REACTIONS OF NITROGEN OXIDES, OZONE AND SULFUR IN POWER PLANT PLUMES

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EXECUTIVE SUMMARY

Potentially harmful chemicals may be generated in the plumes from fossil fuel power plants as they react with ambient air (so-called second generation products). Two chemical species in particular are commonly mentioned in this respect: ozone and sulfate aerosol. While neither of these species is directly emitted into the atmosphere by power plants, fossil fuel plants do generate and emit potential precursors to ozone and sulfates. These precursors may react with chemicals present in the ambient air to form ozone and sulfates downwind of power plants.

Some workers have reported ozone concentrations in power plant plumes exceeding 120 parts per billion (ppb). This is appreciably greater than the Environmental Protection Agency's (EPA) limit of 80 ppb for no longer than 1 hour once per year, and it also exceeds the Occupational Safety and Health Administration's (OSHA) limit of 100 ppb. However, the reliability of these earlier measurements in power plant plumes are questionable because insufficient care was taken to define the ambient ozone level. Due to long-range transport of ozone from urban areas, ozone concentrations can sometimes reach 100 ppb or more even in rural areas. Furthermore, the transport of ozone from the stratosphere to the troposphere can, on occasions, produce ozone concentrations near ground level approaching the federal standards.

The extent of sulfate aerosol production in power plant plumes is likewise controversial. It is additionally complicated by the lack of a definitive health standard. The current OSHA standard for sulfuric acid (generally considered the most synergistic of the sulfates) is 1 mg m\(^{-3}\). However, current indications are that the EPA standard will be considerably
lower than this, possibly around 40-50 μg m⁻³. Natural sulfate production mechanisms rarely, if ever, produce concentrations in excess of 5 μg m⁻³. The highest reported sulfur dioxide-to-sulfate conversion rate in power plant plumes is 10% per hour. Assuming an initial concentration of 500 ppm of sulfur dioxide in a power plant plume, this conversion rate would imply a maximum production of sulfuric acid of about 2 x 10⁴ μg m⁻³ per hour! However, the actual production rate of sulfuric acid in power plant plumes must be much less than this since the highest measured concentrations of sulfuric acid in power plant (or urban) plumes are about 10-20 μg m⁻³.

In view of the sparcity of data on second generation products in power plant plumes, the Cloud and Aerosol Research Group at the University of Washington is undertaking a field and theoretical study of this problem for the Electric Power Research Institute. The present report is concerned mainly with the results which we have obtained on ozone in power plant plumes. Aerosol production in power plant plumes is discussed only briefly.

If the rate of production of a second generation product is slow compared to the rate at which a power plant plume mixes with the ambient air, only rather limited amounts of second generation products will be formed before the concentrations of the precursor chemicals in the plume become diluted to ambient levels. In this case, it is unlikely that second generation products would be produced in sufficient concentrations to exceed federal standards, although they would still contribute to air pollution on a regional scale. On the other hand, if the second generation products are produced at a fast rate compared to the rate at which the plume mixes with the ambient air, high local concentrations of
secondary products might result. In view of these considerations, we have placed emphasis on establishing whether the production of ozone in power plant plumes is limited by chemical kinetics or by the rate at which the plume mixes with the ambient air.

Thirty sets of airborne measurements have been obtained in the plumes from two coal-fired and two gas-fired power plants situated in different climatological areas. On no occasion was above ambient ozone found to be generated in a power plant plume out to distances at which the plume was still distinguishable from the ambient air.

These field observations can be understood as follows. The precursors of ozone in fossil fuel power plants are nitrogen oxides, primarily nitric oxide. Nitric oxide must be converted to nitrogen dioxide in the plume before ozone can be produced. An analysis of our field data reveals that this conversion rate is generally controlled by the rate at which a plume mixes with the ambient air rather than by the relevant chemical reaction rates. Since this mixing rate is slower than the chemical reaction rates for the production of ozone, the conversion of nitric oxide to nitrogen dioxide (and hence to ozone) is slower than would be expected from laboratory or smog chamber experiments. Indeed, the conversion rates are slow enough to make ozone production in power plant plumes unlikely.

As far as the production of aerosol from gases in power plant plumes is concerned, our field measurements indicate a rather slow conversion rate (about 0.3% per hour). More detailed field and theoretical studies on this subject will be reported in a future report to EPRI.
CHAPTER 1

REVIEW OF PREVIOUS WORK AND SCOPE OF STUDY

1.1 Statement of Problem

Industrial plumes, particularly those of power plants, have been studied for a considerable period of time. The majority of these studies, however, have concentrated exclusively on either the dynamics or the chemistry of such plumes. The number of studies dealing with the interaction of plume dynamics and chemistry is relatively small.

The recent emphasis on the construction of plants using increasingly higher sulfur-content coals has prompted several recent studies of the plumes from power plants, with particular emphasis on the nitrogen oxides, ozone, and sulfur chemistry of these plumes. The results of these studies indicate that the pollution potential of such plants is quite high. However, inconsistencies in the available data clearly indicate the need for more careful studies (Tesche et al., 1976).

In this study, an account is given of investigations carried out on several power plant plumes with particular emphasis on the interaction of the dynamics and chemical kinetics of the plumes. Before describing the specific aspects of the problem which will be addressed, a very brief review is given of previous work on plume dynamics and the relevant plume chemistry.
1.2 Previous Plume Studies

1.2.1 Plume Diffusion

The problem of the diffusive spreading of a plume with time was initiated by Taylor (1922) with his now classic application of the single-particle random walk theory. With the notable exception of Richardson (1926), the importance of whose work was not recognized for several decades, most purely theoretical analyses of this problem followed Taylor's approach and employed single particle statistics to describe the diffusion process. This work has been well summarized by Pasquill (1974).

Concurrently with the development of the statistical model, however, several investigators, more interested in application than rigorous theory, have explored the alternative K-theory hypothesis, in which an analogy is drawn between turbulent and molecular diffusion. The possible analytical refinements of this theory are exemplified in the work of Smith (1957). While the theoretical justification for K-theory is not well established, the ease of application has led to its widespread use. Furthermore, recent work by Lamb et al. (1975) has shown that the ability of K-theory to describe atmospheric diffusion compares favorably with the statistical model.

In addition to theoretical work, much effort has been devoted to field studies of plumes (see, for example, Slade, 1968). One result of these studies, which has particular relevance to this report, is the concept of a fluctuating plume. Gifford (1959) has modeled such a plume and his results will be applied to the analysis of data in the present study. The effect of such fluctuations upon the measured concentrations of the constituents of a plume has been demonstrated by Ramsdell (1971).
and the possible effects on the chemical kinetics of a plume have been analyzed by Donaldson and Hilst (1972).

1.2.2 Sulfur Chemistry (Gas-to-Particle Conversion)

It has been known for sometime that various photochemical reactions, particularly those involving sulfur dioxide, can lead to the formation of particles (Leighton, 1961). Several investigators have been able to relate observed aerosol formation in urban air masses to plausible kinetic mechanisms (e.g. Roberts, 1975). However, the question of aerosol formation in power plant plumes is somewhat more complex, due primarily to the short time periods involved and the consequent elimination of many relatively slow aerosol forming reactions of importance in urban smog. Still, aerosol formation has been observed in both coal and oil fired power plant plumes (Tesche et al., 1976; Newman et al., 1975). Harrison et al. (1975) have reviewed various oxidation mechanisms for sulfur dioxide (hereafter referred to as \( \text{SO}_2 \)) in the atmosphere and they point out several mechanisms which may be of importance in power plant plumes. Of particular interest with respect to this study is the Scott-Hobbs heterogeneous oxidation mechanism (Scott and Hobbs, 1967), since most of our field investigations of gas-to-particle conversion have been made in the plume of a coal-fired plant located in a very humid, rainy area (Western Washington).

1.2.3 Nitrogen Oxides and Ozone

The generation of ozone in polluted urban air masses has been both observed in the field and analyzed theoretically for several decades. All of the generation mechanisms involve nitrogen oxides (hereafter
referred to as NO\textsubscript{x}) and most of them involve organic free radicals (Leighton, 1961). The question of above ambient ozone generation in power plant plumes, however, is one of quite recent origin. A research team from the University of Maryland has reported above ambient ozone concentrations (which exceeded federal standards) downwind of a coal-fired power plant at Morgantown, MD (Davis et al., 1974). This report has touched off widespread speculation concerning the mechanisms capable of such generation as well as number of field studies of this phenomenon.

1.3 **Scope of the Present Study**

Under Contract RP 330-1 with EPRI, the Cloud and Aerosol Research Group at the University of Washington is engaged in a three year study of the atmospheric effluents from power plants, with particular emphasis on a large coal power plant located at Centralia, Washington. In addition, under EPRI Contract RP 572-3-1, we have participated in a shorter term study of ozone in coal and gas-fired power plant plumes. In this report we describe our field work and theoretical studies to date on plume diffusion and the chemistry of nitrogen oxides and ozone in power plant plumes. In addition, we present some preliminary results on gas-to-particle conversion in power plant plumes. In a subsequent report we will describe a more detailed investigation of this latter subject.
CHAPTER 2

INSTRUMENTATION AND DESIGN OF FIELD STUDIES

2.1 University of Washington Aircraft Facility

The primary data gathering facility employed in this study is the University of Washington's B-23 research aircraft. A detailed discussion of most of the instrumentation aboard this aircraft (meteorological, cloud physics, and aerosol) is given by Hobbs et al. (1976). Instrumentation not discussed by Hobbs et al. which was used in the present study is described below. A schematic drawing of the instrumentation is shown in Fig. 2.1 and photographs of the instrumentation are shown in Figs. 2.2 and 2.3.

2.1.1 Aerosol Counter

Total aerosol concentrations were measured with an automatic condensation nucleus (hereafter referred to as CN) counter. This instrument is a typical rapid expansion type cloud chamber and has been calibrated against a Polock-calibrated Gardner Counter. This calibration is in satisfactory agreement with the cumulative number concentration of aerosol measured by the full B-23 aerosol system. The CN counter detects all aerosol particles with radius greater than 0.0025 μm. It samples air from a stainless steel plenum chamber (28 liters in volume) described by Hobbs et al. (1976).
AUTOMATIC VALVE SEQUENTIAL BAG SAMPLER (FOR OPC I & EAA)

CLOUD CONDENSATION NUCLEUS (CCN) COUNTER

CONDENSATION (CN) COUNTER

SEAT

ELECTRICAL AEROSOL ANALYZER (EAA)

INTEGRATING NEPHELOMETER

ISOKINETIC PROBE

STATIC PRESSURE TRANSDUCER

30 ° HEATED CHAMBER

ISOKINETIC PUMP

OPTICAL PARTICLE COUNTERS (OPC I & II)

(a) PLAN VIEW

GAS ANALYSIS SYSTEM (NOx, NO, NO2, SO2, AND O3)

PROBE FOR MANUAL BAG SAMPLE

REAR

FRONT

AXIALLY SCATTERING SPECTROMETER PROBE

(b) SIDE VIEW

Fig. 2.1 Arrangement of gas-phase and aerosol analyzers aboard the B-23 aircraft.
Fig. 2.2 View of B-23 aircraft instrumentation: aerosol analyzers are on the right and gas analyzers are visible in the upper left.
Fig. 2.3 Close-up view of the gas analyzers aboard the B-23 aircraft.
2.1.2 Sulfur Analyzer

Total sulfur was measured with a Meloy Laboratories (SA 160-2, FPD) Sulfur Analyzer. Tests conducted in our laboratory indicate that the instrument has a 90% response time of less than 10 seconds (s). Further tests indicated that while the instrument detects sulfur in the gaseous form fairly well it is a relatively inefficient detector of sulfur in the solid phase. In any case, the particulate sulfur in the plumes which were investigated is almost certainly no more than a few percent of the total sulfur. Consequently, the output from the sulfur analyzer was assumed to indicate the gas-phase sulfur concentration (presumably sulfur dioxide, since this was the only sulfur-containing gas emitted in large quantities from the plants investigated).

The sulfur analyzer, as well as the two other gas-phase detectors, sampled from a ram-air line, the intake of which was located beneath the aircraft (Fig. 2.1). The distance from the air intake to the gas instruments was 2 meters (m) or less and, with an average air speed of 60 m s\(^{-1}\), there was a negligible delay in detection of concentration changes compared to the response time of the sulfur analyzer. This was true for all the gas analyzers, and the response time of the sampling system to a gas was simply the instrumental response time for that gas analyzer. The ram-air line itself was 3.8 cm diameter polyethylene tubing and the tap lines were 0.63 cm diameter nylon tubing for the sulfur and \(NO_x\) analyzers and 0.63 cm teflon tubing for the ozone analyzer.

The sulfur analyzer was periodically calibrated against a Meloy model CS-10 sulfur dioxide calibration source. This source is a permeation tube in a temperature-controlled air bath. It was factory calibrated for selectable setting of any \(SO_2\) concentration level between 0.1 and 0.8
parts per million (ppm), and the calibration is warranted correct to within ± 2% of the NBS Certified Standard. The sulfur analyzer has a minimum detectable sensitivity of 0.005 ppm.

2.1.3 Oxides of Nitrogen Analyzer

Nitric oxide and nitrogen dioxide (NO and NO₂ respectively) were measured with a Monitor Labs model 8440 Oxides of Nitrogen Analyzer. This instrument is a chemiluminescent detector with a 90% response time of 5 s on the range (0 - 0.2 ppm) generally used in this study. A higher range (0 - 0.5 ppm) was occasionally used which has a 90% response time of 11.5 s and a 63% response time of 5 s. While the manufacturer quotes a minimum detection limit of 2 parts per billion (ppb), tests in our laboratory indicate that the lower limit for the atmosphere is 7-10 ppb.

The NOₓ analyzer was periodically calibrated against a Monitor Labs model 8500 Permacal calibration source. This source was calibrated by the manufacturer by means of a chemiluminescent analyzer standardized by comparison with gas phase titration. The calibration accuracy is given as ± 5% relative to the titration.

2.1.4 Ozone Analyzer

Ozone (O₃) concentrations were measured with a Monitor Labs model 8410A chemiluminescent Ozone Analyzer. This instrument measures O₃ by sensing light output from the ozone-ethylene reaction. It has a response time of less than 5 s for the scale used in this study (0 - 0.2 ppm) and a detection limit, for the atmosphere, of about 5 ppb. It was periodically calibrated against the Monitor Labs model 8500 Permacal Calibration Source.
This source is essentially an ultra-violet lamp which irradiates air flowing by it to produce ozone in that air flow. It was calibrated by a chemiluminescent ozone analyzer standardized by comparison to neutral buffered potassium iodide. The calibration accuracy is given as \pm 5\% relative to the potassium iodide values. An independent check of the calibration made by employing an ozone analyzer calibrated against the potassium iodide method by the Health Sciences Research Group at the University of Washington showed agreement to within 10\%. However, the ultra-violet source had to be operated for several hours before it stabilized and showed the above agreement.

2.1.5 Ultra-violet Radiometer

Ultra-violet radiation reaching the plume (direct plus sky) was measured by an Eppley ultra-violet radiometer mounted on top of the tail of the aircraft. This instrument gives a continuous measurement of the ambient ultra-violet radiation between 290 and 385 mm. (The photocell sensor has a relative spectral response varying from 0.5 at 290 mm to 1.0 at 385 mm.) The radiometer was calibrated by Eppley Laboratory Inc.

