Appendix M

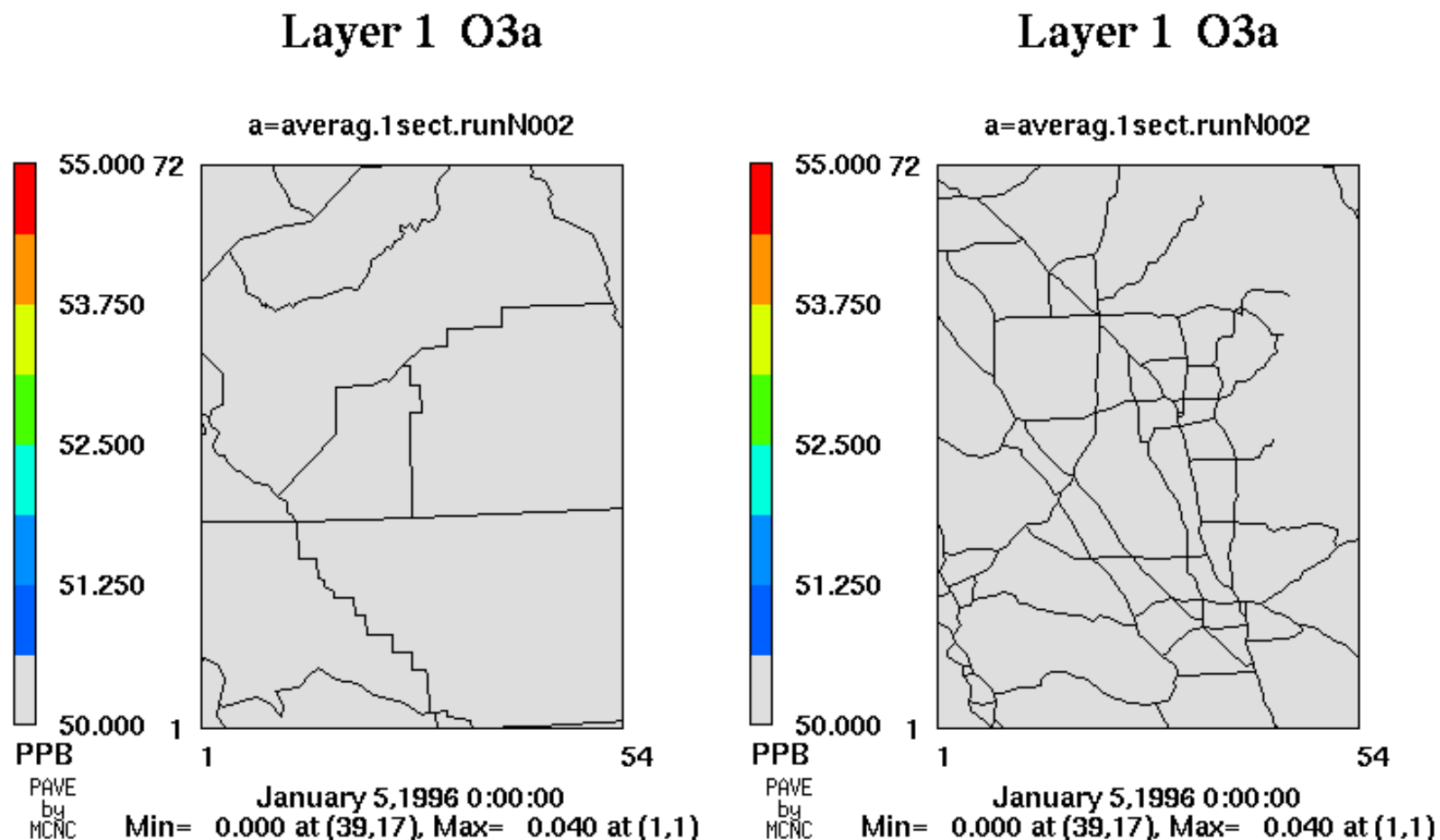# UAM-Aero Documentation for NO$_x$ and Ammonia

1. Introduction:

During the fall and winter of 1995-96, a comprehensive field-monitoring program (the 1995 Integrated Monitoring Study or IMS-95) was conducted in the San Joaquin Valley, California to collect gaseous, particulate, and meteorological data. This was a preliminary field study to support planning of a future large-scale field program to (a) provide an improved understanding of the nature and cause of high particulate matter (PM) concentrations in the Valley, (b) develop tools to help decision-makers in evaluating alternate control strategies, and (c) understand the complex chemical linkage between PM and other pollutants.

Three winter *PM* episodes were captured during the IMS-95. They occurred during December 9-11, 1995, December 24-28, 1995, and January 4-6, 1996. The most complete data set available is for the January episode and, thus, it was the focus of a previous modeling study conducted by the staff of Air Resources Board. Due to the availability of input data the January 4-6, 1996 episode was selected for this modeling effort to support the PM$_{10}$ State Implementation Plan for the San Joaquin Valley.

