

APPENDIX B

APPENDICES TO THE
BASELINE AIR QUALITY CHARACTERIZATION

APPENDIX B1

ROUTINE AIR MONITORING PROGRAMS FOR SULFUR DIOXIDE AND SULFATES

B1.1 The Los Angeles Air Pollution Control District Air Monitoring Program: 1965-1974

Total suspended particulate matter samples have been collected by the Los Angeles Air Pollution Control District by high volume sampling on a regular basis since August 1965. The sampling period was twenty-four hours in duration, at a sample flow rate of 990 to 1270 liters/min (35 to 45 cfm). Samples were collected on glass fiber filters from which water-soluble sulfates were determined by the turbidimetric method. From August 1965 through August 1970, samples were taken from 8:00 a.m. to 8:00 a.m. at intervals ranging from weekly to twice weekly to every fifth day. From September 1970 through the end of 1974, samples were taken from midnight to midnight at least at five day intervals, with a strict five-day sampling schedule prevailing from July 1971 until the end of 1974.

Figure 2.3 in the body of this report shows the location of eight Los Angeles County sulfate air monitoring stations in existence at the end of 1974. The stations at downtown Los Angeles, West Los Angeles, and Lennox have been operated at the same location since August 1965. Sampling commenced at Reseda in late 1967, and at Pasadena and Azusa in July 1971. In January 1974, a monitoring station was added at Lynwood. The APCD also sampled for sulfates at one desert location, Lancaster, outside of the South Coast Air Basin.

Filter type is an important consideration when sampling for sulfates. It has been reported that several percent of the sulfate collected using glass fiber filters may be due to sulfur dioxide gas converted to sulfates on the surface of the filters (Lee and Wagman, 1966). A change in filter type could affect sulfate concentration measurements by altering the extent of this artifact sulfate formation. From 1965 through early 1967, APCD samples were collected on a variety of filter types: MSA 1106 BH; Gelman E, and Gelman A glass fiber filters. From late 1967 through 1974, all samples were reported to be collected on Gelman A filters. The Los Angeles APCD laboratory procedures followed the standard Public Health Service turbidimetric method (U.S. Public Health Service, 1962). Filters are quartered, and water-soluble sulfates are extracted by refluxing the quarter-filter in deionized water for one-and-one-half hours. Sulfate then is precipitated with barium ion in a dilute hydrochloric acid-glycerine-alcohol solution. Light attenuation through the turbid suspension thus formed is measured with a spectrophotometer at a wavelength of 500 nm. Sulfate concentration then is determined by reference to a calibration chart constructed from analysis of known sodium sulfate standard solutions. A quality control study of the accuracy and precision of sulfate measurements made by the LAAPCD laboratories was conducted by Porter et al. (1976). They report an accuracy (coefficient of variation expressed as a percentage) of turbidimetric method sulfate determination made from reference filter strips which averages 11% of the sulfate level being measured, and a precision on standard solutions of

11.8%. The APCD sulfate sampling program is described further by Wadley and MacPhee (1976).

Sulfur dioxide samples also were taken by the LAAPCD at each of their sulfate air monitoring locations.¹ Continuous monitoring instruments employing the conductometric method are used (Thomas, Ivie, and Fitt, 1946). Sulfur dioxide is reacted with an absorbing reagent of hydrogen peroxide (0.003M) and sulfuric acid (0.00005 N) in deionized water. The absorbed sulfur dioxide is oxidized to sulfuric acid, and the increase in conductivity of the solution is measured. Calibration is performed under both static and dynamic conditions. Static calibration involves addition of known amounts of sulfuric acid to the reagent, while dynamic calibration involves simultaneous sampling of sulfur dioxide - air mixtures by both the conductometric and West-Gaeke (1956) methods.

Normal SO₂ instrument range is 0 to 5 ppm on a linear scale. Instrument response is recorded on a continuous strip chart which is later read by a data entry technician and transferred to digital form as an average SO₂ concentration for each hour. The minimum SO₂ concentration discernible on these strip charts is 0.01 ppm (26 µgm/m³). All SO₂ concentrations below that value also would be reported as 0.01 ppm. At the low SO₂ concentrations present in some portions of Los Angeles County, the APCD instruments encounter concentrations at

¹ Sulfur dioxide is also monitored at some locations not equipped for sulfate sampling.

or below their minimum detection limit much of the time. Twenty-four hour averages constructed on days at which the SO₂ instruments measured concentrations below their minimum detection limit thus would be biased high.

B1.2 The Community Health and Environmental Surveillance System (CHESS) Air Monitoring Program: 1972-1974

As part of an effort to assess the health effects of air pollutants in Los Angeles smog, the U.S. Environmental Protection Agency established a series of air monitoring stations in seven Southern California communities in early 1972. These CHESS station locations are shown in Figure 2.3 in the main body of this report.

Total suspended particulate matter samples were collected daily by high volume sampling. The sampling period was twenty-four hours in duration at a sample flow rate of 1130 to 1700 liters/min (40 to 60 cfm). Samples were collected on Gelman A glass fiber filters. Monitoring stations were operated by contractors. Each twenty-four hour sampling period nominally began at 11:00 a.m. daily. The actual time of sample change at a given station may have been as early as 8:00 a.m. or as late as 1:00 p.m. (personal communication, Duckworth, 1976). Sulfate sampling commenced at Vista, Glendora and Anaheim in late January 1972. The sulfate data base at the remaining CHESS air monitoring stations began in early May 1972.

The intended sulfate analysis throughout the sampling program followed the automated methylthymol blue procedure (see Barnard et al., 1976). A strip cut from each filter is refluxed in distilled water,

and the resulting extract is passed through a cation-exchange column to remove interferences. The sample is then reacted with a solution containing barium chloride and methylthymol blue at a known concentration. Sulfate present reacts to form barium sulfate. Excess barium then reacts with the methylthymol blue to form a chelate. The amount of dye remaining is dependent on the amount of barium previously removed as barium sulfate, and provides a means of assessing the amount of sulfate initially present in the solution. Colorimetric measurements are made using a Technion Autoanalyzer. Barnard et al. (1976) state that "The precision and accuracy (of this method) depends upon the region of the absorbance vs. concentration curve in which work is being done."

While the intended laboratory procedures were the same over the period 1972 through 1974, the actual laboratory performing the analyses was changed a number of times. In a retrospective study of laboratory performance, it was found that sulfate analyses reported from October 1972 through May 1974 were probably in error (Heiderscheit and Hertz, 1977). Collaborative reanalysis of more than two hundred archived filters by three different laboratories indicated that the October 1972 through May 1974 sulfate values originally reported should be multiplied by 1.51 in order to match the results of the filter reanalysis. This correction factor was found to be independent of sulfate concentration. In spite of this scale correction, the originally reported October 1972 through May 1974 CHESS sulfate data correlated only 0.86 with the results of the filter reanalysis. CHESS sulfate

data reported during that period of time may be less accurate and precise than normally would result from the sampling procedures intended.

Explicit determination of the accuracy and precision of sulfate measurements made by the CHES network is unreported. However, given the known laboratory problems, it is likely that sampling errors were larger than would normally be expected from the methods employed. Therefore, a study was conducted as part of this research project in an attempt to set a bound on CHES sulfate sampling accuracy.

The Anaheim and Garden Grove CHES monitoring sites are located less than two miles apart. That distance is less than the characteristic dimensions of the grid system to be used in our forthcoming air quality modeling study. Thus these two monitoring locations could have been represented by a single sulfate air quality prediction (if desired) when establishing our modeling grid network. Given the close proximity of these two monitoring sites, and the fact that sulfate concentration gradients are observed to be rather uniform over the South Coast Air Basin, the working hypothesis was adopted that simultaneous sulfate samples taken at Garden Grove and Anaheim could be thought to represent two independent attempts to measure the same event by the CHES standard operating procedure. The coefficient of variation (standard error divided by mean concentration) was determined within each pair of samples representing 830 days of record during 1972 through 1974. The average coefficient of variation was 0.254 (25.4 percent), with highest coefficient of variation in the range

below $5 \mu\text{gm}/\text{m}^3$ and generally lower coefficients of variation above $10 \mu\text{gm}/\text{m}^3$. This compares to an average accuracy of 3.9 percent on reference filter strips and precision of 1.8 percent on standard solutions obtained using the methythymol blue method at the Southern California APCD laboratories (Porter et al., 1976). That is hardly an exact comparison because the CHES stations are not located immediately adjacent to each other, and the coefficient of variation for the CHES data is wrapped around both sample collection, handling, analysis and data reduction, while the APCD measurement errors represent laboratory performance only. Nevertheless, the scatter introduced into individual CHES samples by measurement errors is higher than usually expected. It will be seen in Appendix B4 that this problem was compensated for by the relatively dense (daily) CHES sampling schedule, and that the CHES data are still a useful resource for comparison to monthly mean sulfate predictions as long as the filter reanalysis reported by Heiderscheit and Hertz (1977) succeeded in removing any systematic bias to the mean.

Twenty-four hour average sulfur dioxide measurements also were taken at the same time and locations as the CHES sulfate samples. A procedure similar to the West-Gaeke method was used (West and Gaeke, 1956; see also Barnard et al. (1976) and Benson et al. (1974) for description of CHES modifications). Air containing sulfur dioxide is bubbled through a tetrachloromercurate (TCM) solution to form a solution of dichlorosulfitomercurate. The exposed absorbing reagent is then removed from the bubbler box at the sampling station and sent

to a laboratory for further processing. The dichlorosulfitomercurate ion is subject to slow decomposition. Thus control of the time-temperature history of samples from collection through laboratory processing is important. If proper sample handling procedures are not maintained, a loss of SO_2 is apparent and reported SO_2 values could be below the actual ambient concentrations.

At the laboratory, the exposed absorbing reagent is reacted with formaldehyde and acid-bleached pararosaniline hydrochloride to form a solution the color of which is dependent on the amount of sulfur dioxide collected. Until October 1972, colorimetric determinations were made by manual methods. After that date, a Technicon Autoanalyzer was used for this purpose. From January 1972 through the end of 1973, samples were collected in 35 ml of absorbing TCM solution at an air flow rate of 500 ml/min. It was reported that this solution volume and flow rate combination implies a combined sampling and analysis error of ± 10 percent at SO_2 concentrations below $26 \mu\text{g}/\text{m}^3$, with improved accuracy above $26 \mu\text{g}/\text{m}^3$ (Benson, et al., 1974, Appendix A). Later publications from the CHESS program (Barnard, et al., 1976) disclaim any great accuracy below $25 \mu\text{g}/\text{m}^3$. They state that while instrument response may be recorded as low as $4 \mu\text{g}/\text{m}^3$, sample values below $25 \mu\text{g}/\text{m}^3$ must be viewed as below minimum detection limits unless sample collection efficiency at very low concentrations has been established. In December 1973, SO_2 sampling commenced using a reduction in air flow rate to 200 ml/min and an increase in absorbing solution volume to 50 ml per sample. This change in sample volume and

air flow rate might affect SO₂ collection efficiency at the low SO₂ concentrations encountered in Los Angeles. Minimum detection limits might also have been affected.

CHESS sampling methods are further described by Benson et al. (1974, see their Appendix A). and by Barnard et al. (1976).

B1.3 The National Air Surveillance Network (NASN) Air Monitoring Program: 1972-1974

Total suspended particulate samples have been collected by the National Air Surveillance Network by high volume sampling at locations in Southern California since the mid-1950's. Monitoring stations active during the period 1972 through 1974 are shown in Figure 2.3 in the main body of this report. With one exception, a three year record of sulfate monitoring data can be obtained at each of these NASN locations for the period 1972 through 1974. Sulfate data at Riverside seem unavailable for the years 1973 and 1974.

During the three years of interest to us, NASN stations were operated by volunteers on about 25 pre-selected days per year. The sampling period was midnight to midnight at an air flow rate of 1130 to 1700 liters/min (40 to 60 cfm). Gelman A glass fiber filters were used. Water soluble sulfates were determined by the methylthymol blue procedure.

Sulfur dioxide samples were taken concurrently with the sulfate samples at most NASN locations. Stations apparently not reporting sulfur dioxide data during the period 1972 through 1974 were Burbank,

Ontario and Riverside. Sulfur dioxide sampling followed the methods prescribed in the Federal Register (see Vol. 36, No. 84, April 30, 1971). Air is bubbled at a rate of 200 ml/min through 50 ml of a tetrachloromercurate absorbing reagent. Collected samples are shipped to a laboratory where SO₂ concentration is determined by the West-Gaeke procedure (West and Gaeke, 1956) as modified for the Autoanalyzer by Welch and Terry (1960). Comments made when discussing the CHES^S SO₂ data concerning sample deterioration between field collection and laboratory analysis also apply to the NASN data. The nominal minimum detection limit of the Federal reference method is 25 µgm/m³ although the NASN network attempts to report numerical results well below that value.

The NASN sampling methodology is described by Benson et al. (1974, see their Appendix B).

Bl.4 A Brief Comparison of Monitoring Methods

Each of these three monitoring agencies collected twenty-four hour average total suspended particulate samples by high volume sampling. In all cases during the years 1972 through 1974, the collection media were Gelman A glass fiber filters from which water soluble sulfates were extracted by refluxing with distilled or deionized water. The CHES^S and NASN programs determined sulfate concentrations in these extracts by the automated methylthymol blue procedure. The LAAPCD's laboratory procedures followed the manual turbidimetric method. Recent comparative studies indicate that, when properly executed, these two

analytical methods yield generally comparable results at normal atmospheric sulfate levels (for example, see Porter, et al., 1976). Sulfate determinations by the two methods are highly correlated and typically differ by less than ten percent. However, at very low ambient sulfate concentrations approaching $1.5 \mu\text{gm}/\text{m}^3$, the two methods may not be equivalent, with the turbidimetric method as practiced by the LAAPCD becoming subject to larger percentage errors (Porter et al., 1976). Very low sulfate concentrations are infrequent in the South Coast Air Basin, so this difficulty with the turbidimetric method is not of major practical concern. Sulfate sampling and analysis methods used by these agencies should yield nearly equivalent results. The CHES program is known to have encountered some analytical problems in practice. Laboratories performing their analyses were changed several times between January 1972 and December 1974. As a result of a retrospective re-analysis of high volume sampler filters taken from late September 1972 through early June 1974, CHES states that their raw sulfate data reported for that period must be multiplied by 1.51 in order to correct for a systematic laboratory error.

A notable difference between sulfate data bases lies in the sampling schedules employed. During the period 1972 through 1974, the LAAPCD and NASN networks sampled from midnight to midnight. The CHES network 24-hour sampling period nominally began at 11:00 a.m., but start times at individual stations were said to vary between 8:00 a.m. and 1:00 p.m. CHES samples were taken daily. The LAAPCD sampled for

sulfates once every five days, while the NASN program collected about twenty-five samples per year at each station location.

An attempt has been made to assess the coefficient of variation of sulfate samples representing the same monitoring event. The average coefficient of variation of the CHESSE sulfate samples is thought to be about 0.25 based on comparison of data at two adjacent monitoring sites. The average coefficient of variation due to laboratory analyses by the LAAPCD is about 0.11. It has been shown elsewhere that variation of analyses within laboratories is the major cause of variance in duplicate sulfate determinations in the presence of proper sample handling (Evans, 1977). Therefore the overall coefficient of variation of the LAAPCD sulfate method probably also averages about 0.11. No estimates were found for the coefficient of variation of the NASN sulfate measurements. From the laboratory method employed, the NASN data might be quite accurate, but their volunteer-operated network undoubtedly suffers from sample custody problems of uncertain magnitude. It will be assumed that the NASN measurement system has a coefficient of variation due to sampling errors of 0.11, similar to the LAAPCD method. There is no point in pursuing the accuracy of the NASN analyses much further, as it will be seen from the discussion of Appendix B4 that the NASN's sampling schedule is so sparse that atmospheric fluctuations dominate the confidence interval on mean values constructed from NASN data.

Sulfur dioxide sampling methods employed by separate monitoring agencies are judged to be significantly different. The Los Angeles Air

Pollution Control District never reports SO_2 concentrations lower than $26 \mu\text{gm}/\text{m}^3$ due to minimum detection limit problems with their conductometric instruments. Since 24-hour average SO_2 concentrations at or below $26 \mu\text{gm}/\text{m}^3$ are typical in many areas of the South Coast Air Basin, *average SO_2 results reported by the LAAPCD are almost surely higher than actual.* CHES and NASN stations employed the West-Gaeke colorimetric method. While the nominal minimum detection limit of that method is about the same as the conductometric method, attempts are made to estimate concentrations below $26 \mu\text{gm}/\text{m}^3$. CHES and NASN data thus have the possibility of representing true average SO_2 concentrations. However, sample handling and collection efficiency problems can arise with the West-Gaeke method which result in underestimation of SO_2 concentrations. *NASN and CHES data thus represent a lower limit to likely actual SO_2 concentrations.*

REFERENCES FOR APPENDIX B1

- Barnard, W.D. et al. (1976), Community Health Environmental Surveillance Studies (CHESS) Air Pollution Monitoring Handbook: Manual Methods, Research Triangle Park, North Carolina, Health Effects Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency Publication EPA-600/1-76-011.
- Benson, F.B. et al. (1974), Health Consequences of Sulfur Oxides: A Report from CHESS, 1970-1971, Research Triangle Park, North Carolina, Office of Research and Development, U.S. Environmental Protection Agency Publication EPA-650/1-74-004. See Appendices A and B for monitoring methods.
- Duckworth, S. (1976), California Air Resources Board, personal communication. Provided letter from Gregory Sharp of the Exposure Assessment Branch, Population Studies Division, U.S. Environmental Protection Agency, which outlined the range of variation in CHESS sampling schedules.
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- U.S. Public Health Service (1962), "Air Pollution Measurements of the National Air Sampling Network", U.S. Department of Health, Education and Welfare, Public Health Service Publication No. 978.

- Wadley, M.W., and R.D. MacPhee (1976), "Measurements of Suspended Particulate Matter in the Atmosphere of Los Angeles County, 1965-1974, A Ten-Year Summary," Southern California Air Pollution Control District, Metropolitan Zone, Air Quality Report No. 82.
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- West, P.W., and G.C. Gaeke (1956), "Fixation of Sulfur Dioxide as Sulfimercurate III and Subsequent Colorimetric Determination," Anal. Chem., Vol 28, pp. 1816-1819.

APPENDIX B2

DATA ACQUISITION AND PREPARATION

B2.1 The Los Angeles Air Pollution Control District (LAAPCD) Data Base

Data on suspended sulfate and sulfur dioxide concentrations were hand copied from the files of the LAAPCD. The period covered was August 1965 through December 1974. If duplicate sulfate samples were available for a 24-hour period, then the arithmetic mean of the two observations was recorded. The LAAPCD's daily average sulfur dioxide values were recorded in parts per million for days on which sulfate samples were scheduled. Sulfur dioxide concentrations were subsequently translated to micrograms per cubic meter using the Federal Register reference method calibration conditions of one atmosphere pressure and a temperature of 25°C.

B2.2 The Community Health Environmental Surveillance System (CHESS) Data Base

Xerox copies of computer generated listings of the CHESS data were obtained from the files of the California Air Resources Board. The period covered was 1972 through 1974. Data on suspended particulate sulfates and sulfur dioxide were transcribed into three separate files: sulfates, 35 ml SO₂ samples, and 50 ml SO₂ samples. The two separate sulfur dioxide data bases overlap for a few days at the end of 1973. For the purposes of the computations in this report, the 35 ml SO₂ samples were used exclusively during calendar years 1972 and 1973, while 50 ml SO₂ samples were used in calendar year 1974.

As noted in Appendix B1, some of the raw CHES sulfate data taken from September 1972 through early June 1974 were labeled by CHES as follows:

The sulfate data listed on this page must be multiplied by a factor of 1.51 to correct for an analysis error. The factor was determined by reanalysis of a substantial subset of the affected data.

This correction was incorporated into the data base on the days indicated by CHES.

Since the CHES 24-hour sampling period nominally began at 11:00 a.m. daily, CHES data can not be attributed entirely to a single calendar day. For the purposes of this analysis, the CHES program's convention of assigning the sample's stop date to each data point was adopted. On occasion, the available xerox copies of the CHES data were difficult to read, and a few minor errors in data transcription may have occurred.

B2.3 The National Air Surveillance Network (NASN) Data Base

Xerox copies of the NASN suspended particulate sulfate data for the years 1972 through 1974 were furnished by the California Air Resources Board. Copies of NASN sulfur dioxide data for the same years were obtained on punch cards in SAROAD format from the U.S. Environmental Protection Agency. All data for all stations in the South Coast Air Basin were requested. No sulfate data were received for Riverside in the years 1973 and 1974. No sulfur dioxide data were available for Burbank, Ontario and Riverside.

