



**Receptor Model Allocation of Ozone-Forming Potential to NMOC
Sources in Northeast Illinois**

R. A. Wadden

P. A. Scheff ✓

Environmental and Occupational Health Sciences
University of Illinois at Chicago

I. Uno

National Institute for Environmental Studies
Tsukuba, Japan

To be presented at the 84th Annual Meeting of the AWMA
Vancouver, BC, June 1991

Receptor modeling of ambient NMOC's using component mass balances has been successfully applied in a variety of cities^{1,2,3,4,5,6}. The calculation procedure is a multivariate least-squares fit of ambient concentration measurements with a specified number of source coefficients, each of which represents the contributions from a particular source category. The general equation is

$$Y = Z\beta + E \quad (1)$$

where Y is the vector of i fitting-compound concentrations measured at a receptor site, Z is the pollution source NMOC composition matrix of i compounds for each of the j sources modeled⁷ and E is the vector of i errors (the difference between the measured and predicted component compositions). β is the vector representing the contribution to receptor concentration of NMOC's from each source category included in the model. The least squares fit of Equation (1) was weighted with the variance of the measurement variance for each compound¹⁻⁶.

Source coefficients have been determined for vehicles, gasoline vapor, petroleum refineries, graphic arts, architectural coatings, dry cleaning, vapor degreasing, waste-water treatment, polyethylene plants, and coke ovens. These contributions have been successfully compared with those estimated for emission inventories. In addition, when analyzed using trajectory analysis, large point source contributions, such as petroleum refineries^{1,2,6,8}, graphic art shops⁸, and coke ovens⁶, have agreed well with model predictions.

In this study our interest was to explore the implications which these NMOC predictions have for ozone production, and ultimately for control. To do this we evaluated ambient measurements taken on 9 days from the summer of 1987 in Chicago.

METHODOLOGY

The procedure we used was based on the following steps applied to each ambient sample: (1) Ambient measurement of the less reactive organic species in NMOC (fitting compounds); (2) Application of the chemical mass balance receptor model (CMB) to the ambient sample to determine the distribution of fitting compound emissions among source categories; (3) Determination of the emissions of non-fitting compounds by application of extended source fingerprints, including reactive organics; (4) Prediction of the ozone concentration attributable to each source category by using the source contributions of both fitting and non-fitting components as input to the photochemical smog carbon bond model (CBM-IV)⁹, along with the uv, temperature, pressure, humidity and ambient O_3 , NO_x/NO , and CO concentrations at the monitoring location for each sampling day; (5) Evaluation and validation of predicted O_3 concentrations using wind trajectories; (6) Estimation of the relative effect of each source category by determining the variation in predicted ozone from changes in the NMOC contributions from each source type from -50% to +20% of the base (measured sample) case while holding

the other contributions constant. This analysis resulted in a control region for each type of NMOC source (e.g., vehicles, refineries, graphic arts) which described the effect on ozone concentrations which can be expected for percentage changes in NMOC control of each source category.

Data Set

A series of 4-hour (8:00 am - 12:00 pm) and 20-hour (12:00 pm - 8:00 am) air pollution measurements were carried out at three urban sites from July-September 1987 in Chicago. Ambient air samples were simultaneously collected in six-liter electro-polished stainless steel canisters and on tenax tubes, and subsequently analyzed for 23 organics using gas chromatography. The details of the sampling and analysis have been previously reported^{4,5}. A subset of eighteen 4-hour samples from two inner city sites were used as the basis for this study (SPH and SOUTH SIDE in Figure 1). This subset of nine days included all of the observations which were available for days when O₃ exceeded 0.1 ppm.

Simultaneous measurements of NO_x, NO, O₃, CO, uv radiation, pressure, relative humidity and temperature were also available at the monitoring site. Since the NO measurements were judged to be unreliable, NO_x and NO ambient measurements were used from another location within 2 km.

The fitting compounds included ethane, ethylene, propane, propylene, acetylene, iso- and n-butane, iso- and n-pentane, 2-methyl and 3-methyl pentane, n-hexane, 2,4-dimethyl pentane, benzene, toluene, ethylbenzene, p,m-xylene, o-xylene, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, carbon tetrachloride, and chloroform. Extended NMOC fingerprints were developed for vehicles, gasoline vapor, petroleum refineries, graphic arts, architectural coatings, waste-water treatment, vapor degreasing and drycleaning⁷. Contributions to each sample from these 8 source categories were determined by solving Equation 1 using the fitting compounds.

