# 7. POLLUTANT FLUX ESTIMATES

This section includes a discussion on two methods to estimate the flux of pollutants across a boundary between two air basins. One method uses routine pollutant and wind measurements at one monitoring site to estimate the relative flux of pollutants across an imaginary boundary. Results from using this method can represent the two-dimensional (2-D) transport of pollutants across a boundary only during well-mixed conditions, but the availability of routine data provides pollutant-transport information at many times. The second method uses upper-air meteorological and air quality data to estimate the flux of pollutants across a 2-D plane at the boundary between two air basins; this data is only available during intensive sampling. This section also demonstrates that surface meteorological and air quality measurements at Sutter Buttes (about 640 m msl) are representative of conditions aloft at an equivalent altitude above ground.

## 7.1 SIMPLE OZONE AND $NO_x$ FLUX PLOTS

As part of our analysis we prepared simple ozone flux plots, the product of ozone and wind speed in the direction perpendicular to a plane specific to the measurement site. In our analysis, two flux planes were considered (Figure 7-1): one at Sutter Buttes (an east-west plane) and one at Lambie Road, southeast of Travis Air Force Base (a northwest-southeast plane). The ozone flux plot at Sutter Buttes can be used to represent transport aloft in the Sacramento Valley, while the Lambie Road flux plot represents transport from the San Francisco Bay Area (SF Bay Area) into the Broader Sacramento Area (Broader Sac) near the surface at night and in the mixed-layer during the afternoon. Below, we discuss the flux plots for the two intensive study periods. Flux plots for Sutter Buttes and Lambie Road for June 21 through August 19 are provided in Appendix C.

### July 11-13, 1990 Flux Plots

During the July 11-13, 1990 episode, flux plots for Sutter Buttes (depicted in Figure 7-2), show a very consistent diurnal pattern of morning negative ozone flux followed by afternoon positive flux. That is, northerly flows bring ozone into the Broader Sac from the Upper Sacramento Valley (Upper Sac) in the morning and southerly flow transports ozone from the Broader Sac to the Upper Sac in the afternoon. However, it is important to note that the ozone concentrations at Sutter Buttes also experience a diurnal pattern, such that the highest ozone levels are reached during the afternoon southerly flows. As a result, more ozone is transported to the Upper Sac than is transported to the Broader Sac.

Ozone flux plots at Lambie Road (depicted in Figure 7-3) are also very consistent, but have a very different diurnal pattern from Sutter Buttes. Ozone concentrations at Lambie Road undergo a typical diurnal pattern (early afternoon peak). However, while wind direction at Lambie Road is almost always toward the Broader Sac, wind speeds at Lambie Road do not peak until late afternoon. This offset in timing of wind speed peak and ozone peak limit the ozone transport from the SF Bay Area to the Broader Sac. It is important

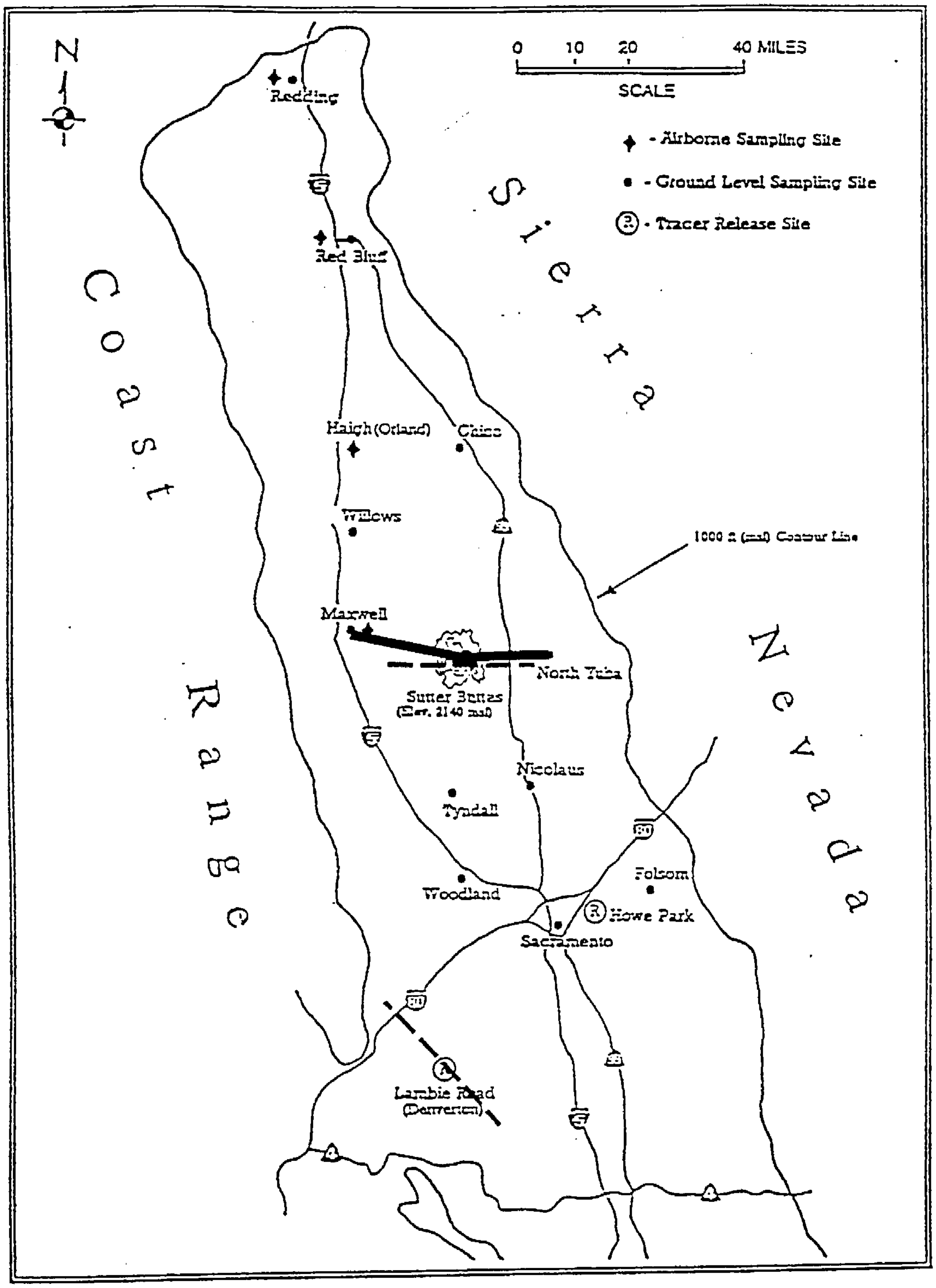



Figure 7-1. Three flux planes investigated in Section 7. The solid line represents a flux plane using aircraft spiral data collected at Maxwell, Sutter Buttes, and North Yuba; the dashed lines represent flux planes using surface measurements at Sutter Buttes and Lambie Road. (Base map from Tracer Technologies, 1991.)

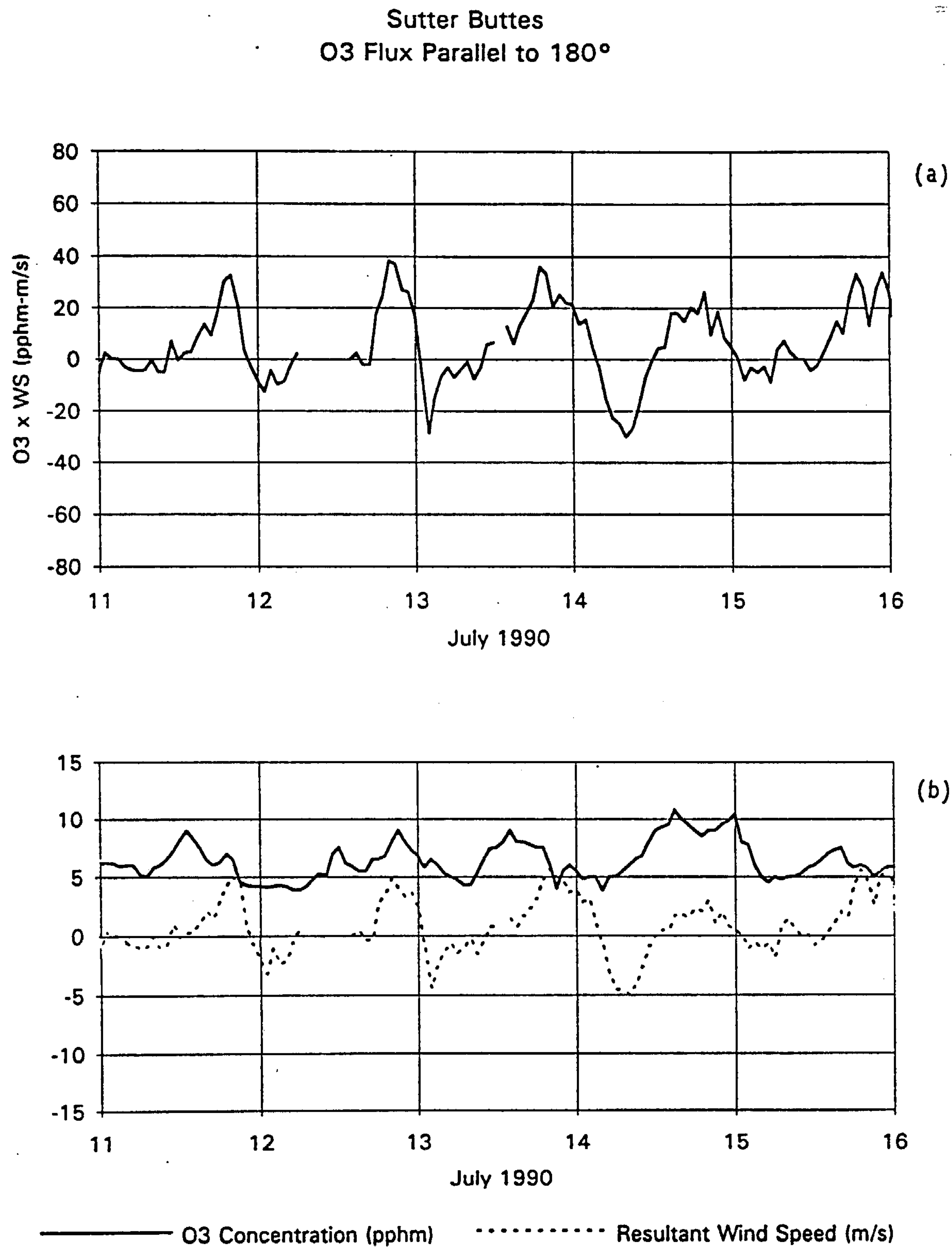



Figure 7-2. (a) Estimated relative ozone flux and (b) ozone concentration and resultant wind speed at Sutter Buttes, July 11-13, 1990.

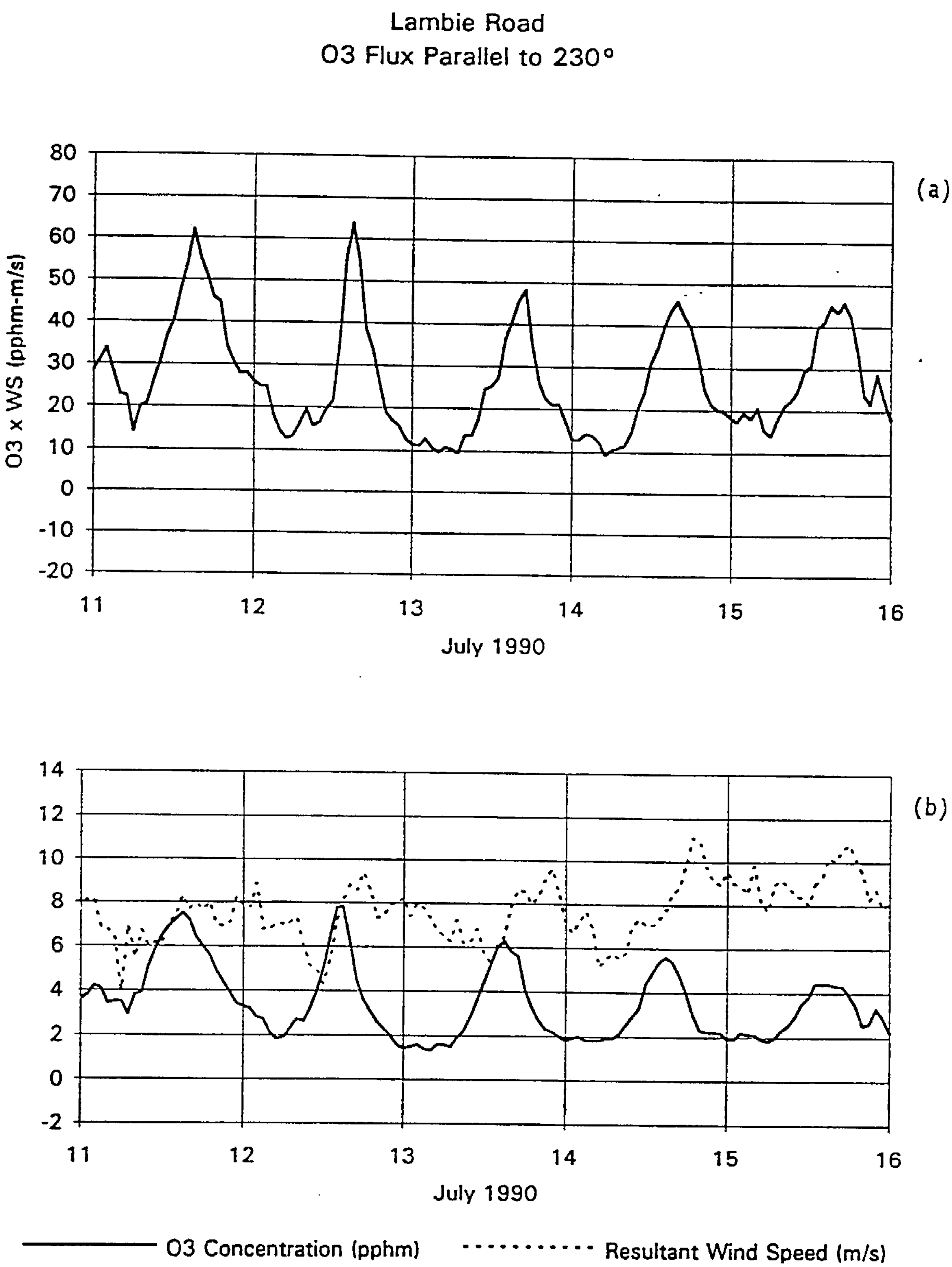



Figure 7-3. (a) Estimated relative ozone flux and (b) ozone concentration and resultant wind speed at Lambie Road, July 11-13, 1990.

to note that on July 10, the day preceding the first Upper Sac tracer release, there was a rare wind reversal at Lambie Road with northeasterly flow toward the SF Bay Area at about noon, with an ozone value of about 9 pphm. Later in the same day, the flow reversed to its more normal southwesterly direction; with an ozone value of about 11 pphm.

A similar flux plot was prepared for $NO_x$ at Lambie Road for the July 11-13, 1990 episode (see Figure 7-4). Note that the diurnal pattern of $NO_x$ concentration is much different than the pattern for ozone: $NO_x$ concentrations are often highest in the morning at this site, and are significantly more jagged and less smooth than ozone concentrations. This results in an early-morning $NO_x$ flux peak about 5 to 6 times lower than the ozone peak, but at a different time of the day. Thus, the highest $NO_x$ fluxes at Lambie Road occur during the morning, while the highest ozone fluxes occur in the late afternoon.

<u>August 10-12, 1990 Flux Plots</u>

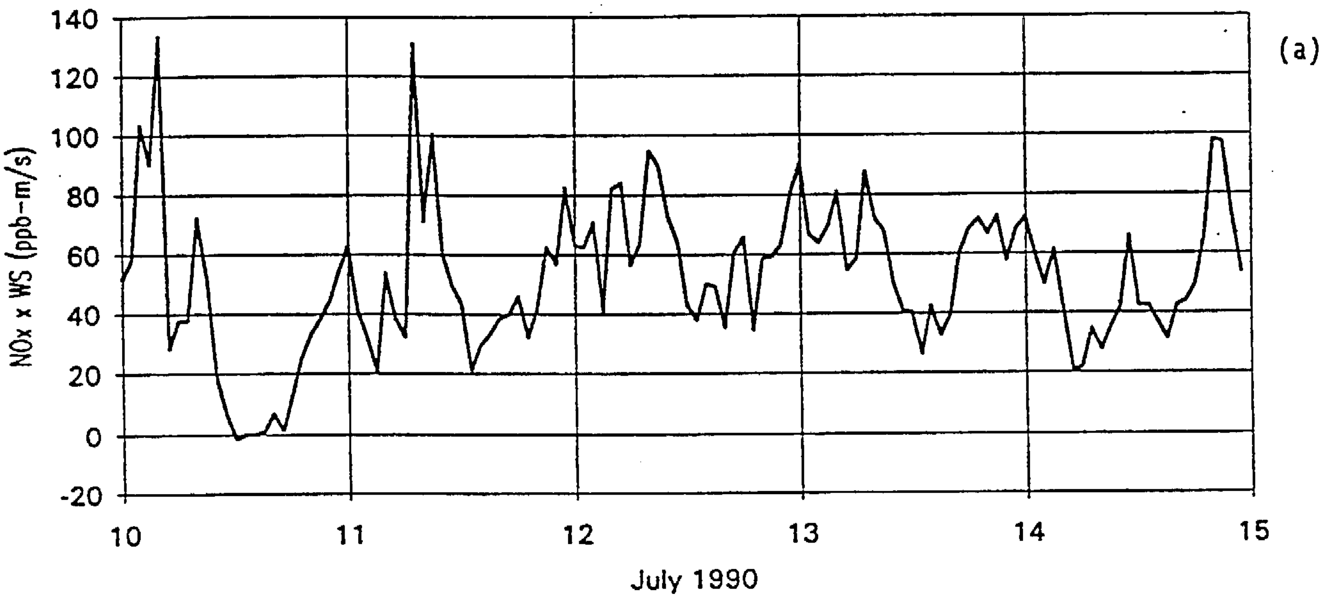
During the August 10-12, 1990 episode, the ozone flux plots at Sutter Buttes (depicted in Figure 7-5), show that the wind patterns resulted in an unusual condition. Rather than the normal diurnal shifting of northerly to southerly wind at Sutter Buttes, a predominantly southerly flow persisted for much of the time. On August 10, the morning northerly flow shifted to southerly before noon and southerly flow continued throughout the next 48-hour period, until mid-day of August 12. Ozone concentrations showed very little diurnal variation, compared to other episodes, and averaged about 5 pphm throughout the period.

During the same time period, Lambie Road ozone flux plots (shown in Figure 7-6) depict the normal diurnal ozone peaks (maximum of 8 pphm on August 11). However, wind speed did not follow the normal diurnal pattern of late afternoon wind peaks, rather the wind speeds remained relatively constant throughout the entire period at about 6 to 8 m/s. The wind direction was toward the Sacramento Valley without interruption for the duration of the episode.

## 7.2 OZONE AND $NO_x$ FLUX ESTIMATES

In order to assess the amount of a given pollutant which is transported into the Upper Sac, we applied a simple model using intensive field study data to estimate the flux of pollutants through a 2-D plane. As described earlier, a simple relative flux can be calculated by multiplying the hourly pollutant concentration by the hourly wind speed in the transport direction. The flux of ozone, for example, is the rate of flow of ozone per unit area which passes from the Broader Sac into the Upper Sac. This flux will depend on the ozone concentration and on the speed (and direction) of the wind which is transporting the ozone. The total amount of ozone transported into the Upper Sac is the sum of the ozone flux over the entire flux plane.

## Lambie Road
## NOx Flux Parallel to 230°



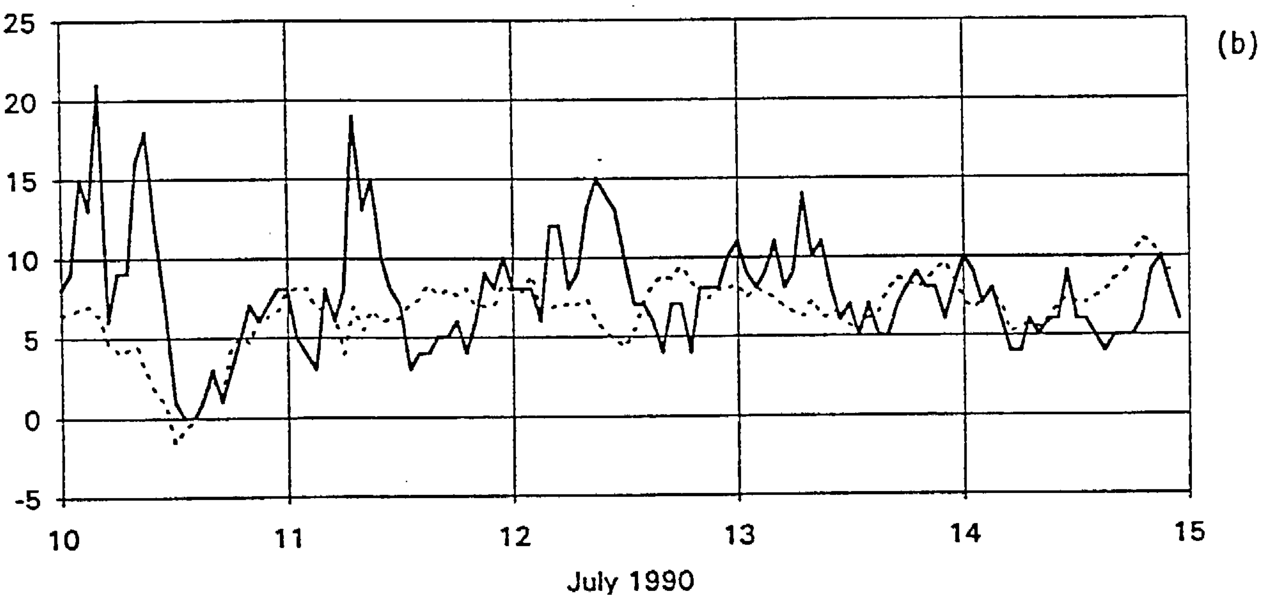




Figure 7-4. (a) Estimated relative $NO_x$ flux and (b) $NO_x$ concentration and resultant wind speed at Lambie Road, July 10-14, 1990.

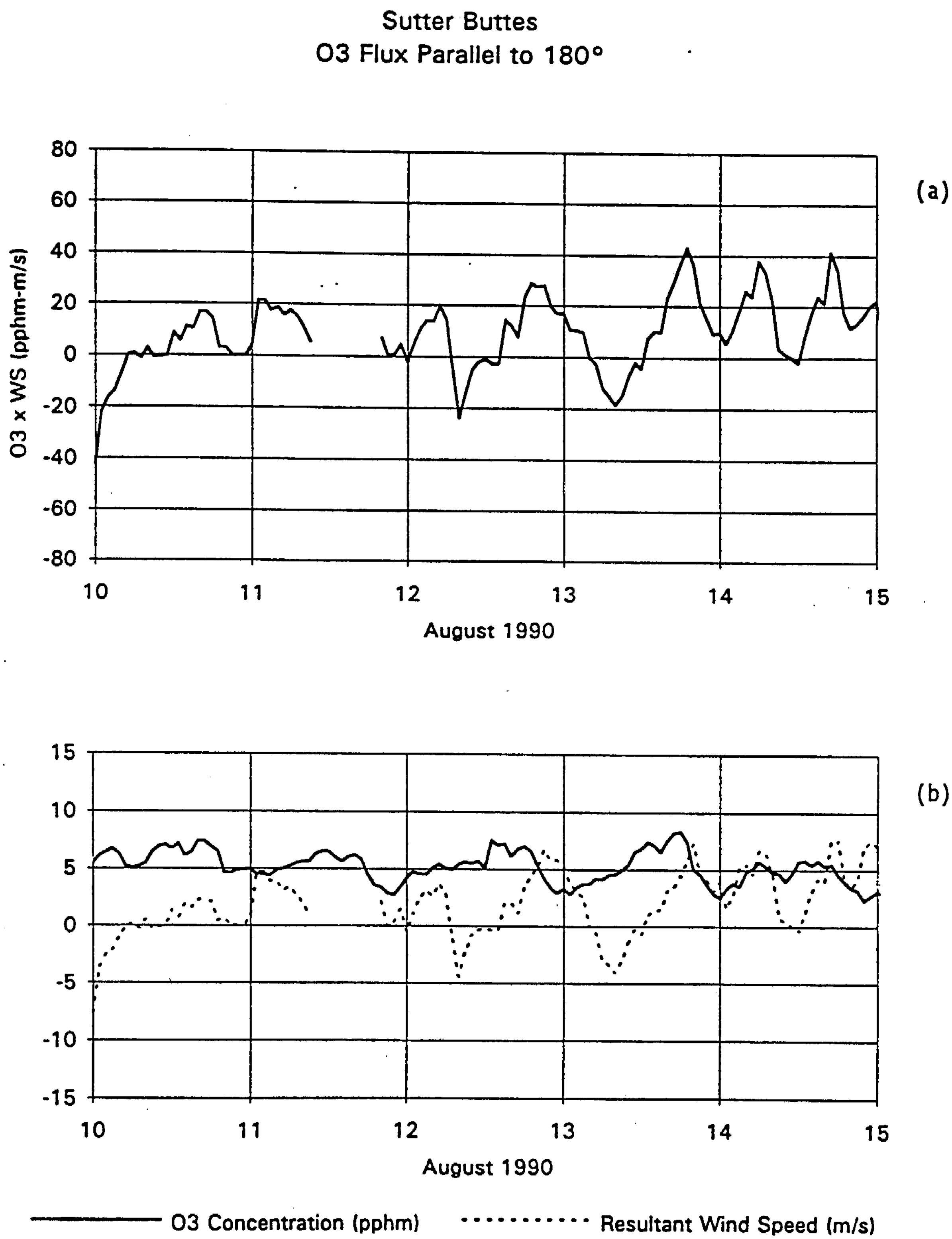
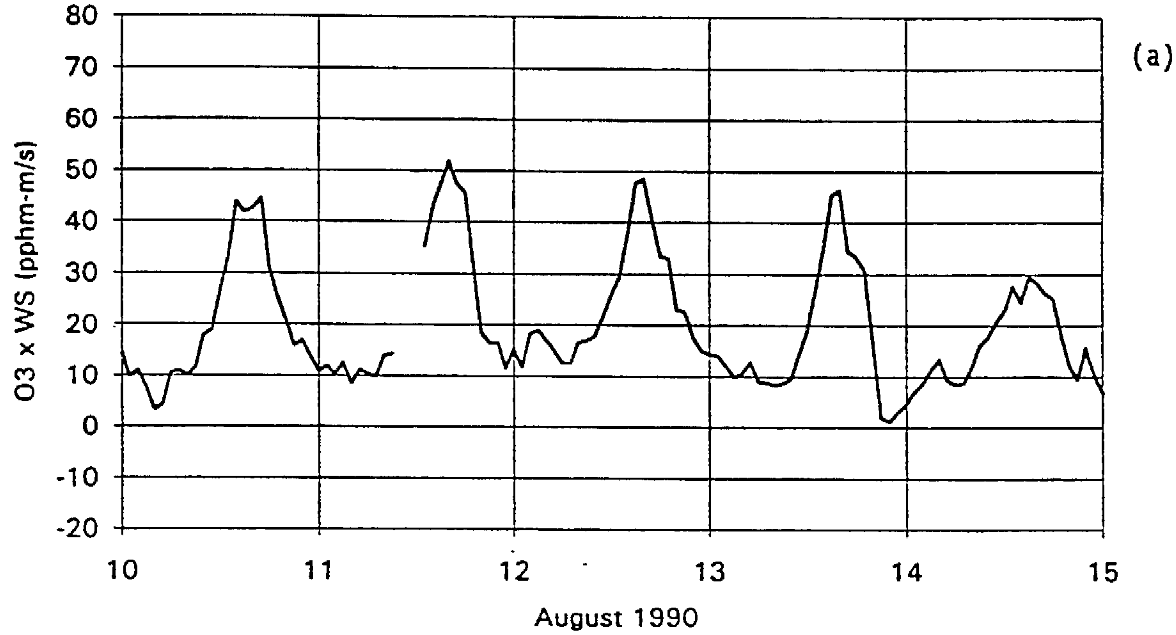



Figure 7-5. (a) Estimated relative ozone flux and (b) ozone concentration and resultant wind speed at Sutter Buttes, August 10-12, 1990.