APPENDIX B3

FREQUENCY OF OCCURRENCE
OF SULFATE CONCENTRATIONS
1972 THROUGH 1974

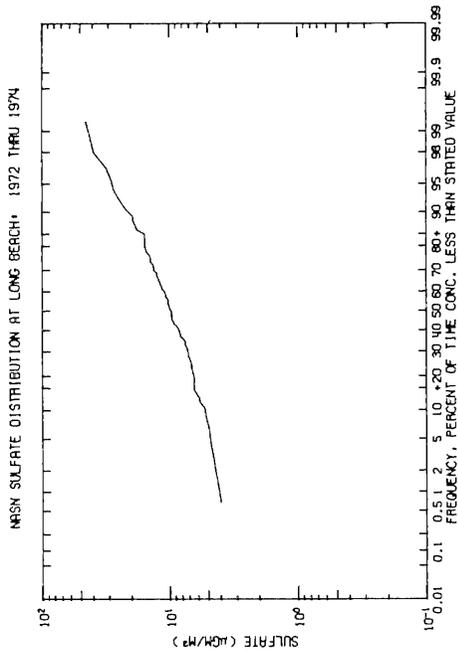


FIGURE B3.2

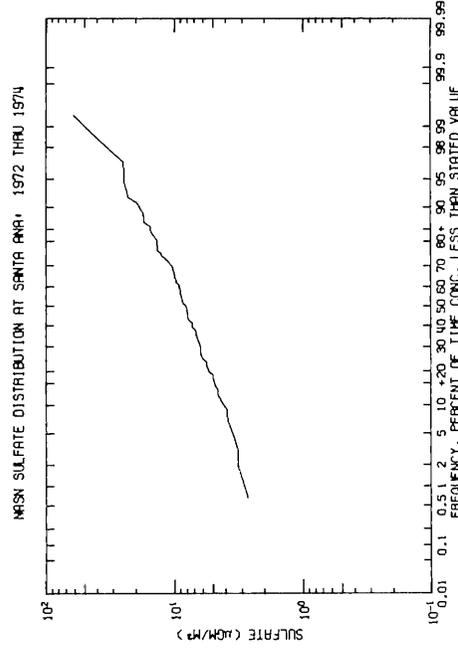


FIGURE B3.4

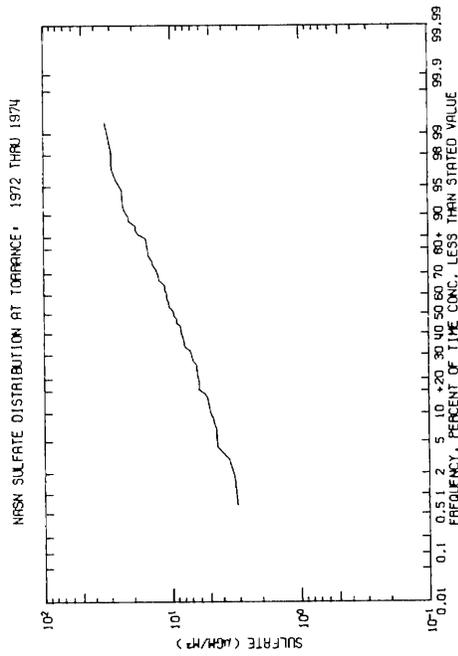


FIGURE B3.1

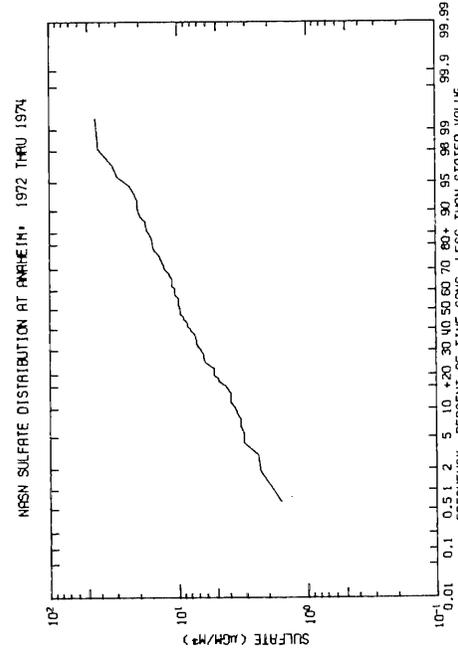


FIGURE B3.3

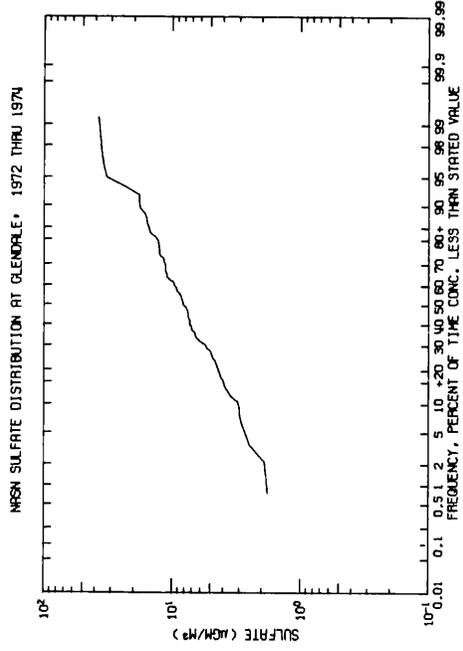


FIGURE B3.6

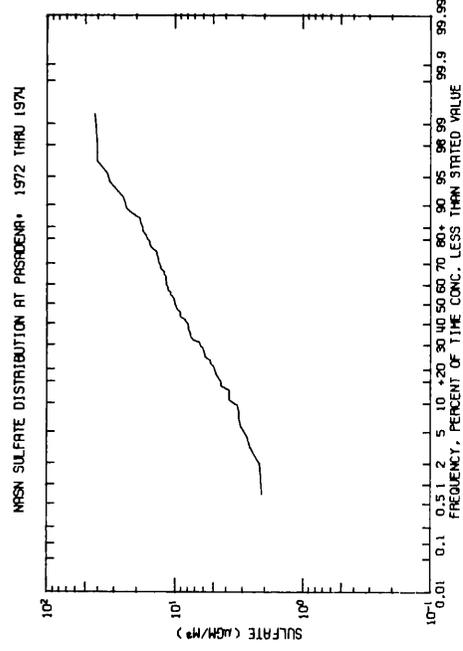


FIGURE B3.8

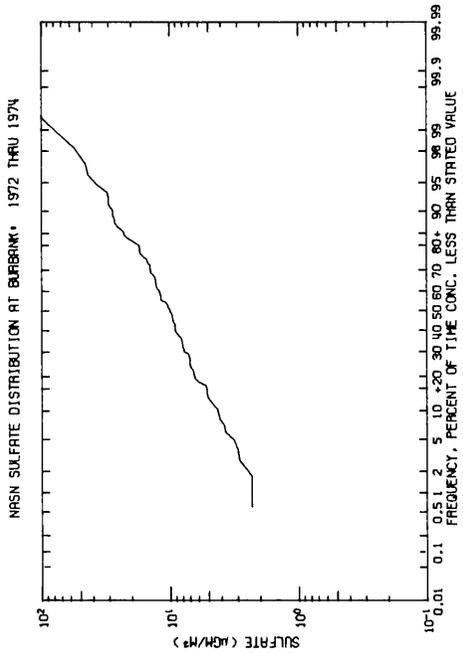


FIGURE B3.5

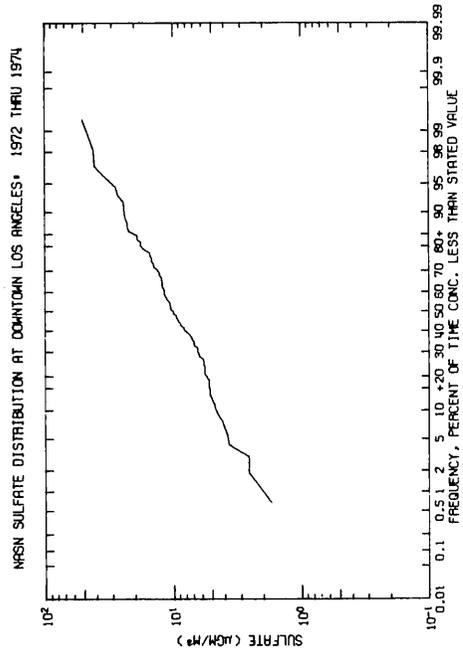


FIGURE B3.7

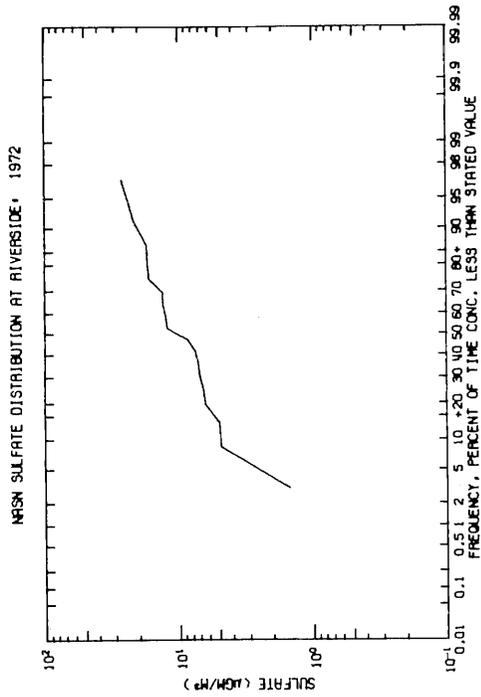


FIGURE B3.10

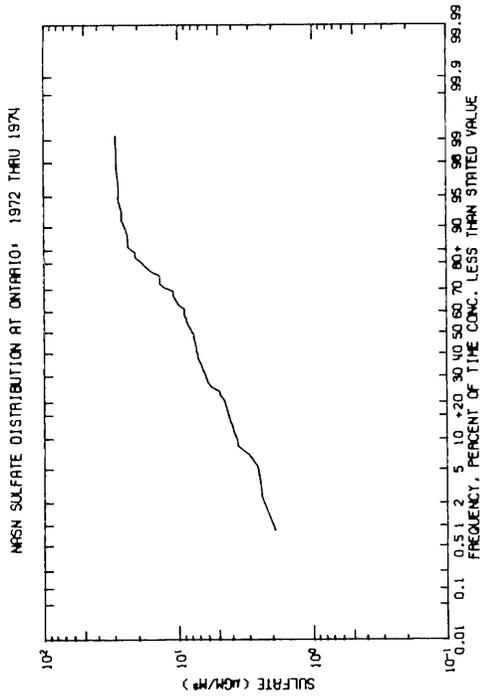


FIGURE B3.9

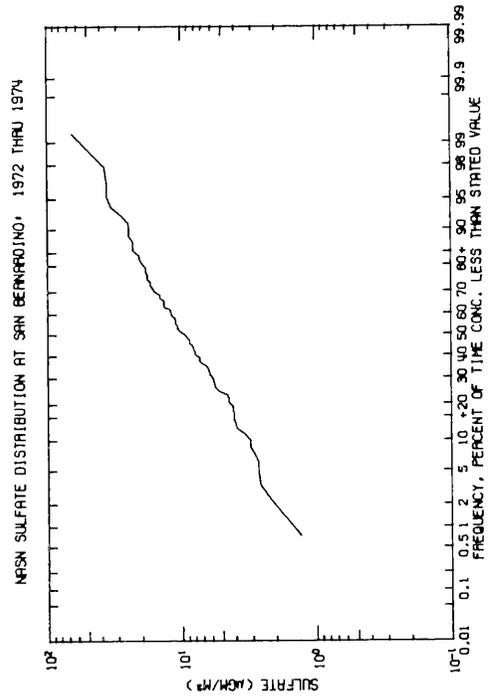


FIGURE B3.11

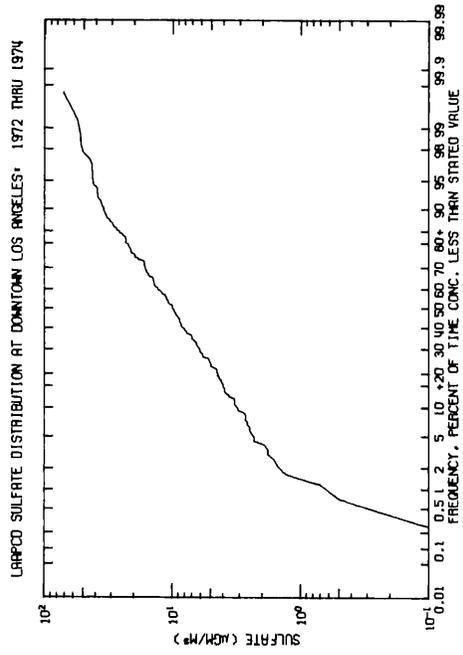


FIGURE B3.13

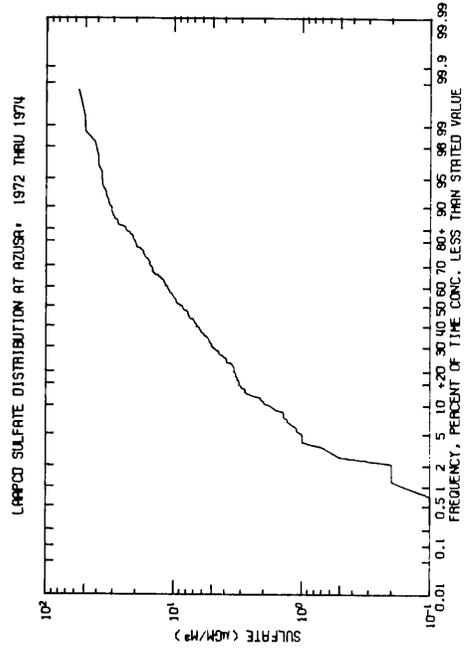


FIGURE B3.15

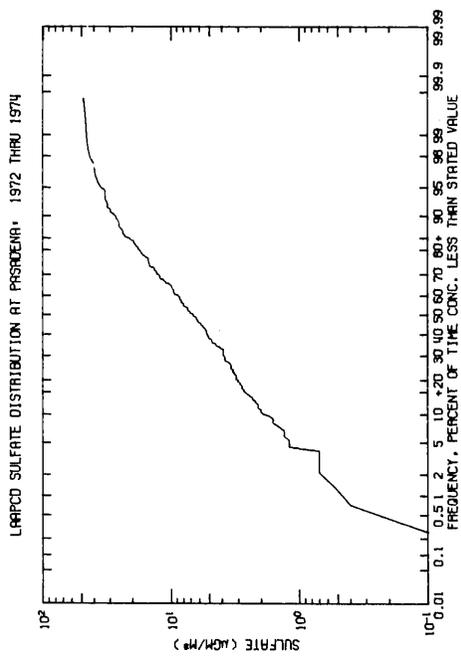


FIGURE B3.12

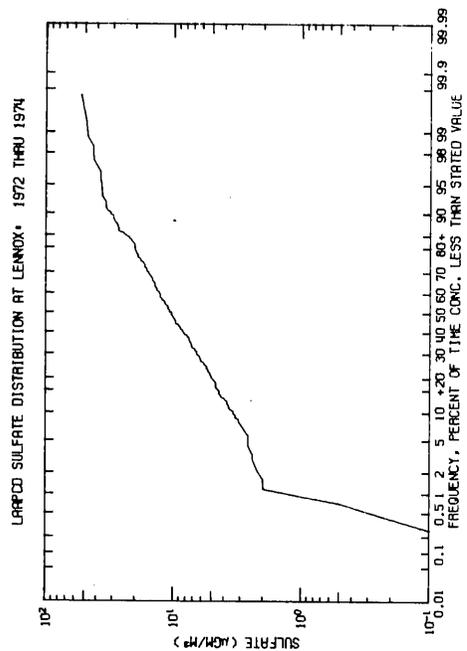


FIGURE B3.14

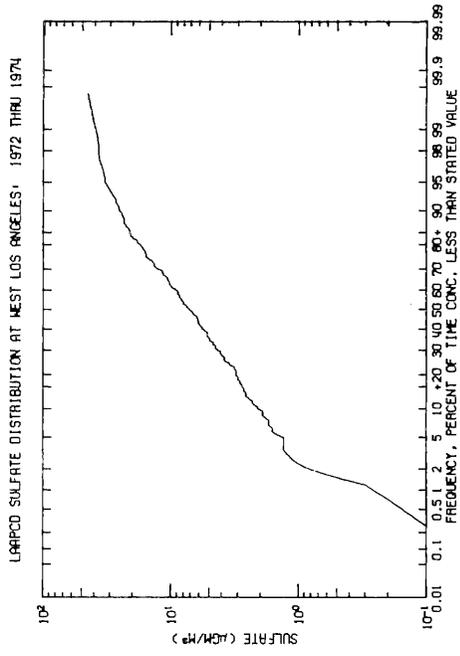


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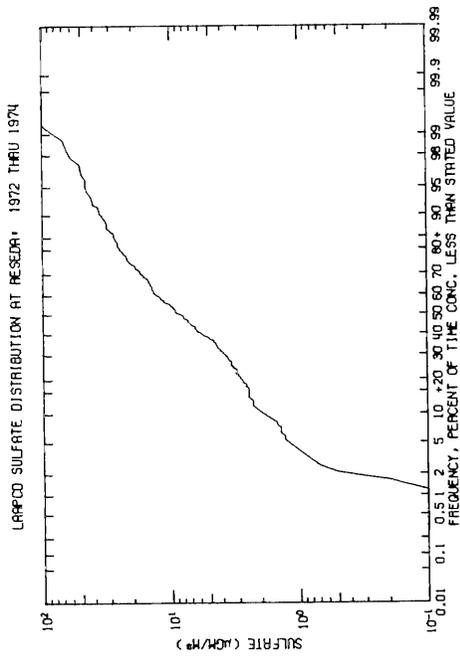


FIGURE B3.16

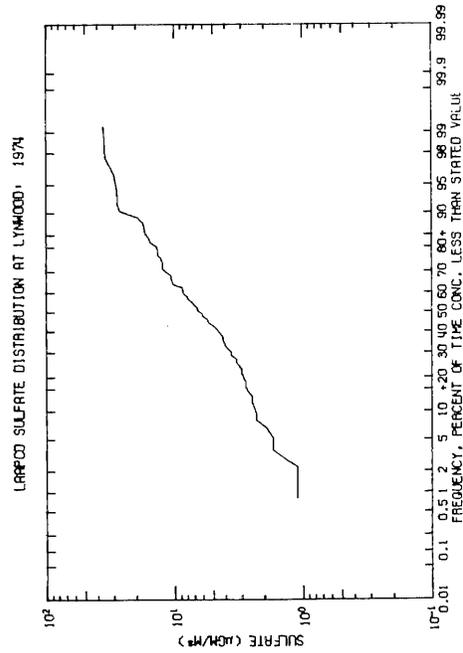


FIGURE B3.18

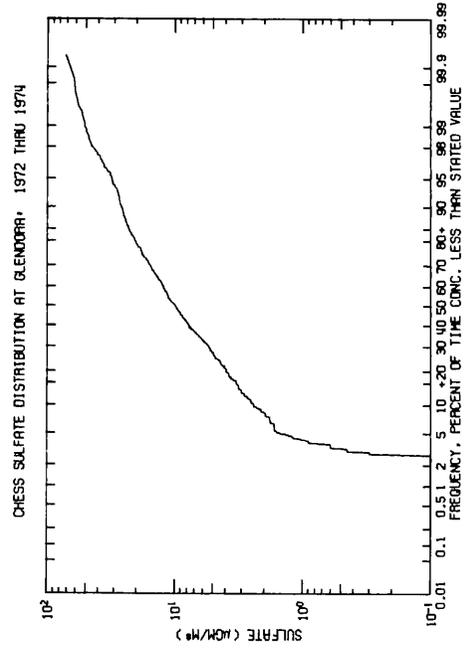


FIGURE B3.20

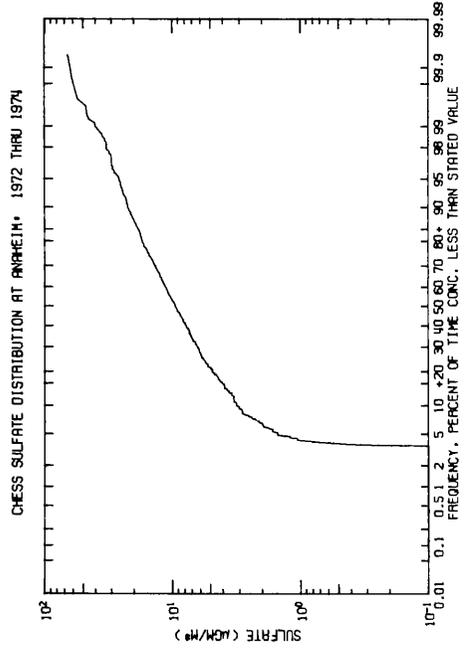


FIGURE B3.22

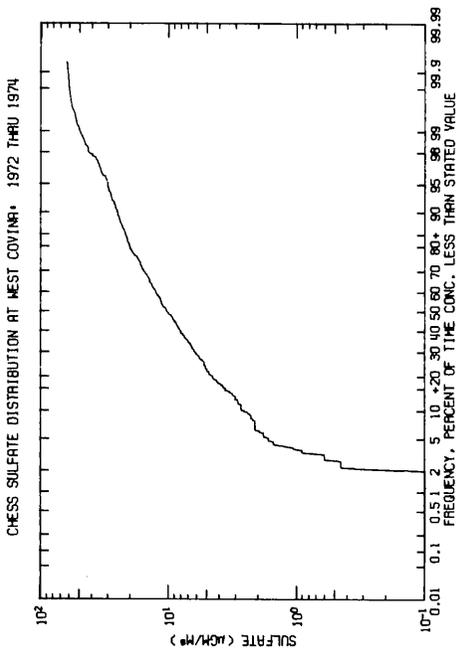


FIGURE B3.19

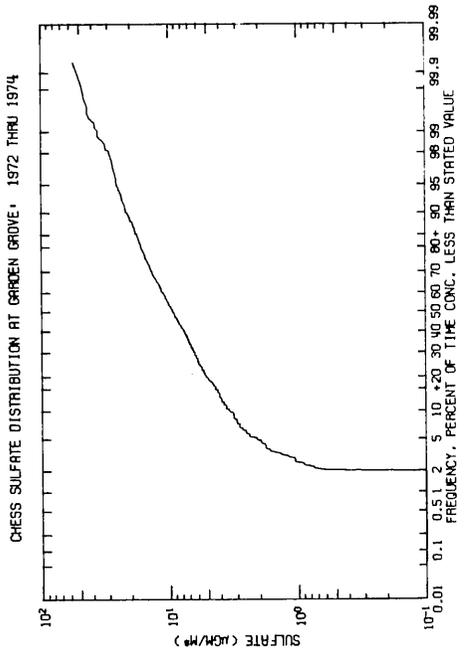


FIGURE B3.21

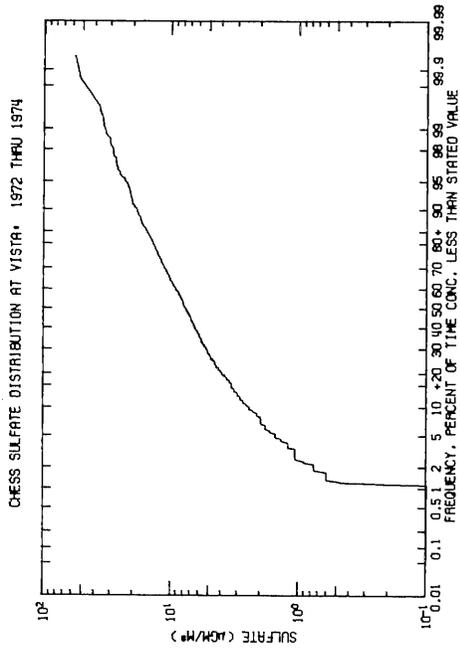


FIGURE B3.24

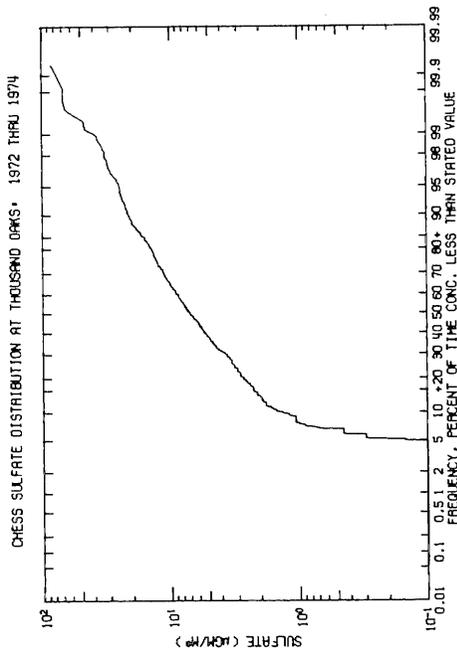


FIGURE B3.23

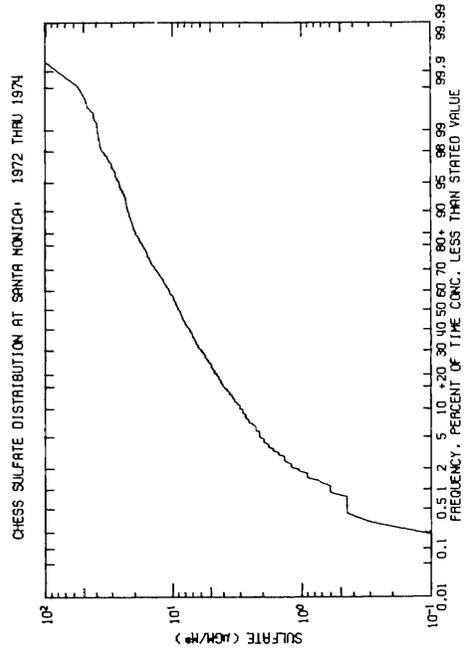


FIGURE B3.25

APPENDIX B4

PARAMETER ESTIMATION PROCEDURES FOR SULFATE AIR QUALITY DATA

Empirical work pioneered by Larsen (1971) suggests that air quality measurements approximately follow a simple two parameter log-normal distribution for all pollutants and all averaging times. Graphs presented in Appendix B3 generally confirm that rule of thumb at sulfate concentrations above $2 \mu\text{gm}/\text{m}^3$. As described in the body of this report, departure from a two parameter log-normal distribution at low concentrations may well be due to minimum detection limit problems arising from the sulfate measurement techniques employed.

Let us establish some nomenclature with which to define the parameters of the log-normally distributed air quality data. Assume that the record at an air monitoring station consists of n stochastically independent observations $y_1, y_2, y_3, \dots, y_n$. The sample arithmetic mean of this data will be referred to as \bar{y} , and the sample variance as s^2 . The true underlying arithmetic mean of the distribution from which these samples were drawn will be called μ , and the true underlying variance is called σ^2 .

