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Project Summary

Effects of Photochemical Kinetic Mechanisms on Oxidant Model Predictions

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The comparative effects of kinetic mechanisms on oxidant model predictions have been tested using the Carbon-Bond Mechanism II (CBM-II) and the Demerjian Photochemical Box Model (DPBM) mechanism, in conjunction with three air quality models, the OZIPM/EKMA, the Urban Airshed Model (UAM), and a trajectory model with the same inputs and chemistry as the UAM. Simulations were performed for the Los Angeles Airshed using a 1974 base case and a 1987 emission inventory (reflecting controls).

To achieve agreement in absolute predictions among the three models, it was necessary to treat two significant processes in the OZIPM/EKMA simulations: surface deposition and the photochemical reaction of material aloft before entrainment by the growing mixed layer. These two processes are not normally modeled in OZIPM/EKMA and could be treated only in a general, averaged fashion. With this treatment, however, results for the three models were within 25 percent overall agreement, and within 10 percent agreement for the peak value when the same kinetic mechanism was used.

The two kinetic mechanisms produced different results. Although the DPBM mechanism produced results similar to those for the CBM-II with the 1974 base case for all three models, it exhibited a greater response to the 1987 control scenario (predicting less ozone). In simulations employing the CBM-II, the ozone reductions predicted using the 1987 emission inventory were 31, 34, and 33 percent for the UAM, trajectory model, and OZIPM/EKMA, respectively. The ozone reductions predicted by the UAM trajectory model and OZIPM/EKMA for the 1987 inventory simulations employing the DPBM were 41, 51, and 53 percent, respectively. Also, reduction of peak ozone anywhere in the UAM simulation grid was 26 percent for the CBM-II/Airshed simulations and 40 percent for the DPBM/Airshed simulations.

The greater response to hydrocarbon control exhibited by the DPBM mechanism compared to that of the CBM-II is contrary to the findings of Jeffries et al. (1981), which indicated a greater response to control for the CBM-II than for the DPBM. However, Jeffries et al. examined uniform control of hydrocarbons, whereas the 1987 emission inventory used in this study included the effects of population growth and differing controls on various source categories. These factors resulted in a shift in hydrocarbon speciation, most notably a decrease in olefins relative to other hydrocarbons. The DPBM demonstrated an overresponse to the olefin component of the hydrocarbon mix. Thus, the difference in the models' response to the control strategy was traced to a specific feature of the DPBM mechanism.

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

A long-term goal of EPA's research program is the development of urban and regional air quality simulation models (AQSMs) to be used in planning accurate and scientifically defensible control strategies. Because the pollutants with the greatest impacts on human health are secondary pollutants formed by chemical reactions occurring in the atmosphere, an understanding of the chemistry that produces these pollutants is critical to the development of AQSMs. In recent years, significant efforts have been made to explain the chemical transformations that occur in photochemical smog systems and to develop chemical kinetic mechanisms that can be used in the AQSMs to explain the formation of ozone and other secondary pollutants. However, comparisons among the various chemical kinetic mechanisms that have been developed for air quality analysis reveal significant differences in performance. Furthermore, different AQSMs frequently give dissimilar predictions, even when the same kinetic mechanism is used.

It would be useful to be able to determine the reasons for discrepancies in AQSM results, i.e., to have procedures for ascribing these reasons to specific portions of the AQSM such as the kinetic mechanism, the model formulation and assumptions, or the data base inputs. The intent of the project reported here was to develop a procedure for analyzing the comparative effects of chemical kinetic mechanisms used in various AQSMs.

Procedure

Three models were selected to test the effects of kinetic mechanism substitution on control strategy assessment: OZIPM/EKMA, which accepts the kinetic mechanism as an input; the Urban Airshed Model (UAM), in which the kinetic mechanism is a module that must be recoded when the substitution is made; and the Airshed Compatible Trajectory Model (ACTM), which uses the same kinetic module as the UAM. The UAM and ACTM already contain the Carbon-Bond II Kinetic Mechanism (CBM-II) and an extensive validation base exists for both these models. Additionally, the CBM-II has been independently validated using laboratory smog chamber data sets for both indoor and outdoor smog chambers. Included in the CBM-II validation set was the Bureau of Mines (BOM) data base used in the calibration and validation of the Dodge/EKMA mechanism.

The Demerjian Photochemical Box Model (DPBM) mechanism was chosen for comparison with CBM-II. The DPBM is a multispecies lumped molecular mechanism that has also been validated with the BOM data set. Both its BOM data validation and its compactness make the DPBM Mechanism a logical candidate for comparison with the CBM-II in UAM simulations.

