United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S3-82-015 May 1982

EPA

Project Summary

Validation of the EKMA Model Using Historical Air Quality Data

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Historical air quality data were used to study the validity of the Empirical Kinetic Modeling Approach (EKMA) model for relating ozone concentrations to precursor control, as a method for evaluating ozone control strategies. Using both emission and ambient air pollution data from the Los Angeles Basin for 1964 to 1978, trends in the ozone precursors nonmethane hydrocarbons (NMHC) and nitrogen oxides (NO_x) were estimated. The estimated trends were entered into the EKMA model to predict historical ozone trends; the results were then compared with actual ozone trends documented from measurements to test the EKMA model. Emission trend calculations showed continual decrease (net reduction of 29%) in basinwide hydrocarbon emissions during the period studied. Basinwide NO_x emissions rose rapidly from 1965 to 1973 and then leveled off, showing a net increase of 34% over the entire period studied. Ambient ozone precursor trends agreed well with the emission trend estimates. Sensitivity analyses indicated that predicted ozone trends were moderately sensitive to the specific EKMA simulation conditions and were extremely sensitive to the NMHC/NO_x ratio. The EKMA validation studies comparing predicted with actual ozone trends showed that the two trends agreed within the error bound designated. However, predicted ozone trends generally underestimated decreases in actual ozone trends. Errors in the estimated precursor trends, or in the meteorological fluctuations in the actual ozone trends, or in the sensitivity to varied EKMA simulation conditions did not account for this discrepancy; it apparently resulted from error in the NMHC/NO_x ratio. The study indicates the importance of accurately estimating the NMHC/NO_x ratio, as well as using the most realistic area-specific EKMA simulation conditions (e.g., inclusion of post-8 a.m. emissions). Further research is recommended to test the EKMA chemical-kinetic mechanism and to check the equivalency of the ambient and the EKMA NMHC/NO_x ratios.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Empirical Kinetic Modeling Approach (EKMA) has recently been proposed by the U.S. Environmental Protection Agency (EPA) as a method for evaluating ozone control strategies. To be accepted as a reliable technique for control strategy analysis, it should be subjected to validation studies. This study tested the EKMA method using historical-trend data for the Los Angeles area. Specifically, trends in the ozone precursors nonmethane hydrocarbons (NMHC) and nitrogen oxides (NO_x) were estimated from emissions and ambient air pollution data for the period 1964 to 1978. These precursor trends were entered into the EKMA model to predict historical ozone trends; the predicted ozone trends were then compared to actual ozone trends to test the EKMA method.

This study showed that analysis of historical-trend data from Los Angeles is an appropriate and useful way of validating the EKMA method. Historical trend analysis also provides a very convenient format for illustrating the sensitivity of EKMA to various inputs, such as the NMHC/NO_x ratio and the choice of specific photochemical-simulation conditions. However, the historical-trend data also have intrinsic interest. By analyzing precursor emission trends in detail, emissions for individual source categories were shown to have changed due to controls and source growth, and how total emissions have changed as a net response to trends for individual source categories. By examining trends in ambient precursor data, emission trend estimates were checked and it was verified that control programs and source growth had the anticipated effects. By analyzing historical ozone trends, investigations showed whether the ozone trends relate rationally to precursor changes and meteorological fluctuations. Thus, the study was useful for validating EKMA and for understanding the air quality effects actually being produced by on-going control programs in Los Angeles.

Based on historical-trend data the Los Angeles region is uniquely excellent for EKMA validation studies. Only Los Angeles can provide nearly two decades of high-quality, spatially-resolved, long-term trend data for ambient concentrations of ozone, hydrocarbons, and NO_x. Although independent data sets regarding the NMHC/NO_x ratio are available from several monitoring programs, the quality of the Los Angeles data for emission-trend analysis is unexcelled. The area has unusually good information regarding existing emission levels, source growth rates, and source control levels. Furthermore, substantial changes in historical precursor levels are required to adequately test EKMA, knowing that Los Angeles has undergone significant decreases in hydrocarbons and increases in NO_x since the middle 1960s. Finally, the severe photochemical smog problem in Los Angeles and the current controversy over the recent lack of air quality improvement enhance the interest of a study in that area.

The EKMA validation studies conducted herein examined the time period 1964 to 1978. To provide robust (statistically stable) data sets for the analysis, 3-year averages (1964-1966, 1967-1969, 1970-1972, 1973-1975, and 1976-1978) of air quality data were used, with 1964-1966 serving as the base period. To test the EKMA model, predicted ozone trends were compared to actual ozone trends for each subsequent 3-year interval.

This study uses four basic data sets: information of the 6 a.m. to 9 a.m. ambient NMHC/NO_x ratio, estimates of historical emission trends, ambient precursor trend data, and ozone trend data. The base period (1964-1966) 6 a.m. to 9 a.m. NMHC/NO_x ratio was determined by examining ambient data for several early seventies monitoring programs and by extrapolating the results back to 1964-1966 based on historical precursor trends. Historical trends in NMHC and NO_x emissions were documented through a new and comprehensive analysis of all major source categories. Ambient precursor trends were examined at 9 sites for NMHC, 10 sites for NO_x, and ambient ozone trend data from 13 sites. The ambient data for NMHC, and NO_x, and ozone were subjected to several correction and adjustment procedures (discussed herein) to ensure consistent data suitable for trend analyses.