Lambie Road
O3 Flux Parallel to 230°



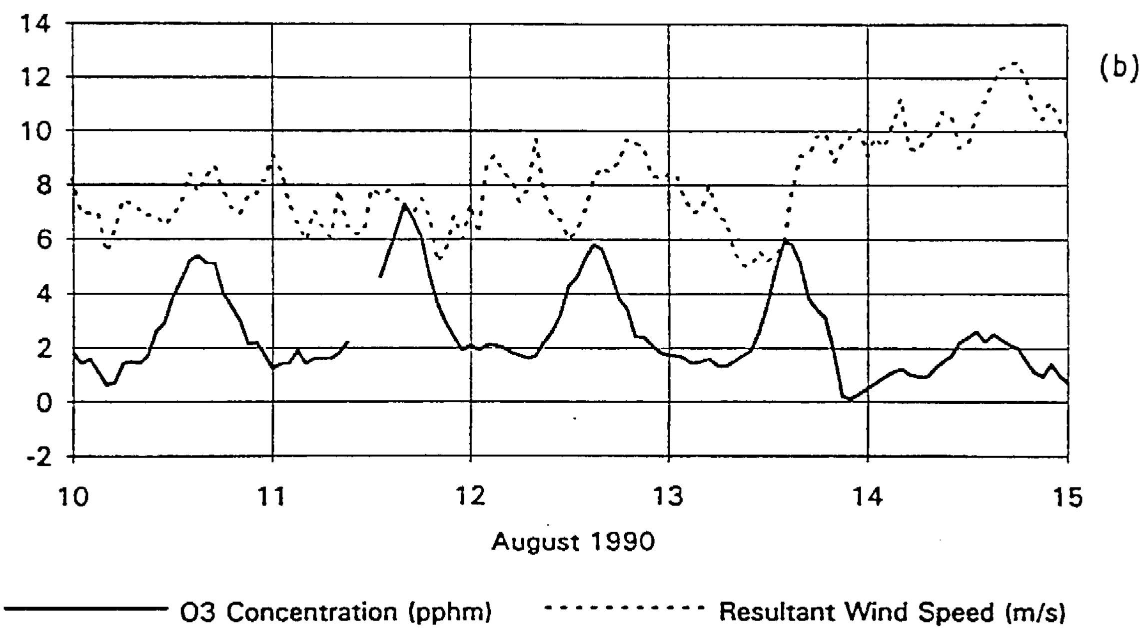




Figure 7-6. (a) Estimated relative ozone flux and (b) ozone concentration and resultant wind speed at Lambie Road, August 10-12, 1990.

To estimate the amount of pollutant (ozone, for example) which is transported into the Upper Sac, we performed the following steps:

- Defined a plane along which air quality and meteorology measurements were available (see Figure 7-1), starting at the ground and continuing vertically to 1500 meters. This is called the flux plane.

- Interpolated meteorological and air quality data between the upper-air meteorological and aircraft air quality measurements taken at the two (upper-air) or three (aircraft) sampling locations along the flux plane.

- Used the interpolated meteorological and air quality data to estimate the pollutant flux over the flux plane.

- Prepared contour plots of the pollutant concentrations and flux.

- Calculated the total ozone flux across the flux plane.

### 7.2.1 Flux Plane Definition

On intensive study days, aircraft air quality measurements were taken at Maxwell, west-northwest of Sutter Buttes, and at North Yuba while upper-air meteorological soundings were made at Maxwell and North Yuba. These three sites lie in a relatively straight line from the western to the eastern side of the valley (Figure 7-1) and span about 60 km. While this flux plane may not be exactly perpendicular to the typical flow into the Upper Sac, it suffices for illustration purposes. The base of the flux plane is at the ground (about 25 m mean sea level, msl), and the height of the flux plane is 1500 m msl, corresponding to the top of most of the aircraft spirals.

To illustrate the calculation of ozone flux across the flux plane, we chose data collected on the afternoon (approximately 1600 PDT) of August 10, 1990. We selected August 10, because ozone concentrations at North Yuba were relatively high aloft (above 100 ppb or 10 pphm) and ozone concentrations in the Upper Sac the next day ranged from 60 to 100 ppb at the surface and greater than 100 ppb aloft.

### 7.2.2 Data Preparation

Table 7-1 lists the data which were collected along the Upper Sac flux plane on August 10, 1990. Note that the aloft air quality and meteorological measurements were made within about two hours of each other. For each aircraft spiral, we averaged the measured ozone concentration into 60-meter vertical bins beginning at 60 m msl. The surface ozone concentration at Maxwell was used to represent the first 35 meters aloft (i.e., from a surface elevation of about 25 m to 60 m msl). Surface ozone concentration data were not available at Yuba City on this date. Therefore, the ozone concentration for the first 35 m was set equal to the concentration used for 60 to 120 m msl. The data from the three spirals were then interpolated and contoured using statistical software to illustrate the pollutant structure aloft along the flux plane. The software package computed its own grid of interpolated values using a distance weighted least squares smoothing technique. Contours are determined using a special technique for contouring data combined with linear interpolation (Wilkinson, 1990).

Table 7-1. Data available for flux calculations along the Upper Sacramento Valley flux plane on August 10, 1990.

| Sampling Location | Time Period, PDT | | | |
|---|---|---|---|---|
| | Surface Ozone | Aircraft Ozone, $NO_x$ | Surface Winds | Upper Air Winds |
| Maxwell | 1400-1500 | 1448-1500 | 1600-1700 | 1608 |
| Sutter Buttes | C | 1418-1429 | C | NA |
| North Yuba | NA[a] | 1348-1359 | S | 1602 |

[a] Surface measurements were made at Yuba City.
S = suspect, not used
NA = not available
C = used for comparison, measured at 640 m msl

The upper-air data are reported as altitude above ground level (agl). These data were first converted to msl. Next, the wind speed component perpendicular to the flux plane was determined. For simplicity, we chose the southerly component for this illustration. Next, the wind speed data were linearly interpolated in the vertical to grid the data to uniform intervals of 60 m to match the gridded ozone concentration data. To obtain the vertically gridded wind speeds at the location near Sutter Buttes, where no upper-air meteorological data were available, we simply averaged the gridded North Yuba and Maxwell data, since the Sutter Buttes aircraft flight was nearly midway on a straight line drawn between Maxwell and North Yuba. Surface wind measurements at Maxwell and North Yuba were used to represent the winds in the first 35 m aloft.

Finally, the gridded wind speeds were multiplied by the pollutant concentration data to obtain the gridded flux at the three locations. These data were then interpolated and contoured to illustrate the flux, in mass/time/area, typically in units of g/s per square meter, aloft along the flux plane.

### 7.2.3 Flux Estimation Results

The two measurement components that are necessary in order to perform ozone and $NO_x$ flux calculations are upper-air winds and ozone and $NO_x$ measurements aloft along the flux plane. As an example, we show results for the afternoon of August 10, 1990.

Figure 7-7a shows a contour plot of the ozone concentration at the flux plane on August 10, 1990 at 1600 PDT. Note that the ground level across the flux plane shown in Figure 7-7a is approximately 25 m msl. Ozone concentrations were highest in the mixed layer at North Yuba. In fact, ozone concentrations were about 30 to 40 ppb higher at North Yuba than at the other two sites. Ozone concentrations were relatively low and spatially uniform above about 600 m msl, ranging from about 55 to 70 ppb.

Figure 7-7b shows the contour plot of the southerly component of the wind speed at the flux plane on August 10. Wind speeds were about a factor of three lower (2 m/s versus 6 m/s) at North Yuba than at Maxwell. Investigation of the wind speeds measured at the surface site on top of Sutter Buttes (about 640 m msl) showed that the interpolated wind speeds used for the central portion of the flux plane were consistent with the measured wind speeds.

The pollutant concentration and the wind speed across the flux plane were combined to produce the flux of pollutant across the plane. Figure 7-7c shows the contour plot of the ozone mass flux across the plane. The flux is reported in $mg/min/m^2$ units for plotting convenience. To obtain the total mass of ozone transported across the plane in mass/time, we determined the average flux and multiplied by the total area of the flux plane as shown in Equation 7-1:

$$\underbrace{(1500-25\ m)}_{\text{altitude}}*\underbrace{(56{,}670\ m)}_{\text{distance}}*\underbrace{(35\ mg/m^2/min)}_{\text{average flux}}*\underbrace{(10^{-6}\ kg/mg)*(min/60s)}_{\text{unit conversions}}= \underbrace{49\ kg/s}_{\text{total ozone mass}} \qquad (7\text{-}1)$$

This is equivalent to an average concentration of 70 ppb being transported into the Upper Sac at about 4 m/s over the total flux plane. Because of the large differences in wind speed between North Yuba (on the eastern edge) and Maxwell (on the western edge) observed on August 10, the highest mass flux of ozone occurred over Maxwell, even though ozone concentrations were a factor of two lower near Maxwell.

To place the flux estimate above into context, we compared it with those of Roberts and Main (1989), which calculated the total ozone flux through the upwind boundary of the San Joaquin Valley (SJV) for eight sets of data. The total ozone flux through the boundary plane during the afternoon in their study varied from a low of 27 kg/s to a high of 65 kg/s for a total flux area of roughly twice the size of the flux plane area defined for the Upper Sac. The average total ozone flux for the upwind SJV boundary, including morning and evening data, was 41 ± 21 kg/s.

Figure 7-8a shows a contour plot of the $NO_x$ concentration at the flux plane on August 10, 1990 at 1600 PDT. $NO_x$ concentrations were highest in the mixed layer, ranging from over 12 ppb at North Yuba to about 9 ppb at Maxwell. $NO_x$ concentrations were lower and spatially uniform above about 600 m msl, ranging from about 3 to 6 ppb. $NO_x$ concentration and the wind speed across the flux plane were combined to produce the flux of $NO_x$ across the plane. Figure 7-8b shows the contour plot of the $NO_x$ mass flux ($mg/min/m^2$) across the plane. The total mass of $NO_x$ transported across the plane was about 4 kg/s. This is equivalent to an average concentration of 5 ppb being transported into

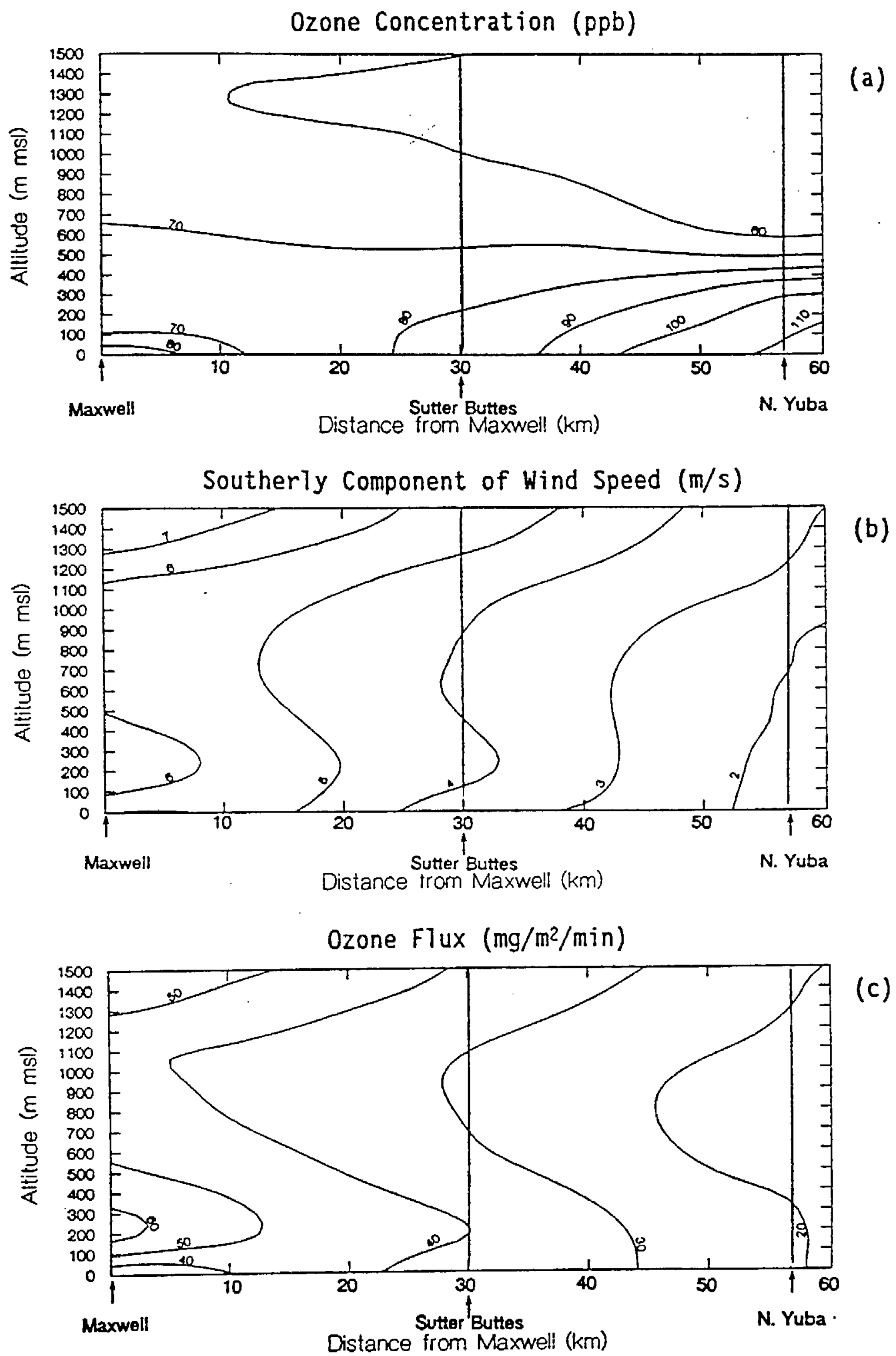



Figure 7-7. (a) Ozone concentrations, (b) wind speed, and (c) ozone flux aloft on August 10, 1990 at about 1600 PDT. Contours were generated along a west-to-east plane from Maxwell to North Yuba using data from aircraft spirals and balloon soundings. The ground level is about 25 m msl.

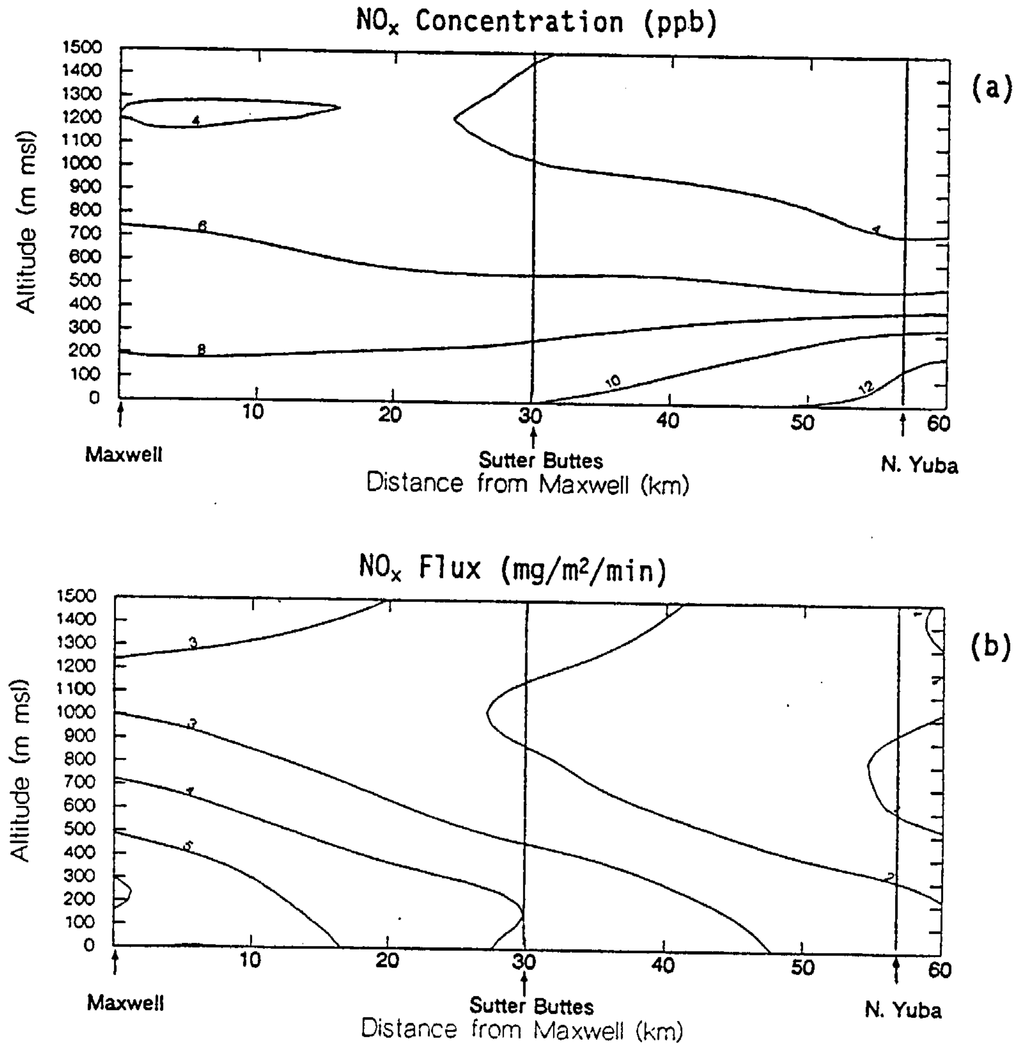



Figure 7-8. (a) $NO_x$ concentrations and (b) $NO_x$ flux aloft on August 10, 1990 at about 1600 PDT. Contours were generated along a west-to-east plane from Maxwell to North Yuba using data from aircraft spirals and balloon soundings. The ground level is about 25 m msl.

the Upper Sac at about 4 m/s over the total flux plane. By comparison, the total $NO_x$ flux through the SJV boundary plane in the afternoons varied from a low of 2.8 kg/s to a high of 8.1 kg/s for a total flux area of roughly twice the size of the flux plane area defined for the Upper Sac (Roberts and Main, 1989). The average total flux for the upwind SJV boundary was 5.5 ± 2.7 kg/s. Note that the $NO_x$ measured by the monitors in the aircraft includes NO, $NO_2$, nitric acid, and some PAN.

Two grab samples, which were later analyzed for volatile organic compounds (VOC), were collected near the top of the mixed layer during 1600 to 1700 PDT along the flux plane. One sample was collected at 437 m msl over Maxwell at 1608 PDT, while the other sample was collected over North Yuba at 485 m msl at 1702 PDT. The VOC composition and concentrations measured over Maxwell were representative of clean air (see Section 8 for more details). In contrast, the VOC composition and concentrations measured over North Yuba were representative of aged urban air. Thus, these VOC samples were consistent with the spatial distribution of ozone and $NO_x$ concentrations and suggest that the higher pollutant concentrations over North Yuba were from the Broader Sac. Only two VOC samples over such a large flux plane were not sufficient to estimate the VOC flux into the Upper Sac; many more samples would be needed.

7.2.4 Summary of Flux Calculation Assumptions

There are a number of assumptions that we made while performing these flux calculations which need to be considered. These are summarized below:

- The wind speeds during ozone and $NO_x$ measurements are similar to those used in the flux estimates. On August 10, the wind speeds were measured one to two hours after the air quality measurements.

- Upper-air winds at the two sampling locations are representative of upper-air winds between locations. In other words, we assumed that the distance-weighting procedure used to spatially interpolate wind speed properly represents aloft winds between locations.

- The distance-weighting procedure that we used to vertically interpolate wind speed properly represents aloft winds.

- The ozone and $NO_x$ distributions over the flux plane did not change significantly during the hour over which aloft air quality measurements were made.

- Any small "clouds" of high or low ozone or $NO_x$ that were missed by the aircraft are small contributors to the total flux.

Important limitations to this flux calculation method include the following:

- We have shown only one example for pollutant flux into the Upper Sac. More calculations are needed during periods of ozone exceedances in the Upper Sac to quantify the range of total flux and the uncertainty.

- This analysis provides only a "snapshot" of the flux through a plane. More frequent data are needed to investigate temporal and spatial variations in the pollutant concentrations, winds, and flux.

- The flux plane used in this example does not account for air flow to the west of Maxwell and east of North Yuba which may impact the Upper Sac.

- This method cannot quantify the ozone that is later formed in the Upper Sac from $NO_x$ and VOC which have been transported into the Upper Sac.

- This method cannot distinguish between background ozone and ozone formed in the upwind air basins. Similarly, this method cannot separately distinguish between ozone formed in the two upwind air basins, the Broader Sac and the SF Bay Area.

### 7.2.5 Discussion of Results

The technique of simple flux plane calculations appears to have been useful in helping to quantify pollutant transport between the Broader Sac and the Upper Sac. However, on the specific episode days monitored in the intensive study period, the afternoon aircraft flights appeared to have missed the ozone "cloud" moving north from Broader Sac toward Upper Sac. We believe, based on analysis of wind speeds and directions, that the bulk of the ozone transport probably occurred prior to the time of the afternoon aircraft sampling period. Nevertheless, the use of a simple flux plane has shown that high concentrations of ozone on the east side of the valley and lower concentrations of ozone on the west side of the valley are carried by relatively consistent wind flow up the valley toward the Upper Sac through the plane parallel to the Sutter Buttes. Furthermore, because of the steady winds, any oxides of nitrogen transported through the plane are likely to contribute to ozone formation in the downwind air basin (e.g., Upper Sac).

### 7.2.6 Applications of the Method to Other Data

In order to determine the pollutant flux from one air basin to another, vertical ozone and wind profiles are needed. Hourly data, collected on multiple days, with adequate spatial resolution, would provide more useful data for the estimation of uncertainty, timing of the peak ozone and $NO_x$ fluxes, and better quantification of the total flux. Ozone profiles may be measured by aircraft, ozone sondes, and ozone dial while winds aloft may be measured by balloon soundings, radar profiler, or doppler sounder (with sufficient height resolution).

To better assess the pollutant structure and pollutant flux aloft into the Upper Sac, we recommend that an ozone dial system paired with a radar profiler be placed at two locations, such as Maxwell and North Yuba, to obtain hourly data over several days. Different flow regimes and ozone concentration ranges should be investigated. Note that in a narrow valley or pass, such as Cajon Pass or Gilroy, only one pair of samplers may be needed.

## 7.3 SUTTER BUTTES METEOROLOGICAL AND AIR QUALITY MEASUREMENTS

One of the methods selected for use in analyzing potential ozone transport or precursor transport from the Broader Sac to the Upper Sac was to examine simple depictions of ozone flux plots at Sutter Buttes. As part of our analysis, we prepared simple ozone flux plots (see Figures 7-2 and 7-5). The ozone flux is defined as the product of ozone and wind speed in the direction perpendicular to a plane specific to the measurement site. One of the key assumptions of this approach is that meteorological and air quality measurements taken at the summit of Sutter Buttes (about 640 m msl) is representative of conditions aloft at an equivalent altitude above ground. The purpose of this discussion is to present the results of the methods we used to demonstrate that the surface measurements from the summit of Sutter Buttes are indeed representative of conditions aloft at an equivalent altitude above ground.

### 7.3.1 Meteorological Measurement Comparisons

Measurements of wind speed and direction were considered for comparisons between Sutter Buttes and two nearby upper-air balloon sounding measurement sites, specifically one near North Yuba and one near Maxwell. The North Yuba and Maxwell locations form a line which laterally crosses the Sacramento Valley with Sutter Buttes in the center. Table 7-2 presents the wind speeds and directions from Sutter Buttes and from the two upper-air sounding locations for all time periods for which data were available during the summer of 1990. The wind speeds and directions for the balloon soundings used in the comparisons were made by visually interpolating values corresponding to the elevation of Sutter Buttes. In addition, surface wind speeds and directions for Maxwell and North Yuba are shown as well. Several general conclusions can be made from these comparisons:

- Wind shear (substantial change in wind direction with increasing altitude) is present in the Maxwell and North Yuba soundings, most notably in the morning hours.

- Average wind speeds aloft at the Maxwell and North Yuba soundings are higher than surface wind speeds.

- Average wind speeds at Sutter Buttes are less than those aloft at the Maxwell and North Yuba soundings, but are equal to or greater than surface wind speeds at Maxwell and North Yuba.

- Mean wind direction at Sutter Buttes is comparable to that of an aloft measurement expected to occur between those aloft at the Maxwell and North Yuba soundings.

