sulfates must be modeled in order to account for total observed sulfate concentrations.

In order to select a chemical modeling approach, atmospheric sulfur oxides air chemistry first was reviewed, then sulfate concentration changes from day to day were compared to fluctuations in the other observable components of the likely chemical oxidation processes.

- Sulfate concentration changes closely track changes in relative humidity and total suspended particulate levels, with intrusion of fog on days of very high sulfate concentration. This suggests that heterogeneous oxidation of  $\text{SO}_2$  on or within wetted particles is important to days of high sulfate concentration in Los Angeles.
- Sulfate concentrations are significantly higher on days of elevated oxidant concentrations. Thus a variety of homogeneous gas-phase sulfate formation mechanisms may also be important.

Sulfate concentrations increase with increases in all of the major observable components of all of the likely  $\text{SO}_2$  oxidation mechanisms.

In light of the complexity of the details of these competitive chemical reactions, it was decided that chemical conversion of  $\text{SO}_2$  to form sulfates should be modeled as a slow pseudo-first order overall reaction within the range of existing experimental data on the rate of  $\text{SO}_2$  oxidation in the Los Angeles atmosphere.

### 8.2.2 Air Quality Model Development

Existing long-term average air quality models lack the ability to reproduce those conditions most important to sulfate air quality in a coastal region like Los Angeles. Pseudo-steady state models which employ a joint frequency distribution of wind speed, wind direction and atmospheric stability have no hope of correctly computing air parcel retention time in an air basin characterized by a daily sea breeze/

land breeze reversal in wind direction. That is because those models contain no information about the serial correlation of the wind vectors.

Therefore a new type of simulation model was derived for directly calculating long-run average sulfate air quality under unsteady meteorological conditions. The model computes pollutant concentrations from long-run average source to receptor transport and reaction probabilities. These transport and reaction probabilities were in turn estimated from Lagrangian marked particle statistics based on the time sequence of historical measured wind speed, wind direction, and inversion base height motion within the airshed of interest. First order chemical reactions and pollutant dry deposition were incorporated. The model was adapted to a multiple source urban setting in a way which permits retention of the air quality impact of each source class contributing to air quality predictions at each receptor site.

Potential sources of error in this model as well as the most advanced trajectory models in use today include:

- Neglect of the vertical component of the wind.
- Neglect of wind shear.

These problems can be overcome mathematically in our model at an increase in computing cost. However, lack of appropriate measurements on winds aloft prevents incorporation of these improvements at present.

The long-run average Lagrangian marked particle air quality model has several particular merits:

- The model need not compute concentration averages from a real-time sequence of events. The order of integration over air parcel

release and transport may be arranged to minimize computing time and intermediate data storage requirements.

- The calculations are very simple and completely stable over time.
- There are no artificial diffusion problems associated with the transport scheme employed.
- Pollutant mass is completely conserved.
- The model builds its own initial conditions by integrating backward to connect all locally-emitted air parcels in the airshed at a given time to their source.
- Air parcels advected beyond the edges of the receptor grid are not lost to the system. Their position is remembered but their magnitude is not accumulated to a receptor cell unless the air parcel is advected back into the region of interest.
- Receptor cells may be specified only over those areas where concentration estimates are desired.

When adapting the air quality model for use in Los Angeles, the following approximations were made as a practical consideration aimed at conserving available computing resources:

- That inversion base height above ground level over the central Los Angeles Basin is spatially homogeneous at any given time.
- That inversion base motion over time may be represented by a stylized diurnal cycle which passes through the known daily maximum and minimum inversion base heights.
- That at any single time, the wind field over our study area may be approximated as a uniform parallel flow.

The first and third approximations above result in a huge savings in computing time by permitting the separation of trajectory and chemical

calculations from detailed dependence on a given starting location in the airshed. Model validation results presented in Chapter 5 indicate that these approximations typically do not lead to errors in sulfate concentration predictions which would exceed the error bounds on the field air quality observations against which the model was tested.

### 8.2.3 An Energy and Sulfur Balance on the South Coast Air Basin

In order to test our modeling approach, a spatially resolved sulfur oxides emissions inventory was constructed for the South Coast Air Basin. Emissions estimates were developed for 26 classes of mobile and stationary sources for each month of the years 1972 through 1974. During 1973, for example,

- $\text{SO}_x$  emissions within that modeling inventory totaled nearly 531 tons per average day.
  - Over 80 percent of that  $\text{SO}_x$  emissions inventory was concentrated in a small number of point source classes: electric utility generating plants, refinery fluid catalytic crackers, chemical plants recovering sulfur and sulfuric acid from refinery wastes, one local steel mill, and petroleum coke calcining kilns.
  - All other stationary sources combined total only 6 percent of the modeling emissions inventory.
  - Mobile sources account for the remaining  $\text{SO}_x$  emissions surveyed.
- Small distributed area sources lying outside of Los Angeles and Orange Counties were neglected for air quality modeling purposes.

