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SOME IMPLICATIONS AND APPLICATIONS OF A NEW OXIDANT CONTROL STRATEGY

by

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PREFACE

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The opinions, findings, conclusions and recommendations expressed in this publication are those of the author and do not necessarily reflect the views of the M.I.T. Energy Laboratory, the Massachusetts Institute of Technology or any other organisation.

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1. BACKGROUND

For many years now those responsible for cleaning smog-ridden cities throughout the world have been concerned with the development of an effective oxidant abatement strategy. Opinion is divided, in some cases sharply divided, on the relative merits of controlling hydrocarbon or nitrogen oxides emissions or both. Even when this decision is made, the precise degree of control necessary to achieve a given goal in any region is uncertain. And over all this hangs the pall of uncertainty about the reductions of nitrogen oxides and hydrocarbons that can be achieved in practice with today's technology.

The Muskie-sponsored Clean Air Act Amendments of 1970 required the newly-created Environmental Protection Agency (EPA) to act quickly to provide guidelines to state air pollution agencies for the control of photochemical smog. In 1971, in the midst of scientific, if not public, controversy, the EPA opted for control of hydrocarbons only, the precise degree of control to be calculated using the now well-known "Appendix J" curve.* There were (and still are) good, practical reasons to favour the strategy of hydrocarbon control over NOx control. Hydrocarbon control is further developed technically, both for mobile and stationary sources than NOx control and generally speaking is more efficient both in terms of cost and energy. In fact hydrocarbon control often conserves energy. However, scientific support for EPA's strategy,

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*The 'Appendix J' method is presented in the Federal Register, 36, 115486-115506, August 14, 1971. For a detailed description of its limitations, see the National Academy of Sciences, Transportation Research Boards' Special Report 167, pp 8-20, published by the N.A.S. in 1976.

particularly the derivation of the Appendix J curve, was always lacking if for no other reason than because understanding of the phenomenon was incomplete. The EPA, it will be remembered, was legally obliged to promulgate guidelines quickly.

Appendix J probably represented the less than satisfactory state of the art at the time. However, it has never been accepted in California, nor has it been used overseas -- an unusual situation given the widespread use in other countries of American-derived standards and procedures in air pollution control. The main weaknesses of the Appendix J curve are that it takes no account of NOx levels and that it was derived from ambient monitoring data of doubtful validity which related morning concentrations of hydrocarbons to afternoon levels of oxidant <u>at the same site</u>. This last point is equivalent to assuming that either the atmosphere never moves or emissions are perfectly evenly distributed. Neither assumption can be supported satisfactorily.

As the weakness of the the Appendix J method have become apparent, a more fundamental relationship between ozone and its precursors has been sought. The goal has been in particular to develop a model that will assist in answering the following three major questions:

1. Is it necessary to control NOx emissions to achieve the oxidant standard? If so, how much?

2. How much hydrocarbon control is necessary to achieve the standard?

3. Are certain areas particularly important as source or receptor areas?

The first of these questions is particularly relevent to energy considerations. NOx control techniques available for use with either mobile or stationary sources result in a quite severe deterioration in efficiency. The final NOx standard for automobiles will have an important influence on future fuel economy standards. This is because the fuel economy standards must be revised if fuel economy penalties in excess of 0.5 mpg are incurred as a result of efforts to meet emission (or safety) standards promulgated after 1975. A stringent NOx standard, of say less than 1 g/mile, would almost certainly incur a penalty in excess of 0.5 mpg and thus be reason to relax the fuel economy standard. The need for a stringent NOx standard depends not only on what oxidant control strategy is adopted but also on levels of NO_2 per se. The EPA intends to revise the NO_2 criteria document in 1977/1978, but present indications are that few areas in the U.S. exceed the current ambient air quality standard for NO_2 and that there seems little reason to change that standard on the basis of health effects. If this situation is confirmed, then a stringent NOx standard for automobiles would not be necessary (nationwide) as a consequence of the NO_2 air quality standard. Hence, if it could be estabilshed that large reductions in NOx emissions are not required to enable the oxidant air quality standard to be met, there would be less pressure to proceed with a stringent NOx emission standard for automobiles.

It is this author's belief that today we are much nearer satisfactory answers to the questions outlined above than we were even two years ago. The remainder of this paper concentrates on the development, use, and implications of the use of a recently developed oxidant control model that does help answer these questions.

2. THE DODGE-DIMITRIADES ISOPLETHS

As the shortcomings of the Appendix J method became more obvious, and particularly after "rural ozone" problems emerged, the EPA began an in-house review of its oxidant control strategy. In 1975, a special task force was set up to investigate alternative approaches. One outcome of this task force was presented at the International Conference on Photochemical Oxidant Pollution and its Control held in Raleigh, North Carolina, in September, 1976, when Dodge[1] and Dimitriades[2] put forward a new set of precursor-oxidant relationships, shown in Figure 1*, that can be used to develop control strategies.