Calculation Procedure

The general approach to modeling ozone production was to consider the volume of air which was characterized by the monitoring point measurements from approximately 8:00 am to 11:00 am. Air which contributes to this volume contains pollutants which have been emitted earlier in the day along the back-trajectory of the wind. The measured concentrations are a consequence of this history, and serve as input to the CBM-IV. Ozone levels were then predicted using the observed 3-hr average concentrations of NO, NO_x, CO, and O₃. The NMOC inputs were the speciated source contributions to the measured 4-hour ambient NMOC concentration from each of the 8 categories in the receptor model averaged over two monitoring sites. Source contributions from non-identified NMOC sources were not included since we did not know the composition of non-fitting organics. The CBM-IV was used to calculate the maximum O₃, and the time to the maximum, which would result from each mixture. Actual hourly values of uv, temperature, relative humidity, and pressure were used. The

concentration of HONO was estimated from an equation suggested by Whitten et al¹⁰. Values of k_1 , the photolytic rate constant for NO_2 , and photolysis rates for other substances were estimated using commonly accepted methods^{11,12}.

The NMOC concentrations reported in Table 1 are only for the fitting compounds. The total contribution of each of the eight source categories was determined by dividing the value of β from Equation 1, by the weight ratio of fitting NMOC compounds to total NMOC for that source. This total contribution had the same composition as the extended source fingerprint. The composition of organics was then allocated to the appropriate carbon bond group¹³.

Essentially, we considered the reaction of the pollutants within the initial air mass to occur within a constant volume. That is, we did not take into account the deepening of the mixing layer, with subsequent increase in volume available for mixing which is likely to occur as the day progresses.

CBM-IV estimates of O_3 in this air mass were then calculated starting at 9:00 am, and were continued, using actual temperature and uv measurements, to the maximum concentration. This typically occurred 6-8 hours later. These are also listed in Table I. In addition the effect of varying the contribution of each of five of the sources was estimated. The organic contribution of each source was varied from -50% to +20% of the value based on the ambient measurement while holding the contributions from the seven other sources constant at the ambient values. This variation in source contribution was examined for each ambient sample for vehicles, refineries, gasoline vapor, architectural coatings, and graphic arts.

RESULTS AND DISCUSSION

Maximum O_3 calculated from CBM-IV are given in Table I. In order to judge whether these estimates were reasonable, we estimated the forward and backward wind trajectories for the monitoring point, and then compared our O_3 maxima values with measured values from "downwind" monitoring stations. These values are also listed in Table I. In one case (9/3/87) the air mass went W out of the region, and it was likely the actual maximum value occurred outside the study area where there were no monitoring stations. For 5 of the days the forward trajectories carried the air mass over Lake Michigan. In two of these cases the wind blew steadily from SW to NE towards Muskegon, MI (7/11/87, 7/24/87). On another two days the air apparently returned from the Lake late in the day; over NW Indiana on 8/7/87 and on 8/17/87 over NE Indiana-SE Michigan (where there were no monitoring stations). A lake breeze was also experienced on 7/30/87 when morning emissions apparently returned over the Chicago area in the afternoon.

Comparison of observed O_3 versus the maximum predicted value for the 6 days for which we had monitoring data downwind are shown in Table I. In general the comparison was reasonable and suggested that, even with the limitations of the methodology, the ozone predictions did reflect what was

going on in the atmosphere. Because of the difficulty of accurate forward trajectory estimation over the Lake, where there are no meteorological measurements, we have less confidence in these projections of the path and speed of the urban plume. Nevertheless, it is of some interest that agreement was found on 7/24/87 for the Muskegon, MI location which was 200 km away NE over the Lake, and which was the only downwind monitoring site. Muskegon itself is on the shore of Lake Michigan, and contains no major sources of NMOC, so it was unlikely that the elevated O_3 levels were self-generated.

Figure 2 shows one type of O_3 response to organic contributions from various sources (8/1/87). The response to vehicle emissions is quite marked. The slope is about 2 ppb $O_3/\mu g$ vehicle NMOC/ m^3 , or a reduction of ~7 ppb O_3/ppb vehicle NMOC. The effect of gas vapor and petroleum refineries is also apparent, but is much smaller in magnitude. The other sources contribute only a small fraction of the NMOC mass which, in turn, does not have a major impact on O_3 response. For this particular day, controlling vehicle emissions would have a significant effect on ambient ozone concentrations.