The natural log of each sample value y_i will be referred to as x_i . The x 's are thus a normally distributed population obtained by direct transformation of the sulfate air quality observations. The sample mean of the x 's will be called \bar{x} . The true underlying mean of the population from which the x 's are drawn will be called α , and the true underlying variance of the x 's will be called β^2 .

The geometric mean, μ_g , and geometric standard deviation, σ_g , of the raw sulfate observations may be estimated from α and β^2 as follows:

$$\mu_g = e^\alpha \quad (\text{B4.1})$$

$$\sigma_g = e^\beta \quad (\text{B4.2})$$

These geometric statistics are often used to describe air quality measurements because long-run changes in pollutant emissions in an air basin are usually expected to affect the geometric mean air quality level while leaving the geometric standard deviation largely unchanged.

One useful relationship between the parameters of the distributions of the x's and y's is that

$$\mu = e^\alpha + \frac{1}{2}\beta^2 \quad (\text{B4.3})$$

This means that given good estimates of α and β^2 , one can make an efficient estimate of the arithmetic mean, μ , of a group of sulfate air quality data. Since it is the arithmetic mean, μ , which our future air quality model will calculate, that is an important expression.

We wish to estimate the parameters α and β^2 of a set of air quality data. Ordinarily, α and β^2 would be obtained easily by taking the moments of the transformed sulfate samples. But the existence of possibly bad data in the LAAPCD and CHESS data bases at sulfate concentrations below $2 \mu\text{gm}/\text{m}^3$ causes us to seek a method by which the existence of those low-valued samples may be acknowledged without explicitly

using the numerical values obtained. In short, we advise censoring the sulfate routine air monitoring data bases below $2 \mu\text{gm}/\text{m}^3$.¹

An analytical approach to estimating the parameters of a censored normal distribution is given by Hald (1952). For the large number of calculations which we have to perform, that procedure is simply too complicated to yield to rapid automation. A variation of the alternate "graphical" method for estimating the parameters of a log-normal distribution was used instead.

In the graphical method, the parameters α and β are estimated from the 50th percentile point and slope, respectively, of the sulfate data when graphed on log-probability paper. In order to plot such a graph, the data are rank ordered and each data point is assigned a probability of occurrence on a normal probability scale. The plotting position for a given data point is obtained from a formula which is usually of the form

$$p = \frac{r-a}{n+(1-2a)} \quad (\text{B4.4})$$

where

r = rank of that data point
 p = probability at which the r^{th} ranked point is plotted
 n = total number of samples considered
 a = a parameter between zero and one selected on the basis of the purpose for which the exercise is being undertaken

¹The background data of Hidy, et al., (1974) will not be censored because there are too few data points to tell what the lower tail of their distribution looks like.

A wide variety of recommended values of the parameter "a" exist in the literature. Koh (1977) has shown that any choice of "a" between zero and one can be defended on theoretical grounds. For small sample populations drawn at random from a large normal distribution with known mean and variance, Koh found empirically that a value of $a = 0.44$ was best suited to re-extracting the original sample variance from a least squares fit to the slope of the data points on probability paper after having regressed sample values on plotting position. That value of $a = 0.44$ has been used throughout this study, along with Koh's computer software which insures maintenance of the empiricism involved in selecting the value of "a" that was used.

In order to automate this "graphical" procedure, the data are rank ordered and plotting positions are calculated for each point in a set of sulfate samples. The plotting positions are next expressed in units of standard deviations above and below the median of a standard normal (0,1) distribution centered on the 50th percentile point. The natural log of each sulfate sample is taken. Then sulfate samples below $2 \mu\text{gm}/\text{m}^3$ were censored from the lower tail of the cumulative probability distribution, while retaining the plotting position for all higher valued samples as if the lower tail were still present. A regression line is next fitted to the rank ordered data by regressing the logs of the sulfate concentrations on plotting position (in standard deviations from the 50th percentile). All of the above calculations are done on an IBM 370/158 computer rather than by actually graphing the data.

Variance estimates were obtained from the square of the slope, b , of this regression line. Since $N = 1096$ consecutive 24-hour samples at a monitoring station would exhaust the entire set of possible days during our three year period (or 31 days within a monthly sample), we are clearly sampling from a finite population of days, and an unbiased estimate of β^2 would be obtained as (reference Hald, 1952)

$$\beta^2 = \frac{N-1}{N} (b)^2 \quad (B4.5)$$

In a similar fashion, α is estimated by the zero standard deviation intercept (50th percentile point) of our regression line fitted to the censored cumulative probability distributions.

As a check on the log-normality assumptions and procedure used in estimating α and β^2 , we can estimate the theoretical arithmetic mean, μ , for a sample population from equation (B4.3). In Tables 2.3, 2.7, 2.8, and 2.9 in the main body of this research report, that computed value of μ is compared to sample arithmetic mean, \bar{y} . The comparison is very close in all cases. An even more stringent test of this parameter estimation procedure is provided by the small sample monthly estimates of \bar{y} and μ given by the o's and +'s, respectively in the figures at the end of this appendix. Even for the LAAPCD data which average only 6 samples per month, the monthly estimates of \bar{y} and μ are still quite close.

Next we wish to calculate a 95% confidence interval about the arithmetic mean of the sulfate data at each air monitoring station. Those confidence intervals are needed if air quality model calculations

are to be compared to observed sulfate concentration measurements. The literature on estimating confidence intervals about the arithmetic mean of log-normally distributed data is not very helpful, particularly for small sample estimation problems. Koch and Link (1970) have surveyed methods in current use for establishing confidence intervals on the arithmetic mean of log-normally distributed data. They located five methods for performing the calculations, and after applying each method to the same data base, they obtained upper confidence limit estimates on their arithmetic mean which ranged over a full order of magnitude from one method to the next. A well agreed upon formula for performing these calculations is not apparent.

In their well known monograph on the properties of log-normal distributions, Aitchison and Brown (1957) state that theory provides no means of obtaining exact confidence intervals for the arithmetic mean and arithmetic standard deviation of log-normally distributed data. Invoking the central limit theorem, about all that can be said is that sample arithmetic mean and sample arithmetic standard deviation are asymptotically normal with means μ and σ , respectively. Therefore they state that a large sample confidence interval for μ may be constructed as

$$\bar{y} - N_{P_1} \sqrt{V\{\bar{y}\}} < \mu < \bar{y} - N_{P_2} \sqrt{V\{\bar{y}\}} \quad (\text{B4.6})$$

Where

$V\{\bar{y}\}$ is the variance of the sample mean

N_{P_1}, N_{P_2} are appropriate percentile points at the upper and lower tails, respectively, of the normal (0,1) distribution

In our case, expression B4.6 will have to serve as a small sample confidence interval as well.

At least two sources of uncertainty contribute to the variance of \bar{y} . The first of these is due to infrequent sampling, particularly at the LAAPCD and NASN monitoring sites. When only a few days are chosen to be sampled from within a month or a year, the mean value of those sulfate concentration measurements is an uncertain estimate of the true population mean. That is because atmospheric concentrations fluctuate from day to day and the entire population was not observed. Secondly, there is an uncertainty introduced into any monitoring program by the accuracy of the measurement technique employed, even if all days of the month or year were sampled.

The problem of attributing components of the variance of \bar{y} to atmospheric fluctuations and to measurement errors will be based on a model of two stage sampling. The first stage consists of drawing a random sample of n_1 primary units (days) from a group of N_1 possible cases (the total number of days of a month or year). The second stage of the sampling process is to choose n_2 measured values from amongst the N_2 results which could have been delivered by a large number of simultaneous attempts to measure that day's atmospheric sulfate concentration by a somewhat inaccurate method. Each observation chosen thus can be thought of as differing from the mean sulfate value due to two fluctuating components

$$y_{i\zeta} = \mu + w_i + z_{i\zeta} \quad (\text{B4.7})$$

where w_i denotes the contribution to the departure from the mean due to fluctuations in atmospheric concentration from day to day

and $z_{i\zeta}$ denotes the contribution to the departure from the mean due to the measurement technique employed.

For a finite population of N_1 possible days to be sampled and N_2 potential samples per day, with experimental values $y_{i\zeta}$, $i = 1, 2, \dots, N_1$, and $\zeta = 1, 2, \dots, N_2$ we obtain (Hald, 1952)

$$\sigma^2 = \frac{1}{N_1 N_2} \sum_{i=1}^{N_1} \sum_{\zeta=1}^{N_2} (y_{i\zeta} - \mu)^2 \quad (\text{B4.8})$$

$$\sigma^2 = \frac{1}{N_1} \sum_{i=1}^{N_1} (\mu_i - \mu)^2 + \frac{1}{N_1 N_2} \sum_{i=1}^{N_1} \sum_{\zeta=1}^{N_2} (y_{i\zeta} - \mu_i)^2 \quad (\text{B4.9})$$

$$\sigma^2 = \sigma_1^2 + \sigma_2^2 \quad (\text{B4.10})$$

Where

$$\mu_i = \frac{\sum_{\zeta=1}^{N_2} y_{i\zeta}}{N_2} \quad (\text{B4.11})$$

$$\mu = \frac{\sum_{i=1}^{N_1} \sum_{\zeta=1}^{N_2} y_{i\zeta}}{N_1 N_2} \quad (\text{B4.12})$$

If a random sample of n_1 days are chosen from amongst the N_1 possible days, then the variance of the mean of the w_i is given by:

$$V\{\bar{w}\} = \frac{\sigma_1^2}{n_1} \left(1 - \frac{n_1 - 1}{N_1 - 1} \right) \quad (\text{B4.13})$$

The latter term on the right hand side of expression (B4.13) is a finite population correction (e.g., if all days of the month are sampled, $n_1 = N_1$, and there is no uncertainty introduced into the monthly mean from having missed sampling a possible event).

For each day sampled, i , we choose n_2 of the experimental results from among the possibly infinite number of samples which could have been measured by simultaneous execution of our sampling protocol. Within each of these days, the variance of the mean of the experimental results is

$$V\{\bar{z}_i\} = \frac{\sigma_{2i}^2}{n_2} \quad (\text{B4.14})$$

Where σ_{2i}^2 is the variance in the underlying measurement technique applied within the context of day i .

Combining these two sources of variation, we get

$$V\{\bar{y}\} = \frac{\sigma_1^2}{n_1} \left(1 - \frac{n_1 - 1}{N_1 - 1} \right) + \frac{\sigma_2^2}{n_1 n_2} \quad (\text{B4.15})$$

where σ_2^2 is the mean of all σ_{2i}^2 's.

For the case of a single measured value per day sampled, $n_2 = 1$, and

$$V\{\bar{y}\} = \frac{\sigma_1^2}{n_1} \left(1 - \frac{n_1 - 1}{N_1 - 1} \right) + \frac{\sigma_2^2}{n_1} \quad (\text{B4.16})$$

The coefficients of variation for individual sulfate measurements made by the LAAPCD, the CHES and the NASN networks were estimated in Appendix B1. For each day i sampled we may estimate σ_{2i} at each monitoring station by:

$$\sigma_{2i} = C\{SO_4\} \cdot \langle c(SO_4) \rangle_i \quad (\text{B4.17})$$

Where $C\{SO_4\}$ is the coefficient of variation of sulfate measurements made by the monitoring network of interest

$\langle c(SO_4) \rangle_i$ is the sulfate concentration measurement available for day i from that monitoring site.

Then σ_2^2 is obtained at each monitoring station by averaging over all σ_{2i}^2 at that site for the time period over which \bar{y} is to be calculated.

Next, the variance σ_1^2 is estimated. Substituting the total sample variance obtained by the method of moments, $s^2 \approx \sigma^2$, into equation B4.10, and rearranging we get:

$$\sigma_1^2 \approx s^2 - \sigma_2^2 \quad (B4.18)$$

Having supplied estimates for σ_1 and σ_2 , the expression for $V\{\bar{y}\}$ in equation B4.18 may be inserted into equation B4.16. The 95% confidence limits estimated for the arithmetic mean of our sulfate air quality data become:

$$\mu_{\text{lower}} = \bar{y} - N_{97.5\%} \sqrt{\frac{s^2 - \sigma_2^2}{n_1} \left(1 - \frac{n_1 - 1}{N_1 - 1}\right) + \frac{\sigma_2^2}{n_1}} \quad (B4.19)$$

$$\mu_{\text{upper}} = \bar{y} + N_{2.5\%} \sqrt{\frac{s^2 - \sigma_2^2}{n_1} \left(1 - \frac{n_1 - 1}{N_1 - 1}\right) + \frac{\sigma_2^2}{n_1}} \quad (B4.20)$$

Confidence intervals estimated for μ at each monitoring station over each of our three years of interest are given in Tables 2.7, 2.8, and 2.9. Figures B4.1 through B4.14 show confidence intervals on μ

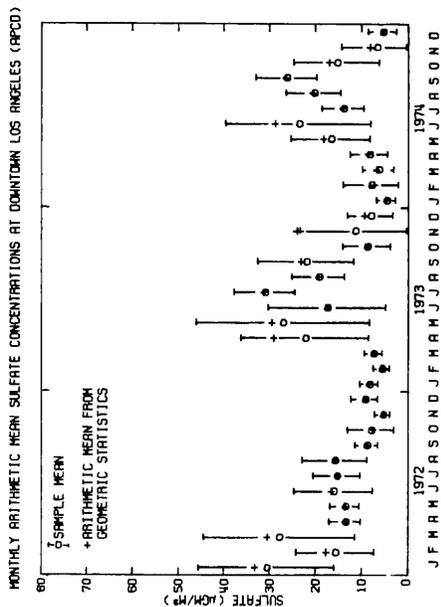


FIGURE B4.2

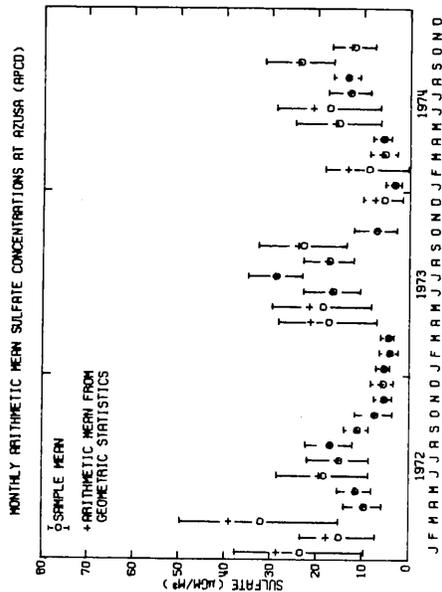


FIGURE B4.4

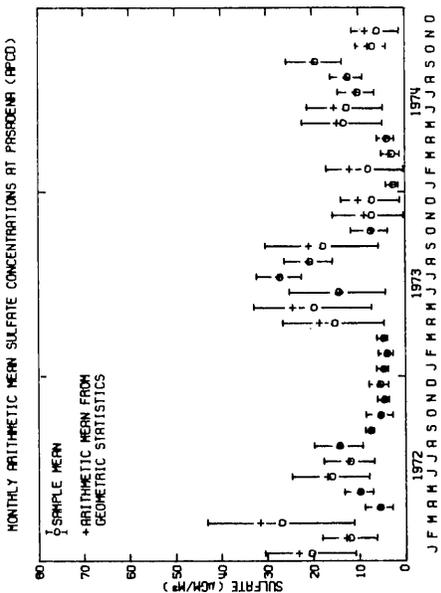


FIGURE B4.1

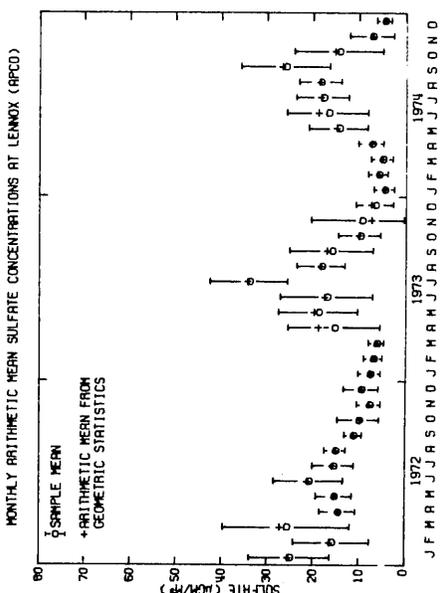


FIGURE B4.3

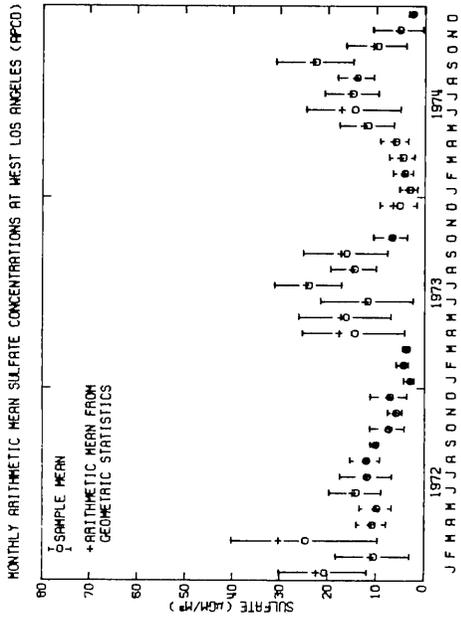


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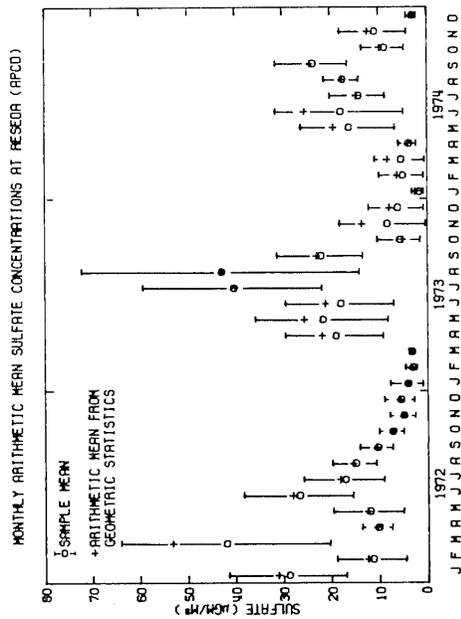


FIGURE B4.5

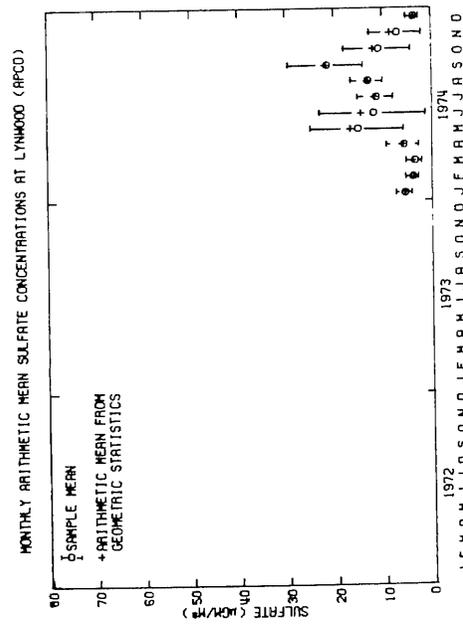


FIGURE B4.7

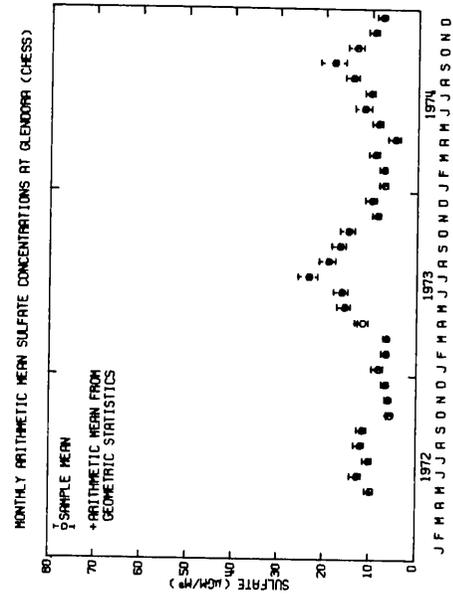


FIGURE B4.9

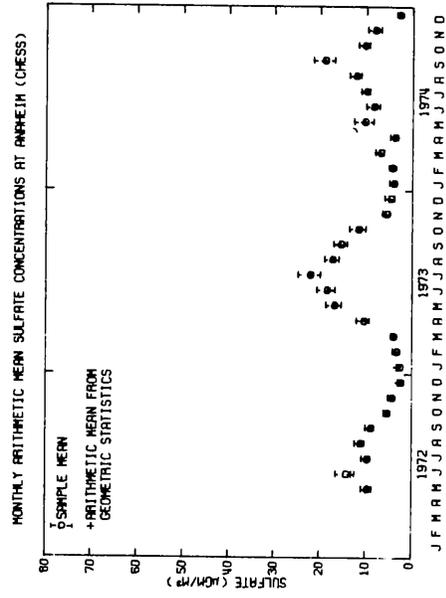


FIGURE B4.11

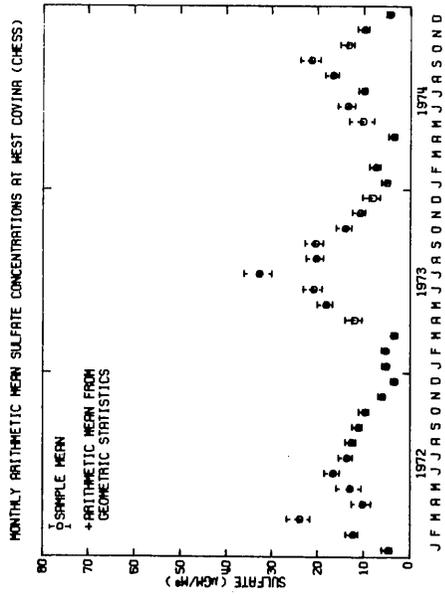


FIGURE B4.8

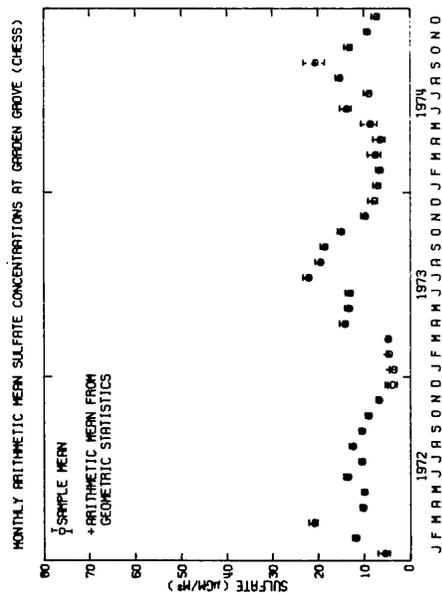


FIGURE B4.10

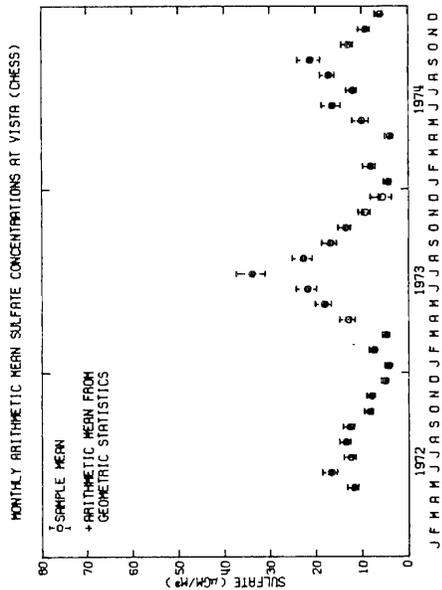


FIGURE B4.13

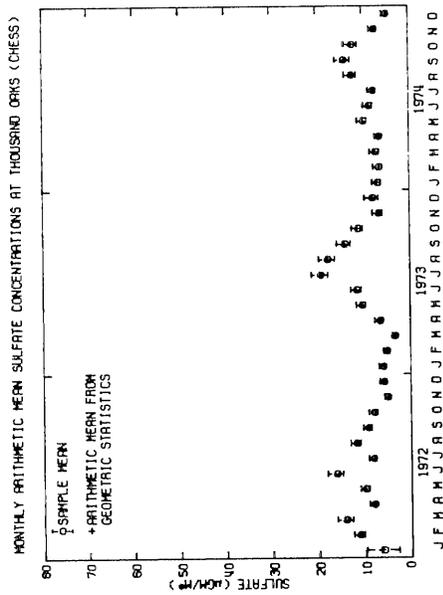


FIGURE B4.12

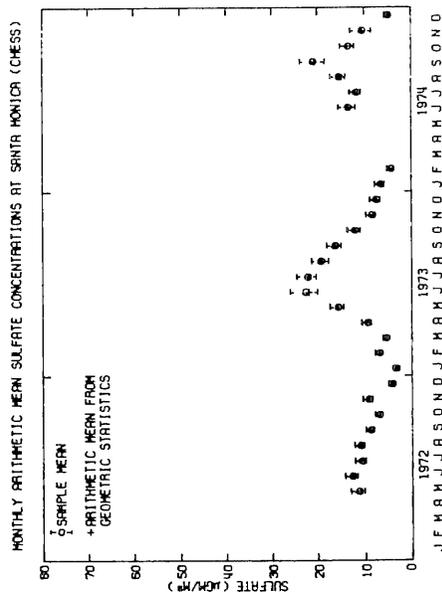


FIGURE B4.14

estimated for each month at all CHESS and LAAPCD air monitoring sites. The NASN stations are not represented because their sampling schedule is too infrequent to support monthly mean determinations.

