1981 Winter Simulation Conference Proceedings
T.I. Ören, C.M. Delfosse, C.M. Shub (Eds.)

TROUBLE SHOOTING A PHOTOCHEMICAL GRID MODEL--THE ST. LOUIS EXPERIENCE

J. P. Killus
Systems Applications Inc.
101 Lucas Valley Road
San Rafael, California 94903

ABSTRACT

Initial application of a photochemical grid model to St. Louis underpredicted ozone formation within the urban area. Analysis indicates that the underprediction was due primarily to an underestimation of hydrocarbon emission reactivity. When emissions reactivity is corrected the model predicts concentrations of ozone similar to those observed. Predicted pollutant peaks are often misplaced, however, probably due to errors and biases in wind monitoring data.

INTRODUCTION

The SAI Airshed Model is a grid-based (Eulerian) photochemical dispersion model whose principal inputs are inventories of pollutant emissions and meteorological data files for mixing depths and wind fields. The major internal components of the model are transport (advection and diffusion, determined by meteorological inputs; see Killus et al., 1980) and chemistry. Chemical transformations in the Airshed Model are computed using the Carbon-Bond Mechanism II (Whitten, Killus, and Hogo, 1980). (See Figure 1)

Of lesser importance, but still significant for some computed results, are the initial concentrations of pollutants and the boundary conditions used in the model. Initial conditions are of importance during the first half day or so of simulation for days modeled in this study. Boundary conditions are important when transported ozone is high, or when ambient concentrations are close to tropospheric background (0.03-0.06 ppm).

Prior to the initiation of this study, application of the SAI Airshed Model to the St. Louis area by both the EPA Meteorology group and the Office of Air Quality Planning and Standards (OAQPS) had shown a persistent tendency for the model to underpredict the ozone concentrations that had been measured by the RAPS (Regional Air Pollution Study) network. This was similar to preliminary results obtained at SAI for St. Louis, prior to delivery of the SAI Air Pollution Simulation Program (APSP) and file preprocessor programs to the EPA. The underprediction problem was, however, contrary to SAI's prior experience with the Airshed Model in other cities: Denver, Colorado, and Los Angeles and Sacramento, California. Further SAI efforts at trouble-shooting had only internal funding and did not have access to current information in the St. Louis Modeling Project, e.g., the full RAPS data base and revised emissions inventories.

The nature of the underprediction problem may be described as follows: A general lack of photochemical ozone production, an apparently large ozone suppression by the urban area which was originally presumed to be caused by the NO-O_3 titration reaction, and a displacement of existent ozone to areas far downwind of the city.

In order to attempt to correct these problems, I was sent by SAI to the EPA research facility at Research Triangle Park, North Carolina.

It may be said that there is a fine line between experience and preconceived notions. At the outset let me describe my main areas of concern and how they differed from EPA staff:

> Programming errors. The computer programs used in the grid model are complex (Figure 2). Errors in the programs would not be surprising. As it happened only one such error was discovered in this project. Its

result was an overestimation of vertical mixing height in the morning. The impact on model results was marginal.

- Atmospheric chemistry. I tended to discount the possibility of major errors in this submodel. The chemical mechanism and computational scheme had been independently validated on laboratory smog chamber experiments, making it one of the few submodels with external verification.
- The emissions inventory, particularly the total mass and reactivity of the hydrocarbons involved.
- Treatment of point sources: The SAI model tends to overestimate vertical mixing in the near source area, and the very large NO_x point sources in St. Louis might be suppressing ozone formation.
- Initial and boundary conditions: Both of these inputs estimate relatively large masses of pollutant inputs from sparse and noisy ambient air quality data.
- Transport; vertical mixing and wind fields: This aspect of the modeling effort did not receive proper attention until late in this project, due to the difficultly of examining model input wind fields as they exist on the binary data file.