The $O_3/NMOC_{source}$ response curves were developed for each day. An important assumption was that the effect of the variation in each source contribution was determined not as if it were a sole source, but rather with the contributions of other sources in place. We believe that consideration of control alternatives for a secondary pollutant such as O_3 requires that the evaluation be carried out with reference to a realistic ambient NMOC mixture. Physically this mixture comes about because of the mix of sources over which the wind trajectory has passed. So control is based on reducing the contributions of one or more sources within the mixture. And, provided the photochemical model is accurate, the calculated variation of O_3 with NMOC from a particular source will reflect the effects such control would have in the actual ambient environment.

Figure 3 shows O_3 response curves for all 9 days for vehicle-generated NMOC. The arrows indicate the base point, corresponding to the initial organic mixture derived from receptor model allocation of the measured ambient NMOC composition. The maximum temperature at the monitoring point is also noted. (Ambient temperature is recognized as an important parameter in O_3 production, and in a past review of 91 days of Chicago summer-time data over two years, no O_3 maxima above 0.08 ppm occurred below maximum temperatures of 25°C averaged over two days¹⁴). As is evident in Figure 3, temperature is an important discriminator between days, but does not explain the differences completely.

Figure 4 shows the effect of two parameters on the pattern of O_3 production. The control surface for maximum ozone is plotted as a function of maximum temperature and the NMOC contribution of ambient organics from vehicles. Although we only have 9 points, the trend is basically an increase in O_3 with both temperature and vehicle NMOC although not with the same slope. The highest concentration is at the highest NMOC and the highest temperature. When total NMOC from all sources was used the pattern was not as clear, which

is an indication of the dependence of ambient O_3 on the organic composition of specific source categories.

Figure 5 is the change in maximum O_3 with change in vehicle NMOC ($\Delta O_3/\Delta NMOC$), plotted against initial NO concentration and temperature. $\Delta O_3/\Delta NMOC$ was calculated as the difference in predicted O_3 at the base point and at the 20% control point divided by the difference between $NMOC_{vehicles}$ at the base point and at the 20% control point. This surface is essentially comprised of the slopes of the control curves for all the observed days. The steeper the slope (i.e., the higher the value of the ratio in the figure), the greater the effect that reduction in vehicular-caused NMOC will have on O_3 reduction. The pattern seems reasonably regular for both parameters, i.e., higher initial NO and high temperatures will result in the highest value of the $O_3/NMOC_{vehicles}$ ratio. Plotting NO_2/NO instead of NO did not provide as regular a pattern.

At this point it is also useful to refer again to the patterns shown in Figure 3. The O_3 - $NMOC_{vehicles}$ response curves for three days, July 11 and 30, and August 1, all occurred at similar temperatures (31-33°C). The slopes of the of the curves are essentially the same. This indicates that the same reduction in vehicle emissions on any of these days would reduce the O_3 the same amount. The difference in total O_3 for the three days occurs because the absolute amount of $NMOC_{vehicles}$ is different for 7/11 and 7/30; and because the contributions from gasoline vapor and refineries are much greater on 8/1 when compared with 7/30, even though the $NMOC_{vehicles}$ is similar (see Table I). This consistency is subsequently reflected in Figure 4.

The curves in Figure 3 express two general conditions. July 11, July 30 and August 1 are days on which the initial NO is high. This condition means that NO molecules are available for reaction with oxygenated organic radicals to produce NO_2 , which in turn leads to the photochemical production of ozone. In other words, $NMOC_{vehicles}$ is the limiting reactant. $NMOC_{vehicles}$ control on such days will bring about a significant decrease in atmospheric O_3 . However, a different situation prevailed on July 24 and August 7 even though the maximum temperatures were similar to those on the high NO days. These are days when the initial NO concentrations were low, probably because of early morning reactions with residual O_3 from the day before. $NMOC_{vehicles}$ is the reactant in excess, and NO is the limiting reactant. Ozone will be formed primarily because of the photochemical conversion of already existing NO_2 . A 20% reduction in $NMOC_{vehicles}$ will have a relatively little effect on the ozone concentration; the slope is quite flat in Figure 3. Changes due to NMOC control will only be realized when 40-50% control is implemented.

