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**USES, LIMITATIONS AND TECHNICAL
BASIS OF PROCEDURES
FOR QUANTIFYING RELATIONSHIPS
BETWEEN PHOTOCHEMICAL OXIDANTS
AND PRECURSORS**

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Executive Summary

The purpose of this document is to describe the technical basis, uses and limitations of several approaches for relating photochemical oxidant (expressed as ozone) to organic compounds and oxides of nitrogen. This document is not intended as a statement of EPA policy concerning which method to use in relating ozone to precursors. By reporting the nature and present status of various analytical techniques, it is hoped that the document will prove useful to agencies and/or individuals wanting (1) to estimate the amount of precursor controls needed to attain the National Ambient Air Quality Standard (NAAQS) for photochemical oxidants ($160\mu\text{g}/\text{m}^3$ hourly average concentration not to be exceeded more than once per year), and (2) to estimate the reduction in ozone concentrations accompanying specified reductions in precursors. Some of the methods described also provide additional measures of improvement in ambient air quality which may accompany precursor controls. These additional capabilities are identified where applicable.

Ambient levels of ozone reflect a complex interaction of locally emitted organic pollutants and oxides of nitrogen with transported ozone and precursors within the framework provided by prevailing meteorological conditions. Conceptually, the role of ambient oxides of nitrogen (NO_x) is to provide the basic means whereby ozone is formed. Ozone results from a series of reactions initiated by the irradiation of nitrogen dioxide by sunlight. In the absence of appreciable amounts of organic compounds, resulting levels of ozone remain low as the result of a chemical equilibrium which is established among ozone, nitric oxide (NO) and nitrogen dioxide (NO_2). Presence of appreciable amounts of organic

pollutants influences this equilibrium so that higher concentrations of ozone prevail. The dependence of ozone concentrations on organic and NO_x precursors can be dominated by meteorological conditions. Sunlight intensity and temperature influence chemical reaction rates and, therefore, the equilibrium among reactants. Mixing height and its diurnal variation determine the extent to which transported ozone and precursors are likely to affect local ozone concentrations. The interaction of locally emitted organic and NO_x precursors with transported pollutants is also influenced by prevailing wind speeds and trajectories.

Given the complexity of the photochemical oxidant problem, it is clear that, in order to be tractable, analytical techniques must incorporate a number of simplifications. The accuracy of methods incorporating such simplifications would be best determined in verification studies which compare estimates against data observed in an urban area which is of interest. Unfortunately, there are few locations in which the data base is sufficient for a comprehensive verification of analytical methods relating oxidant to precursors. A major effort has begun to utilize the data collected in the Regional Air Pollution Study (RAPS) conducted in St. Louis for verification purposes. Still barring the availability of appropriate data for comprehensive verifications, it is possible to estimate the range of uncertainty associated with estimates if the accuracy with which certain key input variables are measured is known. The results of such sensitivity studies suggest that the accuracy of predictions obtained using a photochemical dispersion model is likely to be no worse than $\pm 50\%$ of the actual ozone concentrations. The level of uncertainty associated with the most detailed simple approach described in this report (i.e., the Empirical Kinetic Modeling Approach) is probably no worse than $\pm 70\%$. Because of the manner in which proportional rollback

and statistical approaches are used or derived, it is not possible to speculate about their absolute accuracy. Although the uncertainty bands associated with model predictions of ozone concentrations could under some circumstances be high, there are indications that estimates of precursor reductions needed to reduce oxidant levels from present levels to the NAAQS can be made with considerably greater confidence. Sensitivity studies suggest that the error bands associated with such estimates may be in the order of $\pm 25\%$, with most of the potential error arising from uncertainty about prevailing hydrocarbon/ NO_x ratios. Uncertainty associated with methods which take explicit account of accurately known hydrocarbon/ NO_x ratios may be in the order of $\pm 10\%$.

Four analytical approaches are discussed: photochemical dispersion models, the Empirical Kinetic Modeling Approach (EKMA), linear rollback and application of statistical models. Since EKMA has not been described extensively elsewhere, it is treated in greater detail in this report than are the other approaches. Because of some fundamental questions about the nature of the rural oxidant problem, all the approaches described in this report are only useful in addressing the urban oxidant problem.

Photochemical dispersion models have the greatest potential for evaluating the effectiveness of oxidant control strategies. This potential arises primarily from the spatial and temporal resolution possible with such models and from the ability to relate emissions directly to ambient ozone concentrations as a result of chemistry and atmospheric dispersion. However, data requirements associated with models may be prohibitive in some cases. Simple approaches may therefore be of use.

The Empirical Kinetic Modeling Approach (EKMA) makes use of a kinetics model to express maximum afternoon ozone concentration as a function of morning ambient levels of nonmethane hydrocarbons (NMHC) and NO_x . EKMA is empirical, because it requires the use of observed second high hourly ozone concentrations and morning NMHC/ NO_x ratios to estimate control requirements. The EKMA reflects an effort which has been underway since December 1975 to develop a substitute for the Appendix J approach.

Linear rollback, which is even less data-intensive than EKMA, may also be a possible alternative for estimating bounds on control requirements for organic precursors. However, rollback's failure to consider the dependence of NMHC-ozone relationships on the prevailing NMHC/ NO_x ratio during the base period limits applicability of rollback to a first order approximation.

The fourth approach is really a class of approaches which has been labeled "statistical procedures." Several key features for such procedures are identified. Any one statistical relationship is seen as being site-specific. Further, the use of statistical procedures is most appropriately limited to considering moderate changes from the base control state, since imposition of drastic changes could appreciably modify the functional relationship derived from the base period data.

Although the previously described ozone/precursor relationships can be applied in large urban areas, long range transport still may significantly alter control estimates in some cases. Provided transport can be measured, it can be readily incorporated into photochemical dispersion models and into EKMA. Transport is composed of two components, a natural background and a manmade contribution. Natural background of ozone appears to be about .04 ppm, primarily from slow diffusion from the stratosphere. However, the impact of natural ozone is considerably less in urban areas due to scavenging. The impacts of naturally emitted

organics and NO_x on urban ozone are probably much smaller, if not negligible. A review of a rather limited available data base implies that the principal impact of transport on the urban ozone problem is likely to arise from unscavenged ozone which is trapped aloft overnight as a result of surface-based nocturnal inversions. During the ensuing daylight hours, the atmosphere becomes well mixed near the surface, and ozone aloft reacts with locally generated precursors. This process has been simulated using the chemical kinetics model employed in deriving the EKMA together with several scenarios concerning the rate at which ozone from aloft is mixed in the surface layer and with differing levels of locally generated precursors. The results suggest that ozone transported aloft may be from 20-70% additive in urban areas. For example, if transported ozone were .10 ppm and were 40% additive, the impact on observed downwind maximum ozone would be .04 ppm. In order for control requirements to be equitable, recognition should be allowed for reduced levels of transported ozone from upwind cities having control programs when estimating local control requirements in downwind cities. Procedures for including transport considerations in various analytical methods are presented in this paper.

It is recognized that the data and capabilities for implementing procedures suggested for considering transport may not always be sufficient. An examination of the impact of ignoring transport and natural background, however, indicates that the calculated differences in precursor control requirements may frequently be of little practical significance. An exception to this generalization may occur in the case of a moderately sized city which is downwind from a major city and is observing ambient levels of ozone which are less than about twice the

NAAQS. In such a case, simulations suggest that estimated control requirements may be higher than necessary if transport and background are ignored. A second problem may result from using an approach, such as proportional rollback, which suggests a large reduction in ozone may be forthcoming from initial controls. Significant transport may serve to diminish any actual improvement in air quality resulting from local controls. Therefore, a risk in relying on any such approach is that questions may arise about whether controlling organic emissions will ever be effective in reducing ambient ozone. Many such questions might be the result of using a very simple model which fails to consider several potentially important factors contributing to the urban ozone problem.

Summarizing, a great deal of understanding of the urban photochemical oxidant problem has been gained over the past several years, and though subject to some error and uncertainty, the methods described in this document provide means for making useful approximations in attempts to confront the problem.

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1.0 Background

1.1 Introduction

In the past, Appendix J to Title 40, Part 51 of the Code of Federal Regulations¹ has been used to estimate the degree of reduction in organic emissions needed to achieve the primary National Ambient Air Quality Standard (NAAQS) for photochemical oxidants ($160 \mu\text{g}/\text{m}^3 \approx .08 \text{ ppm}$ 1-hour average not to be exceeded more than once per year). Appendix J was derived from envelope curves enclosing points depicting 6-9 a.m. ambient total and non-methane hydrocarbon concentrations and corresponding daily maximum ambient oxidant concentrations measured at several CAMP sites and in Los Angeles during the late 1960's.² The Appendix J approach has been criticized for a variety of reasons. As a result of acknowledged shortcomings in the envelope curve approach as described in Appendix J, an EPA working group was formed in 1975 to investigate the viability of alternative approaches. Suggestions made as a result of working group sessions have been reviewed periodically by a group of experts outside of EPA. The conclusion reached as a result of these efforts is that it is not possible to recommend a single approach for all applications. The variety of applications, complexity of individual situations, differences in data availability and resources all preclude use of a single procedure nationwide. Therefore, this report describes the technical basis, uses, advantages and disadvantages of several currently available approaches for relating ozone to organic compounds and oxides of nitrogen precursors. Four approaches are described: photochemical dispersion models, the Empirical Kinetic Modeling Approach (EKMA), linear rollback and statistical models. Because the EKMA has evolved largely through the efforts of members of the EPA working group and because it has not been as extensively discussed elsewhere, it is described in greater detail than the other approaches.

1.2 Applicability of Available Procedures

The procedures described in this document address the ozone problem as it exists within and immediately downwind from large urban areas. There are several reasons for limiting the applicability to urban areas. First, although the ozone problem is better understood than it was at the time Appendix J was conceived, certain aspects of the problem are still not well enough understood to allow reliable quantifiable estimates to be made for all situations. For example, present understanding of chemistry occurring within portions of an urban plume trapped aloft by a nighttime radiative inversion does not permit adequate quantitative estimates. The role of less reactive precursors and ozone transported aloft versus that of low concentrations of reactive precursors emitted locally in the synthesis of maximum levels of ozone observed the next afternoon is also difficult to quantify. Thus, situations in which transported ozone and/or precursors are clearly dominant may not be well described by existing methods. The methods described herein are therefore not applicable to the rural ozone problem, nor to cases in which excursions above the NAAQS for oxidant occur during nighttime or early morning hours. Second, the most serious oxidant problem generally occurs downwind of large cities. Ozone concentrations are, as a rule, higher in these locations, where a substantial portion of the population lives. Further, it is likely that strategies which are implemented to reduce ozone levels in and near major cities will produce some (though perhaps less) benefit in more remote areas as well. Third, it is more practical to address initially that portion of the ozone problem which is most readily controlled (i.e., the case where ozone is synthesized by high concentrations of locally emitted precursors subject to control within relatively few political jurisdictions).

An important limitation of the methods described in this report is that adequate comparisons between their estimates and observed levels of ambient ozone have not yet been made. In the absence of such verification studies, definitive statements about the accuracy of the various procedures are difficult to make. The problem of obtaining suitable data for verification of the procedures described in this report is aggravated as a result of the manner in which the procedures would be applied. The analytical procedures are most appropriate for estimating the changes in ambient ozone concentrations accompanying changes in precursor emissions or concentrations. In order to evaluate how accurate procedures are in estimating changes in ambient ozone levels accompanying control measures, it is necessary to have collected ambient data over a period which is long enough to have witnessed significant reductions in precursor levels. Such data are not widely available. In the absence of adequate ambient data, sensitivity studies can be utilized to estimate the range of error in various analytical procedures resulting from uncertainties in key determinants of ambient ozone levels. It must be emphasized that in the absence of verification studies, sensitivity studies can only serve as extremely crude indicators of the accuracy likely with any analytical approach. As described in Section 4.0, sensitivity studies which have been performed with photochemical dispersion models suggest an uncertainty range in absolute predictions of less than $\pm 50\%$ in an area with a reasonably good data base. As a result of some simplifications in the way vertical dispersion is simulated in EKMA, uncertainty in absolute predictions using that approach is probably less than $\pm 70\%$. A considerably higher degree of confidence is likely however, if photochemical dispersion models and EKMA are applied to estimate changes in ozone accompanying changes in precursor levels. Assuming base level emissions

are accurately known, sensitivity studies performed with EKMA imply the uncertainty level attributable to difficulties in estimating light intensity, reactivity, atmospheric dilution rate and diurnal emission patterns may be less than $\pm 10\%$ in areas experiencing serious (e.g., $> .16$ ppm) ozone problems. Failure to consider the appropriate ambient hydrocarbon to oxides of nitrogen ratio (NMHC/NO_x) would increase the error band to about $\pm 25\%$ or more. Obviously, if emissions are not well known, errors associated with all methods are likely to be greater. An important point which needs to be emphasized is that the error bands quoted above are likely to be greater if a technique is applied to simulate a control strategy which is clearly not consistent with the technique's underlying assumptions. For example, the error associated with predictions obtained using the standard isopleths in EKMA might be greater if the estimates were to be compared with observed improvements in air quality accompanying a control strategy which results in substantial alteration of the spatial configuration of emissions.

Despite the limitations described above, a great deal has been learned since the conception of the Appendix J curve. As a result, it is possible to reduce a number of the shortcomings and uncertainties of the Appendix J curve.

1.3 Organization

The remainder of this report is organized in the following manner. Section 2.0 provides a brief assessment of photochemical dispersion models and a more complete description of three (EKMA, rollback, and statistical procedures) non-data-intensive methods for relating ozone to its precursors. Section 3.0 discusses the roles which transported ozone/precursors are thought to play in the urban oxidant problem.

Methods for including transport and natural background in some of the techniques described in Section 2.0 are also presented. It is recognized, however, that the available data base in many urban areas may not be sufficient to implement suggested procedures for considering transport. Thus, the consequences of not considering transport and natural background are also discussed in Section 3.0. Section 4.0 identifies some caveats which should be kept in mind when applying the information presented in earlier sections. This document contains two appendices. Appendix A describes the monitoring network design thought to be most appropriate for assessing a city's oxidant problem as well as salient features of some of the key instrumentation. Appendix B describes in detail the data needs and assumptions of a procedure which can be used to estimate control requirements in specific urban areas. Further documentation of recommended values for natural background and ambient air quality and modeling analyses supporting many of the recommendations presented in this report are contained in a separate report.³

2.0 Methods for Relating Ozone to Precursors

2.1 Use of Photochemical Dispersion Models

Multisource air quality models employing appropriate chemical mechanisms are believed to provide the best approach for relating ozone to precursors. The photochemical dispersion modeling approach has the potential for being theoretically more sound than any of the other approaches described in this report. This results from the attempt to simulate chemical (e.g., transformation of primary species such as NO and non-methane hydrocarbons into secondary species such as NO₂ and ozone) and physical (e.g., atmospheric dilution, diurnal meteorological variations) phenomena. Parameters subject to control (i.e., emissions) are entered directly as input to such models. This facilitates examination

of the impact of hypothetical control strategies.

There are two major types of models. Eulerian models calculate concentrations at fixed locations in space at specified times. As a result of practical limitations and computational expenses, calculated concentrations represent typical concentrations likely to occur over areas of 1 km² or greater. The concentration estimated at each location during each selected time period results from an interaction among emissions, chemical reactions and the transport and dilution introduced by prevailing meteorological conditions. It is then possible to superimpose iso-concentration lines (similar to contour lines on a map) over the area of interest. Such iso-concentration lines can be drawn for ozone or for other pollutants (e.g., NO₂) which participate in the photochemical process and are of interest for regulatory purposes. Eulerian models are thus capable of providing the most complete estimate possible of the impact likely to result from hypothetical control strategies. The spatial resolution afforded by such models is a particularly desirable feature for several reasons. First, a control agency can make judgments about whether control of equal amounts of precursors from different sources will be equally beneficial. For example, is control of a ton of organic emissions from a single point source as effective as control of a ton of organic emissions from motor vehicles throughout a city? For approaches having no spatial resolution, such a question can only be addressed in a more limited fashion.⁴ Second, models with spatial resolution provide greater flexibility in estimating the benefits of precursor controls. For example, reduction in the population exposed to ozone above certain specified levels can be assessed.

The second type of photochemical dispersion model is the Lagrangian model. Lagrangian models estimate the concentration of ozone and other chemical species within a specified parcel of air. These models "follow" an air parcel and estimate pollutant concentrations within the selected parcel during subsequent times. The concentrations which are estimated result from an interaction of chemical reactions among contaminants which are within the parcel at the beginning of a simulation and emissions encountered along the trajectory of the selected parcel. Meteorological variables also play key roles in determining concentrations of ozone and other pollutants in the selected parcel. The trajectory of the parcel (and hence the emissions encountered), the vertical and horizontal exchange with surrounding air and some key chemical reaction rates are all determined by prevailing meteorological conditions. Lagrangian models may be useful in addressing more limited types of questions, such as:

- (1) What is the maximum ozone concentration likely in the vicinity of a city (i.e., will the NAAQS be met)?, or
- (2) What is the impact of a major new source (e.g., a highway) likely to be if it is built in an urban area?

A major advantage enjoyed by Lagrangian models over their Eulerian counterparts is that they are likely to be considerably less expensive to use. Both Eulerian (and to a lesser extent Lagrangian) photochemical dispersion models can provide air quality predictions with temporal resolution. Consequently, they can be used to evaluate strategies resulting in different diurnal emission patterns and impacts on different source categories.

The major limitations to the widespread use of photochemical dispersion models are:

(1) The data base required as input is extremely detailed and extensive and may not be readily obtainable. For example, to obtain the spatial and temporal distribution of ambient pollutants discussed earlier, a large number of meteorological measurements may be needed to characterize the wind field. In addition, spatial and diurnal emission patterns for mobile and stationary sources, the mix of the organic emissions, plume rise characteristics and upper air data, as well as a fairly large oxidant monitoring network to operate and validate the models, are also needed.

(2) In order to utilize photochemical dispersion models incorporating the information described earlier, the user must have access to extensive computational facilities.

(3) Photochemical dispersion models are subject to several of the same shortcomings of less data-intensive approaches (e.g., selection of appropriate boundary and initial conditions to simulate transport).

(4) Photochemical dispersion models have not been extensively verified. Therefore, their ability to simulate temporal and spatial impacts has not been widely demonstrated. Extensive verification efforts will be underway shortly by EPA using the recently completed St. Louis Regional Air Pollution Study (RAPS) data base.

Complete descriptions of individual models are best obtained from the vendors of such models. cursory descriptions of several models and their prior applications are available elsewhere.^{5,6}

2.2 Non-Data-Intensive Methods for Relating Ozone to Precursors

Approaches having less extensive data requirements than photochemical dispersion models may provide useful approximate answers to limited questions. For example, what level of organic emission controls are needed to attain the oxidant standard, or what reduction in maximum oxidant concentration will accompany a specified reduction in ambient levels of hydrocarbons? Three basic approaches for relating ozone* to precursors are described in this section: use of an Empirical Kinetic Modeling Approach (EKMA), linear rollback and statistical techniques. Of these three approaches, the EKMA is believed to have the soundest underlying scientific basis. All of the approaches described in Section 2.2 assume that meteorological conditions in the forecast period are the same as during the selected base period.

2.2.1 Use of an Empirical Kinetic Modeling Approach (EKMA)

The Empirical Kinetic Modeling Approach (EKMA) utilizes a set of ozone isopleths which depict maximum afternoon concentrations of ozone downwind from a city as a function of initial (i.e., morning) concentrations of NMHC and NO_x , NMHC and NO_x emissions occurring later in the day, meteorological conditions, reactivity of the precursor mix and concentrations of ozone and precursors transported from upwind areas.

* Since the Federal Reference Method for photochemical oxidant is specific for ozone, the methods described herein use ozone as a surrogate for oxidant unless stated otherwise.

The physical model underlying EKMA is similar in concept to the previously described Lagrangian model. A column of air consisting of initial concentrations of ozone and precursors is transported along an assumed trajectory. As the column moves, it encounters fresh emissions, which are assumed to be mixed uniformly within the column. The column is assumed to act like a large smog chamber in which the precursors react to form ozone.

EKMA is best used to determine the sensitivity of maximum hourly ozone concentrations observed within or downwind of a city to changes in ambient levels of non-methane hydrocarbon (NMHC) and oxides of nitrogen (NO_x) precursors. EKMA is most suitable for addressing questions like, "how much reduction in local prevailing precursor levels would be needed to attain the .08 ppm standard for oxidants (measured as ozone)?" or, "what reduction in ozone levels is likely to accompany a specified reduction in precursor levels?" The method is less suitable for estimating the impact of strategies which result in substantial changes in source configurations or for questions about what the impact of controlling a single or small group of sources would be.

Many of the underlying principles of EKMA have already been reported in the technical literature.^{7,8,9} The approach is an empirical one, because it requires the use of observed air quality data. The relationships among ozone and its precursors which underlie the approach are based on the application of a chemical kinetics model.^{10,11} The kinetics model used represents a detailed sequence of chemical reactions which has been proposed for a mixture of propylene, n-butane and NO_x . The chemical mechanism used in the kinetics model is based on information

obtained in smog chamber experiments with propylene, n-butane and NO_x conducted primarily at the University of California at Riverside.¹⁰ The kinetics model predictions were matched against Bureau of Mines (BOM) smog chamber data obtained by irradiating automobile exhaust.¹² Initial proportions of propylene and n-butane were then manipulated in the model so that consistently close agreement was obtained with observations in the BOM chamber. Of the available smog chamber studies, the ones using automotive exhaust are thought to use a mix of reactants most representative of the mixes found in urban atmospheres. Automotive exhaust contains a large variety of reactants which are difficult to include in experiments using artificial mixes. One key category of reactants is aldehydes. Aldehyde concentrations identical to those reported in the BOM experiments were used in the kinetics model when the appropriate proportion of initial propylene and n-butane was being determined.