PREVIOUS DIAGNOSTICS

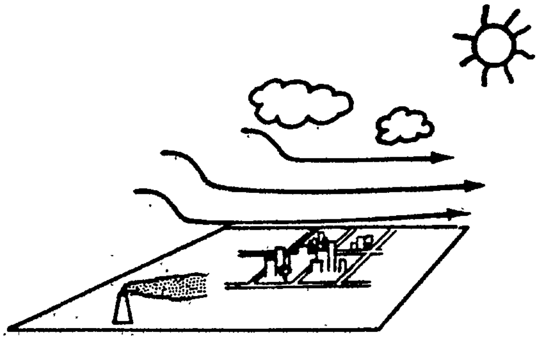
Prior to my visit, a number of diagnostic runs of the APSP had been performed by Ken Schere, of the EPA Meteorology Group, and Hank Cole, of the OAQPS. The most useful of these diagnostic simulations was a run by Ken Schere that, in essence, switched off all chemistry in the APSP.

The "no point source" run showed little difference when compared to the control run in which point sources were included. I have confirmed this result on several runs. At no time, even in the near-source region, did plume impact on O_3 and NO_2 exceed 2 to 3 pphm. Farther downwind the plume impact was negligible. The point sources cannot be the cause of the overall underprediction of O_3.

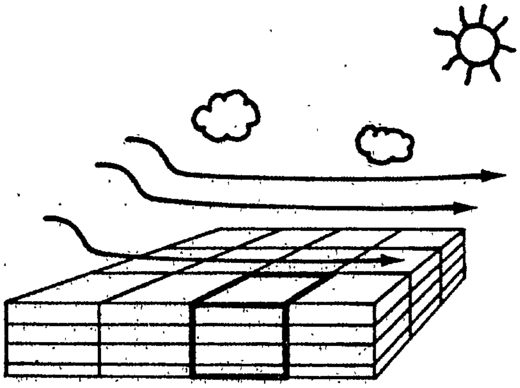
The diagnostic run prepared by Ken Schere, which eliminated all chemical reaction calculations, indicated that the ozone suppression over the city in the model was not due to chemical reaction. Figure 3 shows what seems to be ozone suppression despite the lack of chemical reaction, including the NO-O_3 reaction.

The apparent suppression of ozone was an artifact of temporally varying boundary conditions combined with transport. For the hour 1600 to 1700 (Figure 3), concentrations near the boundaries reflect a boundary condition of about 0.1 ppm. Concentrations at the center of the modeling region are the result of vertical entrainment from aloft and transport from the boundaries that took place in previous hours, when the boundary condition values were lower. The aloft concentration of ozone was 0.06 ppm and the upwind boundaries during the morning were as low as 0.02 ppm. Thus, the central region concentrations of 0.04 ppm are easily explained.

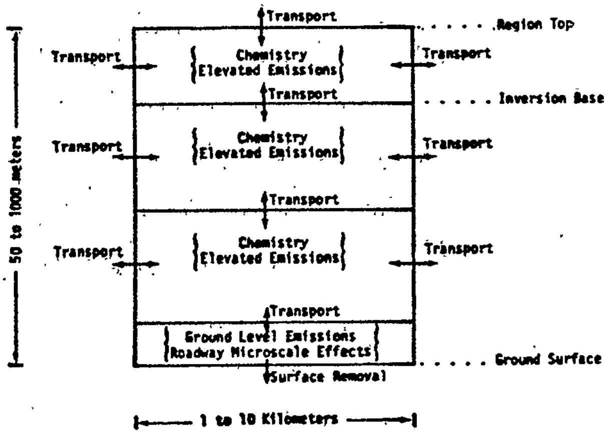
There is reason to believe that the original assumption of 0.06 ppm ozone aloft was incorrect. Upwind



(a) The Area To be Modeled



(b) Specification of the Grid



(c) Atmospheric Processes Treated in a Column of Grid Cells

Figure 1. Schematic Illustration of the Grid Used and Treatment of Atmospheric Processes in the SAI Airshed Model