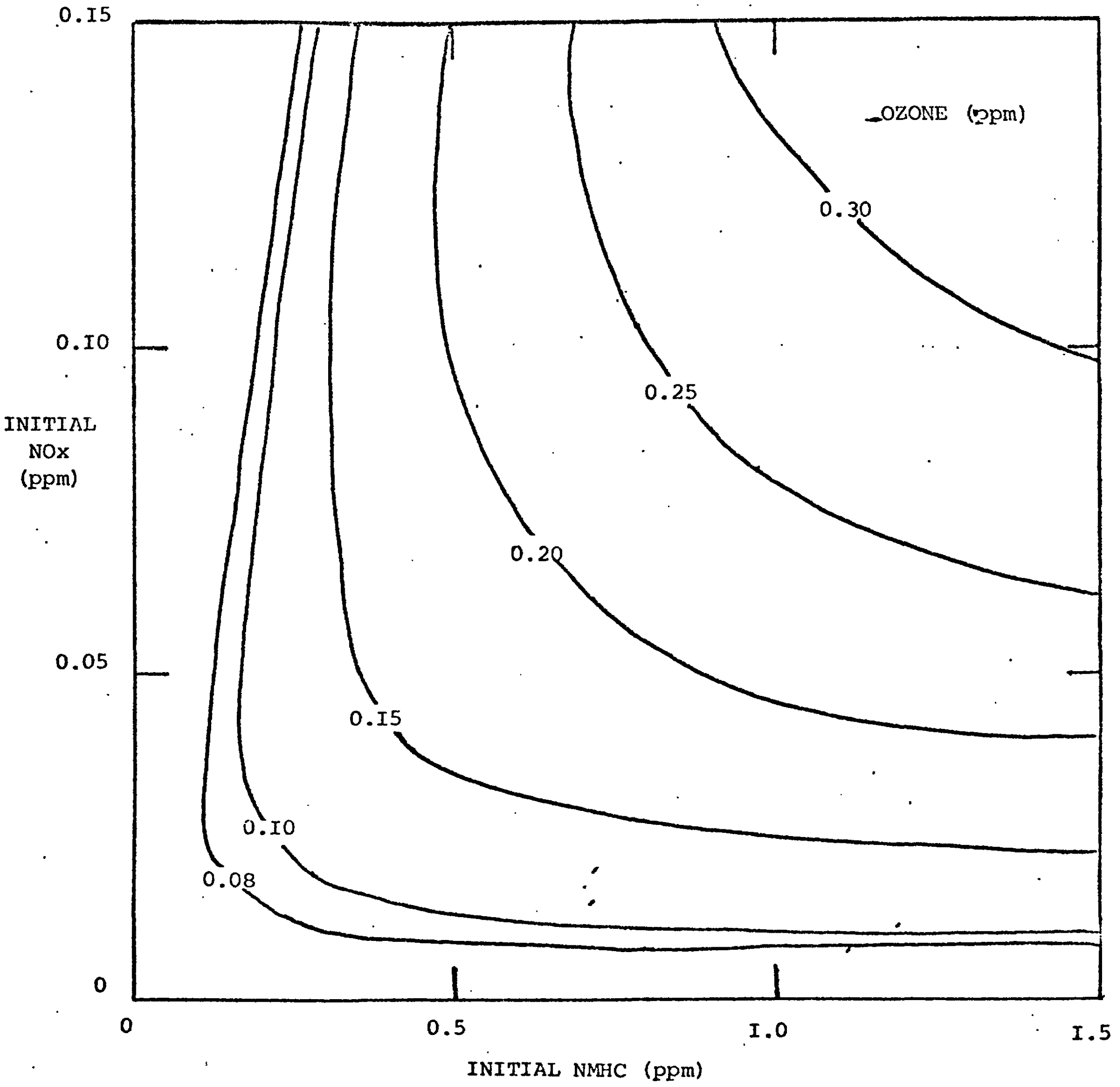

FIGURE 1 OZONE ISOPLETHS DERIVED FROM DODGE (REF. 1)

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*In fact, the isopleths shown in Figure 1 have been derived from the numerical data and drawn to a scale appropriate for most regions other than the Los Angeles basin.

The ozone isopleths in Figure 1 are the result of three stages of research. First, a kinetic mechanism describing ozone formation in propylene-n-butane-NOx mixtures was validated against smog chamber experiments using such mixtures.[3] The mechanism predicted maximum ozone values on average within 5.6 percent of measured levels -- an extremely encouraging result. However, there is still room for improvement in the mechanism as not all species were modelled so accurately.

Secondly, the kinetic model validated in the first step was used to predict ozone formed by irradiating automobile exhaust in a smog chamber. Initial proportions of propylene and n-butane were varied in the model until minimum variation between predicted and measured values of ozone was achieved.* To simulate dirty chamber effects, the chamber walls were assumed to be a source of propylene. This allowed the observed production of ozone from the "blank" run (very low initial hydrocarbon) to be duplicated. Otherwise the conditions that existed in the smog chamber experiments were used in the model.