The 1997 aerosol version of the Urban Airshed Model IV (UAM-AERO) (Lurmann *et al.,* 1996, Kumar *et al.,* 1995) was applied to the IMS-95 modeling domain. This domain covers approximately 215 km east-west and 290 km north-south and extends from the Coastal Range to the crest of the Sierra Nevada and from the Tehachapi Mountains to Merced. Figure 1 shows the modeling domain with sampling sites at South West Chowchilla (SWC), Fresno (FEI), Kern Wildlife Refuge (KWR), and Bakersfield (BFK). The grid resolution used was 4 km^2. The vertical grid structure contained two layers below the mixing height and three above. The top of the domain was placed at 3 km above ground level. The entire modeling domain was assumed to lie in the zone 10 of the Universal Transverse Mercator (UTM) coordinate projection even though about half of the domain lies in the UTM zone 11. The UTM coordinates of the origin of the modeling domain were 705.267 km Easting and 3858.607 km Northing. There were 54 grid cells in the east-west and 72 in the north-south directions.

While there have been other grid-based aerosol modeling studies conducted in California (Lurmann *et al.,* 1996, Seinfeld *et al.,* 1997), this is the first successful attempt to model winter aerosol conditions in Central California with comprehensive sets of 3-D meteorological and spatially and temporally resolved *PM* data.

Figure 1: The modeling domain. The panel on the left shows the county boundaries within the domain. The panel on the right shows the main highways within the domain.

It is important to note, however, that the grid-based photochemical model does not simulate the 24-hour design value of this plan directly. Instead we simulate measurements made five years earlier and those measurements do not represent any violations of the 24-hour PM_{10} NAAQS. The magnitude and relative amounts of emissions for that period may also differ from the design day emissions. This poses a significant difficulty in using the results of these simulations to represent the 24-hour design value. Since these simulations represent only the winter period the results obtained are not applicable to the design value for the annual PM_{10} NAAQS.

However, assuming that the chemical nature of the atmosphere does not change significantly from one winter period to another within a few years, one may be able to argue that the limiting precursor(s) of ammonium nitrate (NH_4NO_3) concentrations of the IMS-95 period may be applicable to the 2000 design value days.

2. Computational Method:

The latest version of UAM-AERO (Lurmann *et al.,* 1996, Kumar *et al.,* 1995, Kumar *et al.,* 1997) was applied to the January 4-6, 1996 IMS-95 episode. This version of the code includes the SAPRC-90 chemical mechanism (Carter, 1990), an implicit-explicit hybrid (IEH) method for numerical integration of gas-phase chemical kinetics (Sun *et al.*, 1994; Kumar *et al.*, 1995), and the SEQUILIB aerosol module (Pilinis and Seinfeld, 1987)

In addition to simulating O_3 and its precursor concentrations, UAM-AERO simulates the formation of secondary *PM* from gaseous precursors. The gaseous inputs to the model are oxides of nitrogen (*NO*x), sulfur dioxide (SO_2), ammonia (NH_3), volatile organic compounds (*VOC*), and carbon monoxide (*CO*). The *VOC*s were further speciated into species required by the SAPRC-90 chemical mechanism (Carter, 1990). The preparation of the emission inventory will be discussed in a subsequent section. The model predicts hourly *PM* size distribution and the chemical composition. The simulated *PM* species are nitrate (NO_3^-), sulfate (SO_4^{2-}), ammonium (NH_4^+), sodium (Na^+), chloride (Cl^-), elemental carbon (*EC*), organic matter (*OC*), crustal matter (*OTR*), and water (H_2O).

Even though the model is capable of simulating up to nine *PM* size fractions, we used the model with one size fraction (0.01-10 µm). It was suggested (Lurmann *et al.,* 1996) that at least nine size fractions should be included in the simulation if the simulated concentrations are to be compared confidently with $PM_{2.5}$ observations. However, due to the lack of *PM* source profiles of that resolution we were unable to prepare the necessary emission inventories for that case.

3. Model Inputs:

The preparation of input information for UAM-Aero is outlined in Appendix K titled SJVAPCD PM10 Modeling Protocol. Thus, we would not repeat that information here except for initial and boundary conditions. Those conditions used for the modeling are shown in Tables 1 and 2.

As seen from these tables both the initial and boundary conditions for gaseous pollutants are nearly clean. Sensitivity simulations indicate that higher boundary conditions would increase the simulated concentrations of pollutants in the domain, but control strategies are not significantly affected by those elevated concentrations. The particle concentrations along the boundaries are significant and vary for each day and each boundary. These values were derived from concentrations observed at boundary sites.

4. Gridded Emissions Inventory:

The preparation of emissions inventories for this study using the EMS-95 emissions processing system (Version 2.01) was described in detail elsewhere (Hughes *et al.,* 1998). In brief, a spatially, temporally, and chemically resolved emissions inventory for the January 4-6, 1996 episode was developed using the base emissions inventory inputs for *CO, NO*x, SO_2, NH_3, PM_{10}, and total organic gases (*TOG*) for area-, motor vehicle-, and point sources. Day-specific emissions input data for use in generating this modeling inventory were not collected during the IMS-95 study period. As a result, annual-average and average-day inventory sources were used exclusively. Biogenic emissions are assumed to be negligible due to low leaf biomass, low solar insolation, and low ambient temperatures during wintertime.