2.2 Meteorology Research Inc. Aircraft Facility

Some of the field work described in this study was carried out in conjunction with Meteorology Research Inc. (MRI). The primary data facility used by MRI was their Cessna 206 aircraft. The instrumentation aboard this aircraft is described by McMurry et al. (1974) and provides measurements of SO\textsubscript{2}, NO, NO\textsubscript{2}, O\textsubscript{3} and CN as well as some meteorological parameters (temperature, pressure, etc.).
2.3 Locations and Characteristics of the Power Plants Studied

The power plant investigated in this study solely by the University of Washington under contract RP330 is the coal-fired power plant operated by the Pacific Power and Light Co. at Centralia, Washington. Three other power plants (the Cunningham gas-fired power plant at Hobbs, New Mexico, the Wilkes gas-fired power plant at Longview Texas, and the Four Corners coal-fired plant at Farmington, New Mexico) were investigated in conjunction with MRI under Contract RP 572-3. The characteristics of these plants are described below.

2.3.1 Centralia

The Centralia coal-power plant is situated in an east-west oriented river valley and is subject to the prevailing rainy weather characteristic of Western Washington. The surrounding vegetation is mostly evergreen trees, primarily fir.

The plant is rated at about 1200 MW electrical output at full load. It emits SO$_2$ with a flue gas concentration of between 300 and 700 ppm and NO$_x$ with a flue gas concentration of about 500 ppm. Aerosol emission from the stack is relatively low due to the installation, in series, of both Kopper and Lodge-Cottrell precipitators. The flue-gas volume flow at full load is about $6.7 \times 10^6$ m$^3$ hr$^{-1}$ (STP). A photograph of the Centralia plant is shown in Fig. 2.4.

2.3.2 Hobbs

The Cunningham gas-fired power plant is located in the relatively arid climate of Hobbs, New Mexico. The electrical output of this plant at full load is about 300 MW. It typically emits NO$_x$ in flue-gas concentrations of 155 ppm. The plant, being gas-fired, emits essentially no SO$_2$. While the particulate loading of the flue gases is unknown, our measurements of CN concentrations a few kilometers downwind indicate that it is rather small.
Fig. 2.4 View of the Centralia power plant. The vapor plume on the right is from the plant cooling towers located on the hillside. The plant plume is invisible.
The flue-gas volume flow from the plant during the study was about $8 \times 10^5 \text{ m}^3 \text{ hr}^{-1}$ (STP).

The terrain around the plant is completely flat and only sparsely covered with light vegetation. A photograph of the plant is shown in Fig. 2.5.

2.3.3 Longview

The Wilkes gas-fired power plant is located near Longview, Texas. This plant has an electrical output of about 900 MW at full load and typically has a flue-gas NO$_x$ concentration of around 250 ppm. It emits no measurable SO$_2$ and relatively little aerosol. The flue-gas volume flow during this study was about $2 \times 10^6 \text{ m}^3 \text{ hr}^{-1}$ (STP).

The Longview area has a very warm and humid climate and has vegetation characteristic of the Southern Gulf states; the only anomaly being a rather high percentage of pine trees. The terrain of the Longview area is quite flat. A photograph of the Wilkes plant and its surroundings is shown in Fig. 2.6.

2.3.4 Farmington

The Four Corners coal-fired power plant is near Farmington, New Mexico. This plant has an electrical output of about 3000 MW at full load but was operating at less than 2000 MW during the period of our measurements (October 1975). The flue-gas NO$_x$ concentration was typically 450-500 ppm and the SO$_2$ flue-gas concentration was about 550 ppm. While the particulate mass loading of the flue gas is rather high, this is due primarily to the large size (5-20 $\mu$m diameter) of a relatively small number of fly-ash particles. The actual number of concentrations are less than a few hundred per cm$^3$ and are
Fig. 2.5 View of the Cunningham gas-fired power plant at Hobbs, New Mexico. The plant plume is invisible.
Fig. 2.6 View of the Wilkes Power Plant at Longview, Texas. The plant plume is invisible.
comparable to background at a range of a few kilometers. The flue-gas volume flow from the plant was around $8 \times 10^6 \text{ m}^3 \text{ hr}^{-1}$ (STP) during the measurement period.

The vegetation and terrain around the Four Corners plant are roughly the same as those around the Hobbs plant. There is, however, considerably more relief in the topography. A photograph of the Four Corners plant is shown in Fig. 2.7.

2.4 Design of Field Studies
2.4.1 Plume Diffusion

The two primary questions addressed in this study, namely, above ambient ozone production and gas-to-particle conversion in power plant plumes, are intimately connected with plume growth. For example, in considering the total aerosol concentration at various ranges from the plant, allowance must be made for decreases in concentrations due to the entrainment of ambient air. Furthermore, the extent of entrainment of ambient hydrocarbons and ozone will have an effect on the NO$_x$ - ozone chemistry of a plume.

The rate of growth of a plume was determined by measuring the change in cross-sectional area of the plume as a function of travel time from the stack assuming the plume to be continuous and the wind velocity to be constant. A dimensionless diffusion parameter was then derived from these measurements in a manner which will be described in § 4.2. This parameter is directly related to the rate of plume growth.

In this type of analysis, a conservative trace of the plume is necessary since the plumes of most modern coal and gas-fired power plants are essentially invisible and the cross-sectional areas cannot be
Fig. 2.7 View of the Four Corners Power Plant at Farmington, New Mexico.
determined photographically. It was assumed that sulfur dioxide was conserved over the time intervals between successive cross-sections (usually an hour or less). While this assumption contradicts, in principle, any hypothesis of oxidation of \( \text{SO}_2 \) to particulate sulfate in the plume, in practice the assumption is reasonable since any conversion process should result, at most, in only a few percent loss of \( \text{SO}_2 \) per hour. Thus \( \text{SO}_2 \) cross-sections were employed as indicators of the actual plume cross sections.

The cross-sectional areas were determined by horizontal traverses of the plume at various altitudes at a particular range from the stack(s) of the plant. The actual range was determined from geographic landmarks and by an automatic radio navigation plotting system (VOR and DME) aboard the aircraft. The ranges so determined are considered accurate to within 0.5 km. The altitudes of the traverses were measured with a pressure altimeter. The internal error of the altimeter is around 5 m. The external error of the altimeter, due to changing surface pressure, was minimized by frequently correcting the zero setting to agree with current airport altimeter settings. However, the correction was generally small since surface pressure does not normally change appreciably over the time scale of a cross-sectional determination (10-20 minutes). The error in relative altitude of traverses within a cross section is thus estimated to be 10 m or less. The traverses were correlated in the vertical by aligning the mid-points of each traverse (half of the distance between the points where the \( \text{SO}_2 \) concentration respectively rose above and then descended to, background). The more common practice of correlating the traverses by correlating the internal concentrations of the traverses was not used for reasons which will be discussed in § 4.3.
The above procedures yielded SO$_2$ concentrations at various relative positions in the plume. These points were then plotted and concentration iso-pleths drawn. The isopleth for the concentration of SO$_2$ which was just measurably above the ambient concentration was taken to be the envelope of the plume; its area was measured with a polar plenimeter. The current$^+$ of SO$_2$ could be determined by an extension of this procedure and measured cross-sectional areas were adjusted to agree with the assumption of constant SO$_2$ current implied by the assumption of conservation of SO$_2$ discussed above. The size of the necessary adjustments can be seen in Table 3.2. Some of the corrections are rather large and are probably due mainly to the fact that the concentration gradient in the outer part of the plume decreased to a value comparable to the sulfur analyzer sensitivity as the plume diffused outward. Thus there was a large uncertainty in the actual position of the SO$_2$ isopleth which was just above ambient SO$_2$ concentrations and consequently of the actual plume envelope.

2.4.2 Gas-to-Particle Conversion

Cross sections of the total aerosol concentrations were determined using the same procedures employed for SO$_2$. However, instead of adjusting the cross-sectional areas to maintain the total aerosol current parameter$^*$ constant (which would contradict the hypothesis of aerosol production), the ratios of successive cross-sectional areas of the aerosol were adjusted to agree with the corresponding SO$_2$ area ratios. Aerosol current parameters were then calculated for successive distances downwind of the stack. By considering total aerosol current parameters rather than aerosol concentrations, the effect of plume dilution is automatically taken into account.

$^+$By current of a trace gas we mean the total volume of the gas flowing per unit time (units: m$^3$ s$^{-1}$).

$^*$Aerosol current is number of aerosol per sec (units: s$^{-1}$). Aerosol current parameter is defined as aerosol current divided by the mean wind velocity and has units of (length)$^{-1}$. 
2.4.3 Nitrogen Oxides and Ozone

Current theory indicates that the amount of $O_3$ that can exist in photochemical equilibrium with any given quantity of NO$_x$ is directly related to the ratio of NO$_2$/NO (Steadman and Jackson, 1974). Furthermore, for a system of either NO$_x$ plus hydrocarbons, or NO$_x$ plus hydrocarbons plus SO$_2$, it has been shown experimentally that $O_3$ generation will not occur to any appreciable extent until the NO$_2$/NO ratio is around 10 to 1 (Kocmond et al., 1975). Therefore, since a power plant plume is in a simplistic sense an NO$_x$ (or NO$_x$ plus SO$_2$) system being emitted into the atmosphere, the ratio of NO$_2$/NO in the plume should give an indication of the ozone generating potential of the plume. Because the NO$_x$ emitted from power plants is mostly NO, the conversion rate of NO to NO$_2$ will also be an important parameter.

The above discussion tacitly assumes that the plumes investigated will, in fact, be in photochemical equilibrium. This is a plausible assumption because the fast rate constants of the NO$_x$-ozone system will result in a very short relaxation time to the equilibrium state. Indeed, the NO$_x$-ozone system has been shown to be in photochemical equilibrium for ambient air (Steadman and Jackson, 1974). However, a diffusing plume, measured at some particular observational spatial scale, may not be in photoequilibrium, due to rapid mixing processes occurring at still smaller spatial scales. Therefore, an analysis of the equilibrium assumption must be made. In principle, if the chemical reactions taking place in the plume are more rapid than the diffusive mixing of the plume with ambient air, then the plume chemistry will be controlled by the diffusion rate and local regions of the plume should be in chemical
equilibrium. Parameters which would indicate whether or not the plume chemistry is diffusion controlled are presented in Chapter 3 (and they indicate that it is diffusion controlled). The assumption of photo-chemical equilibrium is fully discussed in Chapter 4.

The concentrations of NO, NO$_2$, and ozone used in the parameters analyzed in this study were measured along the chemical centerline of the plume (defined as the point of maximum NO$_x$ and/or minimum ozone); this minimizes the error in the NO$_2$/NO ratio due to the instrumental sensitivity limit. Averaging will also reduce this error; average values of NO, NO$_2$, and O$_3$ were determined graphically for various ranges across each traverse, then the horizontal values were averaged in the vertical direction. This procedure allowed an estimate of the average concentrations of the respective chemical species over the plume as a whole at various distances downwind of the stack.

The variation in the concentration of a gas with relative position in the plume was determined by considering the concentration profile of that gas for the various horizontal traverses of the plume at a given range.
CHAPTER 3

RESULTS OF FIELD STUDIES

3.1 The Data Base

A full listing of the flights made by the University of Washington in support of this study is shown in Table 3.1. The MRI data which has been used can be found in Ogren et al. (1976a).

3.2 Plume Diffusion

Cross-sectional areas for all of the plumes studied are given in Appendix D. An example of a cross-sectional area of a power plant plume derived from SO₂ concentrations is shown in Fig. 3.1. A list of all the SO₂ cross-sectional areas calculated in this study is given in Table 3.2. The uncertainty in the area values is estimated at 15% or less on the basis of test calculations on four "bad" cases. The error analysis procedure for the cross-sectional areas, and for other parameters calculated in this study, is given in Appendix A.

3.3 Gas-to-Particle Conversion

The cross-sectional area for the total aerosol concentration corresponding to the SO₂ measurements shown in Fig. 3.1 is shown in Fig. 3.2. It can be seen that the aerosols occupy about the same area as the SO₂. The similarity between the cross-sectional areas of SO₂ and aerosols is characteristic of all of the data and lends support to the procedure of
Table 3.1

Flights of the B-23 Aircraft

<table>
<thead>
<tr>
<th>Date</th>
<th>Power Plant</th>
<th>Measurements</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/13/75</td>
<td>Centralia</td>
<td>Meteorological, SO₂, Aerosol</td>
<td>Good Data</td>
</tr>
<tr>
<td>3/3/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Weather poor, very little data.</td>
</tr>
<tr>
<td>3/4/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>3/6/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Plant shut-down during flight</td>
</tr>
<tr>
<td>3/11/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Plume mixing into cloud layer</td>
</tr>
<tr>
<td>3/20/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>3/24/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Plume rising almost vertically.</td>
</tr>
<tr>
<td>3/26/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Good Data</td>
</tr>
<tr>
<td>4/1/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Good Data</td>
</tr>
<tr>
<td>5/29/75</td>
<td>&quot;</td>
<td>Met., NOₓ, SO₂, Aerosol</td>
<td>&quot;</td>
</tr>
<tr>
<td>6/16/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Excellent data at 3 ranges</td>
</tr>
<tr>
<td>7/29/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Some plume interaction with cloud</td>
</tr>
<tr>
<td>8/20/75</td>
<td>&quot;</td>
<td>Met., NOₓ, O₃, SO₂, Aerosol</td>
<td>Extensive plume interaction with cloud</td>
</tr>
<tr>
<td>10/5/75</td>
<td>Hobbs†</td>
<td>&quot;</td>
<td>Too much interference to track plume</td>
</tr>
<tr>
<td>10/6/75</td>
<td>&quot;†</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>10/7/75</td>
<td>&quot;†</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>10/8/75</td>
<td>&quot;†</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>10/9/75</td>
<td>Longview</td>
<td>&quot;</td>
<td>NOₓ analyzer had fitting leak</td>
</tr>
<tr>
<td>10/11/75</td>
<td>&quot;†</td>
<td>&quot;</td>
<td>Several patches of high ambient ozone</td>
</tr>
<tr>
<td>10/11/75</td>
<td>&quot;†</td>
<td>Met., NOₓ, O₃, SO₂, Aerosol</td>
<td>Patches of high ambient ozone</td>
</tr>
<tr>
<td>10/12/75</td>
<td>&quot;†</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>10/14/75</td>
<td>&quot;†</td>
<td>&quot;</td>
<td>Good Data</td>
</tr>
<tr>
<td>10/15/75</td>
<td>Farmington</td>
<td>&quot;</td>
<td>Survey flight</td>
</tr>
<tr>
<td>10/16/75</td>
<td>&quot;†</td>
<td>&quot;</td>
<td>Excellent data at 3 ranges</td>
</tr>
<tr>
<td>10/17/75</td>
<td>&quot;†</td>
<td>Met., NOₓ, O₃, Aerosol</td>
<td>Plume tracked to 90 km. good NOₓ data</td>
</tr>
<tr>
<td>10/30/75</td>
<td>Centralia</td>
<td>Met., NOₓ, O₃, SO₂, Aerosol</td>
<td>Good Data</td>
</tr>
<tr>
<td>10/31/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>SO₂ analyzer on linear scale</td>
</tr>
<tr>
<td>11/4/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>11/5/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>11/20/75</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

†A simultaneous flight was being made by the MRI Cessna 206.
Fig. 3.1 $\text{SO}_2$ plume cross section at 0.8 km range at Centralia on 16 June 1975. The isopleths give the concentration of $\text{SO}_2$ in ppb.
Table 3.2

$SO_2$ plume cross-sections used in this study. The error in the corrected cross-sections is 15%. Both the Centralia and Farmington plants are coal-fired.