Intermodel comparisons were planned along a high ozone trajectory in Los Angeles for which an extensive UAM data base and numerous control strategy scenarios already exist. A good match of predictions between the UAM and the ACTM along the trajectory was easily obtained since emission inputs, vertical dispersion, and chemical kinetics are identical for the two models, and since factors that would produce discrepancies (such as a high degree of wind sheer) were absent on this simulation day. To obtain a match of OZIPM/EMKA with the UAM and ACTM, however, two phenomena not usually treated in OZIPM/EKMA had to be considered: (1) Reaction of precursor material aloft, which must be considered if the chemical process is not to be retarded by entrainment of unreacted material, was simulated by entraining the average of material as predicted by the ACTM; (2) surface deposition in OZIPM/EKMA was included as a first-order loss process for O_3 and NO_2.

Results

With these modifications to OZIPM/EKMA, good matches were achieved for both the 1974 base case and 1987 control scenario (Figures 1 and 2) among all three models for both kinetic mechanisms. Also, UAM predictions using the DPBM were similar to results obtained with the CBM-II (Figure 3). However, predictions obtained for the 1987 control scenario tended to show a substantially greater reduction in ozone with the DPBM mechanism compared to that predicted with the CBM-II (see Table 1).

Intermodel comparisons using the same mechanism revealed similar ozone reductions with the CBM-II, whereas the UAM with the DPBM predicted somewhat less ozone reduction than the ACTM and OZIPM/EKMA with either mechanism. Reduction of peak ozone predicted anywhere in the UAM grid was less than the trajectory-specific reductions.

The greater response to hydrocarbon control exhibited by the DPBM mechanism compared to that of the CBM-II is contrary to the results of Jeffries et al. (1981), who found that the CBM-II predicted greater response to control than the DPBM. However, Jeffries et al. examined uniform control of hydrocarbons, whereas the 1987 emissions inventory used in this study was a realistic control scenario that included both the effects of population growth and different de-

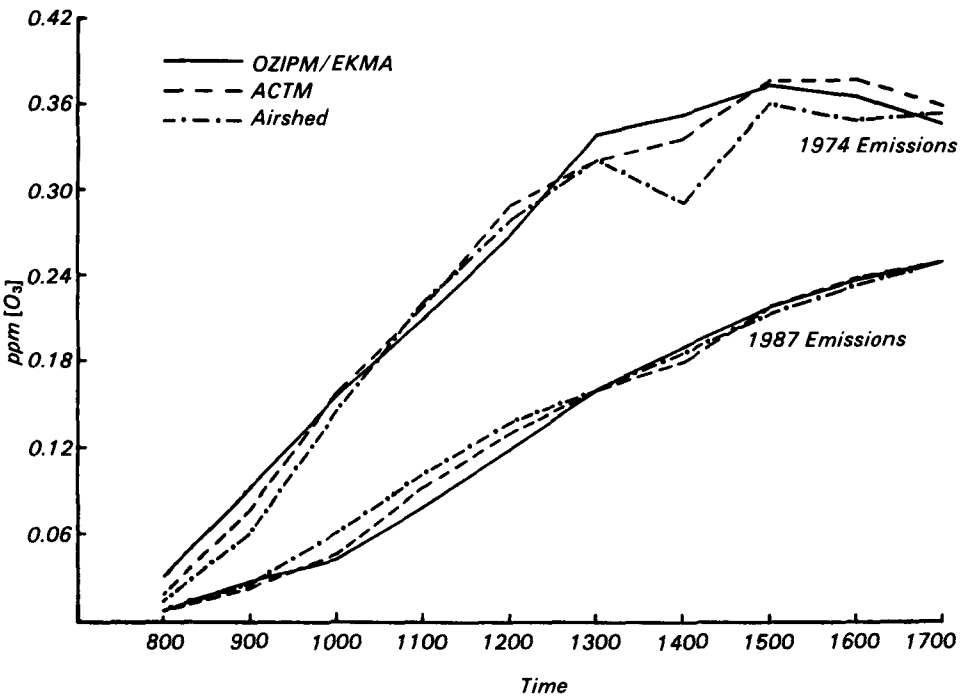

Figure 1. Comparison of model results for the CBM-II simulations.