The ammonia inventory developed by ENVIRON under contract to the Air Resources Board was used for this modeling effort. This is a new inventory that has not been subjected to a rigorous quality assurance process. Area source emissions and temporal inputs for *CO, NO*x, SO_2, PM_{10}, and *TOG* were extracted from the California Emissions Inventory Development and Reporting System (CEIDARS) and processed for the January 4-6 time period (1999 base year back-casted to 1996). SARMAP (DaMassa *et al.,* 1996) spatial surrogates were used to spatially distribute all area source emissions. BURDEN7g (BURDEN7g, 1996) emissions for *CO, NO*x, SO_2, PM_{10}, and *TOG* were distributed along the SARMAP (DaMassa *et al.,* 1996) roadway network using SARMAP-based day-of-week-, temporal- and spatial scalars.

Table 1: The static boundary and initial conditions used for the gaseous model species (ppm).

NO	5.0E-05	OLE1	2.5E-04	CRES	3.0E-06
NO2	1.0E-04	OLE2	2.2E-04	XOOH	1.0E-10
O3	4.0E-02	OLE3	2.9E-05	RNO3	1.0E-10
HO2	1.0E-10	OLE4	1.0E-10	XC	1.0E-10
OH	1.0E-10	ARO1	1.4E-04	NO3	5.7E-06
RO2	1.0E-10	ARO2	8.0E-05	N2O5	5.7E-06
CCO3	1.0E-10	ETHE	4.0E-04	SO2	1.0E-03
PCO3	1.0E-10	HCHO	3.3E-03	HSO4	1.0E-06
HONO	5.0E-06	CCHO	2.6E-04	COC	1.0E-06
HNO3	5.0E-06	RCHO	1.2E-04	FACD	1.0E-10
HNO4	5.0E-06	MEK	3.0E-05	AACD	1.0E-10
H2O2	1.0E-03	MGLY	3.0E-06	HCL	1.0E-06
CO	2.0E-01	PAN	3.0E-06	NH3	1.0E-03
ALK1	1.5E-03	PPN	1.0E-10		
ALK2	8.0E-04	AAFG2	1.0E-10		

Table 2: The boundary conditions used for PM ($\mu g/m^3$) for each boundary for each day.

Boundary	Date	Total	NO_3^-	SO_4^{2-}	NH_4^+	EC	OC	Cl	Na$^+$	H$_2$O	OTR
West	1/4/96	20.4	7.43	1.65	2.73	1.09	2.91	0.02	0.13	0.37	4.12
	1/5/96	33.9	14.6	2.38	5.13	1.55	5.29	0.02	0.16	0.73	4.06
	1/6/96	40.8	20.3	2.20	6.72	1.80	5.11	0.02	0.19	1.02	3.41
South	1/4/96	26.5	9.54	2.15	3.55	1.42	3.78	0.01	0.27	0.48	5.27
	1/5/96	26.4	11.3	1.85	3.99	1.20	4.12	0.01	0.12	0.57	3.16
	1/6/96	29.3	13.9	1.78	4.66	1.95	4.45	0.11	0.11	0.69	1.62
East	1/4/96	41.7	18.8	2.42	6.36	1.85	2.74	0.00	0.11	0.94	8.55
	1/5/96	43.0	17.5	2.55	6.03	2.47	2.72	0.00	0.23	0.87	10.6
	1/6/96	13.3	4.01	0.83	1.47	1.76	2.50	0.00	0.13	0.20	2.43
North	1/4/96	29.8	10.7	2.42	3.99	1.60	4.25	0.46	0.12	0.54	5.64
	1/5/96	42.5	18.0	2.47	5.96	1.86	4.42	0.24	0.07	0.90	8.60
	1/6/96	42.2	17.3	2.31	5.80	2.30	5.74	0.39	0.02	0.86	7.49

5. Model Performance:

While we have looked at the performance of the model with respect to several pollutants, we restrict our discussion here to only a few pollutants.

Figure 2 show the comparison of hourly ozone (O_3) concentrations at four key stations. Note that during this episode, the O_3 concentration never exceeded 40 ppb at any of the four sites. This is due to reduced solar insolation and cooler ambient temperatures during the winter. The model overestimates the O_3 concentrations for all daylight hours except at Bakersfield. Further investigations indicate that the modeling emissions inventory is NOx rich at Bakersfield compared to other sites and that results in a well-understood "ozone hole" around Bakersfield. But, since the ambient observations do not support the presence of such an ozone hole, we believe that our modeling inventory is artificially rich in NO_x in that region. The moderate overestimation of ozone at other sites is not a source of significant concern to us.

Figure 3 shows the comparison of measured and simulated PM_{10} 24-hour concentrations with major chemical species indicated individually. The overall agreement between the measured and simulated concentrations is very satisfactory, perhaps except for the January 03, 1996 at Bakersfield. This disagreement seems to be due to elevated level of primary emissions at that site for that day. The agreement for nitrate, ammonium, and sulfate concentrations is extremely satisfactory at all sites for all days. The organic carbon is consistently over predicted at all sites.