The basinwide EKMA isopleth model (based on the maximum ozone during a 10-hour irradiation) was tested against historical trends for the yearly basinwide 1-hour ozone maximum. To provide greater generality in validating the isopleth approach and to increase the number of test cases, four individual sites for analysis were chosen: Azusa, Downtown Los Angeles (DOLA), Anaheim, and San Bernardino. The validation studies at these four sites were conducted using EKMA isopleths specific to the time of maximal ozone occurrence at the locations. Two ozone air quality indices, yearly maximum 1-hour concentration and 95th percentile of daily maximum concentrations, were used at each of the four sites.

Conclusions

The objectives of this study were (1) to characterize historical precursor trends in the Los Angeles region using both emissions data and ambient data; (2) to document historical ozone trends; (3) to investigate the sensitivity of EKMA predictions to the NMHC/NO_x ratio and to the choice of specific simulation conditions; and (4) to test the EKMA isopleth model by comparing predictions of historical ozone trends with actual ozone trends. The following subsections summarize our findings and conclusions with respect to each of the above four objectives.

Historical Precursor Trends

Estimated basinwide emissions of hydrocarbons decreased continually during the study period, with a net reduction of 29% from 1965 to 1977. This reduction was predominantly due to decreases in emissions from light-duty vehicles (the largest source category). Light-duty vehicle hydrocarbon emissions decreased 40% from 1965 to 1977 despite a 54% increase in traffic levels. Organic solvent emissions also significantly (30%) decreased, with this reduction basically occurring between 1965 and 1974.

Estimated basinwide NO_x emissions rose rapidly from 1965 to 1973 and then essentially leveled off. The net increase over the entire study period, 1965 to 1977, was 34%. This rise was predominantly due to a 55% increase in NO_x emissions from light-duty vehicles, again the largest source category. The net increase in NO_x from light-duty vehicles from 1965 to 1977 basically represented traffic growth. Light-duty vehicle NO_x emission factors for new cars increased sharply in the late 1960s, but by 1977 the fleet-averaged NO_x emission factor was reduced to the 1965 level due to the new car NO_x emission standards of the 1970s. NO_x emissions from heavy-duty vehicles and from residential, commercial, and industrial fuel burning also increased significantly from 1965 to 1977, reflecting growth in traffic and natural gas usage, respectively. Power plant NO_x emissions decreased slightly from 1965 to 1977.

Emission trends differ among the various individual source areas affecting the four ozone study sites, reflecting differences in growth rates and source types within those areas. Comparing estimated emission trends with ambient precursor trends for each source area, we found very good agreement, especially when viewing the data overall from 1965 to 1977. In light of this agreement, we can state with a high degree of confidence that there was a moderate (15 to 30%) reduction in hydrocarbons and a moderate (25 to 35%) increase in NO_x within the Los Angeles Basin from 1965 to 1977.

Historical Ozone Trends

For the EKMA validation studies, using an air quality index that represents high ozone days but has a low year-to-year meteorological variance is desirable. Unfortunately, a trade-off exists in that the indices which represent the highest ozone days tend to be the least robust indices. A satisfactory compromise is the index "95th percentile of daily maximal 1-hour ozone," which was used for the four study sites. To represent worst-case conditions, the index "yearly maximum 1-hour ozone" was used at the four study sites and for a basinwide analysis.

Various adjustments and corrections were applied to the historical ozone and oxidant data base in the Los Angeles area to ensure consistent data for trend analysis. Fortunately, a single monitoring technique was used during the entire period studied at all but one of the four study sites. Thus, ozone trends at these study sites required relatively few adjustments and corrections.

Ozone concentrations at Azusa, DOLA, and Anaheim decreased from the middle 1960s to the early to middle 1970s and then leveled off. All sites in Los Angeles exhibited this historical pattern in ozone trends, except those in the extreme eastern parts of the basin where, as at San Bernardino, ozone increased at a very slight rate during the entire study period.

Selection of Specific Conditions for EKMA Validation

One critical input to the EKMA isopleth model is the base period ambient 6 a.m. to 9 a.m. $NMHC/NO_x$ ratio, and the best estimate for the 1964-1966 base period in Los Angeles was 13:1. This estimate was derived by examining data from several monitoring programs during the early 1970s, and by extrapolating back to 1964-1966 based on historical trends in ambient precursor levels. To make both atmospheric and EKMA NMHC concentrations more nearly equivalent, the ambient NMHC data were adjusted to correspond to measurements made with propane calibration. The contributions from the nearly nonreactive compounds ethane and propane were also subtracted from the ambient NMHC data. Because of discrepancies concerning the $NMHC/NO_x$ ratio among various monitoring programs, there was considerable potential for error in our estimate of the $NMHC/NO_x$ ratio. In sensitivity studies, we considered a range of the ratio from 7:1 to 25:1.