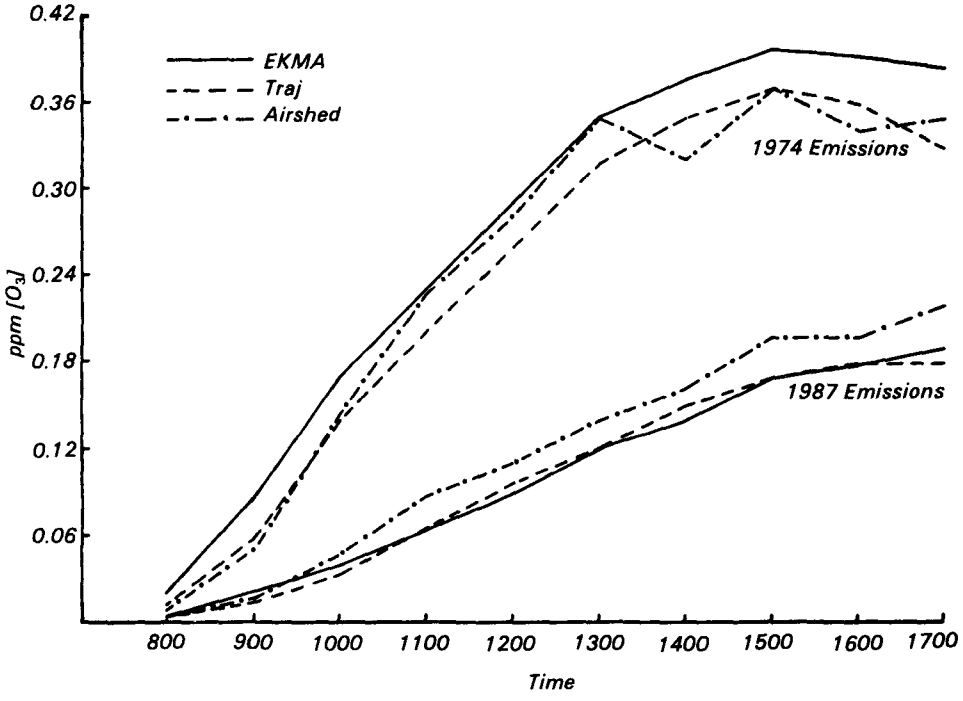

Figure 2. *Comparison of the model results for the DPBM mechanism simulations.*

grees of control on various emission source categories. These factors resulted in a shift in hydrocarbon speciation, including a reduction in the olefin fraction.

The greater reduction of ozone predicted by the DPBM mechanism is attributed to the greater sensitivity of this mechanism to olefinic hydrocarbons. In tests using the DPBM mechanism to simulate smog chamber experiments, the mechanism was shown to overpredict the reactivity of olefins. Correction of this error in the DPBM would probably result in closer agreement between the performance of the two mechanisms.

References

Jeffries, H. E., K. G. Sexton, and C. H. Salmi (1981), "Effects of Chemistry and Meteorology on Ozone Control Calculations Using Simple Trajectory Models and the EKMA Procedure," EPA-450/4-81-034, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