6. The Sensitivity of Nitrate Concentrations to Precursor Reductions:

We now discuss how the concentration of nitrate would change, as precursor concentrations are reduced domain wide. It is important realize that nitrate formation is sensitive to three precursors. They are NOx, ammonia (NH_3), and volatile organic compounds (VOC).

Using the results of several sensitivity simulations, we first observed that the nitrate concentrations in the domain are not very sensitive to VOC concentrations. This fact is illustrated in figure 4, which shows the response of nitrate concentrations to various combinations of domain-wide VOC and NO_x emission reductions. It is interesting to note that rural sites are consistently non responsive to VOC emission controls while the urban sites become increasingly insensitive with time. It is worth noting that the largest response to VOC reductions are in the peak nitrate regions and in areas away from those regions the response is very small and at times slightly disbeneficial. The sensitivities to 50% reductions in precursors are shown in figure 5.

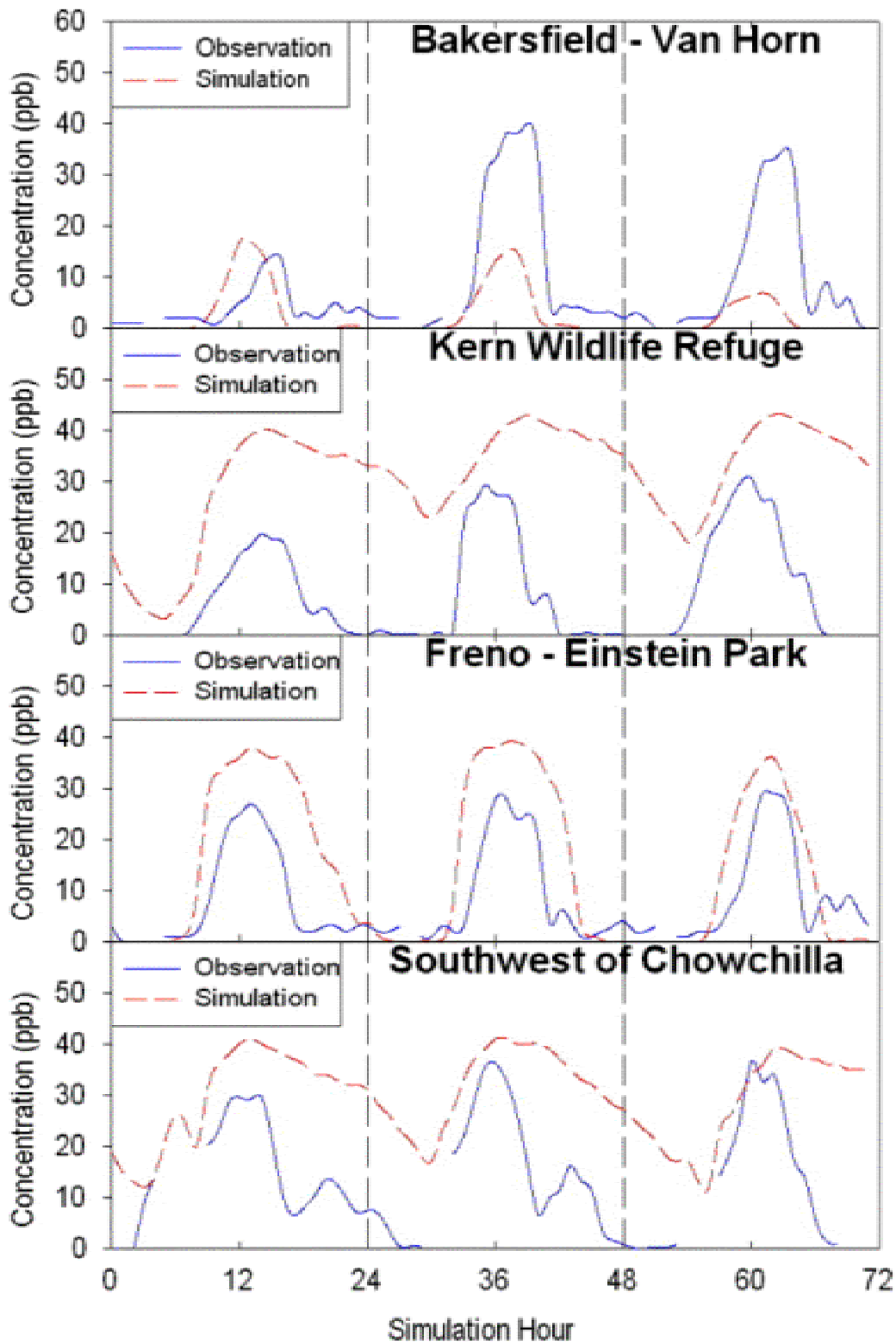**Figure 2:** The comparison of hourly ozone (O₃) concentrations at four key stations.