CONCLUSIONS

Combining the results of mass balance receptor-model allocation of source contributions to ambient NMOC with CBM-IV O_3 predictions provides significant insight into the effectiveness of various O_3 control strategies, at least for the Chicago area. Although the advective and convective

transport of pollutants was not directly taken into account in our evaluations, CBM-IV maximum O₃ predictions were in reasonable agreement with observed downwind concentrations. The reason for this agreement is two-fold: first is the fact that the initial concentrations of NMOC, NO, NO_x, speciated organics, and other pollutants reflect the actual upwind emission history of the air mass which was modeled; and secondly that actual values of uv, temperature, and relative humidity were used in the calculation. Another factor was that dispersion and surface deposition and decay of ozone and precursors were also less likely on many of the days because the air mass spent significant time over Lake Michigan. If these mechanisms are important, ozone prediction requires a more sophisticated treatment of pollutant transport and dispersion. However, summer-time wind directions will often carry the Chicago urban plume over water which physically reflects our model simplifications. In addition, since days of highest ozone in Chicago are frequently associated with lake breeze effects, so that an air mass contaminated by regional emissions is likely to spend time over water, the observations from our simplified model are not atypical.

ACKNOWLEDGEMENTS

This project was partly supported by EPA Grant R-814715-01-0 from the Office of Exploratory Research; and the data were originally collected under EPA Grant R-811936-01-0 from the same Office. We also very much appreciate the contributions Donna M. Kenski made to this evaluation.

REFERENCES

1. Wadden, R.A., Uno, I. and Wakamatsu, S. Source discrimination of short-term hydrocarbon samples measured aloft. Environ. Sci. Technol., 20, 473-483, 1986.
2. O'Shea, W.J. and Scheff, P.A. Validation of a source apportionment model for volatile hydrocarbons. J. Air Pollut. Control Assoc. 38:1020-1026, 1988.
3. Scheff, P.A., and Klevs, M. Source-receptor analysis of volatile hydrocarbons collected in New Jersey, J. Environ. Engin., 113:994-1005, 1987.
4. Aronian, P., Scheff, P.A. and Wadden, R.A. Wintertime source-reconciliation of ambient organics. Atmos. Environ., 23, 911-920, 1989.
5. Hegberg, B.A., Scheff, P.A., Wadden, R.A., Bates, B.A., Aronian, P.F. and Zhou, Qi. Discrimination of source contributions to ambient organics. Paper 89-104.4, Presented at the 82nd Annual Meeting of the Air and Waste Management Association, Anaheim, AC, June 25-30, 1989.

6. Kenski, D.M., Wadden, R.A., Scheff, P.A., and Lonneman, W.A. Receptor modeling of VOC's in Chicago, Beaumont, and Detroit. Paper 91-82.3, Presented at the 84th Annual Meeting of the AWMA, Vancouver, BC, June 1991.
7. Scheff, P.A., Wadden, R.A., Aronian, P., and Bates, B. Source fingerprints for receptor modeling of volatile organics. J. Air Pollut. Control Assoc., 39, 469-478, 1989.
8. Scheff, P.A., Bates, B.A., Wadden, R.A., Zhou, Qi, Kenski, D. M., Lee, Hak Sung. Evaluation of a receptor model for volatile organic compounds using ground-based wind trajectories. Paper 90-78.7, Presented at the 83rd Annual Meeting of the AWMA, Pittsburgh, PA, June 1990.
9. Gery, M.W., Whitten, G.Z., Killus, J.P., and Dodge, M.C. A photochemical kinetics mechanism for urban and regional scale computer modeling. J. Geophys. Res., 94, No. D10, 12,925-12,956, 1989.
10. Whitten, G.Z., Killus, J.P., and Hogo, H. Modeling Simulated Photochemical Smog with Kinetic Mechanism. Vol. 1., EPA-600/3-80-028a, U. S. Environmental Protection Agency, 1980.
11. Zafonte, L., Rieger, P.L., and Holmes, J.R. Nitrogen dioxide photolysis in the Los Angeles atmosphere. Environ. Sci. Technol., 11, 483-487, 1977.
12. Demerjian, K.L., Schere, K.L., and Peterson, J.T. Theoretical estimates of actinic (spherically integrated) flux and photolytic rate constants of atmospheric species in the lower troposphere. Adv. Environ. Sci. Technol., 10, 369-459, 1980.
13. Gery, M.W., Whitten, G.Z., and Killus, J.P. Development and testing of the CBM-IV for urban and regional modeling. System Applications, Inc., SYSAPP-88/002, San Jose, CA, 1988.
14. Wadden, R. A., Ross, E. D., and Quon, J.E. Characterization of ozone episodes in urban air. J. Environ. Eng. Div., ASCE, 105, 621-628, 1979.