To further substantiate the representativeness of the Sutter Buttes wind measurements we performed several statistical comparisons of the data shown in Table 7-2. Particularly, we prepared regressions and correlations of wind speeds and directions comparing Sutter Buttes with both Maxwell and North Yuba sounding data. The results of these statistical comparisons are shown in Table 7-3. Scatter plots of Sutter Buttes wind directions compared to Maxwell and North Yuba upper-air soundings are shown in Figure 7-9. As shown in the

Table 7-2. Surface wind speeds and directions at Maxwell, Sutter Buttes, and North Yuba and aloft winds at Maxwell and North Yuba.

| | Time | Maxwell (surface) | | Maxwell (upper) | | Sutter Buttes (surface) | | N. Yuba (upper) | | N. Yuba (surface) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Date | PDT | WS (m/s) | dir | WS (m/s) | dir | WS (m/s) | dir | WS (m/s) | dir | WS (m/s) | dir |
| 7/11/90 | 1600 | 3.1 | 150 | 2.0 | 180 | 2.1 | 190 | 1.5 | 300 | 0.5 | 160 |
| | 2200 | 3.6 | 270 | 2.5 | 270 | 4.6 | 260 | 4.0 | 180 | 0.5 | 120 |
| 7/12/90 | 400 | 3.1 | 340 | 7.0 | 320 | 2.1 | 350 | 1.0 | 350 | 0.5 | 190 |
| | 1000 | 2.1 | 150 | 6.0 | 350 | | | 3.0 | 320 | 0.5 | 290 |
| | 1600 | 3.1 | 120 | 2.0 | 260 | 2.1 | 280 | 3.0 | 280 | 2.1 | 30 |
| | 2200 | 1.5 | 230 | 4.0 | 180 | 3.6 | 200 | 3.7 | 140 | 3.1 | 140 |
| 7/13/90 | 400 | 3.1 | 10 | 3.5 | 10 | 1.5 | 30 | 3.1 | 20 | 1.0 | 200 |
| | 1000 | 3.6 | 130 | 3.5 | 340 | 0.5 | 360 | 0.0 | 360 | 2.1 | 190 |
| | 1600 | 3.1 | 150 | 3.0 | 140 | 2.6 | 130 | 2.0 | 240 | 1.0 | 110 |
| 8/10/90 | 1600 | 5.7 | 150 | 6.0 | 180 | 2.6 | 150 | 2.0 | 170 | 0.5 | 150 |
| | 2200 | 2.6 | 190 | 4.5 | 240 | 5.7 | 270 | 4.0 | 240 | 0.5 | 90 |
| 8/11/90 | 400 | 1.5 | 240 | 4.0 | 190 | 4.1 | 200 | 5.0 | 160 | 0.5 | 150 |
| | 1000 | 2.1 | 80 | 3.0 | 140 | | | 3.0 | 150 | | |
| | 1600 | | | 3.5 | 180 | | | 5.0 | 200 | | |
| | 2200 | 3.1 | 330 | 2.0 | 200 | 2.1 | 260 | 7.0 | 180 | 4.1 | 140 |
| 8/12/90 | 400 | 1.5 | 100 | 3.5 | 140 | 4.1 | 130 | 8.0 | 150 | 0.5 | 40 |
| | 1000 | 3.6 | 140 | 3.0 | 90 | 2.6 | 70 | 3.0 | 80 | 0.5 | 250 |
| | 1600 | 3.6 | 140 | 2.7 | 100 | 2.6 | 140 | 3.0 | 180 | 3.6 | 150 |
| 9/11/90 | 1600 | 3.1 | 140 | 5.0 | 200 | 2.1 | 190 | 2.0 | 250 | 0.5 | 130 |
| | 2200 | 3.6 | 340 | 3.5 | 280 | 6.2 | 170 | 5.0 | 160 | 1.0 | 110 |
| 9/12/90 | 400 | 1.0 | 280 | 4.2 | | 1.0 | 80 | 6.0 | 140 | 0.5 | 10 |
| | 1000 | 2.1 | 120 | 7.0 | 40 | 1.0 | 60 | 4.5 | 150 | 0.5 | 120 |
| | 1600 | 3.6 | 150 | 4.0 | 170 | 2.6 | 160 | 4.0 | 190 | 2.6 | 160 |
| | 2200 | 2.1 | 310 | 3.5 | 200 | 3.6 | 190 | 6.0 | 160 | 0.5 | 200 |
| 9/13/90 | 400 | 2.1 | 240 | 3.0 | 110 | 7.2 | 110 | 5.0 | 140 | 0.5 | 160 |
| | 1000 | 2.6 | 30 | 3.0 | 90 | 3.6 | 110 | 6.0 | 160 | 0.5 | 230 |
| | 1600 | 4.1 | 140 | 5.0 | 170 | 4.6 | 160 | 7.0 | 190 | 3.6 | 150 |
| Average | | 2.9 | 179.6 | 3.8 | 176.7 | 3.1 | 177.1 | 4.0 | 194.1 | 1.3 | 146.8 |

Table 7-3. Results of linear regressions between surface and upper air wind speed and direction measured at Maxwell, North Yuba, and Sutter Buttes.

| | Maxwell | | North Yuba | | Sutter Buttes | Regression Results | | |
|---|---|---|---|---|---|---|---|---|
| Wind Measurement | Surface | Upper Air | Surface | Upper Air | Surface | Slope | Constant | $r^2$ |
| Direction | | y | | | x | 0.91 | 14 | 0.91 |
| Direction | | | | y | x | 0.72 | 62 | 0.64 |
| Direction | x | y | | | | 0.50 | 96 | 0.26 |
| Direction | | | x | y | | 0.07 | 186 | 0.00 |
| Speed | | y | | | x | -0.12 | 4.2 | 0.02 |
| Speed | | | | y | x | 0.52 | 2.4 | 0.18 |
| Speed | x | y | | | | 0.08 | 3.6 | 0.00 |
| Speed | | | x | y | | 0.24 | 3.7 | 0.02 |

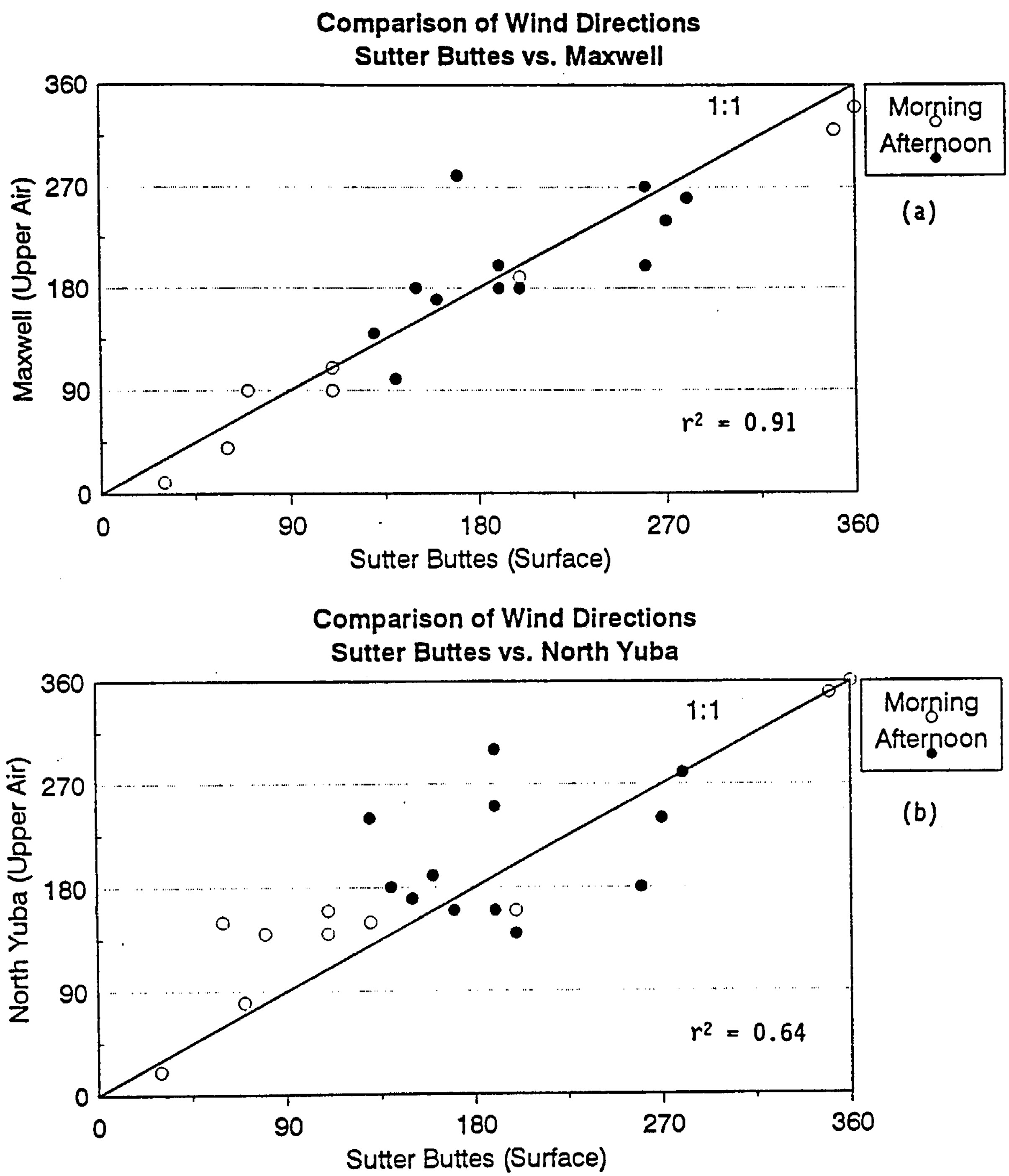



Figure 7-9. Comparison of surface wind directions at Sutter Buttes with aloft wind direction at (a) Maxwell and (b) North Yuba. Sutter Buttes data compare very well with Maxwell data.

table and figures, wind direction measurements at Sutter Buttes compared very favorably with the wind directions from the sounding data (correlation coefficient, $r^2$ = 0.64 for North Yuba and 0.91 for Maxwell). R-square values of this magnitude should be considered as strong evidence of the representativeness of the Sutter Buttes wind direction measurements. Wind speed measurements did not agree as well. However, it is not surprising that wind speeds measured at Sutter Buttes are typically less than wind speeds from nearby aloft measurements due to the influence of the ground which reduce wind speeds due to frictional and other mechanical influences.

### 7.3.2 Air Quality Measurement Comparisons

We compared ozone measurements made at Sutter Buttes with the aircraft samples taken nearby. Table 7-4 presents the ozone concentrations from Sutter Buttes and from the aircraft samples for all time periods for which data were available during the summer of 1990. The ozone concentrations used in the comparisons were made by visually interpolating values from the aircraft spirals corresponding to the elevation of Sutter Buttes (about 640 m msl). In addition, surface ozone concentrations from Maxwell are shown for the corresponding sampling periods. Several general observations may be made from these comparisons:

- Ozone concentrations measured at Sutter Buttes and from the aircraft (28 to 90 ppb) did not vary over the same range as the Maxwell surface ozone concentrations which ranged from 0 to 75 ppb.
- The minimum ozone concentrations aloft, taken from both Sutter Buttes and the aircraft did not show evidence of ground layer ozone depletion from deposition or NO titration. Depletion of ozone was most evident in the morning ozone concentrations at Maxwell.
- Average ozone concentrations at Sutter Buttes were about equal to concentrations measured aloft by the aircraft.
- Average ozone concentrations at Sutter Buttes were considerably higher than concentrations measured at the surface at Maxwell in the morning and were slightly higher than the afternoon concentrations at Maxwell.

To further substantiate the representativeness of the Sutter Buttes ozone measurements we performed several statistical comparisons of the data shown in Table 7-4. Particularly, we prepared regressions and correlations of ozone concentrations comparing Sutter Buttes surface data with Maxwell surface and Sutter Buttes aircraft data. The results of these statistical comparisons are shown in Table 7-5. Sutter Buttes surface ozone concentrations are compared to aircraft and Maxwell surface ozone concentrations in Figure 7-10. As shown in the table and figures, ozone measurements at Sutter Buttes compared very well with the measurements from the nearby aircraft flights ($r^2$ = 0.69) and are consistent in the morning and afternoon. Therefore, the Sutter Buttes ozone measurements are representative of nearby aloft ozone concentrations. In contrast, the Sutter Buttes surface ozone concentrations did not compare well with the Maxwell surface concentrations in the morning. The poor correlation with morning surface Maxwell ozone concentrations should be interpreted as further evidence that Sutter Buttes is representative of

Table 7-4. Ozone concentrations measured aloft near Sutter Buttes, at the surface monitoring station atop Sutter Buttes and at the surface at Maxwell.

| Date | Time (PDT) | Ozone Concentrations (ppb) Sutter Buttes* Aircraft | Sutter Buttes* Surface | Maxwell Surface |
|---|---|---|---|---|
| 7/11/90 | 1400 | 62 | 90 | 75 |
| 7/12/90 | 700 | 32 | 39 | 14 |
| | 1600 | 48 | 55 | 48 |
| 7/13/90 | 700 | 52 | 48 | 8 |
| | 1600 | 80 | 80 | 69 |
| 8/10/90 | 1600 | 72 | 64 | 54 |
| 8/11/90 | 600 | 54 | 50 | 0 |
| | 1600 | 66 | 60 | 39 |
| 8/12/90 | 600 | 48 | 54 | 2 |
| | 1600 | 76 | 72 | 54 |
| 9/11/90 | 1500 | 70 | 80 | 72 |
| 9/12/90 | 600 | 40 | 39 | 0 |
| | 1600 | 60 | 73 | 68 |
| 9/13/90 | 600 | 36 | 28 | 2 |
| | 1600 | 56 | 61 | 65 |

* Measured at about 640 m msl.

Table 7-5. Results of linear regressions between surface and aircraft ozone concentrations measured at Sutter Buttes and Maxwell.

| | Sutter Buttes* | | Maxwell | Regression Results | | |
|---|---|---|---|---|---|---|
| Ozone (ppb) | Surface | Aircraft | Surface | Slope | Constant | $r^2$ |
| Overall | x | y | | 0.69 | 15.5 | 0.69 |
| Morning | x | y | | 0.75 | 11.5 | 0.63 |
| Afternoon | x | y | | 0.41 | 36.8 | 0.21 |
| Overall | x | | y | 1.52 | -52.5 | 0.77 |
| Morning | x | | y | -0.05 | 6.62 | 0.01 |
| Afternoon | x | | y | 0.86 | 0.04 | 0.65 |
| Overall | | x | y | 1.51 | -47.7 | 0.53 |
| Morning | | x | y | -0.26 | 15.5 | 0.17 |
| Afternoon | | x | y | 0.17 | 49.5 | 0.02 |

* Measured at about 640 m msl.

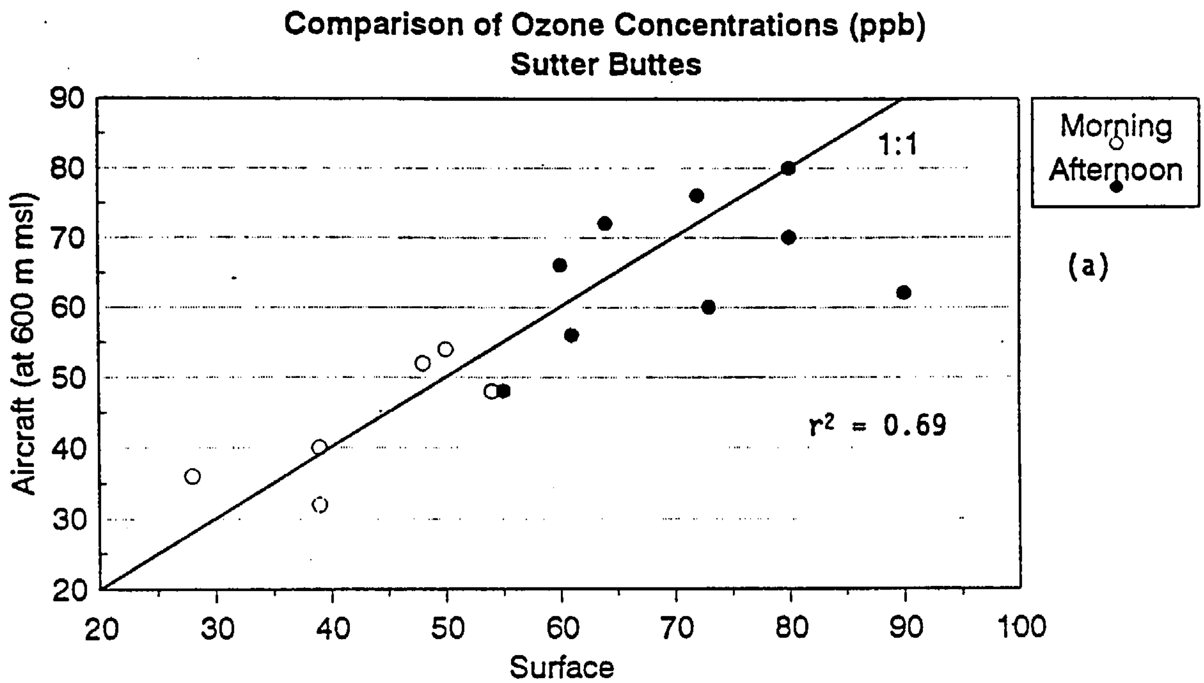
aloft conditions more than it is representative of surface conditions in the Sacramento Valley. Further evidence is provided in Figure 7-11. In this figure we have plotted ozone concentrations at Sutter Buttes during the July-September months of 1989 and 1990. Figure 7-11 depicts the diurnal ozone concentrations for all days as well as those days with ozone peaks greater than 9 pphm. As shown in the figure, on average, ozone concentrations at Sutter Buttes are about 5 to 6 pphm during the night and early morning hours when surface sites typically experience NO titration resulting in ozone concentrations much less than 4 pphm. The plots also show that on some days relatively clean air, with ozone at about 2 to 3 pphm, can be observed throughout the day.

## 7.4 CONCLUSIONS AND RECOMMENDATIONS

Simple Pollutant Fluxes:

- The simple flux plots showed that both ozone and $NO_x$ fluxes vary during the day, with the highest ozone fluxes in the mid- to late-afternoon and the highest $NO_x$ fluxes in the morning. The ozone flux at Lambie Road was about 5 to 6 times higher than the $NO_x$ flux.

- The simple ozone flux at Lambie Road is almost always from the southwest, with the highest flux in the late-afternoon. Peak ozone



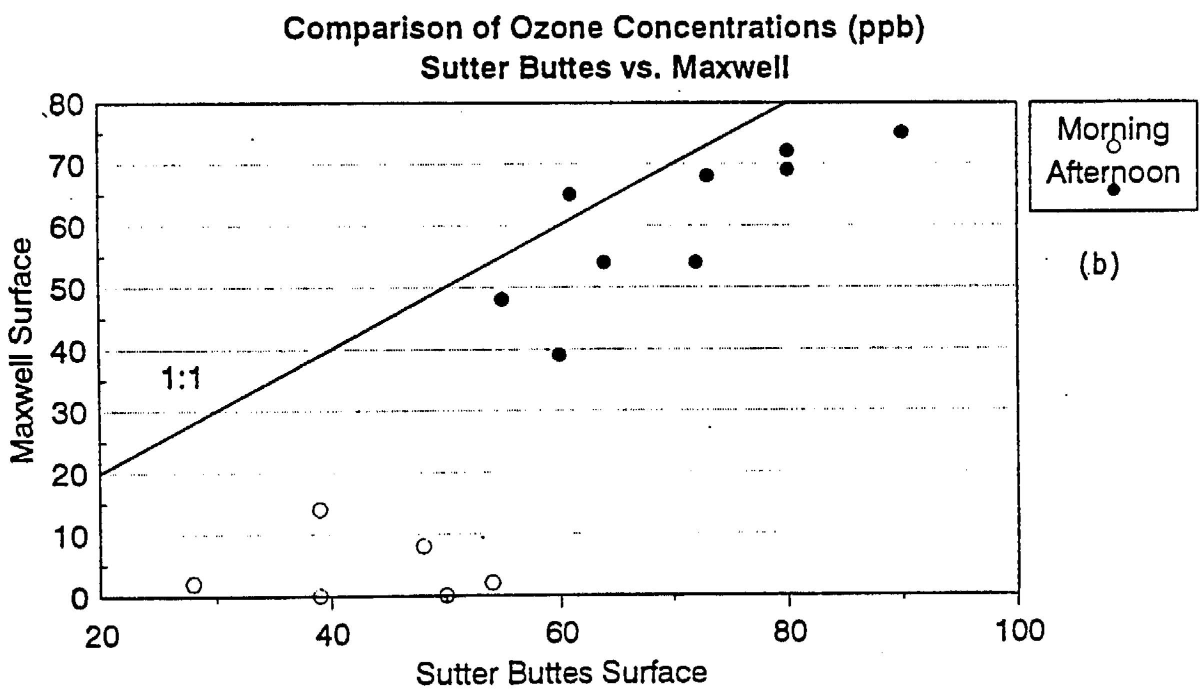




Figure 7-10. Comparison of Sutter Buttes surface ozone concentrations with (a) nearby aloft and (b) Maxwell surface ozone.

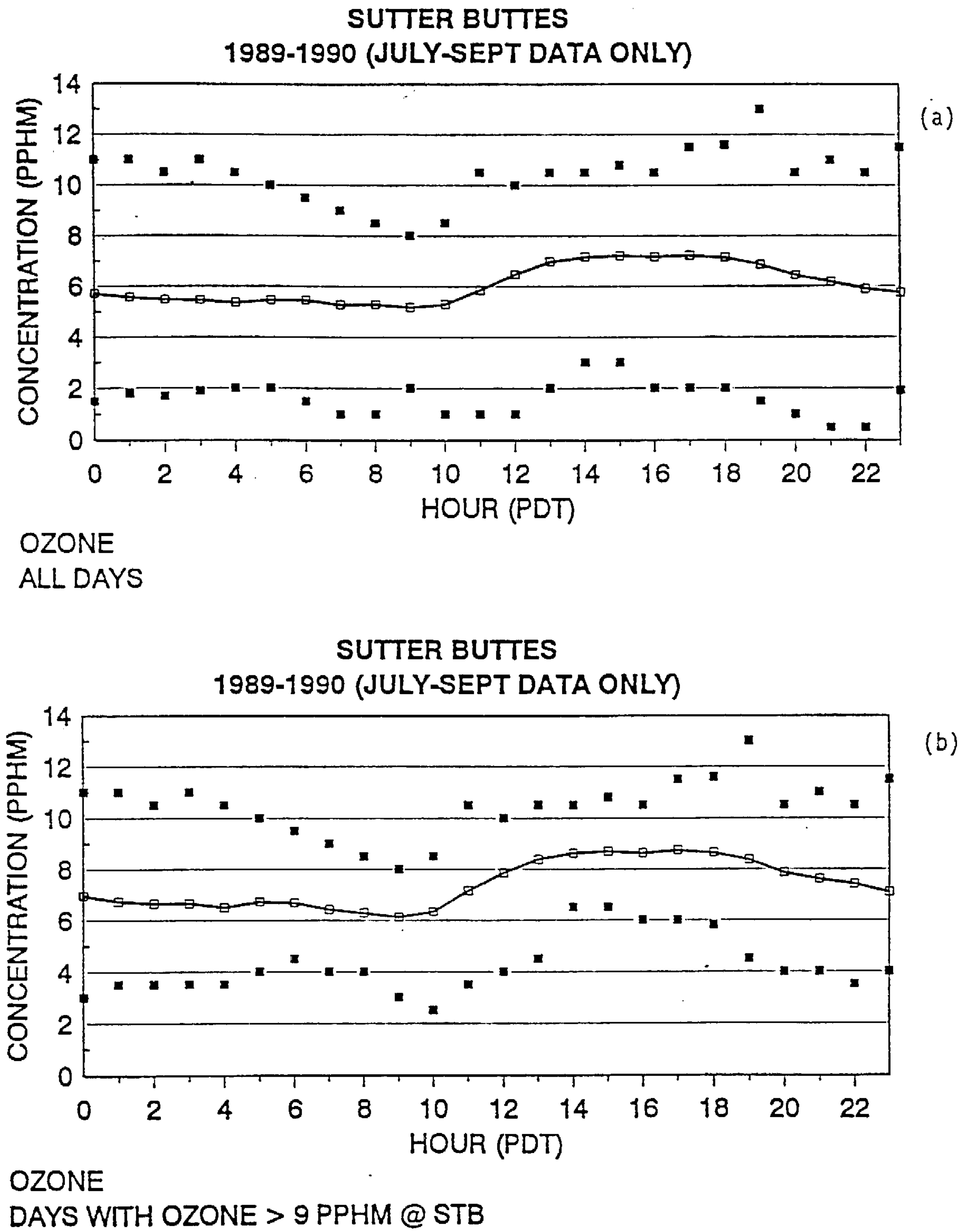



Figure 7-11. Diurnal ozone concentrations for Sutter Buttes during July - September (1989-1990) on (a) all days and (b) days with ozone peaks greater than 9 pphm.

fluxes are typically higher and last longer at Lambie than at Sutter Buttes.

- The simple ozone flux at Sutter Buttes is typically from the north in the morning and from the south in the afternoon; the southerly flux is typically 1 to 2 times higher than the northerly flux, and lasts longer.

Pollutant Flux Estimates:

- The flux of ozone and $NO_x$ into the Upper Sacramento Valley was estimated across a 2-D, east-west plane near Sutter Buttes, using aircraft air quality data and upper-air meteorological data on the afternoon of August 10, 1990. The flux of ozone and of $NO_x$ varied spatially across this plane. The highest mass flux of ozone occurred on the western end of the flux plane, where the wind speed was much higher than on the eastern end, even though the ozone concentration was significantly lower.

- Over the whole flux plane, about 50 kg/s of ozone was transported into the Upper Sac; this is equivalent to an average concentration of 70 ppb being transported at about 4 m/s.

- Over the whole flux plane, about 4 kg/s of $NO_x$ was transported into the Upper Sac; this is equivalent to an average concentration of 5 ppb being transported at about 4 m/s.

- The ozone and $NO_x$ fluxes into the Upper Sac which were measured on the afternoon of August 10, 1990 are similar to the fluxes measured between the SF Bay Area and the San Joaquin Valley (SJV) during August 1988. However, the SJV flux plane covered about twice the area as the Upper Sac flux plane.

General Pollutant Transport:

- The highest pollutant flux can occur in a region of either high pollutant concentration or high wind speeds, or both. Average wind speeds can vary by a factor of five or more, but ozone concentrations in the Sacramento Valley typically vary over a much smaller range; therefore, the regions or times of the highest flux might easily be due to high winds, with only modest ozone concentrations which do not exceed the State standard. In addition, we must remember that concentrations due to transported-ozone can only get lower via dilution and deposition losses. Thus, some cases of high ozone flux, but only modest ozone concentrations, cannot produce an ozone exceedance without additional ozone being formed in the downwind area.