There are two variations of EKMA. The first involves the use of city-specific ozone isopleths. The second utilizes a standard set of ozone isopleths in which fixed assumptions have been made about sunlight intensity, atmospheric dilution rate, reactivity and diurnal emission patterns. There are two main reasons why the city-specific approach is preferable. First, it is possible to use the city-specific version of EKMA to evaluate a wider variety of control measures. Of particular note is the capability to estimate the impact of control measures which are initiated concurrently. For example, questions like, "what would be the impact on maximum O_3 if local organic levels were reduced X% and

transported ozone were reduced Y%?", or "what would happen if the diurnal emission pattern were varied?" can be addressed. The second advantage of the city-specific approach is that it is more desirable to use locally appropriate assumptions about atmospheric dilution rate, sunlight intensity and diurnal emission patterns. This second advantage, however, is probably not as crucial as it might initially appear. As discussed later, proper application of standard ozone isopleths in EKMA should provide estimates for control requirements which are essentially unaffected by use of assumptions about dilution rate, sunlight intensity and diurnal emission patterns which are not locally specific. The advantages of using the standard isopleth variation of EKMA are that less input information is required and it is not necessary to use a computer. Although, on balance, the use of the city specific isopleth version of EKMA is most advantageous, for ease of presentation, the use of standard ozone isopleths in EKMA will be described first.

2.2.1a Use of Standard Ozone Isopleths

Derivation

Figure 1 relates initial concentrations of non-methane hydrocarbons (NMHC) and oxides of nitrogen (NO_x) to maximum ozone (O_3) concentrations formed within 10 hours. The curves in Figure 1 were derived using the previously described kinetics model and the following assumptions:

- (1) simulations were 10 hours long;
- (2) the proportional mix of propylene and n-butane was chosen so that the reactivity of the mix was comparable to that observed for automobile exhaust in the BOM chamber studies (i.e., 25% propylene (ppmC), 75% n-butane (ppmC));
- (3) aldehydes were assumed to be 5% of the initial NMHC levels (in ppmC);

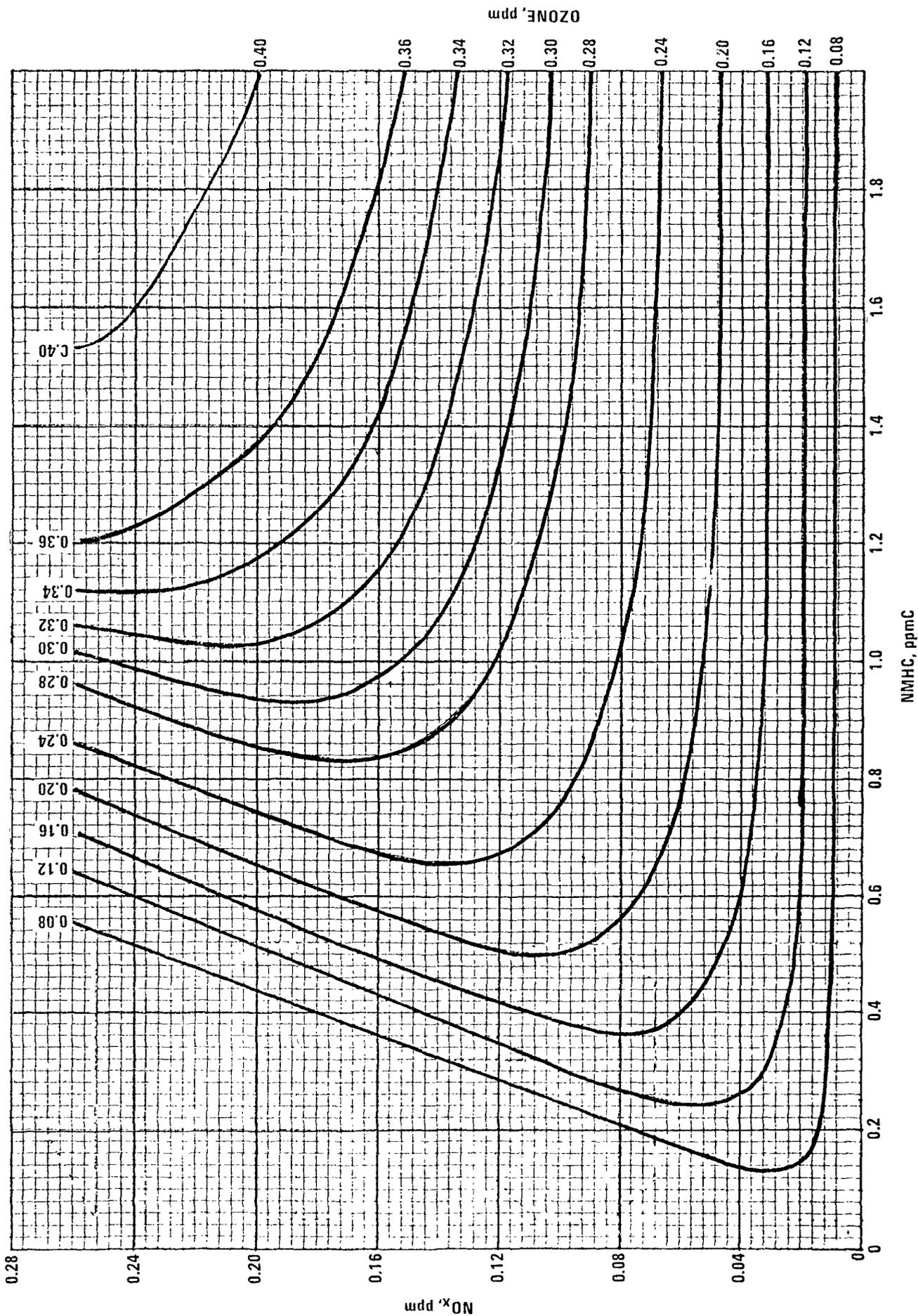


FIGURE 1. Sensitivity of maximum afternoon ozone concentrations to morning precursor levels measured upwind.

(4) photolytic rate constants were varied in accordance with diurnal variation in sunlight intensity during 8 a.m.- 6 p.m. LDT for the summer solstice at 34°N latitude (i.e., similar to the latitude of Los Angeles, Phoenix, Dallas, Atlanta);

(5) an atmospheric dilution rate (caused by lifting of an elevated inversion layer) of 3% per hour was assumed until 3 p.m., with a dilution rate of zero thereafter.

(6) all chemical reactions which had been incorporated within the kinetics model to account for chamber-induced artifacts were disregarded;

(7) no emissions were considered after 8 a.m. LDT.

(8) transported ozone was assumed to be negligible.

Use

Before describing how diagrams such as the one in Figure 1 are used in EKMA, it is necessary to define what is meant by the expressions "absolute sense" and "relative sense." Referring to Figure 1, it can be seen that concentrations of NMHC and NO_x of 0.4 ppmC and .06 ppm respectively correspond with an ozone concentration of .16 ppm. Thus, applying Figure 1 to say that morning concentrations of NMHC and NO_x of 0.4 ppmC and .06 ppm will lead to maximum O_3 concentration of .16 ppm downwind several hours later is an example of applying the diagram in an "absolute sense." In Figure 1, each point on the .16 ppm ozone isopleth has corresponding NMHC and NO_x coordinates. One could also start from an identifiable point on the .16 ppm isopleth and ask the question, "what would be the impact on the maximum O_3 level if NMHC were reduced 50%?" This would represent the application of the diagram in a "relative

sense." In such an application, it is no longer important what level of O_3 will result from specified levels of precursors. What is of interest is what is the change in ozone levels if NMHC and/or NO_x are changed a relative amount. The isopleths in Figure 1 should not be used in an absolute sense, since they reflect specific assumptions about dilution, sunlight intensity, wind speed, emission configuration and patterns and reactivity which may not coincide with what actually occurs on high ozone days in a specific locale.

As will be seen later, however, widespread application of the isopleths is feasible on a relative basis. Thus, Figure 1 should be interpreted as depicting the sensitivity of maximum afternoon ozone concentrations to changes in precursor levels. Consequently the diagram may be used to estimate the degree of reduction in ambient precursor levels needed to attain a specified level of ozone. Conversely, the curves may also be used to obtain a rough estimate of the effect hypothetical reductions in local precursor levels might have on the maximum afternoon ozone concentration observed downwind.

Two pieces of information are needed to apply Figure 1. The first is the design value* of ozone observed in or near the city. The most appropriate location of the instrument measuring this value will depend on prevailing local meteorology during periods conducive to oxidant

*The second highest hourly ozone concentration observed during the base period. If there is more than one ozone monitor in the network, the design value is the highest of the second highest hourly concentrations observed during the base period at all monitors.

formation. Utilizing recommendations of the Standing Air Monitoring Work Group (SAMWG)¹³ as a guide, the ozone concentration used as input to the method should generally be the design value observed within 15-30 km downwind of the central business district. The SAMWG recommendations are, in turn, based on field studies and reviews in which ozone gradients downwind from urban areas were examined.^{14,15,16} Since siting of instruments is a crucial part of assessing the need for and effect of control strategies, it is discussed more fully in Appendix A. Because of previously discussed limitations, only ozone concentrations observed during the afternoon should be considered. The isopleths, as drawn in Figure 1, are appropriate for maximum afternoon O₃ concentrations averaged over periods of an hour. The second piece of information required is the prevailing NMHC/NO_x ratio. Ideally, the most suitable ratio for use would be the one occurring between 6-9 a.m. LDT within the urban core* which is upwind from the site on the day observing the afternoon ozone concentration corresponding to the design value. Because NMHC and NO_x readings are apt to be relatively high in urban areas during 6-9 a.m., more confidence can be placed in the accuracy of these readings. It is therefore recommended that ratios measured in the urban core be used in EKMA. Furthermore, it can be shown that although NMHC and NO_x tend to be higher in the morning, the ratio does not appear to vary nearly so much as individual NMHC and NO_x levels during the course of the day.³

*Urban core is defined as the central city. In large cities this may encompass areas about 3-4 km from the center of the central business district.

The 6-9 a.m. NMHC/NO_x ratio used in the EKMA is viewed as a characteristic of that city which would prevail during the remainder of the morning and early afternoon in the absence of chemical reactions. Thus, use of the 6-9 a.m. ratios is considered to be analogous to the results of smog chamber experiments in which sensitivity of maximum ozone levels to initial combinations of NMHC and NO_x is described. Unfortunately, individual NMHC measurements may be subject to significant error as discussed in Appendix A. Further, 6-9 a.m. measurements of NMHC/NO_x are frequently missing on the days in which highest ozone levels are observed. Therefore, unless there are data from at least two separate monitoring sites, and these data are comparable, a more robust (i.e., less affected by extreme values) and available measurement of the NMHC/NO_x ratio is preferred. It is recommended that the median 6-9 a.m. LDT ratio observed on the days having the five highest ozone values with accompanying NMHC and NO_x data be used. In the event data from more than one site are available, the 6-9 a.m. ratios from each of these sites should be averaged on each of the five days. The median of these five averages should then be used in the EKMA. Close correspondence has been observed between this five-day median ratio* and ratios on the day with maximum ozone in a number of cities.³ It is probable that this close agreement is a result of the similar meteorological conditions which prevail on days experiencing highest ozone levels.

*In following examples, "median NMHC/NO_x ratio" will serve as shortened notation for "median NMHC/NO_x ratio on days experiencing high levels of ozone."

Examples

The following example illustrates the use of standard isopleths in the Empirical Kinetic Model Approach to relate reductions of ambient precursor concentrations in a city to reductions in maximum ozone concentrations downwind. In the examples, letters which are primed reflect the post-control state.

Given: The design value of $O_3 = .28$ ppm;

Median NMHC/ NO_x ratio = 12:1,

Find:

(a) The reduction in ambient organic concentrations needed to attain the .08 ppm oxidant standard if no change in ambient NO_x levels is anticipated.

(b) Same as (a) but with a 50 percent reduction in ambient NO_x anticipated.

(c) The reduction in the second high hourly ozone concentration likely if NO_x concentrations are reduced 30% and organic concentrations are reduced 70 percent.

Solution:

(a) (1) Plot median 6-9 a.m. NMHC/ NO_x ratio line on Figure 2, and note the intersection of this line with the .28 ppm O_3 isopleth.

(2) Likely reduction needed is:

$$R = \frac{(\text{NMHC})_a - (\text{NMHC})_{a'}}{(\text{NMHC})_a} = \frac{1.26 - .26}{1.26}$$

$$R = .79 \text{ or } 79\%$$

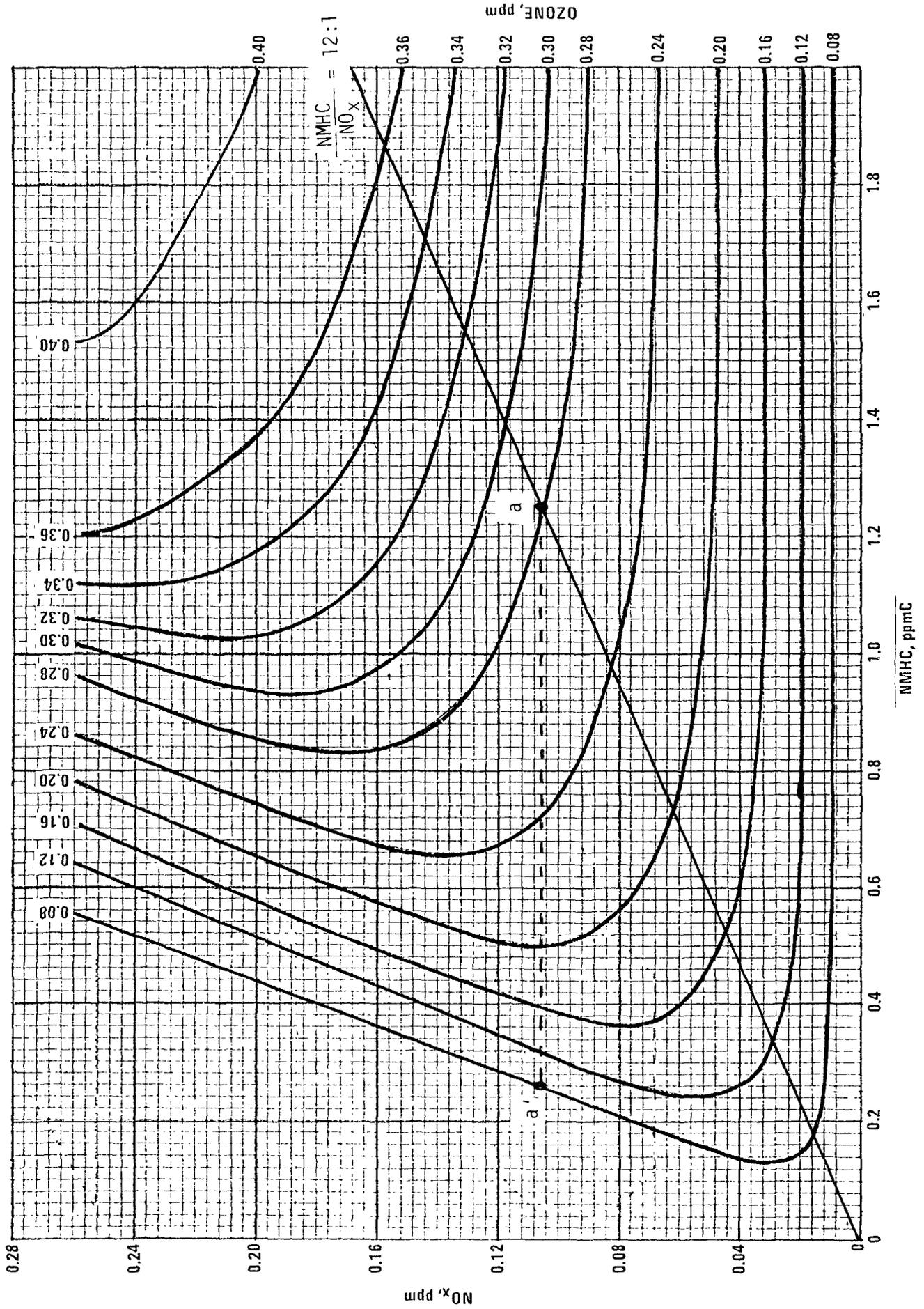


FIGURE 2. Example problem 1a.

(b) If a 50% reduction in NO_x accompanies the needed organic emission controls, the procedure is to:

- (1) Plot the given information on Figure 3 and note the position of the points on the .28 and .08 ppm ozone isopleths.
- (2) Likely reduction needed is:

$$R = \frac{(\text{NMHC})_d - (\text{NMHC})_{d'}}{(\text{NMHC})_d} = \frac{1.26 - .16}{1.26} = .86 = 86\%$$

Note that in this particular example, NO_x control slightly increased NMHC controls needed to meet the standard.

(c) To estimate the impact of a 70% reduction in organic concentrations together with a 30% reduction in NO_x ,

- (1) Plot the given information on Figure 4 (Point g). Note the coordinates of point g (1.26 ppmC, .104 ppm);
- (2) Calculate coordinates of post-control point, g' given the specified reductions in precursor concentration.

$$\begin{aligned} g'_{\text{NO}_x} &= (1 - .30)g_{\text{NO}_x} & ; & \quad g'_{\text{NMHC}} = (1 - .70)g_{\text{NMHC}} \\ &= (.70) (.104) & & \quad = (.30) (1.26) \end{aligned}$$

$$g'_{\text{NO}_x} = .073 \text{ ppm} \quad ; \quad g'_{\text{NMHC}} = .38 \text{ ppmC}$$

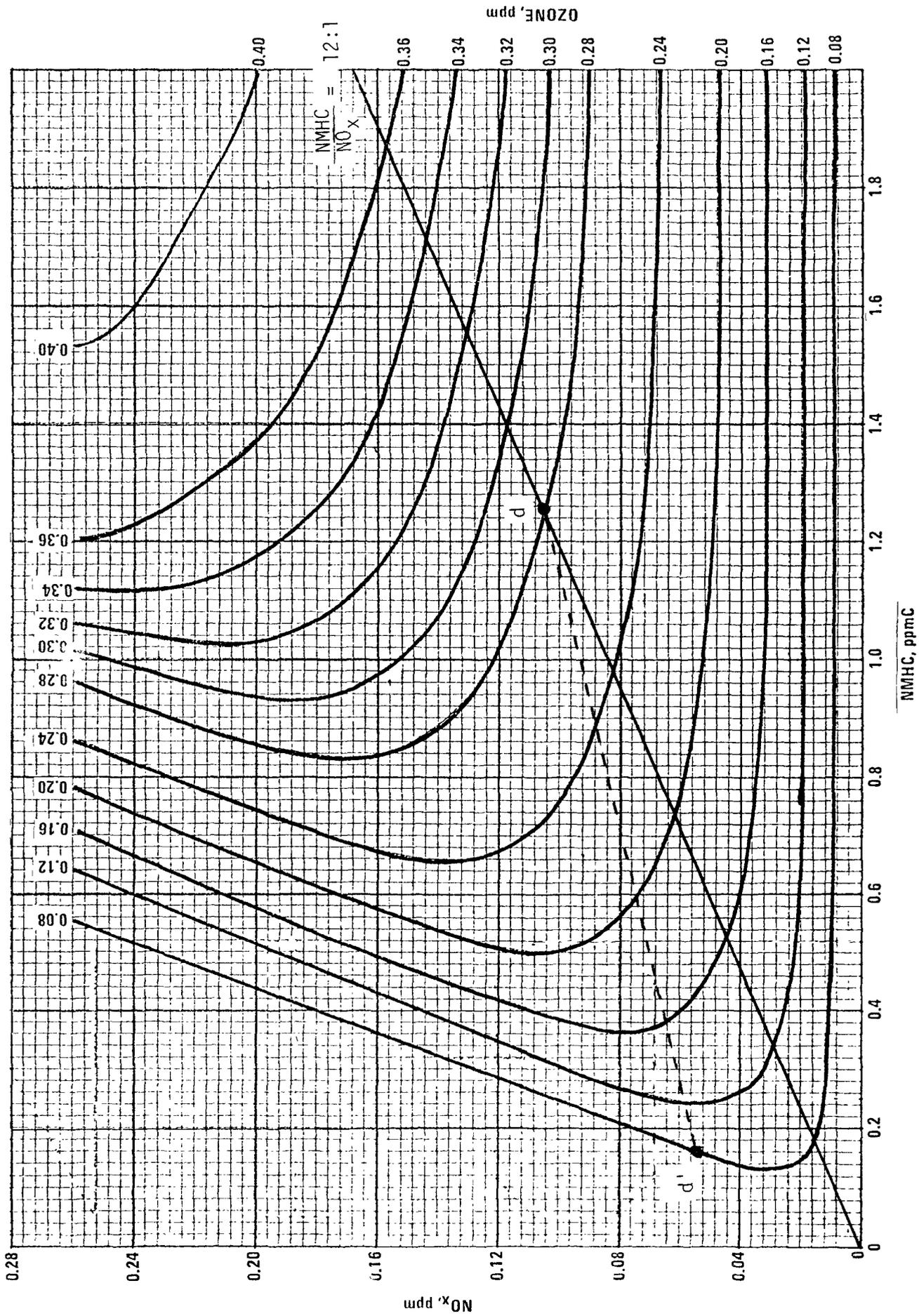


FIGURE 3. Example problem 1b.