Table I. Summary of 1987 summer days which were evaluated

Source, $\mu\text{g}/\text{m}^3$	Date										
	7/1	7/11	7/24	7/30	8/1	8/7	8/11	8/17	9/3		
Gasoline vapor	10.1	4.6	14.1	0.1	27.4	13.6	20.3	0.0	22.0'		
Refinery	16.7	7.8	11.4	1.7	37.4	22.4	35.6	0.0	37.9		
Arch. coatings	0.4	4.0	7.3	4.5	1.2	1.8	2.0	1.3	2.5		
Vehicle exhaust	45.6	34.9	63.7	49.2	45.1	41.4	26.1	54.7	49.4		
Graphic arts	0.3	3.2	5.7	3.5	1.0	1.4	1.2	1.0	2.0		
Initial Conditions											
Total hydrocarbon, $\mu\text{g}/\text{m}^3$	131.3	124.3	263.2	183.6	266.0	187.5	350.4	169.5	288.6		
NO _x , ppb (Cicero)	27	31	25	38	33	20	34	19	12		
NO, ppb (Cicero)	6	11	3	10	6	2	7	5	2		
O ₃ , ppb (UIC)	15	7	21	27	28	45	27	24	15		
CO, ppm (UIC)	0.95	0.65	0.96	2.29	0.59	1.17	1.10	1.08	0.45		
Temp, °C (initial)	20.5	24.9	26.9	26.2	25.3	25.4	22.7	24.6	18.5		
Temp, °C (maximum)	20.8	32.0	31.8	31	33.0	31.0	25.2	28.3	20.6		
Pressure, mbar	1016.7	1014.3	1019.3	1014.9	1012.1	1017.7	1018.9	1014.2	1025.5		
Relative humidity, %	65.3	56.0	74.7	74.7	82.3	55	52.7	56.7	49.0		
Trajectory analysis											
Air parcel direction (wind from ...)	NE	SW	SW	SW	S	SU	SSE	W	SE to ESE		
Air parcel direction (wind to ...)	SW	NE (Lake)	NE (Lake)	SW (Lake & ret.)	NNW	ENE (Lake)	NW	SE (over Lake)	W		
O ₃ prediction, ppb											
Max O ₃ predicted (hour)	57 (16:50)	49 (16:40)	150 (17:40)	110 (17:00)	119 (17:40)	143 (16:00)	60 (15:50)	133 (16:00)	88 (15:40)		

Source, $\mu\text{g}/\text{m}^3$	Date									
	7/1	7/11	7/24	7/30	8/1	8/7	8/11	8/17	9/3	
Max O_3 observed (hour) [Capitalized abbreviations are downwind monitoring stations]	LEHO 44 LOCK 56 ARBO 59 (16:00)	Over Lake Muskegon 90 (15:00) 93 (16:00) 95 (17:00) 88 (18:00)	Over Lake Muskegon 53 (9:00) 61 (10:00) 71 (11:00) 82 (12:00) 87 (13:00) 108 (14:00) 167 (15:00) 178 (16:00) 168 (17:00) 137 (18:00)	SPH 85 CICE 122 (17:00) SPH 120 CICE 148 (16:00) SPH 148 CICE 153 (15:00)	DEER 109 (15:00) BUTT 120 (13:00)	Over Lake (but trajectory suggests that air mass returns over IN Indiana) CHEL 117 (17:00) SEPO 75 (18:00) HAMM 108 (19:00) CALU 117 (19:00) SUPU 84 (19:00) GSAB 112 (19:00)	Over Lake (and parcel probably returned over land of MINE which showed 64 ppb peak at 1:00 a.m.) Muskegon (which would not be expected to be affected) 44 (14:00)	DESP 66 (14:00 - 15:00) TAFI 64 (18:00 but about the same all p.m.)	Over Lake (and parcel probably returned over land of MINE which showed 64 ppb peak at 1:00 a.m.) Muskegon (which would not be expected to be affected) 44 (14:00)	W out of study area ELGI 43 (13:00)