Finally, the model was re-run using conditions more representative of the atmosphere. Instead of being held constant as in the chamber runs, photolytic rate constants were varied in accordance with diurnal variation in sunlight intensity for the summer solstice at 34° of latitude (approximately the latitude of Los Angeles, Tokyo, and Sydney). A dilution rate of 3 percent per hour was used to simulate zero wind speed and the small increase in afternoon mixing depth over morning mixing

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*This occured when the initial proportions were 25 percent propylene and 75 percent n-butane; the model then predicted ozone levels on average within 15 percent of measured values. Since this is the order of accuracy typical of chamber experiments, the results were considered satisfactory.

depth observed in Los Angeles on high oxidant days. The chamber wall effect was removed, but the same ratio of propylene to n-butane (i.e. 25/75) was used that satisfactorily modelled ozone formed from irradiated automobile exhaust. Simulations were carried out for a nine hour period corresponding to the hours 0700-1600 L.D.T. Implied in this treatment was the assumption that all emissions had entered the atmosphere by 0700 and that no further pollutants were emitted in the following nine hours.

The assumptions outlined above are more appropriate for the Los Angeles region than any other, hence the question arises whether the isopleths are appropriate for areas outside of that region. One would expect, for example, lower concentrations of ozone to be predicted at higher dilution rates and reduced solar radiation. To shed light on these and other related questions, Dodge[4] carried out a sensitivity analysis on the model. The parameters included:

Dilution rate: 3% and 20% per hour

Solar energy: 34° summer solstice and 40° September 15

Post-0900 emissions: none and a quantity equal to the 0600-0900 NMHC and NOx emissions

Hydrocarbon reactivity: 25% propylene, 10% propylene (to simulate a relatively unreactive atmosphere) and 50% propylene (a very reactive atmosphere)

As expected, the positions of the isopleths are quite sensitive to the varying assumptions. For example, at initial concentrations of 1.0 ppmC hydrocarbon and 0.1 ppm NOx, the following values are predicted:

base case	0.28 ppm ozone
40° latitude, Sept. 15	0.25 ppm ozone

20% per hour dilution*	0.15 ppm ozone
continuous emissions	0.35 ppm ozone
10% propylene	0.26 ppm ozone
50% propylent	0.28 ppm ozone

Although some of these results could have been predicted in a qualitative sense, the quantitative aspects are far more interesting. Dilution rate dominates all other variables and therein lies the explanation for the significantly higher oxidant levels recorded in Los Angeles than for any other region. Even more important, however, is Dodge's finding that although the absolute positions of the isopleths are affected by the assumptions, the relative positions remain almost constant. This means, as Dodge verified, that the precentage change in hydrocarbons or nitrogen oxides required to reduce one level of ozone (say, 0.28 ppm) to another (say 0.08 ppm) is almost the same irrespective of the underlying assumptions. Or, put another way, although ozone values predicted by the model are sensitive to local conditions, the control strategy deduced from it is not. This increases the usefulness of the model manyfold. The effect of a control strategy may be evaluated using only maximum measured ozone values, measured NMHC/NOx ratios, and predicted percentage changes in hydrocarbon and nitrogen oxides concentrations. The solar energy, dilution rate, or hydrocarbon reactivity in the region under consideration do not have to be known to make use of the model. In the discussions that follow frequent reference is made to the base-case isolpleths. It is

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*A 20 percent per hour dilution rate corresponds, for example, to an increase in mixing height from 100 m at 0700 to 500 m at 1600 and a net wind velocity of zero.

re-emphasized that the conclusions reached as a result of using the base-case conditions are independent of these conditions. The base-case isopleths are used simply because they are the only ones published at the time of writing this paper.

3. USE OF THE MODEL

3.1 General Application

In the previous section the general character of the model was discussed and the fact that the effect of a control strategy could be evaluated using a minimum of local data was emphasized. Presented in Table 1 are the results of using the model to calculate the hydrocarbon or nitrogen oxides reduction required to reduce an ozone level of 0.25 ppm (a common near-maximum for regions other than Los Angeles) to various levels. The calculations were made for the range of NMHC/NOx ratios normally encountered in urban and suburban atmospheres.

From Table 1 it can be seen that the amount of control required of either or both precursors is a function of the non-methane hydrocarbon (NMHC) to nitrogen oxide (NOx) ratio and the degree of control sought. The amount of NMHC control required to achieve a given goal increases as the NMHC/NOx ratio increases while the amount of NOx control decreases as the ratio increases. Of particular importance is the prediction that except when the NMHC/NOx ratio is less than 10, hydrocarbon reductions in excess of 80% are required to reduce ozone levels from 0.25 to 0.08 ppm. NOx reductions in excess of 80% are required at all ratios. Reductions of the order of 80% for either precursor generally cannot be achieved in practice due to technical limitations, deterioration in performance of control devices, and accidental, fugitive, natural and uncontrollable emissions. However because the technology is further advanced for hydrocarbon control reductions of this order are more likely

Table 1

HYDROCARBON AND/OR NITROGEN OXIDE CONTROL REQUIREMENTS TO REDUCE 0.25 PPM OZONE TO 0.16, 0.12, OR 0.08 AS A FUNCTION OF NMHC/NOx RATIO

Reduce to 0.25 ppm ozone to:	Using NMHC Control Only	Using NOx Control Only	Using Both NMHC and NOx Controls
NMHC/NOx = 5			
0.16	43%	71%	no advantage
0.12	51%	88%	no advantage
0.08	66%	93%	no advantage
NMHC/NOx = 10			
0.16	63%	63%	50% each
0.12	69%	83%	62% each
0.08	82%	89%	80% each
NMHC/NOx = 20			
0.16	73%	57%	49% each
0.12	80%	79%	67% each
0.08	90%	85%	81% each
NMHC/NOx = 30			
0.16	78%	54%	little advantage
0.12	84%	74%	little advantage
0.08	92%	82%	little advantage

to be approached for it rather than NOx control.