Techniques were developed and tested for performing both energy balance and sulfur balance calculations on flows of energy resources

containing sulfur throughout the economy of the airshed of interest.

This approach provides five valuable functions.

- It serves as a nearly independent check on the detailed modeling emissions inventory. A formal methodology for validating an  $SO_x$  emissions inventory has been demonstrated.
- It establishes the true current emissions control strategy in the airshed by showing those points in the system where sulfur is captured or segregated into products which will not lead to pollutant emissions. That is important because emissions control may be occurring in ways not obvious from reading local emissions control regulations.
- It connects pollutant emissions to energy flows in a way that control strategy questions involving fuel or process substitution can be addressed.
- By forcing the emissions inventory to be energy consistent, prospects for making plausible emissions forecasts are improved.
- By examining the fate of anthropogenic sulfur prevented from entering the atmosphere, it extends the description of the global sulfur cycle as described by Friend (1973) or Robinson and Robbins (1968).

A material balance on sulfur supplied within energy resources entering the South Coast Air Basin in 1973 shows that:

- Virtually all of the sulfur entering the air basin in that year arrived in a barrel of crude oil.
- Nearly 50 percent of the sulfur arriving was recovered at the refinery level as elemental sulfur or sulfuric acid.

- Approximately 25% of the sulfur was segregated into products like petroleum coke, asphalt and exported high sulfur fuel oil which would not be burned locally.
- 4.4% of the sulfur supply found its way into solid or liquid wastes.
- At least 14% of the sulfur was emitted to the atmosphere.
- The fate of 9.4% of the sulfur supply was undetermined. Over 70% of that sulfur imbalance was due to small percentage differences between two independent estimates of total sulfur supplied in crude oil versus total sulfur reported processed by refiners. This discrepancy would not lead to a significant change in atmospheric  $SO_x$  emissions estimates.

The air quality modeling emission inventory was confirmed to be within about 10% of the atmospheric emissions identified by the sulfur balance. It was further demonstrated that the Los Angeles Basin in 1973 was already achieving greater than 80% overall control of its potential  $SO_x$  emissions. Any future emission control measures adopted must be consistent with maintaining control over all of the sulfur which could get into the air rather than just that portion which currently does become airborne.

#### 8.2.4 Results of the Air Quality Simulation Model

The air quality dispersion model was applied to simulation of Los Angeles sulfate air quality over each month of the years 1972 through 1974. Model results closely reproduced observed sulfate concentration patterns within the central portion of the Los Angeles Basin, particularly during the years 1972 and 1973. The correlation between

observed and predicted sulfate levels is 0.82 in both 1972 and 1973, and rises to 0.89 in 1972 if two biased observations are discarded.

An appropriate test of air quality model performance is whether or not model predictions are statistically indistinguishable from the air quality observations.

- Approximately 80% of the sulfate concentration predictions at LAAPCD air monitoring stations are within the error bounds on the ambient monitoring results.
- Model predictions track observed sulfate levels closely at the critical CHES stations in the eastern San Gabriel Valley at Glendora and West Covina.
- A tendency to underpredict the summer peaks observed near the up-coast and down-coast edges of our study area at Santa Monica and at Garden Grove and Anaheim during 1973 and 1974 was noted.

A seasonal variation in the overall rate of  $\text{SO}_2$  oxidation in the Los Angeles atmosphere was inferred from simultaneous comparison of observations and model predictions at a large number of monitoring sites.

- Monthly mean  $\text{SO}_2$  oxidation rates of between 0.5% per hour and 3% per hour prevail from October through February of our test years.
- During late spring, summer, and early fall,  $\text{SO}_2$  oxidation rates were estimated to jump to an average of about 6% per hour, with individual months ranging  $\pm 2\%$  per hour about that mean value.

Those numerical results must be qualified since a better understanding of seasonal trends in background sulfate concentrations or  $\text{SO}_2$  deposition velocity could alter the outcome somewhat.<sup>1</sup>

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<sup>1</sup>For a sensitivity study of conversion rate calculation dependence on other airshed parameters, see Roberts (1975).

One striking feature of Los Angeles sulfate air quality is that average horizontal concentration gradients are rather small in spite of the highly localized nature of major  $\text{SO}_x$  emission sources. Air quality model results showing individual source class contributions to observed sulfate air quality help to explain this phenomenon. In winter months with a pronounced daily sea breeze/land breeze wind reversal, air parcel trajectories wander widely over the basin. Sulfur oxides emitted from all source classes are dispersed widely within the airshed by the rotation of the wind vectors. In contrast, during mid-summer, onshore flow persists for most of the day. However, the sequential siting of major  $\text{SO}_x$  sources along the coast means that the central portion of the air basin is downwind of one major source group or another at most times. Lateral dispersion of emissions is just about sufficient to balance sulfate formation, with the result that upwind/downwind pollutant gradients are rather small in spite of the direct inland transport from sources to receptors. Annual mean sulfate concentrations are further smoothed by seasonal transport cycles in which peak sulfate concentrations appeared far inland during the summer and near the coast during the winter.