<table>
<thead>
<tr>
<th>Date</th>
<th>Power Plant</th>
<th>Divergence of Current Parameter (ppb m)</th>
<th>Range (km)</th>
<th>Uncorrected Cross-sectional Areas ($m^2$)</th>
<th>Cross-sectional Area Corrected on Assumption of Constant $SO_2$ Current ($m^2$)</th>
<th>Measured $SO_2$ Current ÷ Mean Wind Velocity (ppb m$^2$)</th>
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<tbody>
<tr>
<td>3/13/75</td>
<td>Centralia</td>
<td>--</td>
<td>1.6</td>
<td>3.8\times10^5</td>
<td>3.8\times10^5</td>
<td>2.7\times10^7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1.9\times10^3</td>
<td>4.8</td>
<td>5.2\times10^4</td>
<td>6.7\times10^4</td>
<td>2.1\times10^7</td>
</tr>
<tr>
<td>3/20-75</td>
<td></td>
<td>-1.8\times10^4</td>
<td>9.6</td>
<td>6.1\times10^5</td>
<td>8.9\times10^5</td>
<td>9.7\times10^6</td>
</tr>
<tr>
<td>3/24/75</td>
<td></td>
<td>2.3\times10^3</td>
<td>6.4</td>
<td>1.3\times10^6</td>
<td>7.0\times10^5</td>
<td>2.7\times10^7</td>
</tr>
<tr>
<td>3/26/75</td>
<td></td>
<td>--</td>
<td>1.6</td>
<td>1.1\times10^6</td>
<td>1.5\times10^6</td>
<td>3.5\times10^7</td>
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<tr>
<td>6/16/75</td>
<td></td>
<td>-1.9\times10^3</td>
<td>4.8</td>
<td>1.3\times10^6</td>
<td>1.5\times10^6</td>
<td>3.5\times10^7</td>
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<td></td>
<td></td>
<td>-1.0\times10^4</td>
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<td>1.7\times10^5</td>
<td>4.4\times10^5</td>
<td>1.4\times10^7</td>
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<td>-3.1\times10^2</td>
<td>4.8</td>
<td>2.4\times10^5</td>
<td>5.1\times10^5</td>
<td>1.3\times10^7</td>
</tr>
<tr>
<td>7/29/75</td>
<td></td>
<td>--</td>
<td>0.8</td>
<td>4.7\times10^5</td>
<td>4.7\times10^5</td>
<td>6.3\times10^7</td>
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<td></td>
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<td>6.6\times10^5</td>
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<td>8/20/75</td>
<td></td>
<td>--</td>
<td>0.2</td>
<td>6.0\times10^5</td>
<td>6.0\times10^5</td>
<td>2.1\times10^8</td>
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<tr>
<td></td>
<td></td>
<td>-3.0\times10^4</td>
<td>3.2</td>
<td>1.3\times10^6</td>
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<td>1.2\times10^8</td>
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<td></td>
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<td>6.4</td>
<td>9.3\times10^5</td>
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Table 3.2 (continued)

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<tr>
<th>Date</th>
<th>Power Plant</th>
<th>Divergence of Current Parameter * (ppb m)</th>
<th>Range (km)</th>
<th>Uncorrected Cross-sectional Areas</th>
<th>Cross-sectional Area Corrected on Assumption of Constant SO₂ Current (m²)</th>
<th>Measured SO₂ Current + Mean Wind Velocity † (ppb m²)</th>
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<tbody>
<tr>
<td>10/16/75</td>
<td>Farmington</td>
<td>--</td>
<td>17</td>
<td>2.2x10⁶</td>
<td>2.2x10⁶</td>
<td>4.3x10⁸</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>-2.1x10⁴</td>
<td>30</td>
<td>2.4x10⁶</td>
<td>1.0x10⁷</td>
<td>1.6x10⁸</td>
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<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>-4.2x10³</td>
<td>45</td>
<td>2.6x10⁶</td>
<td>1.9x10⁷</td>
<td>9.7x10⁷</td>
</tr>
<tr>
<td>10/30/75</td>
<td>Centralia</td>
<td>--</td>
<td>0.8</td>
<td>1.2x10⁵</td>
<td>1.2x10⁵</td>
<td>8.9x10⁶</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>1.3x10³</td>
<td>8.0</td>
<td>6.0x10⁵</td>
<td>3.0x10⁵</td>
<td>1.8x10⁷</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>2.0x10²</td>
<td>18</td>
<td>7.5x10⁵</td>
<td>3.4x10⁵</td>
<td>2.0x10⁷</td>
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<td>&quot;</td>
<td>&quot;</td>
<td>-1.5x10³</td>
<td>22</td>
<td>9.9x10⁵</td>
<td>6.4x10⁵</td>
<td>1.4x10⁷</td>
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<tr>
<td>10/31/75</td>
<td>&quot;</td>
<td>2.5x10³</td>
<td>5.6</td>
<td>3.2x10⁵</td>
<td>3.2x10⁵</td>
<td>1.8x10⁷</td>
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<td>&quot;</td>
<td>0</td>
<td>12</td>
<td>8.5x10⁵</td>
<td>5.9x10⁵</td>
<td>2.6x10⁷</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>-1.3x10³</td>
<td>21</td>
<td>7.2x10⁵</td>
<td>9.3x10⁵</td>
<td>1.4x10⁷</td>
</tr>
<tr>
<td>11/5/75</td>
<td>&quot;</td>
<td>--</td>
<td>1.6</td>
<td>3.5x10⁵</td>
<td>3.5x10⁵</td>
<td>9.3x10⁶</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>1.0x10⁴</td>
<td>0.8</td>
<td>1.8x10⁵</td>
<td>1.5x10⁵</td>
<td>1.1x10⁷</td>
</tr>
</tbody>
</table>

†Because the wind velocity is assumed constant during each individual flight, the current divided by the wind velocity is used as a current parameter rather than the current itself. (See text for further explanation.) The current parameter used here, I', is related to the current, I (m³ s⁻¹) by:

\[ I = 10^{-9} \overline{U} I' \]

where \( \overline{U} \) is the mean wind velocity.

*See above footnote for definition of current parameter I'.

Fig. 3.2 Aerosol plume cross section at 0.8 km range at Centralia on 16 June 1975. The isopleths give the aerosol concentrations per cubic centimeter.
adjusting aerosol cross-sectional areas on the basis of SO\textsubscript{2} cross-sectional areas.

Sufficient data were gathered on five flights for aerosol currents to be calculated. However, on one of these five flights (20 August, 1975) there was considerable precipitation and interaction of the plume with clouds. Since insufficient data were available to estimate the extent of the scavanging of aerosols by precipitation, this flight was omitted from detailed aerosol calculations; initial calculations for this flight indicate a substantial decline in the aerosol current parameter with distance downwind. The results of the calculations for the remaining four flights are summarized in Table 3.3.

3.4 Nitrogen Oxides and Ozone
3.4.1 Correlation of NO\textsubscript{2}/NO with NO\textsubscript{x}

A parameter of particular interest with respect to the NO\textsubscript{x} - O\textsubscript{3} chemistry of a plume is the NO\textsubscript{2}/NO ratio. The correlation of this parameter with relative position within the plume yields information relevant to the question of whether or not the plume chemistry is diffusion controlled; this correlation was therefore analyzed. The results of this analysis are summarized in Table 3.4. The correlation parameter employed was the Bravais-Pearson linear correlation coefficient, \( r_{xy} \), defined by:

\[
r_{xy} = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sigma_x \sigma_y (N-1)}
\]

where the \( x_i \)'s and \( y_i \)'s are variables, the \( \sigma \)'s standard deviations. The significance levels were determined by means of tables designed specifically for this purpose (Davies, 1958 or Bevington, 1969). The distinctive
<table>
<thead>
<tr>
<th>Date</th>
<th>Power Plant</th>
<th>Range (km)</th>
<th>Measured Cross-Sectional Area ($\text{m}^2$)</th>
<th>Measured Current Parameter ($\text{m}^2 \text{cm}^{-3}$)</th>
<th>Corrected† Current Parameter ($\text{m}^2 \text{cm}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/16/75</td>
<td>Centralia</td>
<td>0.8</td>
<td>$1.9\times10^5 \text{ m}^2$</td>
<td>$7.0\times10^9$</td>
<td>$(7.0_{-0.7}^{+}1)\times10^9$</td>
</tr>
<tr>
<td>7/29/75</td>
<td>&quot;</td>
<td>1.6</td>
<td>$1.8\times10^5$</td>
<td>$2.3\times10^9$</td>
<td>$(8.2_{-1.0}^{+}1)\times10^9$</td>
</tr>
<tr>
<td>10/31/75</td>
<td>&quot;</td>
<td>1.6</td>
<td>$5.5\times10^5$</td>
<td>$5.9\times10^9$</td>
<td>$(5.0_{-1.8}^{+}0)\times10^9$</td>
</tr>
<tr>
<td>11/5/75</td>
<td>&quot;</td>
<td>0.8</td>
<td>$2.4\times10^5$</td>
<td>$7.9\times10^8$</td>
<td>$(7.9_{-0.2}^{+}0)\times10^8$</td>
</tr>
<tr>
<td>11/5/75</td>
<td>&quot;</td>
<td>1.6</td>
<td>$5.2\times10^5$</td>
<td>$8.7\times10^8$</td>
<td>$(8.7_{-0.7}^{+}0)\times10^8$</td>
</tr>
</tbody>
</table>

†Corrected by comparison with $\text{SO}_2$ cross-sections as explained in the text.

*Corrected for instrument response (see § 4.1).
Table 3.4

Correlation of NO₂/NO with NOₓ in Power Plant Plumes

<table>
<thead>
<tr>
<th>Date</th>
<th>Power Plant</th>
<th>Range (km)</th>
<th>Correlation Coefficient (r_xy)</th>
<th>Significance Level (%)</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/16/75</td>
<td>Centralia</td>
<td>0.8</td>
<td>-0.75</td>
<td>&gt; 90</td>
<td>U.W.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6</td>
<td>-0.92</td>
<td>&gt; 90</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.8</td>
<td>-0.94</td>
<td>&gt; 98</td>
<td>&quot;</td>
</tr>
<tr>
<td>7/29/75</td>
<td>&quot;</td>
<td>0.8</td>
<td>-0.87</td>
<td>&gt; 95</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>1.6</td>
<td>-0.90</td>
<td>&gt; 99</td>
<td>&quot;</td>
</tr>
<tr>
<td>8/20/75</td>
<td>&quot;</td>
<td>0.2</td>
<td>-0.57</td>
<td>&gt; 75</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>3.2</td>
<td>-0.51</td>
<td>&gt; 50</td>
<td>&quot;</td>
</tr>
<tr>
<td>10/10/75</td>
<td>Longview</td>
<td>5.0</td>
<td>+0.98</td>
<td>98</td>
<td>MRI</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>3.0</td>
<td>+0.10</td>
<td>&lt; 50</td>
<td>&quot;</td>
</tr>
<tr>
<td>10/11/75</td>
<td>&quot;</td>
<td>3.0</td>
<td>-0.76</td>
<td>&gt; 90</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>10</td>
<td>+0.99</td>
<td>99</td>
<td>&quot;</td>
</tr>
<tr>
<td>10/17/75</td>
<td>Farmington</td>
<td>20</td>
<td>-0.91</td>
<td>&gt; 90</td>
<td>U.W.</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>40</td>
<td>-0.91</td>
<td>&gt; 95</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>70</td>
<td>-0.54</td>
<td>&gt; 50</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>10</td>
<td>+0.80</td>
<td>80</td>
<td>MRI</td>
</tr>
<tr>
<td>10/30/75</td>
<td>Centralia</td>
<td>8.0</td>
<td>-0.74</td>
<td>&gt; 80</td>
<td>U.W.</td>
</tr>
<tr>
<td>10/31/75</td>
<td>&quot;</td>
<td>2.4</td>
<td>-0.80</td>
<td>80</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>5.6</td>
<td>-0.69</td>
<td>&gt; 80</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
negative correlation shown in Table 3.4 is indicative of diffusive control of the plume chemistry. This correlation, and its significance, is fully discussed in Chapter 4.

3.4.2 Variation of NO$_2$/NO Ratio with Travel Time

Observed ratios of NO$_2$/NO for various travel times from the stack during a particular flight are shown in Table 3.5. The ratios shown are for the centerline of the plume; the centerline ratios were selected because the relatively high concentrations of NO$_2$ and NO along the centerline minimize the uncertainty in the ratio due to instrumental sensitivity limits. This particular flight (10/30/75 at Centralia) is shown for illustration because it contained the highest NO$_2$/NO ratio which was observed. Table 3.6 shows the plume average NO$_2$/NO ratios used in this study.

3.4.3 Nitric Oxide to Nitrogen Dioxide Conversion Rates

The 50% conversion times of NO to NO$_2$ for both the chemical centerline of the plume and the plume as a whole were calculated from the measured NO$_2$/NO ratios with the assumption of conservation of NO$_x$ and the simple formulation:

\[
\frac{(NO_2)_i + \beta(NO)_i}{(1-\beta)(NO)_i} = \frac{(NO_2)_f}{(NO)_f}
\]

(3.2)

where $\beta$ is the fraction of NO converted to NO$_2$ and the $i$'s and $f$'s represent initial and final values of NO and NO$_2$. The value of $\beta$ so determined, divided by the time interval between the initial and final values of NO and NO$_2$, gives the fractional conversion rate from which the 50% conversion
Table 3.5

NO\textsubscript{2}/NO ratios along the centerline of the plume from the Centralia coal power plant on 30 October 1975.

<table>
<thead>
<tr>
<th>Range (km)</th>
<th>Travel Time (min.)</th>
<th>NO\textsubscript{X} (ppm)</th>
<th>NO\textsubscript{2}/NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>1.4</td>
<td>0.42</td>
<td>0.33</td>
</tr>
<tr>
<td>8.0</td>
<td>14</td>
<td>0.099</td>
<td>1.3</td>
</tr>
<tr>
<td>17.6</td>
<td>22</td>
<td>0.065</td>
<td>1.9</td>
</tr>
<tr>
<td>22.4</td>
<td>39</td>
<td>0.055</td>
<td>4.3\textsuperscript{+}</td>
</tr>
<tr>
<td>38.4</td>
<td>65</td>
<td>0.039</td>
<td>2.6</td>
</tr>
</tbody>
</table>

\textsuperscript{+}Highest ratio observed in study.

Table 3.6

Plume average NO\textsubscript{2}/NO ratios with corresponding travel times for various flights at the Centralia coal power plant.