- The time of maximum pollutant flux is important for determining the contribution to ozone exceedances at the downwind receptor site. In particular, if the maximum ozone flux occurs during the late-afternoon at Lambie Road, for example, then it is unlikely that the pollutants which accompany the maximum flux will contribute to an ozone exceedance that day in the Upper Sac (or even the Broader Sac Area), since the peak ozone concentrations at these receptor sites usually occurs before about

1400 PDT. However, it might be that the flux past Lambie Road during the mid-afternoon, or later that evening, might contribute the most to a 1400 PDT ozone exceedance at Red Bluff or Redding on the following day.

- It is critically important to have a non-urban boundary monitoring site, especially if un-titrated ozone and regionally representative $NO_x$ fluxes are to be estimated, since local NO emissions will distort ozone and $NO_x$ concentrations.

- Air quality and meteorological measurements taken at the Sutter Buttes (about 640 m msl) are representative of conditions aloft at an equivalent altitude.

- Frequent air quality and meteorological data aloft across a 2-D flux plane would provide more useful data for determining the timing of the peak ozone and $NO_x$ flux, quantifying the flux over a wide range of conditions, and estimating uncertainty. If possible, hourly data should be obtained.

# 8. ANALYSES USING VOC SPECIES AND TRACERS OF OPPORTUNITY

## 8.1 OBJECTIVES

Volatile organic compound (VOC) species and tracers of opportunity, (also called exotics, mainly chlorofluorocarbons - CFCs) data were collected to investigate source area compositions. Assuming that pollutant transport to the Upper Sacramento Valley (Upper Sac) can occur from the northwest (relatively clean), from the SF Bay Area under northwesterly flow (also relatively clean), from the SF Bay Area under southerly flow, and/or from the Broader Sacramento Area (Broader Sac), we used the VOC and tracers-of-opportunity data to address the following questions:

- Do unique VOC or tracers-of-opportunity signatures for these source areas exist?
- Can we find evidence of pollutant transport into the Upper Sac using these data?
- Can we quantify pollutant transport using these data?

We tested three methods for analyzing the potential ozone or precursor transport: the use of unique VOC and tracers-of-opportunity signatures, the age of air parcels, and statistical analysis. The following sections describe the available data, discuss the investigation of the three methods and their application to Upper Sac data, and recommend potential applications of the methods to other data.

## 8.2 AVAILABLE DATA

We used three data sets containing VOC and tracers-of-opportunity (exotics) data in our analyses, including data collected during the Upper Sac Transport study, the Sacramento Area Ozone Study (SAOS), and the San Joaquin Valley Air Quality Study - AUSPEX (SJVAQS/AUSPEX) study. All three field studies were conducted during the summer of 1990.

During the Upper Sac Transport study, exotics and VOC samples were collected aloft during aircraft spirals flown during the mornings and afternoons of the intensive study periods. The spirals encompassed about 200 to 350 meters vertically over an area about 2 km in diameter, approximately corresponding to a modeling grid square. Air was collected in 3.2-liter stainless steel canisters. The samples were grab samples which were filled within about two minutes. The canisters were then analyzed for methane, CO, and C2-C10 hydrocarbons at the Oregon Graduate Institute (OGI) by R. Rasmussen using gas chromatography - flame ionization detection (GC-FID). Up to about 70 hydrocarbon species are routinely identified by OGI; however, only about half this number of species were typically above detection (about 0.1 ppbC) in the samples. The speciated hydrocarbon data from the study are provided by Rasmussen (1991). Appendix D contains a summary of the nonmethane hydrocarbon (NMHC), olefin, paraffin, and unidentified aromatic hydrocarbon totals for each sample.

The VOC canisters were also analyzed by OGI using GC-electron capture detection (GC-ECD) for the exotics. Nine exotics were identified and these species are listed in Table 8-1. Also included in Table 8-1 are approximate background concentrations observed in remote areas, literature references, and typical sources of these species. The exotics data collected during the Upper Sacramento Valley Transport study are also provided in Appendix D.

Several procedures were used to identify potential outliers in the VOC and exotics data from the Upper Sac Transport study including: examining the data for each species sorted by concentration, examining the relative compositions of the samples, and examining box-whisker plots of species concentrations. Samples containing gross outliers were identified and appropriate validation codes were assigned. The validation codes for each sample are provided in Appendix D, as well as the description of each validation code.

A second source of data used in these analyses were exotics and VOC data collected at surface sites during the SJVAQS/AUSPEX (Blumenthal, 1992). Two-hour samples were collected two-to-four times per day at several locations in the Bay Area and San Joaquin Valley. Samples were also collected at Point Reyes in Marin County over 8-hour periods. The VOC and exotics samples were analyzed at OGI by R. Rasmussen. We obtained a working VOC data set from the Air Resources Board (K. Magliano, 1992); preliminary data validation and quality control procedures were performed by the ARB. Exotics data were available for three sampling periods in July and two sampling periods in August. However, the ARB only provided the VOC data collected during August 3-6, 1990.

Upon examination of the Point Reyes samples, we found that Freon 113 concentrations were significantly higher at Point Reyes than at urban locations, such as San Jose. After discussions with the analytical laboratory, we concluded that the Freon 113 in these samples was probably a result of outgassing from the sampling equipment. Therefore, the Freon 113 data from Point Reyes were flagged as invalid.

We also used exotics and VOC data for six samples collected during the SAOS at Travis, Davis, Folsom, and Auburn. These samples were collected aloft during traverses and spirals using procedures identical to those used for the Upper Sac samples. These samples were analyzed by OGI. The exotics data from these samples are listed in Appendix D with the Upper Sac Transport study data.

## 8.3 METEOROLOGICAL SETTING

Meteorological analyses established that a northwesterly flow pattern in the SF Bay Area would transport mainly clean air through Petaluma, Vallejo, and Travis to the Upper Sac (see Section 4). None of the intensive sampling days in the Upper Sac coincided with a southerly flow regime in the SF Bay Area which could transport pollutants from portions of the SF Bay Area with higher emissions to the Upper Sac. Wind flow patterns showed that transport from the Broader Sac to the Upper Sac could have occurred during some of the intensive study days.

Table 8-1. List of exotic species names, background concentrations, and sources.

| Formula | Species Name | Approximate Background Concentration (ppt) | Background Literature Reference |
|---|---|---|---|
| $N_2O$ | Nitrous Oxide | 307 | Rasmussen & Khalil (1986) |
| $CCl_2F_2$ | Freon 12 | 230-384 | Seinfeld (1977), Rasmussen & Khalil (1986) |
| $CCl_3F$ | Freon 11 | 133-223 | Seinfeld (1977), Rasmussen & Khalil (1986) |
| $CCl_2FCClF_2$ | Freon 113 | 19 | Seinfeld (1977) |
| $CHCl_3$ | Chloroform | 14 | Seinfeld (1977) |
| $CH_3CCl_3$ | 1,1,1-Trichloroethane | 113-158 | Seinfeld (1977), Rasmussen & Khalil (1986) |
| $CCl_4$ | Carbon Tetrachloride | 122-130 | Seinfeld (1977), Rasmussen & Khalil (1986) |
| $C_2HCl_3$ | Trichloroethylene | 16 | Seinfeld (1977) |
| $C_2Cl_4$ | Perchloroethylene | 40 | Seinfeld (1977) |

| Species Name | Typical Sources* |
|---|---|
| Freon 12 | Refrigeration, Air Conditioning |
| Freon 11 | Air Conditioning, Blowing Agent |
| Freon 113 | Manufacturing |
| Chloroform | Manufacturing, Cooling Towers |
| 1,1,1-Trichloroethane | Wastewater Treatment, Degreasing |
| Carbon Tetrachloride | Manufacturing |
| Trichloroethylene | Wastewater Treatment, Degreasing |
| Perchloroethylene | Dry Cleaning |

* Reference: SCAQMD, 1991

## 8.4 UNIQUE SOURCE AREA SIGNATURES

To assess transport to the Upper Sac, the first method we investigated was how to identify a source region by its VOC and exotics composition (also called a fingerprint or signature). We examined the data to find a unique signature for the SF Bay Area, for relatively clean air originating in Marin and Sonoma Counties, and for the Broader Sac.

We first investigated the exotics data to determine a unique SF Bay Area signature. We examined relationships among species and species ratios and the composition of individual samples collected at Pittsburg and Richmond during the SJVAQS/AUSPEX. The exotics data were highly variable from sample to sample and appeared to be influenced by nearby sources; some species concentrations varied over two orders of magnitude. This is consistent with measurements of exotics in the South Coast Air Basin (SoCAB) where ratios of exotic species at locations throughout the SoCAB varied significantly, while ratios at the Cajon Pass (outlet from the SoCAB) were similar from day to day (e.g., Bastable et al., 1990).

Since a unique signature was not identified, we stratified the data by SF Bay Area wind flow types. The Richmond VOC and exotics data showed slightly different average compositions for southerly and northwesterly flows. In fact, average concentrations for most species were slightly higher for the southerly flow conditions. We concluded that additional data are needed to properly characterize the SF Bay Area signature for use in other comparisons.

As discussed earlier, a northwesterly flow pattern in the SF Bay Area would transport mainly clean air through Petaluma, Vallejo, and Travis to the Upper Sac. We chose the Point Reyes data to investigate the background for this northwesterly wind flow pattern. Five 8-hour samples were available from the SJVAQS/AUSPEX study. The Point Reyes data were generally consistent from sample to sample, with apparently little or no dependence upon the SF Bay Area flow regime. These data probably well represent the background for the northwesterly flow pattern. The exotics and VOC composition profiles and concentrations showed some evidence of local emissions. For example, most of the exotic species concentrations were above literature background values. Some samples had compositions similar to vehicle emissions, although concentrations were relatively low; VOC concentrations ranged from 10 to 70 ppbC.

We also subjected the Point Reyes data to screening criteria which we established in a boundary study (Main et al., 1990) to identify clean air. Our concept of clean air is air that has been transported for numerous days without any fresh emission inputs, such as might be expected for air that is transported across the ocean. The screening criteria are shown in Table 8-2. These criteria were similar to criteria employed by Moore et al. (1989). Samples in which none of the six species concentrations exceeded the criteria concentrations were considered clean. The cut-off concentrations are somewhat greater than concentrations considered to be representative of tropospheric background concentrations. One criterion was different from Moore et al. (1989): a total xylene concentration of 2.0 ppbC, instead of 0.2 ppbC was used. A 2 ppbC cut-off concentration for xylenes is considered sufficiently

Table 8-2. Clean air criteria for hydrocarbon samples.

| ROG Species | Clean Air Cut-off Concentrations (ppbC) |
|---|---|
| Methane ($CH_4$) | ≤ 2000 |
| CO | ≤ 200 |
| Ethane ($C_2H_6$) | ≤ 10 |
| Ethene ($C_2H_4$) | ≤ 2 |
| Acetylene ($C_2H_2$) | ≤ 2 |
| Total xylenes | ≤ 2 |

stringent for identifying relatively clean samples. We found that eight of the ten Point Reyes VOC samples met all the screening criteria; only two samples failed to meet the xylenes criterion.

Having established that the Point Reyes data could characterize the northwesterly flow background and relatively clean air, we needed samples collected farther downwind during northwesterly flow for comparison. Only one sample met our criteria: the July 13 Travis sample was collected at 1453 PDT at 457 m msl during northwesterly flow in the SF Bay Area. Figure 8-1 compares the Travis VOC and exotics composition with the average Point Reyes composition of samples collected on August 6 (northwesterly SF Bay Area flow regime). The VOC composition is provided for 24 typically abundant species. For the VOCs, the Travis and Point Reyes average data were similar in both composition and concentration except that the Travis sample had higher concentrations of acetylene, toluene, ethylbenzene, and xylenes. We might expect higher concentrations at Travis because of nearby vehicle traffic and Travis Air Force Base activities (automobile emissions, degreasing activities, etc.). One species comparison which was not consistent with other data was CO; the Point Reyes average CO concentration was higher than the Travis sample. Note, however, only one Travis sample was available. For comparison to SF Bay Area samples, Figure 8-2 shows that the Richmond VOC and exotics composition and concentrations were significantly different from Travis samples.

Additional Davis-Travis traverse samples were collected on July 30 during southerly SF Bay Area flow. We anticipated that these samples might be representative of SF Bay Area southerly flow and therefore, might be different from samples collected during northwesterly flow. However, one of the samples was collected at too high an altitude (1500 m msl) to represent the mixed layer. The other samples were collected at about 450 m msl, which was within the mixed layer. However, all the samples showed low VOC and exotics concentrations and ratios similar to the Travis and Point Reyes data. It is possible that the area had already been "cleaned out" by strong winds.

We had two samples available to possibly characterize the Broader Sac VOC and exotics signature. Two samples were collected during aircraft spirals over Folsom and Auburn on the afternoon of July 11 and July 13, respectively (during SAOS). The SF Bay Area flow pattern on both these days was northwesterly, so that relatively clean air, with little SF Bay Area contribution, was transported to the Sacramento Valley. Therefore, the Folsom and Auburn samples should be representative of the Broader Sac signature. Figure 8-3 shows that the two samples had very similar VOC and exotics concentration and composition. VOC and exotics concentrations were slightly higher at Folsom than at Auburn, except isoprene, which had a higher concentration at Auburn. These samples differed significantly from the Travis, Point Reyes, and Richmond data. For example, note the differences between the relative composition of isoprene, butane, propane, acetylene, ethene, and ethane in the Folsom and Auburn samples compared to samples collected at Richmond.

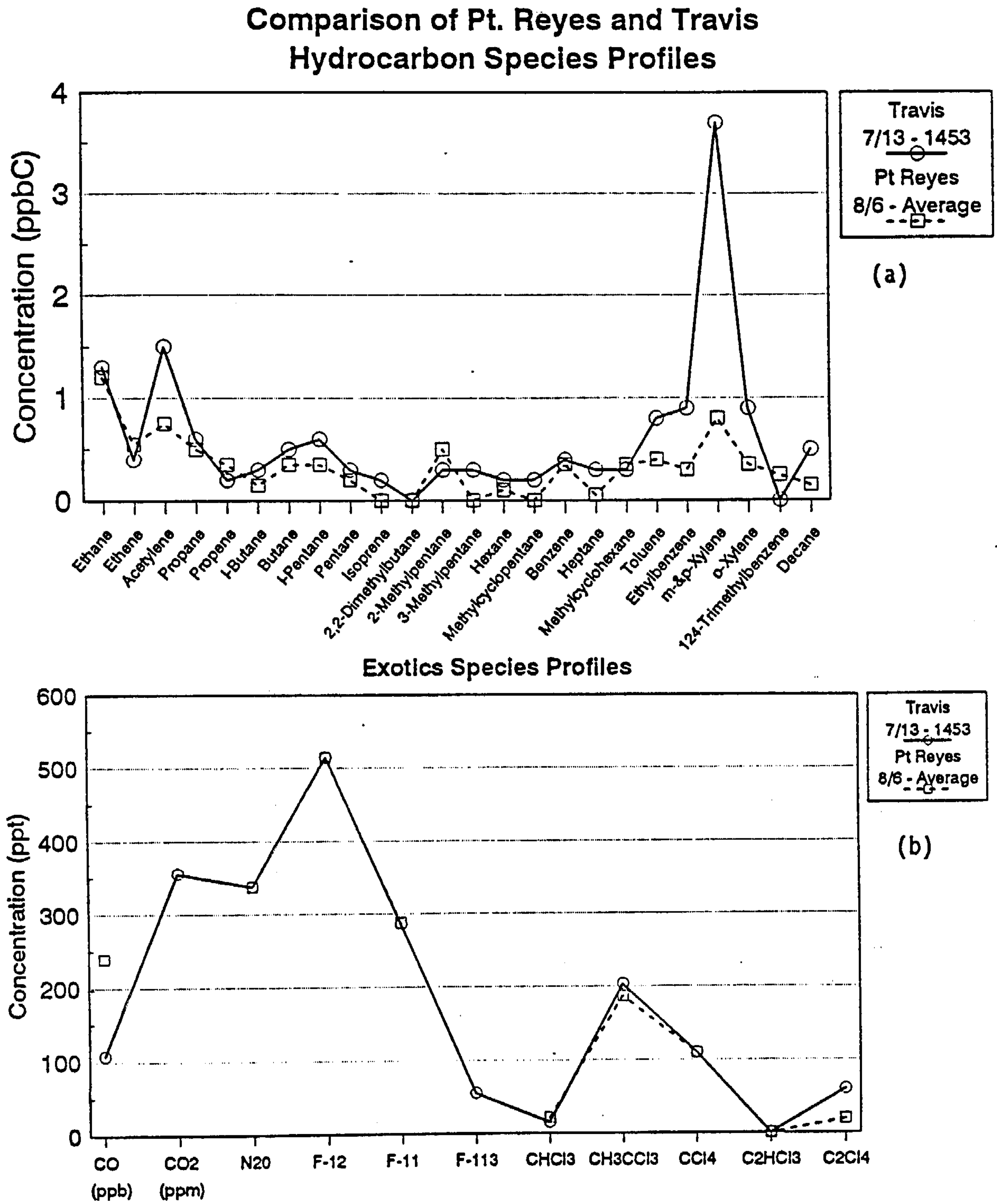



Figure 8-1. Comparison of Point Reyes and Travis (a) VOC and (b) exotics data in 1990. The July 13 Travis sample was collected by aircraft (457 m msl) at 1453 PDT. Two 8-hour Point Reyes samples were collected at the surface on August 6. Northwesterly wind flow occurred in the San Francisco Bay Area on both dates. Note that the exotics concentrations at both locations were nearly identical.

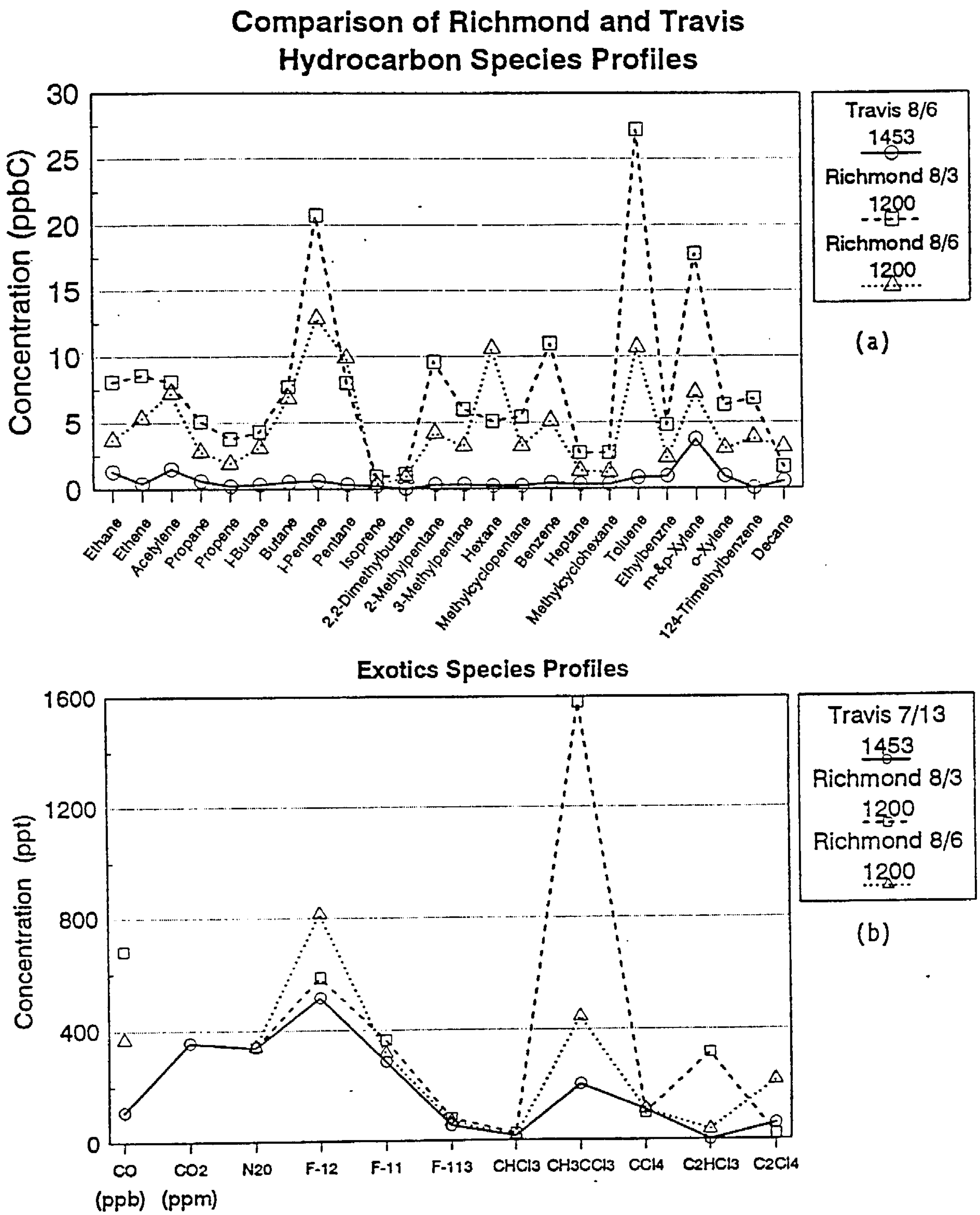



Figure 8-2. Comparison of Travis and Richmond (a) VOC and (b) exotics data in 1990. The July 13 Travis sample was collected by aircraft (457 m msl) at 1453 PDT. The 2-hour Richmond samples were collected at the surface on August 3 and 6. The SF Bay Area experienced southerly winds on August 3 and northwesterly winds on August 6.

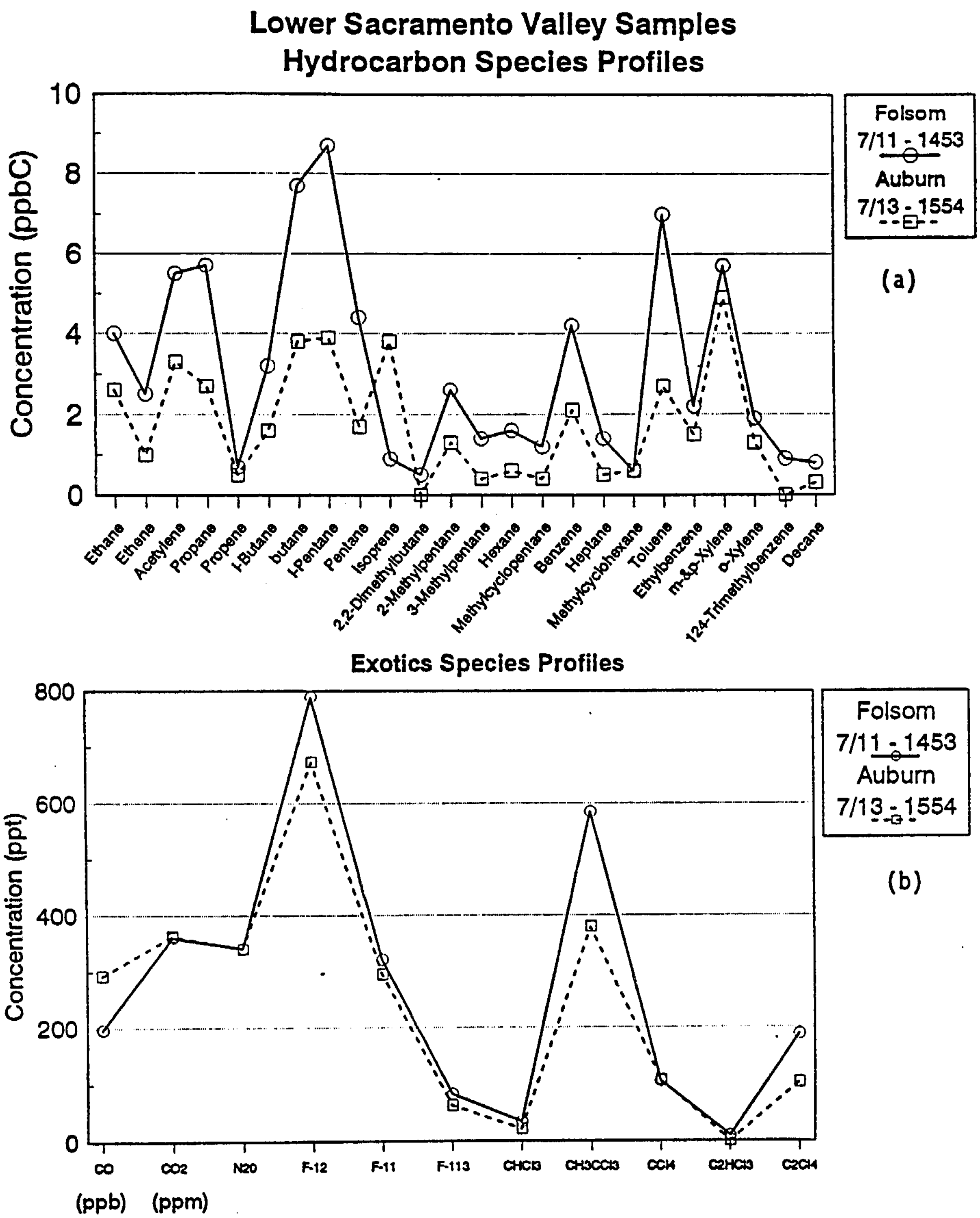



Figure 8-3. The composition of two (a) VOC and (b) exotics samples collected downwind of the Broader Sacramento Area at Folsom and Auburn. Wind flow in the SF Bay Area was northwesterly, therefore, these samples probably well represent the Broader Sac signature.

## 8.5 COMPARISON OF UPWIND SIGNATURES TO UPPER SACRAMENTO VALLEY SAMPLES

Having identified a VOC and exotics signature for the Broader Sac and the SF Bay Area northwesterly flow, the next step was to compare the Upper Sac samples with these signatures in an attempt to find evidence of transport. All of the Upper Sac samples were collected under northwesterly SF Bay Area flow conditions; therefore, pollutant transport from the urban/industrial parts of the SF Bay Area to the Upper Sac was not very important during the field study intensive days. However, flow conditions did support transport from the Broader Sac to the Upper Sac. Note that surface ozone concentrations in the Upper Sac were relatively low during the field study; intensive measurements were not made on the days with the highest ozone concentrations or with typical wind flow characteristics (see Section 4).

We compared each Upper Sac sample to the Travis and Folsom data to determine whether the exotics or VOC concentrations and relative compositions were similar to northwesterly (clean) flow, Broader Sac, or other source data such as forest fires or local emissions. We were modestly successful in matching VOC and exotics signatures to possible source areas. Many of the samples were relatively clean (concentrations and composition similar to Travis), some samples showed evidence of influence from the Broader Sac (concentrations and composition similar to Folsom), some samples showed a combination of influences (either exotics or VOC concentrations or composition similar to Folsom, but not both), while other samples showed evidence of more local emissions (very high concentrations of some species). Figure 8-4 shows a clean sample, Figure 8-5 shows a sample with a composition similar to the Folsom sample (Broader Sac influence), and Figure 8-6 shows a sample with a signature which was difficult to classify.