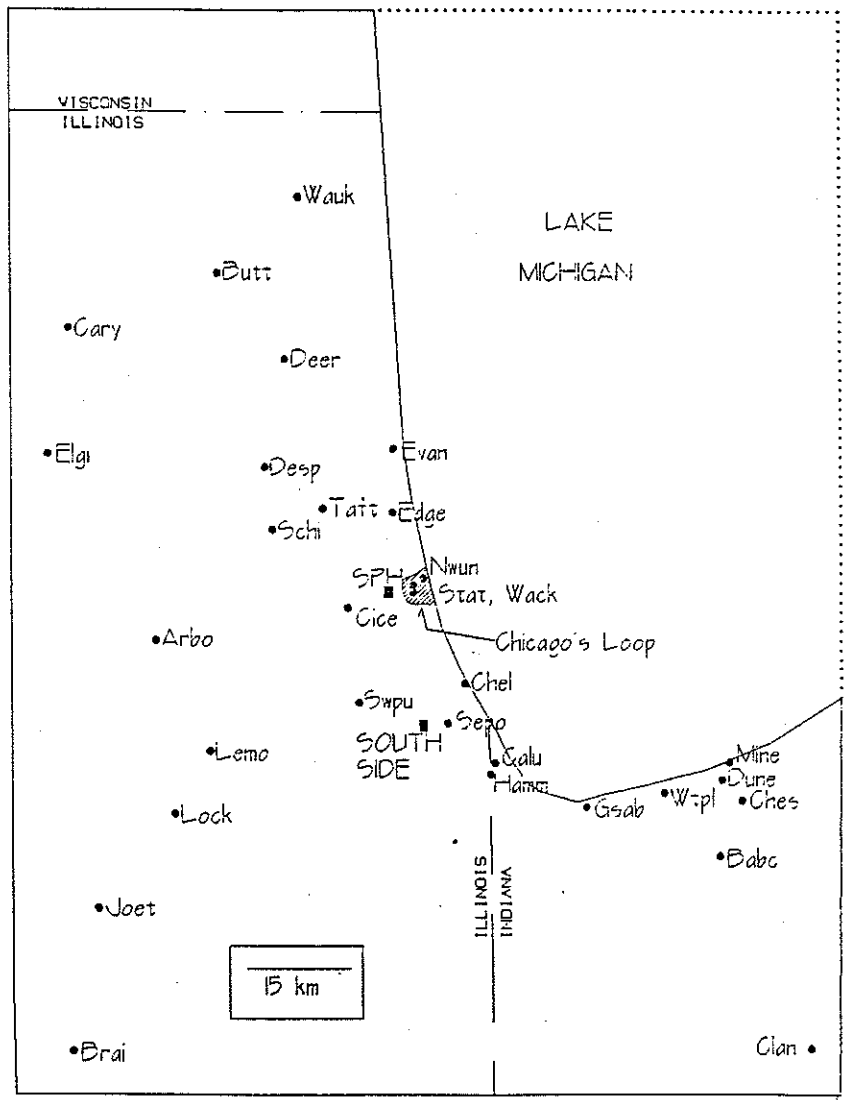


Figure 1. Chicago Area Monitoring Stations

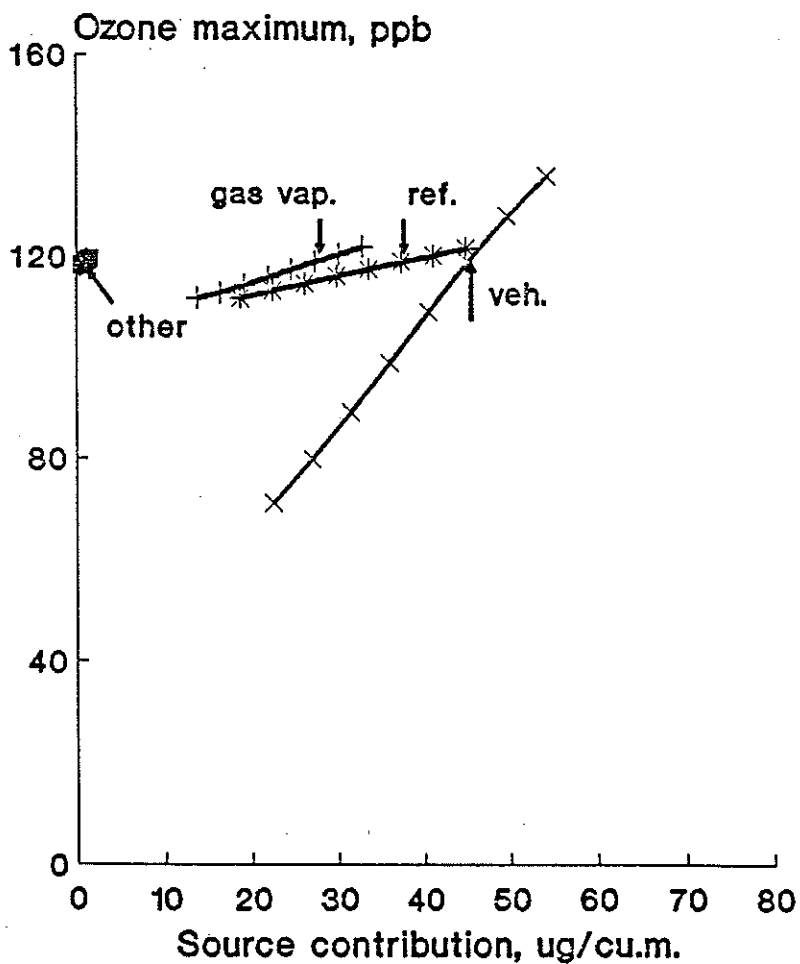


Figure 2. Ozone Maxima vs VOC Control Options for August 1, 1987. (Max. temp., 33°C; Predicted O₃, 119 ppb; Observed maximum O₃ downwind, 109-120 ppb; Arrows show base case (ambient conc.)).