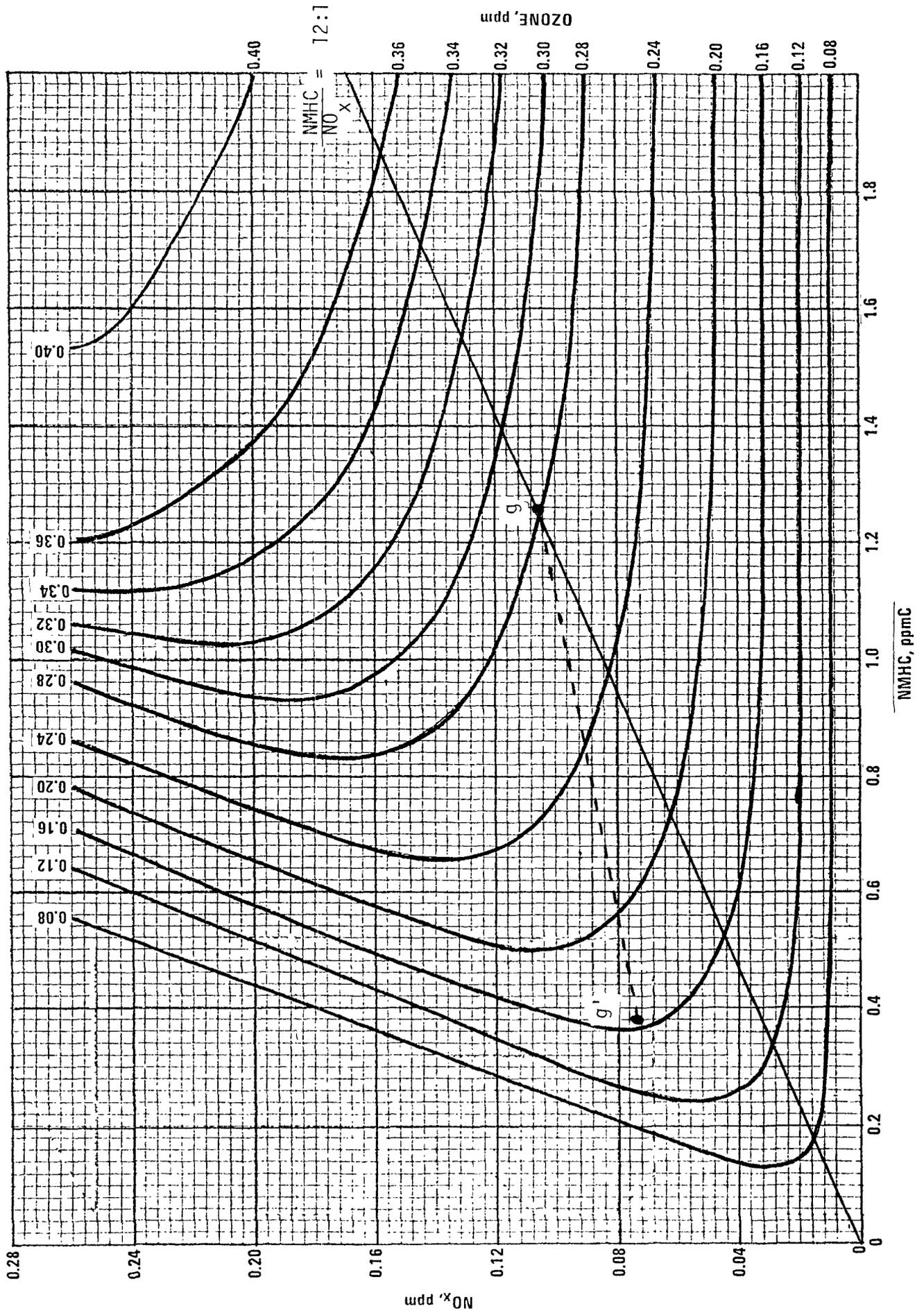


FIGURE 4. Example of problem 1c.

(3) Plot the post-control point on Figure 4. Results indicate that the second high hourly ozone concentration would be about .16 ppm.

In the preceding examples, it has been assumed that sufficient data exist to estimate the representative median ratio in an urban core area. Frequently, however, this information may not be available. The issue of how to estimate an appropriate NMHC/NO_x ratio for specific cities is discussed further in Appendix A. It may ultimately be necessary to assume default values for the ratio. Data from a number of monitoring sites are presented in a separate document.³ Fourteen of these sites are considered to have a large enough sample size and are located either:

- (1) in a highly populated urban area (which may or may not contain substantial stationary sources of organic pollutants), or
- (2) in a suburb which is not dominated by stationary sources.

These sites are presented in Table 1. Best estimates of typical 6-9 a.m. NMHC/NO_x ratios, based on an examination of these sites, would be a median ratio of about 9.5:1. The 10th and 90th percentile NMHC/NO_x ratios observed in the cities in Table 1 may be used to provide a measure of the uncertainty introduced by using default ratios. These data suggest 10th and 90th percentile ratios of about 6:1 and 16:1 respectively are appropriate. In this case, Figure 5 may be used to relate the sensitivity of maximum afternoon ozone levels downwind to changes in upwind ambient precursor levels in the absence of appropriate ambient precursor data.

TABLE 1. AMBIENT DATA FOR URBAN SITES OR SUBURBAN SITES NOT DOMINATED BY STATIONARY SOURCES

(1) Site	(2) Sample Size (Days)	(3) Sampling Period	(4) Mean NMHC, ppmc (0600-0900)	(5) Mean NO _x ppm (0600-0900)	(6) Median NMHC/NO _x Ratio (0600-0900) (Total Period)	(7) Median NMHC/NO _x Ratio on Five Highest Days (0600-0900) (Total Period)	(8) 90th Percentile Ratio (Total Period)	(9) 10th Percentile Ratio (Total Period)	(10) Maximum Observed Afternoon Ozone (ppm)	(11) Remarks
Austin	42	7/1-9/30/75	.27	.026	10.1:1	10.0:1	20.0:1	7.1:1	.10	Station located 8 miles N of CBD
Corpus Christi	44	7/1-9/30/75	.65	.035	18.5:1	21.3:1	37.5:1	10.8:1	.08	Pop = 205,000 w/many, major point sources
El Paso (1)	35	7/1-9/30/75	.59	.067	9.3:1	9.8:1	13.2:1	4.8:1	.15	Station 2-3 mi. S of Franklin Mtn. CBD
Houston (Mae Dr.)	39	7/1-9/30/75	1.14	.156	7.5:1	7.5:1	15.0:1	4.5:1	.20	In heavily industrialized and populated area
Los Angeles	58	7/1-9/30/75	1.48	.147	9.8:1	10.2:1	16.8:1	6.2:1	.25*	Station located in Downtown LA
San Antonio	37	7/1-9/30/75	.22	.022	11.2:1	7.8:1	33.3:1	6.1:1	.07	Station located 8 mi. NW of CBD
Aldine, Texas	10	7/1-9/30/75	.48	.047	11.9:1	10.0:1	40:1	7.1:1	.21	Houston suburb, 12 mi. N of CBD and 13 mi. NW of an industrial complex
Azusa, CA	86	7/1-9/30/75	1.23	.146	8.5:1	8.0:1	15:1	5.9:1	.32*	LA suburban city (25,000), 20 mi ENE of LA CBD
Canton, OH	20	7/1-7/21/74	.56	.076	7.3:1	9.5:1	13.8:1	4.2:1	.14	Site on Malone College Campus 2 mi. N of CBD
Dayton, OH	16	7/18-8/12/74	.59	.049	12.9:1	11.8:1	23.8:1	8.0:1	.13	Huber Hts. site, 9 mi. NE of Dayton (pop. 243,000) CBD
El Paso (Ascarte Park)	29	7/1-9/30/75	.46	.028	10.0:1	14.0:1	40.9:1	4.0:1	.17	In park, 4 1/2 mi. ESE from El Paso CBD and 3 mi. NE of Juarez, Mexico
Groton, CT	15	7/18-8/21/75	.24	.029	9.5:1	8.8:1	14.7:1	5.6:1	.18	SE CT, 2 mi. S of Groton-New London (pop. 40,000)
St. Louis	150	6/1-10/31/76	.62	.077	7.6:1	8.5:1	12:1	5.8:1	.24	Composite of 7 Stations located within 4 km of CBD
Washington, D.C.	43	7/1-8/31/76	.62	.086	7.2:1	9.2:1	13:0	3.5:1	.15	Camp Station

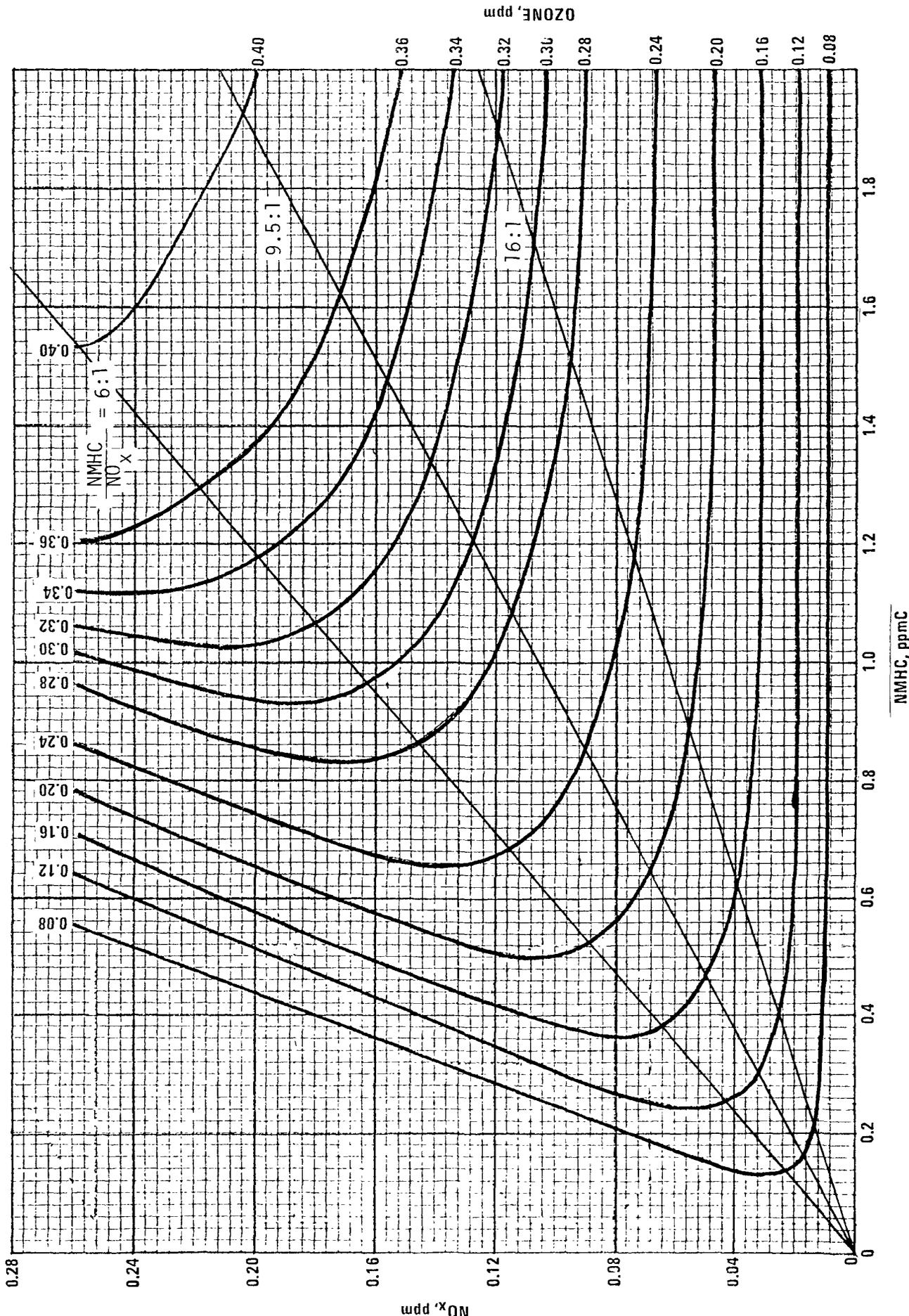


FIGURE 5. Sensitivity of maximum afternoon ozone concentrations to precursor concentrations given default NMHC/NO_x ratios.

For several reasons, isopleth diagrams such as those in Figures 1-5 are most properly interpreted when used in a relative rather than an absolute sense. First, as described previously, the absolute position of the isopleths depends upon a number of underlying assumptions concerning meteorological conditions and emission patterns. Unless the meteorological conditions and emission patterns corresponding to those assumed in deriving the isopleths in Figures 1-5 are similar to those occurring in the city of interest on smoggy days, there is no reason to expect the absolute position of the isopleths to be correct. The relative positions of the isopleths, however, should be less sensitive to these differences. As discussed elsewhere, sensitivity tests have indicated that predicted control requirements for organic emissions are not very sensitive to changing dilution rates, solar intensity, diurnal emission patterns and changes in reactivity when the isopleths are applied in a relative sense.¹⁷ One advantage to beginning with the observed design value of O_3 as input to the EKMA is that this parameter inherently reflects the local prevailing meteorology on the smoggiest days. In this respect, the standard isopleth approach is area-specific. It is crucial, of course, that the O_3 monitoring data have been collected at sites likely to observe the maximum O_3 . Therefore, it is important to consider local meteorology in designing monitoring networks likely to observe high ozone values. The important issue of instrument location is discussed further in Appendix A. A second reason for applying the isopleths in a

relative sense is that the isopleths reflect the behavior of one fixed mixture of automotive exhaust. Therefore, use of these isopleths in an absolute sense in areas having drastically different mixes of organic pollutants may be unreliable. Relative positions of the isopleths are less sensitive to the mix of organic precursors assumed.¹⁷ Third, simulations in which the kinetics model was used to derive the isopleths in Figures 1-5 did not include allowance for any injection of precursors after 8 a.m. LDT. Sensitivity tests conducted with the model indicated that the maximum O_3 concentration formed on the first day of the simulation is increased by post-8 a.m. precursor emissions.¹⁷ However, these same sensitivity studies indicated that estimated control requirements (using the isopleths in a relative manner) were insensitive to differing diurnal emission patterns. It is important to point out that in the sensitivity studies described in Reference 17, post-8 a.m. emissions were reduced in proportion to reductions in initial NMHC concentrations. Thus, in using the standard isopleths, proportional reductions in all emissions (both 6-9 a.m. and post-9 a.m.) must be assumed in order for the curves to be applied properly. No distinction can be made between 6-9 a.m. emissions and other emissions with the standard isopleths. Fourth, it should be kept in mind that the isopleths have been primarily validated against smog chamber data. Smog chambers represent a simplification of the urban atmosphere in that several contaminants which may have a potential impact on maximum O_3 may have been excluded from either

the chamber or the model or both. Finally, a limitation in this method, as well as in linear rollback or any other empirical technique, is that there will always be some uncertainty about whether the maximum O_3 concentration is measured. On any given day it is unlikely that the O_3 monitor is at the precise location experiencing the maximum O_3 concentration.

2.2.1b Use of City Specific Isopleths

As indicated in Section 2.2.1a, the diagrams presented in Figures 1-5 were derived using a fixed set of assumptions concerning sunlight, atmospheric dilution rate, reactivity and diurnal emission patterns. Figures 1-5 also assume that the impact of transported ozone and precursors is negligible. Possible means for considering transport using the standard isopleths are discussed in Section 3.0, as are the consequences of ignoring transport. The fixed assumptions inherent in using standard isopleths limit the flexibility of that variation of EKMA in considering the impact of precursor control strategies. Several of these limitations can be easily overcome by using isopleths which have been derived using city specific data. Generally, it is appropriate to derive isopleths for two types of situations: (1) isopleths derived specifically for the base period (i.e., that situation corresponding to conditions on the day in which the design value of ozone is recorded in a city), and (2) isopleths derived for a controlled state (those conditions which are expected to prevail in the city being reviewed after controls are initiated). This section describes a model which can be used to derive

sets of ozone isopleths reflecting specific assumptions concerning sunlight intensity, atmospheric dilution rate, diurnal emission patterns and transport. The use of city-specific isopleths in EKMA provides one with the important capability of being able to consider different changes (e.g., reduction in local precursors plus reduction in ozone transported into a city or gross changes in diurnal emission patterns) which occur concurrently. This capability will be illustrated in Section 3.3.

Figure 6 is a conceptual view of the model used to generate city-specific isopleths for use in EKMA. The model considers an imaginary column of air which extends from the earth's surface to the base of an elevated inversion. The diameter of this column is large enough so that horizontal exchange of air in and out of the column is ignored. Air within the column is uniformly mixed at all times. The column is moved, at a speed determined by the wind, along a specified trajectory. As the column moves, its volume is increasing (decreasing) in accordance with the diurnal raising (lowering) of the atmospheric mixing depth. As the column encounters precursor emissions along its trajectory, these are assumed to be mixed instantaneously and homogeneously within the column. The column is assumed to behave like a large reaction vessel. The previously described kinetics model is used to simulate the transformation of precursors into ozone within the column. For a fixed set of assumptions about sunlight intensity, dilution rate, diurnal pattern of emissions injected into the column, reactivity and transported ozone, maximum afternoon ozone can be plotted as a function of initial NMHC and NO_x

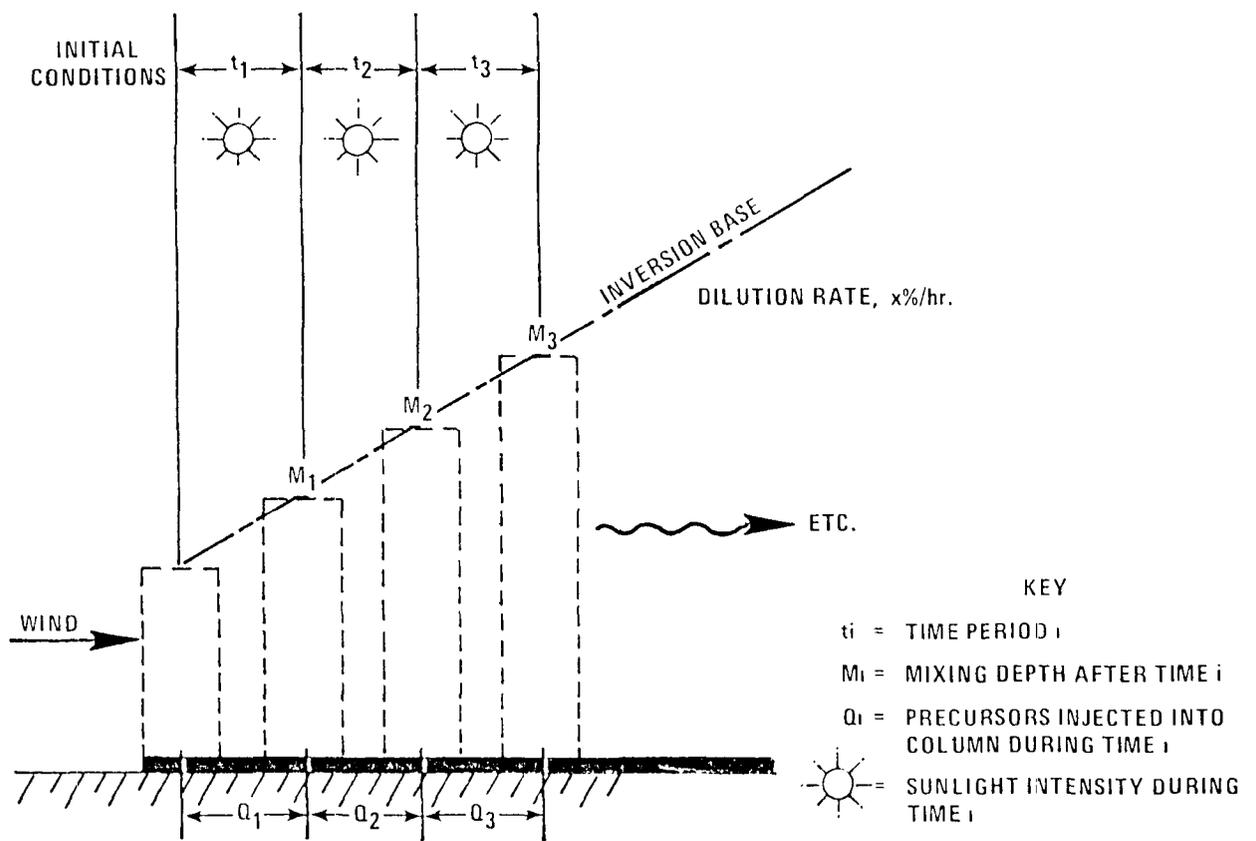


Figure 6. Conceptual view of the column model.

concentrations, as was done in Figures 1-5. This procedure is then repeated using a set of assumptions which is consistent with the post-control situation.