REFERENCES FOR APPENDIX B4

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APPENDIX B5

SEASONAL TRENDS IN SULFATE AIR QUALITY
IN THE SOUTH COAST AIR BASIN
1972-1974

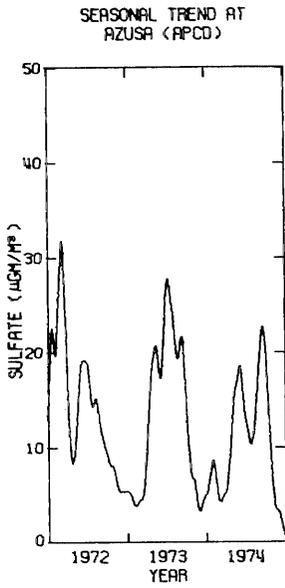


FIGURE B5.1

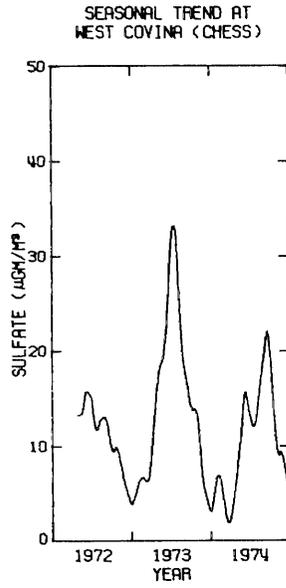


FIGURE B5.2

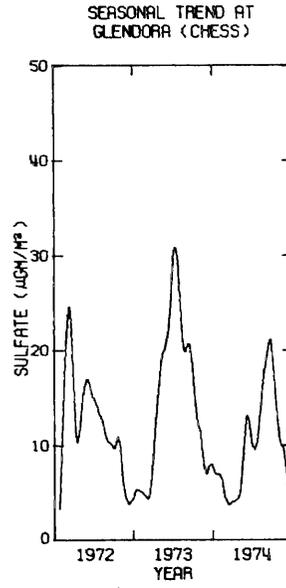


FIGURE B5.3

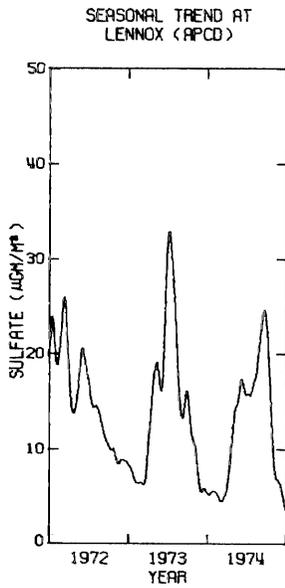


FIGURE B5.4

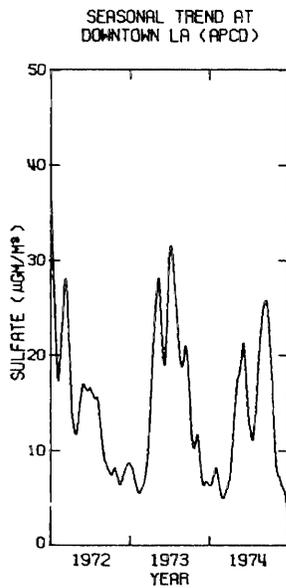


FIGURE B5.5

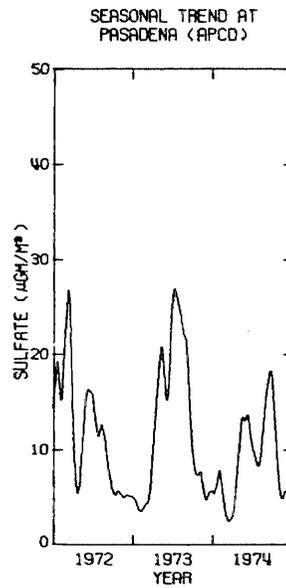


FIGURE B5.6

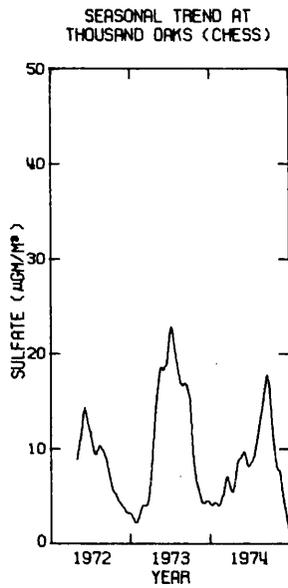


FIGURE B5.7

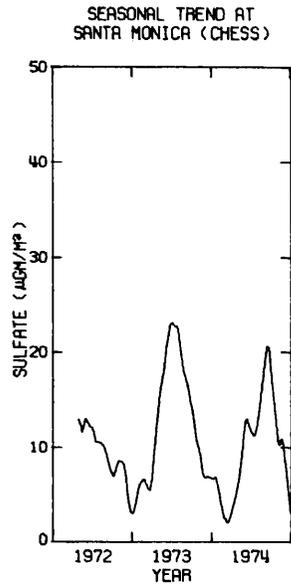


FIGURE B5.8

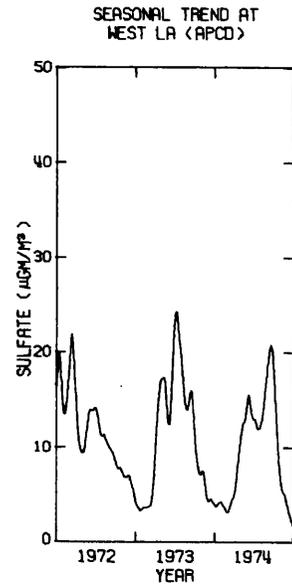


FIGURE B5.9

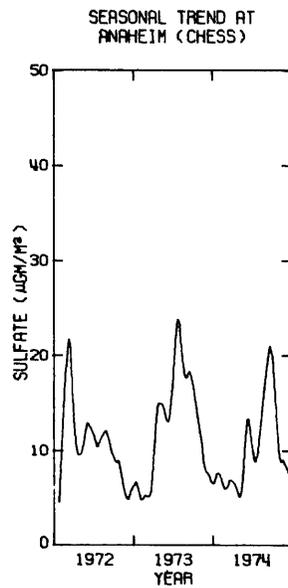


FIGURE B5.10

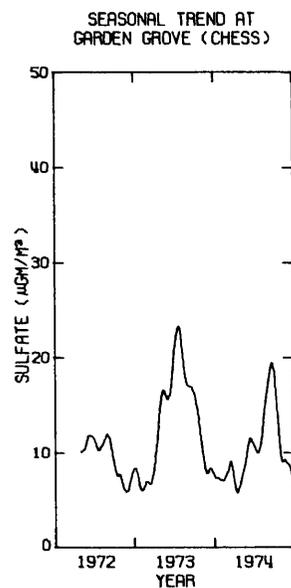


FIGURE B5.11

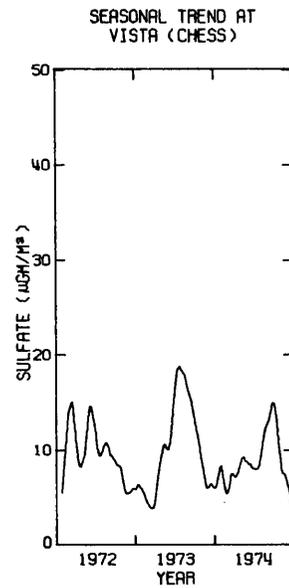


FIGURE B5.12

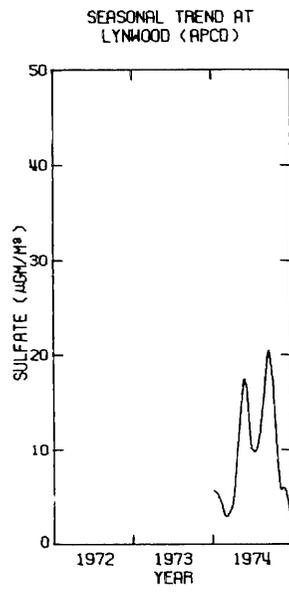


FIGURE B5.13

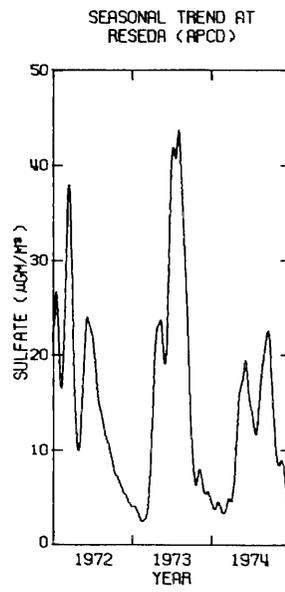


FIGURE B5.14

APPENDIX B6

FREQUENCY OF OCCURRENCE OF VALUES OF THE RATIO OF PARTICULATE
SULFUR TO TOTAL SULFUR, f_s , 1972 THROUGH 1974

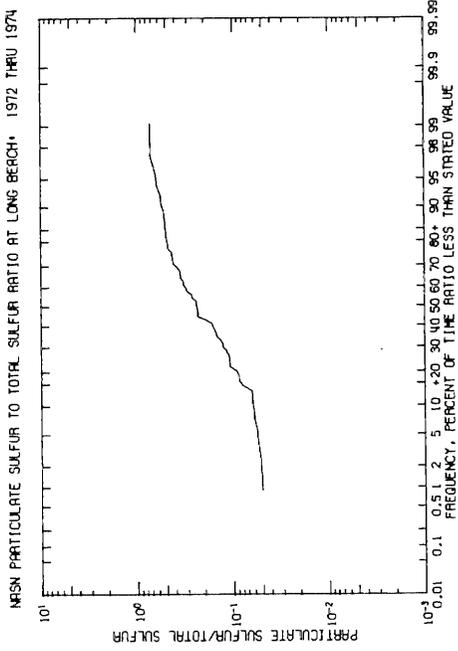


FIGURE B6.2

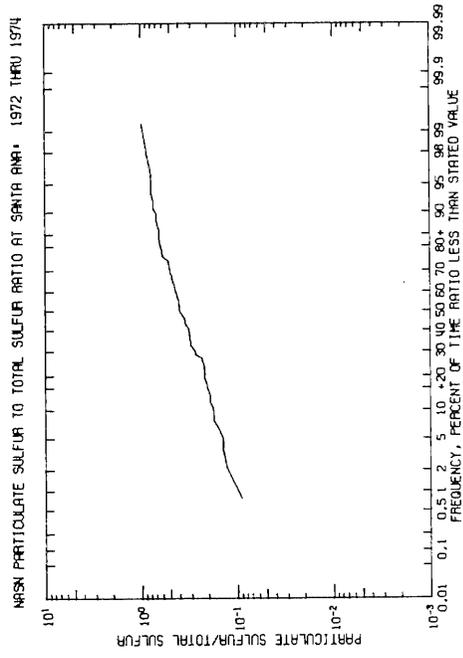


FIGURE B6.4

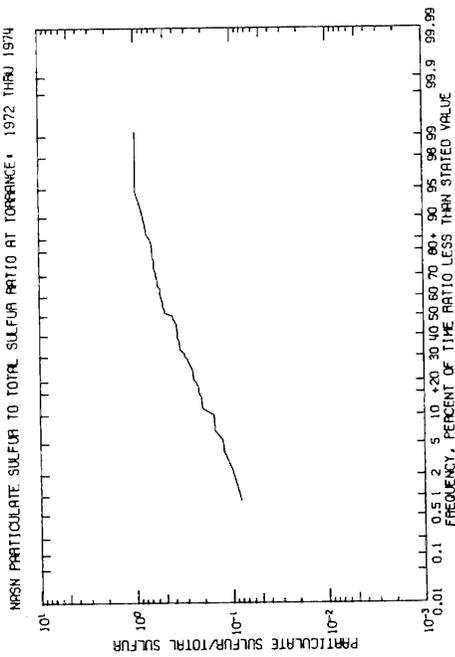


FIGURE B6.1

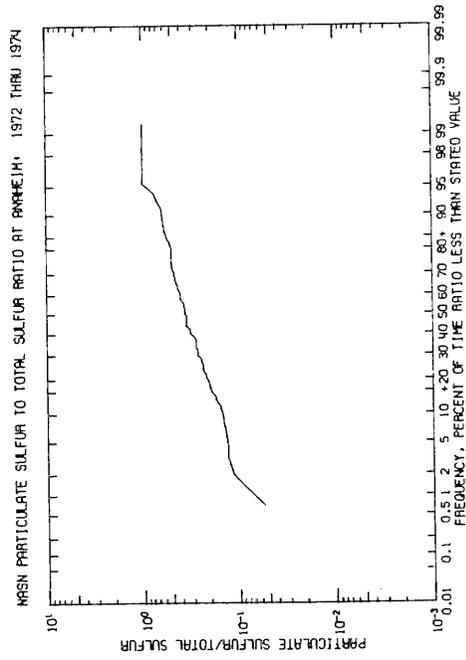


FIGURE B6.3

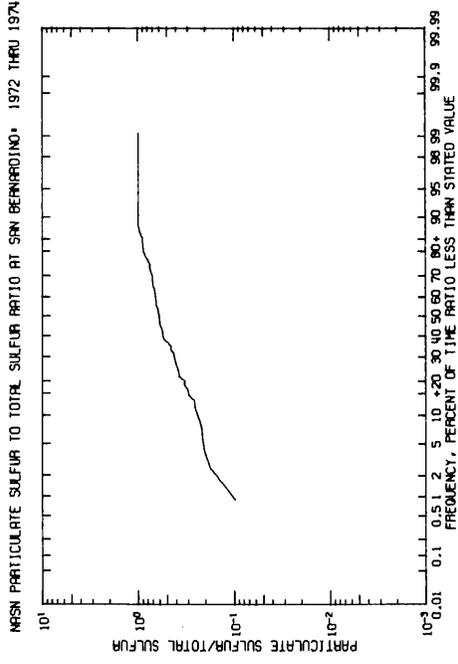


FIGURE B6.6

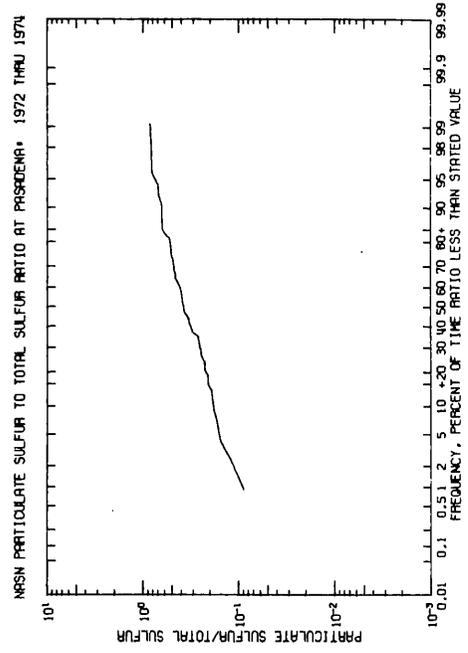


FIGURE B6.8

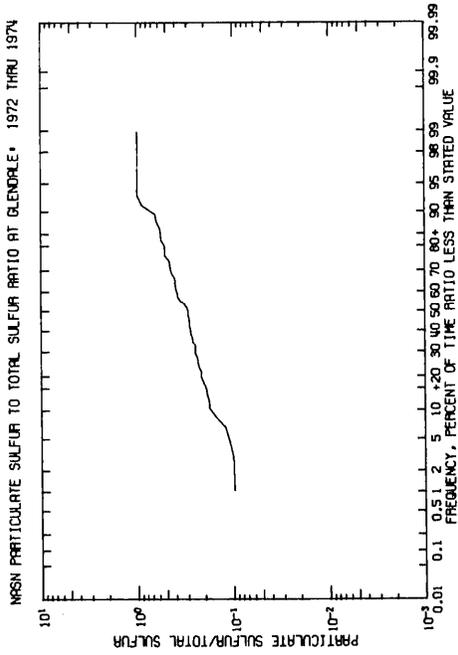


FIGURE B6.5

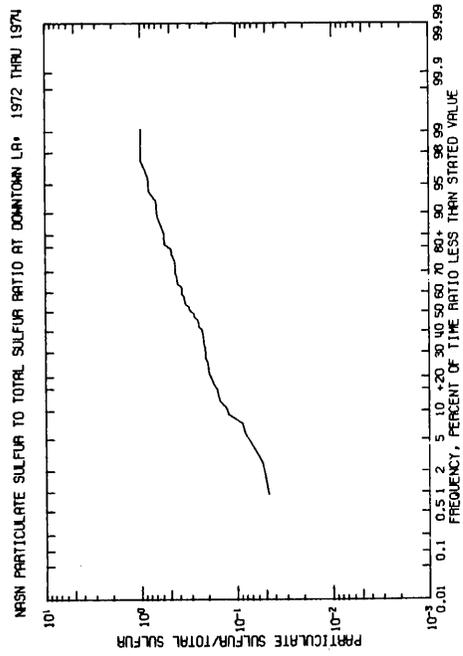


FIGURE B6.7

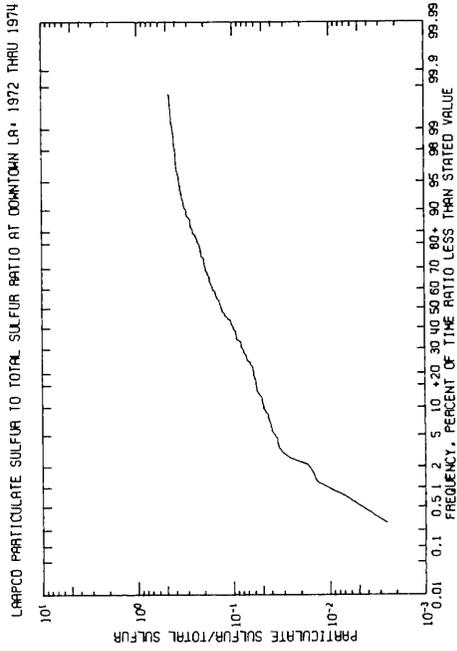


FIGURE B6.10

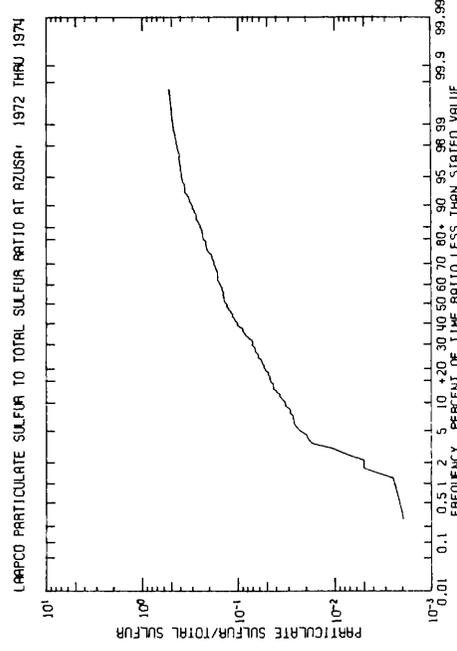


FIGURE B6.12

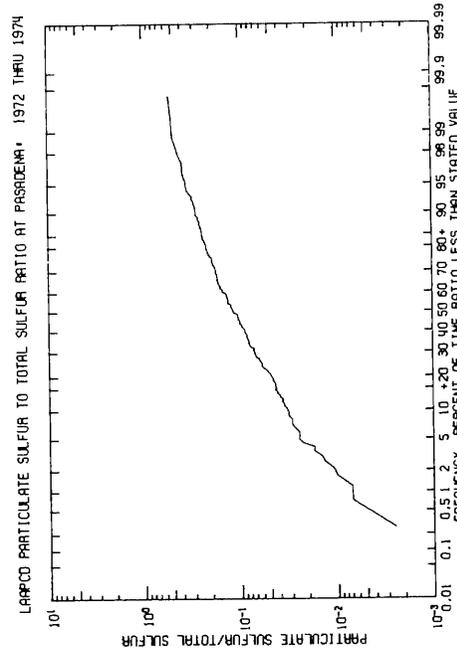


FIGURE B6.9

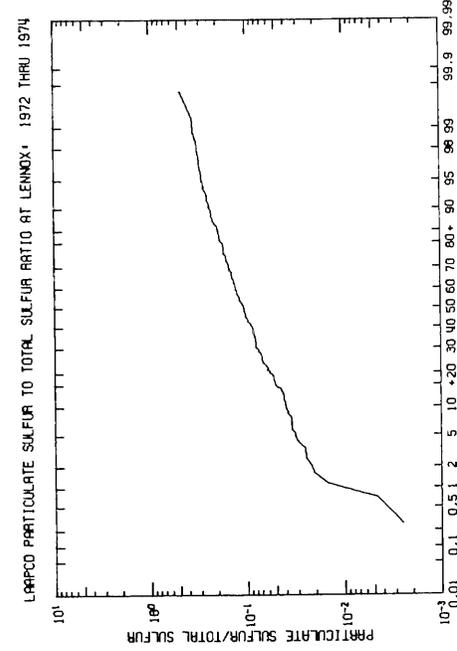


FIGURE B6.11

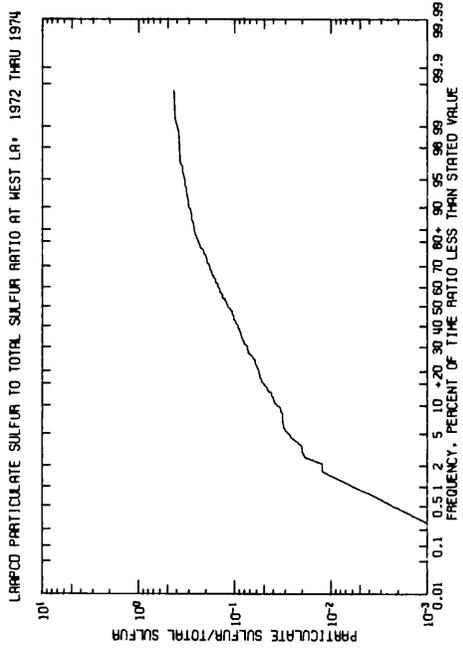


FIGURE B6.14

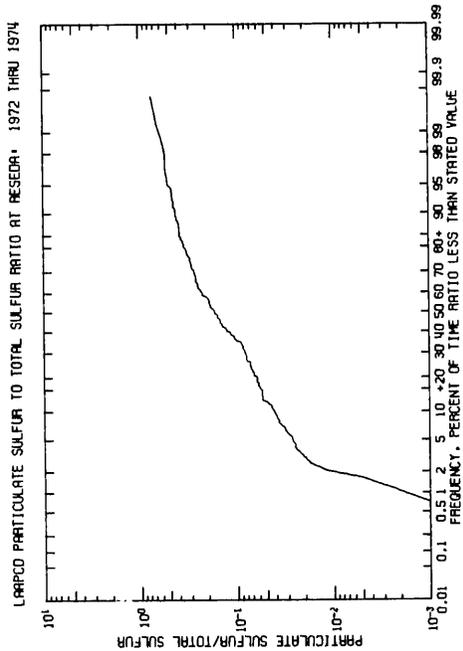


FIGURE B6.13

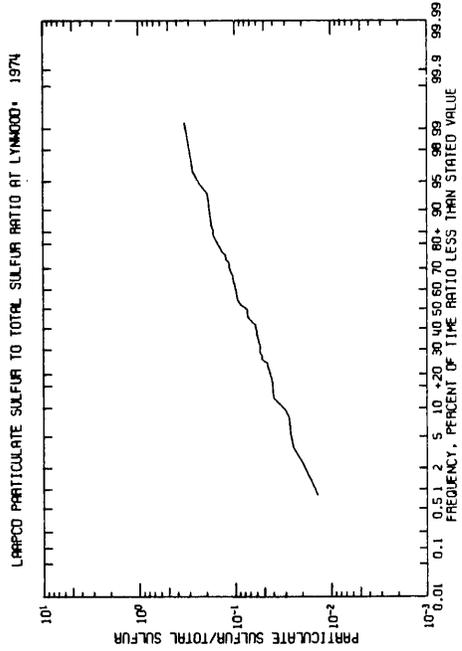


FIGURE B6.15

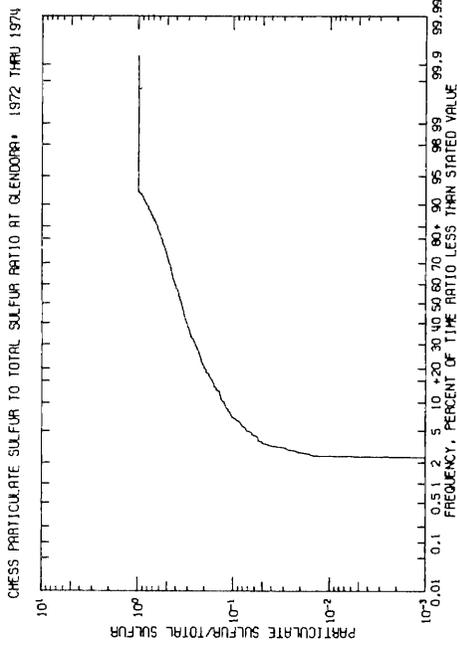


FIGURE B6.17

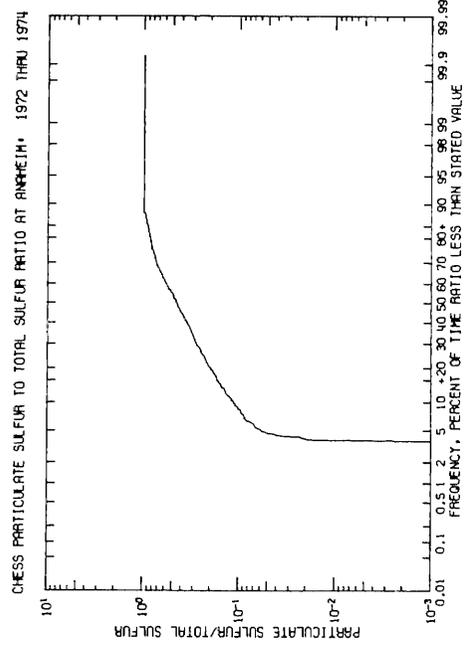


FIGURE B6.19

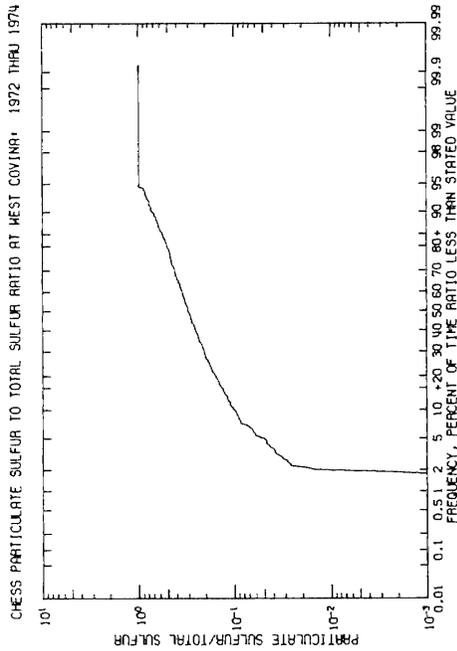


FIGURE B6.16

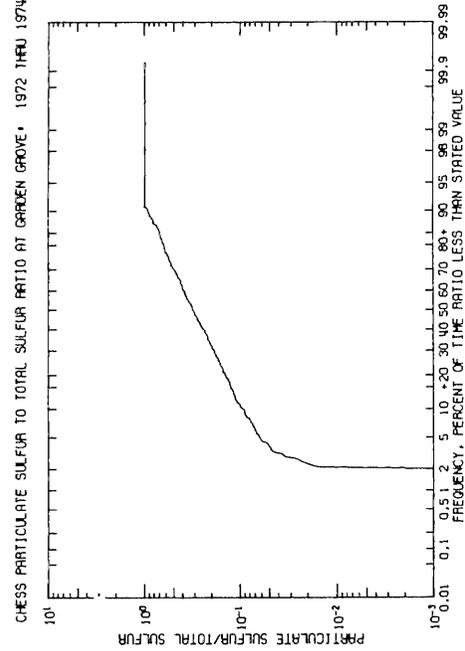


FIGURE B6.18

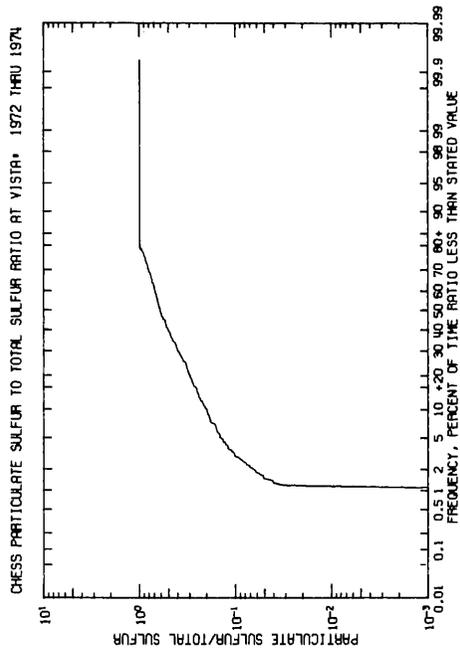


FIGURE B6.21

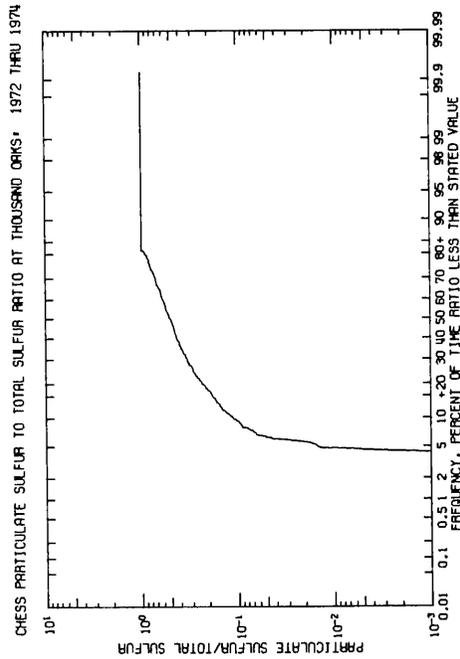


FIGURE B6.20

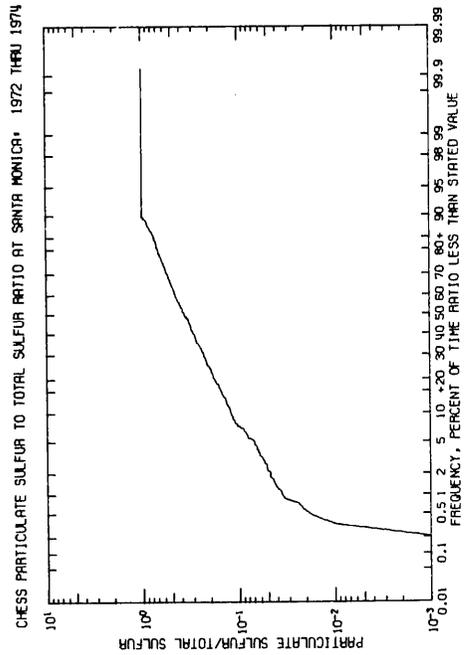


FIGURE B6.22

APPENDIX B7

MONTHLY MEAN VALUES OF THE RATIO OF PARTICULATE SULFUR TO
TOTAL SULFUR, COMPARED TO MONTHLY VALUES OF THE RATIO OF MEAN
PARTICULATE SULFUR TO MEAN TOTAL SULFUR: 1972 - 1974

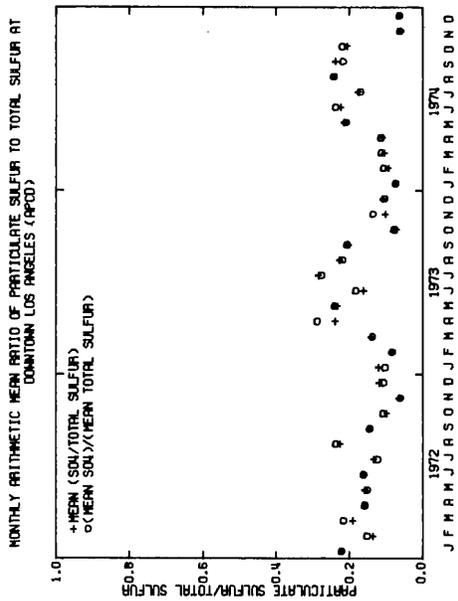