<table>
<thead>
<tr>
<th>Date</th>
<th>Travel Time (min.)</th>
<th>NO\textsubscript{X} (ppm)</th>
<th>NO\textsubscript{2}/NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/29/75</td>
<td>15</td>
<td>0.13</td>
<td>0.25+0.03</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.07</td>
<td>0.27+0.05</td>
</tr>
<tr>
<td>6/16/75</td>
<td>3.3</td>
<td>0.27</td>
<td>0.24+0.02</td>
</tr>
<tr>
<td></td>
<td>6.7</td>
<td>0.11</td>
<td>1.14+0.07</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.05</td>
<td>1.08+0.14</td>
</tr>
<tr>
<td>8/20/75</td>
<td>3.5</td>
<td>0.38</td>
<td>0.27+0.01</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.06</td>
<td>0.26+0.03</td>
</tr>
<tr>
<td>11/5/75</td>
<td>1.5</td>
<td>0.07</td>
<td>0.47+0.07</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.05</td>
<td>0.70+0.10</td>
</tr>
</tbody>
</table>
time is derived in the obvious way. Calculated values of the 50% conversion times are listed in Table 3.7.

3.4.4 The Effect of Liquid Water on Effluent Gases

One point of interest, only briefly touched on in this study, is the effect of rain or cloud on the chemical reactions in power plant plumes. While recent studies (e.g., Hales, 1972) have emphasized the reversible nature of gas scavanging by liquid water and the consequent uncertainty as to the net effect of liquid water on gases, liquid water probably has some effect on the chemical reactions in plumes. Measurements of the ratio of $\text{NO}_2/\text{NO}$ for a plume partially in cloud and the same plume completely out of cloud are shown in Table 3.8. A decrease in the $\text{NO}_2/\text{NO}$ ratio in cloud relative to out of cloud is clearly shown.
Table 3.7

Times required for 50% of NO to be converted to NO₂ in power plant plumes

<table>
<thead>
<tr>
<th>Date</th>
<th>Power Plant</th>
<th>Travel Time (min.)</th>
<th>50% Conversion Time Along Centerline (min)</th>
<th>Average 50% Conversion Time for Plume (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/16/75</td>
<td>Centralia</td>
<td>5.0</td>
<td>5.9 - 7.6</td>
<td>3.6 - 4.3</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>14</td>
<td>Indeterminate</td>
<td>Indeterminate</td>
</tr>
<tr>
<td>7/29/75</td>
<td>&quot;</td>
<td>23</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>8/20/75</td>
<td>&quot;</td>
<td>30</td>
<td>366 - 1002</td>
<td>&quot;</td>
</tr>
<tr>
<td>10/11/75</td>
<td>Longview</td>
<td>18</td>
<td>24 - 53</td>
<td>48 - 82</td>
</tr>
<tr>
<td>10/17/75</td>
<td>Farmington</td>
<td>96</td>
<td>119 - 160</td>
<td>93 - 126</td>
</tr>
<tr>
<td>10/31/75</td>
<td>Centralia</td>
<td>7.9</td>
<td>11.6 - 120</td>
<td>Indeterminate</td>
</tr>
<tr>
<td>11/4/75</td>
<td>&quot;</td>
<td>14</td>
<td>29 - 320</td>
<td>--</td>
</tr>
<tr>
<td>11/5/75</td>
<td>&quot;</td>
<td>2.3</td>
<td>2 - 3.4</td>
<td>3.3 - 16.7</td>
</tr>
</tbody>
</table>
Table 3.8

Effect of liquid water on NO$_2$/NO ratio of the power plant plume at Centralia on 20 August 1975.

<table>
<thead>
<tr>
<th>Range (km)</th>
<th>Altitude (m)</th>
<th>NO$_2$/NO</th>
<th>Liquid Water Content (g m$^{-3}$)</th>
<th>In Visible Cloud?</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>600</td>
<td>0.35</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>&quot;</td>
<td>690</td>
<td>0.21</td>
<td>0.02</td>
<td>Yes</td>
</tr>
<tr>
<td>&quot;</td>
<td>780</td>
<td>0.23</td>
<td>0.16</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>870</td>
<td>0.21</td>
<td>0.22</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>930</td>
<td>0.25</td>
<td>0.28</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>1020</td>
<td>0.42</td>
<td>0.02</td>
<td>No</td>
</tr>
<tr>
<td>6.4</td>
<td>780</td>
<td>0.40</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>870</td>
<td>0.56</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>930</td>
<td>0.44</td>
<td>0</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
4.1 Effects of Instrument Response Times

The response times of the instruments used in this study have been given in § 2.1. The longest response time was that of the sulfur analyzer, about 10s, which implies an e-folding time of about 5s. Since the aircraft flies at 60 m s\(^{-1}\) during sampling, this implies a spatial resolution of 300 m for the sulfur analyzer and somewhat shorter distances for the other instruments. Because the plume diameter was frequently of the same order of magnitude as 300 m, the actual concentration profile of a species will be distorted in a manner similar to that which a changing voltage signal undergoes when passing through an excessive cable capacitance. The values of the corrections necessary to retrieve the true concentration profiles have been calculated and the effects of these corrections on the parameters utilized in this study have been determined. These calculations are given in Appendix B. The only parameter which underwent a net significant change was the plume cross-sectional area (which was 55% overestimated). However, since the errors in the area of the plume result in errors in \(\alpha\) and the currents which are within the calculated uncertainties of the uncorrected values of these parameters (with one exception indicated in the text), the areas employed and shown in this study are left uncorrected.
4.2 Plume Diffusion

The basis for the plume diffusion parameter mentioned in § 2.4 and discussed below is a dynamic-kinetic plume model developed by Gelinas and Walton (1974) for analyzing the effects of aircraft exhausts on the stratosphere. Their model equation is:

\[
\frac{d C_i(t)}{dt} = P_i[C(t)] - L_i[C(t)]C_i(t) - \left( \frac{3\ln\mathcal{V}(t)}{\theta t} \right) \\
\times [C_i(t) - C_i^A(t)] + S_i^{\text{ext}}(t)
\] (4.1)

where \( C_i \) represents the concentration of species \( i \), the terms \( P_i[C(t)] \) and \( L_i[C(t)]C_i(t) \) represent interactive production and removal terms for the \( i \) species, \( S_i^{\text{ext}} \) is the net source (or sink) rate of the \( i \) species, and the third term on the right hand side allows for the effects of plume dilution and entrainment (this term is derived by considering the plume as an expanding Lagrangian box). The symbol \( \mathcal{V} \) represents the plume volume, and the superscript \( A \) indicates ambient air in this third term. The actual dilution coefficient, \( 3\ln\mathcal{V}(t)/\theta t \), can be reduced to a particularly simple form, readily determined empirically, by means of the following arguments.

The box volume, \( \mathcal{V}(t) \), can be considered as some constant multiple of \( \sigma_x \sigma_y \sigma_z \), where the \( \sigma \)'s are the standard deviations of the plume (i.e., the root-mean-square displacement of a particle from the plume axis) in the \( x, y, \) and \( z \) directions, that is,

\[
\mathcal{V}(t) = K \sigma_x(t) \sigma_y(t) \sigma_z(t).
\] (4.2)
Thus, if the true variations of the $\sigma$'s are known, $V(t)$ and $\frac{\partial \ln V(t)}{\partial t}$ can be evaluated. Further, if

$$\sigma_x(t) = C_1 t^A$$
$$\sigma_y(t) = C_2 t^B$$
$$\sigma_z(t) = C_3 t^D$$

then,

$$V(t) = K C_1 C_2 C_3 t^{A+B+D}$$

and

$$\frac{\partial \ln V(t)}{\partial t} = \frac{A+B+D}{t} = \frac{\alpha}{t}$$

where $\alpha$ is the diffusion parameter referred to in § 2.4; it gives a measure of the rate of increase in the volume of the plume. Now consider a continuous, steady-state plume as illustrated in Fig. 4.1. If the plume is considered as consisting of Lagrangian disc, volume elements moving in the $x$ direction with the mean wind velocity ($U$), diffusion in the direction of the mean wind is negligible compared to advection in this direction, the Lagrangian discs are very thin and growing radially with time, then the volume of a disc at time $t$, is given by

$$V(t) = L_0 \beta \sigma_1 \sigma_2 = L_0 A_1$$

where $\beta$ is a constant, the value of which depends on the geometry of the plume, and $L_0 = U \Delta t$ where $\Delta t$ is the small time interval required to traverse the thickness of the disc at the mean wind velocity. Clearly, for a constant wind velocity, $L_0$ can be held constant and the change in the box volume with time then becomes a function of the change in the plume cross-sectional area with time. Thus,
Fig. 4.1 Geometry of a continuous, steady-state plume. The mean wind velocity $\langle \bar{U} \rangle$ is constant and flows from left to right in the diagram. $L_0$ is the width of a Lagrangian disc.
\[
\frac{\Delta \ln V}{\Delta t} = \frac{\Delta \ln V}{\Delta t} = \frac{\ln V_2 - \ln V_1}{\Delta t} \approx \frac{\alpha}{t}
\]  (4.7)

and,
\[
(ln A_2 - ln A_1) \frac{t}{\Delta t} \approx \alpha
\]  (4.8)

The \( t \) value chosen for purposes of calculation was the midpoint of the \( \Delta t \) interval. Values of \( \alpha \) calculated from this procedure are shown in Table 4.1.

Ideally, values of \( \alpha \), using the above procedure but with NO\(_x\) as a conservative plume tracer, could be derived for comparison with the values of \( \alpha \) derived from SO\(_2\) concentrations. However, this was generally not possible owing to large uncertainties in the NO\(_x\) cross-sectional areas resulting from signal saturation close to the stack, and instrument insensitivity to small concentration variations on the scales which had to be used near the stack. A few values of \( \alpha \), derived from the NO\(_x\) data, are shown in Table 4.1. These were derived from the NO\(_x\) data of Table 3.6 by means of the following procedure. From Eqn. (4.7):

\[
\frac{\Delta \ln V}{\Delta t} = \frac{\alpha}{t},
\]

but
\[
V = \frac{K}{C},
\]  (4.9)

therefore,
\[
\frac{\Delta \ln V}{\Delta t} = \frac{\Delta \ln (1/C)}{\Delta t} = \frac{\alpha}{t}
\]  (4.10)

where the parameter \( C \) is the mean concentration, in volume \( V \), of whatever gas is being used as a conservative plume tracer (in this case NO\(_x\)).

The values of \( \alpha \) shown in Table 4.1 can be compared to the \( \alpha \)'s derived from various theories. For example, in most semi-empirical plume models
Table 4.1

Calculated values of the diffusion parameter $\alpha$ for power plant plumes

<table>
<thead>
<tr>
<th>Date</th>
<th>Local</th>
<th>Range Interval</th>
<th>$\alpha$($SO_2$)$^+$</th>
<th>$\alpha$($NO_x$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/13/75</td>
<td>Centralia</td>
<td>1.6 - 4.8 km</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>3/20/75</td>
<td>&quot;</td>
<td>4.8 - 9.6</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>3/24/75</td>
<td>&quot;</td>
<td>0.8 - 6.4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>3/26/75</td>
<td>&quot;</td>
<td>1.6 - 4.8</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>6/16/75</td>
<td>&quot;</td>
<td>0.8 - 1.6</td>
<td>2.0</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>1.6 - 4.8</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>7/29/75</td>
<td>&quot;</td>
<td>0.8 - 1.6</td>
<td>0.3</td>
<td>0.9</td>
</tr>
<tr>
<td>8/20/75</td>
<td>&quot;</td>
<td>0.2 - 3.2</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>3.2 - 6.4</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>10/16/75</td>
<td>Farmington</td>
<td>17 - 30</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>30 - 45</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>10/30/75</td>
<td>Centralia</td>
<td>0.8 - 8.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>8.0 - 18</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>18 - 22</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>10/31/75</td>
<td>&quot;</td>
<td>2.4 - 5.6</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>5.6 - 12</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>12 - 21</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>11/5/75</td>
<td>&quot;</td>
<td>0.8 - 1.6</td>
<td>1.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

$^+$The uncertainty in $\alpha$ is estimated to be $\leq 0.5$. 
(the form of which is almost always derived from the statistical approach of Taylor) \( \sigma_y \approx C_1 t \) and \( \sigma_z \approx C_2 t^{1/2} \) (Slade, 1968) which implies that \( \alpha = 1.5 \). For K-theory, Smith gives \( \sigma_y = \sigma_z = C_3 t^{1/2} \) which implies that \( \alpha = 1.0 \). Of course, the \( t \) dependence of the \( \sigma \)'s, particularly \( \sigma_z \), will vary with atmospheric stability for all empirical models; however, the variability is not large. The value of \( \alpha \) for the Pasquill-Hay model varies roughly between 1.2 and 3 (Slade, 1968). The values of \( \alpha \) listed in Table 4.1 indicate that plumes commonly diffuse at slower rates than those predicted by current models. This agrees with the findings of several recent studies (e.g., Raynor et al., 1975). However, perhaps the most important point illustrated by the results in Table 4.1 is the variability of plume diffusion rates in the atmosphere. The high value for the uncertainty in \( \alpha \) and the disparity between the values of \( \alpha \) derived from the SO\(_2\) and NO\(_x\) concentrations suggest that part of the variability in the results is due to the measurement technique. However, the range of values of \( \alpha \) listed in Table 4.1 is considerably greater than the uncertainty in the value of \( \alpha \) for SO\(_2\) (0.5) --see Appendix A. Therefore, much of the variability in the value of \( \alpha \) is probably real.

4.3 Fluctuations in Concentration of Constituents of a Plume

Since the model for plume diffusion described in § 4.1 is based on the concept of a Lagrangian box moving with the mean wind, it must be considered to be essentially an instantaneous plume model. However, the plume cross-sections upon which the calculation of \( \alpha \) (and the SO\(_2\) and aerosol currents) is based are determined by sampling which extends over a substantial time interval, often as long as 20 minutes. They are therefore time-averaged cross-sections. While this does not change the
conceptual significance of $\alpha$, it can introduce a large source of error into the determinations of mean cross-sectional concentrations. This error is due to the fact that the concentrations of $SO_2$ and aerosol will fluctuate because of fluctuations or meandering of the instantaneous plume within the time-averaged plume envelope. The error will affect the current calculations and thus, in turn, the cross-sectional areas since they are adjusted on the assumption of a constant $SO_2$ current. Finally, this can result in an error in $\alpha$ itself. The potentially large size of the error (or variance) from this source is illustrated in a study by Ramsdell (1971). Ramsdell found that the time-averaged concentrations in a plume could differ from the instantaneous concentrations by as much as an order of magnitude.

The first attempt to treat the problem of concentration fluctuations due to plume meandering was apparently that of Gifford (1960). Gifford modeled a plume as a series of Lagrangian discs in the plane normal to the mean wind direction. These discs were assumed to have a definite concentration distribution within them and to fluctuate randomly around the time-averaged centerline of the plume. In this model, the variance of the time-averaged concentration distribution would simply be the sum of the variance (with respect to the center of the disc) of the distribution within the discs and the mean square displacement of the centers of the discs from the time-averaged centerline. While Gifford carries his analysis further than this, as far as the present study is concerned, the important point is that the effect of plume meanderings on the time-averaged concentrations within the plume can be evaluated in terms of the variance of the time-averaged concentration distribution itself.
Since the measured cross-sections essentially give the time-averaged concentration distribution, the variance of the concentration distribution in a cross-section will give the variance to be associated with each individual concentration point in the cross-section. Thus variances which include the effects of plume meandering can be associated with the plume currents, cross-sections, and with \( \alpha \).