The conceptual model underlying the generation of city-specific isopleths is capable of considering data in various degrees of detail. If the data are very detailed (i.e., the trajectory is determined by wind field data, diurnal emission patterns are broken down by source type and location, etc.), the model begins to approach in sophistication the Lagrangian models described in Section 2.1. The most serious limiting factor is the instantaneous homogeneous mixing which is assumed in the column model. The model which was implicit in the derivation of the standard isopleths described in Section 2.2.1a represents a much simpler application of the column model (e.g., no emissions after 8 a.m. were considered).

Application of City-Specific Isopleths

A computer program to generate ozone isopleth diagrams using locally appropriate assumptions and an accompanying User's Manual¹⁸ is expected to be available shortly. Appendix B discusses in detail considerations used in estimating appropriate input parameters to this computer model. Once an appropriate isopleth diagram is generated by the program, it is applied in EKMA exactly the same way as the standard set of isopleths. The procedure is somewhat more complicated if changes in transport, diurnal emission patterns, etc., accompany a control strategy. This procedure will be discussed in Section 3.3, where procedures for integrating transport into approaches relating ozone to precursors are addressed.

As discussed above, use of city-specific isopleths in EKMA has potential advantages over the standard isopleth approach. The most important advantage of using city-specific isopleths is the ability to consider several factors (e.g., changes in transport, local emissions, diurnal emission patterns, etc.) concurrently. However, it should be remembered that flexibility to consider locally appropriate factors such as atmospheric dilution rate (caused by lifting of the mixing depth), diurnal emission patterns and the amount of transported ozone is only an advantage if one is able to estimate these parameters accurately.

2.2.2 Use of Linear Rollback

Linear rollback is simply the intuitively appealing concept that ambient concentrations of a pollutant are directly proportional to emissions of that pollutant. Furthermore, the relationship between the ambient concentration of a pollutant and its emission is a constant as shown in Equation (1).

$$x = aQ \quad (1)$$

where

x = concentration variable

Q = emission variable

a = constant of proportionality

If a significant portion of the pollutant is transported into the area of interest, Equation (1) becomes:

$$x = aQ + b \quad (2)$$

b = Concentration of the pollutant which is not attributable to local emissions.

If an air quality goal, x' , is established, emissions must be reduced to the corresponding level, Q'

$$x' = aQ' + b \quad (3)$$

Combining equations (2) and (3), the reduction needed to attain the air quality goal is

$$\frac{Q - Q'}{Q} = \frac{(x - x')}{(x - b)} \quad (4)$$

Since there are no appreciable emissions of ozone, however, Q and Q' must represent emissions of ozone precursors (i.e., organics).

For the linear rollback relationship to hold for organics and ozone, Equations (2) and (3) must be valid. That is, there must be a single proportionality constant, "a", between organic emissions and maximum ozone. Re-examining Figure 1, shows that this is not always the case. Even if it were assumed that the isopleths in Figure 1 are not absolutely correct, the proportionality "constant" between NMHC and O_3 depends on (1) the prevailing level of NO_x and (2) the changes in NO_x accompanying hydrocarbon control strategies. For example, for $O_3 = .28$ ppm, according to Figure 1 the proportionality constant, "a" can be anything from .33 on down. Proceeding from the $O_3 = .28$ isopleth down to the $O_3 = .08$ ppm isopleth at a constant NMHC/ NO_x ratio of 10:1, one finds proportionality constants between NMHC and O_3 varying between .25 and .50. Despite the questionable physical basis for rollback, linear rollback can be shown to agree reasonably well with trend data reported

TABLE 2. COMPARISON OF NMHC REDUCTIONS NEEDED TO ATTAIN THE OXIDANT NAAQS ESTIMATED BY THE ROLLBACK AND EKMA APPROACHES

2nd High Hourly Ozone Concentration	NMHC NO _x Ratio	Constant NO _x EKMA	Rollback	Constant NMHC/NO _x EKMA
(a) Using Typical NMHC/NO _x Ratios				
.10	10:1	36%	22%	27%
.15	9.8:1	67%	46%	62%
.20	7.5:1	64%	59%	75%
.25	10.2:1	76%	68%	85%
.21	11.9:1	77%	62%	77%
.32	8.0:1	72%	75%	90%
.14	9.5:1	63%	42%	58%
.13	11.8:1	62%	40%	55%
.18	8.8:1	67%	55%	70%
(b) Using Low NMHC/NO _x Ratios				
.10	7.1:1	33%	22%	33%
.15	4.8:1	44%	46%	59%
.20	4.5:1	48%	59%	72%
.25	6.2:1	62%	68%	81%
.21	7.1:1	63%	62%	77%
.32	5.9:1	63%	75%	87%
.14	4.2:1	38%	42%	59%
.13	8.0:1	56%	40%	53%
.18	5.6:1	54%	55%	70%
(c) Using High NMHC/NO _x Ratios				
.10	20.0:1	53%	22%	28%
.15	13.2:1	73%	46%	65%
.20	15.0:1	80%	59%	77%
.25	16.8:1	85%	68%	85%
.21	40:1	91%	62%	81%
.32	15.0:1	85%	75%	89%
.14	13.8:1	72%	42%	62%
.13	23.8:1	78%	40%	53%
.18	14.7:1	78%	55%	72%

from Los Angeles.¹⁹ Table 2 compares estimates obtained with rollback versus those obtained using Figure 1 for ambient data typical of those observed in a number of cities. Rollback is compared with EKMA for two scenarios:

- (a) NO_x levels are kept constant while NMHC levels are reduced;
- (b) the NMHC/ NO_x ratio is kept constant while NMHC levels are reduced (i.e., NO_x is reduced proportionally).

Table 2 indicates that, with the exception of cases having very low NMHC/ NO_x ratios, needed NMHC reductions estimated with rollback are almost always less than those obtained with the standard isopleth version of EKMA. Thus, the main justifications for using linear rollback are that it is simple, and that under NMHC/ NO_x ratios believed to prevail in most U. S. cities, it appears to be useful in serving as a lower bound for estimates of hydrocarbon controls needed to attain the oxidant standard.

Example

The example presented in Section 2.2.1 will be repeated.

Given: The Design Value of $\text{O}_3 = .28$ ppm.

- Find:
- (a) The reduction in ambient organic concentrations needed to attain the .08 ppm oxidant standard if no change in ambient NO_x levels is anticipated.
 - (b) Same as (a), but with a 50% reduction in ambient NO_x .
 - (c) The reduction in second high hourly ozone concentrations likely if NO_x concentrations are reduced 30% and organic concentrations are reduced 70%.

Solution:

(a) Using Equation (4),

$$R = \frac{.28 - .08}{.28} = .71 = 71\%$$

(b) Answer is the same as in (a), since the rollback approach assumes differences in NO_x levels are irrelevant. It will be remembered that the reductions calculated with the isopleths in parts (a) and (b) were 79% and 87% respectively.

(c) if NMHC is reduced 70 percent,

$$.70 = \frac{.28 - x}{.28}$$

$$x = .08 \text{ ppm}$$

This is more optimistic than the estimate of about .16 ppm obtained with the Empirical Kinetic Modeling Approach.

An assumption in rollback is that the amount of organic emission controls needed to attain the oxidant standard is independent of the prevailing NMHC/ NO_x ratio. However, smog chamber experiments suggest that the lower the ratio, the more effective the hydrocarbon reduction is in reducing the maximum ozone formed. Thus, at very low NMHC/ NO_x ratios, linear rollback may underestimate the effectiveness of organic controls. Conversely, at high ratios, estimates obtained with linear rollback may be overly optimistic. From Table 2 it can be seen that, with the prevailing ambient conditions which appear to be typical in many cities, the net effect of the rollback assumptions is to estimate that less control is needed to attain the oxidant standard than would be implied by the EKMA. Under the ambient conditions which apparently prevail in most cities, rollback is likely to differ most from predictions of kinetics models during the period in which initial control increments

are exercised (i.e., when the NMHC/NO_x ratio is still relatively high). Thus, for example, if organic emission reductions of 30% were implemented in a city experiencing moderate (10:1) NMHC/NO_x ratios, the corresponding improvement in maximum ozone concentrations may be considerably less than the 30% predicted with linear rollback. The risk in relying on rollback is that when the corresponding 30% reduction in ozone levels failed to materialize, questions may arise about whether controlling organic emissions will ever be effective in reducing ambient ozone. Many of these questions would arise because a model which is not based directly on cause-effect relationships between ozone and its organic and NO_x precursors is used.

2.2.3 Use of Statistical Models

There are a number of statistical procedures which could conceivably be applied to attempt to describe ozone/precursor relationships at specific sites.²⁰ Examples of such procedures include simple log linear regression equations, empirically derived envelope curves for individual cities, stochastic models and complex multiple regression systems. The use of statistical models offers two major advantages. First, there exists a close relationship to the actual atmospheric data upon which they are based, and second, because these models are relatively simple, development and use costs are low. It is not the intent of this document, however, to enumerate every possible approach which could be pursued and its accompanying advantages/disadvantages. Instead, a general discussion follows of the fundamental features that such approaches should incorporate.

At the present time, statistical modeling of ozone/precursor relationships can be viewed as both an art and a science. There is, however, a considerable body of information on empirical relationships between ozone and meteorological and emissions variables which is already available to aid in the formulation of such models.^{20,21,22,23} If a statistical model is to be used for the purposes of control strategy development and evaluation, then obviously the model must include variables that are subject to control by agency officials. Therefore, a functional relationship between ozone concentrations and precursor emissions and/or ambient concentrations must be a fundamental feature of any statistical model used for control strategy purposes. As noted earlier in this document, a number of studies have found that maximum afternoon ozone concentrations are sensitive to prevailing meteorological conditions. Thus, some accounting for meteorological differences should be incorporated into the statistical model, either directly or indirectly, with particular emphasis on those times of the year and those meteorological conditions which are conducive to high ozone levels. In addition to the above considerations, some attempt should also be made to account for the impact of the transport of ozone and its precursors as well as the impact of natural background.

Once a statistical model has been derived, it is relatively simple and inexpensive to use, resulting primarily from the small input data requirements. Perhaps the best example of small input data requirements is the use of an empirically derived envelope curve where the only input required is the ozone design value. As noted previously, this is one of

the major advantages of statistical models. The problem with the use of these models for control strategy development/assessment is the question of reliability in extrapolating the model predictions beyond the range of conditions contained in the data from which the model was derived. This problem arises because the very purpose of a control strategy is to change existing conditions such that emission levels are often substantially reduced. Therefore, statistical models may be most appropriately used to consider moderate movements from existing control states and to indicate the direction of change rather than to make absolute numerical predictions.

The motivation for the use of statistical models comes from the assumption that a model derived from actual ambient data will enable one to successfully predict ozone concentrations even when the understanding of the complex photochemical process is incomplete. That these models are derived from ambient data, however, is also a cause for concern. Questions concerning instrument reliability, accuracy and representativeness (e.g., the absence of local NO_x interferences, etc.) must be resolved through a comprehensive quality assurance program. Similar quality assurance procedures should also be applied to the emissions and meteorological data. Where indicated, appropriate tests should be performed for the basic assumptions in some of the statistical procedures, such as linear regression, used to estimate model coefficients. The most critical assumption in the use of a statistical model for oxidant control strategy evaluation is that the functional relationship derived from the base period data would hold for future time periods. If the new control strategy drastically changes the emissions pattern from this base period, then the error in the prediction of the change in ozone level due to this new strategy is difficult, if not impossible, to assess.

3.0 Consideration of Transport and Natural Background

This section is organized in the following manner. First, possible roles of transported ozone and precursors in contributing to high levels of ozone observed in or near an urban area during the afternoon are discussed. Second, means for measuring transported ozone and interpreting the measurements are described. Third, procedures for assessing the impact of transport in an urban area and suggestions for incorporating transport into the methods described in Section 2.0 are presented and illustrated. Finally, possible consequences of not considering the roles of transport and background as contributors to the ozone problem near large cities are addressed.

3.1 Possible Roles of Transported Ozone/Precursors in the Urban Oxidant Problem

There are several possible means whereby transported ozone and/or precursors could affect ozone concentrations observed in urban areas during the afternoon.

3.1.1 Transport of Precursors

Observations concerning transported levels of organic pollutants (including manmade and natural) are sparse. One means for estimating concentrations of transported organic precursors is to measure levels of organic pollutants at moderate distances downwind from urban areas. Concentrations of organic pollutants measured 40 km downwind from St. Louis and in Wilmington, Ohio, (about 60 km downwind of Cincinnati and Dayton) revealed organic concentrations considerably less than those found in urban areas.³ For example, organic concentrations downwind from St. Louis are in the order of 20% of central city levels. Best

estimates of transported organics based on these measurements would be in the order of 0.1-0.3 ppmC. For example, highest 6-9 a.m. NMHC readings 40 km downwind from St. Louis appear to be slightly less than 0.3 ppmC. Readings at sites which do not reflect the impact of any obvious urban plume from an upwind city are in the order of 0.1 ppmC.³ The previously described chemical kinetics model was used to estimate the impact of such levels. As described in Reference 3, the impact of .1 ppmC of transported organics was at most .02 ppm of ozone. However, the impact was generally less than .01 ppm. Under some circumstances, transported hydrocarbon concentrations of 0.26 ppmC were estimated to increase maximum ozone concentrations by as much as .08 ppm. However, a more typical impact was in the order of .03-.05 ppm. Available measurements suggest that even in remote areas hydrocarbons emitted from vegetation constitute but a small fraction of measured NMHC. Therefore, the impact of naturally emitted organics on the formation of ozone in urban areas is expected to be negligible. Scenarios which were tested with the kinetics model also suggest that aldehydes which are transported from upwind areas have a negligible impact on maximum ozone levels formed downwind of a city.³

Most available evidence suggests that ambient NO_x in areas not within or immediately downwind from cities is at or below the detection limits of commercially available instrumentation (.005 ppm). Hence, the impact of NO_x which is presently transported over long distances on the formation of ozone in urban areas is expected to be negligible.

Transported ozone is best considered as consisting of 2 layers; (1) ozone transported within the morning mixing layer (i.e., "ground level transport", usually within a few tens of meters of the surface) and (2) ozone which is transported above the morning mixing height but below

the afternoon mixing height (e.g., in a layer 100-2000 m aloft). This second category of transported ozone is referred to as "transport aloft" in the subsequent discussion. "Ozone transported at ground level" is subject to surface reactions and scavenging by other species (e.g., NO) emitted during the night. As a result of nighttime atmospheric stability, "ozone transported aloft" does not come into contact with the earth's surface, nor does it come into contact with scavengers emitted during the night.

3.1.2 Transport of Ozone at Ground Level

The chief impact of ozone transport near ground level is expected to be the more rapid conversion of NO to NO₂. When incoming ozone near the ground was simulated, using the kinetics model, the impact on maximum ozone concentrations was generally found to be negligible. This finding held true for incoming concentrations as high as .12 ppm. Only when locally generated organic and NO_x precursor levels were decreased to about .3 ppmC and .04 ppm respectively did the impact of transported surface ozone become perceptible. Even in these extreme cases, the incoming surface ozone was less than 20% additive (e.g., incoming O₃ of .12 ppm increased the downwind maximum O₃ by .02 ppm). Thus the impact of ozone transported overnight near the surface on maximum O₃ levels is essentially negligible in the large urban areas for which the methods described in Section 2.0 are most appropriate.

3.1.3 Transport of Ozone Aloft

A series of simulations was performed with the previously described chemical kinetics model used to develop the EKMA. The kinetics model was combined with the column model described in Section 2.2.1b to simulate scenarios considering different dilution rates (resulting from

increases in the atmospheric mixing depth during the course of the day), different levels of NMHC, NO_x and NMHC/ NO_x ratios. As described in Reference 3, all scenarios considered the impact of post-8 a.m. emissions of NMHC and NO_x . A typical scenario is pictured conceptually in Figure 7. Air trapped aloft overnight which contains relatively high ozone levels is homogeneously mixed into an imaginary surface-based column of air as the mixing depth lifts during the day as a result of surface heating. The imaginary column of air is regarded as a reaction vessel in which the kinetics model is applied. This reaction vessel is transported by the mean wind in such a way that it reaches the edge of the most built-up area by noon. Emissions into the column of air thereafter are assumed to have a negligible impact, partly because of the very much lower emissions assumed and partly because of the larger volume of air into which these emissions are diluted. The results of these simulations are reported in detail in Reference 3. Depending on the assumptions made, ozone aloft was found to be generally between 20-70% additive. The higher the dilution rate assumed, the greater the impact of ozone aloft. If the local emissions decrease, the impact of ozone transported aloft tends to increase as a result of less scavenging. This latter observation implies the need to reduce local emissions and transported ozone in order to most effectively reduce the urban ozone problem. Simulations described in Reference 3, as well as simulations conducted by Seinfeld,⁵ suggest that one of the impacts of post 8 a.m. emissions is to diminish the importance of ozone transported aloft. However, it should also be noted that post-8 a.m. emissions contribute to maximum ozone levels as the result of increased synthesis which occurs.

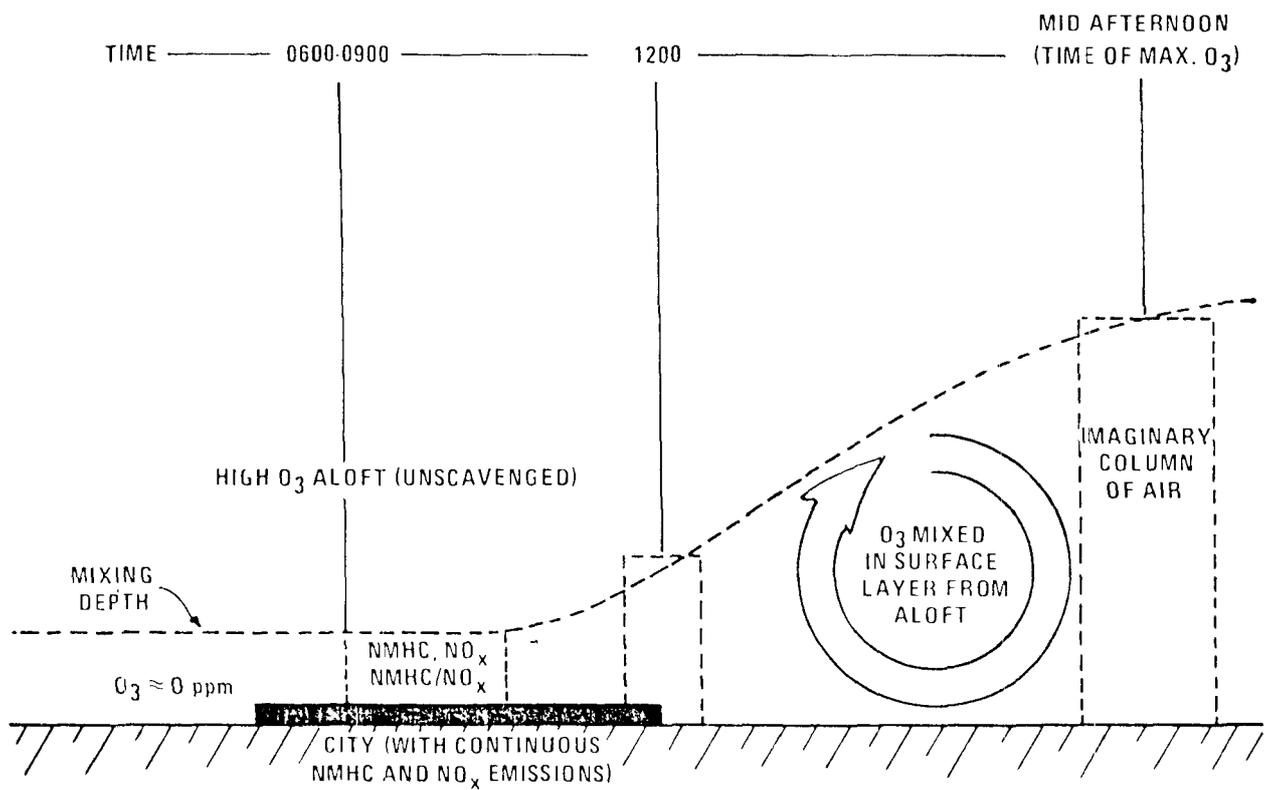


Figure 7. Role of ozone aloft on maximum surface ozone levels: a conceptual view.

Measurements conducted in remote locations suggest that natural background ozone is about .04 ppm, primarily as a result of stratospheric sources.³ Combining this information with the previously described simulation results suggests that the impact of natural ozone on peak hourly ozone values in urban areas ranges from .01-.03, with .02 ppm being most likely.

Summarizing the information presented in Section 3.1, it appears that unscavenged ozone transported aloft is likely to be the component of transport having the greatest impact on maximum afternoon ozone levels observed downwind from cities. Measurements concerning transported organics are very sparse, but they indicate that these organics may be in the order of 0.1-0.3 ppmC, with concentrations near 0.1 ppmC typically found in rural areas upwind from major cities. Simulations described in Reference 3 suggest the role of such levels would typically be to contribute about .01 ppm to observed maximum O_3 levels near major cities. The only significant source of natural background in urban areas appears to arise from ozone transported above nocturnal surface-based inversions. This ozone occurs as the result of slow diffusion from the stratosphere, and may exert an impact of about .01-.03 ppm on maximum urban surface concentrations of ozone.