FIGURE B7.2

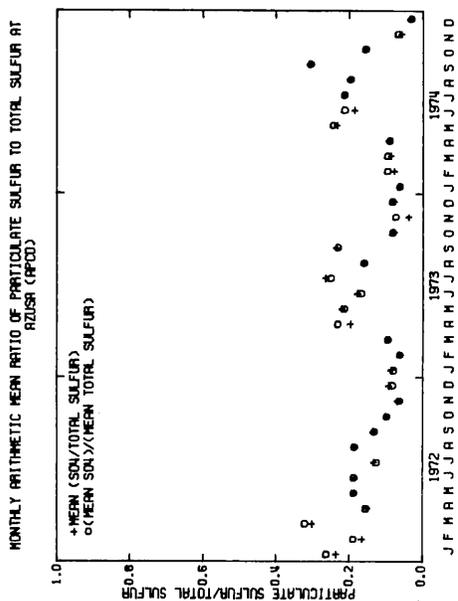


FIGURE B7.4

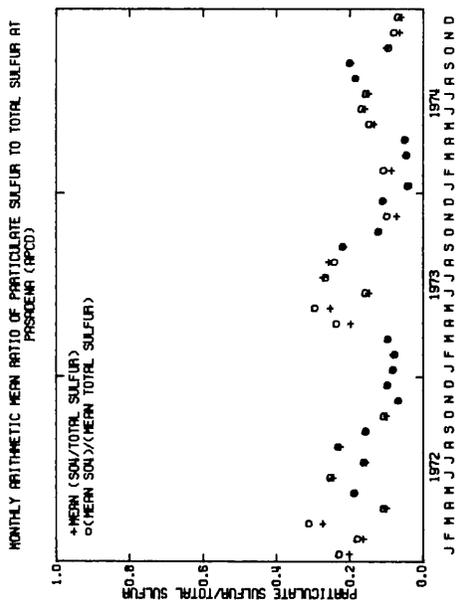


FIGURE B7.1

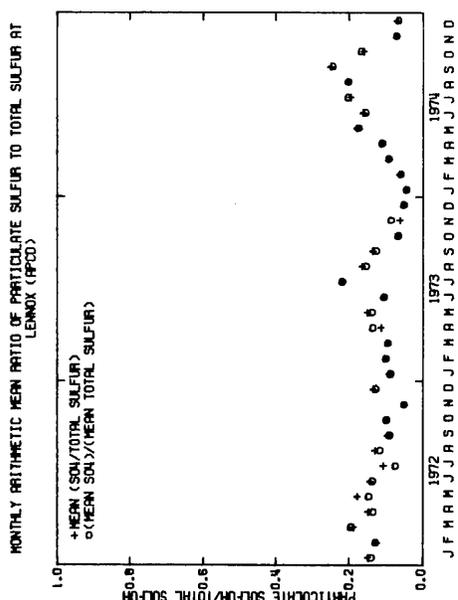


FIGURE B7.3

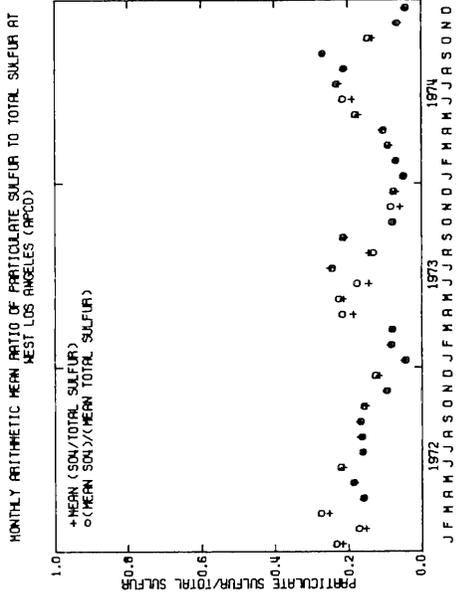


FIGURE B7.6

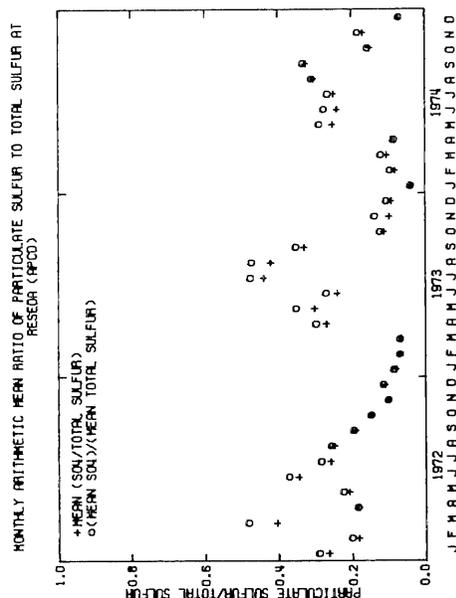


FIGURE B7.5

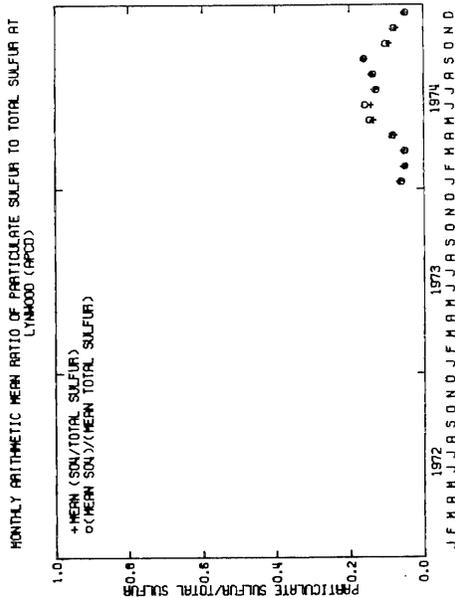


FIGURE B7.7

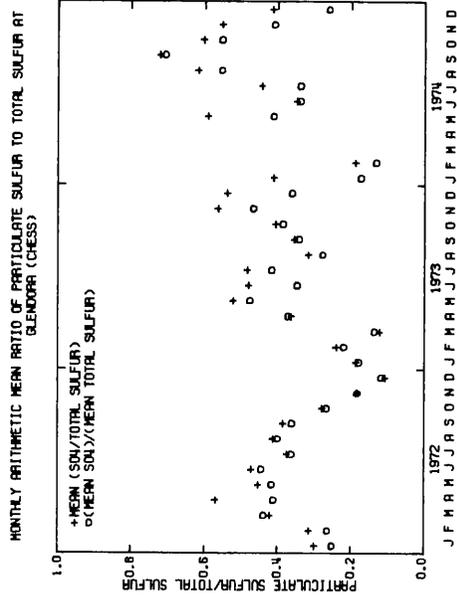


FIGURE B7.9

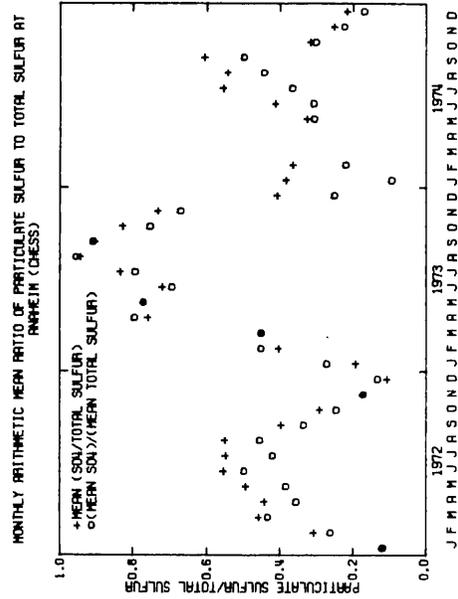


FIGURE B7.11

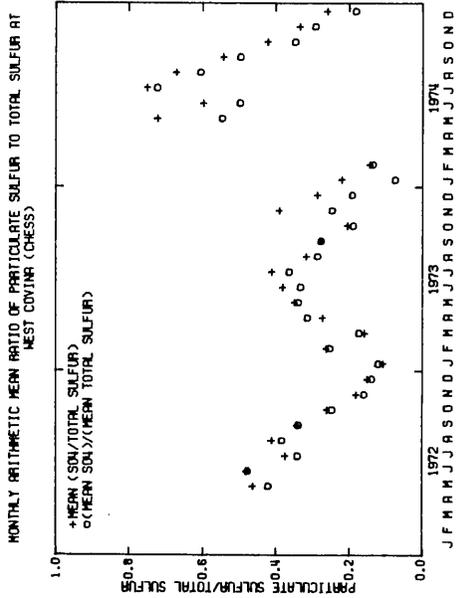


FIGURE B7.8

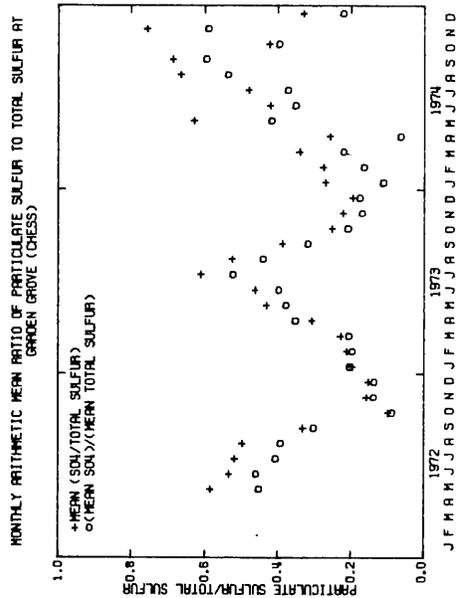


FIGURE B7.10

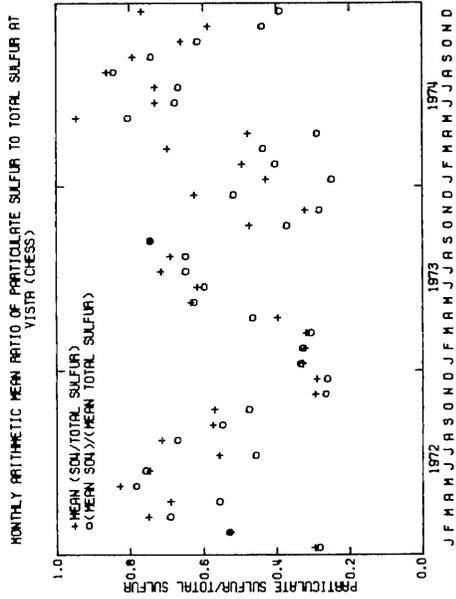


FIGURE B7.13

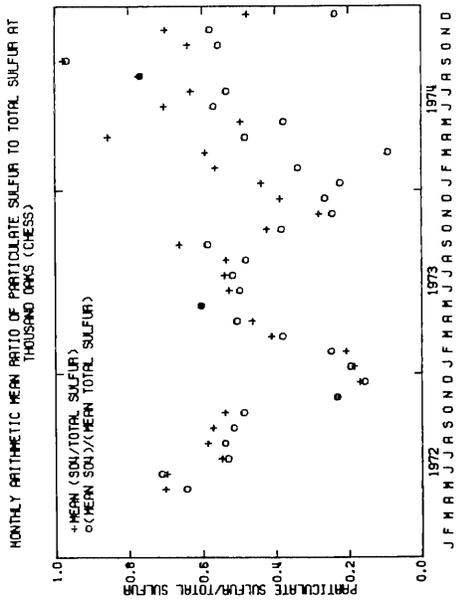


FIGURE B7.12

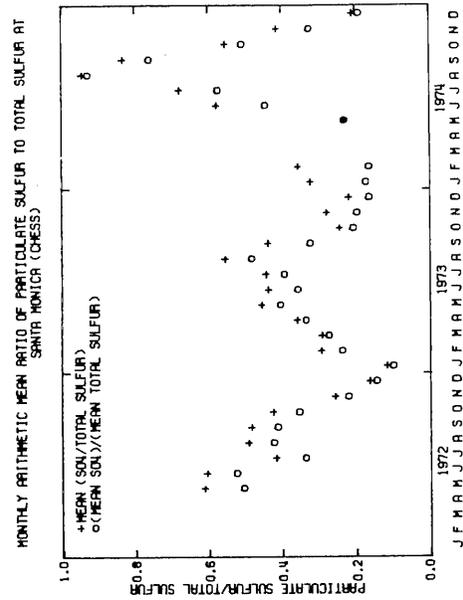


FIGURE B7.14

APPENDIX B8

DESCRIPTION OF THE DATA BASE USED
IN THE STUDY OF SULFATE CORRELATION WITH METEOROLOGICAL
AND POLLUTANT VARIABLES

Symbol	Description	Units in Which Value is Stated	Averaging Time
SO ₄	Water soluble sulfate ion concentration extracted from hi vol filter	µgm/m ³	24 hr
Inv. Max.	Height of afternoon inversion base over downtown LA (estimated from morning sounding) ^b	100's ft above msl	
Inv. Base	Height of early morning inversion base at LA Int'l Airport ^b	100's ft above msl	
Wind Sp	Scalar average wind speed at downtown LA	mph	24 hr
Sol Rad	Solar radiation intensity at downtown LA	$\frac{\text{gm cal}}{\text{cm}^2 \text{ hr}}$	24 hr
Max Temp	Maximum temperature reached at downtown LA	°F	
O3 Max	Instantaneous maxima of daily oxidant observations at downtown LA	pphm	
Avg O3	Average of daily oxidant observations at downtown LA	ppm	24 hr
NO ₂	Average of daily NO ₂ observations at downtown LA	ppm	24 hr
Total HC	Average of daily total hydrocarbon observations at downtown LA	ppm	24 hr
SO ₂	Average of daily SO ₂ observations at downtown LA	ppm	24 hr
TSP	Total suspended particulate concentration at downtown LA	µgm/m ³	24 hr
(1-RH)	One minus the average of relative humidity observations at downtown LA. Relative humidity expressed in percent/100		24 hr

Notes: (a) Averages are taken for the 24 hour period corresponding to the sulfate sample schedule. Missing hourly data were replaced by linear interpolation between adjacent data points prior to averaging. 24 hour average relative humidity values are approximate since observations are taken for 14 hours daily, thus necessitating extensive interpolation.
(b) Detailed estimates of mixing depth for observations with inversion height above 5000 ft are not available. Mixing depth on those occasions will be estimated as 6667 ft.