Control of both precursors is advantageous for ratios between 10 and 20, but careful economic analysis would need to be carried out in each individual case. For example, a reasonable mid-term goal for a region with a ratio of hydrocarbons to nitrogen oxides of 10 and current ozone levels of 0.25 ppm might be to reduce that to 0.12 ppm. According to the model, this can be achieved by reducing hydrocarbons by 69 percent, nitrogen oxides by 83 percent, or both by 62 percent. The cost of reducing nitrogen oxides by 62 percent would need to be weighed against the marginal cost of reducing hydrocarbons 69 percent instead of 62 percent. Although it is unlikely the nitrogen oxide control would be cost-effective, a reduction in emissions of this pollutant may be deemed necessary for reasons other than ozone control.* It should be noted, however, with respect to ozone control that until the reduction of nitrogen oxides approaches 60 percent there is little offset against the required hydrocarbon control. But neither is there a penalty, which should be reassuring to control agencies concerned with controlling nitrogen oxides for purposes other than to reduce ozone concentrations.

3.2 Application to Los Angeles

The U.S. EPA[5] has compared the model's predictions with measured ozone levels in the Los Angeles basin since 1968. The median 0600-0900

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*There is a body of scientific opinion that some other oxidant products, including PAN and aerosols as well as nitrogen dioxide might be reduced effectively by controlling nitrogen oxides emissions.

precursor concentrations at nine sites within the basin on the highest oxidant day each year were used to predict ozone concentrations. The precursor concentrations and the predicted ozone and measured oxidant are compared in absolute terms in Table 2, where it can be seen that the agreement is close. However, the fact that the agreement is close in absolute terms is not important -- if precursor levels other than the median 0600-0900 are used, or if the isopleths taking into account continuous emissions are used, the absolute agreement is not good. However, the ability of the model to account for year-by-year changes in ozone levels in relative terms is notable and augers well for the use of the model in the L.A. region.

EPA also used the model in a strictly relative sense. In performing these comparisons, data from years 1968-71 were lumped to define the base state. This was done as a precaution against any freak meteorlogical occurrences during a single year which might disrupt the trend analysis (although an examination of the results in Table 2 indicates this was hardly necessary). Similarly, data from 1972-75 were combined to serve as a basis for comparison with the model predictions. The median third quarter (highest ozone period) values for the median 0600-0900 readings from all stations in the basin were used to derive the precursor ratios and percentage change in concentrations from one period to the other. The oxidant concentration used was the median maximum value in each four-year period. Table 3 summarizes the data.

The oxidant and NMHC/NOx ratio for 1968-71 were used to establish Point A on Figure 2. Next, 19 percent reductions in NMHC and NOx were

Table 2

COMPARISON OF PREDICTED AND MEASURED OZONE LEVELS IN L.A.[5]

Year	1968	1969	1970	1971	1972	1973	1974	1975
Median NMHC	2.64	2.45	3.41	2.36	1.71	1.86	2.12	1.14
Median NOx	.257	.253	.413	.318	.152	.307	.207	.163
Measured Ox	0.49	0.54	0.58	0.53	0.49	0.46	0.48	0.33
Predicted Ozone	0.51	0.50	0.66	0.53	0.37	0.48	0.45	0.34
Difference %	+4.0	-7.4	+14.0	0.0	-24.5	+4.4	-6.3	+3.0