We also applied the clean air criteria to the Upper Sac samples as an independent means of identifying clean samples. The results from this screening procedure are shown in Table 8-3. Most of the data failed to meet the xylenes criterion. However, in most cases, the samples which met all of the other clean air criteria were also the samples which were identified as having a VOC and exotics signature similar to Travis (and thus to Point Reyes).

One of the confounding problems with the Upper Sac VOC data was the occurrence of forest fires in the Chico area during the August episode. The aircraft measured high $b_{scat}$ levels attributable to the smoke, but ozone and $NO_x$ concentrations did not appear to be elevated (or depressed). Many of the samples during this time period had relatively high CO concentrations. In most of these samples with high CO, several VOC species had disproportionately high concentrations, which probably masked evidence of influence from the Broader Sac. The forest fire smoke did not appear to affect the exotics concentrations.

## 8.6 AGE OF AIR PARCELS

The ratios of more reactive species concentrations to less reactive species concentrations are indicative of the relative changes in species composition and age. Lower ratios correspond to more aged VOC mixtures (for

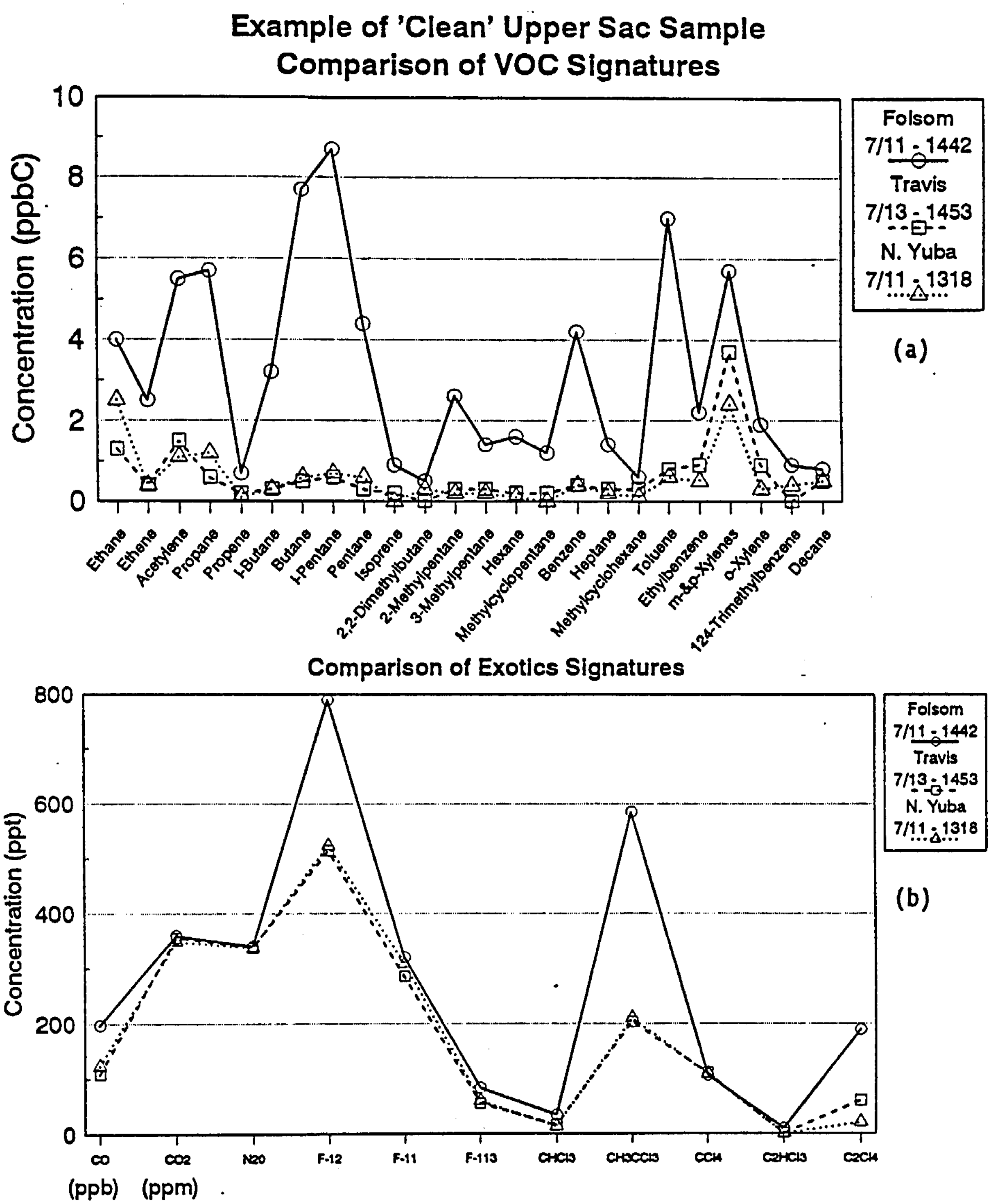



Figure 8-4. Comparison of (a) VOC and (b) exotics signatures at North Yuba, Folsom, and Travis. The North Yuba sample has similar species concentrations and composition to the Travis sample and is considered "clean."

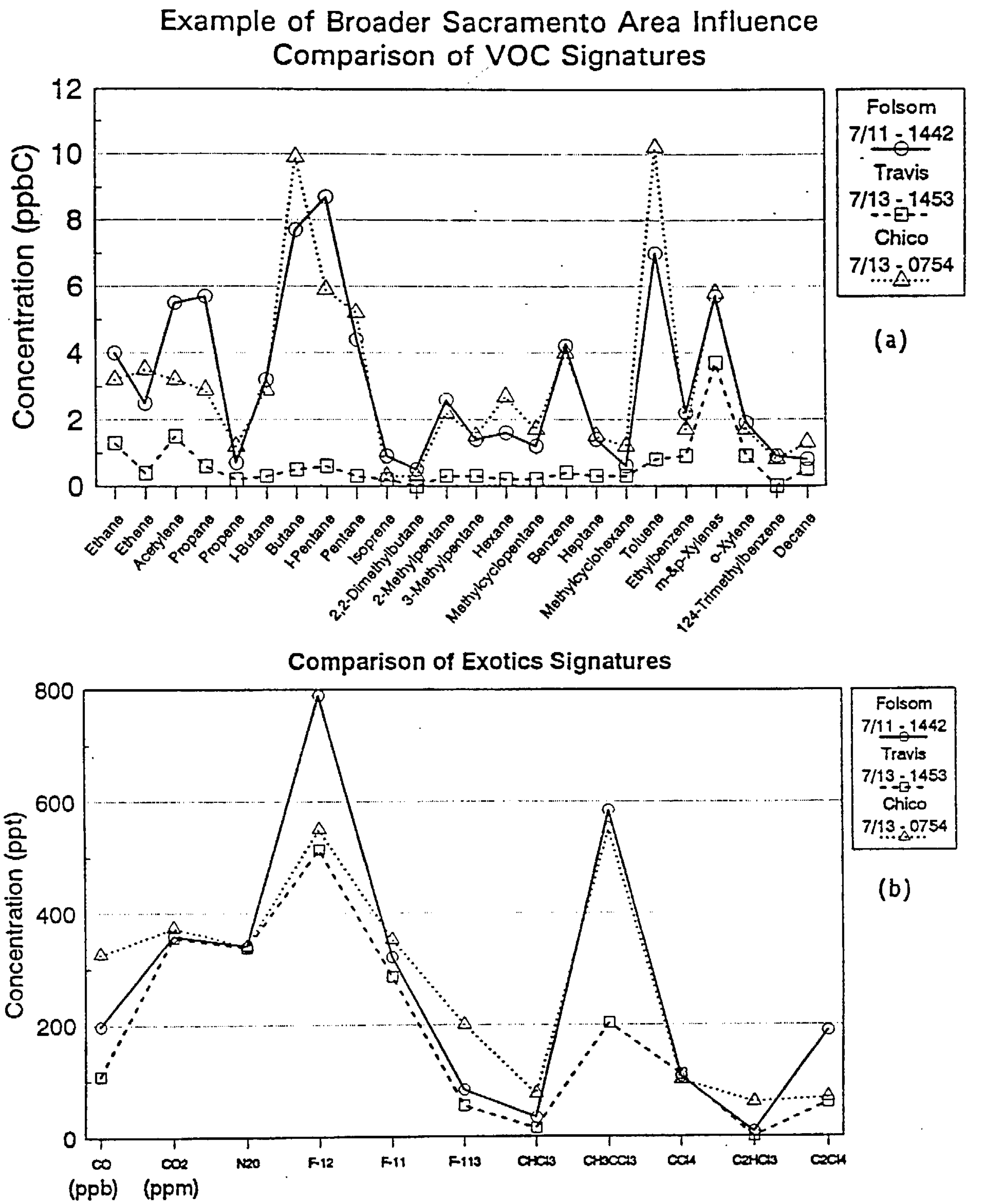



Figure 8-5. Comparison of (a) VOC and (b) exotics signatures at Chico, Folsom, and Travis. The Chico sample has similar species concentrations and composition to the Folsom sample and appears to have been influenced by the Broader Sacramento Area emissions.

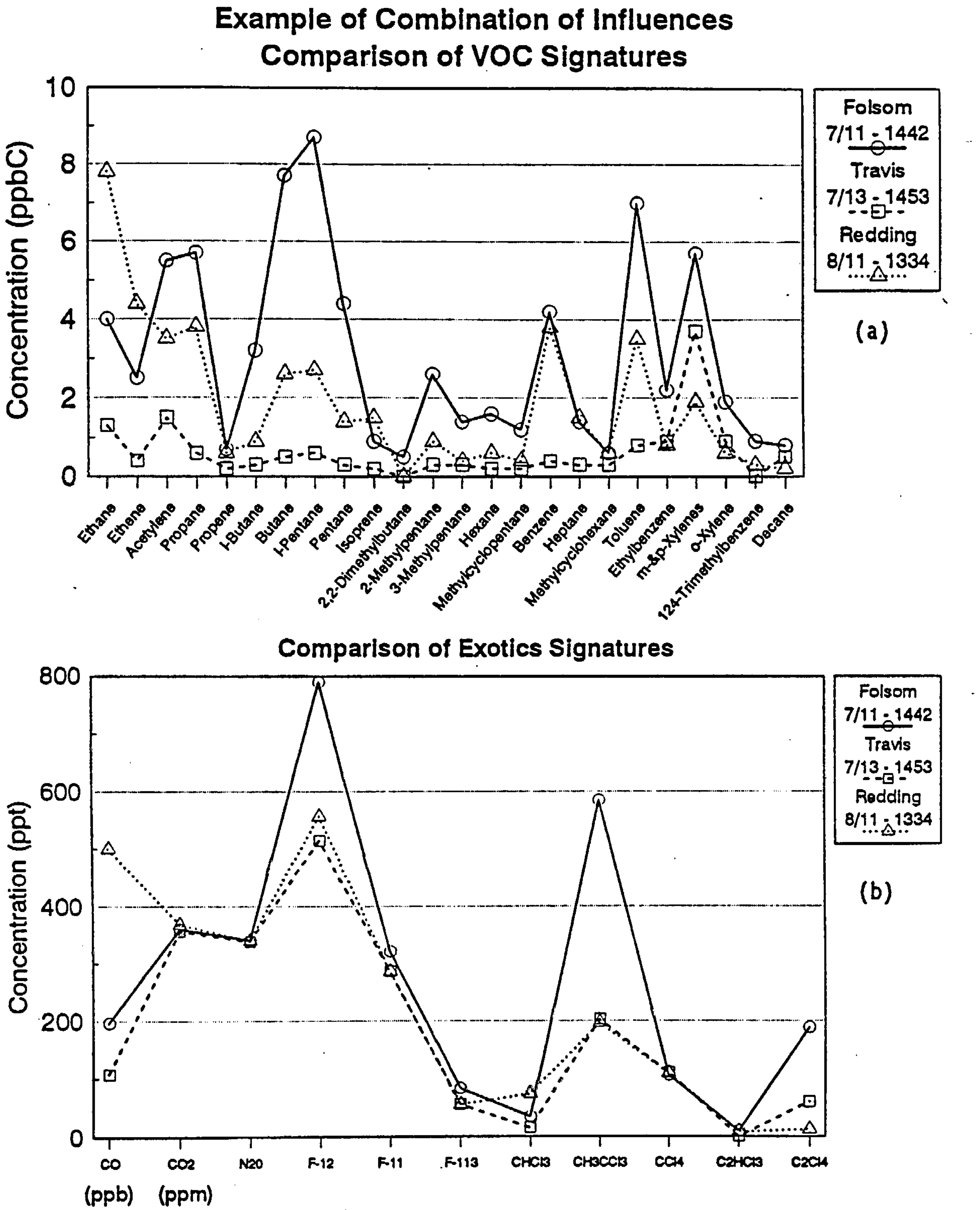



Figure 8-6. Comparison of (a) VOC and (b) exotics signatures at Redding, Folsom, and Travis. The Redding sample was collected in or near a smoke cloud and shows evidence of a combination of influences: clean air (most exotics and some VOC concentrations), smoke (high CO and possibly VOCs), and upwind urban area emissions (e.g., benzene, toluene).

Table 8-3. Application of clean air criteria to Upper Sacramento Valley and source signature hydrocarbon samples.

| | Number of Samples Remaining | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Criteria (ppbC) | N. Yuba | Maxwell | Haigh | Chico | Red Bluff | Redding | Folsom | Auburn | Davis/Travis | Pt. Reyes |
| None Applied | 18 | 17 | 12 | 12 | 10 | 14 | 1 | 1 | 4 | 10 |
| $CH_4 < 2000$ | 18 | 17 | 12 | 11 | 10 | 14 | 1 | 1 | 4 | 10 |
| $CO < 200$ | 14 | 15 | 10 | 7 | 7 | 8 | 1 | 0 | 4 | 10 |
| $C_2H_6 < 10$ | 17 | 14 | 11 | 10 | 9 | 12 | 1 | 1 | 4 | 10 |
| $C_2H_4 < 2$ | 15 | 12 | 10 | 5 | 8 | 4 | 0 | 1 | 4 | 10 |
| $C_2H_2 < 2$ | 16 | 15 | 10 | 9 | 9 | 10 | 0 | 0 | 4 | 10 |
| Xylenes < 2 | 3 | 1 | 2 | 1 | 3 | 1 | 0 | 0 | 0 | 8 |
| All Applied | 3 | 1 | 2 | 1 | 3 | 1 | 0 | 0 | 0 | 8 |

example, Nelson and Quigley, 1983). Examining these types of ratios in a data set may provide confirming evidence to other methods. For example, consider a VOC sample collected aloft near a receptor site which has a VOC signature similar to an upwind source region. Investigation of VOC ratios might indicate that the air parcel is from aged emissions, which provides additional evidence that transport occurred. This information and other data, such as the ozone concentration of the air parcel, may indicate that the hydrocarbons are of local origin. We investigated one Upper Sacramento Valley sample which had a relatively high ozone concentration (110 ppb). Unfortunately, other data showed this sample had been collected in a smoke cloud and therefore, it was inappropriate to apply this method because of the presence of hydrocarbons in the smoke.

We have had some success in applying this ratio technique to other data, such as the Southern California Air Quality Study (SCAQS) VOC data (Lurmann and Main, 1992). One of the ratios often used is the sum of o-, p-, and m-xylenes to benzene (X/B). Xylenes and benzene are emitted primarily by motor vehicles and, based on OH rate constants, the xylenes are expected to react about 14 times faster than benzene (Atkinson, 1990). We therefore expect xylenes to be depleted relative to benzene or toluene. Hence, it was surprising to find such high concentrations of xylenes compared to benzene in most of the available data, including Point Reyes, Travis, SAOS, and the Upper Sac samples.

We also investigated the morning X/B, toluene/benzene, and other ratios in the Upper Sac data. Unfortunately, the ratio analysis provided results with no clear patterns.

## 8.7 STATISTICAL ANALYSES

Factor and cluster analyses were used to investigate spatial and temporal relationships in the VOC and exotics data. Cluster analysis is a multi-variate procedure for detecting groupings in data. Principal component (PC) analysis is a form of regression analysis used to identify the linear combination of variables that explain most of the variability in the data. This analysis method is used to reduce the number of variables needed to explain variance in the data. Factor analysis extracts PC's for variables and usually provides similar results to PC analysis. The Pearson correlation method was used to measure similarity in patterns across profiles regardless of overall magnitude, an important feature since the VOC and exotics concentrations spanned a range from parts-per-trillion to parts-per-million.

We performed these analyses using all the exotic species and the 24 most abundant VOCs. We applied cluster and factor analyses to the complete data set to investigate the spatial relationships among individual samples. The analyses were applied to the VOC data only, exotics data only, and VOC and exotics data combined.

Cluster analysis showed several groupings which agreed relatively well with our observations from the comparison of Travis and Folsom VOC and exotics signatures with the Broader Sac samples. For example, several samples identified as having some evidence of influence from the Broader Sac or the forest fire were grouped together (including the Chico sample collected on the morning of July 13, shown in Figure 8-5, and the Redding sample collected on the afternoon of August 11, shown in Figure 8-6). Other groupings included samples with high concentrations of a single species, such as $CHCl_3$, ethene, or isoprene.

Factor analysis showed similar results to cluster analysis. Most of the samples which appeared clean were grouped with the Travis sample, accounting for about 35 percent of the variance in the VOC data. Samples showing some influence from the fire or the Broader Sac were present in two factors, accounting for about 11 percent of the variance. Two other groups consisting of samples with high ethene or high isoprene concentrations accounted for another 6 percent of the variance. Less than half the variance was accounted for in the five factors (covariance became a problem when more than five factors were considered). Most of the variance in the exotics data was explained by a single factor (72 percent).

Overall, the cluster and factor analyses identified similar groupings of samples to those identified in the direct comparison of Travis and Folsom VOC and exotics signatures with the Upper Sac samples.

## 8.8 CONCLUSIONS AND RECOMMENDATIONS

### 8.8.1 Application of Methods to Upper Sacramento Valley Data

With the limited available data, we identified unique VOC and exotics signatures for different source regions including the Broader Sac and clean air resulting from northwesterly flow in the SF Bay Area. While we were unable to identify a unique source signature for the more urban/industrial SF Bay Area for use in this analysis, the technique appears promising for future applications. Species ratios (including assessment of the relative age of air parcels), clean air screening criteria, and statistical analyses were useful to augment the analysis of unique signatures.

Comparisons of receptor area samples to source area signatures showed evidence of transport of VOC and exotics from the Broader Sac to the Upper Sac. Unfortunately, the intensive study meteorology did not favor transport from the urban/industrial parts of the SF Bay Area to the Upper Sac and therefore, we could not investigate evidence of transport from this source region. Because we did not have transport from both the SF Bay Area and the Broader Sac to the Upper Sac, we did not attempt to quantify the relative contribution of each source region to the receptor VOC or exotics signatures. However, quantification may be possible with additional data.

To better assess the origins of transport into the Upper Sac using VOC and exotics data, the following data and analyses are recommended:

- Collect additional data to confirm characterization of the Broader Sac and the SF Bay Area northwesterly flow (Travis area).
- Conduct additional analysis of the SJVAQS/AUSPEX VOC and exotics data to provide an appropriate SF Bay Area signature.

- Collect data under different SF Bay Area wind flow regimes, specifically, southerly flow. With these data, assess the SF Bay Area signature and differences between VOC and exotics signatures during the various wind flow regimes. It may be possible to quantify the relative contribution of the SF Bay Area and the Broader Sac to the hydrocarbon concentrations using species ratios and exotics concentrations and ratios when both source area signatures are present. A statistical analysis approach, such as cluster analysis, may be useful to determine possible groupings of the data. This data may be available in existing ARB VOC data sets. In addition, the new EPA PAMS (photochemical assessment monitoring stations) requirements will likely include upwind, source region, and downwind VOC speciated monitoring in many air basins.

- Collect data during Upper Sac ozone exceedances. Ozone concentrations at Redding and Red Bluff were relatively low during the intensive study days in 1990.

The clean air screening procedure is useful for screening samples collected at background locations and identifying samples which may have had little contribution from upwind sources. Additional criteria could be added for the exotics to aid in the screening process. However, an investigation of appropriate background concentrations is required.

### 8.8.2 Application of Methods to Other Data

Investigating unique signatures and air parcel age may be useful in interpreting the SJVAQS/AUSPEX data set. Depending upon the meteorology and specific siting of the sampling location, the SF Bay Area source signature may be characterized by the Livermore, Altamont, and/or Pacheco Pass data. There were 30 samples collected at each of these locations at various times during the day. Crows Landing (12 samples), Collegeville (25 samples), and Yosemite (34 samples) could be interesting receptor sites to investigate. These data could also be useful for assessing transport from the SF Bay Area to other air basins, such as the Broader Sac.

# 9. SACRAMENTO VALLEY TRANSPORT STUDY TRACER EXPERIMENTS

One of the methods selected for use in analyzing potential ozone transport or precursor transport from the San Francisco Bay Area (SF Bay Area) and from the Broader Sacramento Area (Broader Sac) to the Upper Sacramento Valley (Upper Sac) was to perform a series of tracer experiments. Three tracer experiments were conducted to track the transport from the SF Bay Area and the Broader Sac. Because of low ozone concentrations in the Upper Sac during the third tracer experiment, none of the field samples were analyzed and thus will not be discussed here. Further details of the tracer studies can be found in Tracer Technologies (1991).

## 9.1 TRACER STUDY DESIGN

The tracer studies were designed to quantify the contribution of ozone and its precursors from the upwind air basins (SF Bay Area and Broader Sac) to the receptor region (Upper Sac). Of particular interest were three separate transport categories:

- Same-day transport;
- Overnight transport; and
- Transported pollutants which remain overnight in the receptor region.

To address these objectives, tracers were released simultaneously from two locations: (1) Lambie Road (representing SF Bay Area transport) and (2) Howe Park (representing Broader Sac transport). Tracer experiments were conducted during two ozone episodes in the summer of 1990: July 11-13 and August 10-12. The tracer releases were made at two different time periods for 3-hour durations during each experiment: 1400 to 1700 PDT (to represent overnight transport), and 0600 to 0900 PDT (to represent same-day transport of morning emissions). The sampling period for each experiment was from 1200 PDT on the day of the first tracer release until 1800 PDT 2 days later. Figure 9-1 depicts the study domain and shows the locations of the releases, as well as the surface and aircraft sampling sites. Because of the large area covered in these experiments, perfluorocarbon tracers were selected for use in this study due to their measurability at very low concentrations and their low global background level.

Before interpreting the results of any tracer study, it is important to have an understanding of the uncertainty (e.g., accuracy, precision, and consistency) of the collected tracer data. Although no specific analysis of uncertainty was conducted in this study, an uncertainty analysis of tracer data collected in a parallel study conducted by Tracer Technologies using the same four tracer materials was available for our review (see Richards et al., 1991 and Richards and Blumenthal, 1990). The parallel tracer study was conducted to determine source attributions to visibility degradation in the desert southwest. Using collocated samplers, replicate analysis, and statistical analysis techniques, it was concluded that the uncertainty of the measured tracer material was inversely related to the quantity of material

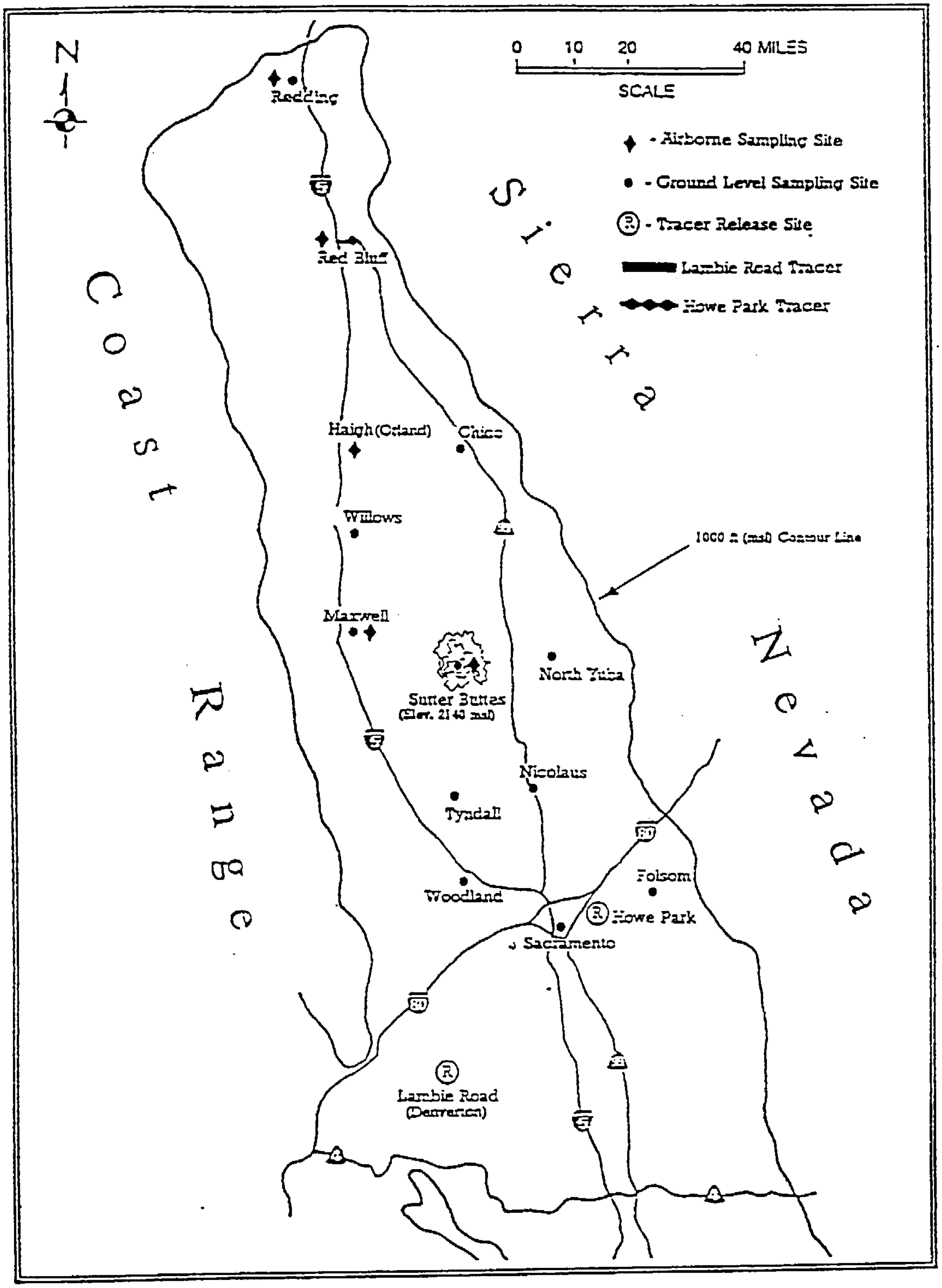



Figure 9-1. Tracer release, aircraft, and surface sampling locations.

measured. That is, greater certainty (conversely lower uncertainty) is associated with higher concentrations than with lower concentrations. Review of the statistical results for the complete 3-month tracer data set suggest that tracer concentrations greater than 100 parts-per-quadrillion (ppq) have a high degree of confidence and concentrations less than 50 ppq should be used with caution, but the results varied widely for different subsets of data. In fact, several subsets of tracer data were much better than the overall data set. In these cases, tracer concentrations down to about 20 ppq were consistent with $SO_2$, $NO_x$, particle scattering, and air-parcel trajectory results (Richards and Blumenthal, 1990). Since our tracer results were consistent between sampling locations, including aloft, and with air-parcel trajectories in this study, we have used tracer concentrations greater than approximately 25 ppq to indicate the presence of tracer.