TABLE B8.1(a)

Statistical Description of Data Base
Used in Study of Sulfate Correlation with Meteorological
and Pollutant Variables

A. Data Base Incorporating all Complete Sets of Observations													
Sampling Station is Downtown Los Angeles													
Number of Complete Sets of Observations = 342													
Time Period Spanned is August 1965 through December 1974													
	SO ₄ ²⁻	Inv Max	Inv Base	Wind Speed	Solar Rad	Max Temp	Ozone Max	Avg Ozone	NO ₂	Total Hydrocarbons	SO ₂	TSP	(1-RH)
Average	13.97	40.57	18.51	5.36	18.48	75.72	11.77	0.032	0.083	3.32	0.019	157.26	0.36
Standard Deviation	11.60	17.09	19.55	1.19	6.80	10.08	7.67	0.017	0.039	1.11	0.007	59.20	0.17
Linear Correlation Between Variables													
SO ₄ ²⁻	1.00												
Inv Max	-0.55	1.00											
Inv Base	-0.04	0.30	1.00										
Wind Sp	-0.04	0.11	0.45	1.00									
Soi Rad	-0.04	-0.16	-0.08	0.31	1.00								
Max Temp	-0.07	-0.15	-0.39	-0.10	0.42	1.00							
O3 Max	0.09	-0.24	-0.36	-0.17	0.45	0.59	1.00						
AVG O3	0.18	-0.29	-0.24	-0.03	0.51	0.52	0.92	1.00					
NO ₂	0.11	-0.12	-0.46	-0.51	-0.15	0.24	0.34	0.17	1.00				
Total HC	-0.06	-0.08	-0.47	-0.58	-0.13	0.25	0.33	0.17	0.73	1.00			
SO ₂	0.25	-0.27	-0.39	-0.42	-0.10	0.19	0.22	0.10	0.49	0.42	1.00		
TSP	0.31	-0.32	-0.37	-0.39	-0.10	0.16	0.32	0.22	0.64	0.61	0.47	1.00	
(1-RH)	-0.49	0.46	-0.26	-0.06	0.02	0.33	0.11	-0.02	0.27	0.31	0.04	0.09	1.00
SO ₄ ²⁻	1.00												
Inv Max	-0.60	1.00											
Inv Base	-0.02	-0.02	1.00										
Wind Sp	-0.03	0.09	0.48	1.00									
Soi Rad	-0.03	-0.12	0.02	0.36	1.00								
Max Temp	0.009	-0.12	-0.24	-0.05	0.37	1.00							
O3 Max	0.22	-0.32	-0.21	-0.12	0.57	0.49	1.00						
AVG O3	0.31	-0.33	-0.02	-0.04	0.57	0.45	0.91	1.00					
NO ₂	0.14	-0.16	-0.50	-0.56	-0.09	0.20	0.30	0.15	1.00				
Total HC	-0.01	-0.10	-0.55	-0.63	-0.08	0.21	0.27	0.10	0.70	1.00			
SO ₂	0.22	-0.29	-0.35	-0.45	-0.06	0.16	0.24	0.13	0.47	0.43	1.00		
TSP	0.38	-0.35	-0.33	-0.44	-0.03	0.15	0.35	0.24	0.66	0.62	0.48	1.00	
(1-RH)	-0.50	0.44	-0.48	-0.09	0.16	0.27	0.04	-0.06	0.25	0.27	0.04	0.10	1.00
Correlation Between Natural Log of Variables													
SO ₄ ²⁻	1.00												
Inv Max	-0.60	1.00											
Inv Base	-0.26	-0.02	1.00										
Wind Sp	-0.03	0.09	0.48	1.00									
Soi Rad	-0.03	-0.12	0.02	0.36	1.00								
Max Temp	0.009	-0.12	-0.24	-0.05	0.37	1.00							
O3 Max	0.22	-0.32	-0.21	-0.12	0.57	0.49	1.00						
AVG O3	0.31	-0.33	-0.02	-0.04	0.57	0.45	0.91	1.00					
NO ₂	0.14	-0.16	-0.50	-0.56	-0.09	0.20	0.30	0.15	1.00				
Total HC	-0.01	-0.10	-0.55	-0.63	-0.08	0.21	0.27	0.10	0.70	1.00			
SO ₂	0.22	-0.29	-0.35	-0.45	-0.06	0.16	0.24	0.13	0.47	0.43	1.00		
TSP	0.38	-0.35	-0.33	-0.44	-0.03	0.15	0.35	0.24	0.66	0.62	0.48	1.00	
(1-RH)	-0.50	0.44	-0.48	-0.09	0.16	0.27	0.04	-0.06	0.25	0.27	0.04	0.10	1.00

TABLE B8.1(b)

Statistical Description of Data Base
Used in Study of Sulfate Correlation with Meteorological
and Pollutant Variables

B. Data Base Incorporating Observations Since Change in Sampling Schedule of September, 1970
Sampling Station is Downtown Los Angeles
Number of Complete Sets of Observations = 186
Time Period is September 1970 through December 1974

	SO ₄	Inv Max	Inv Base	Wind Speed	Solar Rad	Max Temp	Ozone Max	NO ₂	Total Hydrocarbons	SO ₂	TSP	(1-RH)
Average	16.15	40.84	20.15	5.56	17.49	75.46	9.67	0.028	3.15	0.019	151.19	0.36
Standard Deviation	13.11	16.67	20.19	1.31	6.68	11.12	6.32	0.015	1.04	0.008	61.26	0.16

	SO ₄	Inv Max	Inv Base	Wind Speed	Solar Rad	Max Temp	Ozone Max	NO ₂	Total Hydrocarbons	SO ₂	TSP	(1-RH)
SO ₄	1.00	-0.54	-0.05	-0.13	-0.04	-0.13	-0.13	-0.19	-0.12	-0.007	0.33	-0.55
Inv Max	-0.54	1.00	0.35	0.20	-0.09	-0.14	-0.23	-0.22	-0.19	-0.16	-0.39	0.40
Inv Base	0.05	0.35	1.00	0.44	-0.20	-0.38	-0.41	-0.25	-0.45	-0.65	-0.38	-0.26
Wind Sp	-0.13	0.20	0.44	1.00	0.27	-0.05	-0.14	0.02	-0.47	-0.56	-0.39	0.06
Soi Rad	-0.04	-0.09	-0.20	0.27	1.00	0.50	0.51	0.55	-0.12	-0.11	-0.06	0.11
Max Temp	-0.13	-0.14	-0.38	-0.05	0.50	1.00	0.59	0.50	0.18	0.14	0.17	0.35
O3 Max	0.13	-0.23	-0.41	-0.14	0.51	0.59	1.00	0.91	0.24	0.20	0.26	0.18
Avg O3	0.19	-0.22	-0.24	0.02	0.55	0.50	0.91	1.00	0.02	-0.03	0.12	0.01
NO ₂	0.12	-0.19	-0.45	-0.47	-0.12	0.18	0.24	0.02	1.00	0.77	0.51	0.68
Total HC	-0.007	-0.16	-0.45	-0.56	-0.11	0.14	0.20	-0.03	0.77	1.00	0.42	0.27
SO ₂	0.34	-0.39	-0.38	-0.39	-0.06	0.17	0.26	0.12	0.51	0.42	1.00	-0.06
TSP	0.33	-0.35	-0.37	-0.35	-0.09	0.06	0.18	0.02	0.68	0.67	0.50	1.00
(1-RH)	-0.55	0.40	-0.26	0.06	0.11	0.35	0.15	0.01	0.25	0.27	-0.06	1.00

Linear Correlation Between Variables

Correlation Between Natural Log of Variables

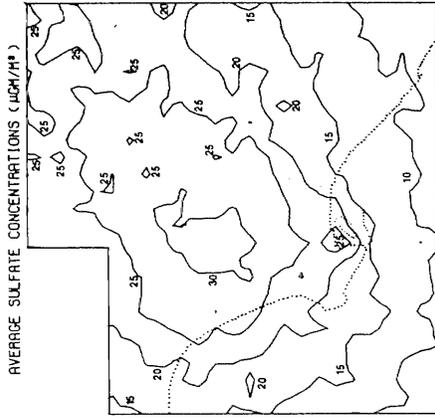
SO ₄	1.00	-0.62	0.27	-0.09	-0.007	-0.10	0.26	0.32	0.08	0.004	0.37	-0.66
Inv Max	-0.62	1.00	0.07	0.19	-0.07	-0.08	-0.33	-0.26	-0.21	-0.14	-0.42	0.40
Inv Base	0.27	0.07	1.00	0.43	-0.13	-0.25	-0.34	-0.09	-0.50	-0.51	-0.31	-0.51
Wind Sp	-0.09	0.19	0.43	1.00	0.31	0.01	-0.10	0.12	-0.52	-0.61	-0.42	0.01
Soi Rad	-0.007	-0.07	-0.13	0.31	1.00	0.38	0.59	0.58	-0.05	-0.05	-0.03	0.22
Max Temp	0.10	-0.08	-0.25	0.01	0.38	1.00	0.43	0.37	0.13	0.12	0.13	0.28
O3 Max	0.26	-0.33	-0.37	-0.10	0.59	0.43	1.00	0.89	0.24	0.20	0.32	0.07
Avg O3	0.32	-0.26	-0.09	0.12	0.58	0.37	0.89	1.00	0.00	-0.05	0.15	-0.06
NO ₂	0.08	-0.21	-0.50	-0.52	-0.05	0.13	0.24	0.00	1.00	0.71	0.51	0.27
Total HC	0.004	-0.14	-0.51	-0.61	-0.05	0.12	0.20	-0.05	0.71	1.00	0.42	0.27
SO ₂	0.37	-0.42	-0.31	-0.42	-0.03	0.13	0.32	0.15	0.51	0.42	1.00	-0.08
TSP	0.35	-0.39	-0.37	-0.41	-0.01	0.04	0.26	0.06	0.69	0.67	0.54	1.00
(1-RH)	-0.66	0.40	-0.21	0.01	0.23	0.28	0.07	-0.06	0.27	0.28	-0.08	0.09

APPENDIX C

APPENDICES TO THE
AIR QUALITY MODEL VALIDATION STUDY

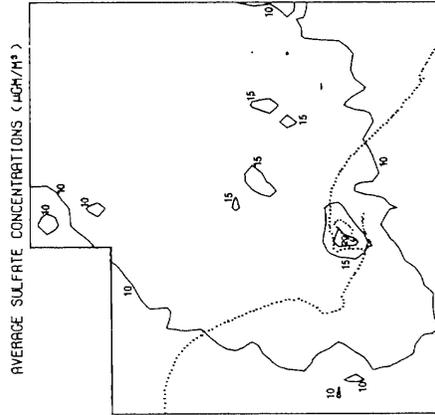
APPENDIX C1

MONTHLY ARITHMETIC MEAN SULFATE
CONCENTRATION ISOPLETHS FOR THE PERIOD 1972 THROUGH 1974



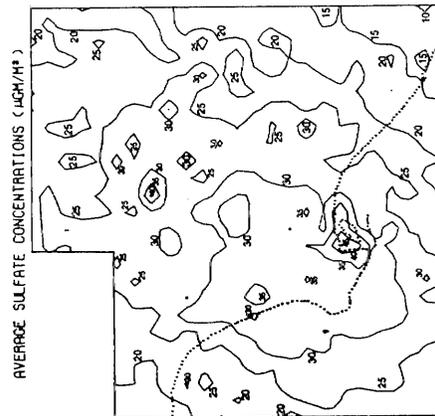
MARCH, 1972

FIGURE C1.3



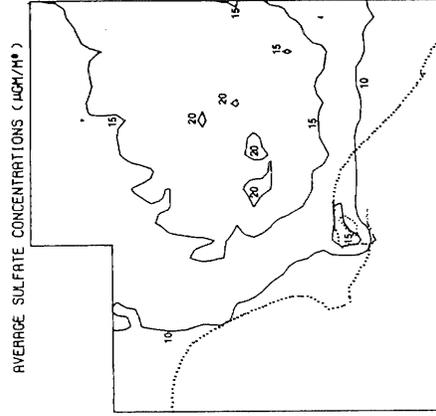
FEBRUARY, 1972

FIGURE C1.2



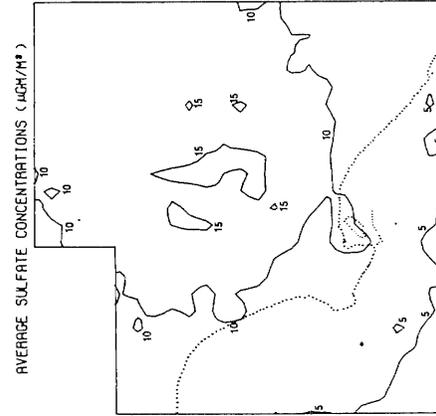
JANUARY, 1972

FIGURE C1.1



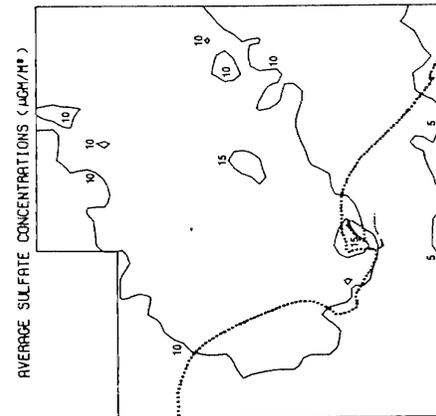
JUNE, 1972

FIGURE C1.6



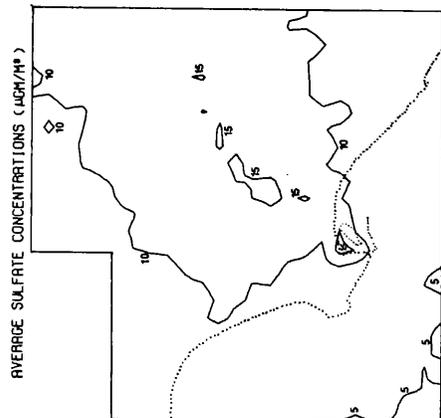
MAY, 1972

FIGURE C1.5



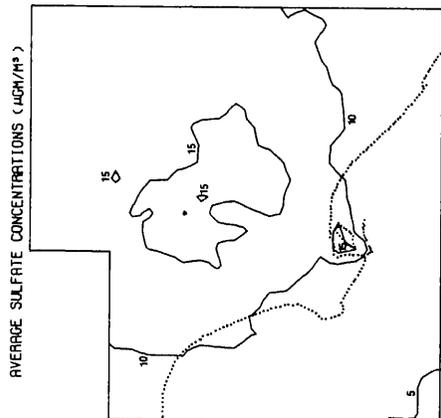
APRIL, 1972

FIGURE C1.4



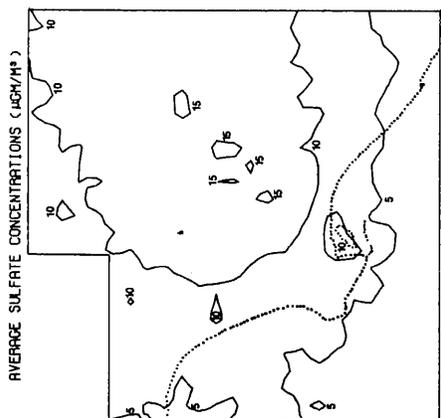
SEPTEMBER, 1972

FIGURE C1.9



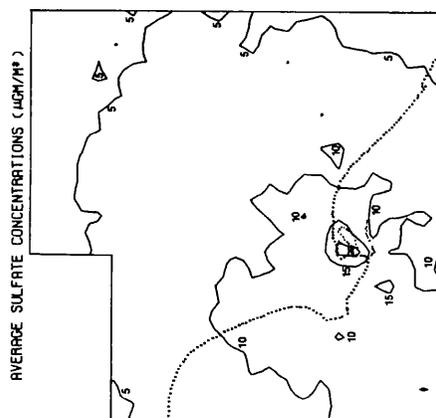
AUGUST, 1972

FIGURE C1.8



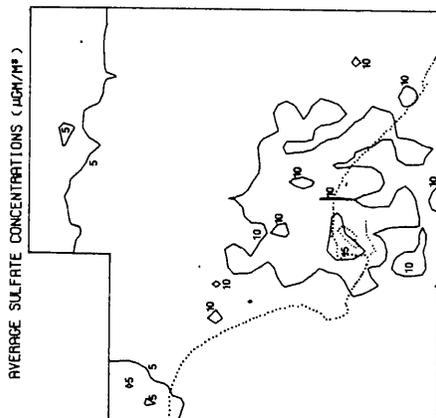
JULY, 1972

FIGURE C1.7



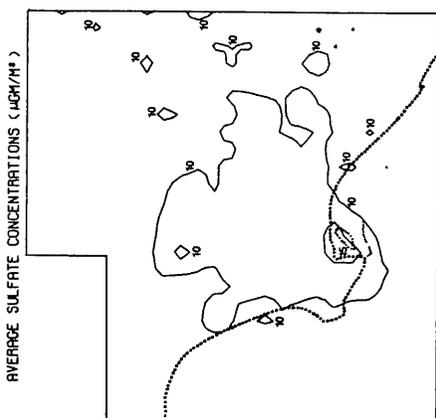
DECEMBER, 1972

FIGURE C1.12



NOVEMBER, 1972

FIGURE C1.11



OCTOBER, 1972

FIGURE C1.10

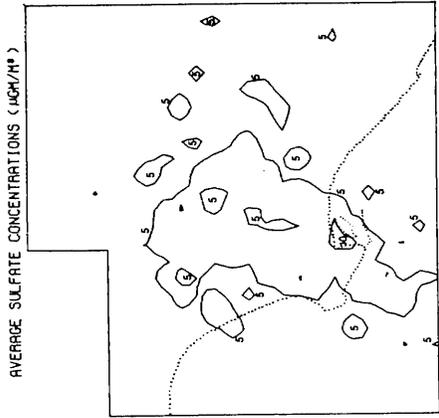


FIGURE C1.15

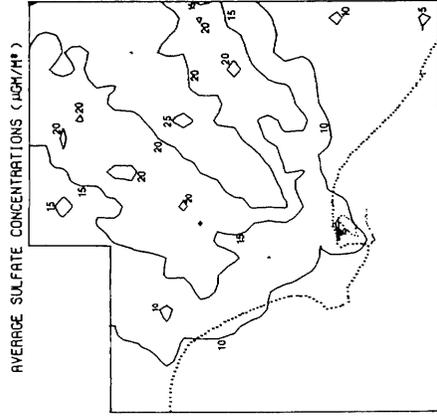


FIGURE C1.18

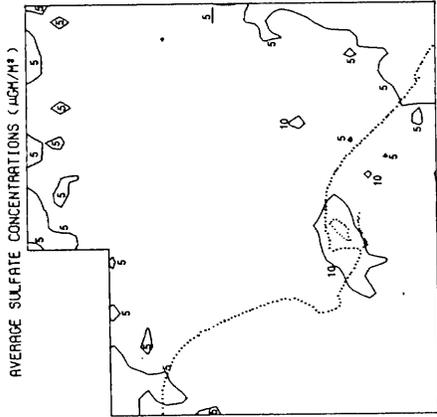


FIGURE C1.14

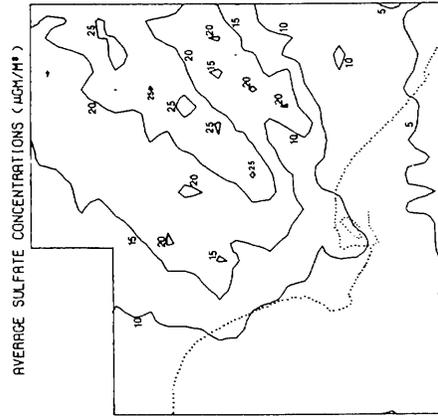


FIGURE C1.17

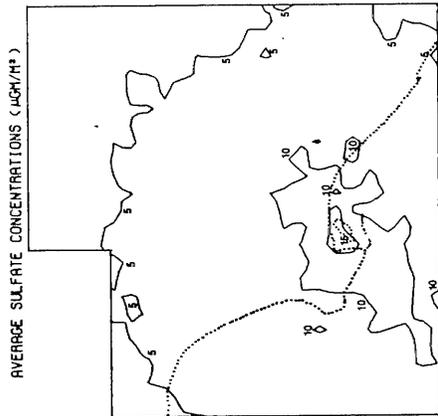


FIGURE C1.13

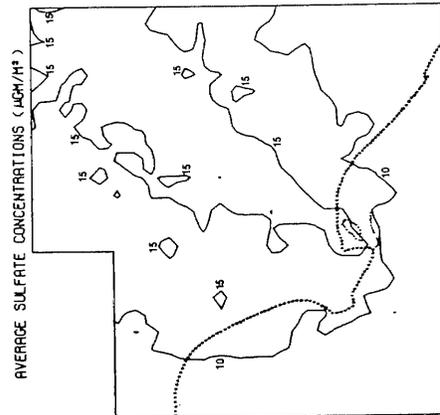
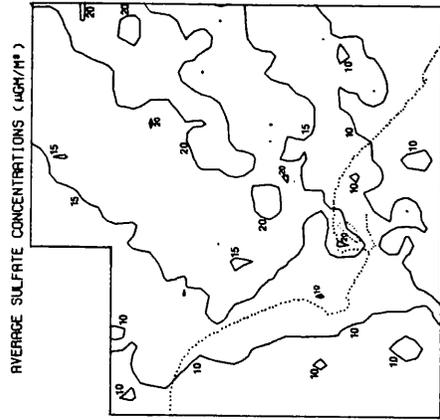
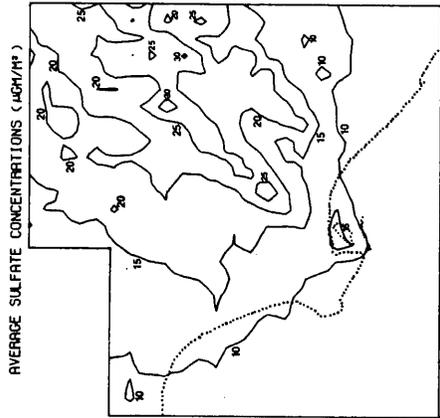