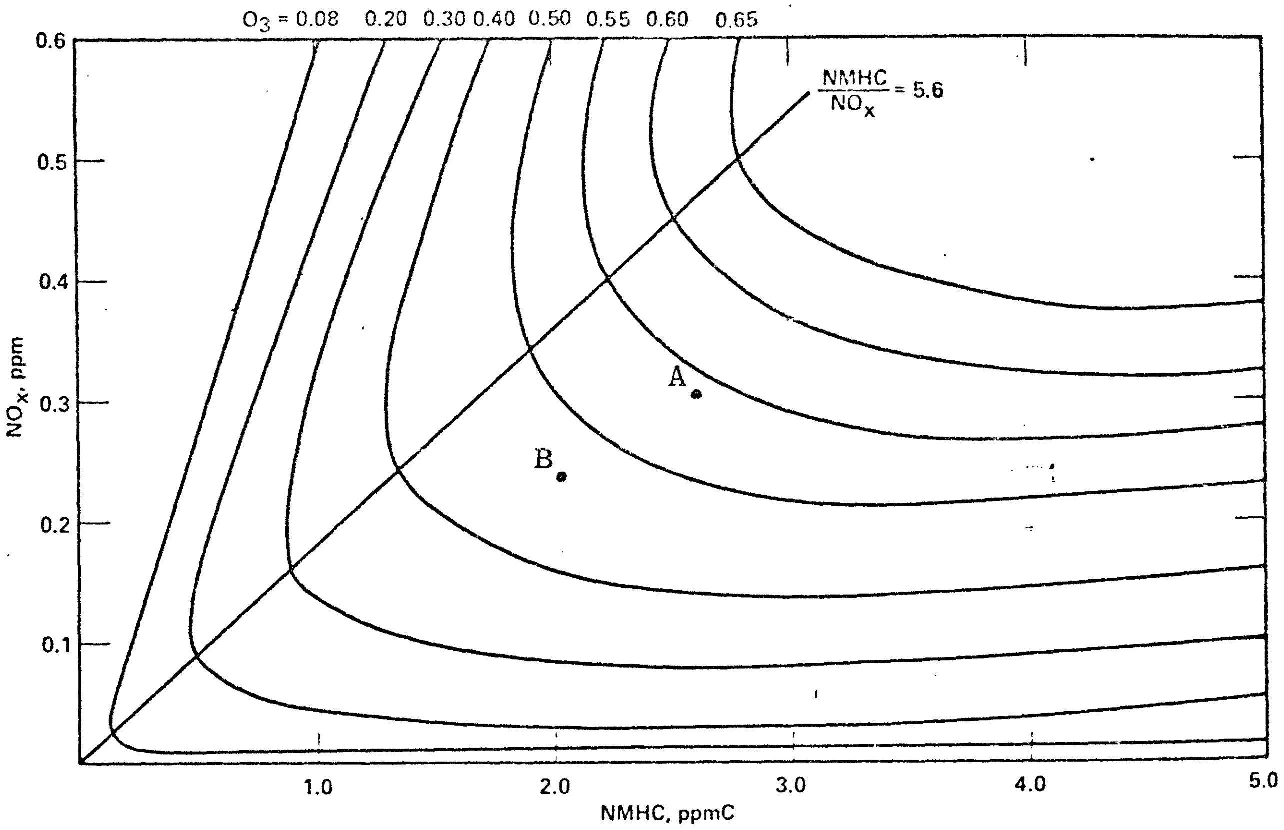

FIGURE 2 ISOPLETHS APPLIED TO THE LOS ANGELES REGION. POINT A REPRESENTS THE SITUATION IN 1968-71, POINT B IN 1972-75. SEE TEXT AND TABLE 3 FOR ADDITIONAL INFOMATION.

used to identify the post-control point on the diagram, Point B. The agreement between the predicted post-control maximum oxidant (0.47 ppm) and the observed value (0.47 ppm) is exact, again emphasizing the usefulness of the model when used in a relative sense.

3.3 Application to Regions Where Ozone Transport is Important

In the past three years considerable attention has been focused on the problem of "rural" or transported ozone. It is now clear that ozone generated in a city's plume can persist for hundreds of kilometers downwind. Explanation of this phenomenon is still not complete, but sufficient work has now been done to rule out in most cases the much-vaunted theories that the elevated rural ozone levels are due to either the intrusion into the atmosphere of stratospheric ozone or the photochemical reactions of natural precursors.*

One of the most graphic demonstrations of the transport of ozone downwind from a city was obtained during the Project DaVinci II balloon flight.[6]** Project DaVinci II was a manned, balloon-borne air chemistry experiment conducted in the vicinity of St. Louis during early July, 1976. The experiment was set up so that the balloon moved with the air current from a region of relatively high pollutant density (St. Louis)

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*This is not to say that ozone is not formed from these processes. However, it is rare for such phenomenon by themselves to raise the ground-level ozone concentration above 0.08 ppm for one hour.

**The following description of the DaVinci II experiment is paraphrased from Reference 6.

Table 3

DATA USED IN RELATIVE COMPARISONS OF OBSERVED AND PREDICTED MAXIMUM OXIDANT IN LOS ANGELES[5]

Parameter	1968-71	1972-75	% Change
Ambient NMHC (ppmC)	1.50	1.22	-19%
Ambient NOx (ppm)	.177	.143	-19%
Median Ratio Maximum Oxidant	8.5	8.5	0
Measured (ppm) Maximum Oxidant	0.54	.47	-13%
Predicted from Figure 2		0.47	

to the adjacent low emission rural regions. Measurements of ozone and ozone precursors were made so that changes in their relative proportions could be determined as the balloon drifted with the wind. Concurrently, a mobile ground-based laboratory was driven as nearly as possible, beneath the balloon, also measuring ozone and precursor concentrations. At regular intervals an aircraft equipped to monitor various pollutants including ozone flew above and beside the balloon.

The balloon system consisted of a double-decked gondola approximately three meters square and four meters high with sleeping quarters on the lower deck), connected to a 5000 m^3 balloon by a 22 meter suspension harness. Nearly one ton of scientific equipment was on board. The flight commenced at an airport 24 kilometers west of St. Louis at 0900. The balloon drifted around the western part of St. Louis for five hours (until 2000), and finally drifted across the southern Illinois plains for thirteen hours before landing in a wheat field in southwestern Indiana at approximately 0900 the following morning. The experiment was conducted while an almost stationary high pressure system prevailed over the region. The airborne (balloon) and ground-based ozone values are compared in Figure 3.