To simplify the determination of the cross-sectional variance, the concentration distributions are assumed to be roughly Gaussian. Plots of the cross-sectional plume concentrations are then plotted against the percent of the plume they occupy on semilog-cumulative probability paper and the standard deviation of the distribution is determined as the difference of the concentrations at the 50th and 84th percentiles.

Another matter in which meandering (although not exactly plume meandering) must be taken into account is that of the vertical correlation of the horizontal traverses of the plume. As described in § 2.4, this was done by aligning the mid-points of the traverses, rather than by the more normal procedure of concentration correlation (i.e., essentially aligning the points of maximum concentration in each traverse). This method was settled upon because analysis of the horizontal traverses revealed that the concentration distribution was not only commonly skewed, but the direction of skewness was random. In other words, the relative position within the plume of the area of highest concentration was fluctuating. The reason for this is as follows. The high concentration "core" of the plume clearly has a smaller characteristic linear dimension than the plume itself. Thus the turbulence spectra effective in translating the "core" of the plume will include smaller and shorter time
scale eddies than the spectra which will effectively translate the plume as a whole. This results in "meandering" of the "core" of the plume relative to the plume as a whole. Thus, if the points of maximum concentration of the horizontal traverses were aligned, a plume cross-section of considerably greater area than is actually the case would result. In view of this, rather than align points of maximum concentration, it seemed more reasonable to align the mid-points of the traverses. This merely assumes that the time-averaged plume envelope is symmetrical in the direction transverse to the mean wind.

One interesting consequence of this view of internal plume fluctuations is that the commonly observed Gaussian distributions in even very short time-averaged plumes may be due to random fluctuations caused by turbulent eddies which cause the "cores" of plumes to move.

4.4 Gas-to-Particle Conversion

4.4.1 Current Calculations

The aerosol current parameter data shown in Table 3.3 indicate that there was only one clear-cut case (the flight of 10/31/75) of a net increase in the total aerosol current in the plume from the Centralia coal power plant and one case (the flight of 7/29/75 also in the plume from the Centralia power plant) of a significant decrease in the aerosol current parameter.

In order to calculate an aerosol mass production rate (or the percentage conversion rate from the gas phase) in the plume, both the size distribution and the chemical composition of the aerosol that is produced should be known. Unfortunately, neither of these parameters could be determined owing to the apparently quite small size of the aerosol produced in the plume. Thus on 10/31/75 the aerosol-size
analyzers showed no increase in aerosol concentration over the ranges measured (0.012 - 30 μm radius), although the CN counter (which measures aerosol down to about 0.0025 μm radius) did detect an increase. Hence, aerosol that was produced in the plume must have been smaller than 0.012 μm radius. (Several more recent flights have shown an increase in the concentration of 0.02 μm radius particles at travel times of about 30 min. from the Centralia plant.) While chemical analysis of such small particles is possible, the necessary equipment (e.g., mass spectrometers) was not available for this study. However, by making several reasonable assumptions, a rough gas-to-particle conversion rate can be determined.

Since the divergences of the aerosol current parameters shown in Table 3.3 were determined ignoring any coagulation, the particle size assigned to the newly created aerosol should be no greater than the size at which coagulation begins to supplant condensation as the dominant growth process. Luria et al. (1974) give this size as about 0.0072 μm when the particles are those produced from the photolysis of SO₂ - light hydrocarbon mixtures. This particle radius (which is consistent with the above discussion, i.e., < 0.012 μm radius) was therefore chosen as the size of the photochemically produced aerosol observed on the flight of 10/31/75.

A likely composition for such small particles, produced in the absence of liquid water, can be inferred from the large number of laboratory studies of aerosol formation in SO₂ - NOₓ mixtures. For example, Cox (1973) states that with an average SO₂ concentration of 0.1 ppm and a relative humidity greater than 30%, enough sulfuric
acid (1-10 ppb hr\(^{-1}\)) is produced to cause rapid heteromolecular nucleation of sulfuric acid (H\(_2\)SO\(_4\)) droplets in less than 1 min. Sulfuric acid was therefore chosen as a likely chemical species for the aerosol produced in the plume from the Centralia coal power plant on 10/31/75.

Assuming the particles to be spherical and of density 1.5 g cm\(^{-3}\), straightforward calculations with the above assumptions yield an SO\(_2\) conversion rate to sulfuric acid of about 0.02%/hr. for the flight of 10/31/75. While faster conversion rates of SO\(_2\) to sulfate have been observed in coal-fired power plant plumes (Newman et al., 1975), this relatively slow rate is much easier to explain. However, another factor which should be discussed is the possible "masking" of aerosol production by coagulation.

### 4.4.2 Coagulation

The problem of determining the extent of coagulation of aerosol in the atmosphere is essentially that of determining a value for the turbulent coagulation coefficient. Very little work, either experimental or theoretical, has been carried out on this problem. An attempt was therefore made to determine, by means of a simple model, the effect of coagulation on the data listed in Table 3.3.

The change in number concentration of a stationary system of aerosol due to coagulation is given by (Fuchs, 1964):

\[
\frac{dn}{dt} = -K_0 n^2
\]  

(4.11)

where \(K_0\) is the coagulation coefficient and \(n\) is the number concentration of aerosol. Substituting this result into Eqn. (4.1) gives:
\[
\frac{dn}{dt} = -K_0 n^2 - \frac{3\ln V}{\alpha} (n - n_A) + S
\]

where \( n_A \) is the ambient aerosol concentration and \( S \) is a (constant) unspecified source of aerosol. In this study, \( S \) is taken to be photochemical production of aerosol.

Unfortunately, Eqn. (4.12) cannot be solved analytically. However, assuming \( n \gg n_A \) over the time scale of interest, the approximate asymptotic solution of Eqn. (4.12) for \( t > 180 \) s is

\[
n = \sqrt{S/K_0} - \frac{\alpha}{2K_0 t}
\]

where \( \alpha \) is the diffusion coefficient defined by Eqn. (4.5). (The derivation of (4.13) is given in Appendix C.)

Since values of \( \alpha \) and the cross-sectional areas of the plume are available for all the cases listed in Table 3.3, it was possible to perform a regression on the data in Table 3.3 against Eqn. (4.13) with \( S \) and \( K_0 \) to be determined as regression coefficients. The values of \( S \) and \( K_0 \) were determined to be,

\[
S = 100 \pm 9 \text{ cm}^{-3} \text{s}^{-1}
\]

\[
K_0 = (3.16 \pm 0.49) \times 10^{-7} \text{ cm}^3 \text{s}^{-1}.
\]

These values were found to be quite insensitive with respect to \( \alpha \) and insensitive to variance in \( n \) of the order of magnitude of the calculated variance. It is interesting to note that this value for \( K_0 \) agrees quite well with the theoretical value \((7 \times 10^{-8} \text{ cm}^3 \text{s}^{-1})\) for particles of about the same size derived by extrapolating Beal's (1972) curve (Fig. 2) to 00072 \( \mu \)m. However, it should be noted that the multiple correlation coefficient
for the regression was only about 0.3 ($R^2 \approx 0.3$) and consequently the regression equation (Eqn. 4.13) itself cannot be considered particularly accurate.

Using the above value of $S$ with the same assumptions employed in the calculation of the $SO_2$ to sulfuric acid conversion rate on the flight of 10/31/75 yields a conversion rate, corrected for coagulation, for this flight of 0.34% per hour. This is still quite modest compared to the upper limit of 5% per hour for coal-fired plants given by Newman et al. (1975) but more than an order of magnitude larger than the rate obtained ignoring coagulation. Thus, the above calculations suggest that coagulation of photochemically produced aerosol in plumes from coal power plants must be taken into account if valid conversion rates are to be obtained.

4.5 Nitrogen Oxides and Ozone

4.5.1 Correlation of $NO_2/NO$ with $NO_x$

A plume of $NO_x$, initially mostly NO, interacting with an atmosphere containing ozone (or any other species which has a comparable reactivity with nitric oxide) may be viewed as a bimolecular reaction, with initially unmixed reactants, in a turbulent fluid. This problem has been treated theoretically with some success and, in addition, some laboratory results are available (Hill, 1976; O'Brien, 1974). However, a real plume, ejected into an obviously inhomogeneous, turbulent atmosphere containing many potentially important reactants, may depart so far from the ideal theoretical case as to render any analogy unprofitable. The important step, therefore, in any analysis of $NO_x - O_3$ chemistry in atmospheric plumes is to determine if there are any similarities between the real and ideal cases.
Assuming that the bimolecular reaction is fast compared to plume mixing (for \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \), \( \tau_{\text{NO}_3} \approx 1 \text{ min.} \) for typical NO concentrations), which was tacitly assumed in §2.4, theory indicates that the reactant species should be spatially segregated with the reaction occurring entirely within a relatively narrow reaction zone between the two spatial regions (Hill, 1976). The well known ozone deficits associated with power plant plumes are, in fact, manifestations of exactly this spatial segregation. Fig. 4.2 shows an example of this effect.

Further evidence for the diffusive control of the plume chemistry, and for the relative location of the reaction zone, can be obtained from a consideration of the spatial distribution of the \( \text{NO}_2/\text{NO} \) ratio. Since \( \text{NO}_2 \) is the product of the reaction of \( \text{NO} \) and \( \text{O}_3 \) (and most other NO oxidation reactions), the ratios of \( \text{NO}_2/\text{NO} \) should be highest at the reaction zone and, if the chemistry is the diffusion-controlled, and bimolecular reactions hypothesized, this zone should be located at the edge of the plume between the regions of high \( \text{NO} \) and \( \text{O}_3 \). Assuming this to be the case, the ratio of \( \text{NO}_2/\text{NO} \) should then be negatively correlated with the total concentration of \( \text{NO}_x \) (which is assumed to be conserved in the plume). (See Table 3.4.)

It should be noted that the more direct method of determining the location of the reaction zone by determining the location of peak nitrogen dioxide is not necessarily valid for the cases examined in this study. In-stack (or pre-stack) reactions such as

\[
\text{NO} + \text{NO} + \text{O}_2 + 2\text{NO}_2
\]

with \( \tau_{\text{NO}} \approx 30 \text{ min.} \) (at stack NO concentrations)
Fig. 4.2 Profiles of (a) nitric oxide and (b) ozone across the plume of the Four Corners coal-fired power plant on 16 October 1975. The range was 1 km and the altitude 1950 m.
can result in the formation of appreciable NO\textsubscript{2} in or near the stack itself due to the high concentration of NO (~ 500 ppm for most of the study cases). This initial concentration of NO\textsubscript{2} will clearly bias the peak NO\textsubscript{2} concentration towards the plume center. Probably even more important, appreciable NO\textsubscript{2} may be formed near the plume centerline during the period of rapid entrainment as the plume leaves the stack and before diffusive control is well established. The location of the peak NO\textsubscript{2} concentration is therefore not a particularly good indicator of the location of the reaction zone.

The results of the correlation analysis between NO\textsubscript{2}/NO and NO\textsubscript{x} are shown in Table 3.4. In fourteen out of eighteen cases there was a negative correlation between NO\textsubscript{2}/NO and NO\textsubscript{x}. In eight of these cases the correlation is significant at the 90% level and in three others at the 80% level. Considering only those correlations at the 80% or higher level to be significant, there was still a significant correlation in the majority of cases studied. These results suggest that the NO\textsubscript{x} - O\textsubscript{3} chemistry in power plant plumes is indeed often diffusion controlled and that an analogy with the ideal bimolecular-turbulent chemistry referred to at the beginning of this section has some validity.

4.5.2 Nitric Oxide to Nitrogen Dioxide Conversion Rates

If the plume chemistry is diffusion controlled, as the results indicate, the conversion rate of NO to NO\textsubscript{2} will be considerably slower than the kinetic rate for this reaction would lead one to believe. Indeed, since the rate of turbulent entrainment of ambient air decreases with time (to some constant value) as the radius of the plume grows, the NO to NO\textsubscript{2} conversion rate should also decrease with travel time from
the stack. The centerline 50% conversion times (Table 3.7) are plotted against travel time in Fig. 4.3. Even with the large uncertainties in the conversion times, the results show a roughly inverse-squared decrease in conversion rate with travel time. Since the average conversion times listed in Table 3.7 agree with the centerline times, a similar relationship between NO-to-NO₂ conversion time and travel time is postulated for the plume as a whole. This relationship implies that the conversion time, τᵣ, is proportional to the square of the travel time, τₜ, that is:

\[ τᵣ \propto τₜ², \quad (4.14) \]

This further implies that the reaction-zone width, Lᵣ, grows approximately linearly with time, t, that is:

\[ Lᵣ \propto τₜ = t. \quad (4.15) \]

This last relationship is easily explicable in terms of the equation defining the reaction-zone width,

\[ Lᵣ \approx Vₑ τᵣ \quad (4.16) \]

where \( Vₑ \) is an eddy velocity (assumed constant) and \( τᵣ \) is a relaxation time to chemical equilibrium. (Equ. (4.16) will be fully discussed in § 4.5.4.) The reaction time, \( τᵣ \), must be of the form,

\[ τᵣ \propto \frac{1}{kC} \quad (4.17) \]

where \( k \) is a rate constant and \( C \) is a concentration of the plume. The concentration of a steady-state plume, however, will vary inversely as the cross-sectional area (§ 4.2), which implies:
Travel time (minutes) from stack to midpoint of conversion interval

Fig. 4.3 NO-to-NO₂ 50% conversion times versus travel time from the plant. The circles indicate data from the Centralia coal power plant, the triangles data from the Longview gas power plant, and the squares data from the Farmington coal power plant.
\[ \tau_R \propto \frac{t}{k'} \]  
(4.19)

and

\[ L_R \approx V_k \tau_R \propto k'' \]  
(4.20)

where \( k'' \) is \( VE/k' \). Thus the inverse-square dependence of the NO-to-NO\(_2\) conversion rate on travel time (illustrated in Fig. 4.2) is shown to be a consequence of the diffusive control of the plume chemistry.

4.5.3 Ratio of Nitrogen Dioxide to Nitric Oxide

The rapidly decreasing conversion rates of NO to NO\(_2\) with travel time shown in Fig. 4.2 imply that the ratio of NO\(_2\)/NO should only increase slowly with time. An examination of these ratios, which are contained in Tables 3.5 and 3.6, shows that the ratio do indeed increase only slowly. The value of 4.34 for this ratio, shown in Table 3.5, was the highest value recorded during this study. Since, as discussed in § 2.4.3, appreciable ozone generation is unlikely to occur before this ratio reaches 10, and since most of the plumes included in this study were tracked until they were indistinguishable from the background, the observed ratios indicate that the probability of ozone generation in these plumes, before they dilute to background (and only before), must be quite low.

4.5.4 Chemical Equilibrium and Turbulent Kinetics

Another question suggested by the analogy between plume chemistry and a bimolecular reaction in turbulent mixing is the degree to which turbulent fluctuations affect the plume kinetics.

It has been shown (e.g., Donaldson and Hilst, 1972) that when concentration fluctuations of the two reactants in a bimolecular reaction
are negatively correlated, as nitric oxide and ozone fluctuations are in
the plumes studied in this thesis, the reaction rate may be appreciably
slowed. The extent to which this effect contributes to a reduction in
the rate of conversion of NO to NO\textsubscript{2} is clearly of interest with respect
to the generation of ozone in power plant plumes. To assess the possible
importance of turbulent fluctuations in the production of ozone, the
extent to which a power plant plume is in chemical equilibrium must
first be determined.