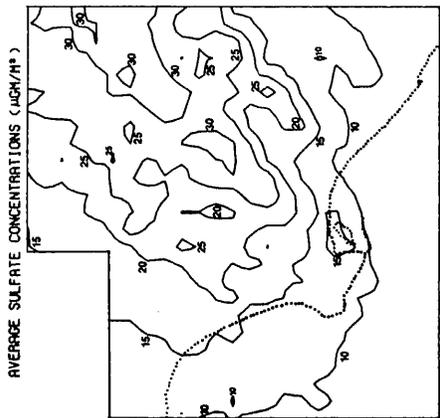
FIGURE C1.16



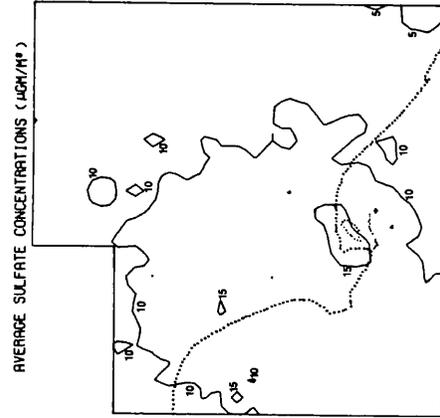
SEPTEMBER, 1973
FIGURE C1.21



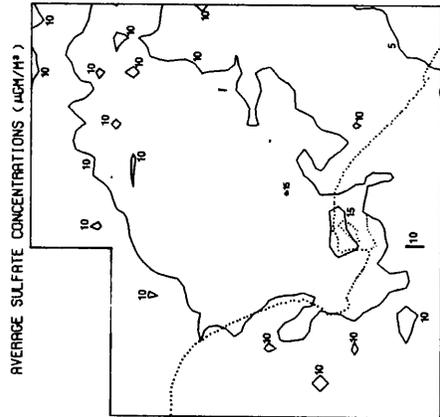
AUGUST, 1973
FIGURE C1.20



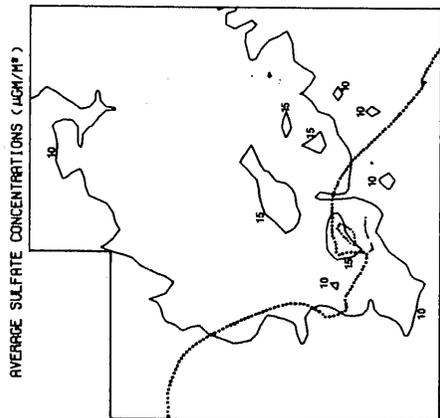
JULY, 1973
FIGURE C1.19



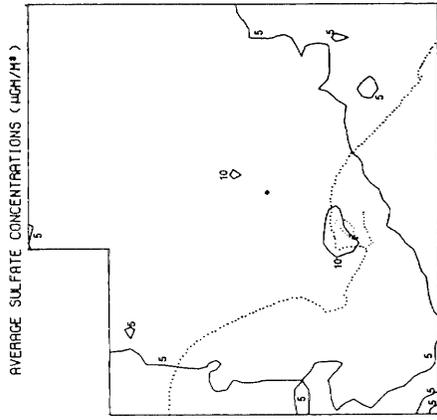
DECEMBER, 1973
FIGURE C1.24



NOVEMBER, 1973
FIGURE C1.23

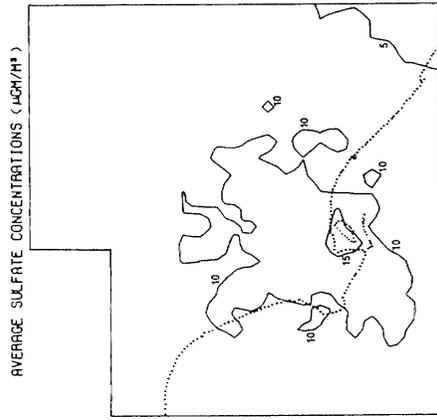


OCTOBER, 1973
FIGURE C1.22



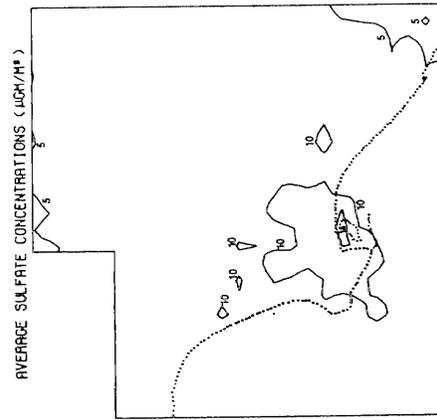
MARCH, 1974

FIGURE C1.27



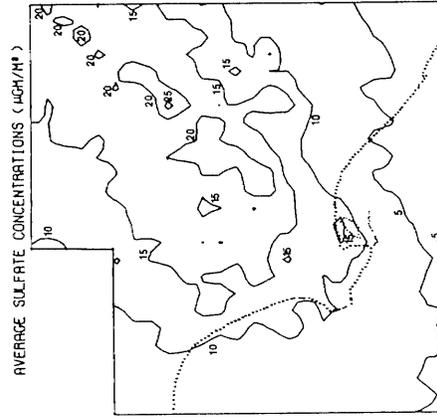
FEBRUARY, 1974

FIGURE C1.26



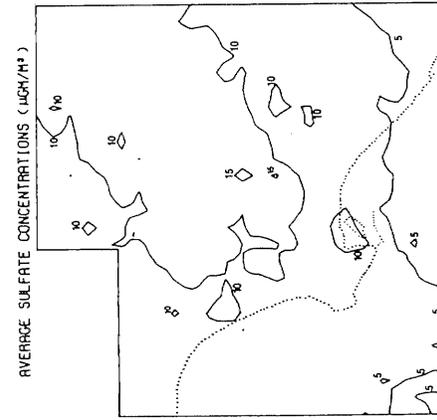
JANUARY, 1974

FIGURE C1.25



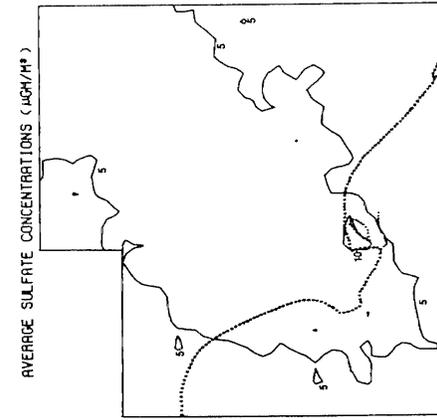
JUNE, 1974

FIGURE C1.30



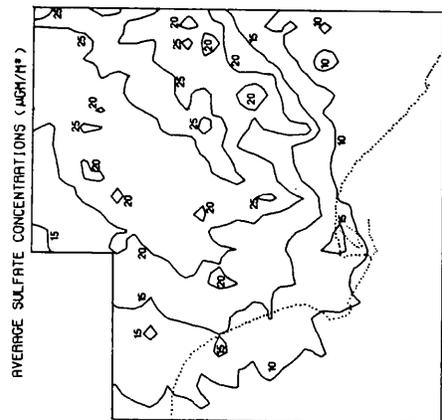
MAY, 1974

FIGURE C1.29



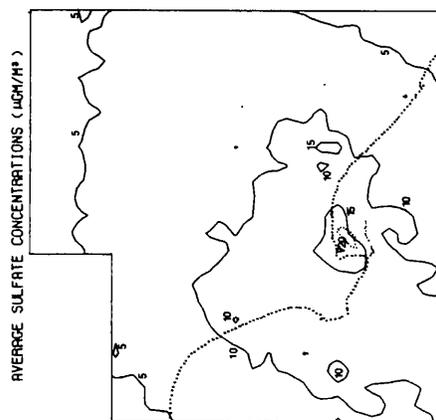
APRIL, 1974

FIGURE C1.28



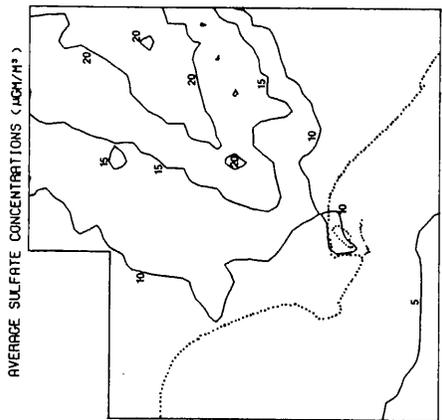
SEPTEMBER, 1974

FIGURE C1.33



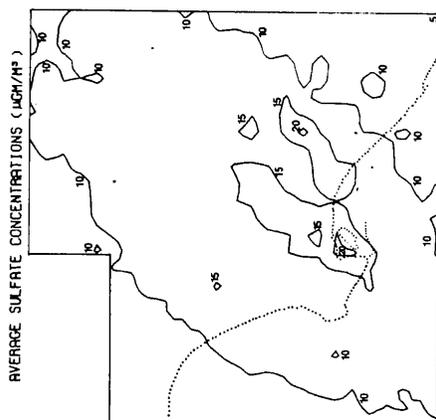
DECEMBER, 1974

FIGURE C1.36



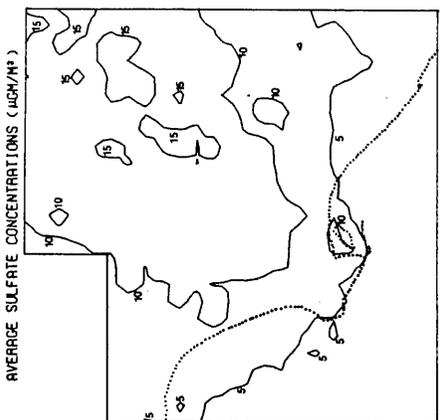
AUGUST, 1974

FIGURE C1.32



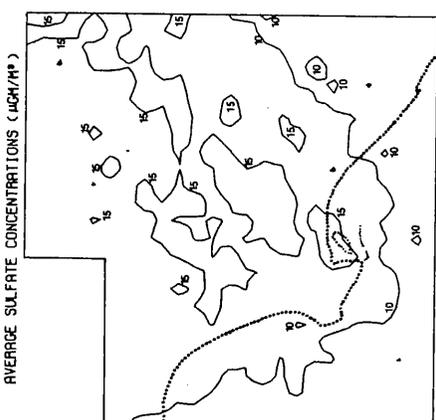
NOVEMBER, 1974

FIGURE C1.35



JULY, 1974

FIGURE C1.31



OCTOBER, 1974

FIGURE C1.34

APPENDIX C2

OBSERVED VERSUS PREDICTED VALUES OF
THE RATIO OF SULFATES TO TOTAL SULFUR OXIDES

As was noted in Chapter 2, it is more convenient to model the ratio of average sulfate to average total sulfur, f_s^- , than it is to predict average values of f_s for each month. These two particulate sulfur to total sulfur ratio statistics were compared in Appendix B, and found to display similar seasonal trends. Figures C2.1 through C2.11 compare simulation model results for monthly values of f_s^- to observations on f_s^- at all CHES and LAAPCD monitoring stations within our receptor zone.

A comparison of f_s^- predictions to observations in the Eastern San Gabriel Valley at Azusa and Glendora serves to test our hypotheses about the nature of the sampling network biases. Air quality model results for f_s^- at these nearby locations are very similar, as shown in Figures C2.1 and C2.2. The LAAPCD monitoring network rounds SO_2 measurements which are below their minimum detection limit up to $26 \mu\text{gm}/\text{m}^3$. This raises the average of total SO_x observations at Azusa and lowers the value of f_s^- observed. As expected, model predictions for f_s^- at Azusa fall above the reported observations. Predictions and observations on f_s^- at Azusa both display similar seasonal trends, which is encouraging. The CHES monitoring station at Glendora used a sulfur dioxide sampling method which also has minimum detection limit problems. In contrast to the LAAPCD practice, the CHES network

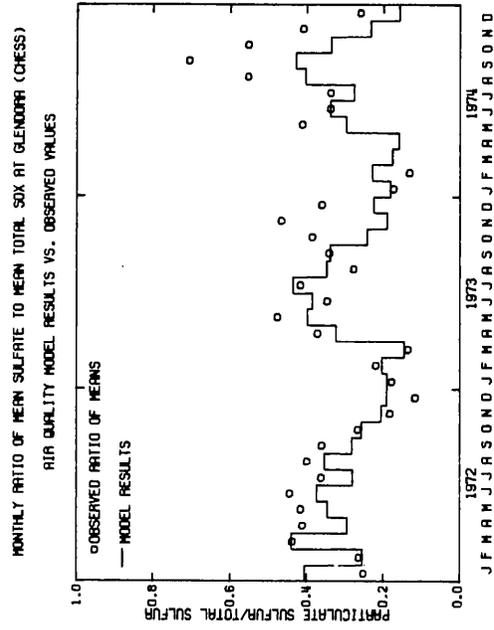


FIGURE C2.2

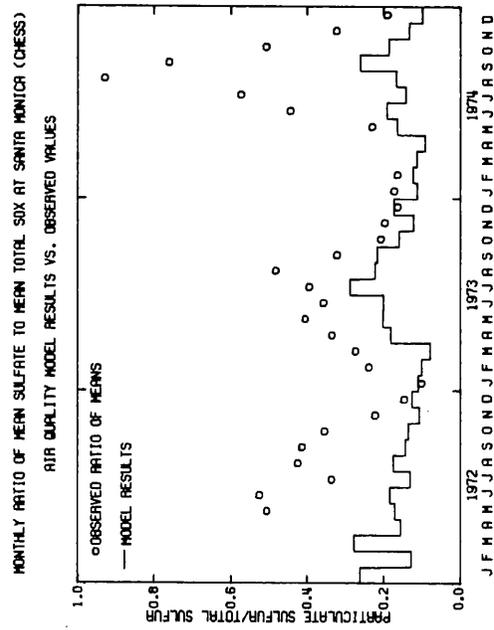


FIGURE C2.4

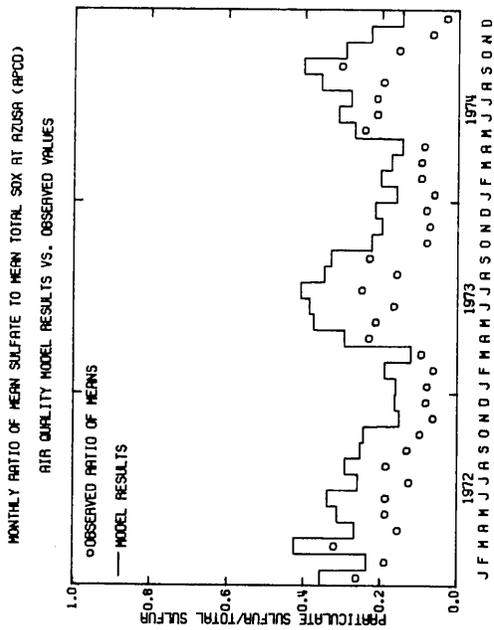


FIGURE C2.1

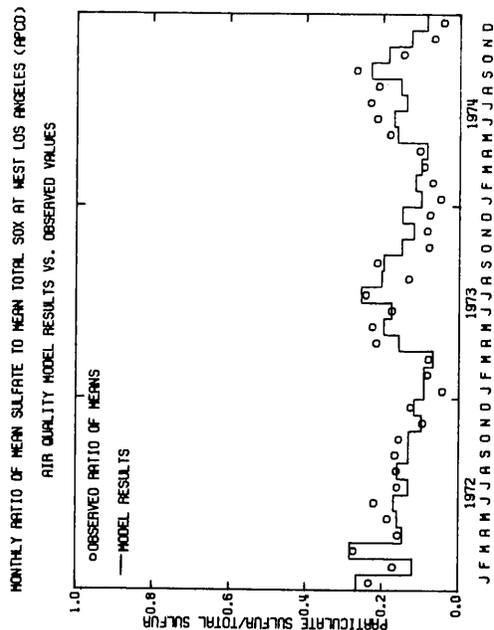


FIGURE C2.3

attempts to report a closest estimate of SO_2 concentrations which are below their nominal detection limit without truncation or round-up. However, systematic underestimation of SO_2 levels at low SO_2 concentrations is likely using the West-Gaeke SO_2 sampling method if reagent volume and airflow rate are not matched to the expected ambient SO_2 concentrations, or if close control is not maintained over the time-temperature history of the sample. Model results for f_s^- at Glendora are generally lower than observations, as expected. Observations on f_s^- match predictions closely at Glendora until late 1973. In October 1973, model predictions at both locations and measured f_s^- values at Azusa begin a short term decline, while f_s^- measurements at Glendora begin to rise. From that point onward, comparison of model results to f_s^- observations at Glendora becomes erratic. One suspects that the CHES sampling protocol was changed.

A second comparison of nearby CHES and LAAPCD air monitoring station data to model predictions for f_s^- is possible near West Los Angeles. Figures C2.3 and C2.4 show results obtained at the CHES station in Santa Monica versus the measurements made at the LAAPCD station in West Los Angeles. Model results closely match LAAPCD observations at West Los Angeles and fall below CHES data at Santa Monica.

In order to test the accuracy of model predictions for f_s^- , it is going to be necessary to find a monitoring site which is known to experience high enough SO_2 concentrations that detection limit problems will be minimized. None of the CHES stations are located near major

SO₂ sources. However the LAAPCD station at Lennox is adjacent to a busy freeway and is directly downwind of two power plants, an oil refinery, and Los Angeles International Airport. When model results at Lennox are compared to observations in Figure C2.5, excellent agreement is noted.

Model predictions for f_s fall below the LAAPCD monitoring results at downtown Los Angeles. That is the only LAAPCD station where model predictions do not confirm the suggested sampling bias in the LAAPCD SO₂ data. Reference to the emissions inventory of Chapter 4 and Appendix A2 suggests one likely source for this problem. SO_x emissions at downtown Los Angeles are dominated by a mobile source SO_x emission density comparable to many of our industrial point sources. With such large emissions rates located at ground level, total SO_x air quality at the downtown monitoring site will be controlled by mobile sources located within the same receptor cell as the monitoring station. As mentioned in Chapter 5, the air quality simulation was not constructed with the intention of accurately reproducing concentrations in the extreme near-field. No sub-grid scale processes are embedded in the model. In spite of that, the model reproduces reasonable total sulfur concentration in most parts of the airshed.

Therefore, the emissions inventory was reviewed to see if there was anything unusual about the emissions estimates at downtown Los Angeles. It was found that a large fraction of the SO_x emissions from within the receptor cell containing the downtown monitoring site arise from one of the few railroad switching yards in the air basin.

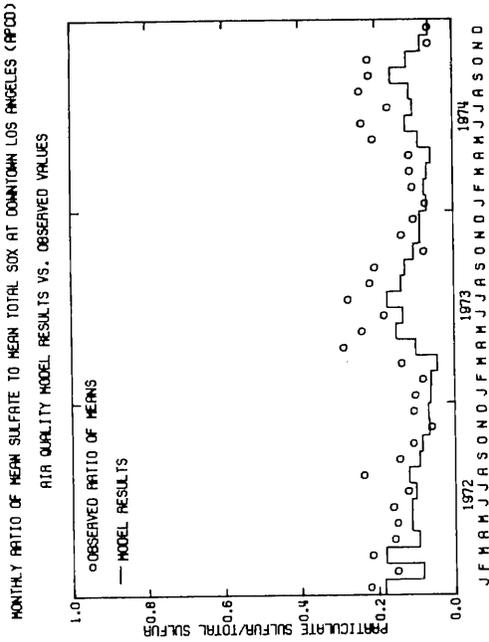


FIGURE C2.6

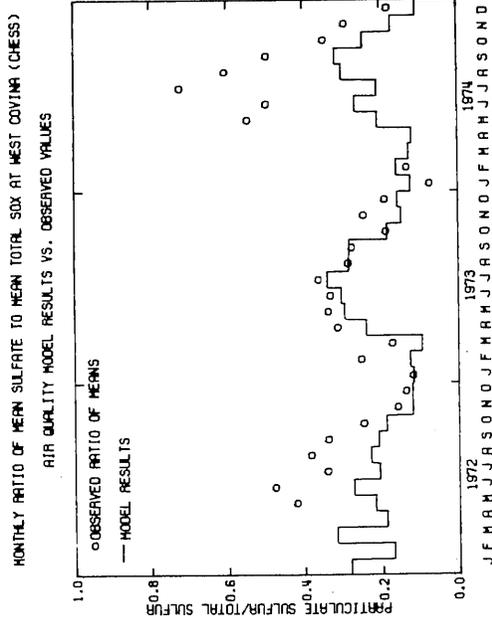


FIGURE C2.8

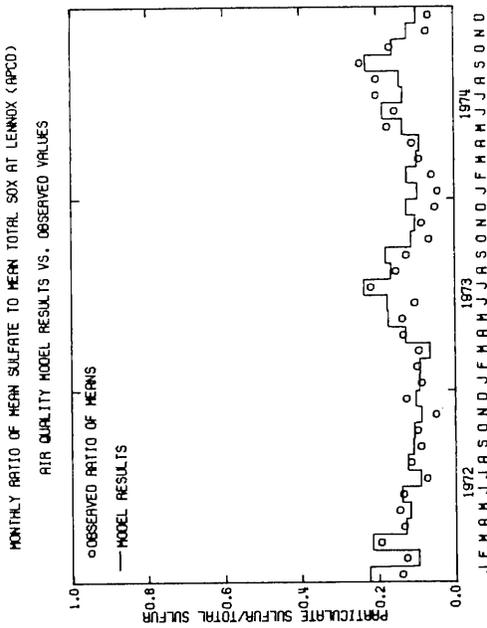


FIGURE C2.5

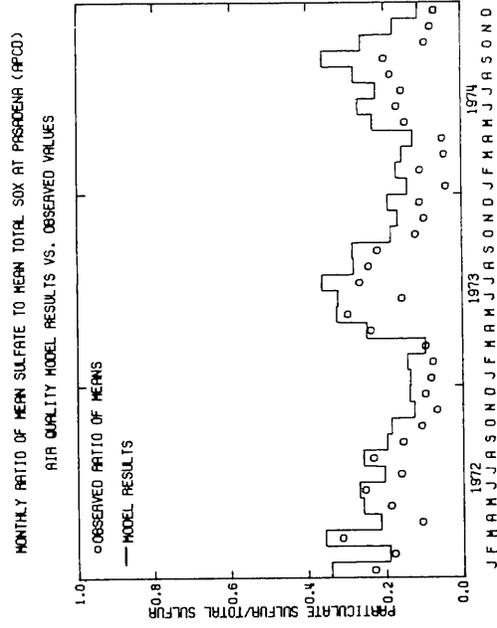


FIGURE C2.7

Emissions estimates for railroads were obtained in Appendix A2 by a rapid survey emission inventory technique and not from the higher quality site-specific information used throughout most of our other source classes. That railroad switching yard may well account for much of the over-estimate in total SO_x air quality at the downtown monitoring site.

It is also worth noting that the downtown Los Angeles monitoring station is located on the upper floors of a tall building, about 20 meters above ground level. While that is still below the minimum mixing depth reported by the LAAPCD, the actual minimum mixing depth at night might be lower on occasion. Such surface inversions at night could trap pollutants below the level of the monitoring station, yielding lower SO_2 concentration measurements than would be the case at a ground level monitoring site in the same location.