In January 1972, extreme resultant wind stagnation occurred during a period of high  $\text{SO}_x$  emissions. The highest localized sulfate concentration predictions for any month of our three year period occurred at that time. While such extended stagnation is unusual, the fact that it can occur means that sulfate air quality control strategy design must consider avoidance of wintertime as well as summertime pollution episodes in Los Angeles.

Source class increments to predicted sulfate air quality were examined in time series at each air monitoring station. It was found

that three to five source classes of roughly equal impact, plus background sulfates, must be considered simultaneously in order to come close to explaining sulfate levels observed at most locations. For example, during the year 1973 at downtown Los Angeles, contributors to the annual mean sulfate concentrations observed were estimated to be:

- Background sulfates - 28%
- Electric utility generating stations - 23%
- Heavy duty mobile sources - 15%
- Sulfur recovery and sulfuric acid plants - 12%
- Petroleum refining and production - 11%
- Autos and light trucks - 4%
- Petroleum coke calcining kilns - 3%
- All remaining sources - 4%

The relative importance of particular source classes varies from one monitoring site to another, but no single source class clearly dominates the observed sulfate concentrations. The implication is that a mixed strategy targeted at a combination of source types will be needed if significant sulfate air quality improvements are to be achieved in this airshed through precursor  $SO_x$  control.

#### 8.2.5 The Relationship Between Sulfate Air Quality and Visibility

Techniques were developed for analysis of the long-run impact of pollutant concentrations on visibility at downtown Los Angeles. Existing statistical models which use particle chemical composition as a key to particle size and solubility were reviewed. An analysis of vapor pressure lowering over solutions of electrolytes was used to add structure to these models so that the relative humidity dependence of light

scattering by hygroscopic aerosols could be represented in a more physically realistic manner. Light absorption by  $\text{NO}_2$  was added to the analysis. Coefficients were fit to the model based on air pollution control agency routine air monitoring data taken at downtown Los Angeles over the decade 1965 through 1974. It was found that:

- The principal contributors to visibility reduction at downtown Los Angeles include sulfates and oxides of nitrogen ( $\text{NO}_2$  and nitrates).
- There is a pronounced increase in light scattering per unit sulfate solute mass on days of high relative humidity, as would be expected for a hygroscopic or deliquescent substance. Light extinction by SULFATES was quantified as  $0.107 (1-\text{RH})^{-0.53} (10^4 \text{m})^{-1}$  per  $\mu\text{gm}/\text{m}^3$ , where RH stands for relative humidity in (%/100) and SULFATES is taken as 1.3 times the measured  $\text{SO}_4^{2-}$  concentration in order to account for the mass of associated cations.
- That functional relationship between light extinction by sulfates and relative humidity was compared to theoretical calculations for light scattering by ammonium sulfate aerosols. Our results were found to be similar in shape but slightly higher than the theoretical calculation would indicate.

These small differences between theory and analysis of Los Angeles observations may be due to the deviation of an actual human observer's visual acuteness from that assumed by Koschmieder.

Having developed and fitted a model representing a decade of atmospheric events, it becomes possible to examine the likely long-run response of visibility in the Los Angeles basin to altered levels of particulate sulfates. It was estimated that the visibility impact of

reducing sulfates to a half or to a quarter of their measured historic values on each past day of record would be manifested most clearly in a reduction of the number of days per year with average visibility less than three miles. For example, a 75 percent reduction in sulfate levels on a daily basis would have reduced the number of days with worse than three-mile visibility by about two-thirds, while improvement in the number of days of average visibility greater than ten miles would be much smaller, about 10 percent.

#### 8.2.6 Toward Emission Control Strategy Analysis

The results of the air quality and visibility models can be used to evaluate sulfate air quality control strategy options. Example calculations worked for the year 1973 show that a 43% reduction in annual mean sulfate concentrations at downtown Los Angeles could have been achieved in that year through application of the SO<sub>x</sub> emission control technologies suggested by Hunter and Helgeson (1976). A second strategy predicated in part on deregulation of the price and availability of new natural gas supplies to industry could have achieved about a 49% decrease in sulfate concentrations in 1973 at lower cost than a purely technological solution to the Los Angeles sulfate problem.

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- (2) "Sulfur Balance - Los Angeles County Refineries - 1974"
- (3) "Sulfur Recovery and Sulfuric Acid Plant Operations - Los Angeles County - 1973"
- (4) "Sulfur Recovery and Sulfuric Acid Plant Operations - Los Angeles County - 1974"

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