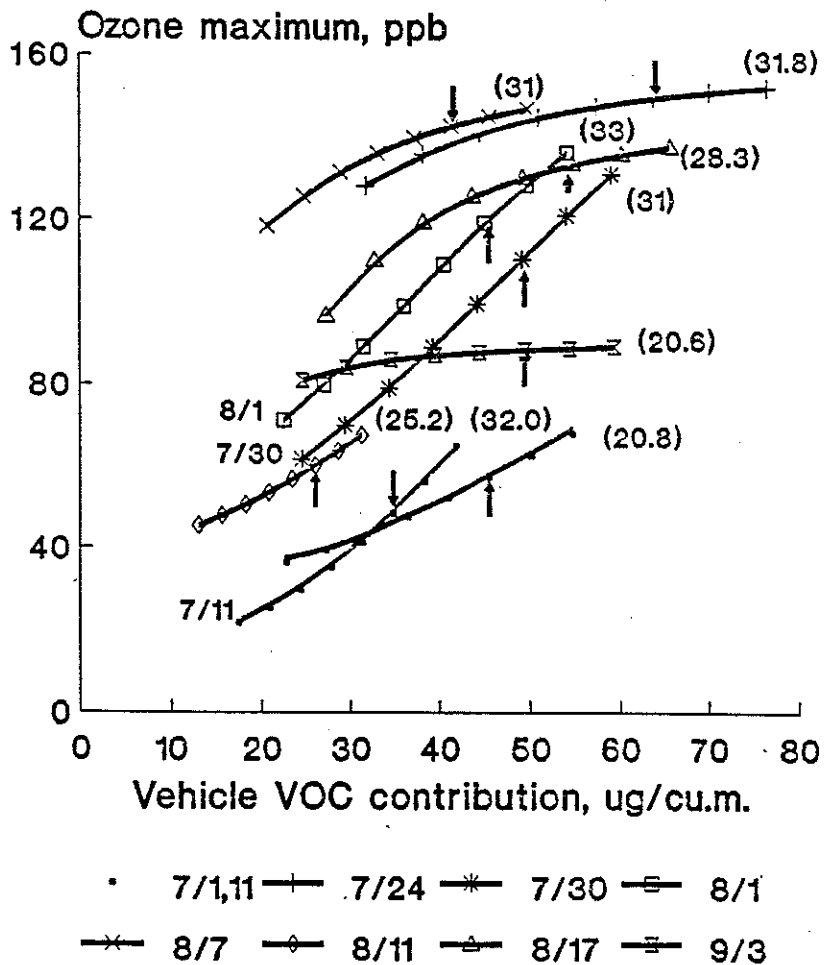


Figure 3. Ozone Maxima vs Vehicle VOC Control for July-September, 1987. (Maximum temperature in °C ()); Arrows show VOC contribution to atmospheric concentration from receptor model and ambient measurement).