Figure 3: The comparison of measured and simulated PM$_{10}$ 24-hour concentrations for major chemical species.
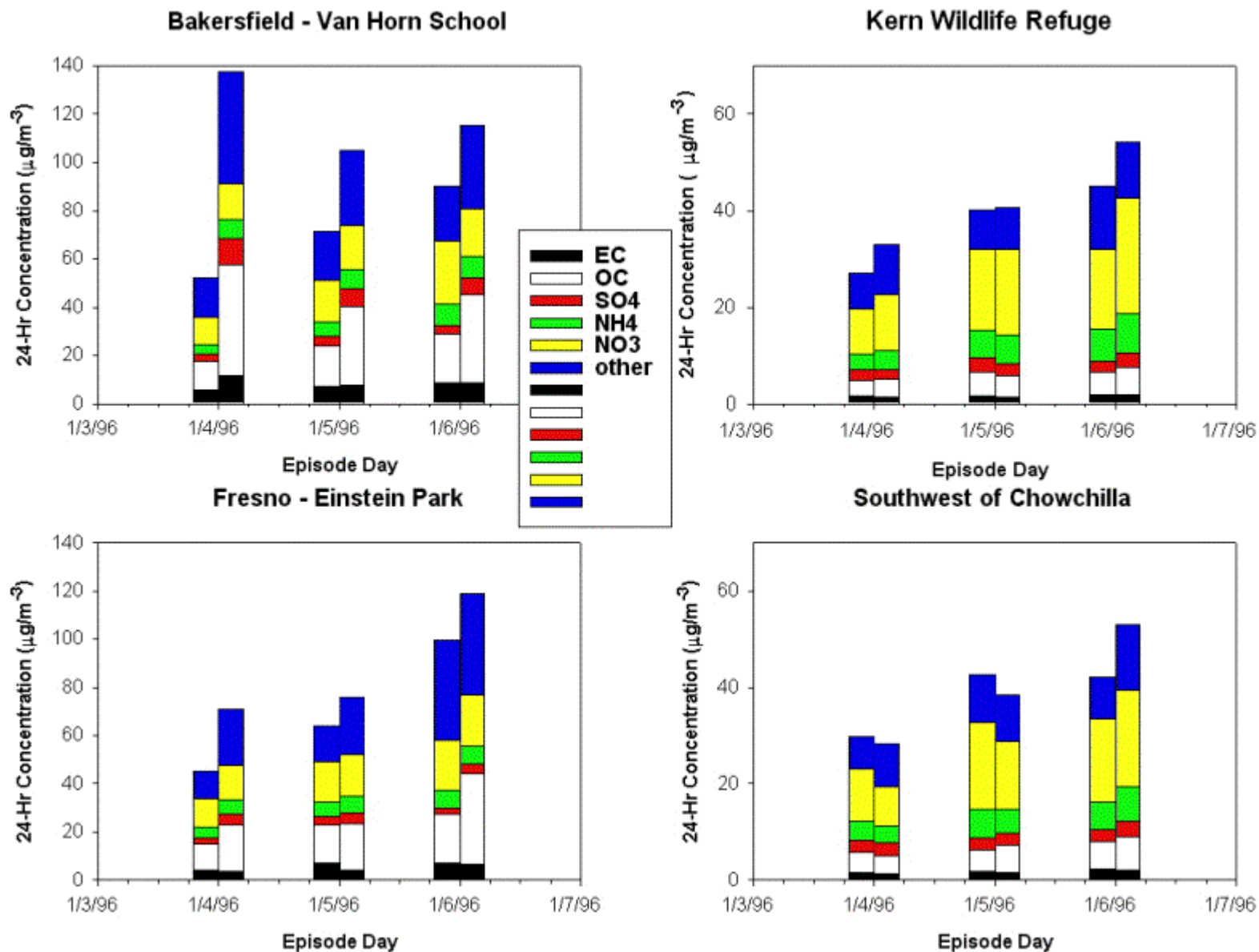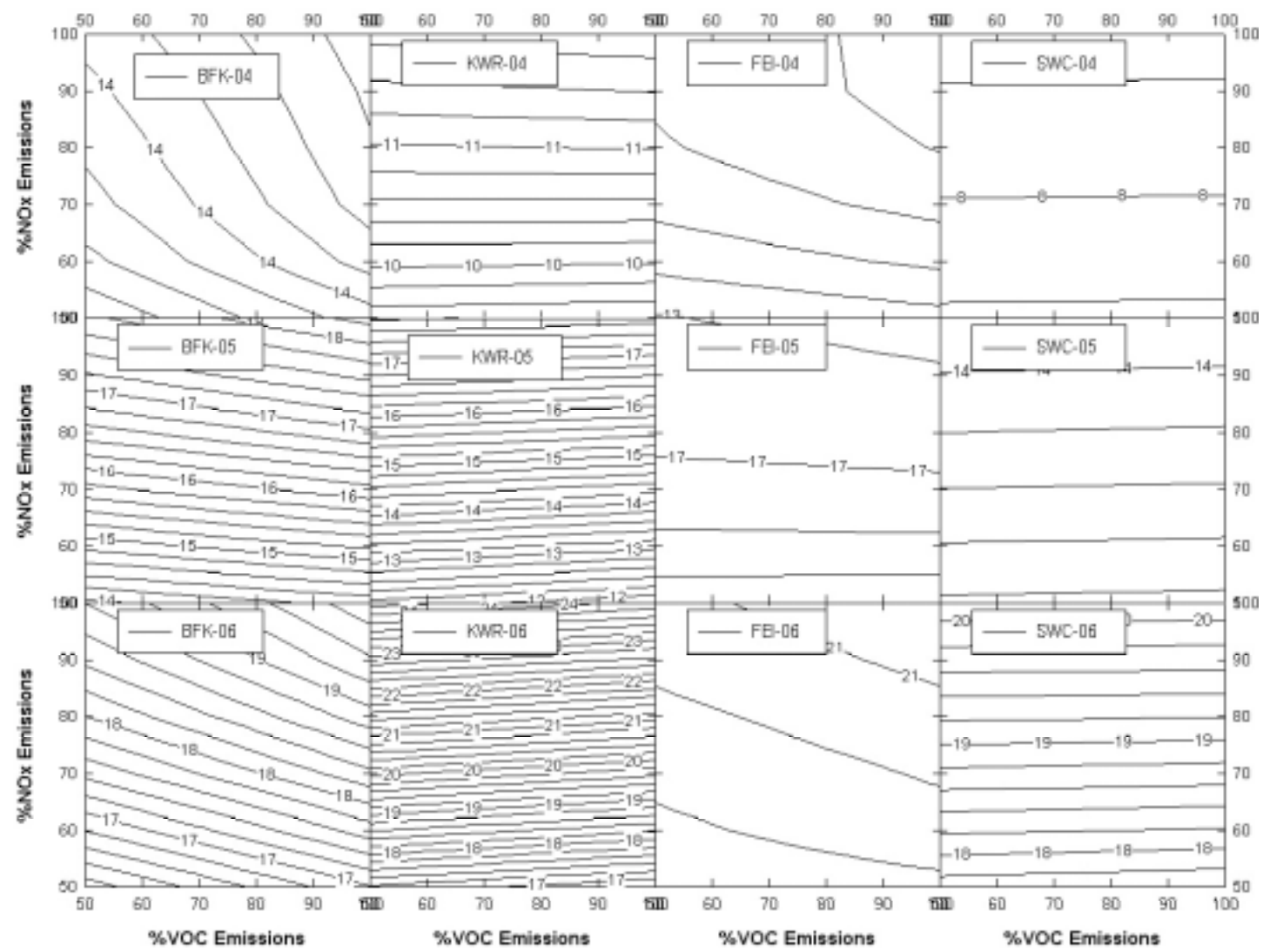
Figure 4: The response of nitrate concentrations to various combinations of domain-wide reductions of VOC and NOx emissions. Each panel represents a day and a monitoring site. (BFK- Bakersfield (Van Horn School), KWR – Kern Wildlife Refuge, FEI – Fresno (Einstein Park), SWC – South West Chowchilla, 04 - January 04, 1996, 05 – January 05, 1996, 06 – January 06, 1996). Note that emission controls are up to 50% only.
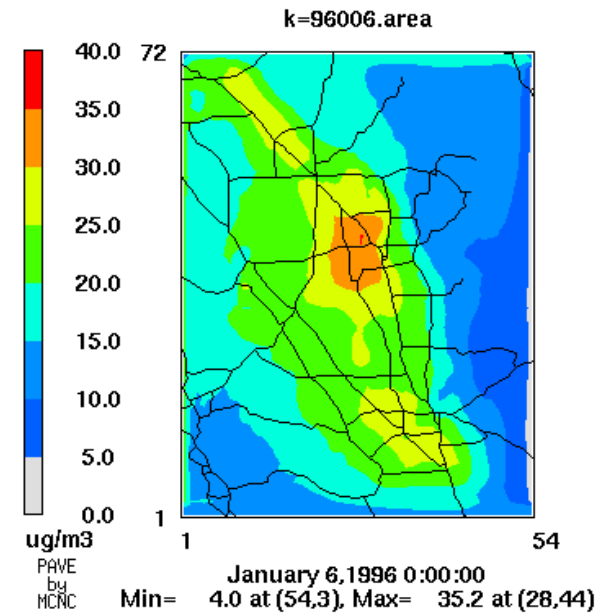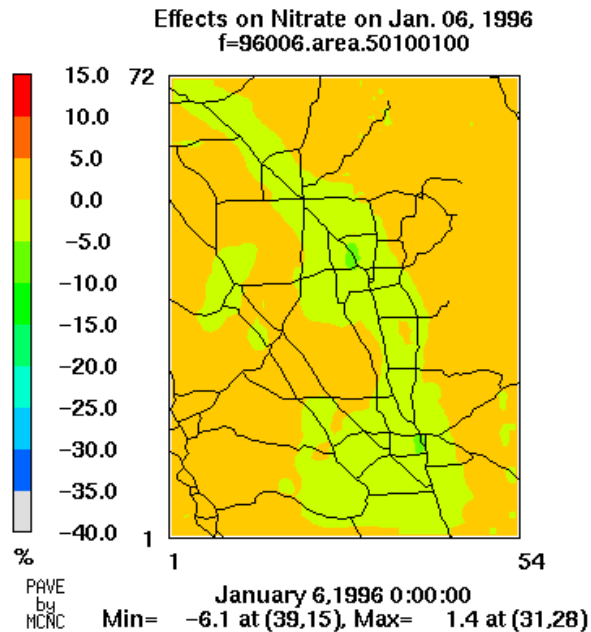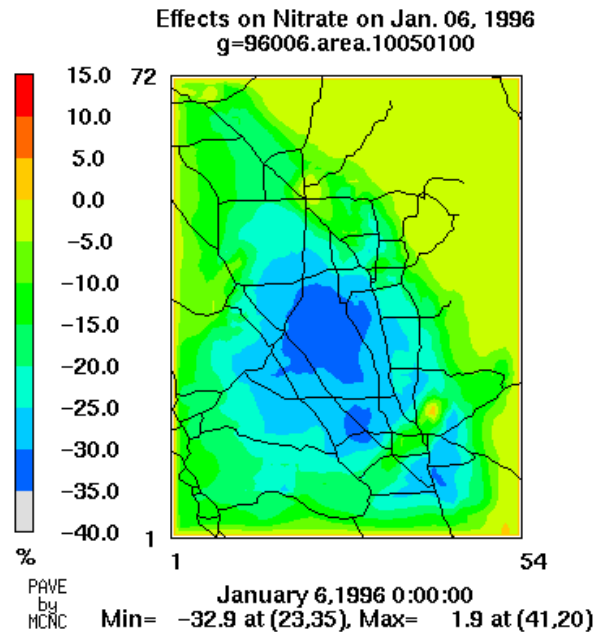
Base–Case Nitrate