3.2 Measurement and Interpretation of Transported Ozone

In Section 3.1, it was concluded that unscavenged ozone remaining aloft at night is the facet of transport likely to exert the greatest impact on maximum ozone concentrations in urban areas, with a smaller impact also arising from transported organics. While issues concerning monitoring network design most suitable for estimating oxidant control requirements are discussed more fully in Appendix A, it is appropriate to enumerate some of the difficulties in measuring transported ozone and in interpreting the measurements. The principal difficulty lies in having to rely primarily on surface measurements to estimate ozone levels aloft. As exemplified in Figure 8, there is a distinct difference between ozone 2000 feet aloft and surface ozone which accompanies night-time atmospheric stratification.²⁵ A second complication is introduced by photochemical synthesis which is most pronounced near the surface where precursor sources are located. Figure 9 is contained in a review by Vukovich and illustrates the respective roles of atmospheric mixing and photochemical synthesis as the day progresses.^{26,27} To obtain surface readings which are most indicative of ozone aloft, measurements should be made upwind or outside of the urban plume after breakup of the nocturnal radiative inversion, but prior to the time at which photochemical synthesis results in higher ozone concentrations near the surface than aloft. Because it is necessary to obtain a representative indication of transported ozone, measurements of several hours duration (i.e., 3) are suggested. The exact time to make such measurements would vary somewhat depending on local meteorological conditions. Data such as those presented in Figure 9 suggest that surface measurements obtained

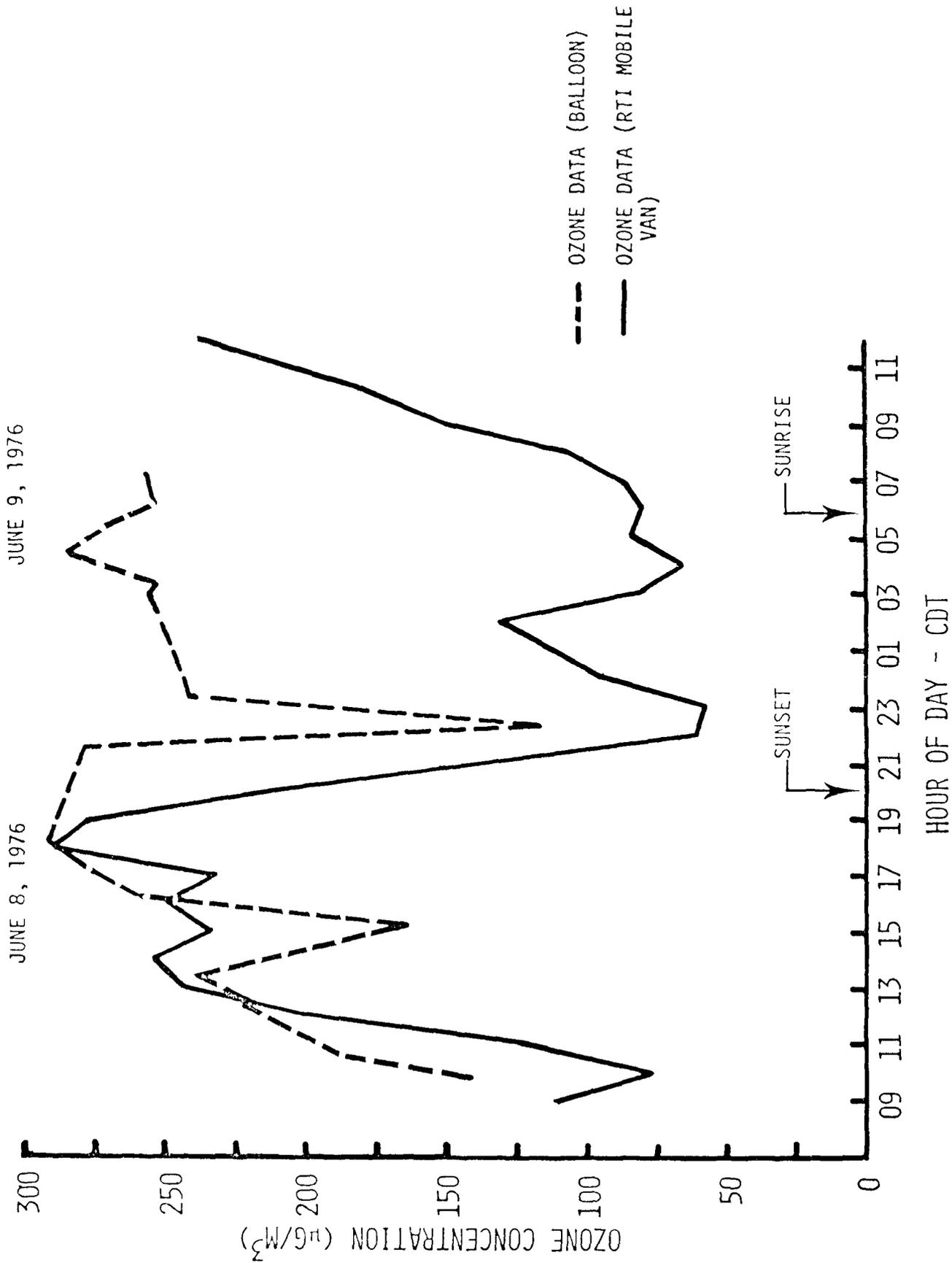


Figure 8. Airborne and ground-level ozone concentrations during the flight of Davinci II (June 8-9, 1976).

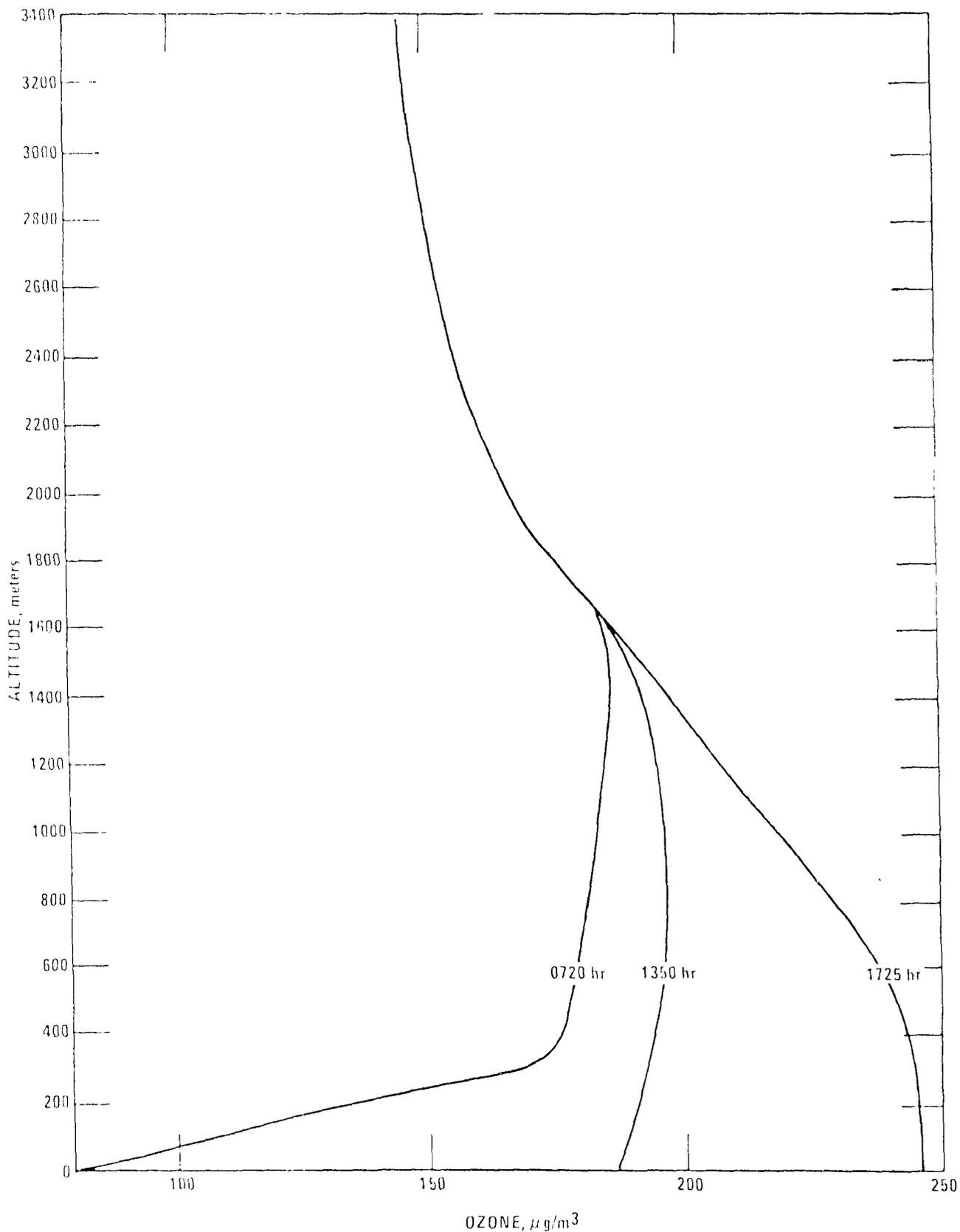


Figure 9. Diurnal variation of the vertical distribution of ozone at Wilmington, Ohio, on 1 August 1974. These profiles have been smoothed using both the ascent and descent portions of flights where possible. The indicated times are the mean time (EDT) of each profile. Altitude is measured from the surface. (Unsmoothed data are in Reference 27).

between about 1100 and 1300 LDT would be most indicative of ozone levels aloft. Therefore, in the absence of locally appropriate data on the breakup of nocturnal inversions, surface measurements of ozone between 11-1300 LDT are suggested for use in estimating ozone which is advected aloft. Some of the difficulties concerning the measurement of transported ozone could be circumvented by mounting an ozone monitor on some tall structure, such as a TV tower. The monitor should be high enough so that it samples air which is insulated from the surface at night. Generally, elevations of 1000-2000 feet above the surface should suffice. Siting of these monitors is described more fully in Appendix A, but as a general guide, they should be located far enough upwind to minimize the impact of pollutants which may be recirculated from the city under review.

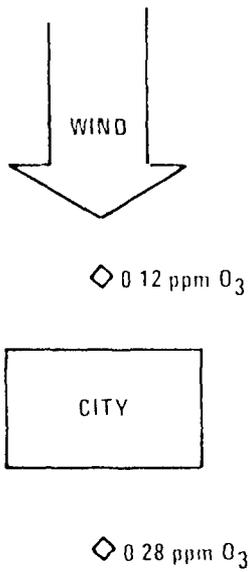
3.3 Procedures for Accounting for the Impact of Transport and Natural Background in Oxidant/Precursor Relationships

The purpose of this section is to describe procedures for integrating transport and natural background into ozone/precursor relationships presented in Section 2.0. The role of transport and natural background in estimating regulatory requirements will first be discussed conceptually. This discussion will be followed by a more complete description of how transport and natural background can be considered in photochemical dispersion models, EKMA, and rollback.

Discussion

Figure 10 depicts the base state and the post-control state in a hypothetical city. The .08 ppm reduction (i.e., .12 - .04) in the upwind (transported) ozone concentrations pictured would have to result from controls initiated upwind. The goal of local control programs would be to ensure that the impact attributable to local emissions is not greater than the difference between the NAAQS and the impact of future transport in the urban area. If, for example, the impact of the .04 ppm transported ozone concentration on the maximum afternoon concentration of .08 ppm shown in Figure 10(B) were .02 ppm, the goal of the city should be to reduce local emissions so that the net ozone produced by the city does not exceed .06 ppm (i.e., .08-.02). If it is assumed that incoming or transported ozone can never be less than natural background, it is apparent that accounting for natural background should increase the estimated local emission control requirements. However, it is also likely that a portion of the .28 ppm ozone concentration shown downwind of the hypothetical city in Figure 10(A) is attributable to the .12 ppm shown as transported ozone. It should be noted that the impact of the transported ozone shown in Figure 10(A) on maximum ozone observed downwind from the city is likely to be considerably less than .12 ppm. This less-than-100% additivity is largely due to chemical reactions which the incoming ozone undergoes with precursors emitted within the city. If transported ozone were reduced as shown in Figure 10(B), it is likely that maximum downwind ozone would be reduced also (though to a smaller extent). Therefore, the initiation of upwind control programs (thereby reducing transport) should lower local control requirements. Conversely, if transport remains constant, control requirements are greater, since

(A) BASE STATE



(B) CONTROLLED STATE

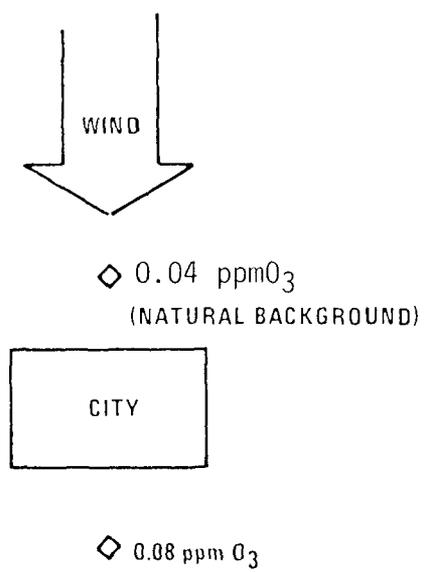


Figure 10. Conceptual view of base and controlled states.

local controls alone must be used to reduce the ozone design value (which reflects both local synthesis and transport) to .08 ppm. Since the goal of control programs is to reduce ozone design values to .08 ppm, and it is unlikely that this design value will occur immediately upwind of a second city after controls have been implemented in upwind cities, assumption of post control transport levels which approach natural background ozone concentrations (.04 ppm) may frequently be appropriate. Potential implications of the apparently opposite impacts of natural background and reducing transport will be elaborated upon in Section 3.4. Because of the potential role played by reducing transport through upwind controls, use of the second high hourly ozone concentrations as the ozone design value may not always result in the highest estimated control requirements. For example, if there were little transport occurring on the day with the fifth highest hourly ozone value, more local controls may be needed to attain the NAAQS than if there were a significant contribution from transport on the day with the second highest hourly value. Therefore, it may sometimes be advisable to review data from several days with high ozone to ensure that calculated control requirements are sufficient to meet the NAAQS.

3.3.1 Photochemical Dispersion Models

Transport is considered in models by assuming boundary and initial conditions which coincide with measurements or estimated transport. Incorporation of these estimated or measured values in the models is a straightforward process which proceeds within the computer software for the model. The impact of transport of manmade pollutants per se can be simulated by a second model run in which transport has been reduced to natural background. As described in Section 3.2, a far more difficult

problem arises in trying to determine what boundary and initial values to enter as input to the model being utilized.

3.3.2 EKMA

Transport can be readily considered by using the city-specific isopleth version of EKMA described in Section 2.2.1b. Transported ozone or precursor concentrations are just two of several specific assumptions which can be made in utilizing the kinetics model underlying EKMA to generate city-specific isopleths. If transported pollutants are assumed not to change, the city-specific isopleths are applied exactly as described in Section 2.2.1b. Reference 18 specifies how the transported ozone concentration may be input into the kinetics model.

If a reduction in transported pollutant concentrations occurs concurrently with emission reductions (as shown for the hypothetical city in Figure 10), it is generally necessary to conduct separate model runs for the base and controlled states. For reasons discussed in Appendix B, it frequently shall be adequate to exercise this procedure considering only changes in transported ozone concentrations. The following is a step-by-step procedure which should be used in the determination of emission reduction requirements based on city-specific isopleths that consider reductions in transported ozone:

1. Gather the data described in Appendix B.
2. Using the data from Step 1, operate the kinetics model to generate an isopleth for the design value of ozone. Unless locally applicable information to the contrary is available, this isopleth should be based on the assumption that the transported ozone concentration is equal to the average from 11 a.m. to 1 p.m. LDT of the upwind ozone concentration on the day the design value occurs.

3. Using the data from Step 1, operate the kinetics model to generate an ozone isopleth for $O_3 = .08$ ppm. This isopleth should ordinarily be based on the assumption that the transported ozone concentration is equal to natural background (.04 ppm).

4. Determine the 6 - 9 a.m. NMHC/ NO_x ratio using procedures outlined in Section 2.2.1a of this report.

5. Using the ozone-precursor graph generated in Step 2, determine the location of the intersection of the line for the NMHC/ NO_x ratio of Step 4 with the isopleth for the design value of ozone. Label the coordinates of this location as the "base initial NMHC concentration" and the "base initial NO_x concentration."

6. Estimate the percentage reduction of NO_x that will occur by the time the ozone NAAQS is met. Reduce the "base initial NO_x concentration" accordingly to estimate the "controlled initial NO_x concentration."

7. Determine the location along the isopleth for .08 ppm ozone which has the appropriate "controlled initial NO_x concentration." The coordinates of this location are the "controlled initial NMHC concentration" and the "controlled initial NO_x concentration."

8. Hydrocarbon emission control requirements are determined by this formula:

$$\% \text{ Reduction Req'd} = \left[1 - \frac{\text{"controlled initial NMHC concentration"}}{\text{"base initial NMHC concentration"}} \right] \times 100$$

Note that it is possible to interchange the roles of NMHC and NO_x in Steps 6-8 of the above procedure. If one is solely interested in assessing the impact of changing transport on local emission control requirements, all other variables (e.g., diurnal emission patterns) must stay constant. It is also possible, however, to assess the impact of

several concurrent changes on local emission control requirements using the above 8-step procedure. For example, one could generate the .08 isopleth described in Step 3 assuming reduced transport and a different diurnal emission pattern.

Example

Figure 11 is used to illustrate how city-specific isopleths may be used in EKMA to estimate the implications of concurrent changes on precursor control requirements. The solid isopleths in Figure 11 depict ozone as a function of initial NMHC and NO_x in the presence of ozone which has been transported aloft overnight. The dashed line depicts the .08 ppm isopleth as a function of initial NMHC and NO_x , when transported ozone has been reduced to natural background levels as the result of upwind control programs. The amount of organic control needed (keeping NO_x constant) to attain the .08 ppm standard is estimated by line AB'. In the example shown,

$$A_{\text{NMHC}} = 1.02 \text{ ppmC}, B'_{\text{NMHC}} = .27 \text{ ppmC} \text{ and } B_{\text{NMHC}} = .18 \text{ ppmC}.$$

$$AB' = \frac{1.02 - .27}{1.02} = .74 = \underline{74\%}$$

If transported ozone had remained unchanged, the amount of organic control needed to attain the oxidant standard would be represented by line AB. In the example shown,

$$AB = \frac{1.02 - .18}{1.02} = .82 = \underline{82\%}$$

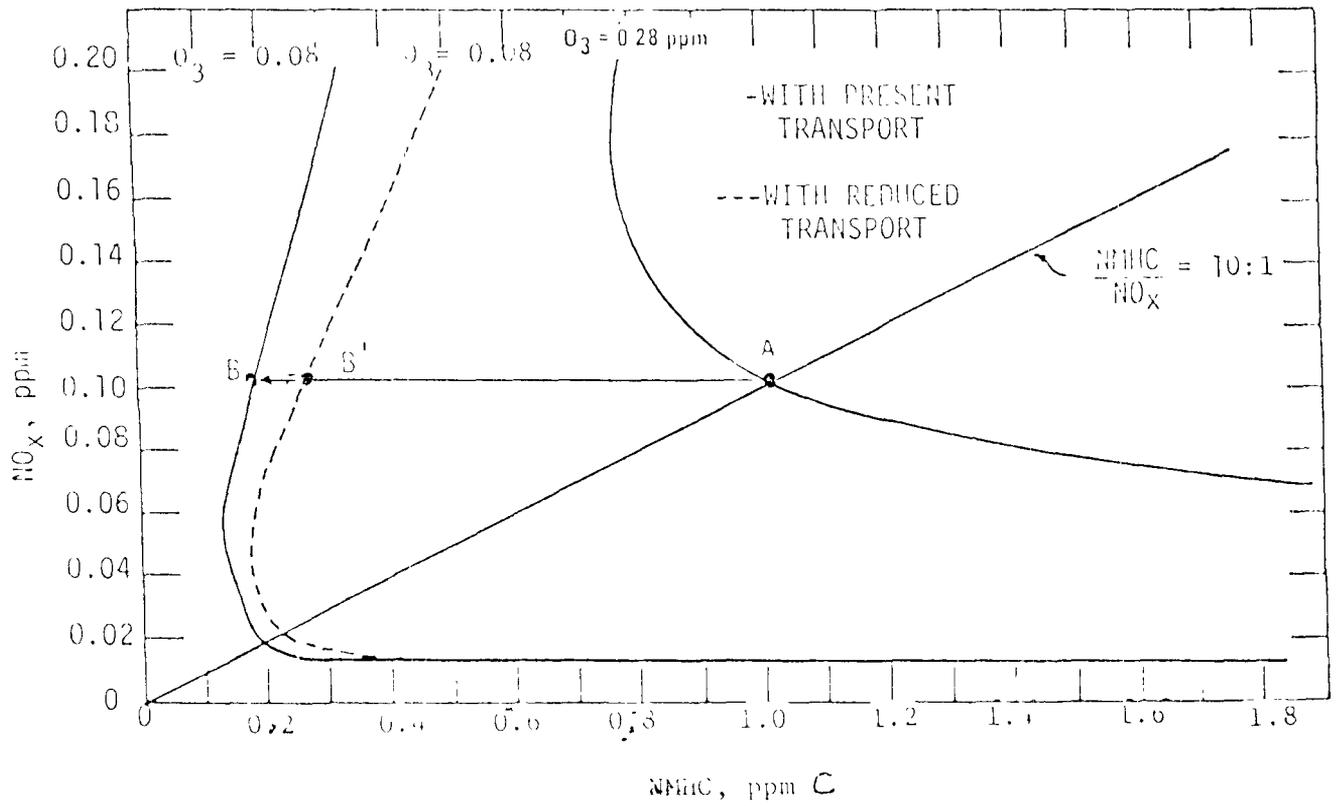


Figure 11. Procedure for considering two or more impacts of control strategies simultaneously using city-specific isopleths.