Data at the remaining LAAPCD and CHES air monitoring stations fall to the expected side of the model predictions for f_s . The comparison between model results and observations at the CHES stations at Garden Grove and Anaheim is poor in the summer. This is due in part to our underprediction of sulfate levels at those locations. But more importantly, the f_s values measured at these two locations are extremely suspect. Those stations are located within two miles of each other, which means that they could have been located within a single grid cell if desired when our grid system was established. Observations on f_s at those two sites are so

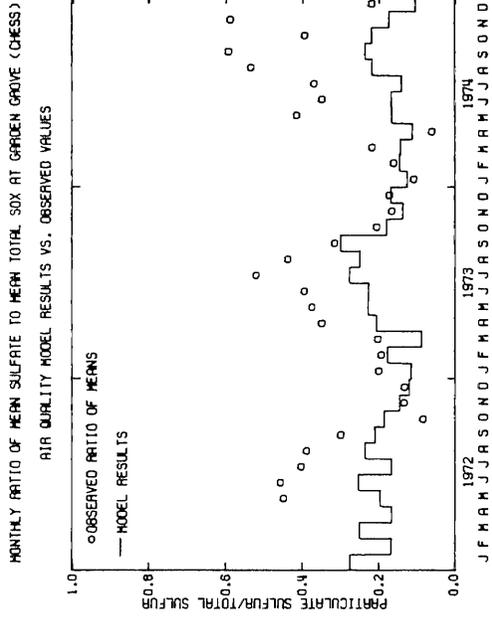


FIGURE C2.10

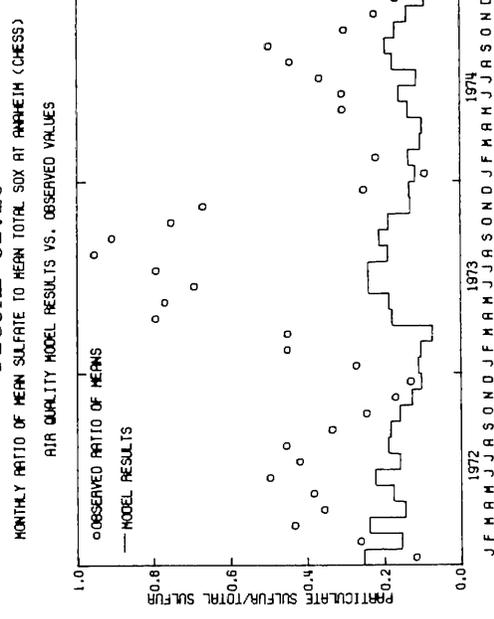


FIGURE C2.11

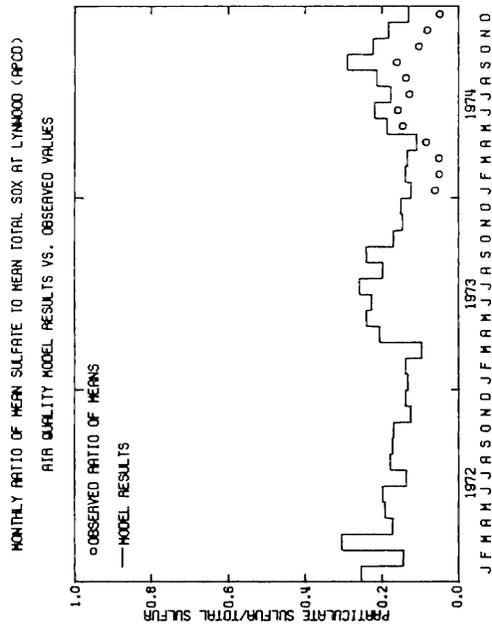


FIGURE C2.9

different that one suspects the accuracy of the SO₂ measurements involved, or the representativeness of the monitoring site locations.

Additional data on f_s which are relatively free of minimum detection limit problems are available from the ACHEX Study (Hidy, et al, 1975). These data are compared to model predictions in Table C2.1. Close agreement is obtained at Dominguez Hills and Pomona. ACHEX values for West Covina are below model estimates during July 1973. Differences of that magnitude could easily arise from the fact that the ACHEX program did not sample for the entire month or from the fact that model results are for the ratio of mean sulfate to mean total sulfur oxides, while the ACHEX data are for the average of the ratio of particulate sulfur oxides to total sulfur.

It is concluded that model predictions for the ratio of particulate sulfur oxides to total sulfur oxides cannot be verified as closely as model predictions for sulfate air quality. This situation arises from the unavailability of sensitive sulfur dioxide air quality data. However, on the basis of what can be said from comparison to available monitoring data, most indications are that the model is working well within the context of this application.

TABLE C2.1
 Particulate Sulfur to Total Sulfur Ratios:
 Comparison of Simulation Model Results
 to Measurements from the ACHEX Study

Location	Month	ACHEX Data on $\frac{f}{s}$ (a)		Simulation Model $\frac{f}{s}$	Grid Square
		Day	Night		
Dominguez Hills	October 1973	0.119	0.119	0.13	I11-J11
West Covina	July 1973	0.18	0.24	0.34	I21-J18
Pomona	August 1973	0.27	0.31	0.29	I25-J18

(a) From Table 4-1 of Volume IV of the ACHEX Study (Hidy, et al., 1975)

APPENDIX C3

ERRATA FOR CHAPTER 5:
A SULFUR OXIDES OMISSION INVENTORY

A series of quality control checks were performed on the model results to detect any minor errors which might escape a visual screening of the data. It was found that emissions from a subset of members of the miscellaneous stationary source category had been inadvertently deleted during the source class recombination step prior to execution of the model. The error occurred only in alternate months (February, April, June, etc.) and involved only 2% of the emissions within the inventory when it did occur. From a comparison of model results for months with and without the truncated inventory, an upper limit could be placed on the effect of the omission. The loss to the three year average sulfate air quality level predicted at pollutant monitoring stations ranged from 0.08 to 0.29 $\mu\text{g}/\text{m}^3 \text{SO}_4$, with an average reduction over all stations of 0.15 $\mu\text{g}/\text{m}^3$. To put that in perspective, the bias introduced is about 1% of the total average sulfate level in the air basin, and would alter the graphs of Chapter 5 section 5.4 by about the width of the pen used to plot them. Model output from one repetition to another varies by more than that amount due to the random number generators employed. None of our peak sulfate months (January 1972, March 1972, July 1973, September 1974) were affected. It was concluded that model validation results are insensitive to the omission. Corrective action will be taken prior to control strategy analysis.

APPENDIX D

APPENDICES TO THE VISIBILITY STUDY

APPENDIX D1

SOME PREVIOUS INVESTIGATIONS OF VISIBILITY AT LOS ANGELES

A number of investigators have reviewed visibility observations at Los Angeles with an eye toward determining the causes of reduced visual range. Long-term trends in visibility at Los Angeles are discussed by Neiburger (1955); Kauper, Holmes and Street (1955); Keith (1964); and Keith (1970). These studies conclude that visibility definitely deteriorated at Los Angeles during the period of industrialization which accompanied World War II. Several of these authors observe that this trend toward reduced visibility had been partially reversed by the early 1950's as a result of the initial imposition of pollution controls following the war years. This improvement was apparently not permanent. The most recent study (Keith, 1970) concludes that average noontime visibility at downtown Los Angeles had deteriorated over the past 37 years, and that the trend in this average was still downward as of 1969. Keith (1970) shows that this decline in average visibility is accompanied by a strong increasing trend in the number of days per year with visibilities falling into the ranges 1-1/2 to 2-1/2 miles, and 3 to 6 miles. It is of interest to note that this is the same portion of the cumulative distribution of visibilities which our regression model predicts will be most affected by alterations in atmospheric sulfate levels. (See Figures 6.8 and 6.9 in the main body of this study.)

Studies of visibility in relation to meteorological parameters have been performed by Renzetti, et al. (1955) and by Neiburger (1955). Documentation of the effects of high relative humidity on light extinction by Los Angeles smog aerosols is provided, and the variations of visibility with wind direction are discussed.

The relation of pollutant concentrations to visibility reduction has been explored. Early research efforts by the Los Angeles Air Pollution Control District led to the statement that,

"It has been established that a significant percentage of the sulfur dioxide in the atmosphere oxidizes to sulfur trioxide. Preliminary evidence indicates that this acid mist could account for thirty to sixty percent of the total reduction in visibility." (Los Angeles Pollution Control District, 1950)¹

Upon further study, the class of compounds in the aerosol phase potentially responsible for light extinction was found to be quite complex, including a wide variety of hygroscopic liquid droplets, carbon, "tar", opaque particles, plus soluble and insoluble transparent solids (Stanford Research Institute, 1954). The study of Renzetti, et al. (1955) attempted to correlate particulate loading of the atmosphere at Los Angeles and Pasadena with transmissometer measurements of visibility, but with limited success. The statistical section of that report showed that visibility was significantly negatively correlated with a wide variety of pollutant gases and other smog manifestations.

¹It is interesting to compare this statement with the fraction of light scattering at downtown Los Angeles attributed to SULFATES by White, Roberts and Friedlander (1975), as shown in Figure 6.3 in the main body of this study.

Undoubtedly some of the most interesting investigations are those which sought to relate pollutant emissions to visibility. In 1958, the Los Angeles Air Pollution Control District adopted Rule 62 which resulted in a rapid large scale change from high sulfur fuel use to natural gas combustion by industry in the Basin during the period May through September 1959 (Thomas, 1962). An improvement in visibility due to lowered levels of sulfur-bearing particulates was expected to accompany the SO₂ emission reductions. In a retrospective study of the effects of Rule 62 (Los Angeles Air Pollution Control District, 1959), little or no improvement in minimum visibility at Los Angeles or Burbank was noted. However, only data at 50 percent or lower relative humidities were considered.² At Los Angeles and Long Beach airports, which are closer to major point source locations, significant reduction in the number of days with minimum visibilities of about five miles or less at relative humidity of 60 percent or less was noted. Only about a 4 percent improvement in days of greater than ten-mile minimum visibility occurred at these airport locations. Another study prompted by Rule 62 was performed by Thomas (1962). He correlated visibility at downtown Los Angeles and Burbank, Long Beach and Los Angeles International airports with daily fuel oil consumption on days of poor meteorological dispersion. A small but statistically significant reduction in visibility due to fuel burning was found at Los

² At least over the decade following 1965 for which a nearly continuous record of sulfate data is available, days of high sulfate are significantly positively correlated with days of high relative humidity. (See Appendix D2, this chapter.) By discarding the data for observations above 50 percent relative humidity, many of the high sulfate days may have been overlooked by the LAAPCD.

Angeles International and Long Beach airports. At downtown Los Angeles and Burbank, there was no apparent negative correlation between visibility and fuel oil consumption. Neither of the above studies correlated atmospheric sulfate concentrations with visibility. The lack of visibility improvement at downtown Los Angeles was thus not demonstrated to have accompanied a drop in sulfate levels at that location.

REFERENCES FOR APPENDIX D1

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APPENDIX D2

VISIBILITY STUDY DATA PREPARATION

High volume sampler data on total suspended particulate, sulfate ion and nitrate ion concentrations at downtown Los Angeles was hand copied from the files of the LAAPCD. The period covered was August 1965 through December 1974. If duplicate samples were available for a 24-hour period, then the arithmetic mean of the two observations was recorded. Following White and Roberts (1975), it was assumed that SULFATES equals 1.3 times $\text{SO}_4^{=}$ concentration and NITRATES equals 1.3 times NO_3^{-} concentration in order to account for the mass of associated cations. Each total suspended particulate (TSP) sample was then subdivided into SULFATES, NITRATES, and (TSP-SULFATES-NITRATES). All units are in micrograms per cubic meter. Data for days on which rain was recorded at downtown Los Angeles were discarded.

Hourly observations on prevailing visibility in miles, relative humidity as a fraction of complete saturation, and NO_2 concentration in ppm were extracted from LAAPCD data tapes. Data for days on which no corresponding particulate samples existed were discarded. Each remaining day's visibility data were examined, and only those days for which 9 hours of consecutive visibility observations existed were retained. Daily relative humidity and NO_2 data strings were then edited to retain only those hours for which a corresponding visibility observation existed. Since the NO_2 instrument was typically

recalibrated around noontime daily, at least one hour of missing NO_2 data was embedded in each NO_2 data string corresponding to consecutive visibility observations. Missing hourly NO_2 and relative humidity data corresponding to available visibility observations were replaced by the linear interpolation between adjacent valid data points. If more than three embedded consecutive hourly observations were missing, the day's data were discarded. Missing end points in the NO_2 and relative humidity data strings were replaced by the adjacent value. If the next point adjacent to a missing end point was also missing, the day's data were discarded. The atmospheric extinction coefficient at each hour, b_i , was then estimated from prevailing visibility at that hour by equation (6.9). Finally the t hour average (nominally $t = 9$) of the extinction coefficient, NO_2 concentration ($\overline{\text{NO}_2}$), and relative humidity ($\overline{\text{RH}}$) was taken for each day of interest. It is important to note at this point that the average extinction coefficient computed in this manner is not equal to the inverse of the average of the day's prevailing visibility observations scaled in proportion to the constant of equation (6.9). For use in forming the non-linear functions of relative humidity in equation (6.19), each hourly relative humidity value, RH_i , was retained. At the end of this editing process, 413 days of useful data on all selected variables remained spanning the period August 1965 through December 1974.

A second data base for use with the low humidity model was constructed by a similar procedure. In this case, however, hourly extinction coefficient, NO_2 , and relative humidity observations were

edited prior to averaging to remove all data for those hours where relative humidity exceeded 70 percent. If fewer than five hours of low humidity observations remained in a day after this editing procedure, the day's data were discarded. In this second data base, 390 days of observation on all selected variables remained spanning the period August 1965 through December 1974. A statistical description of these data bases follows.

TABLE D2.1

Statistical Description of the Data Used in the Visibility Study
(Unrestricted Data Base Incorporating all Relative Humidity Values)

Number of Complete Sets of Observations = 413 Days

Time Period Spanned is August 1965 through December 1974

	Average** Extinction Coefficient [10 ⁴ m] ⁻¹	<u>Variable</u>				Average**	
		SULFATES* µgm/m ³	NITRATES* µgm/m ³	(TSP-SULFATES -NITRATES)* µgm/m ³	NO ₂ ** ppm	Relative Humidity %/100	DUMMY one or zero
Average	6.62	17.54	13.92	127.18	0.100	0.53	0.52
Standard Deviation	5.52	14.80	10.77	50.59	0.050	0.17	0.50

Correlation between Variables

	Extinction Coefficient	SULFATES	NITRATES	(TSP-SULFATES -NITRATES)	NO ₂	RH%/100	DUMMY
Extinction Coefficient	1.00	0.62	0.09	0.25	0.42	0.38	0.11
SULFATES	0.62	1.00	-0.03	0.08	0.22	0.48	-0.17
NITRATES	0.09	-0.03	1.00	0.29	0.42	-0.14	-0.21
(TSP-SULFATES -NITRATES)	0.25	0.08	0.29	1.00	0.48	-0.29	0.14
NO ₂	0.42	0.22	0.42	0.48	1.00	-0.14	-0.15
RH%/100	0.38	0.48	-0.14	-0.29	-0.14	1.00	-0.11
DUMMY	0.11	-0.17	-0.21	0.14	-0.15	-0.11	1.00

*24 hour average.

**t hour average, where t corresponds to the 9 hours of visibility observations available in each day selected.

TABLE D2.2

Statistical Description of Data Used in this Visibility Study
(Restricted Data Base Incorporating only those Hours with
Relative Humidity Below 70%)

Number of Complete Sets of Observations = 390 Days

Time Period Spanned is August 1965 through December 1974

	<u>Variable</u>						
	Average** Extinction Coefficient [10 ⁴ m] ⁻¹	SULFATES* μgm/m ³	NITRATES* μgm/m ³	(TSP-SULFATES -NITRATES)* μgm/m ³	NO ₂ ** ppm	Average** Relative Humidity %/100	DUMMY one or zero
Average	5.65	16.30	14.28	129.47	0.099	0.48	0.51
Standard Deviation	3.83	13.83	10.70	50.37	0.052	0.14	0.50

Correlation between Variables

	Extinction Coefficient	SULFATES	NITRATES	(TSP-SULFATES -NITRATES)	NO ₂	RH%/100	DUMMY
Extinction Coefficient	1.00	0.67	0.11	0.39	0.52	0.31	0.12
SULFATES	0.67	1.00	0.003	0.14	0.24	0.44	-0.13
NITRATES	0.11	0.003	1.00	0.26	0.39	-0.07	-0.25
(TSP-SULFATES -NITRATES)	0.39	0.14	0.26	1.00	0.47	-0.25	0.14
NO ₂	0.52	0.24	0.39	0.47	1.00	-0.13	-0.14
RH%/100	0.31	0.44	-0.07	-0.25	-0.13	1.00	-0.12
DUMMY	0.12	-0.13	-0.25	0.14	-0.14	-0.12	1.00

*24 hour average.

**t hour average, where t = number of hours of visibility observations available
that day; nominally t = 9; t_{min} = 5.

APPENDIX D3

SUMMARY OF NEIBURGER AND WURTELE'S APPROXIMATION
RELATING PARTICLE SIZE TO PARTICLE SOLUTE MASS

Light scattering by aerosols is a strong function of particle size. Particle size in turn is heavily influenced by atmospheric humidification if the aerosol material is water soluble.

Relative humidity is defined as the prevailing ambient vapor pressure of water divided by the saturation vapor pressure over a plane pure water surface at the same temperature. Three factors altering the equilibrium vapor pressure over atmospheric droplets from that prevailing over a plane pure water surface are surface curvature, electric charge and dissolved substances. The effect of surface curvature is to raise the equilibrium vapor pressure while the effect of electric charge and dissolved substances is to lower it. If the solution effect dominates, then droplets containing liquid water can persist in the atmosphere at relative humidities below 100 percent.

Neiburger and Wurtele (1949) examined these factors as they affect atmospheric solution droplets of approximately one micron particle diameter. They conclude that the vapor pressure lowering effect of the dissolved substances in such particles will control particle size at humidities below 100 percent. Relying on laboratory data for vapor pressure over solutions of electrolytes, they constructed an expression for the vapor pressure over a solution droplet:

$$\frac{P}{P_0} = 1 - CM \quad (D3.1)$$

where

p = the vapor pressure of water over a solution droplet.

p_0 = the vapor pressure over a plane surface of pure water.

M = concentration of solute in the droplet, expressed as¹ gram formula weights of solute per gram of solution.

C = a factor which can be computed from experimental data presented in the International Critical Tables. C is not a constant; rather it is a function of concentration, temperature, and the nature of the solute involved.

For the droplet to remain in equilibrium in the atmosphere, the left-hand side of equation (D3.1) is equated to the ambient relative humidity, RH, as follows:

$$RH = 1 - CM \quad (D3.2)$$

The mass concentration of solute in the drop is given by:

$$c = wM \quad (D3.3)$$

where

c = mass concentration of solute in the drop expressed as grams of solute per gram of solution.

w = solute molecular weight, in grams per gram formula.

The mass of solute in one drop is related to its mass concentration, c , by:

$$m_s = \frac{4}{3} \pi r^3 \rho c \quad (D3.4)$$

¹The system of units used in Neiburger and Wurtele's paper was not spelled out explicitly. In this recapitulation of their argument, a set of consistent units is supplied. Please note that this unit system differs from that used in the International Critical Tables, and that M as used in (D3.1) is based on solution weight, not solvent weight.

where

m_s = mass of solute in the droplet, grams.

r = droplet radius, in centimeters.

ρ = droplet density, grams of solution per cubic centimeter.

Solving equation (D3.4) for c :

$$c = \frac{3}{4} \frac{m_s}{\pi r^3 \rho} \quad (\text{D3.5})$$

Substituting equations (D3.5) and (D3.3) into equation (D3.2),

Neiburger and Wurtele developed an expression for droplet radius:

$$r = K[m_s/(1-RH)]^{1/3} \quad (\text{D3.6})$$

The factor $K = (3C/4\pi\rho w)^{1/3}$ was described by Neiburger and Wurtele as "... a parameter of the nuclear substance which has a variation of the order of 1 percent with temperature and concentration." Checking that statement as it applies to solutions of ammonium sulfate and ammonium nitrate, one finds that K is not quite that well behaved. For ammonium nitrate at a reference temperature of 100°C, K decreases by roughly 10 percent as the concentration of solute in the solution is diluted from 24 molal down to about 0.6 molal. The change in K^3 , for example, would be correspondingly more pronounced. Still, the order of magnitude of the change in K seems small compared to the order of magnitude of changes in solute concentration.

The reader should thus be cautioned that the assumption that K is constant is an empirically-based approximation. This approximation is attractive because it yields an uncomplicated hyperbolic expression in relative humidity which is practical for use in a simple non-linear

regression model while at the same time preserving some sense of the underlying relationship between particle size and light scattering. For a theoretically-based discussion relating the particle size of solution droplets to ambient relative humidity, see Byers (1965). The reader might also be interested in a recent review article by Hänel (1976) which explores the relationship between theoretical and approximate treatments of particle size as a function of relative humidity.

REFERENCES FOR APPENDIX D3

- Byers, H. R. (1965), Elements of Cloud Physics, Chicago, The University of Chicago Press.
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- Neiburger, M. and M. G. Wurtele (1949), "On the Nature and Size of Particles in Haze, Fog and Stratus of the Los Angeles Region," Chemical Reviews, Vol. 44, No. 2, April (1949).

APPENDIX D4

SUMMARY OF RECOMMENDATIONS FOR DESIGN OF ROUTINE AIR MONITORING PROGRAMS
AIMED AT ASSESSMENT OF THE CAUSES OF VISIBILITY DETERIORATIOND4.1 Introduction

Analysis of existing air pollution control agency routine air quality measurements is not only cost-effective; it is usually the only way in which one can say anything about the long-term behavior of an air basin without designing an experiment from scratch and then waiting for the long-term to repeat itself. However, air pollution control agency air monitoring programs usually have not been designed with a visibility study in mind. In attempting to use existing data to reveal the relationship between sulfate air quality and visibility deterioration at a particular air monitoring site, a number of difficulties were encountered and tackled. Comments made in passing on the means for eliminating some of these difficulties are summarized in this appendix.

D4.2 Particle Size Determination

As shown in Figure 6.1 of this study, the light scattering potential of a given mass of atmospheric particulate matter is a strong function of particle size. Particles in sizes between one-tenth microns and two microns in diameter are responsible for the bulk of the light scattering in the Los Angeles atmosphere. In this study, aerosol chemical composition has been used as a key to particle size and solubility. It would be more desirable, however, to obtain data on particle

size directly from physical measurements. This can be done by incorporation of inertial impactors into an agency's air monitoring program. Before beginning a size-segregated particulate sampling program, a careful intermethod study would be necessary to select or design an impactor with a sharp cut-off between adjacent stages, and a high enough flow rate to collect a sample volume suitable for chemical analysis.

D4.3 Chemical Resolution

In this study, the results of comprehensive chemical analysis of particulate samples taken from the Los Angeles atmosphere as part of previous short-term special studies (e.g., those of Hidy, et al, 1975) served as a pre-survey of the important chemically distinguishable fractions of the local submicron aerosol. Before establishing visibility analysis as one of the goals of its particulate sampling program, an agency should assure itself that data will be collected on all of the abundant submicron chemical species. For example, in the study performed as part of this research effort, the lack of availability of ammonium ion and organic particulate data required that major assumptions be made (based on the findings of others) before the analysis could proceed. When a pre-survey indicates that additional important pollutants require measurement before the visibility study's success can be assured, then the agency should consider allotting resources sufficient to develop laboratory practices and capacity for performing those analyses.

Once the monitoring program is underway, it should be possible to check the chemical measurements against visibility observations to see

if any unexpected relationships hint at sampling trouble. In the case of the study pursued in Chapter 6 of this report, a near zero correlation between NITRATES and extinction coefficient, plus an exaggerated estimate of the extinction coefficient per ppm for NO_2 , indicate a possible problem with sample collection or analysis which should be investigated further.

D4.4 Temporal Resolution

A visibility study requires simultaneous information on particulate characteristics, nitrogen dioxide data, relative humidity information, and an estimate of the atmospheric extinction coefficient. Air monitoring and meteorological data bases should be designed so that each necessary measurement can be computed over the same averaging time. Ideally, one would like periodic instantaneous readings on each variable of interest, but that is not feasible with present particulate sampling technology. Data taken over two-hour averaging times by Hidy, et al. (1975) allowed White and Roberts (1975) to obtain excellent statistical confidence tests in their visibility study. At longer averaging times, information can still be extracted from a statistical study of visibility in relation to aerosol composition, but the unexplained variance in regression model results will possibly increase. Increased sampling frequency is of course more expensive. Perhaps intensive short-term sampling should be confined to a few monitoring stations at which the meteorological measurements needed by a visibility study are also readily available.

D4.5 Extinction Coefficient Determination

Visual range and extinction coefficient estimates can be made either by instrumental methods or a human observer. Each of these approaches has its own advantages and disadvantages. However, if one wishes to use these measurements interchangeably, it is important to run a comparative study between the agency's trained observer and instrumentally determined b_{scat} values. As mentioned in the body of this report, less than ideal availability of visibility markers, plus the requirement that markers be clearly recognized and not just seen could lead to a minimum contrast level for reported prevailing visibility observations that deviates from Koschmieder's assumptions.