k=96006.area

Figure 5: The panel on the upper right shows the spatial distribution of nitrate concentrations throughout the domain for January 06, 1996. The first panel on the bottom row shows the response to 50% reduction in VOC emisions. The middle panel is for 50% reductions in NOx emissions and the panel on the lower right is for 50% reductions in ammonia emissions.
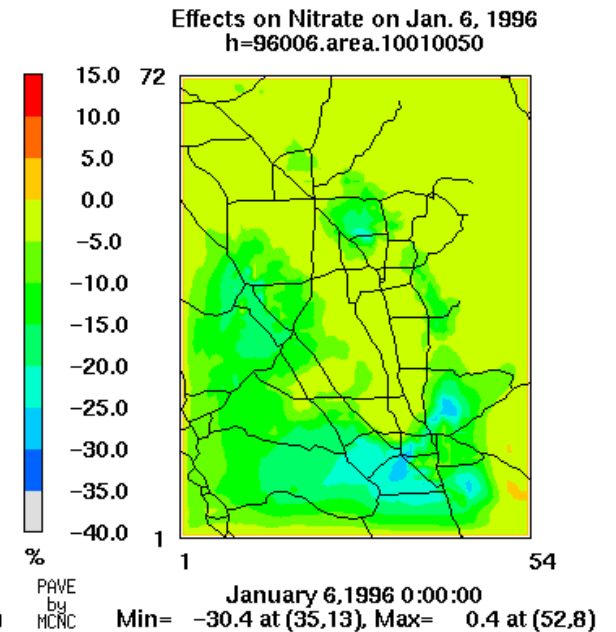
January 6,1996 0:00:00
Min=   4.0 at (54,3), Max=   35.2 at (28,44)

50% VOC Reduction

Effects on Nitrate on Jan. 06, 1996
f=96006.area.50100100

January 6,1996 0:00:00
Min=   −6.1 at (39,15), Max=   1.4 at (31,28)

50% NOx Reduction

Effects on Nitrate on Jan. 06, 1996
g=96006.area.10050100

January 6,1996 0:00:00
Min=   −32.9 at (23,35), Max=   1.9 at (41,20)

50% NH3 Reduction

Effects on Nitrate on Jan. 6, 1996
h=96006.area.10010050

January 6,1996 0:00:00
Min=   −30.4 at (35,13), Max=   0.4 at (52,8)