## 9.2 TRACER STUDY RESULTS

### 9.2.1 July 11-13, 1990 Tracer Study Results

<u>Description of Afternoon Release:</u> The tracer released on the afternoon of the first day (July 11, 1990) from Lambie Road was not observed at any sampling location until late that night (actually 0200 PDT at North Yuba). Additional tracer from Lambie Road was observed after sunrise in Chico and aloft near Maxwell. By noon on July 12, Lambie Road tracer was seen at nearly all sites south of Willows. Concentrations slowly diminished and eventually disappeared at all sites. The tracer released on the afternoon of the first day from Howe Park was also not observed at any sampling location until late that night (actually 0200 PDT at Nicolas). Additional tracer from Howe Park was observed after sunrise aloft and at the surface at North Yuba. This tracer also appeared at Nicolas the next day (July 12) as well. Neither tracer was observed at Red Bluff or Redding, either aloft or at the surface.

<u>Discussion:</u> Figure 9-2 depicts a schematic view of the movement of the tracer material. The pattern of tracer observations suggests that the tracer material was entrained aloft into an up-valley flow during the afternoon and cutoff from the surface layer after sunset. Some of the tracer material was brought back down to the surface near North Yuba, possibly in a downslope flow off of the Sierra foothills. On the morning of July 12, widespread re-entrainment of tracer material from aloft into the growing mixed layer took place as a result of surface heating. It appears likely that the bulk of the tracer material released from Howe Park was carried eastward into the Sierra foothills in the afternoon westerlies.

<u>Description of Morning Release:</u> The tracer released on the morning of the second day (July 12, 1990) from Lambie Road was not observed at any sampling location until late that night and only in small quantities throughout the Broader Sac. Tracer released on the morning of the second day from Howe Park was observed nearby in Sacramento at noon and again at Nicolas the following morning, but was not seen elsewhere.

<u>Discussion:</u> Figure 9-3 depicts a schematic view of the movement of the tracer material. The pattern of tracer observations suggests that the tracer material from both Lambie Road and Howe Park moved easterly or southeasterly

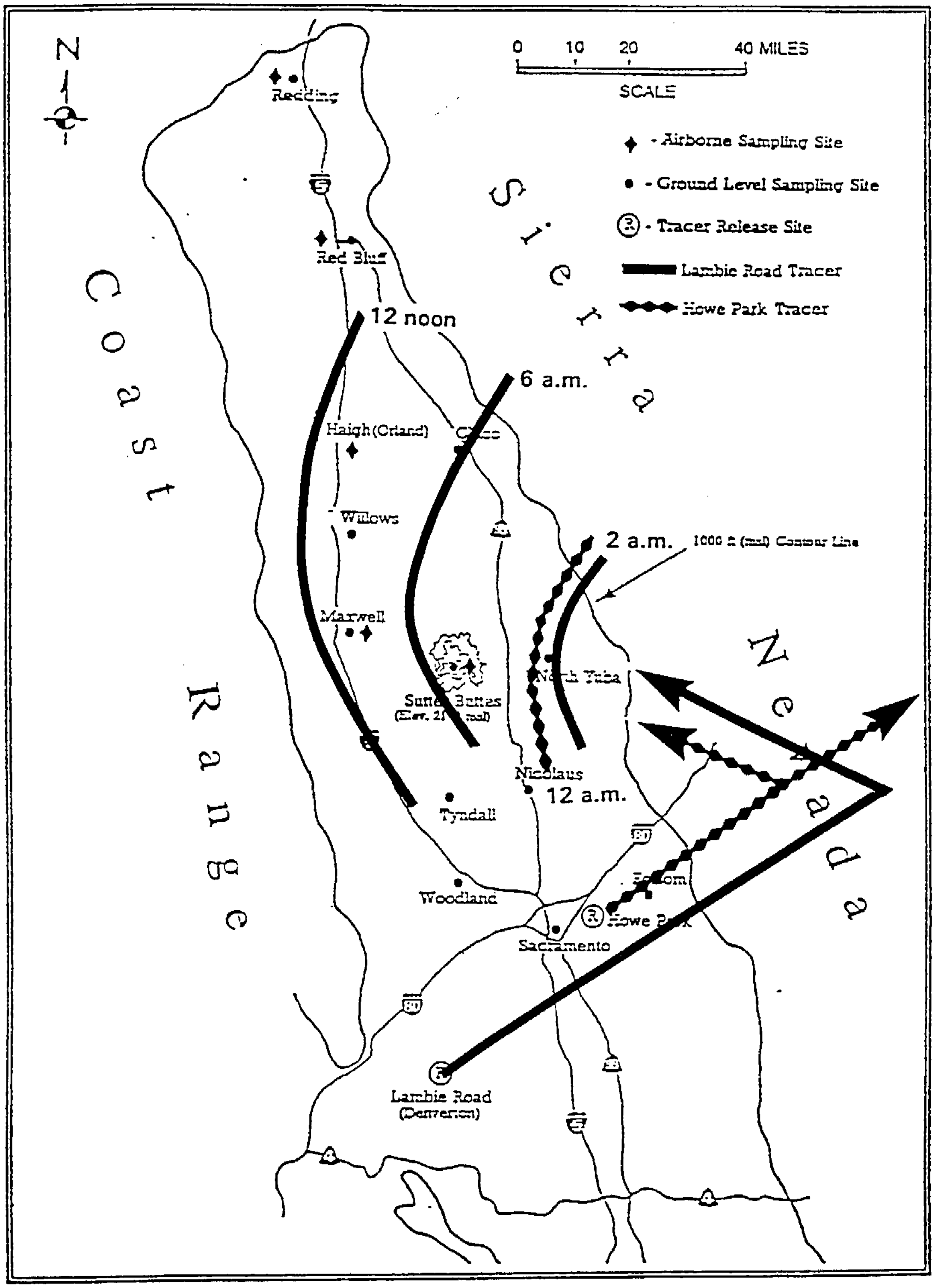



Figure 9-2. July 11th afternoon release.

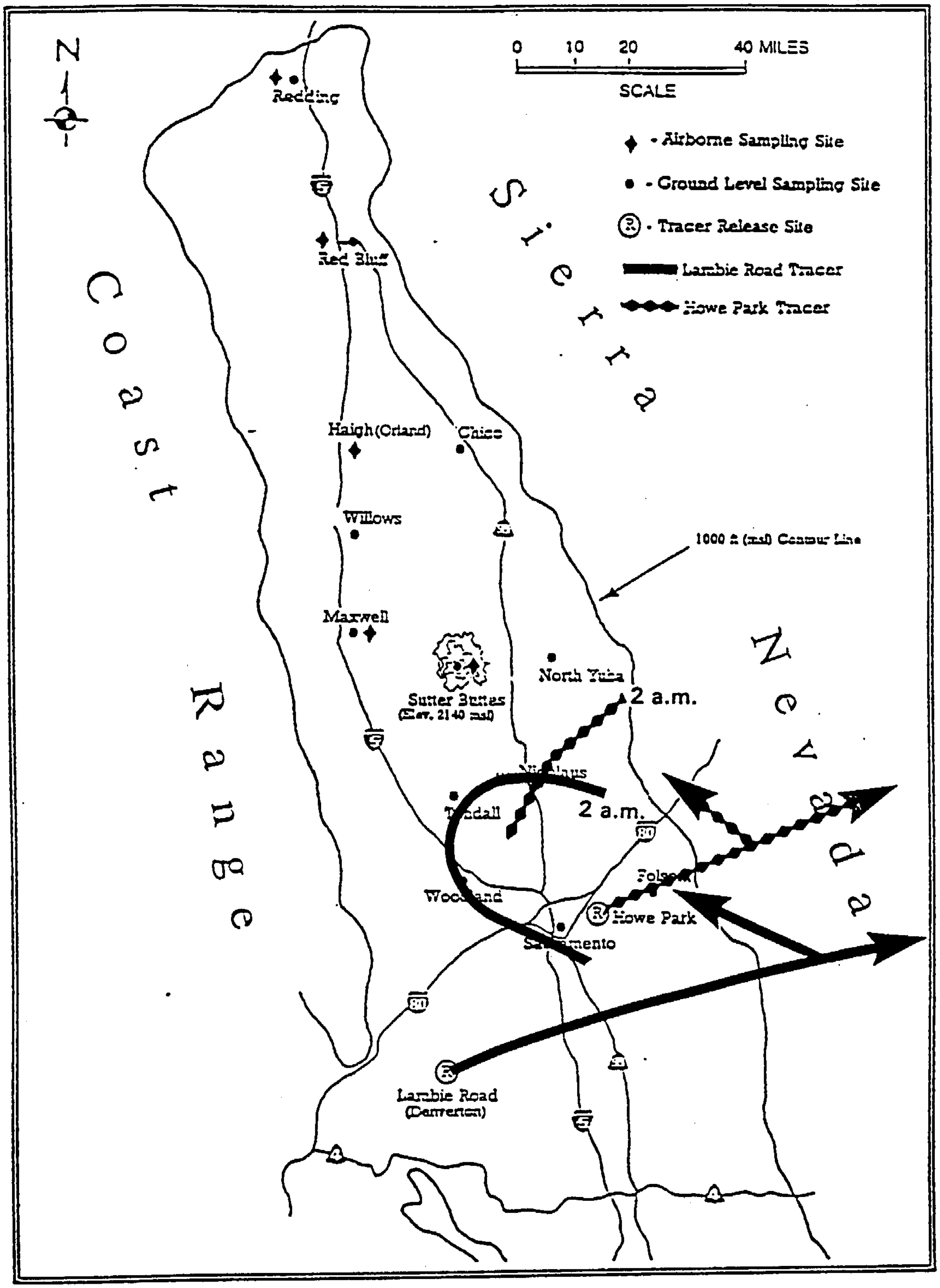



Figure 9-3. July 12th morning release.

away from the sampling sites and that only small quantities were recirculated back over night.

### 9.2.2 August 10-12, 1990 Tracer Study Results

Description of Afternoon Release: The tracer released on the afternoon of the first day (August 10, 1990) from Lambie Road was observed overnight at North Yuba, Chico, and at Sutter Buttes. Additional tracer from Lambie Road was observed aloft near North Yuba and Chico the following morning. On August 11, Lambie Road tracer was seen as far north as Redding: aloft at about 1330 PDT and it was mixed down to the surface at noon. Tracer released on the afternoon of the first day from Howe Park was first observed overnight at Nicolas. Additional tracer from Howe Park was observed after sunrise aloft at Sutter Buttes, North Yuba, and Red Bluff.

Discussion: Figure 9-4 depicts a schematic view of the movement of the tracer material. The pattern of tracer observations suggests that the tracer material was entrained aloft into an up-valley flow aloft during the afternoon and cutoff from the surface layer after sunset as was the case in the July episode. However, in this case the tracer material was carried as far north as Redding and Howe Park tracer material was also carried northward to North Yuba at the surface and Red Bluff aloft.

Description of Morning Release: The tracer released on the morning of the second day (August 11, 1990) from Lambie Road was observed in small quantities at only a few locations in the Broader Sac. Tracer released on the morning of the second day from Howe Park was observed in very high concentrations at Nicolas on the same morning, but not at other nearby sites between Howe Park and Nicolas.

Discussion: The pattern of tracer observations suggests that the tracer material from Howe Park moved in a very compact plume in the morning hours, and seems to have spread northward. Figure 9-5 depicts a schematic view of the movement of the tracer material as discussed above.

## 9.3 CLIMATOLOGICAL COMPARISONS

In designing the tracer study experiments we considered the summertime mean wind flow patterns in the SF Bay Area, the Broader, the Upper Sac, and the San Joaquin Valley (SJV). Figure 9-6 depicts the path of tracer material and expected time of arrival at various distances from the points of release, assuming the wind flow pattern is the summertime mean wind. Comparisons of the summertime mean wind flow expected paths with those in Figures 9-2 through 9-5 lead to the conclusion that the wind speeds and directions were not typical on the intensive days during which the tracer experiments were conducted. In fact, it appears that the onshore gradient was much stronger than normal on most of the days, causing the tracer material to be carried eastward into the Sierra foothills. These gradients were stronger than forecasted. As a result, most of the Howe Park tracer material was not effective in "tagging" the Broader Sac contribution to the Upper Sac ozone. Furthermore, on the morning of August 11, winds carried the tracer from Lambie Road east and/or south away from the Sacramento Valley altogether.

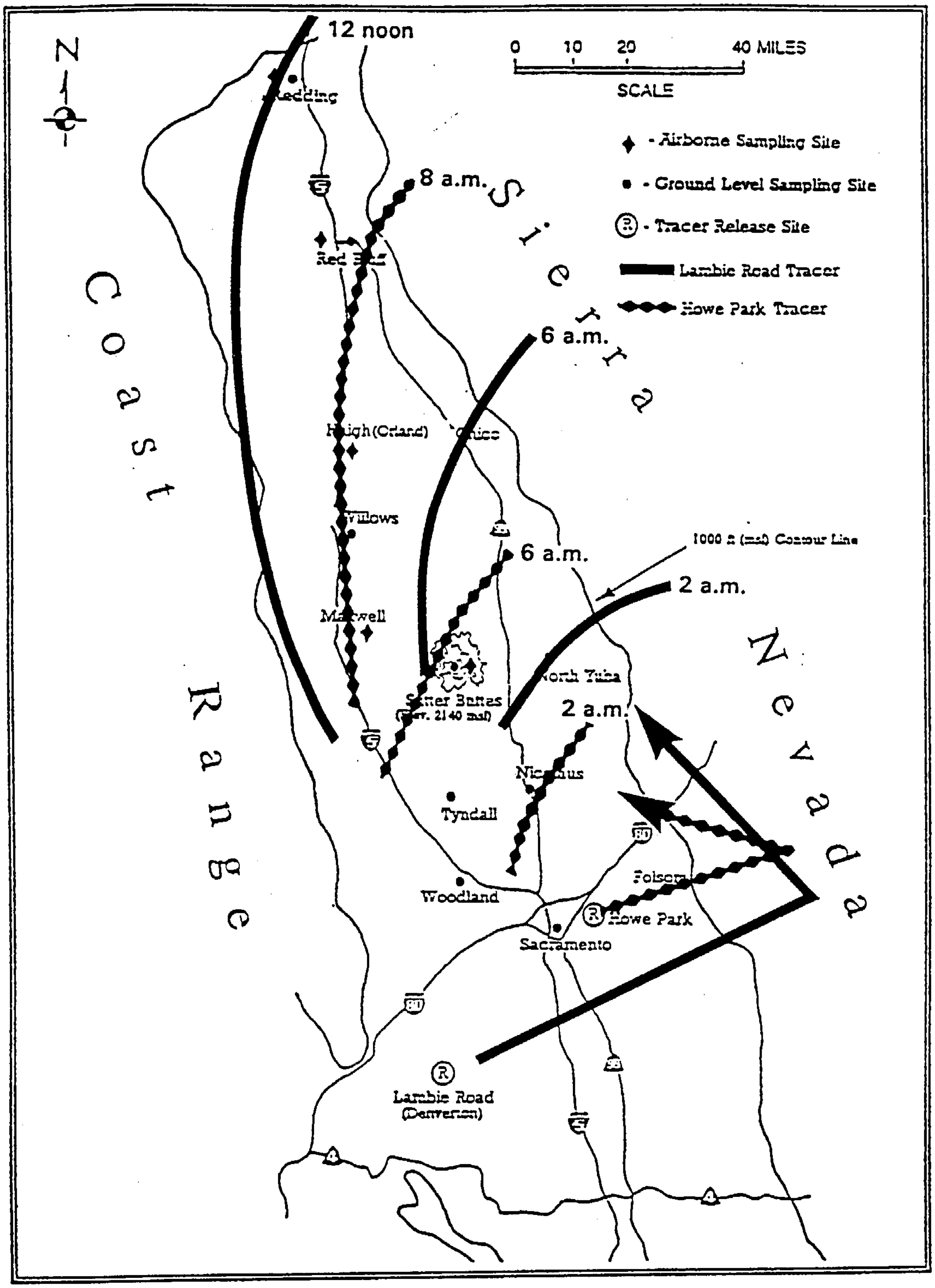



Figure 9-4. August 10th afternoon release.

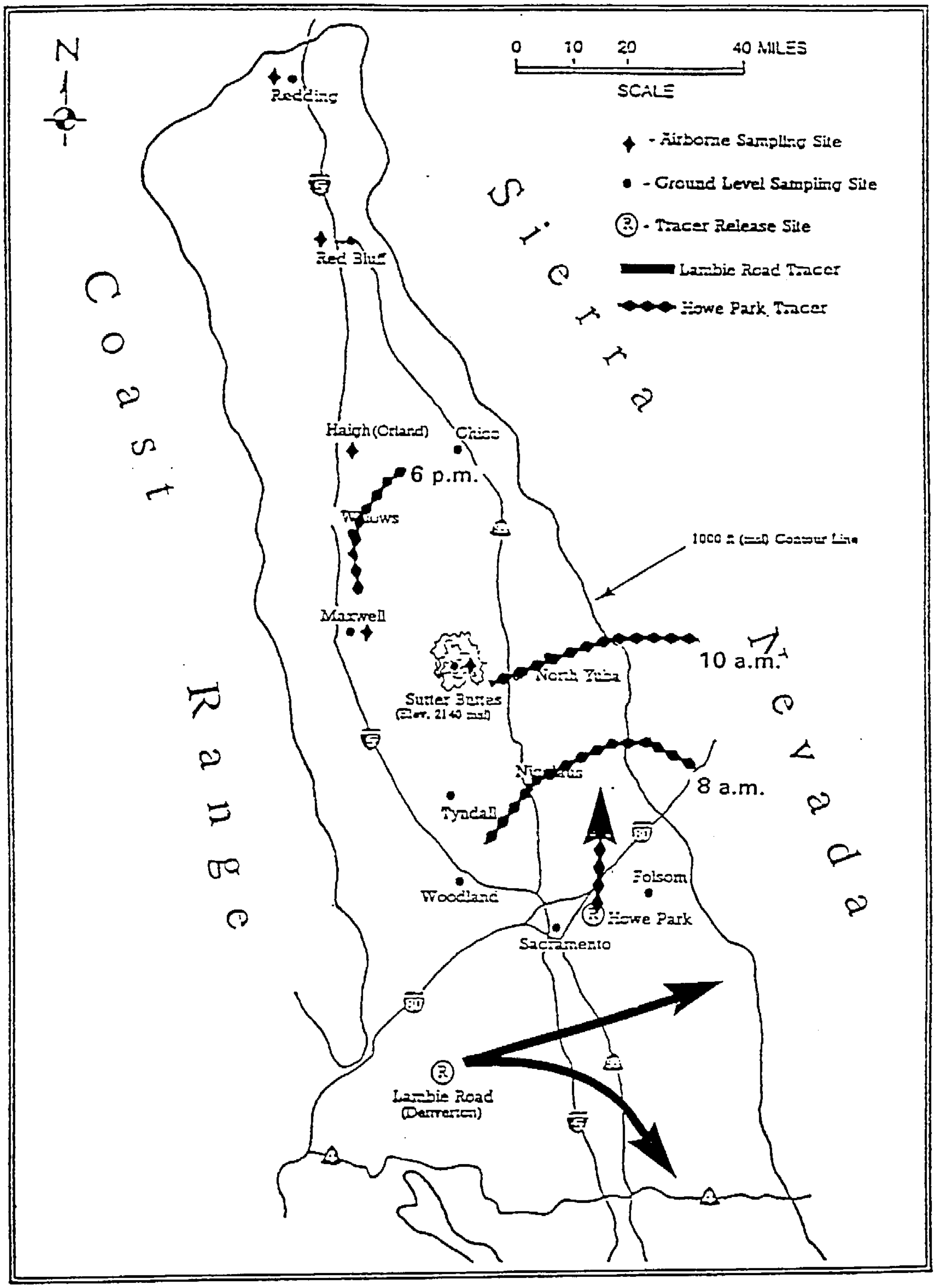



Figure 9-5. August 11th morning release.

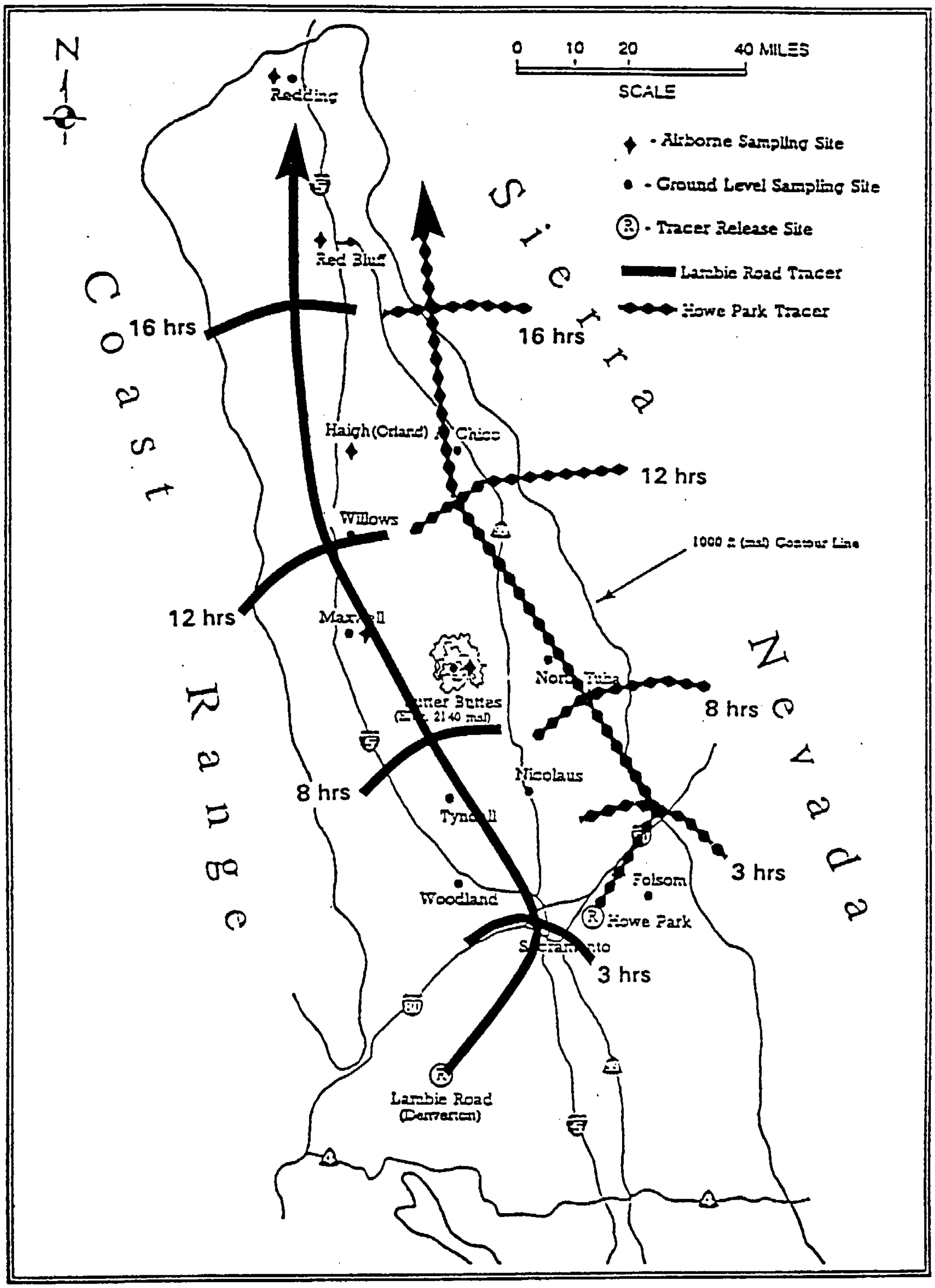



Figure 9-6. Expected tracer observations from climatological flow pattern.

## 9.4 IMPLICATIONS FOR OZONE AND PRECURSOR TRANSPORT

Despite the fact that the wind flow patterns were not typical on the intensive monitoring days as discussed above, the tracer releases described above were able to provide evidence of ozone and precursor transport from the SF Bay Area and the Broader Sac to the Upper Sac. To illustrate the specific relationship between tracer and ozone transport we present a specific case study for August 11, 1990. Figure 9-7 depicts the observed ozone and Lambie Road tracer concentrations at the surface in Red Bluff and Redding. The ozone concentrations are hourly average values whereas the tracer concentrations were made over 2 hours. Note that on August 11, no tracer from Howe Park was observed in Red Bluff or Redding. As shown in the figure, ozone peaked at 100 ppb at Red Bluff and 90 ppb at Redding. The tracer concentrations observed at the surface in both Red Bluff and Redding were below detection (shown as zero) until noon. Tracer concentrations in Red Bluff at noon were above 20 ppq and in Redding were above 120 ppq.

In Figure 9-8, we have added the ozone and tracer measurements obtained from morning and afternoon aircraft spirals above Red Bluff and Redding. Note that in each spiral, two samples were taken and are labeled with the appropriate altitude. As shown in the figure, aircraft measurements of ozone and tracer closest to the ground (<450 m) in the morning match those of the surface measurements. Tracer and ozone concentrations measured by aircraft further from the ground provide interesting data. In particular, note that the tracer aloft above Red Bluff in the morning (about 130 ppq) was almost identical to the surface concentration of tracer measured in Redding at noon. Also notice that ozone aloft near Redding at 1330 PDT was about 110 ppb, which is 20 ppb higher than at the surface, while the aloft tracer concentrations were less than that at the surface. This implies that not all of the tracer material has mixed down to the surface and indirectly, that not all of the ozone aloft has mixed down to the surface either.