In addition to the use of EKMA for determining emission control requirements, Section 2.2.1 of this report also discusses its application in determining the reductions in peak ozone concentrations corresponding to a given reduction in precursor emissions. If transported ozone concentrations during the base period are assumed to be at natural background levels, it is possible simply to generate a set of isopleths all based on the transport of .04 ppm. These isopleths may then be used as discussed in Section 2.2.1a to determine the impact of a given emissions reduction. However, if transported ozone concentrations during the base period exceed natural background concentrations, such a determination is made more difficult by the need to estimate the concentration of ozone that is transported at the time the given emissions reductions have occurred. If estimates can be made of an appropriate transported ozone concentration, it is then possible to operate the kinetics model in order to estimate the ozone concentration that would result, given the appropriately reduced initial precursor concentrations and the estimated transported ozone concentration. As stated previously, it is also possible to estimate the reductions in downwind ozone attributable to local emissions simply by assuming constant transport levels, although such a procedure tends to overestimate the ozone concentration that may be expected.

The following step-by-step procedure should be used in determining the impact of a given emission reduction (based on the assumption that current transport levels are greater than natural background levels):

1. Steps 1, 2, 4 and 5 of the procedure for determining emission control requirements using city-specific isopleths should be done to determine the "base initial NMHC concentration" and the "base

initial NO_x concentration."

2. Reduce the base initial precursor concentrations by the percent emission reductions that apply to the respective precursors in order to determine the respective "intermediate initial precursor concentrations."

3. Estimate the transported ozone concentration that may be expected at the time the given emission reductions have occurred. The intermediate level of transport may be assumed equal to the base level of transport or, preferably, will be some reasonable concentration between the base transported ozone concentration and the natural background concentration.

4. Operate the kinetics model in order to determine the peak ozone concentration that corresponds to the "intermediate initial precursor concentrations" from Step 2 and the transported ozone concentration from Step 3. This peak ozone is the second highest concentration of downwind ozone that may be expected when the given emission reductions have occurred.

3.3.3 Standard Isopleth Version of EKMA and Rollback

In order to consider the impact of altering transport on the effect of local emission controls using the standard isopleths or rollback, it is first necessary to estimate the additivity of the transported ozone to maximum ozone concentrations which are synthesized by locally emitted precursors. As described earlier (and in greater detail in Reference 3), additivity of transported ozone depends on the interaction of a number of factors. Hence, the best approach for estimating the additivity of transported ozone is through simulations with an atmospheric diffusion model or with the column and kinetics models underlying EKMA. However,

if one has the capability for implementing either of these procedures, it makes little sense to use the standard isopleths or rollback. Therefore, if available resources do not permit the use of photochemical dispersion models or the city-specific version of EKMA, less satisfactory means for considering transport will, by necessity, have to be incorporated in the standard isopleth or rollback approaches. It is suggested that Section 5.0 in Reference 3 first be reviewed to gain a more complete appreciation of how factors such as prevailing NMHC/NO_x ratio, local precursor levels, dilution rate, and diurnal emission patterns affect the additivity of transported ozone. The range of additivity reported in Reference 3 was roughly .20 - .70. Table 3 is adapted from Reference 3 and indicates the impact of various factors on additivity. The factors are listed in order of their impact on additivity (greatest impact is listed first). The additivity of transported ozone can be estimated subjectively by beginning at the midpoint of the observed .20 - .70 range of values (i.e., .45) and adjusting this value upward or downward according to the nature of the four factors presented in Table 3. For example, if the dilution rate were low (e.g., < 13%/hour), the city of interest were a major one with many sources, the prevailing NMHC/NO_x ratio were low (e.g., 6:1 or less), and high ozone occurred on days with atmospheric stagnation (i.e., so that air parcels tended to stay near areas of high emission density all day), one would choose an additivity value (A) near the low end of the scale (e.g., A = .20). In some cases, several of the factors in Table 3 may be high while others are low. In this event, greater weight should be attached to those factors at the top of the table in choosing a value for the additivity of transported ozone. Once the additivity of transported ozone has

TABLE 3. IMPACT OF VARIOUS FACTORS ON THE ADDITIVITY (A) OF TRANSPORTED OZONE TO MAXIMUM OZONE CONCENTRATIONS IN URBAN AREAS

<u>Factor</u>	<u>Factor Value</u>	<u>Additivity</u>
1) Dilution Rate (i.e., the extent and rate at which the diurnal mixing depth increases).	Relatively High (e.g., > 13%/hour)	Relatively High (>.45)
2) Quantities of locally emitted precursors	Relatively Low (e.g., small city ~ 200,000)	Relatively High (> .45)
3) NMHC/NO _x Ratio	Relatively Low (e.g., < 6:1)	Relatively High (> .45)
4) Importance of post 9 a.m. emissions (This reflects both diurnal emission patterns and the larger atmospheric dilution capacity which generally occurs during the mid-morning and afternoon)	Relatively High (e.g., significant NO emissions in the afternoon such as would occur if an air parcel remained within the city limits in the afternoon during a stagnation period)	Relatively Low (<.45)

been estimated using this rather subjective procedure, the second high hourly ozone concentration observed during the base period should be adjusted downward in accordance with the following formula.

$$(O_3)_{ADJ} = (O_3)_{design} - A (T_o - T_f) \quad (5)$$

where $(O_3)_{ADJ}$ is the adjusted (reduced) ozone concentration to be used in estimating control requirements;

$(O_3)_{design}$ is the 2d high hourly ozone concentration observed during the base period.

A is the additivity factor for transported ozone.

T_o is the concentration of transported ozone estimated for the base period.

T_f is the future concentration of transported ozone which, presumably has been reduced from present levels as the result of upwind controls. T_f is frequently assumed to approach natural background.

Controls required to attain a specified air quality goal, x' , may be estimated with rollback using the following formula:

$$R = \frac{[(O_3)_{ADJ} - x']}{[(O_3)_{ADJ} - (A) (T_f)]} \quad (6)$$

Example

Given: Design Value for $O_3 = .28$ ppm. Present transported ozone is estimated to be .12 ppm. It is assumed that upwind controls will reduce future levels of transport to .04 ppm.

Find: Amount of reduction of local organic precursors needed to reduce the 2d high hourly ozone concentration to .08 ppm.

Solution:

(1) Since nothing is given about any of the factors influencing additivity, assume a value of $A = .45$ (i.e., the middle of the observed range of values).

(2) From Equation (5),

$$[O_3]_{ADJ} = .28 - (.45)(.12 - .04)$$

$$[O_3]_{ADJ} = .24 \text{ ppm.}$$

(3) Using Equation (6), the required reduction is

$$R = \frac{[.24 - .08]}{[.24 - (.45)(.04)]} = .73 \text{ or } \underline{73\%}$$

Note that in accordance with Table 3, the value of "A" in the denominator in Equation (6) should probably be somewhat higher than ".45." As will be illustrated in the next section, however, this is probably an unnecessary refinement in cities presently experiencing a serious oxidant problem.

Using the standard isopleth version of EKMA, transport is considered by first reducing the ozone design value in accordance with Equation (5). Control requirements are estimated by entering the isopleth diagram (e.g., Figure 12) at the intersection of the $[O_3]_{ADJ}$ isopleth and the prevailing NMHC/NO_x ratio line. Control requirements needed to attain the standard are calculated by estimating the reductions needed to reach the isopleth which is $.08 - A(b)$. For example, if the additivity of transported ozone were .45 and natural background were .04 ppm, control

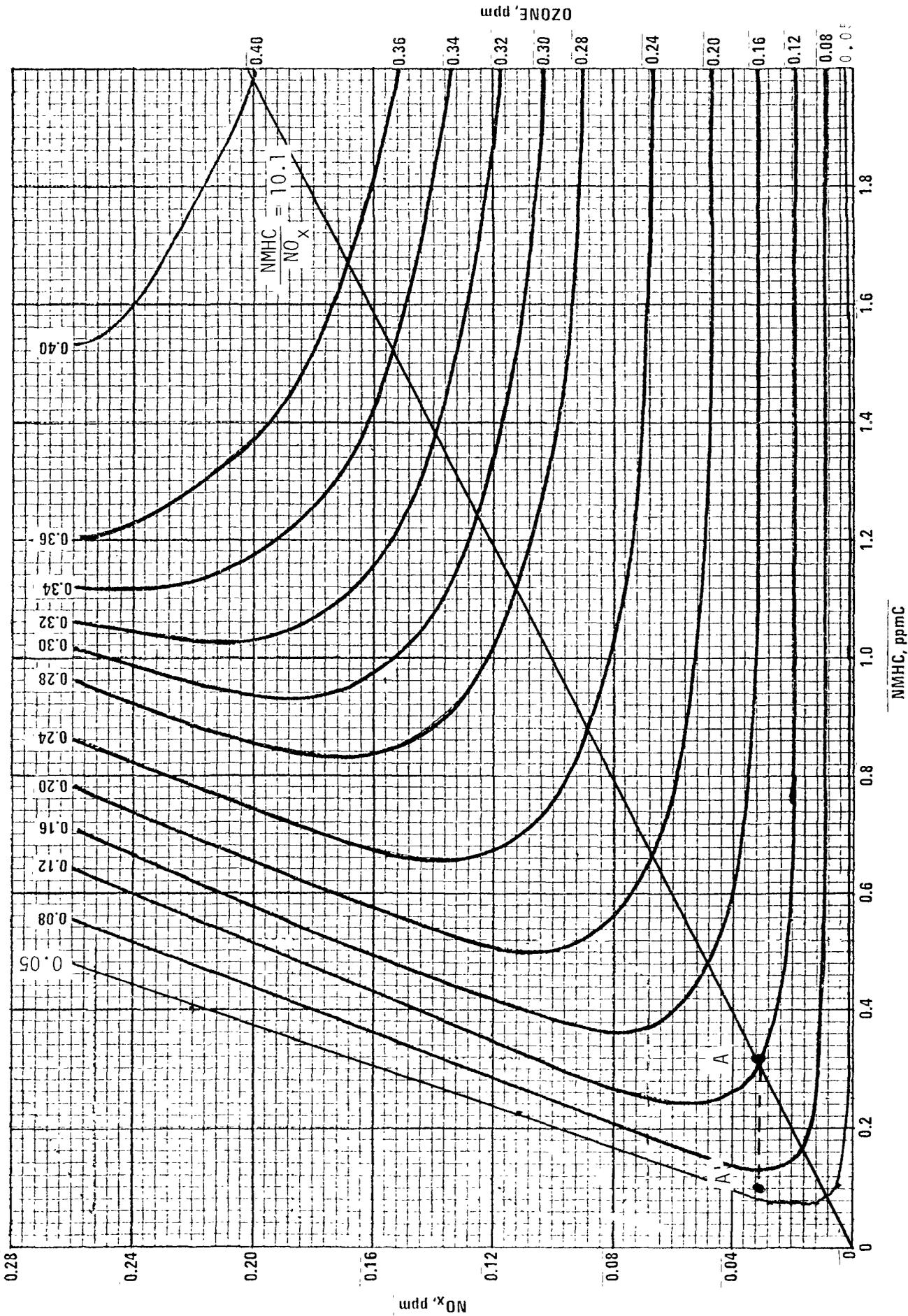


FIGURE 12. Consideration of Transport Using the Standard Isopleth Version of EKMA

requirements would be estimated by NMHC and/or NO_x reductions needed to reach the .06 ppm isopleth. This procedure is illustrated in Figure 12.

As previously discussed, transport can not be accounted for as readily with the standard isopleths or with rollback as it can using models or the city-specific version of EKMA. It is not possible to readily account for the impact of transported precursors using the standard isopleths or rollback. Neither is it possible to account for the role of other changes, such as changes in diurnal emission patterns, using these procedures.

3.4 Data Limitations and Resulting Consequences

Section 3.0 has described what appears to be the role of transport in the urban ozone problem. Procedures for incorporating transport into the methods presented in Section 2.0 have also been described. However, when attempts were made to use existing air quality data to estimate transported ozone, difficulties were frequently encountered.³ These difficulties arose principally because of the lack of upwind data or inappropriate siting of upwind instruments. Such problems are understandable, since the primary purpose of existing monitors is seldom to obtain an estimate of representative ozone concentrations entering a city. Therefore, it may not always be feasible to incorporate transport considerations until monitoring programs have been developed. Hence it is pertinent to examine how ignoring transport might affect estimated control requirements. There are two situations which should be considered. The first occurs if transported ozone concentrations remain unaltered. If this situation prevails, ignoring transport will likely cause one

to underestimate local control requirements using the simple approaches described in Section 2.2. The reason for the low estimate is that, in order to attain the NAAQS, local emissions would have to be reduced such that the sum of locally synthesized ozone and the combined impact of manmade and natural transported ozone is .08 ppm or less.

The second (and more important) situation occurs if transported ozone is diminished concurrently with local emission control programs. Ideally, this reduction would result in ozone transported to downwind cities being reduced to levels approaching natural background. Since transport and natural background affect maximum ozone via a similar mechanism (i.e., from aloft), to be consistent, natural background should be ignored if transport is ignored. For the situation in which transport is actually reduced, ignoring both transport and natural background may frequently result in calculated control requirements which are similar to those in which both transport and natural background are considered. These assertions are illustrated in the following example.

Example

Four hypothetical situations are presented:

Case I -- A moderate size city downwind from a major city in an area where diurnal variations in the atmospheric mixing depth are substantial. In this case, for illustrative purposes, transported ozone will be assumed to be .20 ppm and 60% additive.

Downwind concentrations from the moderate size city will be assumed to be .24 ppm, with $\text{NMHC}/\text{NO}_x = 10:1$

Case IA -- Same assumptions as Case I, except that the problem is more moderate, with downwind and upwind ozone of .16 ppm and

.14 ppm respectively.

Case II -- A major city within a megalopolis in an area with moderate diurnal variations in atmospheric mixing depth. In this case, transported ozone is assumed to be .12 ppm and 40% additive. Downwind concentrations are assumed to be .24 ppm. NMHC/NO_x = 10:1

Case III -- A major city which is relatively isolated in an area with moderate diurnal variations in atmospheric mixing depth. In this case, transported ozone is assumed to be .10 ppm and 20% additive. Downwind concentrations are assumed to be .18 ppm with NMHC/NO_x = 10:1.

Because the computer program for generating city specific isopleths was not available at the time this report was being prepared, calculations for the above cases were made using the standard isopleth version of EKMA and assumptions about additivity. As indicated in Section 3.3, this is not the best way to account for transport in EKMA.

For Case I, the following data apply,

- Present transported ozone, T_o = .20 ppm
- Future transported ozone (natural background), T_f = .04 ppm
- Design value of ozone, (O₃)_{design} = .24 ppm
- Assume that the fraction of additivity, A, has already been determined to be .60, as given.

Solution

(1) Adjust ozone design value downward to reflect the impact of transported ozone

$$(O_3)_{ADJ} = [O_3]_{design} - A(T_o) \quad (5)$$

$$(O_3)_{ADJ} = .24 - (.60)(.20)$$

$$(O_3)_{ADJ} = .12 \text{ ppm}$$

(2) Note that if, in the future, natural background were only 60% additive, local controls would have to ensure that synthesis of local emissions were less than

$$.08 - (.60)(.04) = .06 \text{ ppm}$$

(3) Using the standard isopleth version of EKMA, enter Figure 12 (Section 3.3) and find the intersection of the .12 ppm ozone isopleth with the NMHC/NO_x = 10:1 ray.

(4) Note the NMHC and NO_x coordinates of this point are (.32 ppmC, .03 ppm). If NO_x is kept constant, and only NMHC is reduced, the corresponding (NMHC, NO_x) coordinates at the .06 ppm ozone isopleth are (.10 ppmC, .03 ppm).

$$(5) \text{ Required NMHC control} = \frac{.32 - .10}{.32} = .69 = \underline{69\%}$$

(6) Ignoring transport and background, Figure 1 would be entered at the intersection of the .24 ppm ozone isopleth with the 10:1 NMHC/NO_x ratio line, and the percent reduction needed in NMHC levels estimated is:

$$\text{Required Control} = \frac{.88 - .25}{.88} = .72 = \underline{72\%}$$

Similar procedures can be followed for Cases IA, II and III. The sensitivity to transport considerations for each of the three cases is depicted in Table 4. In these examples, NO_x was assumed to remain constant, and a natural background concentration of .04 ppm was assumed for ozone.

It can be concluded that for the cases pictured in Table 4, the calculated difference in needed controls is practically imperceptible, except in the cases where a moderate size city is impacted by a major city upwind such that measured upwind and downwind concentrations are almost identical.

TABLE 4. THE IMPACT OF IGNORING TRANSPORT ON ESTIMATED ORGANIC CONTROL REQUIREMENTS

<u>Case</u>	<u>Considering Transport and Natural Background</u>	<u>Ignoring Transport and Natural Background</u>
I	69%	72%
IA	31%	69%
II	76%	75%
III	71%	70%

4.0 Caveats

In addition to the limitations already described in connection with each analytical approach, there are several which apply generally to all simple approaches described. Some of these limitations apply to photochemical dispersion models as well. Limitations are of three categories: 1) inability to make accurate, appropriate measurements; 2) inability to account for measured phenomena properly in analytical approaches (models); 3) limited availability of data for verification of the analytical approaches.

The EKMA, rollback and statistical approaches all require the use of observed ambient ozone data to relate oxidant to precursors. Thus, a key limitation arises if ozone monitors are not properly sited. Selecting the proper location for instruments depends on local meteorology and the configuration of sources. For economic reasons, ozone instruments are frequently co-located with instruments measuring other pollutants. Ideal siting criteria for ozone instruments are not, as a rule, entirely consistent with the criteria for other instruments. Even if the instrument locations were consistent with available guidance, however, it is conceivable that the concentration measured at a point in space would be less than the actual maximum O_3 concentration. Further, if there are any local sources of precursors, the monitoring data may not represent concentrations predicted over the somewhat larger spatial scales assumed in available models. These limitations have implications concerning control requirements estimated by using the simplified procedures described herein and with regard to attempts to validate both complex and simple models. Even the most sophisticated Eulerian grid models do not attempt to predict pollutant concentrations for grid squares less than 1 km^2 in area.

Methods such as the EKMA and some statistical approaches also rely on measured NMHC data. Existing instrumentation for NMHC produces estimates which are subject to large errors. Because these errors appear random and less severe on days experiencing high levels of ozone, use of robust estimates like median 6-9 a.m. NMHC values on high O_3 days reduces this error considerably. However, using such a procedure reduces some of the advantage of the cause-effect nature of the EKMA. All methods are limited by inadequate emission inventories. If known emissions are responsible for only 50% of the ambient organic concentrations found in urban areas, reducing the known emissions a given amount will not have the impact anticipated by the analytical procedures described herein. The impact of transported organic material is not very well documented. This problem arises, in part, because of the difficulties in measuring low levels of organics and various types of organic pollutants. If the major impact of transported material comes from ozone advected aloft, as suggested in Section 3.0, utilization of surface measurements to derive numbers for use in analytical procedures has uncertainties associated with it.

An important set of limitations of the simple models arises from the lack of spatial resolution. Thus, these procedures do not, in their present form, enable evaluation of strategies which result in different spatial emission patterns. Further, the 1:1 relationship assumed between ambient precursor concentrations and emissions does not enable one to consider the relative effectiveness of controlling particular source categories. The simple procedures do not readily allow consideration of other indicators of the oxidant problem, such as population exposed to high levels, frequency of high concentrations,

etc. Such other indicators may prove useful in assessing the benefits accompanying precursor controls. All of the models proposed are limited to urban areas. The rural problem and the impact of ozone and/or precursors on areas whose local emissions are small is not well described by the EKMA or rollback approaches (or by photochemical dispersion models either, for that matter). Also, the impact of urban control strategies on the transport of ozone and precursors overnight is not considered. Certain smog chamber experiments, for example, suggest that drastic control of organic precursors may increase the transport of NO_2 downwind from cities.²⁸ In addition, it may be difficult to simulate complex meteorological phenomena such as land-sea breezes and urban heat island effects using the procedures described herein. Difficulties of this sort stem both from data availability and from simplifications which have been made in computational schemes.

Perhaps the most important shortcoming of the methods described in Section 2.0 is the limited extent to which their accuracy has been assessed. Major efforts are underway at EPA to verify several Eulerian and Lagrangian photochemical dispersion models, using the St. Louis RAPS data base. As reported in Reference 3, many uncertainties are introduced when one attempts to compare EKMA and rollback with Los Angeles trend data. Further investigation of the Los Angeles data is underway. Another possible way to assess the accuracy of the EKMA approach would be to use ambient NMHC, NO_x and ozone data collected in and near a city. This may be very difficult to do in practice, however, since the isopleth curves in EKMA are based on the premise that meteorology does not

vary. If different meteorological conditions occur from day to day, there is little reason to expect the isopleths to agree with the observations in the data base. The reason for this is that changing ozone levels are not solely a function of changing precursor levels, but of changing meteorological conditions as well.