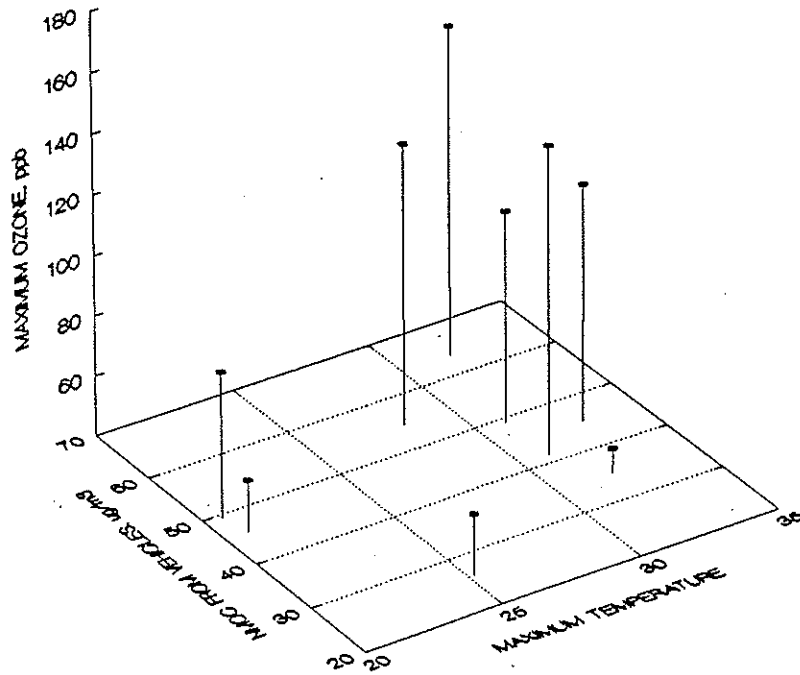


Figure 4. Control Surface for Maximum Ozone and Vehicular NMOC

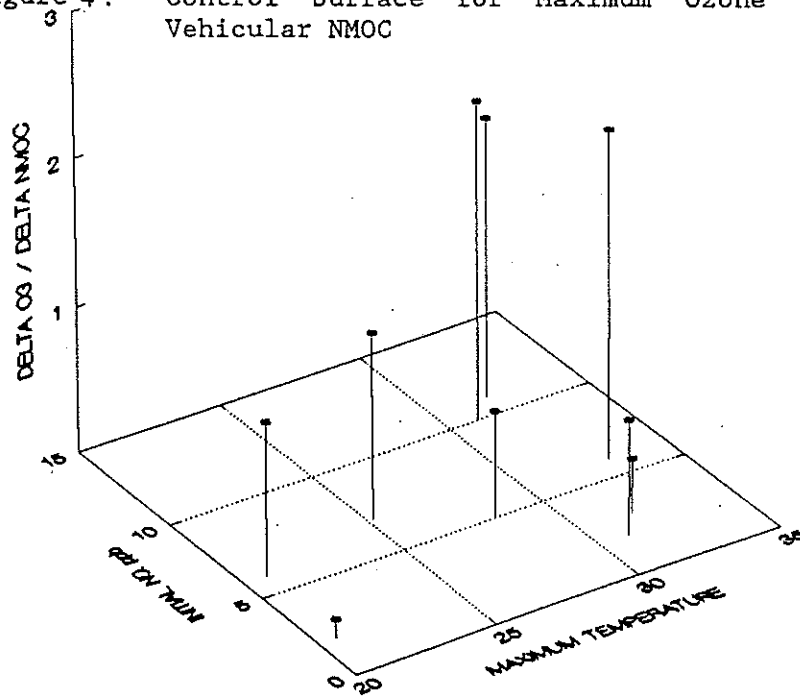


Figure 5. Change in O₃ with change in Vehicle NMOC and initial NO