## 9.5 OZONE/TRACER REGRESSION ANALYSIS RESULTS

We performed a simple regression analysis on data from receptor samples containing Lambie Road tracer during the August 10-12, 1990 field period. The tracers released at Lambie Road and Howe Park on the afternoon of August 10, 1990 were designed to tag SF Bay Area and Broader Sac emissions, respectively. The ozone/tracer regression analysis concept (see White et al., 1976 and Richards et al., 1981) is illustrated in Figure 9-9, where two sets of data points are plotted: the upper set (circles) for the two aircraft samples taken during a vertical spiral over Redding at about 1330 PDT and the lower set (squares) for the surface samples taken at 1200 to 1400 PDT and 1400 to 1600 PDT at Redding. The slope of the line drawn for each set of points represents the contribution of the source represented by the tracer, in this case the SF Bay Area. The intercept of the line drawn for each set of points represents the ozone contributed by all other sources, i.e., background, Broader Sac, and Upper Sac. This type of analysis must be limited to a set of

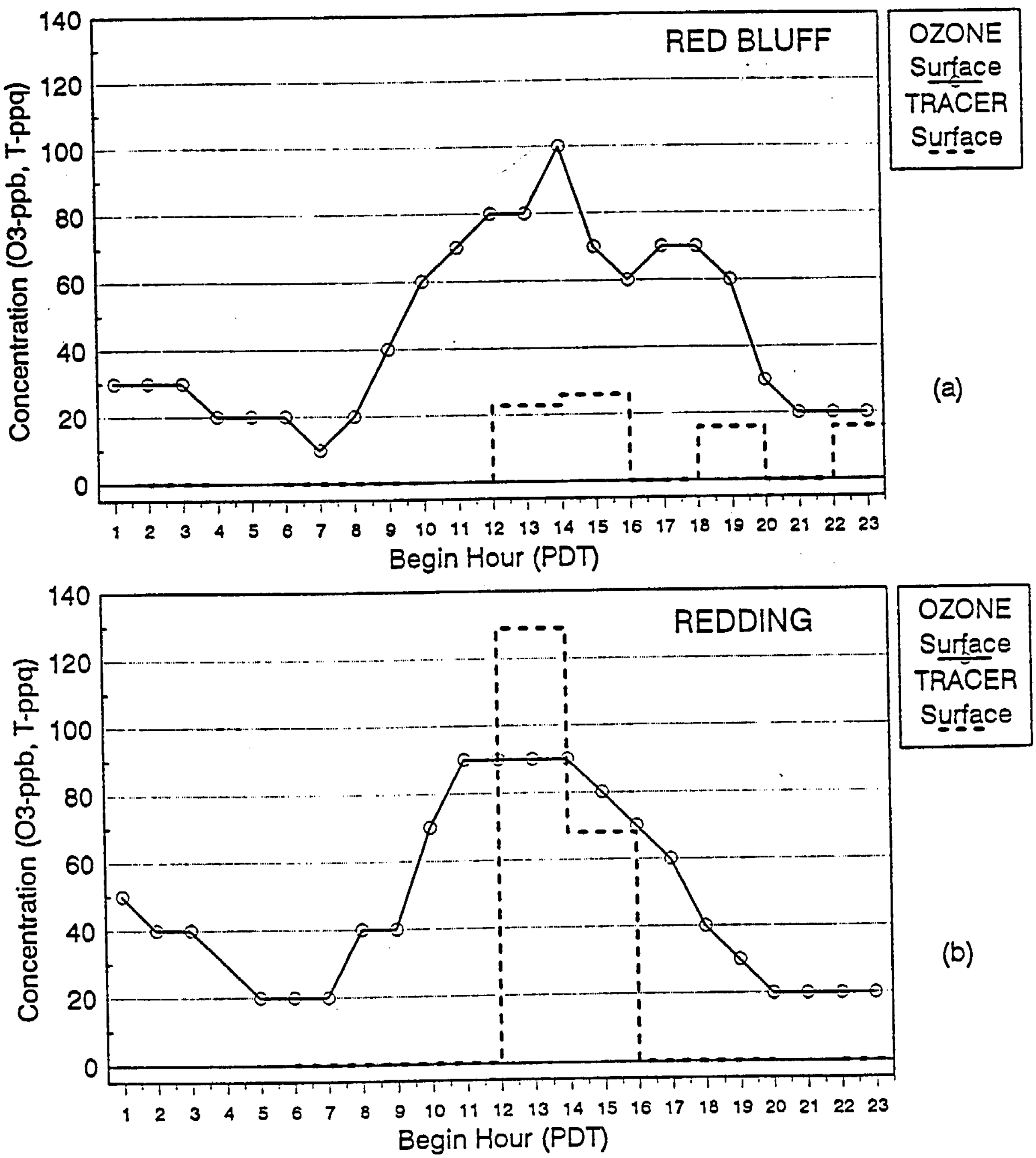
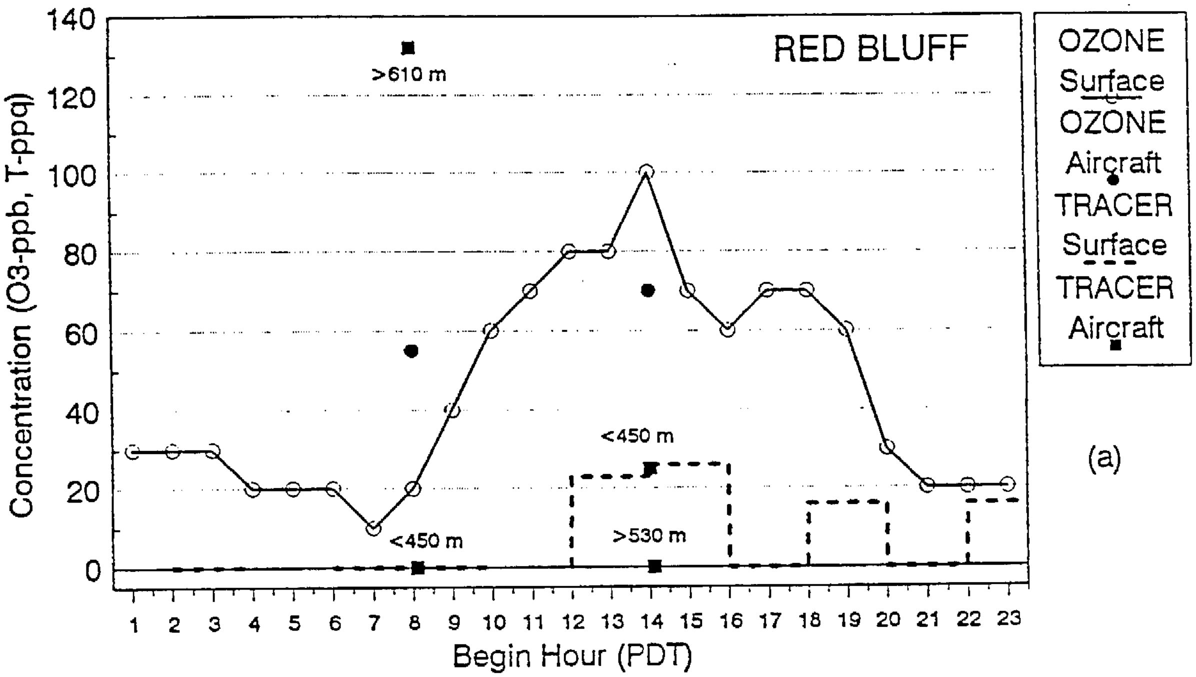



Figure 9-7. Ozone and Lambie Road tracer concentrations measured on August 11, 1990 at the surface at (a) Red Bluff and (b) Redding. Tracer concentrations were 2-hour averages. No Howe Park (Sacramento) tracer was measured at either location on this day. Note that the Red Bluff ozone data used here was corrected (see Appendix E).



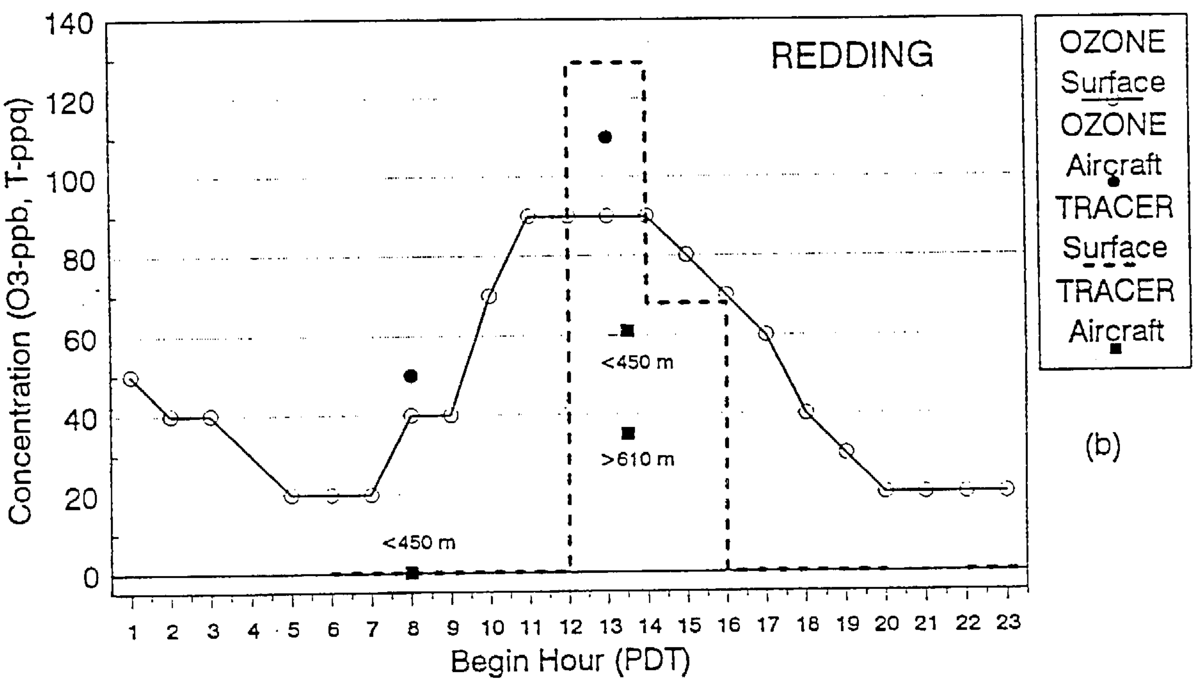




Figure 9-8. Ozone and Lambie Road tracer concentrations measured on August 11, 1990 at the surface and aloft at (a) Red Bluff and (b) Redding. Aloft ozone and tracer measurements were made in the morning and afternoon at two altitude ranges (tracer concentrations are labeled with the altitude). Ozone concentrations were similar at both altitudes, while tracer concentrations varied.

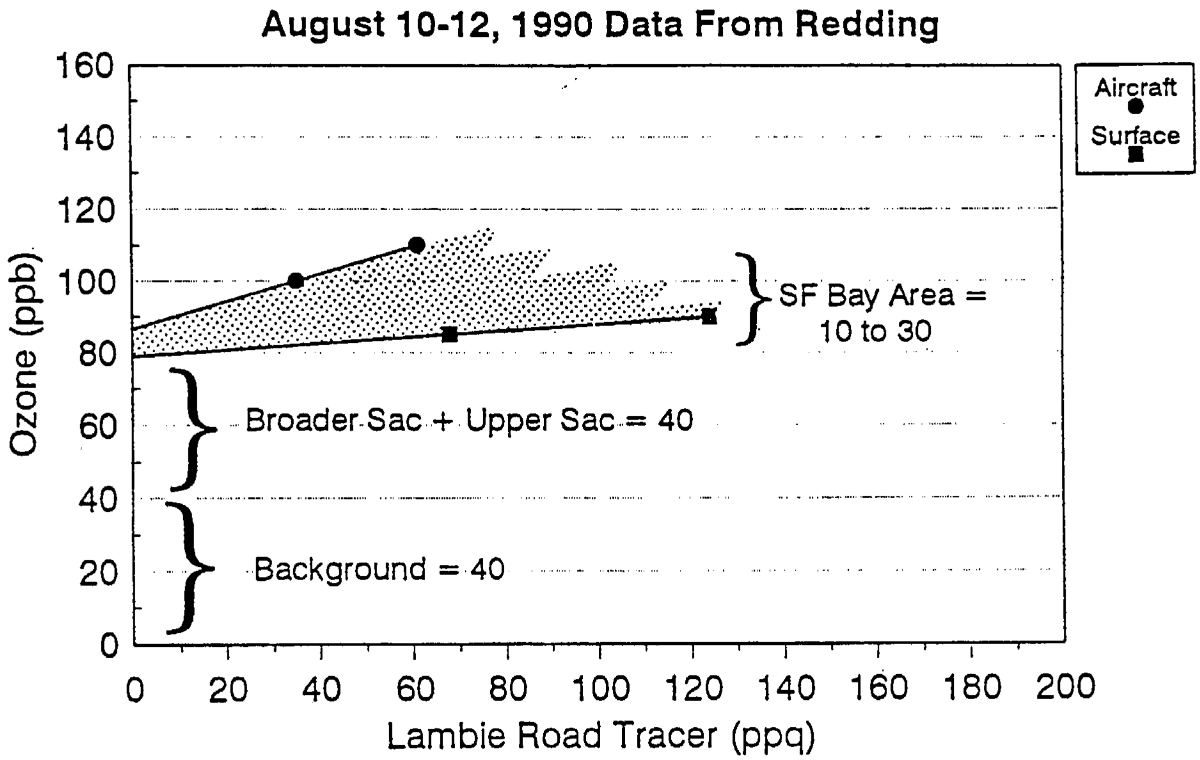



Figure 9-9. Ozone/tracer regression results using August 10-12, 1990 data from Redding.

data which was collected during just a few hours, in order to meet the following assumptions:

- The contribution of all other sources to the measured ozone concentration must be the same for each set of points used in the analysis.

- Ozone concentrations for each set of points are influenced to an equal degree by deposition and reaction along the transport path.

- Ozone concentrations should be high for all of the samples used, in order to avoid periods when ozone concentrations are reduced due to NO titration.

Typically, these assumptions are met during the 1000 to 1600 PDT period at Upper Sac monitoring sites such as Redding, Red Bluff, and Chico.

In the example shown in Figure 9-9, the intercepts for both the aircraft samples and the surface samples are similar: about 80 ppb ozone. In addition, an envelope defined by the aircraft and surface lines illustrates the bounds of the estimated SF Bay Area contribution to ozone at Redding. Thus, the estimated SF Bay Area contribution to ozone at Redding, which arrived from aloft, was about 10 to 30 ppb. Since the background ozone concentration is typically assumed to be about 40 ppb (see Main et al., 1991), the estimated contribution by Upper Sac and Broader Sac to ozone at Redding, by difference, was about 40 ppb. Since these samples did not contain Howe Park tracer, the contributions of Upper Sac and Broader Sac could not be separated.

However, if these same samples had included significant Howe Park tracer concentrations, then the relative contributions for Upper Sac, Broader Sac, and SF Bay Area could all have been estimated. This is illustrated hypothetically in Figures 9-10a and 9-10b. For these figures, it was assumed that three 1-hour midday tracer samples are available at an Upper Sac receptor site and all three samples contain significant tracer concentrations for both upwind air basins, SF Bay Area and the Broader Sac. It was also assumed that ozone concentrations were available for the 3 hours. The lines indicate that the maximum Broader Sac contribution was about 30 ppb (Figure 9-10a) and the maximum SF Bay Area contribution was about 20 ppb (Figure 9-10b). Assuming that the background ozone concentration was about 40 ppb, then by difference the intercepts indicate that the Upper Sac contribution is about 30 ppb.

The results for Redding illustrated in Figure 9-9 are consistent with similar ozone and tracer concentration results for Chico on the afternoon of August 11, 1990; even though the 1000 to 1200, 1200 to 1400, and 1400 to 1600 PDT surface samples and the 1430 PDT aircraft samples probably represented the tail-end of the Lambie tracer cloud. For these Chico samples, the SF Bay Area contribution to ozone concentrations was small (0 to 20 ppb) and other sources (Upper Sac and Broader Sac) contributed about 30 ppb, assuming that the background contribution was about 40 ppb. Again, no Howe Park tracer was measured in these samples.

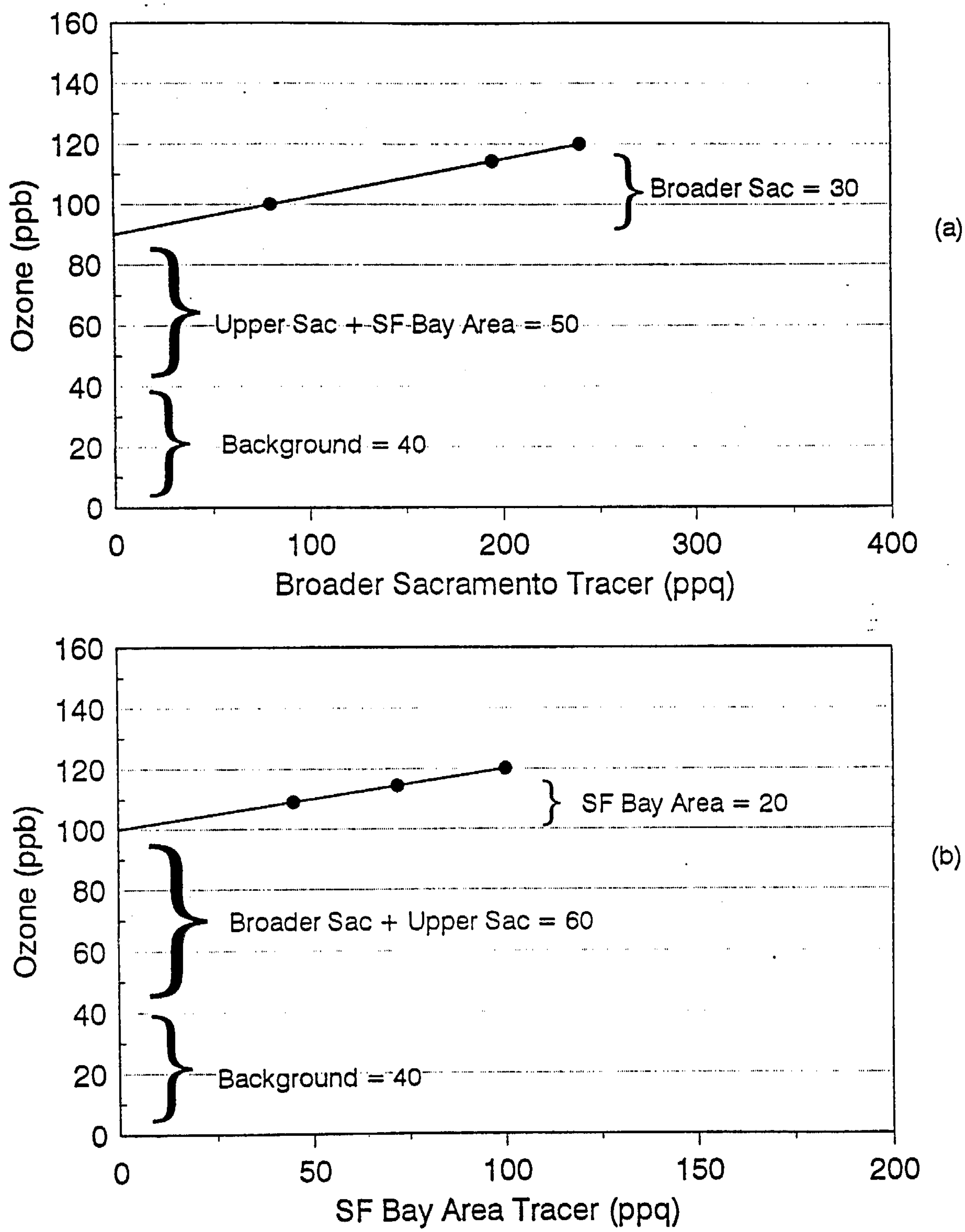



Figure 9-10. Hypothetical example of ozone/tracer regression at an Upper Sacramento Valley monitoring site for (a) tracer representing the Broader Sacramento Area and (b) tracer representing the SF Bay Area.

The general conclusions of the ozone/tracer regression analysis for both Redding and Chico are consistent with the results of other analyses, including the following:

- General transport paths (see Section 4);
- Trajectory analyses (see Section 6); and
- VOC and exotics signature analyses (see Section 8).

## 9.6 TRACER STUDY RESULTS AND RECOMMENDATIONS FOR FUTURE WORK

The following is a summary of the tracer study results and recommendations for future work.

<u>Tracer Study Results</u>

- Much of the tracer material released during the July and August studies was carried into the Sierra and not up the Sacramento Valley.

- Even though the wind flow patterns were not typical on the intensive monitoring days, the tracer releases did provide evidence of ozone and precursor transport from the SF Bay Area and the Broader Sacramento Area to the Upper Sacramento Valley.

- The tracer released on the afternoon of August 10, 1990 at Lambie Road was transported by aloft winds up the Sacramento Valley to Red Bluff and Redding. The tracer mixed to the surface at about noon on August 11, 1990 in both locations and likely contributed additional ozone from aloft to the peak concentration at the surface. The Lambie Road tracer was also measured at Chico on August 11, 1990.

- A simple ozone/tracer regression analysis using the Redding data provided estimates of the relative amounts of ozone contributed by various areas: the SF Bay Area contributed about 10 to 30 ppb and the Broader Sac plus Upper Sac areas contributed about 40 to 45 ppb to the measured Redding ozone concentrations of 90 to 110 ppb, assuming a background contribution of about 40 ppb ozone. Since these samples did not contain Howe Park tracer, the contributions of Broader Sac and Upper Sac could not be separated.

- However, if the Redding samples had included significant Howe Park tracer concentrations, then the relative contributions for Upper Sac, Broader Sac, and SF Bay Area could all have been estimated.

- The general conclusions of the ozone/tracer regression analyses for Redding and Chico are consistent with the general results of other analyses, including air flow patterns (Section 4), trajectory and precursor contribution estimates analyses (Section 6), flux analyses (Section 7), and VOC and exotics signature analysis (Section 8).

Recommendations for Future Work

- When planning and executing the tracer tests, it was difficult to match the 3-hour release time with the air parcel which would eventually arrive at one of the Upper Sac receptor sites during the ozone peak. If the tracers were released continuously, but the tracer was switched every few hours, then all air parcels would be tagged with tracer, including the ones which eventually arrive at the receptor site. Another alternative release schedule might include 4 to 6 hour releases of two tracers back-to-back.

- In order to use the ozone/tracer regression analysis method, one needs as many ozone/tracer data pairs as possible on as many high-ozone days as possible. One way to accomplish this is to release tracer continuously, as discussed above, and to collect tracer samples over shorter time periods (like 1 hour) during the peak ozone time.

- During this study, the onshore gradients were significantly stronger than the forecast gradients; better forecasting is needed in future studies.

- Tracer studies were being conducted for the SJVAQS/AUSPEX during the same period and using the same tracers as the Upper Sac tracer studies. Since the SJVAQS/AUSPEX study had priority over release times and about 3 days had to be allowed for tracer cleanout, the Upper Sac tracer releases were not performed on the preferred days. Future studies should deal equally with this problem.

- During this study, budget constraints limited the number of tracer samples, the number of sampling locations, and the amount of tracer released. If future studies could increase these quantities, then significantly more cases with quantified pollutant transport would be available for analysis. Additional sampling should be done in the intermediate basin (Broader Sac, in this case). Likely locations in the Broader Sac area include locations upwind, slightly downwind, and far downwind of the urban area: Davis, Meadowview, Rocklin, Auburn, and Folsom, for example.

- Additional transport analyses should be performed using the SJVAQS/AUSPEX air quality, tracer, and speciated VOC and exotics data set.

# 10. CONCLUSIONS AND RECOMMENDATIONS

This section summarizes the results and conclusions of our analyses and presents the recommendations for future data analysis work on pollutant transport. It is organized into three parts. Listed first is information on each individual method, including how well the method worked, the results of applying the method to Upper Sacramento Valley (Upper Sac) receptors, an evaluation of the method results, and recommendations specific to that method. Next is a summary of comparisons between method results. Last is a summary of overall project conclusions; including a discussion of which methods worked and which methods show promise for future applications, and a list of recommendations for future methods applications in the Upper Sac.

## 10.1 CONCLUSIONS AND RECOMMENDATIONS ON EACH METHOD

Flow Characteristics

- The air flow and ozone concentration patterns provided a basic understanding of how, when, and where pollutant transport might occur; this understanding was a useful component of all other analysis methods.
- Under typical afternoon wind flow conditions, pollutants from the San Francisco Bay Area (SF Bay Area) and the Broader Sacramento Area (Broader Sac) can reach Upper Sac monitoring sites. However, a convergence zone occurs regularly (15 to 25 percent of the time) overnight and in the early morning in the Sacramento Valley, thus restricting the surface transport of pollutants to Upper Sac monitoring sites.
- Ozone episodes during the summer of 1990, during which intensive monitoring was conducted, were not characterized by typical wind flow patterns. Although there was significant potential for SF Bay Area impact at the Upper Sac sites during the summer of 1990 as a whole, due to the greater-than-normal occurrences of southerly flows in the SF Bay Area associated with urban area emissions, the two intensive periods were characterized by northwesterly flow in the SF Bay Area (associated with relatively clean air). In addition, the onshore gradient was stronger than normal on most of the intensive days, causing ozone and precursor emissions from the SF Bay Area and the Broader Sac to be carried into the Sierra foothills, rather than to Upper Sac receptor sites. On other intensive days, air flow patterns either carried SF Bay Area emissions to the San Joaquin Valley (SJV) or prevented those emissions from reaching the Upper Sac because of a persistent convergence zone near Sutter Buttes.

The following is recommended for future work:

- A complete understanding of flow characteristics is essential for understanding how, when, and where pollutant transport might occur. Thus, this method is an important first step in any transport study.

Statistical Analysis of Ozone and Meteorological Data

- The statistical techniques tested for this project included analysis of diurnal ozone concentration patterns, site-to-site ozone concentration correlations, and stepwise regression of ozone at selected receptor sites against meteorological variables and ozone concentrations at other locations. These techniques were not fully successful in quantifying ozone and precursor transport from the Broader Sac to the Upper Sac, but they were helpful in understanding ozone transport.

- Examination of diurnal ozone concentrations did show that the timing of ozone peaks on all high ozone days was a useful tool for distinguishing sites influenced by same-day transport from sites where ozone results from other sources. These other sources could include ozone produced from local precursor emissions, ozone held aloft overnight entrained into the mixed layer, and overnight transport of precursor emissions. This approach suggests that Tyndall, West Nicolaus, and Yuba City were likely affected by same-day transport from Sacramento; Chico was potentially affected by same-day transport from Sacramento, and Redding was not likely to be affected by same-day transport from Sacramento.