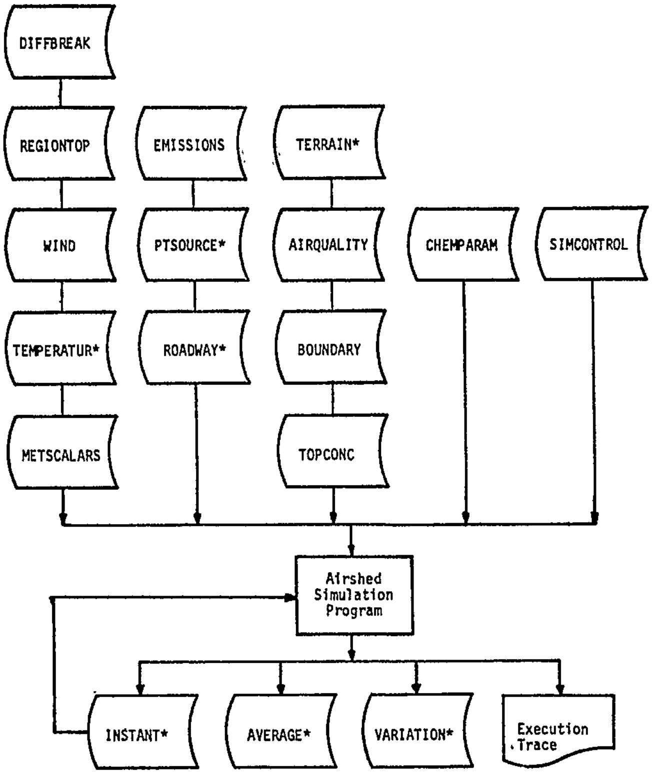
ground monitoring stations observed values of ± 2 to 4 pphm O_3 in the early morning, which rose to a peak of around 10 pphm by midday. Given the absence of upwind precursors of ozone, it seems clear that these numbers reflect the entrainment of a layer of ozone aloft. I have examined the ozone and NO_2 monitoring data and the estimated inversion rise and have concluded that the morning measurements of ozone, prior to the time when photochemical generation becomes important (about 10 to 11 a.m.), are entirely consistent with 0.1 ppm ozone aloft. Accordingly, I have made that correction to the initial and boundary conditions for day 195.

EMISSIONS INVENTORY

After first checking the overall mass balances in the pollutant emissions inventory files (to insure that this material had not somehow vanished between inventory and computation), I turned my attention to hydrocarbon reactivity.

The overall hydrocarbon splits in the emissions inventory input to the APSP in the St. Louis modeling project simulations were:

Species	Carbon Fraction
Olefins	0.06
Ethylene	0.06
Aromatics	0.08
Carbonyls	0.01
Paraffins	0.79



* Optional files.