The EKMA simulation conditions chosen for this study were standard except for including post-8 a.m. emissions and using a special dilution pattern. For the studies at individual monitoring sites, isopleths that represented ozone at fixed irradiation times rather than maximum ozone over the entire irradiation period were also useful. A sensitivity analysis using six types of EKMA isopleths indicated that predicted ozone trends were moderately sensitive to the specific simulation conditions. In particular, adding post-8 a.m. emissions to the model significantly improved the agreement between predicted and actual ozone trends in Los Angeles.

For the specific EKMA simulation conditions that were used, and for the type of historical precursor changes that were examined (decreasing NMHC with increasing NO_x), predicted ozone trends were extremely sensitive to the base period $NMHC/NO_x$ ratio. Potential errors in the $NMHC/NO_x$ ratio alone obviously could account for any discrepancy between predicted and actual ozone trends. Bearing this conclusion in mind, the EKMA validation studies were studied under stringent test conditions which did not allow for potential errors in the $NMHC/NO_x$ ratio.

Validation of the EKMA Isopleth Method

In the validation studies, historical precursor trends of either emission or ambient precursor trends and the EKMA isopleth model were used to predict historical ozone trends. These predicted ozone trends were then compared to actual ozone trends. Error bars representing the error in historical precursor trends were included on the predicted ozone trends; error bars representing meteorological fluctuations were included on the actual ozone trends. The validation studies were conducted for basinwide maximum ozone as well as for two ozone air quality indices (yearly maximum 1-hour concentration and 95th percentile of daily maximum concentrations) at the four individual study sites.

The results of the EKMA validation studies were nearly the same whether one uses emission trends or ambient precursor trends to derive predicted ozone trends. In both cases, the validation study results were not poor considering the stringent test conditions which did not include potential errors in the $NMHC/NO_x$ ratio. For most sites and years, the predicted and actual ozone trends agree within the error bars representing both variance in precursor trends and meteorological fluctuations in ozone trends. However, predicted ozone trends generally underestimated decreases in actual ozone trends at all sites except San Bernardino, and the discrepancy was rather large for certain sites and years.

Three possible explanations for the observed discrepancy that predicted ozone levels which tended to underestimate historical improvements in actual ozone levels were rejected. The cause was not errors in the historical precursor trends, because the precursor trends error bars were small, and because the precursor trends were confirmed by two independent data bases (emissions data and ambient data). Studies of met-adjusted ozone (i.e., data adjusted for influences of varying meteorology) strongly suggest that the discrepancy was also not due to meteorological fluctuations in actual ozone trends. Also, further refining EKMA simulation conditions (improved dilution patterns, improved estimates of post-8 a.m. emissions, addition of carry-over ozone) will probably not eliminate the discrepancy because our predicted ozone trends were not sensitive enough to changes in the simulation conditions.

The obvious factor that can account for observed discrepancies between predicted and actual ozone trends is error in the $NMHC/NO_x$ ratio. Using a 10:1 ratio rather than a 13:1 ratio eliminates all of the discrepancies. There are two ways to account for error in the $NMHC/NO_x$ ratio. First, we could have a random error in our estimate of the ratio, which would not necessarily recur when applying EKMA to other areas. Second, there could be a systematic error in the EKMA chemical-kinetic mechanism or in matching sthe atmospheric $NMHC/NO_x$ ratio with the EKMA

$NMHC/NO_x$ ratios, which might improve the EKMA mechanisms or the guidelines for adjusting atmospheric $NMHC/NO_x$ ratios before use in EKMA.

This study has pointed out two potentially significant sensitivities of the EKMA isopleth method. The predictions of EKMA can be moderately sensitive to the $NMHC/NO_x$ ratio, and thus, in some applications, it may be important to ensure that the most realistic, area-specific EKMA simulation conditions are used. Also, accurately estimating the EKMA-equivalent $NMHC/NO_x$ ratio is important. Predictions of future ozone trends will likely be less sensitive to both the simulation conditions and to the $NMHC/NO_x$ ratio, because future emission reductions are likely in both NMHC and NO_x, and because the predictions of EKMA are much less sensitive to the simulation conditions and the $NMHC/NO_x$ ratio when both precursors undergo similar changes.

As a postscript to this study, the controversial lack of improvement in Los Angeles ozone air quality since the middle 1970s was studied. Several possible explanations for this apparent lack of improvement were considered: source growth, failure of catalytic converters, meteorological fluctuations, reversal in the historical trend of a decreasing $NMHC/NO_x$ ratio, and overall failure of control programs. Source growth and catalyst failures were not reasonable explanations considering available data. Other potential explanations seemed reasonable to a degree, but each also appeared to contradict certain observations. We recommend taking new data and conducting further analyses to resolve this controversy.

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***Basil Dimitriades** is the EPA Project Officer (see below).*

The complete report, entitled "Validation of the EKMA Model Using Historical Air Quality Data," (Order No. PB 82-197 187; Cost: $13.50, subject to change) will be available only from:

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☆ U S GOVERNMENT PRINTING OFFICE, 1982 — 559-017/0727