The plumes studied are similar in chemical structure to plumes in
which bimolecular reactions are diffusion controlled. Therefore, the
chemical equilibrium of the plume may be considered in terms of the
three fast reactions:

\begin{align*}
\text{ka} & \quad \text{NO}_2 + h\nu \rightarrow \text{NO} + 0 \\
\text{k}_2 & \quad 0 + 0_2 + M \rightarrow 0_3 + M \\
\text{k}_3 & \quad \text{NO} + 0_3 \rightarrow \text{NO}_2 + 0_2
\end{align*}

where the k's are rate constants. One can now consider the chemical
equilibrium of the plume in terms of a photostationary state concept
(Stedman and Jackson, 1974). If the system is in the photostationary
state, then:

\begin{align*}
\frac{\text{NO}_2}{\text{NO}(0_3)} &= \frac{k_3}{k_a} & (4.22) \\
\frac{(\text{NO}_2)k_a}{k_3(\text{NO})(0_3)} &= 1 & (4.23)
\end{align*}

Since all of these parameters can be determined from the airborne
measurements, any departures of the measured values of \(\frac{(\text{NO}_2)k_a}{k_3(\text{NO})(0_3)}\)
(hereafter represented by \(\Psi\)) from unity will indicate a departure from
chemical equilibrium. The relationship between any such departure of \( \Psi \) from unity and some parameter which will reflect the effects of turbulent fluctuations on \( \Psi \) must now be derived.

Returning to the theory of a bimolecular reaction, with initially unmixed reactants, undergoing turbulent mixing, the following argument can be employed. A turbulent eddy, \( E \), can be considered to transfer ozone into the plume with a velocity \( V_E \) and to transfer NO out of the plume with a velocity \(-V_E\) (Fig. 4.4). As the \( O_3 \) first enters the plume and encounters higher than ambient NO, it begins to react with the NO to form \( NO_2 \); the concentrations of the three species tending towards their equilibrium values as the reaction proceeds. Thus, as the eddy penetrates deeper into the plume, the magnitude of the perturbing \( O_3 \) concentration decreases to zero. The reaction zone (defined as the area where NO and ozone are actually coming into contact with one another and reacting) thus has a width, \( L_R \), given approximately by:

\[
L_R = V_E \tau_R
\]  

(4.24)

where \( \tau_R \) is the relaxation time to the equilibrium state. It follows from this conception of the mixing plume that the area of the plume outside of the reaction zone will be in photochemical equilibrium very shortly after its formation because, by definition, it contains no correlated concentration fluctuations of NO and \( O_3 \). The reaction zone, on the other hand, will, by definition, not be in chemical equilibrium because of eddy diffusion. In addition, the reaction-zone chemistry may be further from equilibrium due to negatively correlated NO and \( O_3 \) concentration fluctuations. The plume as a whole, therefore, will be out
Fig. 4.4 Schematic diagram to illustrate a bimolecular reaction in a turbulent plume. The view is cross-sectional. The reaction zone is an annulus of area $A$ and width $L_R$. The interior of the plume, where the concentration of NO is high, has area $B$. Area $C$ is the exterior region of ozone (or other similar reactants). $E$ is a mixing turbulent eddy of velocity $V_E$ and scale $\lambda$. 
of equilibrium to an extent dependent on the percentage of the plume which is included in the reaction zone, which in turn is dependent on the chemical and turbulent time scales, and on the extent to which the zone itself is out of chemical equilibrium. In order to quantitatively examine these effects, a model which relates the effects of diffusion and the negatively correlated fluctuations of NO and ozone to the $\Psi$ parameter is derived in terms of chemical and diffusive time scales.

Consider a simple bimolecular reaction:

$$k$$

$$\begin{align*}
A + B &\rightarrow C \\
\left(4.25\right)
\end{align*}$$

where $k$ is the chemical rate constant. Then,

$$\frac{d\bar{A}}{dt} = K_r \frac{\partial^2 \bar{A}}{\partial r^2} - k(\bar{A} \bar{B} + \bar{A}'B') \left(4.26\right)$$

where $K_r$ is the eddy diffusion coefficient along the radius of the plume (cylindrical symmetry is assumed), and the bars indicate spatial averages and the primes fluctuations. Eqn. (4.26) can be approximated as:

$$\frac{d\bar{A}}{dt} = \frac{\beta \bar{A}}{\tau_D} - \frac{\bar{A}}{\tau_c} - k \bar{A}'B' \left(4.27\right)$$

where $\tau_c$ is the kinetic time scale and $\tau_D$ is defined by:

$$K_r \frac{\partial^2 \bar{A}}{\partial r^2} = K_r \bar{A} \frac{1}{r^2} = \frac{\bar{V}'^2 \tau_T A}{\bar{V}^2 \tau_D} \left(4.28\right)$$

where $\tau_D$ is a time scale characteristic of the turbulent fluctuations in the plume, $\tau_T$ is the turbulent time scale, and $V'$ the turbulent velocity fluctuation. The value of $\beta$ is then given by:
\[ \beta = \frac{\overline{v'^2}}{\overline{v'^2} \tau_D}. \]  

(Since the value of \( \overline{v'^2}/\overline{v'^2} \) will be constant and determinable for any given turbulence state, the ratio of \( \tau_T/\tau_D \) can be determined once \( \beta \) is known.)

The real problem in solving (4.27) is the determination of \( \overline{A'B'} \) in terms of the time scales. Donaldson and Hilst (1972) give:

\[ \frac{\partial \overline{A'B'}}{\partial t} = -2 \frac{K}{\lambda^2} \overline{A'B'} \]  

which assumes slow chemistry and where \( \lambda \) is a spatial scale which will be absorbed in \( \tau_D \). Thus

\[ \overline{A'B'} = \overline{A'B'}_0 e^{-2K \tau/\lambda^2} = e^{-2t/\tau_D} \]  

For an extreme case, let:

\[ \overline{A'B'}_0 = - \overline{A B} \]  

then,

\[ \frac{d \overline{A}}{dt} = \frac{\beta \overline{A}}{\tau_D} - \frac{\overline{A}}{\tau_c} + \frac{\overline{A}}{\tau_c} e^{-2t/\tau_D} \]  

and,

\[ \ln \frac{\overline{A}}{A_0} = \beta \frac{\tau_c}{\tau_D} - 1 + \frac{1}{\tau_c} \int_0^{\tau_c} e^{-2t/\tau_D} dt \]

\[ = \beta \frac{\tau_c}{\tau_D} - 1 - \frac{\tau_D}{2\tau_c} (e^{-2\tau_c/\tau_D} - 1) \]  

Hence,

\[ \overline{A} = A_0 \exp \{ \beta \frac{\tau_c}{\tau_D} - 1 - \frac{\tau_D}{2\tau_c} (e^{-2\tau_c/\tau_D} - 1) \} \]
and,

$$\psi_1 = \frac{k_a}{k_3} \frac{c}{A} \bar{B} \approx \alpha \exp\{-\beta \tau_c/\tau_D + 1 + \frac{\tau_D}{2\tau_c} (e^{-2\tau_c/\tau_D} - 1)\} \quad (4.36)$$

This solution must assume the extreme case of Eq. (4.32). A more general solution for $A'B'$, which has been derived by Harrison (1976), is:

$$A'B' = -\bar{A} \bar{B}/(1 + \tau_c/\tau_D) \quad (4.37)$$

In this case:

$$\psi_2 \approx \alpha \exp\{-\beta \tau_c/\tau_D + (\tau_c/\tau_D)/(1 + \tau_c/\tau_D)\} \quad (4.38)$$

If one assumes a priori that the fluctuations have no effect, then:

$$\psi_3 \approx \alpha \exp\{-\beta \tau_c/\tau_D + 1\} \quad (4.39)$$

Table 4.2 lists values of $\psi$ and of $\tau_c/\tau_D$. The value of $\tau_c$ was determined from the formula of Stedman and Jackson (1974), namely:

$$\tau_c = \{k_a + k_3(NO) + k_3(O_3)\}^{-1}. \quad (4.40)$$

The value of $\tau_D$ was determined as:

$$\tau_D = R/2V_E \quad (4.41)$$

where $R$ is the radius of the plume, and $V_E \approx 0.4\bar{U}$, where $\bar{U}$ is the mean wind velocity (Pasquill, 1974).

Least square regressions of the data in Table 4.2 to each of the above three $\psi$ functions were run with the following results:

$$\psi_1: \alpha_1 = 0.54 \pm 0.08; \beta_1 = 4.1 \pm 1.4; R_1^2 = 0.61$$

$$\psi_2: \alpha_2 = 0.54 \pm 0.08; \beta_2 = 4.5 \pm 1.5; R_2^2 = 0.61$$

$$\psi_3: \alpha_3 = 0.2 \pm 0.03; \beta_3 = 4 \pm 1 \quad ; R_3^2 = 0.61$$
Table 4.2
Values of $\tau_c/\tau_D$ and corresponding values of $\Psi$

<table>
<thead>
<tr>
<th>Date</th>
<th>Power Plant</th>
<th>Range (km)</th>
<th>$\tau_c/\tau_D$</th>
<th>$\Psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/17/75</td>
<td>Farmington</td>
<td>20</td>
<td>0.034</td>
<td>0.60 ± 0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>0.002</td>
<td>0.84 ± 0.11</td>
</tr>
<tr>
<td>10/31/75</td>
<td>Centralia</td>
<td>2.4</td>
<td>1.17</td>
<td>0.13 ± 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.6</td>
<td>0.44</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>10/11/75</td>
<td>Longview</td>
<td>3</td>
<td>0.17</td>
<td>0.13 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>0.18</td>
<td>0.12 ± 0.02</td>
</tr>
<tr>
<td>10/31/75</td>
<td>Centralia</td>
<td>21</td>
<td>0.39</td>
<td>0.17 ± 0.05</td>
</tr>
<tr>
<td>10/30/75</td>
<td></td>
<td>0.8</td>
<td>0.88</td>
<td>0.15 ± 0.03</td>
</tr>
<tr>
<td>10/16/75</td>
<td>Farmington</td>
<td>17</td>
<td>0.005</td>
<td>0.54 ± 0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.010</td>
<td>0.37 ± 0.05</td>
</tr>
<tr>
<td>10/30/75</td>
<td>Centralia</td>
<td>18</td>
<td>0.45</td>
<td>0.18 ± 0.03</td>
</tr>
</tbody>
</table>
where $\beta$ is defined by Eqn. (4.29) and $\alpha$ by Eqn. (4.36). The equal correlation coefficients ($R^2$) for the three cases and the stability of the regression coefficients ($\alpha_3$ differs from $\alpha_1$ and $\alpha_2$ because the exponential of $\psi_3$ has a different limit from those of $\psi_1$ and $\psi_2$) indicate that the concentration cross-correlations $A'B'$ have a negligible effect on the chemical kinetics. Furthermore, considering the uncertainties in the determination of $\psi$ and $\tau_c/\tau_D$, the correlation of the data of Table 4.2 with the $\psi$ functions is considered to be fairly good.

4.5.5 Effects of Liquid Water on Effluent Gases

The results shown in Table 3.8 indicate that the presence of liquid water reduces the $\text{NO}_2/\text{NO}$ ratio. While this may be due to some reaction of $\text{NO}_2$ and water (or a water derivative), preferential absorption of $\text{NO}_2$ relative to NO into liquid water droplets is a more likely cause. Since $\text{NO}_2$ dissolves in liquid water, this effect might even be irreversible and thus have an influence on the increase in the ratio of $\text{NO}_2/\text{NO}$. However, even if the gases eventually desorbed, the delay in the increase of the $\text{NO}_2/\text{NO}$ ratio should have an effect on the generation of ozone in the plume. One can even envision cases, involving the presence of large quantities of liquid water in the plume for substantial periods of time, where the $\text{NO}_2/\text{NO}$ ratio would remain essentially constant until the plume had diffused down to background levels, even if the plume were not diffusion controlled. This question clearly needs further study.

4.5.6 Observations of Ozone Concentrations In This Study

The above discussion leads one to believe that above ambient ozone concentrations in power plant plumes should be quite rare due to the
low $\text{NO}_2/\text{NO}$ ratio in these plumes. In this study, which included observations at two coal and two gas-fired power plants, above ambient ozone concentrations which could definitely be associated with the power plants were never observed. However, above ambient ozone was observed on three occasions. These observations will now be discussed in order to point out some of the pitfalls in associating occasional above ambient ozone measurements in power plant plumes with the plant itself.

The three observations of above ambient ozone occurred in the vicinity of the Wilkes gas-fired power plant near Longview, Texas. The above ambient ozone was initially thought to be associated with the plume of this plant. Fig. 4.5, for example, shows above ambient ozone which was observed downwind of the Wilkes Power Plant on 10/11/75. Because these observations occurred at a reasonable distance downwind of the plant, and in a region through which the Wilkes plume was meandering back and forth, it seemed reasonable to associate them with the plant. Furthermore, comparison with approximately simultaneous airborne observations made upwind of the plant indicated that ozone concentrations were much higher downwind than upwind. However, when a more detailed analysis of the ozone measurements made upwind of the plant was made (including vertical ozone profiles), it was found that very high concentrations of ozone were in fact present upwind of the plant. They were not initially detected because the high concentrations were not uniformly distributed in the vertical but situated in a "blob" just above the mixing layer. This effect is illustrated in Fig. 4.6. The high ozone concentrations observed downwind of the Wilkes plant occurred at the same altitudes as those at which the high ozone concentrations were observed
Fig. 4.5 Concentrations of ozone measured downwind of the Wilkes gas-fired power plant on 11 October 1975. The measurements do not represent a cross-section of the plume because the aircraft orbited for a period in the region of high ozone.
Aged upper layer, disconnected from surface. Ozone and b\textsubscript{scat} well correlated.

Wind shear zone velocity increases above

Surface mixing layer - ozone depleted by fresh emissions during night and morning hours.

Fig. 4.6 Vertical profile of ozone 1 km upwind of the Wilkes Power Plant on 11 October 1975. (From Ogren et al., 1976b)
upwind of the plant. Furthermore, the high ozone concentrations measured both upwind and downwind of the plant were equal. Thus it seems clear that the above ambient ozone concentrations were in the form of an ozone "blob" which had been transported into the plume region from upwind. A more detailed discussion of this topic is given by Ogren et al. (1976b), who have reached similar conclusions.

The main point resulting from this discussion is that great care must be taken in analyzing the meteorological situation and the overall ambient conditions before reaching any conclusions on the concentrations of chemical species in power plant plumes. The determination of the ambient concentrations of a particular species is very important in this respect and cannot be done on the basis of a few point measurements. This is particularly true in urban areas where ambient conditions are generally not uniform and may well be changing with time.

4.5.7 Other Observations of Ozone Concentrations in Power Plant Plumes

The only really well documented case of above ambient ozone in a power plant plume is that reported by Davis et al. (1974) for the coal-fired power plant at Morgantown, Maryland. In view of the results of this study, a re-evaluation of the measurements described by Davis et al. is in order.