Figure 2. Airshed Simulation Program with Input and Output Files

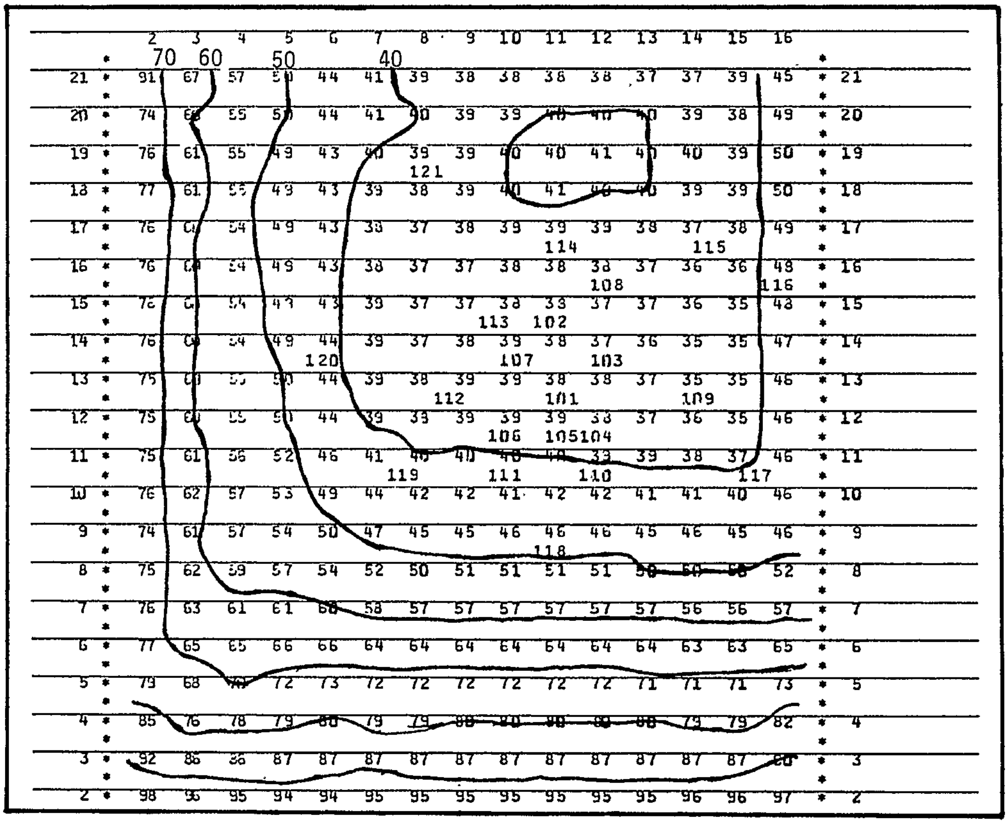


Figure 3. RAPS Day 135--4-Hour Run, 13 July 1976--No Chemistry Average Ambient Concentrations (ppb) of Ozone Between the Hours of 1600-1700

These numbers are the carbon fraction associated with the appropriate chemical bonds as required by the Carbon Bond Mechanism formulation.

Overall, this mixture would be expected to be only moderately reactive in contrast to the high reactivity one might expect for St. Louis air. The aromatics fraction, in particular, is lower than the fraction measured by Kopczynski et al. (1975) for St. Louis air, and it is much lower than the aromatics fraction observed in other cities such as Los Angeles, Denver, and New York (see Table 1).

Table 1. Ambient Hydrocarbon Speciation Data for Several Cities

	ETH	OLE	PAR	ARO	CARB*
St. Louis Highways	0.094	0.053	0.59	0.21	0.038
Downtown	0.076	0.044	0.64	0.16	0.033
Denver Expressway	0.059	0.033	0.68	0.16	0.027
Los Angeles Underpass	0.05	0.028	0.57	0.33	0.023
Lincoln Tunnel	0.085	0.049	0.62	0.21	0.035
Downtown Los Angeles	0.05	0.027	0.72	0.18	0.026

* CARB category includes only "surrogate carbonyl," highly reactive internal olefins which immediately react to form carbonyl compounds. Recent estimates (Killus and Whitten, 1981) suggest aldehyde and ketones to be at least 50 percent of emissions.

Data for aldehydes and other carbonyls are rather sparse, but various review studies at SAI have suggested tha aldehydes, ethylene, the higher olefins, and acetylene are emitted at similar molar rates. Because olefinic carbon has two carbon atoms to a single carbonyl carbon atom (per mole), the estimated aldehyde carbon fraction is approximately 0.03 (Killus et al., 1980). By way of comparison, the carbon fraction associated with automobile exhaust aldehydes in the EKMA model is 0.05.

We view the 0.03 carbonyl fraction as a lower limit for emissions. A carbonyl fraction as low as 0.01 definitely retards the rate of chemical reaction.

The reason for the difference between the SAI assumptions and the EPA assumptions seems to be that the data used in preparation of the RAPS inventory show few carbonyl products other than formaldehyde. The SAI mechanism requires inputs of all carbonyls, including ketones. Also, very reactive olefins, such as trans-2-butene, are treated as carbonyls because of the very fast rate of reaction of those species.

In order to bring the SAI/RAPS model into agreement with other SAI studies (Killus et al., 1980; Anderson et al., 1977), as well as to reflect auto exhaust reactivity as shown by smog chamber studies, I boosted the aldehyde emissions rates by a factor of 3 and resplit the other hydrocarbons to show a 0.24 fraction for aromatics and a 0.63 fraction for paraffins. All other emissions were left unchanged. The change in aldehyde emissions increases the overall reactivity problem in the SAI model for day 195. Peak ozone calculated in the airshed model now came to within about 10 percent of the observed ozone values on that day (see Figure 4).