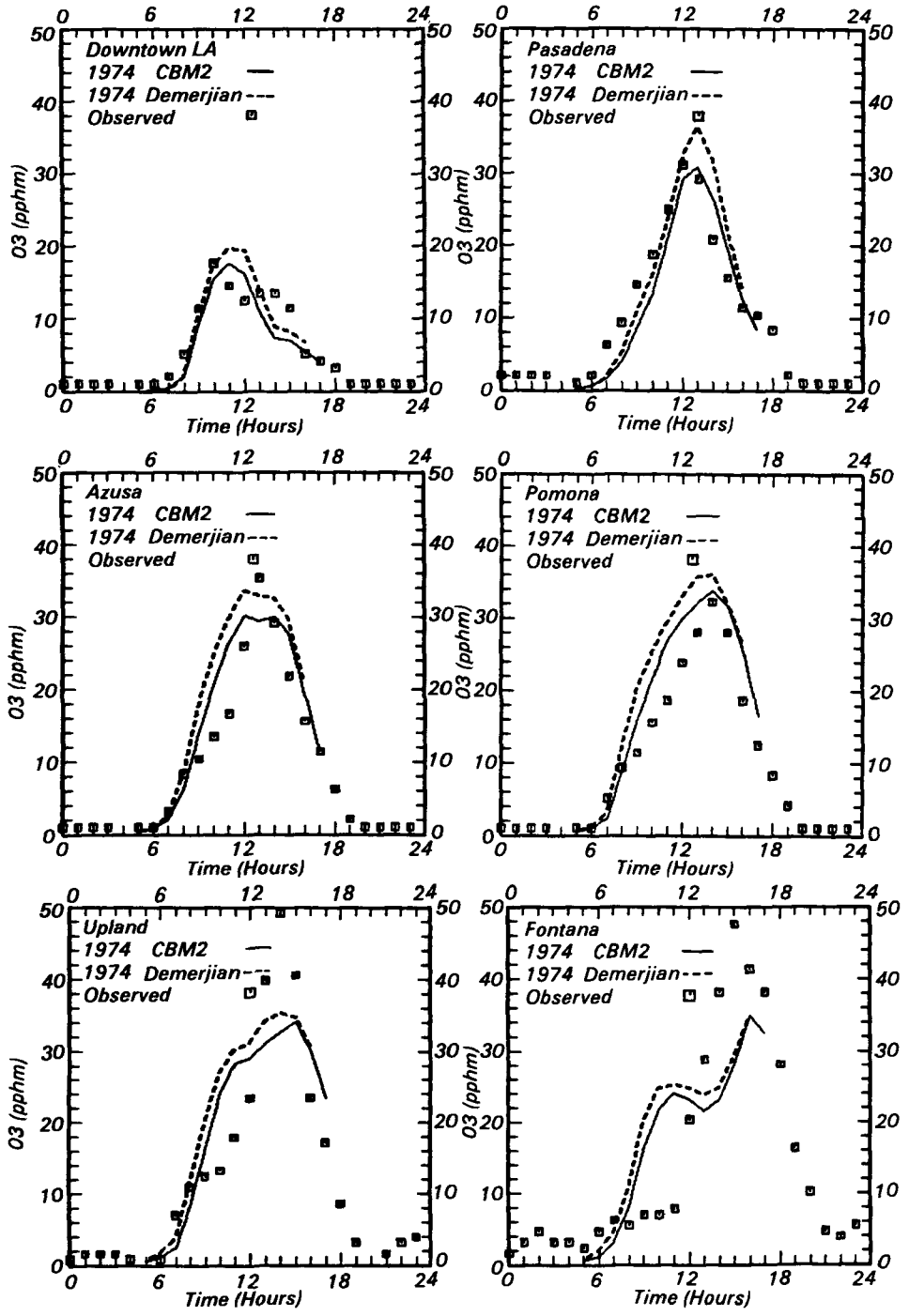

Figure 3. *Comparison of O_3 results for Los Angeles, June 1974, (Airshed base case) for the DPBM mechanism and CMB-II.*

Table 1. *Effect of Controls on ACTM, Airshed, and OZIPM/EKMA Model Predictions for the Fontana Trajectory*

(a) Carbon-Bond Mechanism

	1974 Ozone Prediction (ppm)			1987 Ozone Prediction (ppm)			1987/1974 Ratio			Percent O_3 Reduction		
Time	ACTM	Airshed	OZIPM/ EKMA	ACTM	Airshed	OZIPM	ACTM	Airshed	OZIPM/ EKMA	ACTM	Airshed	OZIPM/ EKMA
1500	0.376	0.36	0.375	0.22	0.21	0.22	0.59	0.58	0.59	41	42	41
1600	0.376	0.35	0.367	0.24	0.234	0.24	0.64	0.67	0.65	36	33	35
1700	0.36	0.36	0.36	0.25	0.25	0.25	0.69	0.69	0.69	31	31	31
Peak trajectory value	0.376	0.36	0.375	0.25	0.25	0.25	0.66	0.69	0.66	34	31	33
Peak value anywhere in Airshed grid		0.39 (at 1700 near Fontana)			0.29 (at 1700 near Fontana)			0.74			26	

(b) DPBM Mechanism

	1974 Ozone Prediction (ppm)			1987 Ozone Prediction (ppm)			1987/1974 Ratio			Percent O_3 Reduction		
Time	ACTM	Airshed	OZIPM/ EKMA	ACTM	Airshed	OZIPM/ EKMA	ACTM	Airshed	OZIPM	ACTM	Airshed	OZIPM/ EKMA
1500	0.37	0.37	0.40	0.17	0.20	0.17	0.46	0.54	0.42	54	46	58
1600	0.36	0.34	0.40	0.18	0.20	0.18	0.30	0.59	0.45	50	41	55
1700	0.33	0.35	0.39	0.18	0.22	0.19	0.54	0.63	0.49	45	37	51
Peak trajectory value	0.37	0.37	0.40	0.18	0.22	0.19	0.49	0.39	0.47	51	41	53
Peak value anywhere in Airshed grid		0.40 (at 1400 near Fontana)			0.24 (at 1600 near Fontana)			0.60			40	

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***Marcia C. Dodge** is the EPA Project Officer (see below).*

The complete report, entitled "Effects of Photochemical Kinetic Mechanisms on Oxidant Model Predictions," (Order No. PB 84-113 752; Cost: $10.00, subject to change) will be available only from:

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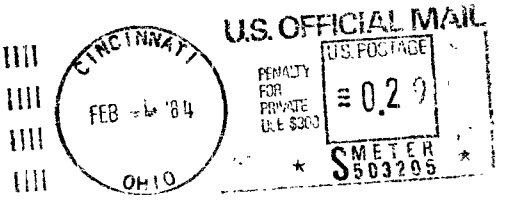

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