The Morgantown power plant is not, as stated by Davis et al., an "isolated plant." Figure 4.7 shows the area surrounding Morgantown. It can be seen that Morgantown is in the Washington, D.C. - Baltimore urban area. There is a great deal of recent work (e.g., Cox et al., 1975) which shows that ozone can be transported over distances orders of magnitude greater than those depicted in Fig. 4.6. Consequently,
Fig. 4.7 Map of the area surrounding the Morgantown Power Plant. The numbers plotted on the map represent ozone concentration in ppb. The outlines of the plumes from various power plants are also shown. (From Tesche et al., 1976)
Morgantown can certainly be affected by other urban sources of ozone. Furthermore, work by Anlauf et al. (1975) demonstrates that three-dimensional circulation patterns, rather than the mean wind field at a particular level, must be specified in interpreting ozone measurements and the assigning of sources for high ozone concentrations.

Davis et al. (1974) further state, "that the $O_3$ bulge was, in fact, representative of the power plant plume is supported by the $SO_2$ profiles: as shown in Fig. 1b [Fig. 4.8 of this study], significant negative or positive profiles of $O_3$ were observed only when positive $SO_2$ profiles were detected, thus marking the location of the plume." However, it is clear from Fig. 4.8 that the total current of $SO_2$, which was used as a plume tracer, is drastically increasing with increasing distance downwind of the plume. This is indicative of interference from some other source(s) of $SO_2$. This same source(s) might also be a source of high ozone; for example, most urban "plumes" have both high ozone and high $SO_2$. Superhighways (such as I-95, Fig. 4.7) could also produce both high ozone and high $SO_2$. This suggests the possibility that a situation similar to that described above for the Wilkes Power Plant may have occurred at Morgantown.

In light of the above discussion, the conclusion of Davis et al. that ozone was produced in high concentrations in the power plant plume at Morgantown is questionable.
Fig. 4.8 Profiles of SO₂ and ozone concentrations across the plume from the Morgantown Power Plant. (From Davis et al., 1974)
CHAPTER 5

SUMMARY AND CONCLUSIONS

This study has focused on two major problems with respect to power plant plumes, namely, gas-to-particle conversion and the nitrogen oxides-ozone chemistry. With respect to particle formation, the preliminary results of this study suggest that, under the condition of our measurements, the conversion rate of $SO_2$ to aerosol is relatively slow ($\leq 0.34\%$ per hour). Furthermore, it has been shown that aerosol coagulation due to turbulence must be allowed for in determining the rate of gas-to-particle conversion in plumes and a theoretical model has been developed which allows this to be done. Considerably more sophisticated instrumentation than was available for this study must be used if the exact aerosol forming mechanism is to be identified. Such instrumentation is currently being employed by the Cloud and Aerosol Research Group in their continuing studies of power plant plumes; the results of these studies will be described in a later report.

The analysis of nitrogen oxides-ozone chemistry in power plant plumes suggests that the plume chemistry is commonly diffusive controlled and that the rate of conversion of NO to $NO_2$ is generally quite slow. Consequently, ozone is probably not formed until the plume has been diluted to almost background concentration levels. Ozone production was never observed in the power plant plumes investigated in this study and the few observations by other workers of ozone production in power plant plumes seem dubious.
To obtain more definitive information on the question of ozone formation in power plant plumes, field studies should be carried out over a wide range of meteorological as well as ambient chemical conditions. The important question of how often power plant plumes are diffusive controlled could then be answered and perhaps even a predictive methodology developed.
REFERENCES


APPENDIX A

ANALYSIS OF VARIANCES

A.1 General Equation

The determination of all variances and standard errors in this study was done using the following general equation (Davies, 1958):

\[
V(\Psi) = \left( \frac{\partial \Psi}{\partial x_1} \right)^2 V(x_1) + \left( \frac{\partial \Psi}{\partial x_2} \right)^2 V(x_2) + \ldots \\
+ \left( \frac{\partial \Psi}{\partial x_1} \right) \left( \frac{\partial \Psi}{\partial x_2} \right) \text{cov}(x_1, x_2) + \left( \frac{\partial \Psi}{\partial x_1} \right) \left( \frac{\partial \Psi}{\partial x_3} \right) \text{cov}(x_1, x_3) + \ldots \\
+ \text{higher differential terms},
\]

where \( \Psi \) is the function whose variance is to be determined, and \( x_i \) are independent variables of \( \Psi \). The higher differential terms were considered negligible throughout this report.

A.2 Errors in Cross-Sections

The relative change in the cross-sectional area of a plume is an important parameter in this study. It was computed assuming the SO\(_2\) (or NO\(_x\)) current to be constant in the plume. If the measured currents at two successive ranges were not in fact equal, the second cross-sectional area was adjusted until the currents at the two ranges were equal. Thus the first cross-sectional area is considered to be exact, and all of the relative variance between the two cross sections is combined in the second cross-sectional area. Hence,

\[\text{See page 19.}\]
\[ I_1 = \overline{C}_1 A_1 \]

and,

\[ I_2 = \overline{C}_2 A_2 \]

therefore,

\[ A_2 = \frac{\overline{C}_1}{\overline{C}_2} A_1, \quad (A.2) \]

where the \( \overline{C}_1 \)'s are mean cross-sectional concentrations, the \( A_1 \)'s are cross-sectional areas, and the \( I_1 \)'s are currents divided by wind velocity (assumed constant). If \( V(A_1) = 0 \), then from (A.1),

\[ V(A_2) = A_1^2 V\left(\frac{\overline{C}_1}{\overline{C}_2}\right) \quad (A.3) \]

and, also from (A.1),

\[ V\left(\frac{\overline{C}_1}{\overline{C}_2}\right) = \frac{1}{(\overline{C}_2)^2} \{ V(\overline{C}_1) + \left(\frac{\overline{C}_1}{\overline{C}_2}\right)^2 V(\overline{C}_2) - \left(\frac{\overline{C}_1}{\overline{C}_2}\right) \sigma_{\overline{C}_1} \sigma_{\overline{C}_2} \} \quad (A.4) \]

where the \( \sigma_{\overline{C}_1} \)'s are the standard deviations of the mean cross-sectional concentrations and it has been assumed that \( \overline{C}_1 \) and \( \overline{C}_2 \) have a correlation coefficient, \( r_{x,y} \), equal to unity. This assumption appears reasonable and was made to simplify the calculations. In any case, the third term on the right of Eqn. (A.4) is typically only 25% of the first two. Typical values for \( V(\overline{C}_1/\overline{C}_2) \) are 0.01-0.02.

It should be noted that \( V(\overline{C}_1) \) and \( V(\overline{C}_2) \) are variances of mean concentrations and are therefore defined as:

\[ V(\overline{C}_1) = \sigma_{\overline{C}_1}^2/N_1 \quad (A.5) \]

where \( \sigma_{\overline{C}_1} \) is the standard deviation determined from the cross sections and \( N_1 \) is the number of statistically independent observations. In order to estimate \( N_1 \), which will in general be less than the number of observations, a lag correlation analysis was performed on the real concentration
points measured during a traverse of a plume. By real points is meant points further apart than the spatial resolution of the aircraft instrumentation (~300m). The analysis indicated that the number of statistically independent observations per traverse was one less than the number of real points per traverse. This was taken into account in the calculation.

A.3 Errors in the Diffusion Parameter $\alpha$

From (A.1),

$$V(\alpha) = \left( \frac{\partial \alpha}{\partial A} \right)^2 V(A_2) \text{ (} V(A_1) = 0, \sigma(A_1) = 0 \text{).}$$

(A.6)

Rather than calculating the errors in all of the derived $\alpha$'s, a conservative estimate of the error for all cases was determined by analyzing the error (synonymous with standard deviation in this study) for the flight of 6/16/75 for which turbulence was relatively high. The derived error was 0.50, as quoted in the text.

A.4 Errors in Aerosol Currents

The errors in the aerosol current parameters, $I_1$, are related to the errors in the mean concentrations of aerosols determined from the cross sections, and to the errors in the cross-sectional areas. Since the ratio of successive aerosol cross-sectional areas is equated with the corresponding ratio of $SO_2$ cross-sectional areas to determine a corrected current parameter, one can assume $V(A_1) = 0$, and since

$$A^A_2 \approx A^A_1 \frac{A^{SO_2}_2}{A^{SO_2}_1},$$

it is clear that:
Hence, from (A.1),
\[
v(I_i) = A_1^2 V(C_1) + C_1^2 V(A_1) + A_1 C_1 \text{cov}(A_1, C_1). \tag{A.8}
\]

In order to simplify the calculations, the reasonable assumption that
\[
\text{cov}(A_1, C_1) = r_{A_1 C_1} \sigma_{A_1} \sigma_{C_1} \approx -\sigma_{A_1} \sigma_{C_1}
\]
was made. This covariance term contributes at most 20% to \(V(I_i)\). Values of \(V(I_i)\) were typically \(10^{16} - 10^{18} \text{ (ppbm)}^2\).

A.5 Errors in \(\text{NO}_2/\text{NO}\) and the Conversion Rates of \(\text{NO}\) to \(\text{NO}_2\)

Letting \(\text{NO}_2/\text{NO} = \psi\) and the subscripts \(i\) and \(f\) refer to the initial and final ranges, respectively, from (A.1),
\[
v(\psi) = \frac{V(\text{NO}_2)}{(\text{NO})^2} + \frac{(\text{NO}_2)^2}{(\text{NO})^4} V(\text{NO}) - \frac{(\text{NO}_2)}{(\text{NO})^3} \text{cov}(\text{NO}_2, \text{NO}).
\]

Since, from the data \(V(\text{NO}_2, \text{NO}) \approx 1\),
\[
\text{cov}(\text{NO}_2, \text{NO}) \approx \sigma_{\text{NO}_2} \sigma_{\text{NO}}.
\]

Therefore,
\[
v(\psi) = \frac{1}{(\text{NO})^2} \{V(\text{NO}_2) + \left(\frac{\text{NO}_2}{\text{NO}}\right)^2 V(\text{NO}) - \left(\frac{\text{NO}_2}{\text{NO}}\right) \sigma_{\text{NO}_2} \sigma_{\text{NO}}\}. \tag{A.9}
\]

The values for \(\sigma_{\text{NO}_2}, \sigma_{\text{NO}}\), and hence \(V(\text{NO}_2)\) and \(V(\text{NO})\) can be determined from the concentration traces. The values of \(\sigma_{\text{NO}_2}\) and \(\sigma_{\text{NO}}\) visually determined for any particular traverse were equal and of the order of 10 ppb. Values of \(V(\psi)\) range from 0.00005 to 0.5. The third term on the right of A.9 is typically 30% of this value. Also,
\[ \beta = \frac{\psi_f}{1 + \psi_f} \]  

(A.10)

where \( \beta \) is the functional conversion of NO to NO\(_2\) as stated in the text.

Hence, from (A.1) and (A.10)

\[ V(\beta) = \frac{V(\psi_f)}{(1 + \psi_f)^2} + \frac{1}{(1 + \psi_f)} V(\psi_f). \]  

(A.11)

This assumes that cov(\( \psi_f \), \( \psi_f \)) = 0, which appears justified by the data.

This procedure can be applied to determine the errors in the conversion rates of NO to NO\(_2\) for both the centerline and plume average values.

Values of V(\( \beta \)) range from .0008 to .081.

A.6 Errors in the Value of \( (\text{NO}_2)k_a/k_3(\text{NO})(0_3) \)

The general procedure for estimating the variance of this parameter is exactly the same as for the other parameters in this study. The only point which must be clarified is the assigning of an error to \( k_a \) and \( k_3 \).

These constants are determined from the measured UV and temperature data, respectively. While the relationship between temperature and \( k_3 \) has been experimentally determined, the relationship between total UV radiation and \( k_a \) involves several assumptions in a largely theoretical derivation (see Leighton, 1961). The magnitude of the error in \( k_a \) is therefore difficult to estimate and a standard deviation of 10% was arbitrarily attributed to both \( k_a \) and \( k_3 \).
APPENDIX B

INSTRUMENT RESPONSE CORRECTION

B.1 The Correction Factor

Because the response times of the instruments used in this study are in many cases comparable to the plume traverse times, the actual spatial profile of a species is distorted in a manner very similar to that of perceiving a changing voltage signal through the distortion of an excessive cable capacitance. A first derivative correction for this effect would be of the form:

\[ e_i = e_0 + \lambda \frac{de_0}{d\theta} \]  \hspace{1cm} (B.1)

where \( e_i \) is the actual signal, \( e_0 \) is the perceived signal, \( \theta \) is a phase angle, and \( \lambda \) is a correction coefficient dependent on the instrument response. In this study it is assumed that the actual signal is roughly of the form of a cosine bell, that is,

\[ e_i = 1 + \cos \theta \quad \pi \leq \theta \leq \pi. \]  \hspace{1cm} (B.2)

The perceived signal will then be of the form (Harrison, 1976)

\[ e_0 = 1 + \frac{1}{1+\lambda^2} \cos \theta + \frac{\lambda}{1+\lambda^2} \sin \theta \]  \hspace{1cm} (B.3)

The value of \( \lambda \) appropriate for this study is:

\[ \lambda = \frac{\bar{U} \pi \pi}{\sigma} \]  \hspace{1cm} (B.4)
where $\bar{U}$ is the aircraft speed, $\tau$ is the $e^{-1}$ decay time of the instruments and $\sigma$ is the measured plume radius.

Because the distortions in the plume area and plume concentrations cancel out, the plume current need not be corrected. However, since the plume cross-sections themselves are used in the determination of the diffusion parameter $\alpha$, this must be corrected. This correction can be determined by considering the plume radii as standard deviations of the plume distribution functions for the perceived and real plumes given by equations (B.3) and (B.2), respectively. The correction factor for the plume areas will then be of the form $\sigma_i^2/\sigma_0^2$ where

$$\sigma_i^2 = \int_{-\pi}^{\pi} \theta^2 (1 + \cos \theta) d\theta / \int_{-\pi}^{\pi} (1 + \cos \theta) d\theta$$

(B.5)

and

$$\sigma_0^2 = \frac{\int_{-\pi}^{\pi} \theta^2 \left(1 + \frac{1}{1+\lambda^2} \cos \theta + \frac{\lambda}{1+\lambda^2} \sin \theta\right) d\theta}{\int_{-\pi}^{\pi} (1 + \frac{1}{1+\lambda^2} \cos \theta + \frac{\lambda}{1+\lambda^2} \sin \theta) d\theta}$$

(B.6)

Performing the indicated integrations yields,

$$\frac{\sigma_i^2}{\sigma_0^2} = \frac{1.3(1+\lambda^2)}{3.3(1+\lambda^2)-2}$$

(B.7)

It remains to determine the manner in which this correction should be applied to the parameters dependent on the measured plume cross-sectional areas. (The value of $\sigma_i^2/\sigma_0^2$ from Eqn. (B.7) is the value given to $\gamma_i$ of Eqn. (B.11) and, with the appropriate change from $\lambda_{SO_2}$ to $\lambda_{aerosol}$, to the parameter $\phi$ of Eqn. (B.13))
B.2 Sulfur Dioxide Cross sections and the Diffusion Parameter

The ratio of cross sections at successive ranges was to be determined. The assumption was made that the currents and thus the current parameters, \( I \), at successive ranges were equal, that is,

\[
I_{1P} = I_{2P}
\]

where the subscript \( P \) stands for perceived (the subscript \( R \) will stand for real). Therefore,

\[
C_{1P}A_{1P} = C_{2P}A_{2P}.
\]  
(B.8)

Because the currents at successive ranges were not exactly equal, the area \( A_{2P} \) was adjusted to make them so, that is,

\[
C_{1P}A_{1P} \neq C_{2P}A_{2P}
\]

but

\[
C_{1P}A_{1P} = C_{2P}A_{2P}K
\]

where

\[
K = \frac{C_{1P}A_{1P}}{C_{2P}A_{2P}}.
\]  
(B.9)

The ratio of cross sections, \( \beta_p \), was then given as:

\[
\beta_p = \frac{A_{1P}}{A_{2P}K} = \frac{A_{1P}}{A_{2P}} \cdot \frac{C_{2P}}{C_{1P}} \cdot \frac{A_{2P}}{A_{1P}} = \frac{C_{2P}}{C_{1P}}.
\]  
(B.10)

This value of \( \beta \) was used in the determination of the diffusion parameter, \( \alpha \), as indicated in the text. The question is, if one corrects the \( C \)'s and \( A \)'s for the instrument response time, how will this change \( \beta \)?