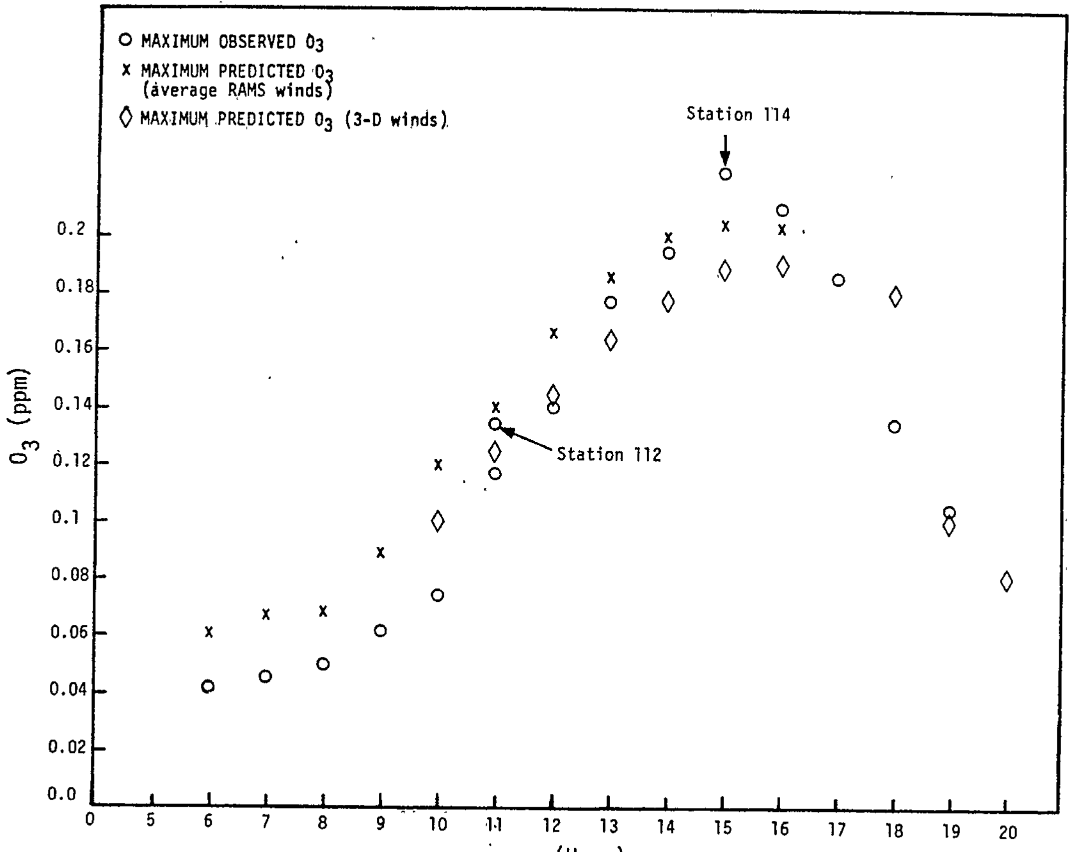


Figure 4. Peak Ozone Observed (Anywhere in Region) Compared to Peak Ozone Predicted (Anywhere in Region) for Day 195