Given the lack of extensive observations with which to compare estimates obtained with the procedures discussed previously, it is difficult to generalize about the accuracy of these procedures. One means for estimating the uncertainty inherent in various procedures is to test the sensitivity of estimates to errors in input values. If the potential error in input variables can be estimated, the degree of uncertainty in estimated ozone concentrations can also be assessed. The more fundamental question about the appropriateness of an analytical procedure as applied to a specific area can only be completely resolved after verification studies have been conducted, however. Errors associated with key input variables to photochemical dispersion models have been summarized in a review by Seinfeld⁶ for the Los Angeles area. This information is then used to infer that errors in Eulerian photochemical dispersion model estimates of absolute ozone concentrations are less than $\pm 50\%$ if input variables are known with a reasonable degree of accuracy. Comparisons between single cell and multi-cell models (in the vertical) suggest that single cell models (such as the column model in EKMA) may be subject to an additional error as high as 20%.⁶ This information implies that errors associated with predictions of absolute levels of ozone using EKMA are less than $\pm 70\%$. Such numbers, of course, are extremely rough estimates. It is likely that careful collection

of appropriate input data would result in more accurate predictions. Conversely, if key variables such as emission inventories are poorly known, errors can be much higher. Since it is not possible to apply rollback in anything but a relative sense, it is not possible to comment on the absolute accuracy of that approach. Neither is it possible to comment on the accuracy of statistical approaches using anything other than observed data.

The degree of error or uncertainty can be appreciably reduced when models are applied in a relative sense.⁶ Additional sensitivity studies conducted utilizing the kinetics model underlying EKMA bear this assertion out.¹⁷ Reviewing the results of the sensitivity studies reported in Reference 17, uncertainties concerning reactivity, diurnal emission patterns, sunlight intensity and atmospheric dilution rate result in less than a 10% difference in estimated organic control requirements (with constant NO_x). As shown in Reference 17, the degree of uncertainty concerning control requirements is greater if there is uncertainty concerning prevailing NMHC/ NO_x ratios. Errors in estimated NMHC control requirements in the order of $\pm 25\%$ are implied if NMHC/ NO_x ratios lie somewhere between 5:1 and 20:1. Since rollback makes no attempt to consider prevailing NMHC/ NO_x ratios, atmospheric chemistry or changes in transported ozone concentrations, estimates obtained using this approach may be subject to somewhat greater error than those which attempt to consider these factors (e.g., models, EKMA).

A final caveat to keep in mind is that estimates obtained with simple approaches may be subject to additional errors if they are used to assess the impact of strategies which are clearly inconsistent with

their underlying assumptions. Thus, if the standard isopleth version of EKMA or rollback were used to assess the impact of strategies involving a substantial rearrangement of source configurations, additional errors could occur.

For the reasons cited above, there are uncertainties associated with the estimates obtained by using simple approaches and complex models as well. However, these uncertainties are more of degree than of direction. For example, all methods indicate that substantial reductions in organic precursors are needed to reduce ozone levels appreciably. In addition, there is no evidence that controlling organics and NO_x at the NMHC/ NO_x ratios which appear to exist in most cities will not be beneficial in reducing maximum levels of ozone. Therefore, the procedures described herein can be regarded as approximations, subject to some error, which may nevertheless be useful in assessing the magnitude of the oxidant problem.

5.0 Acknowledgements

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APPENDIX A

MONITORING NETWORK DESIGN AND INSTRUMENTATION

A comprehensive discussion of this topic is beyond the scope of this document. Nevertheless, proper design, collection and interpretation of ambient monitoring data is a crucial part of the previously discussed approaches for relating ozone to precursors and for considering the role of transport. The purpose of this Appendix is to outline considerations for designing an appropriate air quality monitoring network to enable assessment of control requirements for oxidant. In addition, some limitations in available instrumentation and their resulting implications are identified.

A.1 Network Design

This discussion will proceed by first outlining appropriate siting guidance associated with the least data-intensive method (linear rollback) and then build upon that discussion with advice concerning additional data which are desirable for other approaches (e.g., the Empirical Kinetic Modeling Approach with transport considerations). The fundamental piece of ambient air quality information required by linear rollback (and all other simple approaches) is a good estimate of the design value of ozone.* Hence, it is necessary to exercise great care in siting the ozone monitor(s) so that there is a reasonable chance of observing the higher O_3 levels near the city. The prime sites should be in areas which are most frequently downwind on summer days between mid-morning and mid-afternoon.

* The highest second highest hourly concentration observed at all monitoring sites during the base period.

"Downwind" should be determined from meteorological data which are not unduly influenced by very localized phenomena such as land-sea breezes. Each ozone site should preferably not be located within 200 meters of major ground level sources of NO. The monitoring site should not be obstructed by buildings or have any restrictions to uniform flow in at least 3 of the 4 major directions. The monitoring instrument itself should be a reference method or equivalent. The distance of the monitor from the center of the urban core* should be determined by how far a parcel of air over the urban core might be expected to travel between 6-9 a.m. to mid-afternoon with summer/fall winds in the prevailing direction. Therefore, the most appropriate distance and orientation would vary according to the local meteorology. As a general guide, the Standing Air Monitoring Work Group (SAMWG) has recommended that two permanent ozone monitoring sites be established in each city to be reviewed. On days with light winds, one site should be within 15-30 km of the center of the urban core in the predominantly downwind direction (afternoon).² A second monitoring site might be located on the fringes of the urban core in the predominate summer/fall downwind direction. A review of air quality data collected in St. Louis as part of the Regional Air Pollution Study (RAPS) has revealed that highest O₃ concentrations may occur very near or within the urban core during atmospheric stagnations.³

*Urban core is defined as the central city. In large cities, this may encompass areas as much as 3-4 km from the center of the central business district.

Obviously, the greater the number of monitoring sites, the better the chance of observing high concentrations of ozone in the vicinity of a city. Furthermore, imposition of controls may have as one of its effects a shifting of the location of maximum ozone concentrations. Therefore it is recommended that additional ozone monitors be deployed. For very large cities (e.g., New York City), maximum O_3 concentrations frequently appear to occur somewhat farther downwind than the 15-30 km SAMWG guidance suggests.⁴ Therefore, if sufficient resources exist, a third ozone monitor might be placed somewhat farther (40 + km) from a city in the predominate summer/fall daytime wind direction.

In addition to the requirements for monitoring O_3 , it may be desirable to monitor non-methane hydrocarbons and NO_x if the EKMA or certain statistical approaches are utilized. Since NMHC and NO_x data are needed to calculate prevailing NMHC/ NO_x ratios, the instruments should be co-located. Because it is important to obtain representative values for the ratio in locations likely to have the highest smog-forming potential, it would be preferable to have more than one NMHC and NO_x monitor located in the urban core and preferably at least 200 m from any important sources. Analysis of the RAPS data confirms that NMHC/ NO_x ratios in the St. Louis urban core do not vary appreciably from each other during the day.³ It is recommended that NMHC and NO_x ratios observed during 6-9 a.m. be used. The reasons for this are that concentrations measured at this time best reflect initial conditions prior to the onset of photochemical reactions. Further, concentrations of NMHC and NO_x are apt to be higher during these hours. Hence, the reliability of the monitoring data is greater. As described later, there are serious problems with the available measurement techniques for

ambient NMHC. For this reason, the Agency cannot recommend the use of individual NMHC readings from single monitoring sites in analytical approaches relating oxidant to precursors. As will be discussed later, more robust measures such as the median NMHC/NO_x ratio on days experiencing high ozone may be used, with smaller associated errors.

If it is not possible to monitor NMHC and/or NO_x, default values for the NMHC/NO_x ratio based on ambient observations presented in Table 1 could be used in EKMA. These default values were obtained using NMHC and NO_x data from a number of cities. The data were obtained either as part of EPA field studies or as a result of State or local monitoring efforts.

In order to consider the role of transported ozone, as discussed in Section 3.0, additional ozone monitoring sites are needed. It is suggested that at least one such site can be located predominantly upwind of the urban core of the city during late morning (e.g., 1100-1300 LDT) on sunny summer/fall days. The site should be located in as rural a location as possible so as not to be appreciably affected by local sources of precursors. The goal to strive for is to obtain a representative indication of the ozone concentrations in incoming air aloft. The distance such upwind sites should be located from a city would depend on the degree of urban sprawl. It is desirable not to measure pollutants which are recirculated from the city under review. Limited experience with the RAPS data base suggests that a distance of 40 km or more upwind from the urban core should be sufficient. This distance perhaps could be reduced for smaller cities. Figure A-1

depicts orientations for acceptable upwind sites. Note that it is not essential for an "upwind" site to be "upwind" provided it is not influenced by emissions from the city under review. The inherent assumption is that the "upwind" sites in Figure A-1 are measuring representative air quality levels resulting solely from remote sources. Since SAMWG has indicated that only two ozone monitoring sites in high concentration areas need to be maintained on a permanent basis, additional sites may be operated on a seasonal basis or as part of a special study.

Use of mobile monitors should be subject to the same guidance as that previously discussed for stationary sites. In the event tower data are used to estimate transported ozone, as suggested in Section 3.0, the tower should preferably be located as far upwind from the city as feasible to reduce the measured impact of recirculated pollutants. Instruments located 1000 feet or more above the ground should provide a good indicator of ozone transported aloft.

A.2. Limitations of Existing Instrumentation

The instrumentation used to measure ambient NO_x should be capable of estimating hourly concentrations. The most widely available NO_x instruments are sensitive down to levels of about .005 ppm. This degree of sensitivity does not present serious difficulties in estimating urban NO_x levels. However, it exists as one of the technical barriers to understanding fully the rural oxidant problem where exceedingly low levels of NO_x prevail.

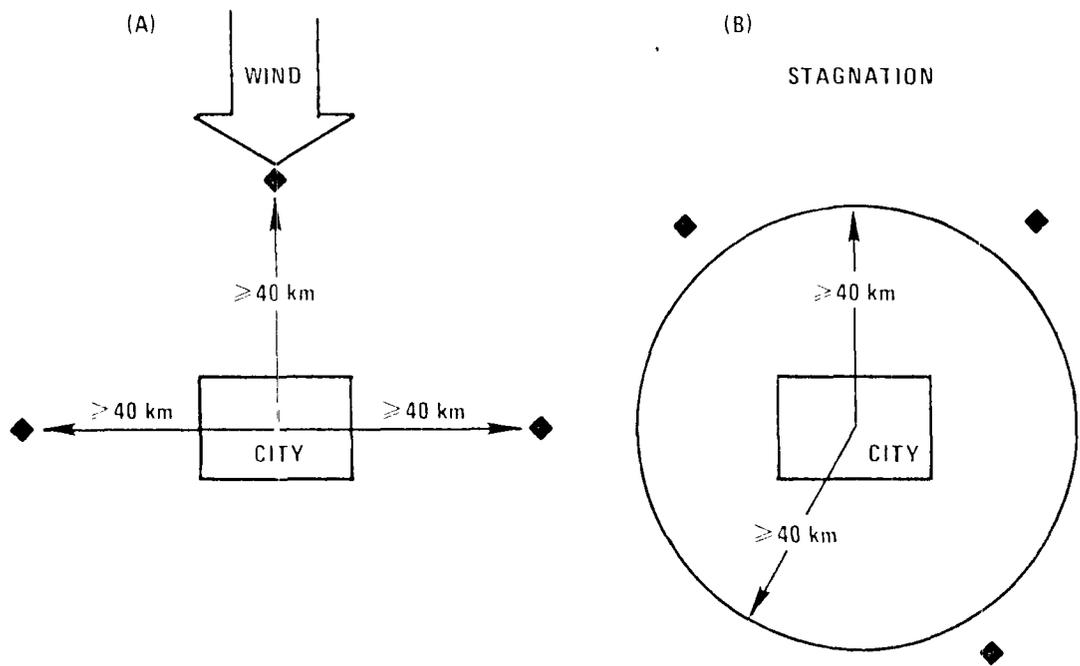


Figure A-1. Examples of acceptable monitoring locations for estimating transported ozone.

Far more serious problems exist with the methods available for estimating ambient non-methane organic concentrations. Within the past several years, there has been increasing awareness of the problems associated with measuring ambient non-methane hydrocarbons. These problems center on the Flame Ionization Analysis (FIA) method used in continuous field instruments for NMHC. According to this method, NMHC are not measured directly, but are computed by determining the difference between measured methane concentrations and the total hydrocarbon (THC) concentration of the sample. Thus, possible errors in the individually measured methane and THC are compounded in the calculated NMHC value. When methane and THC are similar in magnitude, there can be a large error in their difference. This may occasionally result in negative estimates of NMHC.

The causes of error in the methane and THC measurements are attributable to a wide range of mechanical and operational problems with the FIA instruments.^{5,6} For example, system flow valves tend not to regulate effectively the pressure in the sampling loop. This inability to maintain stable hydrogen, combustion air, and carrier gas flow rates results in an unstable flame and inaccurate instrument response. Other problems such as deterioration of the analytical columns, contamination of the sample due to adsorption and desorption of hydrocarbons in the system, and sample loss in inlet lines and plumbing contribute to the response unreliability.

These problems are further complicated by the highly sensitive nature of the instruments.^{5,6} Instrument response varies if, during calibration, span gases are not in air, not correctly analyzed for methane, or contain unknown amounts of higher hydrocarbons. Additionally, THC measurements are sensitive to the oxygen content of the calibration gas and tend to be depressed by high ambient relative humidity. The mixture of light and heavy hydrocarbons in the sample also affects the instrument's response. The FIA will produce a greater response in air to methane than to the same number of carbon atoms of higher hydrocarbon species. The response to carbon-oxygen bonds is weaker still. These mechanical fluctuations, together with the sensitivity problems of the instruments result in drift and instability of response. In addition, the instruments are highly erratic, requiring that a skilled technician be assigned to maintenance during all operations. Small oversights and errors in operating and calibrating the analyzer contribute to the inaccuracy in recorded values. Further details on the problems and complexity of operating the FIA field instruments are discussed in References 5 and 6.

The inconsistent response of hydrocarbon instruments leads to imprecision and repeatability errors in recorded NMHC data. Because no commercially available instruments measure NMHC directly, existing field instruments must be evaluated with laboratory test mixtures or against the response of other field instruments. This presents some difficulties in quantifying the errors, since each test method has substantial limitations. Using laboratory mixtures can test instrument response to

known hydrocarbon levels, but that eliminates variability due to ambient conditions. Comparing data from different analyzers sampling ambient air solves this problem but eliminates a reference NMHC value.

An EPA study using the latter approach estimates (by assuming most instruments have equal total error) that the error in hourly NMHC data may be 5 to 10 percent of the 10 ppm full scale range of the instrument. This leads to the assumption that there may be at least $\pm 100\%$ error in values below 0.5 ppmC, $\pm 50\%$ error in values around 1.0 ppmC, and $\pm 25\%$ error in values around 2.0 ppmC.⁵ A look at instrument response to known NMHC concentrations gives slightly different results. Based upon a study by Scott Labs for EPA,⁶ the difference between known NMHC concentrations and values (peak response) measured by 13 users of Flame Ionization Devices (FID) ranged from +350% to -110% (1.04 ppmC maximum observed, -0.02 ppmC lowest observed) for an actual concentration of 0.23 ppmC, and +28% to -32% (3.70 ppmC maximum, 1.98 ppmC minimum) for 2.90 ppmC.

In summary, measurement of NMHC by the available commercial FID instruments yields unreliable individual measurements. Inaccuracy in individual hourly values may be as high as \pm several hundred percent in the range of concentrations below 0.5 ppmC. At higher levels, the error is considerably less, but may still be $\pm 25\%$ at up to 2.0 ppmC.

Because of the unreliability of individual NMHC measurements, there was cause for concern about whether any approach (such as EKMA or potential statistical approaches) which relies on ambient NMHC data could be used. NMHC data which were observed on days experiencing high ozone levels

were reviewed for several cities.³ Ambient NMHC levels occurring on such days tend to be high (with correspondingly small relative errors). As demonstrated in the examples in Section 2.2.1, for NMHC/NO_x ratios prevailing in most cities, this magnitude in estimating the prevailing ratio would not be of serious consequence in relating ozone changes to precursor changes with the EKMA.

In summary it has been demonstrated that the error in individual NMHC data recorded from FIA instruments does not, in most cases, produce a significant impact upon the application of the EKMA methodology under actual ambient conditions. occurring on days experiencing high ozone levels. Because of this, the FIA instruments could be used by State/local agencies to obtain NMHC data, but only if the data are used to compute median and mean NMHC/NO_x ratios. Alternatively, if close agreement is found among several sites on the day in which the ozone design value is observed, the mean of such measurements could be used in the EKMA as well. Any use of individual NMHC concentrations at single sites for single days is not recommended, because of the large error that is present in the data. Existing field instruments should only be used until a more precise technique is developed. Therefore, if a city does not have FID instruments, it should rely on default ratios presented in this document or on estimates obtained in special contractual studies performed by qualified specialists.

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APPENDIX B
GUIDELINES FOR USE OF A KINETICS MODEL IN ESTIMATING
CITY-SPECIFIC OZONE-PRECURSOR RELATIONSHIPS

B.1 An Overview of City-Specific Studies

This appendix provides guidance in collecting the necessary data to use the city-specific isopleth version of EKMA as described in Sections 2.2.1b and 3.3. This appendix also discusses the use of these data in a kinetics model to derive the necessary isopleths required by EKMA. The kinetics model which should be used is described briefly in Section 2.2.1a and in depth by Dodge¹ and Whitten and Hogo.² This model has been successfully validated against smog chamber data and represents the state-of-the-art for mathematically simulating the production of photochemical oxidant without requiring large quantities of input data.

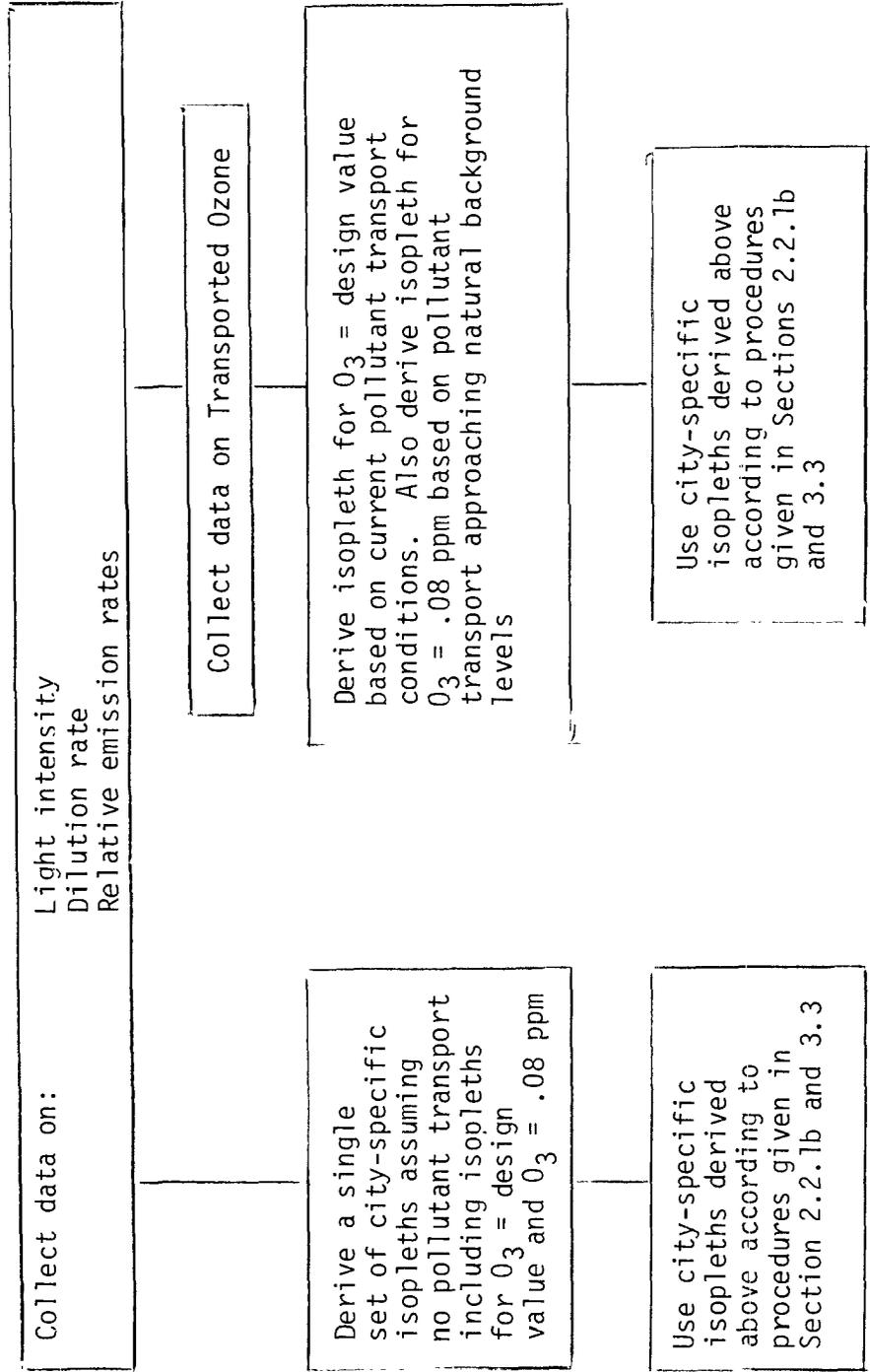
The procedures discussed herein use the kinetics model to generate isopleths representing ozone-precursor relationships for the specific conditions applicable to a given city. Procedures are discussed separately for (1) analyses which consider pollutant transport, and (2) analyses which do not consider pollutant transport. Table B-1 summarizes the procedures necessary to determine emission control requirements both with and without the consideration of pollutant transport. This table shows the three phases that comprise each such analysis (i.e., data collection, kinetics model use, and determination of emission control requirements). Similar analyses may also be conducted to determine the reduction in downwind ozone concentrations that occur with a given emission reduction, although the analysis is more difficult if pollutant transport is being considered.