M-10

As seen in Figure 5, the most beneficial and widespread reductions of nitrate concentrations would be due to NOx reductions. Thus, the limiting precursor of nitrate formation in the San Joaquin Valley is NOx. These reductions are largest near the peak nitrate concentrations. These are also the areas where the ammonia is most abandoned. It is also interesting to note that the southern Valley shows a non-negligible sensitivity to ammonia reductions.
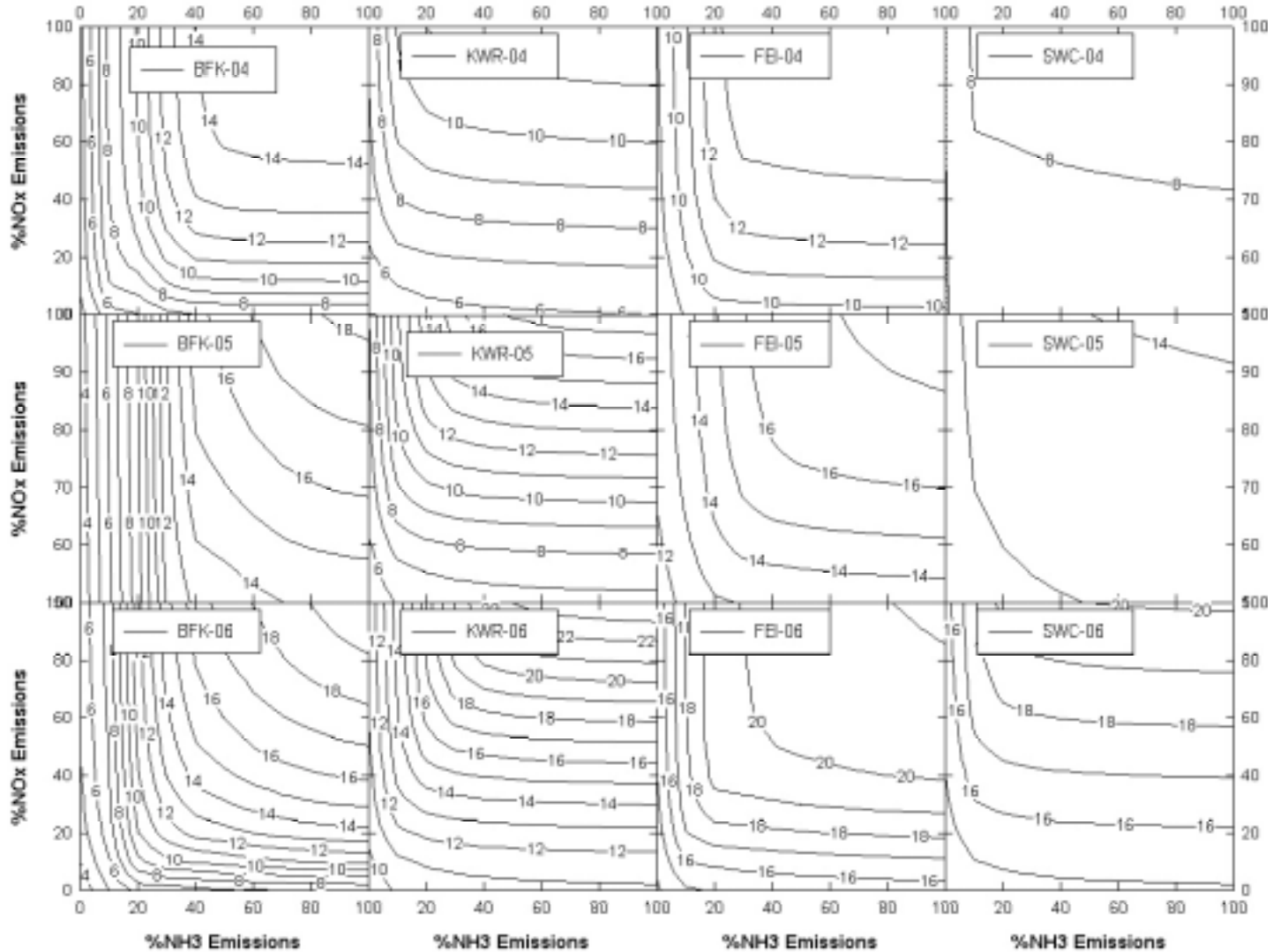
Figure 6 shows the sensitivity of nitrated concentrations to various reductions in NOx and ammonia emission reductions. Similar to figure 4, the rural sites show sensitivity to only NOx reductions until the ammonia concentrations are very low. After that point the response becomes insensitive to NOx controls and almost entirely depend on ammonia controls. The urban sites are more responsive to ammonia controls at higher NOx emissions. At Bakersfield on January 06, 1996, the reductions of nitrate are nearly equal for equal amount of emission reductions of NOx and ammonia. This is contrary to the previous findings based on data analysis and limited modeling efforts. We will comment on this disparity next.

7. Further Investigations to Assess the Apparent Ammonia Limitation at Bakersfield on January 06, 1996:

There are two analyses known to us indicating that the nitrate formation in the San Joaquin Valley is not ammonia limited. But, our grid-based photochemical modeling effort indicates that urban sites could exhibit ammonia limitations at times. Based on sensitivity simulations we performed, we believe that this apparent ammonia limitation is due to the artificially low ammonia emissions in the southern San Joaquin Valley.

To further support our finding, we have also performed additional data analysis during this episode. Here, we employed a simple mass balance concept, based on the thermodynamic equilibrium of ammonium nitrate and sulfate formation, to see if there was any deficiency of ammonia in the domain. Our findings suggest that there was excess ammonia (~0.25 to 0.3 μmoles per cubic meter on a 24-hour basis) at the Bakersfield site during the episode. This indicates that there was no ambient ammonia deficiency at Bakersfield during the IMS-95 episode. This corroborative analysis together with the observation that there were no other ammonia limitations elsewhere in the domain strongly suggests that in emissions inventory had an ammonia deficiency at Bakersfield.

Figure 6: The response of nitrate concentrations to various combinations of domain-wide reductions of NOx and ammonia emissions. Each panel represents a day and a monitoring site. (BFK- Bakersfield (Van Horn School), KWR – Kern Wildlife Refuge, FEI – Fresno (Einstein Park), SWC – South West Chowchilla, 04 - January 04, 1996, 05 – January 05, 1996, 06 – January 06, 1996). Note that emission controls are up to 100%.

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