- Correlation analysis of daily maximum ozone concentrations showed that sites as close to Sacramento as Yuba City and Woodland were likely to be influenced by same-day transport from Sacramento; Redding, Red Bluff, Chico, and Willows were not likely to be influenced by same-day transport from Sacramento; and Maxwell appeared to be somewhere between these two regimes.

- Step-wise regression analysis of daily maximum ozone concentrations also showed that Redding, Red Bluff, and Willows were not likely to be influenced by same-day transport from Sacramento; sites as close to Sacramento as Yuba City and Woodland were likely to be influenced by same-day transport from Sacramento; and Chico may have been influenced by overnight transport from Sacramento.

- In summary, the timing of ozone peaks, correlations using daily maximum ozone concentrations, and step-wise regression of daily maximum ozone concentrations showed that same-day transport from the Broader Sac likely influenced ozone concentrations at Tyndall, West Nicolaus, Yuba City, and Woodland and was unlikely to influence concentrations at Redding, Red Bluff, and Willows. The analyses also showed that ozone concentrations at Maxwell sometimes were influenced by same-day transport and that concentrations at Chico were not likely influenced by same-day transport, but were possibly influenced by overnight transport.

The following is recommended for future work:

- Statistical techniques should be applied to help identify qualitatively which receptor sites are influenced by pollutant transport.

- In future studies, it may be possible to extend these methods and combine them with other methods to provide quantitative estimates of the influence of transported material on downwind concentrations. For example, trends in upwind source region precursor emissions could be compared with emission and concentration trends at downwind receptor regions. For small (but statistically significant) changes in emissions, a regression model may provide an adequate fit to the data and allow one to estimate the relative contribution of upwind emissions to downwind ozone concentrations.

Transport-path Analyses

- Generating large numbers of air-parcel trajectories was a good method to identify the consensus transport paths for each receptor. Air-parcel trajectories generated from surface wind measurements were consistent with expected transport paths based on results from past field, analysis, and modeling studies.

- Aloft transport to Redding seemed to occur on a number of days, even though a convergence zone was often present at the surface between Redding and the Broader Sac. For example, on August 7, 1990, aloft trajectories indicate transport from the south, but surface trajectories show transport from the northwest most of the day.

- Transport paths using upper-air wind measurements were often consistent with those generated from surface winds, but they were also sometimes different, especially at the 800-meter level. When transport paths using upper-air winds were consistent with those using surface winds, the transport aloft was much faster than the transport at the surface.

- For most receptor sites, we identified one major transport path. However, for Redding, and possibly Red Bluff on some days, transported pollutants could arrive via either the surface or aloft.

The following is recommended for future work:

- Ozone exceedances at Redding often occur when there is a convergence zone in the Upper Sac and when there is the potential for nighttime transport aloft. A complete understanding of how these exceedances occur will require surface measurements at sites on both sides of the convergence zone, both near the convergence zone and 10 to 30 km away; and aloft meteorological measurements north of the convergence zone, preferably near Redding.

Precursor Contribution Estimates

- The precursor contributions of upwind and downwind areas were estimated for two ozone precursors: reactive organic gases (ROG) and nitrogen oxides ($NO_x$). The relative contribution estimates of the upwind and downwind areas using ROG were very close to those using $NO_x$.

- Precursor contribution estimates were made for cases with and without the loss of precursors via reaction and deposition. Including losses via reaction and deposition increased the precursor contributions from the local area and decreased the contributions from the upwind area. Using daytime and nighttime first-order reaction rates for both ROG and

$NO_x$ was more realistic than not using any reaction rates and should be done in future applications. Thus, results are reported for cases with reaction included.

- When compared with surface transport, fast transport aloft increased the precursor contribution of the upwind area, relative to the downwind area. However, this increase was small if same-day transport or transport over short distances was involved. The largest differences between precursor contribution estimates using surface data and those using aloft data occurred when there was overnight transport.

- When pollutant transport to a receptor site well away from the upwind boundary (i.e., Chico, Red Bluff, and Redding) occurred, at least 30 to 40 percent of the precursor contributions usually came from the local air basin. This occurs because biogenic emissions are significant in the Upper Sac and because significant amounts of $NO_x$ are lost over time via reaction and deposition. However, an exception occurred when there was transport from the upwind air basins to Arbuckle, a monitoring site just across the boundary into the Upper Sac, on October 7, 1987. This resulted in about 90 percent precursor contribution from the upwind air basins; we defined this as overwhelming transport to Arbuckle.

- For Chico, Red Bluff, and Redding, we identified ozone violation days with both local and transport contributions. However, none of these days had overwhelming transport.

- Precursor contribution estimates using aloft trajectories resulted in larger contributions from the upwind area than did estimates using surface trajectories. This is because the aloft trajectories result in faster transport with less time for precursors to be lost via reaction and deposition.

- The combined surface trajectory/precursor contribution estimate method worked best when applied to pollutant transport to Chico, versus transport to Red Bluff or Redding. This was due to the possibility of regular aloft transport to Redding and Red Bluff; when appropriate aloft data are available, the method should work as well for transport to Red Bluff and Redding.

- Precursor contribution estimates for surface transport to Chico on eleven days in 1987 and seven days in 1989 were quite consistent:

| Area | Contribution to ROG and NOx (%) |
|---|---|
| Upper Sac | 30-55 |
| Broader Sac | 30-40 |
| SF Bay Area | 15-25 |

- Pollutant transport to Chico on August 5, 1989 was examined because this was the day with the highest ozone concentration and when we have both surface and aloft wind data, although the maximum ozone concentration was only 9 pphm. Precursor contribution estimates for this day were quite consistent, based on both surface and aloft trajectories:

| Area | Contribution to ROG (%) | Contribution to NOx (%) |
|---|---|---|
| Upper Sac | 60-70 | 65-85 |
| Broader Sac | 10-30 | 5-15 |
| SF Bay Area | 10-20 | 2-25 |

- Precursor contribution estimates for surface transport to Red Bluff on ten days in 1987 (see Table 6-1) were quite consistent:

| Area | Contribution to ROG and NOx (%) |
|---|---|
| Upper Sac | 55-70 |
| Broader Sac | 15-20 |
| SF Bay Area | 15-20 |

- Local days at Upper Sac receptors were defined as ones where the back trajectories had remained within about 75 km of the receptor. Precursor contribution estimates for local days at Chico, Red Bluff, and Redding in 1987 were over 90 percent from the Upper Sac. However, all of these cases were based on surface trajectories; whereas aloft transport and/or carryover may have occurred and significantly modified the definition of local or transport and the relative contributions.

The following are recommended for future work:

- In this study, upper-air meteorological data were critical for determining transport paths and estimating precursor contributions. These aloft data were obtained during special short-term field studies, but the data were not always available on ozone violation days or at the appropriate locations. Programs to obtain aloft meteorological and air quality data are critical for determining transport paths and estimating precursor contributions in the future.

- Consider using an emissions-accumulation box which is narrower than 45 km at distances within about 50 km of the receptor area. This would reflect the narrower area of potential influence close to a receptor site. Decreasing the box width gradually from 45 to 5 km might be a reasonable choice.

- Prepare additional precursor contribution estimates using an emissions inventory with fewer biogenics and with no biogenics, as a bounding estimate of the actual effect of biogenics on ozone concentrations. With the current biogenics inventory, the Upper Sac contributions remained high even when obvious transport occurred.

Simple Pollutant Flux Estimates

- The simple flux plots showed that both ozone and $NO_x$ fluxes vary during the day, with the highest ozone fluxes in the mid- to late-afternoon and the highest $NO_x$ fluxes in the morning. The ozone flux at Lambie Road was about 5 to 6 times higher than the $NO_x$ flux.

- The simple ozone flux at Lambie Road is almost always from the southwest, with the highest flux in the late-afternoon. Peak ozone fluxes are typically higher and last longer at Lambie than at Sutter Buttes.

- The simple ozone flux at Sutter Buttes is typically from the north in the morning and from the south in the afternoon; the southerly flux is typically 1 to 2 times higher than the northerly flux, and lasts longer.

- Note that although the flux method can estimate the pollutant transport at the boundary, it cannot quantify the contributions of the upwind areas separately.

The following are recommended for future work:

- Ozone monitoring along potential transport paths is often critical to understanding when and by what route transport takes place. Ozone and nitrogen oxides monitoring should be performed at a few more sites between the Broader Sac and the Upper Sac besides at the receptor sites of Redding and Chico, especially on the sides of the Sacramento Valley; data at Red Bluff, either Arbuckle or Colusa, and northeast of Yuba City would be very useful.

- Prepare simple relative ozone and nitrogen oxides flux estimates using data from additional monitoring sites along potential transport paths; install additional monitors at critical locations in order to prepare such estimates.

- It is critically important to have a non-urban boundary monitoring site, especially if un-titrated ozone and regionally representative $NO_x$ fluxes are to be estimated, since local NO emissions will distort ozone and $NO_x$ concentrations.

2-D Pollutant Flux Estimates

- The flux of ozone and $NO_x$ into the Upper Sacramento Valley was estimated across a 2-D, east-west plane near Sutter Buttes, using aircraft air quality data and upper-air meteorological data on the afternoon of August 10, 1990. The flux of ozone and of $NO_x$ varied spatially across this plane. The highest mass flux of ozone occurred on the western end of the flux plane, where the wind speed was much higher than on the eastern end, even though the ozone concentration was significantly lower.

- Over the whole flux plane, about 50 kg/s of ozone was transported into the Upper Sac; this is equivalent to an average concentration of 70 ppb being transported at about 4 m/s.

- Over the whole flux plane, about 4 kg/s of $NO_x$ was transported into the Upper Sac; this is equivalent to an average concentration of 5 ppb being transported at about 4 m/s.

- The ozone and $NO_x$ fluxes into the Upper Sac which were measured on the afternoon of August 10, 1990 are similar to the fluxes measured between the SF Bay Area and the SJV during four afternoons in August 1988.

- The highest pollutant flux can occur in a region of either high pollutant concentration or high wind speeds, or both. Average wind speeds can vary by a factor of five or more, but ozone concentrations in the Sacramento Valley typically vary over a much smaller range; therefore, the regions or times of the highest flux might easily be due to high winds, with only modest ozone concentrations which do not exceed the State standard. In addition, we must remember that concentrations due to transported ozone can only get lower via dilution and deposition losses. Thus, some cases of high ozone flux, but only modest ozone concentrations, cannot produce an ozone exceedance without additional ozone being formed in the downwind area.

- The time of maximum pollutant flux is important for determining the contribution to ozone exceedances at the downwind receptor site. In particular, if the maximum ozone flux occurs during the late-afternoon at Lambie Road, for example, then it is unlikely that the pollutants which accompany the maximum flux will contribute to an ozone exceedance that day in the Upper Sac (or even the Broader Sac Area), since the peak ozone concentrations at these receptor sites usually occurs before about 1400 PDT. Therefore, it might be that the flux past Lambie Road at 2000 PDT, for example, contributes the most to a 1400 PDT ozone exceedance at Red Bluff or Redding, the following day.

- Air quality and meteorological measurements taken at the Sutter Buttes (about 640 m msl) are representative of conditions aloft at an equivalent altitude in the mid-Sacramento Valley.

- Note that although the flux method can estimate the pollutant transport at the boundary, it cannot quantify the contributions of the upwind areas separately.

The following are recommended for future work:

- Frequent air quality and meteorological data aloft across a 2-D flux plane would provide more useful data for determining the timing of the peak ozone and $NO_x$ fluxes, quantifying the fluxes over a wide range of conditions, and estimating uncertainty. If possible, hourly data should be obtained.

- Perform additional analyses of the August 7-8, 1990 ozone episode in the Sacramento Valley, including flux calculations, once the SACOG modeling is finished.

Analyses Using VOC and Tracers-of-Opportunity (Exotic) Species

- We identified unique VOC and exotics signatures for different source regions including the Broader Sac and clean air resulting from northwesterly flow in the SF Bay Area. However, we were unable to identify a unique source signature for the more urban/industrial SF Bay Area, although the technique appears promising for future applications. Species ratios, including assessment of the relative age of air parcels; clean air screening criteria; and statistical analyses were useful to augment the analysis of unique signatures.

- Comparisons of receptor area samples to source area signatures showed evidence of transport of VOC and exotics from the Broader Sac to the Upper Sac. Unfortunately, the intensive study meteorology did not favor transport from the urban/industrial parts of the SF Bay Area to the Upper Sac and therefore, we could not investigate evidence of transport from this source region. Because we did not have transport from both the SF Bay Area and the Broader Sac to the Upper Sac, we did not attempt to quantify the relative contribution of each source region to the receptor VOC or exotics signatures. However, quantification may be possible with additional data.

To better assess the origins of transport into the Upper Sac using VOC and exotics data, the following data collection and analyses efforts are recommended:

- Collect additional data to confirm characterization of the Broader Sac and the SF Bay Area northwesterly flow (Travis area) source signatures.

- Collect data under different SF Bay Area wind flow regimes, specifically, southerly flow. With these data, assess the SF Bay Area signature and differences between VOC and exotics signatures during the various wind flow regimes. It may be possible to quantify the relative contribution of the SF Bay Area and the Broader Sac to the hydrocarbon concentrations using species ratios and exotics concentrations and ratios when both source area signatures are present in a receptor site sample. A statistical analysis approach, such as cluster analysis, may be useful to determine possible groupings of the data. These data may be available in existing ARB VOC data sets. In addition, the new EPA PAMS (photochemical assessment monitoring stations) requirements will likely result in upwind, source region, and downwind VOC speciated monitoring in many air basins.

- Collect data during Upper Sac ozone exceedances. Ozone concentrations at Redding and Red Bluff were relatively low during the intensive study days in 1990.

- The clean air screening procedure is useful for screening samples collected at background locations and identifying samples which may have had little contribution from upwind sources. Additional criteria could be added for the exotics to aid in the screening process. However, an investigation of appropriate background concentrations is required.

<u>Tracer Study</u>

- Much of the tracer material released during the July and August 1990 studies was carried into the foothills of the Sierra and not up the Sacramento Valley.

- Even though the wind flow patterns were not typical on the intensive monitoring days, the tracer releases did provide evidence of ozone and precursor transport from the SF Bay Area and the Broader Sacramento Area to the Upper Sacramento Valley.

- The tracer released on the afternoon of August 10, 1990 at Lambie Road was transported by aloft winds up the Sacramento Valley to Red Bluff and Redding. The tracer mixed to the surface at about noon on August 11, 1990 in both locations and likely contributed additional ozone from aloft to the peak concentration at the surface. The Lambie Road tracer was also measured at Chico on August 11, 1990.

- A simple ozone/tracer regression analysis using the Redding data provided estimates of the relative amounts of ozone contributed by various areas: the SF Bay Area contributed about 10 to 30 ppb and the Broader Sac plus Upper Sac areas contributed about 40 to 45 ppb to the measured Redding ozone concentrations of 90 to 110 ppb, assuming a background contribution of about 40 ppb ozone. Since these samples did not contain Howe Park tracer, the contributions of Broader Sac and Upper Sac could not be separated.

- However, if the Redding samples had included significant Howe Park tracer concentrations, then the relative contributions for Upper Sac, Broader Sac, and SF Bay Area could all have been estimated.

The following are recommended for future tracer work:

- When planning and executing the tracer tests, it was difficult to match the 3-hour release time with the air parcel which would eventually arrive at one of the Upper Sac receptor sites during the ozone peak. If the tracers were released continuously, but the tracer was switched every few hours, then all air parcels would be tagged with tracer, including the ones which eventually arrive at the receptor site. Another alternative release schedule might include 4 to 6 hour releases of two tracers in sequence.

- In order to use the ozone/tracer regression analysis method, one needs as many ozone/tracer data pairs as possible on as many high-ozone days as possible. One way to accomplish this is to release tracer continuously, as discussed above, to collect tracer samples over shorter time periods (like 1 hour), and to monitor for ozone and $NO_x$ at important boundary and receptor locations.

- During this study, budget constraints limited the number of tracer samples, the number of sampling locations, and the amount of tracer released. If future studies could increase these quantities, then significantly more cases with quantified pollutant transport would be available for analysis. Additional sampling should be done in the intermediate basin (Broader Sac, in this case). Likely locations in the Broader Sac area include locations upwind, slightly downwind, and far downwind of the urban area: Davis, Meadowview, Rocklin, Auburn, and Folsom, for example.

- During this study, the onshore gradients were significantly stronger than the forecast gradients; better forecasting is needed in future studies.

- Tracer studies were being conducted for the SJVAQS/AUSPEX during the same period and using the same tracers as the Upper Sac tracer studies. Since the SJVAQS/AUSPEX study had priority over release times and about three days had to be allowed for tracer cleanout, the Upper Sac tracer releases were not performed on the preferred days. Future studies should deal equally with this problem.

## 10.2 COMPARISON OF METHODS RESULTS

Listed below is a summary of comparisons between method results.

### Comparison of Qualitative Methods

Results from meteorological characterization, statistical analyses, and transport-path methods using surface data are generally consistent with each other:

- Receptor sites such as Tyndall, West Nicolaus, Yuba City, and Woodland are often influenced by same-day surface transport from Broader Sac.
- Receptor sites such as Redding, Red Bluff, and Willows are not likely to be influenced by same-day surface transport from Broader Sac.
- Receptor sites such as Maxwell and Chico seem to be influenced by same-day surface transport from Broader Sac on some days and not on other days.

### Comparison of Qualitative Methods During the July 11-13 and August 10-12, 1990 Field Intensives

The spatial and temporal pattern of surface tracer concentrations was consistent with the meteorological characterization and transport-path methods using surface data:

- Most of the Lambie and Howe Park tracers were transported by surface winds into the foothills of the Sierra and not up the Sacramento Valley.
- Surface back trajectories from Redding, Red Bluff, and Chico on August 11 indicate that the air parcels arriving at the surface at these sites had been in the Upper Sac during the previous 18 to 24 hours. This is consistent with the surface tracer data, which did not show measurable concentrations of Lambie tracer at Willows, Red Bluff, and Redding until after the tracer had mixed to the surface from aloft at Redding and Red Bluff about noon on August 11.

The spatial and temporal pattern of aloft tracer concentrations was consistent with the aloft wind data at Maxwell and North Yuba on August 10-11; these results indicated that the Lambie tracer was transported aloft to Red Bluff and Redding on the morning of August 11 and mixed to the surface about noon.

The results of the meteorological characterization, transport-path, and VOC/exotics methods using surface data were consistent: they all indicated transport from the Broader Sac to Chico during both the July 11-13 and August 10-12 intensive monitoring periods. The Howe Park tracer was not measured at Chico during these tests; these releases did not seem to have properly tagged the Broader Sac emissions which were transported to Chico.

Comparison of Quantitative Methods During the July 11-13 and August 10-12, 1990 Field Intensives

- The general conclusions of the ozone/tracer regression analyses for Redding and Chico, and the flux analysis at the Broader Sac/Upper Sac boundary on August 10-11, 1990 are consistent with the general results of other analyses, including air flow patterns, trajectory analysis and precursor contribution estimates, and VOC and exotics signature analysis.

- The 2-D flux plane analysis indicates that an average of about 70 ppb ozone and 5 ppb $NO_x$, including a background contribution of about 40 ppb ozone, was being transported into the Upper Sacramento Valley on the afternoon of August 10, 1990. The ozone/tracer regression analysis for Redding indicates that more than 50 to 80 ppb of the ozone measured at Redding was due to sources upwind of the Upper Sac, including a background of about 40 ppb. These results are consistent, but are not exactly comparable.

Note that during the July 11-13 period, the conditions were poor for transport methods applications: no tracers were measured at either Red Bluff or Redding and only one minor "hit" was measured at Chico, and the unusual north-south sloshing which occurred between the Broader Sac and the Upper Sac made analyses difficult.

Also, note that aloft trajectories, and thus precursor contribution estimates using aloft data, were not available for the August episode because upper-air meteorological data were available at only two sites; this data was not sufficient to calculate aloft trajectories in the Sacramento Valley.

## 10.3 OVERALL PROJECT CONCLUSIONS AND RECOMMENDATIONS

Listed below is a summary of overall project conclusions, including a discussion of which methods worked and which methods show promise for future applications, and a list of recommendations for future methods applications in the Upper Sacramento Valley.

Overall Project Conclusions

- Characterizing the air flow of the region provided a basic understanding of how, when, and where pollutant transport might occur; this understanding was essential as a first step in any transport study. In addition, statistical techniques can help identify which receptor sites are likely influenced by pollutant transport.

- Generating large numbers of air-parcel trajectories was a good method to identify the consensus transport paths for each receptor. However, both surface and aloft wind measurement data are needed to generate air-parcel trajectories for all receptor sites and situations, since aloft pollutant transport can often occur.

- During this project, the combined surface trajectory/precursor contribution estimate method worked best when applied to pollutant transport to Chico, versus transport to Red Bluff or Redding. This was due to the possibility of regular aloft transport to Redding and Red Bluff, but we did not have sufficient aloft data to apply these methods. If appropriate aloft data were available, the method should work as well for transport to Red Bluff and Redding.

- Simple pollutant flux estimates were very useful in identifying the temporal characteristics and relative magnitude of pollutant fluxes at a boundary site between two air basins. This method is also useful in designing a measurement program to collect data for tracer and 2-D flux plane studies.

- Estimating pollutant fluxes using 2-D flux plane measurements was a direct and useful method to quantify pollutant transport. However, more frequent pollutant and wind measurements aloft (than three times per day) are required in order to capture the appropriate conditions which relate to peak ozone at a downwind receptor.

- Routine air quality and meteorological measurements taken at an isolated, elevated location, such as a radio tower or Sutter Buttes, for example, are representative of conditions aloft at an equivalent altitude. Data from such a site represent a cost-effective method for collecting pollutant flux data aloft.

- Since we did not collect data during typical flow conditions in the Sacramento Valley, we were not able to quantify the relative contributions of the SF Bay Area and Broader Sac to an Upper Sac ozone exceedance. We did identify unique VOC and exotics signatures for Broader Sac and clean air resulting from northwesterly flow in the SF Bay Area, but not for the more urban/industrial SF Bay Area; the method appears promising for future applications.

- The tracer releases provided evidence of both surface and aloft pollutant transport from the SF Bay Area and the Broader Sac to Upper Sac receptor sites, even though the wind flow patterns were not typical and much of the tracer was carried into the foothills of the Sierra and not up the Sacramento Valley.

- A simple ozone/tracer regression analysis using the Redding data provided estimates of the relative amounts of ozone contributed by various areas. Since these samples did not contain Howe Park tracer, the contributions of Broader Sac and Upper Sac could not be separated. If the Redding samples had included significant Howe Park tracer concentrations, then the relative contributions for Upper Sac, Broader Sac, and SF Bay Area could all have been estimated.

Recommendations for Future Methods Applications in the Upper Sacramento Valley

The data analysis methods which could be applied in future applications for the Upper Sac include transport paths and precursor contribution estimates using surface and aloft trajectories, 2-D pollutant flux estimates, ozone/tracer regressions, and analyses of unique VOC and exotics signatures. In addition, air flow patterns should be characterized as a basis for any of the other methods. At least two of the methods should be applied at the same time, in order to strengthen the results. If routine, hourly measurement techniques are used; then the selected methods can be applied to a wide range of high-ozone cases over a complete range of air flow characteristics.

If additional pollutant transport quantification for Upper Sac is desired on more days and/or under a broader range of flow characteristics than addressed in this project, then we make the following recommendations:

- If future applications for the Upper Sac are limited to the use of existing aerometric monitoring, then only one method that we studied is possible: precursor contribution estimates for $NO_x$ and ROG using surface trajectories (see Section 6). This method is not applicable to all Upper Sac receptors, but only to those receptors which are influenced by same-day surface transport. This would include receptor sites south of a diagonal line between Maxwell and Chico. In addition, air flow patterns should be characterized for all days of interest as a basis for understanding and interpreting the analysis results.

- If new routine monitoring is installed to meet EPA's PAMS (Photochemical Assessment Monitoring Stations) requirements for the Sacramento Metropolitan Air Quality Management District (see EPA, 1992), then VOC signature analyses could be performed to quantify precursor transport. The PAMS requirements include hourly VOC-speciation measurements at upwind, Sacramento urban, and downwind locations. If a similar monitor was also installed at one or more Upper Sac receptors (for example, Redding, Chico, and/or Red Bluff), then the VOC-signature analysis described in Section 8 could be performed. In addition, air flow patterns should be characterized for all days of interest as a basis for understanding and interpreting the analysis results.

- Based on analyses in this study, if additional measurements can be taken such that 2-D flux plane and VOC-signature analysis methods can be employed, the combination of these techniques provides the most reliable quantification of ozone and ozone precursors. These methods are reliable because they are based on calculations and comparisons using physical parameters such as wind speed, wind direction, ozone concentration, and VOC speciation rather than relying on purely statistically related parameters which may not be physically related such as the timing of ozone peaks. To apply these two methods, intensive field measurements would be needed on potential transport days, including the following:

    - Upper-air meteorological and air quality data at the Upper Sac upwind boundary to quantify the ozone and $NO_x$ flux into the Upper Sac;

- Upper-air meteorological and air quality data at the Broader Sac upwind boundary to quantify the ozone and $NO_x$ flux from other upwind air basins; and

- Speciated VOC measurements to represent the upwind areas (Broader Sac and SF Bay Area) and at Upper Sac receptor sites; data from the EPA PAMS network (mentioned above) could possibly be used to provide some of this data.

Note that the measurement locations for any of the studies mentioned above will depend on the then-current definition of the Upper Sac and Broader Sac areas.

The data needed to apply these methods could be acquired during a field study with the components selected from the list below; additional details are provided in Section 10.1 and Sections 6 through 9 on the individual methods.

- Surface meteorological and air quality data.

- Upper-air meteorological data collected throughout the Sacramento Valley, in order to calculate aloft trajectories to Upper Sac receptor sites.

- Upper-air meteorological and air quality data across a 2-D flux plane between Upper Sac and Broader Sac; use routine, hourly measurement techniques, if available.

- A tracer test with the following components:

  - 4 to 6 hour releases of two different tracers in sequence at locations to represent the SF Bay Area and Broader Sac, beginning in the afternoon.

  - Samples over the next 36 hours: 1-hour tracer samples during the peak ozone period (say 1100 to 2000 PST, for example) and 2-hour samples during the rest of the time. Samples should be collected at Upper Sac receptor sites, plus a range of sites in Broader Sac, including locations upwind, slightly downwind, and far downwind of Sacramento.

- If data analysis of routine VOC samples has identified an unique signature for the industrial/urban SF Bay Area, then collect samples for speciated VOC analyses during the periods of peak ozone concentrations at receptor sites of interest.

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