The concentration of ozone at flight altitude (approximately 800 meters) remained in the range of 0.11-0.15 ppm from 1700 on the evening of June 8th until the gondola monitor was turned off at 0700 the next morning, with the exception of the time interval between 2141 and 2310 on June 8th. The decrease at this time coincided with the observation by the flight crew of a pungent hydrocarbon odor and occurred when the balloon

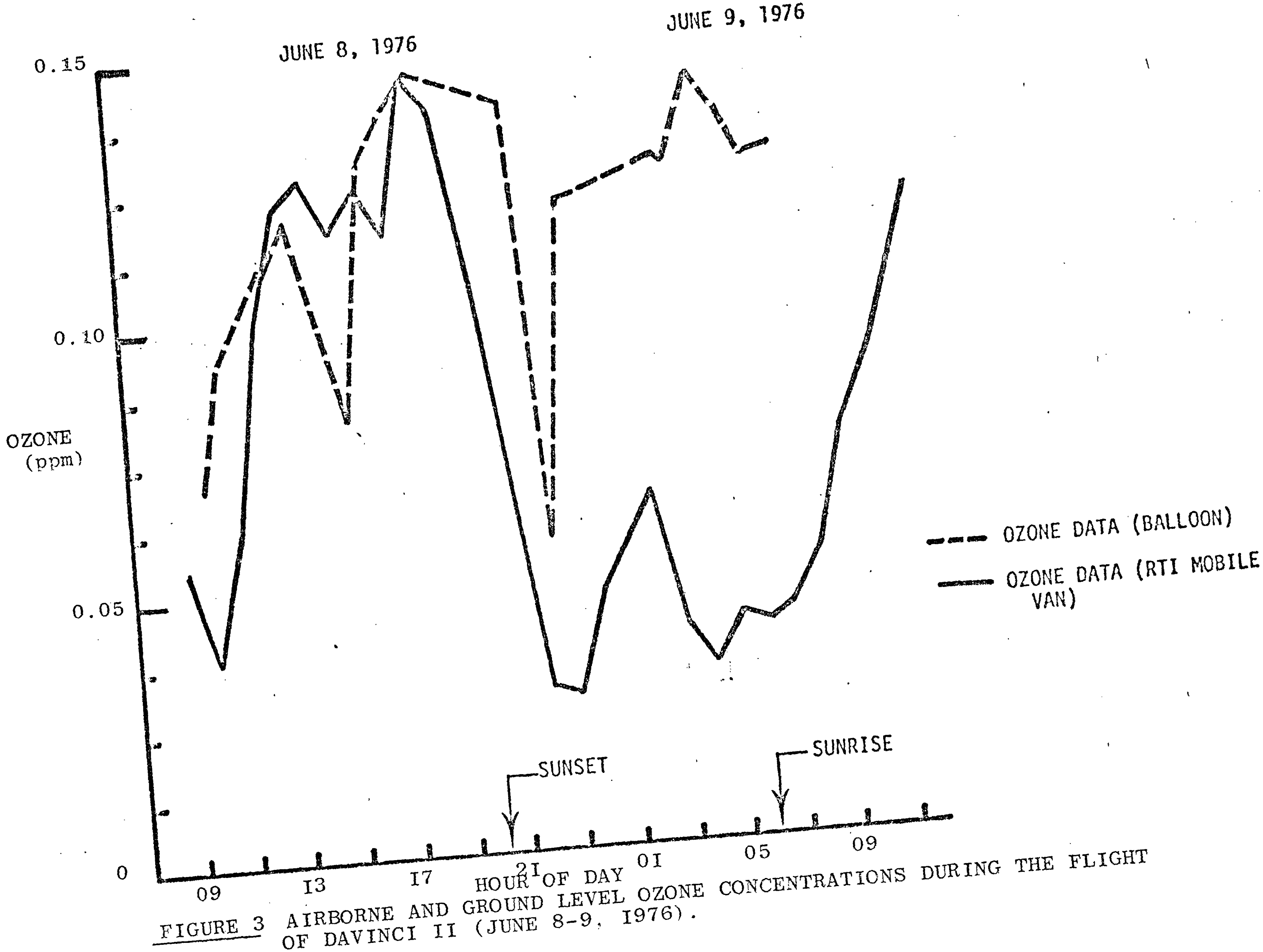

FIGURE 3 AIRBORNE AND GROUND LEVEL OZONE CONCENTRATIONS DURING THE FLIGHT OF DAVINCI II (JUNE 8-9, 1976).

was 30 kilometers downwind of the refining region (and 50 kilometers) downwind of a power plant). The results demonstrate well the transport aloft of ozone with minimum dilution and/or destruction during the nighttime regime. At ground level, ozone concentrations decreased rapidly with nightfall to a minimum of about 0.03 ppm. From other monitoring data this decrease was probably due to reaction with nitric oxide emissions. A strong radiative inversion separated the flow aloft from the air at ground level, and this inversion prevented the fresh emissions of nitric oxide from mixing upwards and the ozone aloft from mixing downwards.