One can represent the real concentrations and cross sections in terms of the perceived ones by:
\[ C_{iR} = \gamma_i^{-1} C_{iP} \]  
\[ A_{iR} = \gamma_i A_{iP} \]  

Substituting the relations (B.11) into (B.10) yields:
\[ \beta_R = \frac{\gamma_2^{-1} C_{2P}}{\gamma_1^{-1} C_{1P}} = \frac{\gamma_1}{\gamma_2} \beta_p. \]  
(B.12)

Thus the value of \( \beta_p \) must be corrected by the factor \( \gamma_1/\gamma_2 \) to give the true value \( \beta_R \).

B.3 Aerosol Currents

Aerosol production was analyzed by considering the current divergence between two ranges:
\[ I_{2P}^A - I_{1P}^A = C_{2P}^A A_{2P}^A - C_{1P}^A A_{1P}^A. \]  
(B.13)

Since,
\[ I_R^A = \phi^{-1} C_{P}^A \phi A_{P} = C_{P}^A A_{P} = I_P^A, \]
(\( \phi \) is the aerosol analog of \( \gamma \) in Eqn. B.11) if no correction were made to any of the C's or A's in (B.13), the effect of instrument response time would cancel out. However, while an assumption of constant current could not be made, it was assumed that the aerosol cross-sectional area ratios should be the same as the corresponding \( \text{SO}_2 \) cross-sectional area ratios, that is:
\[ \frac{A_{1P}^A}{A_{2P}^A} = \beta_p. \]

Because,
\[ \frac{A_{1P}^A}{A_{2P}^A} \neq \beta_p, \]
it was necessary to make another correction, this time to $A_{2P}^A$, namely,

$$\frac{A_{1P}^A}{A_{2P}^A D} = \beta_p$$  \hspace{1cm} (B.14)

where

$$D_p = \frac{1}{\beta_p A_{2P}^A}.$$  

Substituting (B.14) into (B.13),

$$I_{2P}^A - I_{1P}^A = C_q^{A_{2P}^A A_{2P}^A} - C_{1P}^{A_{1P}^A A_{1P}^A}.$$  \hspace{1cm} (B.15)

If one now corrects the values of the aerosol cross sections for instrument response and further substitutes $\beta_R$ for $\beta_p$ in (B.14), then

$$D_R = \frac{1}{\beta_R^A A_{2P}^A} = \left(\frac{\gamma_2^{A_2} \phi_1}{\gamma_1^{A_1} \phi_2}\right) \frac{1}{\beta_p^A} \frac{A_{1P}^A}{A_{2P}^A}$$

$$= \left(\frac{\gamma_2^{A_2} \phi_1}{\gamma_1^{A_1} \phi_2}\right) D_p.$$  \hspace{1cm} (B.16)

Substituting this into (B.15) gives the corrected value for the aerosol current divergence, namely:

$$I_{2P}^A - I_{1P}^A = C_q^{A_{2P}^A A_{2P}^A} \left(\frac{\gamma_2^{A_2} \phi_1}{\gamma_1^{A_1} \phi_2}\right) D - C_{1P}^{A_{1P}^A A_{1P}^A}.$$  \hspace{1cm} (B.17)

The corrected and uncorrected values of the current parameters and the diffusion parameters used in this study are shown in Table (B.1).

With the exception of the current parameter of flight 10/31/75, the corrections for instrument response are within the calculated uncertainty of the parameters $\alpha$ and $I_i$. Therefore, only this exceptional case was corrected in the text.
Table B.1

Corrections for Instrument Response to $\alpha$ and $I_{2P}\Delta$

<table>
<thead>
<tr>
<th>Date</th>
<th>Range Interval (km)</th>
<th>$\alpha$</th>
<th>$\alpha$ (corrected)</th>
<th>$I_{2P}\Delta$ ($m^2 cm^{-3}$)</th>
<th>$I_{2P}\Delta \left[ \frac{\gamma_2 \phi_1}{\gamma_1 \phi_2} \right]$ ($m^2 cm^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/13/75</td>
<td>1.6 - 4.8</td>
<td>0.4</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/20/75</td>
<td>4.8 - 9.6</td>
<td>1.8</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/24/75</td>
<td>0.8 - 6.4</td>
<td>0.6</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/26/75</td>
<td>1.6 - 4.8</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6/16/75</td>
<td>0.8 - 1.6</td>
<td>2.0</td>
<td>2.0</td>
<td>(8.2±1)$\times 10^9$</td>
<td>(8.2±1)$\times 10^9$</td>
</tr>
<tr>
<td></td>
<td>1.6 - 4.8</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7/29/75</td>
<td>0.8 - 1.6</td>
<td>0.3</td>
<td>0.3</td>
<td>(5.0±0.8)$\times 10^9$</td>
<td>(5.2±0.8)$\times 10^9$</td>
</tr>
<tr>
<td>8/20/75</td>
<td>0.2 - 3.2</td>
<td>0.8</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.2 - 6.4</td>
<td>1.4</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/16/75</td>
<td>17 - 30</td>
<td>0.9</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 - 45</td>
<td>1.8</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/30/75</td>
<td>0.8 - 8.0</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.0 - 18</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18 - 22</td>
<td>2.7</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/31/75</td>
<td>2.4 - 5.6</td>
<td>0.4</td>
<td>0.5</td>
<td>(3.4±0.1)$\times 10^9$</td>
<td>(3.2±0.1)$\times 10^9$</td>
</tr>
<tr>
<td></td>
<td>5.6 - 12</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12 - 21</td>
<td>0.8</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/5/75</td>
<td>0.8 - 1.6</td>
<td>1.3</td>
<td>1.3</td>
<td>(8.7±0.7)$\times 10^9$</td>
<td>(8.3±0.7)$\times 10^9$</td>
</tr>
</tbody>
</table>

†Uncertainty in $\alpha$ is ± 0.5
APPENDIX C

SOLUTION TO EQN. (4.12)

Restating Eqn. (4.12) from § 4.4.2 of the text as:

\[
\frac{dn}{dt} = K_0 n^2 - \frac{31nV}{3t} (n - n_A) + S.
\]

Substituting Eqn. (4.10) into the above equation gives,

\[
\frac{dn}{dt} = -K_0 n^2 - \frac{\alpha}{t} (n - n_A) + S \tag{C.1}
\]

which is a form of Riccati's equation. Thus let,

\[
n = \frac{u'}{K_0 u}, \text{ where } u' = du/dt, \tag{C.2}
\]

then (C.1) becomes,

\[
u'' + \frac{\alpha}{t} u' - \left(\frac{\alpha n_A + S}{t}\right) K_0 u = 0 \tag{6.3}
\]

and,

\[
t^2 u'' + \alpha t u' - (\alpha n_A t + SK_0 t^2) u = 0. \tag{C.4}
\]

(C.3) does not have an analytic solution. However, if \( S = 0 \), this equation is a form of Bessel's equation with solutions:

\[
u = t^{(1-\alpha)/2} \left\{ C_1 I_{1-\alpha}(\sqrt{\alpha n_A K_0} t^{1/2}) + C_2 K_{1-\alpha}(\sqrt{\alpha n_A K_0} t^{1/2}) \right\} \tag{C.5}
\]

Substitution of Eqn. (C.5) into Eqn. (C.2) results in a function for \( n \) which is not particularly easy to visualize, and does not take into account \( S \) in any case. However, if \( S \) is retained, Eqn. (C.3) can be transformed into:
\[ W'' + \left( -\alpha \frac{n_A^0}{t} - SK_0 \frac{\alpha^2}{4t^2} + \frac{\alpha}{2t} \right) W = 0 \]  \hspace{1cm} (C.6)

where \( W = ut^{\alpha/2} \). While Eqn. (C.6) does not have even an asymptotic solution, a review of the cases shown in Table 3.3 indicates that \( n_A \) is at least half an order of magnitude less than \( n \) and that \( n_A \) can be considered negligible compared to \( n \) in Eqn. (C.1). Therefore,

\[ W'' + (-SK_0 + \frac{2\alpha - \alpha^2}{4t^2}) W = 0 \]  \hspace{1cm} (C.7)

which looks ideal for an asymptotic series solution. As \( t \to \infty \) this equation reduces to:

\[ W'' + SK_0 W = 0 \]  \hspace{1cm} (C.8)

and therefore,

\[ W = e^{\sqrt{SK_0} t} \]  \hspace{1cm} (C.9)

This suggests that Eqn. (C.7) has a solution of the form:

\[ W \approx e^{\sqrt{SK_0} t} \sum_{n=0}^{\infty} a_n t^{-n} \]  \hspace{1cm} (C.10)

Substitution of this series into Eqn. (C.7) and solving for the coefficients yields,

\[ a_{n+1} = \left\{ (n[n+1] + \frac{2\alpha - \alpha^2}{4})/2(n+1)\sqrt{SK_0} \right\} a_n \]  \hspace{1cm} (C.11)

Setting \( a_0 = 1 \),

\[ W = e^{\sqrt{SK_0} t} \left\{ 1 + \frac{(2\alpha - \alpha^2)}{8\sqrt{SK_0}} t^{-1} + \ldots \right\} \]  \hspace{1cm} (C.12)

Since \( \alpha \) varies between 0 and 2 for the cases of interest (implying that \( 2\alpha - \alpha^2 \leq 1 \)), the first order and greater terms in Eqn. (C.12) may be
neglected if \( t \approx \frac{1}{\sqrt{SK_0}} \). The reasonableness of this can be determined after the regression values of \( S \) and \( K_0 \) are found. For \( t > \frac{1}{\sqrt{SK_0}} \):

\[
W = e^{\sqrt{SK_0} t} \quad (C.13)
\]

and,

\[
U = t^{-\alpha/2} e^{\sqrt{SK_0} t} \quad (C.14)
\]

Substituting Eqn. (C.14) into Eqn. (C.2),

\[
n = \frac{u'}{uK_0} = -\frac{\alpha}{2K_0 t} + \frac{\sqrt{SK_0}}{K_0}
\]

thus,

\[
n = \sqrt{S/K_0} - \frac{\alpha}{2K_0 t} \quad (C.15)
\]

The regression values for \( S \) and \( K_0 \) were found to be \( S \approx 100 \text{ cm}^{-3} \text{s}^{-1} \) and \( K_0 \approx 3 \times 10^{-7} \text{ cm}^{3} \text{s}^{-1} \) implying \( 1/\sqrt{SK_0} = 180 \text{s} \). Clearly this is reason- able for data at \( t \geq 180 \text{s} \).
APPENDIX D

This appendix contains all of the cross sections used in this study with the exception of the two already shown in the text as examples. The cross sections are vertical cross sections through the plume. The SO$_2$ cross sections have concentrations isopleths in ppb and the aerosol cross sections have concentration isopleths in particles per cm$^3$. The cross sections are uncorrected for instrument response.
Fig. D.1 SO$_2$ plume cross section at Centralia on 3/13/75. The range is 1.6 km.
Fig. D.2  $SO_2$ plume cross section at Centralia on 3/13/75. The range is 4.8 km.
Fig. D.3 $SO_2$ plume cross section at Centralia on 3/20/75. The range is 4.8 km.
Fig. D.4 $SO_2$ plume cross section at Centralia on 3/20/75. The range is 9.6 km.
Fig. D.5 SO$_2$ plume cross section at Centralia on 3/24/75. The range is 0.8 km.
Fig. D.6  \( \text{SO}_2 \) plume cross section at Centralia on 3/24/75. The range is 6.4 km.
Fig. D.7 SO\textsubscript{2} plume cross section at Centralia on 3/26/75. The range is 1.6 km.
Fig. D.8 $\text{SO}_2$ plume cross section at Centralia on 3/26/75. The range is 4.8 km.
Fig. D.9  $SO_2$ plume cross section at Centralia on 6/16/75. The range is 1.6 km.
Fig. D.10 SO₂ plume cross section at Centralia on 6/16/75. The range is 4.8 km.
Fig. D.11  $\text{SO}_2$ plume cross section at Centralia on 7/29/75. The range is 0.8 km.
Fig. D.12 $\text{SO}_2$ plume cross section at Centralia on 7/29/75. The range is 1.6 km.
Fig. D.13 $\text{SO}_2$ plume cross section at Centralia on 8/20/75. The range is 0.2 km.
Fig. D.14 SO$_2$ plume cross section at Centralia on 8/20/75. The range is 3.2 km.
Fig. D.15 $\text{SO}_2$ plume cross section at Centralia on 8/20/75. The range is 6.4 km.
Fig. D.16 SO$_2$ plume cross section at Farmington on 10/16/75. The range is 17 km.
Fig. D.17 SO$_2$ plume cross sections at Farmington on 10/16/75. The range is 30 km.
Fig. D.18 SO$_2$ plume cross section at Farmington on 10/16/75. The range is 45 km.
Fig. D.19  SO$_2$ plume cross section at Centralia on 10/30/75. The range is 0.8 km.
Fig. D.20 $SO_2$ plume cross section at Centralia on 10/30/75. The range is 8.0 km.
Fig. D.21 $SO_2$ plume cross section at Centralia on 10/30/75. The range is 18 km.
Fig. D.22  $SO_2$ plume cross section at Centralia on 10/30/75. The range is 22 km.
Fig. D.23 $SO_2$ plume cross section at Centralia on 10/31/75. The range is 2.4 km.
Fig. D.24  \( \text{SO}_2 \) plume cross section at Centralia on 10/31/75. The range is 5.6 km.
Fig. D.25 $SO_2$ plume cross section at Centralia on 10/31/75. The range is 12 km.
Fig. D.26 \( \text{SO}_2 \) plume cross section at Centralia on 10/31/75. The range is 21 km.
Fig. D.27 $\text{SO}_2$ plume cross section at Centralia on 11/5-75. The range is 0.8 km.
Fig. D.28  $\text{SO}_2$ plume cross section at Centralia on 11/5/75. The range is 1.6 km.
Fig. D.29 Aerosol plume cross section at Centralia on 6/16/75. The range is 1.6 km.
Fig. D.30 Aerosol plume cross section at Centralia on 7/29/75. The range is 0.8 km.
Fig. D.31 Aerosol plume cross section at Centralia on 7/29/75. The range is 1.6 km.
Fig. D.32 Aerosol plume cross section at Centralia on 10/31/75. The range is 2.4 km.
Fig. D.33 Aerosol plume cross section at Centralia on 10/31/75. The range is 5.6 km.
Fig. D.34 Aerosol plume cross section at Centralia on 11/5/75. The range is 0.8 km.
Fig. D.35 Aerosol plume cross section at Centralia on 11/5/75. The range is 1.6 km.