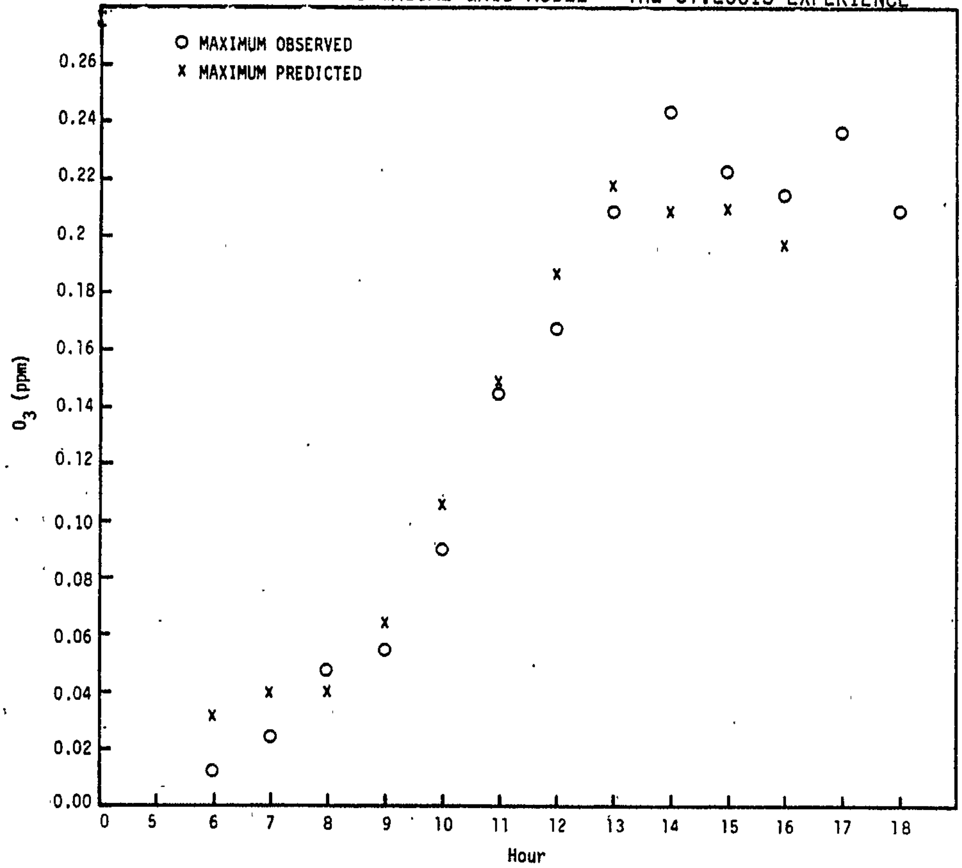


Figure 2. Peak Ozone Observed (Anywhere in Region) Compared to Peak Ozone Predicted (Anywhere in Region) for day 275

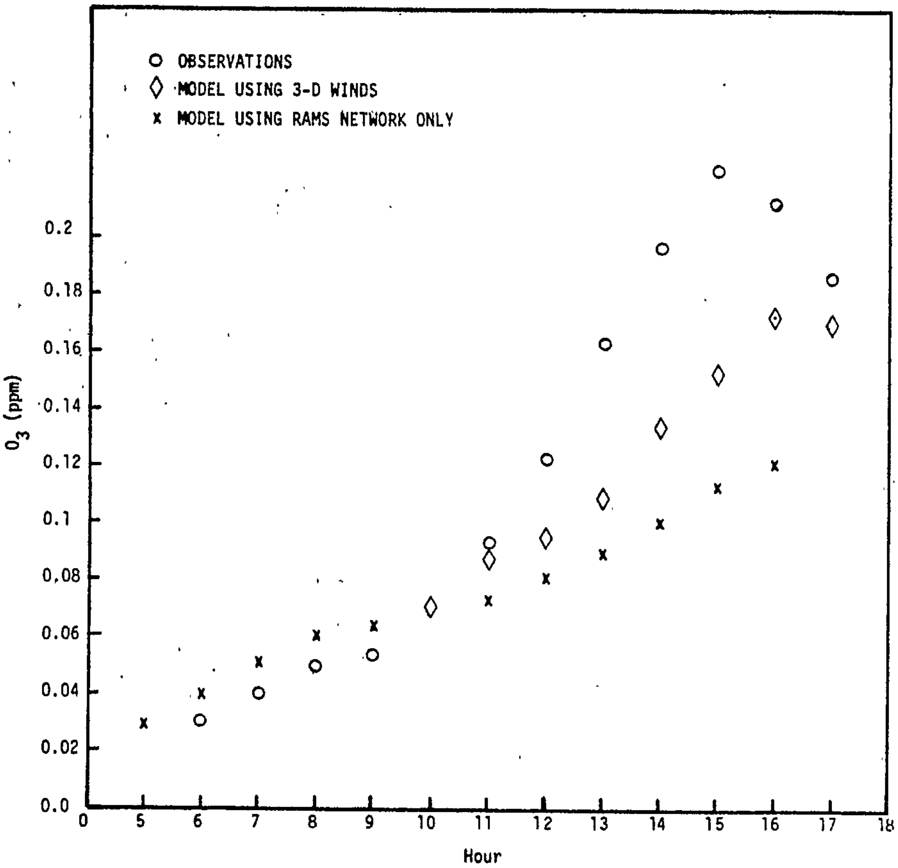


Figure 6. Ozone Observations Compared to Predictions (Two Sets of Wind Fields) for Station 114 on Day 195

A problem still remained with the overall spatial pattern of model predictions. Peak ozone was displaced somewhat farther downwind than the observed values would indicate, and the downtown station ozone values were still underpredicted. These problems could be caused by a variety of errors in in model inputs: spatial errors in emissions, greater transport of ozone from aloft than was assumed, or errors in the wind field. In order to test these factors, I chose to model day 275, an intense stagnation episode with little transport and high photochemical generation of ozone.