Within a few hours after sunrise, the radiative inversion was broken up and this allowed the ozone aloft to mix downwind. Because of the rural nature of the area, nitric oxide concentrations were now too low to destroy any ozone and normal photochemical activity could serve to maintain the high ozone levels.

In the absence of these detailed data, it has been impossible to pick between the various theories proposed to explain the observation of high ozone values in rural areas. In this particular case (and there is no reason to believe it is atypical), there is no need to invoke stratospheric ozone, photochemcial reaction of natural precursors, or the transport of anthropogenic precursors to explain the observations. The explanation simply seems to be that ozone, generated from anthropogenic precursors the day before and isolated from fresh emissions of nitric oxide by a radiative inversion, can be transported a considerable distance before it ultimately mixes downwind on the breakup of the inversion. No doubt renewed photochemical activity with whatever precursors are around helps sustain the ozone concentrations during the daytime in rural regions.

Given that this is one of the more common mechanisms by which ozone is transported, can the Dodge-Dimitriades model handle it? The break-up of the inversion doesn't have to coincide with the ozone-laden air being over a rural region. In the eastern United States and in Western Europe, the upper layer of ozone-rich air will frequently mix with air above and around another city. The questions then arise: Is the newly added ozone additive to that generated by the second city's emissions? Or does it simply accelerate the conversion of nitric oxide to nitrogen dioxide, causing maximum ozone levels to be observed earlier in the day?

To examine this question Dodge carried out a number of simulations whereby dilution of urban air with clean and ozone-laden air were compared. For a variety of conditions it was found that about 30 percent of the ozone in the air aloft was destroyed. For example, with a hydrocarbon concentration of 1 ppmC and a nitrogen oxides concentration of 0.1 ppm diluted with clean air at 20 percent per hour commencing after 1000, the model predicted that 0.2 ppm ozone would form.* When the air is diluted with air containing 0.09 ppm of ozone, the model predicts not 0.29 ppm which would occur if the ozone concentrations were additive, but 0.26 ppm. Hence in establishing how much ozone has been formed as a result of a region's emissions (locally generated ozone) a quantity equal to 70% of

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*Note that this compares with 0.15 ppm ozone predicted when dilution at 20 percent per hour commences at 0800 LDT. Clearly the time of onset of dilution is an important factor in determining absolute levels of ozone.

the ozone measured to be entering the system upwind (background ozone) should be subtracted. This then represents the amount of ozone that is controllable by emission reductions in that region. The background ozone can be reduced only by implementation of controls in upwind regions.

3.4 The St. Louis Case -- Correcting for Background Ozone

The occurrence of photochemical pollution in the St. Louis region is worth examining because, after the Los Angeles region, it is one of the most intensively monitored regions in the world. Twenty-five fully equipped monitoring stations extend from the inner city to 40 kilometers distant, covering all points of the compass. The results presented here were derived by the author from 1975 summer data.*

Each high ozone day (ozone > 0.1 ppm) was examined to see if the precursor concentrations responsible for the ozone measured later in the day could be identified with reasonable assurance. Because of the large number of monitoring sites and, in most cases, the well-defined wind field, this was usually possible. Table 4 summarizes the data obtained in this way. The background ozone was taken as the value recorded upwind of the city at about 1100. The numbers in parantheses refer to the monitoring site.** The results are presented here for the eight days

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*This data was made available by Ken Demerjian of the EPA to whom many thanks are due.

**In fact the monitoring sites in the RAPS study are numbered 101-125 with lower numbers generally located nearer downtown St. Louis. Nos. 122-125 are all about 40 km from the downtown region in different directions. In Table 4 the one hundred numeral is dropped.

Table 4

Summary of St. Louis, 1975 Summer Ozone and Precursor Data

			0600-0900 Precursors	
Date	Max. Ozone	Background Ozone	NMHC	NOx
July 4	0.1 (18,24)	0.08 (22)	.35 (2)	.025 (4)
July 15	0.16 (14,22)	0.06 (24)	.8 (1)	.1 (7)
July 26	0.18 (6,12,13,14)	0.06 (17)	.9 (5,12)	.07 (4,7)
July 27	0.135 (23)	0.05 (25)	.4 (7)	.055 (2)
July 28	0.2 (18)	0.08 (22,23)	.6 (5)*	.065 (5)
August 10	0.14 (21)	0.05 (17)	.35 (4)	.04 (3,4)
August 17	0.16 (19)	0.04 (17)	.6 (4)	.05 (7)
August 19	0.23 (21)	0.05 (22)	.9 (3,4)	.085 (3)

* Hydrocarbon concentration two hours before ozone maximum

where the ozone reached values near to those predicted by the Dodge-Dimitriades Model (base-case). There were twenty-four days in July and August 1975, when maximum hourly ozone values of 0.1 ppm or more were recorded in the St. Louis region. On sixteen of these days, however, ozone levels did not approach their apparent potential (as indicated by the model), probably because of meteorological factors.