Table B-1

City-Specific Procedures for Determining Emission Control Requirements

City-Specific Procedure not
Considering Pollutant Transport

City-Specific Procedure
Considering Pollutant Transport



Data Collection

Kinetics Model
Use

Determination of
Emission Control
Requirements

The specific procedures that should be followed in each type of analysis have been discussed in Sections 2.2.1b and 3.3 of the main text. As shown in Table B-1, the first phase of any analysis is data collection. All analyses require data on light intensity, dilution rate, and relative emission rates. Data on light intensity for the day the design value of ozone* occurs are necessary to simulate the diurnal variation of photolytic rate constants. Data for determining dilution rate are necessary to simulate entrainment of relatively clean air as the mixing height increases. Relative emission rates are necessary to simulate variations of emissions into the air parcel over space and time. If the information is available, it is also desirable to consider the concentrations of ozone and other pollutants being transported into the city.

B.2 Data Requirements

The first step in any determination of the city-specific ozone-precursor relationship is data collection. Table B-2 shows the data required in order to use the kinetics model. Information should be obtained on light intensity, dilution rate and relative emission rates. Information should also be obtained on transported pollutant concentrations (particularly ozone) if pollutant transport is being considered. Dodge¹ discusses the variables in more detail and discusses the values that are used in generating the standard set of isopleths presented in Section 2.2.1a. Whitten and Hogo² discuss the format required for use of these variables in the kinetics model. The following subsections provide procedures for determining city-specific values of these variables.

*The design value of ozone is the highest second-highest ozone concentration measured in or near a city.

Table B-2

Input Requirements of the Kinetics Model

<u>Data Required</u>	<u>Values Used in Standard Isopleths</u>	<u>Source of City-Specific Value</u>
Light intensity as defined by latitude, longitude, and day of year	34°N, 118°W June 21	Latitude and longitude is determined using a local map; day of year is based on times of highest measured data
Mixing height data	Dilution rate = 3%/hr	Local mixing height measurements or data from Holzworth ³
Relative emission rates	Emission rates after 8 a.m. LDT are zero	Local emissions and meteorological data (default values for missing data provided in this Appendix)
Ozone concentration transported into city (optional)	0.0 ppm	Ambient measurements

B.2.1 Light Intensity

The kinetics model discussed by Whitten and Hogo² requires data on latitude, longitude and day of the year. These data are used to calculate the appropriate diurnal variation of photolytic rate constants. Local latitude and longitude (for the center of the city) should be readily available. The date used should be the day on which the design ozone concentration occurs.

Adjustments for attenuation of light intensity due to cloud cover are not provided for in the kinetics model package. If quantitative information exists which suggests a different level of light intensity is more appropriate, this information may be used by modifying the kinetics model. However, it should ordinarily be assumed that the highest ozone concentrations occur on days without significant cloud cover.

B.2.2 Dilution Rate

Dilution in the kinetics model represents the entrainment of relatively "clean" air from aloft into the primary "dirty" column of air. The kinetics model uses data on mixing height to determine the rate of dilution. The model assumes uniform mixing throughout the column of air at all times. Thus, for example, if the mixing height doubles over some time period, dilution by a factor of two is assumed to occur. The extent to which the air above the original mixed layer contains pollutants is considered separately and is discussed in the section on data requirements for considering pollutant transport. Wind speed and lateral diffusion are not considered, because the pollutant concentrations in the air surrounding the imaginary column of air are assumed to be similar to those within the column. Thus, it is assumed that horizontal mixing does not cause any significant dilution of the concentrations within the column.

The kinetics model as described by Whitten and Hogo² requires data for a minimum mixing height, a maximum mixing height, and a time period over which the mixing height is increasing. Ideally, these data should be observed on the day experiencing the design value of ozone. However, it is usually necessary to use some other indicator of these mixing height data.

If the information is available, a suitable surrogate for design day data is median data based on several of the days with the highest ozone concentrations. Nevertheless, the only available data often are seasonal mean morning and afternoon mixing heights as provided by Holzworth.³ If no local information is available on the time of day over which the mixing height is increasing, it may be assumed that increases in mixing height typically occur primarily between the hours of 8 a.m. and 3 p.m. local daylight time.

B.2.3 Relative Emission Rates

Relative emission rates express the rate of emissions into the imaginary column of air for each hour of simulation relative to the emissions into the air column prior to the beginning of the simulation (8 a.m. LDT). In the kinetics model, emissions prior to the time a kinetics model simulation begins (8 a.m. LDT) are represented by initial precursor concentrations. Post-8 a.m. emissions are represented by additions to these precursor concentrations. Relative emission rates are used by the kinetics model to determine the appropriate rate at which to add to the initial precursor concentrations in order to simulate post-8 a.m. emissions.

Relative emission rates are required for each hour of simulation. A rigorous calculation would require a precise specification of: (1) the location of the air parcel, (2) the spatial variation in emissions, and (3) the temporal

variation in emissions. Unfortunately, none of these items can be specified accurately with the limited data normally available. The task then becomes to derive reasonable approximations with data which are available.

The most practical approach is to develop a hypothetical air parcel trajectory, and then to roughly approximate the spatial and temporal variations in emissions along this trajectory. Normally it is appropriate to first consider spatial variations along the trajectory, and then separately adjust for temporal variations. The following discussion indicates the types of assumptions that may be used in estimating these variations. Note that it is important to use information and assumptions that pertain to the local area wherever possible. The assumptions and the values discussed below are included primarily for illustrative purposes and should be used only if local information is unavailable.

A typical set of assumptions might be that: (1) the emission distribution is Gaussian in the direction of the wind (i.e., emissions = $Q_0 e^{-ax^2}$, where "Q₀" is the emissions in the center of the city, "a" is a constant, and "x" is the distance from the center of the city); (2) the air parcel meanders around the center of the city until 8 a.m. and then moves at a constant velocity until it leaves the urban area three hours later (a conservative estimate), and (3) the emissions distribution is calculated on the basis that the emissions at the edge of the urban area are e^{-2} (approximately 0.14) of the emissions in the center of the city. These assumptions result in the following hourly factors expressing the emissions at the location of the air parcel relative to the emissions in the center of the city:

prior to 8 a.m. LDT	:	1.0
8 - 9 a.m.	:	.95
9 - 10 a.m.	:	.61
10 - 11 a.m.	:	.25
after 11 a.m.	:	negligible

These emissions are calculated at the midpoint of each hour (e.g. 8:30 a.m.). This generally provides an adequate estimate of the average emissions for each hour.

In the absence of site-specific data, a city-wide average may generally be used for the temporal distribution of emissions. This distribution may be calculated as an average of the temporal distribution of mobile and stationary sources. Nevertheless, the temporal distribution of automotive emissions should ordinarily be an adequate representation of the temporal distribution of the total emissions. If local information on the temporal distribution is not available, Tittlemore et. al.⁴ suggest that the following hourly percentages of a day's automotive emissions may be typical (times are in LDT):

Midnight - 8 a.m.:	16.9%	(the concentration at 8 a.m. is assumed to reflect emissions over these eight hours)
8 - 9 a.m.:	6.4%	
9 - 10 a.m.:	4.4%	
10 - 11 a.m.:	4.8%	

(for the sample calculation, the air parcel is assumed to be outside the city after 11 a.m. and thus no longer receiving emissions).

In this example it is not necessary to consider the hours prior to 8 a.m. separately since the air parcel is assumed to remain stationary and because the mixing height is assumed constant during this time period.

Once the above data are obtained, relative emission rates may be determined by adjusting the relative emissions for the air column location each hour according to the fraction of the day's emissions that occurs during that hour. An important subsequent step is to normalize these emission rates relative to the emissions that have entered the air column prior to 8 a.m. The calculation of normalized relative emission rates is illustrated in Table B-3 with sample values of spatial and temporal emissions variations. Normalized relative emission rates are required as input to the kinetics model. Note that the values shown in Table B-3 should be used only if no city-specific information is available.

The rates of precursor concentration addition derived by the kinetics model are dependent upon the emission rate and the height over which these emissions are mixed. The kinetics model uses input data on normalized relative emission rates and changes in mixing height to determine post-8 a.m. rates of concentration addition as a fraction of the 8 a.m. concentrations. If the mixing height is variable prior to 8 a.m., the pre-8 a.m. emissions (against which later emissions are normalized) must be adjusted accordingly. It may be noted that changes in wind speed affect the location of the air parcel, the corresponding emission density, and the length of time spent traversing an area; however, changes in wind speed do not affect the mass per unit time added to the air parcel due to emissions from a given area. That is, if the air parcel remains for an hour over an area with a given average emission rate, the total mass added to the air parcel is independent of the wind speed. Thus the kinetics model requires only normalized relative emission rates and the mixing height data used in determining dilution rate to calculate the rates of concentration addition appropriate for simulating post-8 a.m. emissions.

Table B-3
 Derivation of Sample Values for Relative Emission Rates

Time (LDT)	Spatial Adjustment	Percent of Day's Emissions	Composite Relative Emission Rate	Normalized Relative Emission Rate*
12 - 8 a.m.	1.0	16.9%	16.5%	100%
8 - 9 a.m.	.95	6.4	6.1%	36%
9 - 10 a.m.	.61	4.4%	2.7%	16%
10 - 11 a.m.	.25	4.8%	1.2%	7%
after 11 a.m.	negligible	-----	negligible	negligible

$$\left. \begin{array}{l} 16.5\% \\ 6.1\% \\ 2.7\% \\ 1.2\% \end{array} \right\} \times \frac{100\%}{16.9\%} = \left. \begin{array}{l} 100\% \\ 36\% \\ 16\% \\ 7\% \end{array} \right\}$$

*The composite relative emission rate normalized relative to the 8 a.m. composite rate.

B.2.4 Transported Ozone Concentrations

Section 3.1 discusses the transport of ozone in two atmospheric layers, viz. transport in a layer near the ground and transport aloft. Section 3.2 discusses means of estimating the ozone concentrations transported into a city in these two layers. Ideally, one should have measurements of the transported ozone concentration at several heights. However, ground-level measurements are generally the only available data. The best ground-level measurements for indicating ozone concentrations transported aloft are generally upwind measurements taken in the late morning and early afternoon, after mixing has extended well above the morning mixed layer. Therefore, unless better information is available, the ozone concentration transported aloft into the urban area for the current situation should generally be assumed to equal the upwind ground level measurements between 11 a.m. and 1 p.m. LDT.

Ozone transported in the surface layer in the early morning is generally much less significant than ozone transported aloft. Scavenging may at times significantly reduce ozone concentrations transported in the surface layer. Furthermore, a kinetics model analysis⁵ suggests that even high ozone concentrations transported in the surface layer have little effect on the peak ozone concentration in the afternoon. Nevertheless, if information is available on the current ozone concentrations transported in the surface layer early in the morning, e.g. if upwind measurements are available between 6-9 a.m., this information may be considered. Substantially similar results should be obtained using any reasonable assumption, for example, that the ozone concentration transported in the surface layer equals the concentration transported aloft.

When ozone isopleths representing future conditions are being generated, it is necessary to estimate the corresponding transported ozone concentrations. When an isopleth for the NAAQS for oxidants is being generated, it is reasonable

to assume that upwind cities are also meeting the NAAQS. Therefore, for this case, the ozone concentration transported aloft can be assumed to be generally close to the natural background concentration but in some cases as high as 0.08 ppm. An examination of the ozone concentrations found in isolated areas suggests that natural ozone concentrations are approximately 0.03 - 0.05 ppm, with 0.04 ppm. most likely.⁵ Thus, in deriving the isopleth for $O_3 = 0.08$ ppm, the ozone concentration transported aloft should normally be assumed to be 0.04 ppm but may be assumed to be as high as 0.08 ppm. The relationship between the ozone concentration transported in the surface layer and the ozone concentration transported aloft should be similar to the relationship used in simulating current conditions.

B.2.5 Other Variables

The discussion of pollutant transport in this Appendix has focused exclusively on the transport of ozone. If data are available to indicate both current and future transported precursor concentrations, these data may also be considered. However, consideration of precursor transport is not considered essential for several reasons. First, transported precursor concentrations, particularly NO_x concentrations, tend to be significantly below the concentrations attributable to an urban area.⁵ Second, due to rapid reactions of the more reactive hydrocarbon species, the mix of transported organic species is likely to be less reactive than an urban emissions mix. Third, transport of precursors from an upwind city decreases as the upwind city controls its emissions. To the extent these reductions parallel the emissions reductions of the city under review, precursor transport has little if any impact on the relative effect of local emission reductions.

In order to assess the potential impact of precursor transport, a kinetics model analysis of transport⁵ considered the impact of precursor transport on a hypothetical city located within 40 kilometers of St. Louis. This was assumed to represent a worst case example of transported precursors. Simulations were conducted based on two different assumptions: (1) the concentrations transported aloft were equal to those transported at ground level, and (2) the concentrations aloft were minimal. These simulations suggested that the impact of transported precursors is usually less than the impact of transported ozone. Thus for any reasonable assumption about future transported precursor concentrations, consideration of precursor transport is likely to have only minimal effect on estimated emission control requirements. If data on precursor transport are available, these data may be considered. However, in the absence of these data, the failure to consider precursor transport in most cases should not greatly affect the estimated impact of local emission reductions.

In general, consideration of other variables is not specifically recommended, either because consideration of the variable is likely to have little, if any, effect on the estimated peak ozone concentrations or because it is difficult to quantify the variable. One such variable is the initial NO_2/NO_x ratio. The standard isopleths presented in Section 2.2.1a are based on the assumption that NO_2 is 25% of NO_x . Ground level transport of ozone is likely to be the most significant factor affecting the initial NO_2/NO_x mix, but the kinetics model analysis⁵ has suggested that the effect on peak ozone concentrations is small. Other factors that affect the initial NO_2/NO_x mix are likely to have less effect on this mix and negligible effect on peak ozone concentrations, as shown by Dodge.⁶

Consideration of reactivity is not recommended, due to the serious difficulties involved in determining an appropriate hydrocarbon mix. These difficulties stem both from the limited knowledge about the mixes of hydrocarbons that exist in urban areas and from the uncertainties about how to represent these mixes in the kinetics model. In particular, there are generally no data available--either through measurement or through estimation using an emissions inventory--on what mix of paraffins, olefins, aldehydes and aromatics can be expected in individual urban areas. Even in cases where the data are available, the kinetics model cannot directly use the data. The kinetics model is based on a detailed chemical mechanism using two hydrocarbon species, specifically n-butane and propylene. Unfortunately, there is very little information with which to specify what butane-propylene mix should be used to simulate different atmospheric hydrocarbon mixes. The only atmospheric mix for which a corresponding butane-propylene mix has been established is the automotive mix used in the Bureau of Mines smog chamber, which is best represented with a 75% butane-25% propylene mix. Unless correspondence between other atmospheric and kinetics model mixes can be established, the 75% butane-25% propylene mix should ordinarily be used in generating city isopleths.

Consideration of transported aldehydes or variations in the initial aldehyde mix is also not recommended. The standard isopleths assume that formaldehyde represents 2% and acetaldehyde represents 3% of the total initial nonmethane hydrocarbon concentration (all in ppmC). In some situations, these proportions might be slightly higher. However, consideration of these variables is likely to have little effect on peak ozone concentrations.⁵ In addition, aldehydes are difficult to measure reliably. Therefore, unless contrary

information is available, the assumptions about aldehyde concentrations used in deriving the standard isopleths should be used.

B.3 Summary

This appendix has outlined the data requirements necessary to generate city-specific isopleths. In particular, various assumptions and potential sources of data have been discussed for determining light intensity, dilution rate, relative emissions rates, and transported pollutant concentrations. Once the appropriate data are obtained, the kinetics model described by Whitten and Hogo² may then be used to generate city-specific isopleths. These city-specific isopleths may then be used to estimate emission control requirements and the benefits of given levels of emission reduction as discussed in Sections 2 and 3.

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TECHNICAL REPORT DATA

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15 SUPPLEMENTARY NOTES

16. ABSTRACT

Approaches for relating ozone to non-methane hydrocarbon and oxides of nitrogen controls are discussed. All procedures are only applicable in addressing the oxidant problem in urban areas. Available procedures include use of Eulerian and Lagrangian photochemical dispersion models, a new approach called the Empirical Kinetic Modeling Approach (EKMA), proportional rollback and statistical approaches. EKMA, rollback and statistical models are most useful in estimating the degree of reduction needed to attain the National Ambient Air Quality Standard (NAAQS) for oxidant and for estimating reduction in maximum hourly ozone concentration accompanying specified levels of precursor controls. Models are useful for these purposes as well as others. The issue of long range transport of ozone/precursors is discussed. It is concluded that ozone transported above the surface-based nocturnal inversion layer is likely to be the facet of transport exhibiting the greatest impact on maximum ozone levels in urban areas. Procedures for integrating transport considerations into the previously mentioned analytical approaches are discussed.

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12 April 1978

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been estimated using this rather subjective procedure, the second high hourly ozone concentration observed during the base period should be adjusted downward in accordance with the following formula.

$$(O_3)_{ADJ} = (O_3)_{design} - A (T_o) \quad (5)$$

where $(O_3)_{ADJ}$ is the adjusted (reduced) ozone concentration to be used in estimating control requirements;

$(O_3)_{design}$ is the 2d high hourly ozone concentration observed during the base period.

A is the additivity factor for transported ozone.

T_o is the concentration of transported ozone estimated for the base period. T_o consists of both manmade and natural ozone.

Controls required to attain a specified air quality goal may be estimated with rollback using Equation (6).

$$R = \frac{[(O_3)_{ADJ} - x']}{[(O_3)_{ADJ}]} \quad (6)$$

x' is an air quality goal; x' is the impact attributable to local sources which will insure the NAAQS is attained. Hence x' is the NAAQS itself minus whatever the impact of transported ozone is in the future $[A(T_f)]$.

$$x' = .08 \text{ ppm} - A(T_f) \quad (7)$$

T_f may be assumed to be .08 ppm or less. In the examples herein it is assumed to approach natural background (i.e., approximately .04 ppm).

Example

Given: Design Value for $O_3 = .28$ ppm. Present transported ozone is estimated to be .12 ppm. It is assumed that upwind controls will reduce future levels of transport to .04 ppm.

Find: Amount of reduction of local organic precursors needed to reduce the 2d high hourly ozone concentration to .08 ppm.

Solution:

(1) Since nothing is given about any of the factors influencing additivity, assume a value of $A = .45$ (i.e., the middle of the observed range of values).

(2) From Equation (5),

$$[O_3]_{ADJ} = .28 - (.45)(.12)$$

$$[O_3]_{ADJ} = .23 \text{ ppm.}$$

(3) Using Equations (6) and (7), the required reduction is

$$R = \frac{.23 - [.08 - (.45)(.04)]}{.23} = .74 \text{ or } 74\%$$

Note that in accordance with Table 3, the value of "A" in the denominator in Equation (6) should probably be somewhat higher than ".45." As will be illustrated in the next section, however, this is probably an unnecessary refinement in cities presently experiencing a serious oxidant problem.

Using the standard isopleth version of EKMA, transport is considered by first reducing the ozone design value in accordance with Equation (5). Control requirements are estimated by entering the isopleth diagram (such as the one shown in Figure 12) at the intersection of the $[O_3]_{ADJ}$ isopleth and the prevailing NMHC/NO_x ratio line. Control requirements needed to attain the standard are calculated by estimating the reductions needed to reach the isopleth which is $.08 - A(T_f)$. For example, if the additivity of transported ozone were .45 and future transported ozone approached the natural background value of .04 ppm, control

requirements would be estimated by NMHC and/or NO_x reductions needed to reach the .06 ppm isopleth.

As previously discussed, transport can not be accounted for as readily with the standard isopleths or with rollback as it can using models or the city-specific version of EKMA. It is not possible to readily account for the impact of transported precursors using the standard isopleths or rollback. Neither is it possible to account for the role of other changes, such as changes in diurnal emission patterns, using these procedures.

3.4 Data Limitations and Resulting Consequences

Section 3.0 has described what appears to be the role of transport in the urban ozone problem. Procedures for incorporating transport into the methods presented in Section 2.0 have also been described. However, when attempts were made to use existing air quality data to estimate transported ozone, difficulties were frequently encountered.³ These difficulties arose principally because of the lack of upwind data or inappropriate siting of upwind instruments. Such problems are understandable, since the primary purpose of existing monitors is seldom to obtain an estimate of representative ozone concentrations entering a city. Therefore, it may not always be feasible to incorporate transport considerations until monitoring programs have been developed. Hence it is pertinent to examine how ignoring transport might affect estimated control requirements. There are two situations which should be considered. The first occurs if transported ozone concentrations remain unaltered. If this situation prevails, ignoring transport will likely cause one