TEST FOR DAY 275

Day 275 was the day of the highest observed ozone concentrations for St. Louis in 1976. The highest ozone values were measured at the downtown stations in the area of maximum emissions, indicating the occurrence of stagnation conditions.

It is fairly surprising that day 275 was so high in ozone. Sunlight is weaker in October than during the summer, and the period of sunlight was much less than in other photochemical runs. Also, on many of the other days, ozone transport into St. Louis was a significant factor in smog formation, while on day 275 this was not the case.

The first simulation of day 275 for this study, using the new emissions splits, again underpredicted ozone formation, though not as badly as prior simulations. I examined the initial conditions for day 195 and day 275 using a utility program that we had transferred to the EPA facility for this purpose. For day 195 the mass of pollutants in the initial condition field was insignificant. For day 275, however, the initial pollutant mass was a significant factor in the day's pollutant burden. The hydrocarbon splits used in the preprocessor inputs that prepared the initial conditions still reflected the emissions inventory assumptions concerning aromatic hydrocarbons, though the aldehyde fraction was higher than in the emissions inventory. About 7 percent of the NMHC in the initial conditions is assumed to be aldehydes.

Examination of winds from day 274 indicates that the stagnation conditions began in the evening of that day. To estimate the pollutant burden that should exist in the airshed at the beginning at the simulation, I performed simple ventilation calculations based upon the mean average wind speed of the wind station network, assuming that a 1 m/sec wind corresponded to a 4 percent per hour ventilation. The result was that the initial condition field at 5:00 a.m. on day 275 should have contained about 35 percent of a full day's emissions, about 250 metric tons NMHC and 100 metric tons NO_X. About two-thirds of this mass came from post-sunset emissions on day 274.

This mass of pollutants would be contained in the initial condition field if the ground station values of NMHC and NO_X were interpolated and extended to a height of about 100 meters (originally the polluted layer was terminated at 50 m). Some above-background concentrations were extended above this to represent carryover from the previous day's elevated mixing region. The precursors aloft were at low concentrations, generally less than 50 ppb above background.

The paraffins and aromatics were resplit to conform to our new assumptions about emissions. The aldehyde fraction for initial conditions was left unchanged. The aging of smog does increase the aldehyde fraction, though the olefins and, to a lesser extent, the aromatics and ethylene should be slightly reduced to account for this. The difference should not affect the simulation results noticeable, however. The reactivity of a hydrocarbon mix is less sensitive to aldehyde emissions above 3 percent than it is to emissions less than 3 percent.

The second run of day 275 reproduced the peak ozone concentration fairly well (<20 percent underprediction) see figure 5) but again was spatially misaligned. The peak concentration in the simulation was located about 16 km to the north of the city center, while peak ozone was observed at the downtown sites. This seems to confirm the supposition that there may be a problem with the wind field, as noted in the previous discussions of the results for day 195.

DESCRIPTION OF MODELED TRANSPORT ON DAYS 195 and 275

In an analysis of the results for day 195, Dr. K. Demerjian of EPA noted what seemed to be an inconsistency between the pattern of morning precursor concentrations and observed pollutant levels. After satisfying ourselves that there was no misplacement of the emissions grids, we hypothesized that the simulated pattern could result from an overestimation of the wind velocities.

In the afternoon on day 195, a wind shear situation seemed to develop, with the winds aloft differing greatly in direction from those measured by the RAMS network. The upper air data indicate a turning of the winds at noon when a flow from the south was established. The RAMS network indicates a flow from the southeast.

In the actual observations, the shift in pollutant advection to the north resulted in a rapid rise in oxidant readings for stations in that sector (see Figure 3 for station 114). The model underestimates this rise, probably because of a misalignment of the advected pollutant cloud. This misalignment is emphasized if the RAMS data are used alone (see Figure 6).

On day 275, as noted above, peak predicted ozone was found some 16 km north of the city, while peak was observed in the downtown area.