In Table 5 the ozone level predicted by the model (base-case conditions) is compared with both the measured and locally generated ozone. The locally generated ozone was calculated by subtracting 70 percent of the background ozone from the maximum recorded ozone as outlined in Section 3.3.

From Table 5 it can be seen that the maximum ozone recorded in St. Louis was between 78 and 103 percent of the value predicted by the base-case model on six days in 1975. However, when account is taken of the background ozone, the locally generated ozone is found to be between 42 and 80 percent of the value predicted by the model for these conditions. This is a sensible and intuitively reasonable result and illustrates the importance of considering background ozone concentrations.

3.5 Effect of Urban Controls on Downwind Ozone

The Dimitriades-Dodge model predicts only what will happen on the first day of irradiation of smog components. In Section 3.3 a method of handling the influx of ozone from sources outside the region under consideration was discussed. However, the question remains -- Will the hydrocarbon control strategy predicted to be effective in the urban and suburban regions be effective in downwind rural regions? There is little hard evidence either way on this question. It is possible that neither

Table 5

MEASURED AND LOCALLY GENERATED OZONE
IN ST. LOUIS AS A PERCENTAGE OF THE
OZONE PREDICTED FROM THE DIMITRIADES-DODGE MODEL

Date	Max. Ozone (ppm)	Percent of Potential*	Locally Generated Ozone (ppm)	Percent of Potential*
July 4	.1	83	.05	42
July 26	.18	78	.14	61
July 27	.135	84	.105	66
July 28	.2	103	.15	77
August 10	.14	100	.11	78
August 17	.16	91	.13	74
August 19	.23	92	.2	80

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*Potential in this case means the value predicted by the model for base-case conditions. The real potential ozone for St. Louis is unknown at present. Again the base-case serves for comparison purposes.

a hydrocarbon nor a nitrogen oxide control strategy will be as effective in rural regions as in city areas. This is because of the so-called dilution effect -- demonstrated most graphically in outdoor smog chambers. In one such experiment the original mixture of precursors (and subsequently formed oxidants) were diluted 95 percent in twenty-four hours.[8] The products were then irradiated for a second day. A maximum ozone concentration of 0.31 ppm was measured on the first day but the second day maximum of 0.20 ppm instead of being 95 percent was less than 40 percent below the first day maximum.*

There is insufficient data to determine whether NOx or hydrocarbon control is to be preferred in achieving rural ozone reductions. The evidence from outdoor smog chambers is not conclusive but supports the hypothesis that less rural ozone would be formed if either hydrocarbons or nitrogen oxides were reduced.[8] Other studies[9] suggest that the hydrocarbon control predicted to be effective in urban and suburban regions will also be effective in reducing rural concentrations. This will certainly be the case if most of the rural ozone results from the transport of urban ozone as described in Section 3.3. If the urban ozone is reduced, there is less to be transported to the rural regions and lower concentrations (in the absence of other formation mechanisms) must result. It seems reasonable to conclude then that the control of urban hydrocarbons will assist in lowering rural ozone concentrations.

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*This argument depends of course on the observed chamber data being representative of the ambient atmosphere at these very low concentrations and not a consequence of experimental artifacts. And because of the possible effect of dirty chamber walls there must be some doubt about the validity of the results at such low concentrations.

4. SUMMARY

The need to base oxidant control strategies on something more fundamental than EPA's Appendix J method led to the development of ozone isopleths. These isopleths were developed from kinetic modeling of smog chamber data with appropriate allowances made for smog chamber artifacts. The outstanding feature of the isopleths is that they have been shown to be homothetic -- that is, although the absolute position of the isopleths change when different assumptions are made about radiation intensity and dilution rate, etc., their relative positions do not. This feature allows the isopleths to be used to develop control strategies with a minimum of data. In fact all that is needed to evaluate a proposed control program are the existing ozone concentration (maximum or near maximum) and non methane hydrocarbon to nitrogen oxide ratio and the predicted percentage changes in hydrocarbon and nitrogen oxide concentrations as a result of the control program. When used in this way, the model fits well the historical data obtained in the Los Angeles basin.

For NMHC/NOx ratios typical of urban regions afflicted with photochemcial pollution (5-15) hydrocarbon control is found to be a more practical approach than NOx control. This is because generally hydrocarbons are more easily and more cheaply controlled than nitrogen oxides for a given level of control. For NMHC/NOx ratios of 5-15 the level of control required using either strategy is about the same hence the hydrocarbon strategy is more practical. However, NOx control is not predicted to have a deleterious effect on ozone levels if it were to be implemented for reasons other than ozone control.

Background ozone can and should be taken into account as this gives added perspective to the problem of calculating the amount of ozone reduction that is possible by controlling precursor emissions in a given region. The methodology is not suited to calculating the effect of urban and suburban control strategies on distant rural ozone concentrations. However, if most of the rural ozone occurs because of the transport of urban and suburban ozone as recent experiments and surveys indicate, then the strategy that reduces urban ozone will also reduce rural levels. For most regions this means a hydrocarbon reduction policy can be expected to lower ozone concentrations in urban, suburban, and rural areas.

5. REFERENCES

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