These results are consistent with the hypothesis that there is a bias in the RAMS network wind field. This bias does not have to be large. An overall bias of about 1 m/sec from the south on day 275 is sufficient to explain the misalignment. A bias that is similar in magnitude but directed from the east or southeast would explain the misalignment on day 195.

Spatial misalignment is not an uncommon feature of wind fields based on ground data. In our simulations of Denver, Colorado, we noted a misalignment of the pollutant field of about 60 degrees

(Anderson et al., 1977; Killus, Anderson, and Hayes, 1980), which results in a poor spatial correlation compared to temporal correlation. (The all-station temporal correlation coefficient for a typical Denver simulation was 0.88, while the spatial correlation was only 0.4. If pollutant values above 0.08 ppm only are considered, the spatial correlation coefficient becomes negative).

DISCUSSION

The SAI Airshed Model is a set of general programs that can be manipulated by a competent user to produce realistic wind fields, emissions files, and airshed simulations. The data preparation programs, straightforwardly applied, produced an airshed simulation that was, after some troubleshooting, minimally acceptable. Errors in the spatial alignment of model predictions may be traced to the wind fields.

If, as we hypothesize, there is a bias in the wind station data, or even a large random error factor, what may be done to improve the simulations? Clearly, some wind wind algorithms are more sensitive to input errors than others. Choice of a new wind algorithm might improve matters. Perhaps an entirely new wind field preparation methodology, e.g., wind modeling, would be useful.

However, I resist the "black box modeling" orientation of such an approach. It is my opinion that operator judgment is required regardless of the methodology used. Large simulation programs are an aid to analytical thinking, not a substitute for it. I believe that the present airshed model and data preparation programs are a sufficient starting point for the production of an adequate simulation.

All air pollution model users are still in a learning curve. The models are complex tools and require as much experience in their use as other more hardware-oriented processes require. One should expect a learning curve for use of an airshed model to be similar to that for use of an electron microscope or a sophisticated gas chromatograph. On the basis of past experience at SAI, I would say that the St. Louis modeling exercise is proceeding as well as one would expect; the present results for St. Louis are similar in quality to those obtained at the preliminary stages in modeling projects for Denver, Los Angeles, and Sacramento. Results should improve as the operators gain experience with the model.

CONCLUSIONS

> The reactivity problem that caused this study to be initiated has been corrected.

> A problem with the spatial alignment of the pollutant cloud remains, at least for days 195 and 275.

> The misalignment of the pollutant cloud is inherent in the use of the wind station data. However, some wind field algorithms are more sensitive to data biases than others.

RECOMMENDATIONS

> That the wind station data be carefully examined for biases and cross correlations.

> That operator judgment be used in preparing the wind fields from data.

REFERENCES

Anderson, G.E., et al. (1977), Air Quality in the Denver Metropolitan Region 1974-2000, EPA-908/1-77-002, Research Triangle Park, North Carolina

Calvert, J.G. (1976), Hydrocarbon Involvement in Photochemical Smog Formation in the Los Angeles Atmosphere, Environ. Sci Technol., Vol. 10, No. 3.

Killus, J. P., G. E. Anderson, and S. R. Hayes (1981), Simulation of Ozone Formation in Denver, Colorado, Using a Photochemical Grid Model, 62nd Annual Meeting of Pacific Division AAAW, 14-19 June 1981, Eugene, Oregon.

Killus, J. P., and G. Z. Whitten (1981), A User's Guide to the Carbon-Bond Mechanism, SAI. No. 75-81-EF81-90, Systems Applications, Inc., San Rafael, California.

Killus, J. P. , et al. (1980), Continued Research in Mesoscale Air Pollution Simulation Modeling--Vol. V, EF77-142A Systems Applications, Inc., San Rafael, California.

Whitten, G. Z., J. P. Killus, and H. Hogo (1980), Modeling of Simulated Photochemical Smog with Kinetic Mechanisms. Vol. 1, Final Report EPA-600/3-80-028a, U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina.

Whitten, G. Z., H. Hogo, and J. P. Killus (1980), The Carbon-Bond Mechanism: A Condensed Kinetic Mechanism for Photochemical Smog, Environ. Sci. Technol., Vol. 14, p. 690.