2009-2010 Del Paso Manor Winter $PM_{2.5}$ Study

Breathe California of Sacramento-Emigrant Trails

Health Effects Task Force,

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Presented to

Sacramento Metropolitan Air Quality Management District

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Executive Summary

Fine particulate matter ($PM_{2.5}$) mass values reach their highest levels in winter throughout the Sacramento Valley. While far less work has been done in the southern Sacramento Valley than the intensively studied San Joaquin Valley, many similarities exist. The first is that in winter, the Central Valley is usually decoupled from the Bay Area, except during synoptic storm events. Cold subsidence winds come down from the mountains almost every evening and pool on the valley floor, where they then slowly migrate downhill towards the lowest point, the San Joaquin/Sacramento Delta (see Figure 1). The net result is a strong inversion that traps valley pollutants, sometimes for weeks at a time, until interrupted by synoptic winter storms.

However, the regional situation is heavily modified in urban regions by the addition of residential wood smoke to the aerosol mix. Urban wood smoke sources are emitted at low elevation, and thus are efficiently trapped by the inversions that occur frequently in winter. These inversions are strongest during cold periods – which is also when residential wood burning is most likely.

Figure 1. Map of California with winter stagnation wind patterns (ARB 1984)

One of the consequences of the weather pattern in winter is that $PM_{2.5}$ mass north of the Delta only rarely is influenced by pollution from south of the Delta, and vice versa. Only on a few days each winter does San Joaquin Valley air impact Sacramento.

Particulate mass rises steadily from low values in the far north, Redding, to the highest values in the southern San Joaquin Valley, such as at Bakersfield. Below we show this pattern during a period of 17 days stagnation in January 5 to January 22, 2009.

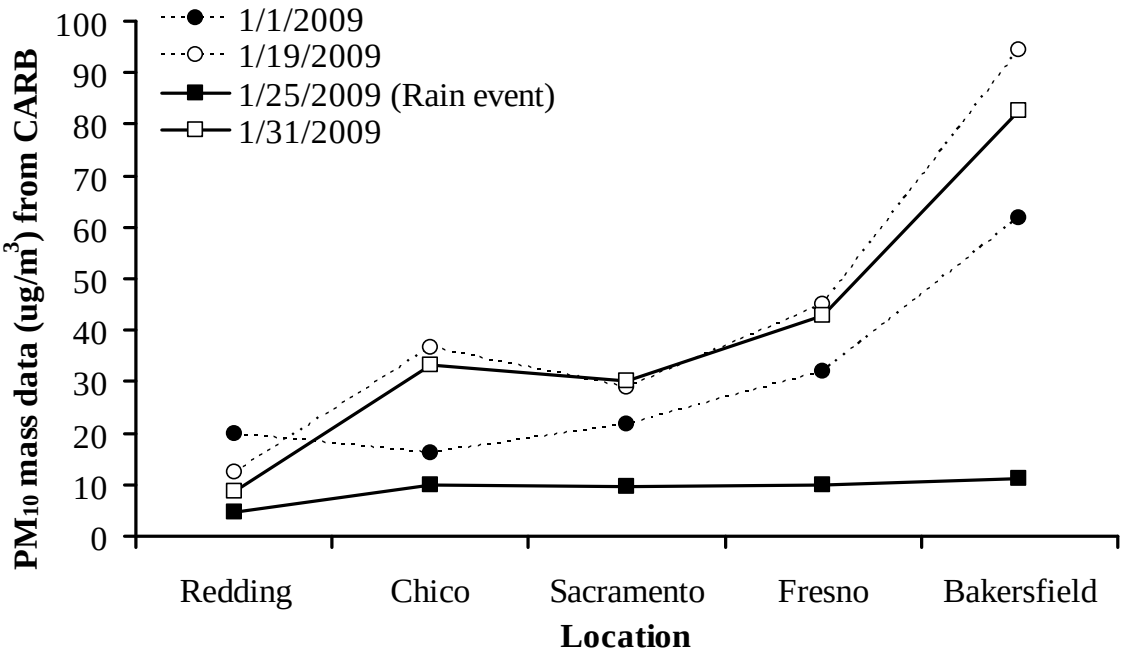

Figure 2. PM_{10} mass values (circa 95% $PM_{2.5}$) before (1/1), during (1/19), and after (1/25, 1/31) an intensive aersol study, January 2009 (Cahill TM 2010).

A synoptic rain event that moved into the entire Central Valley by January 25 ended the stagnation episode as seen in the January 25 mass data, but by January 31, the north - south gradient was once again established.

One key point to understanding Central Valley particulate matter in winter is that extensive studies in the San Joaquin Valley from 1998 to about 2004, and monitoring data since that time, show that the aerosol mass is mostly ammonium nitrate. The major source is vehicular NO, mostly from diesel trucks,trains, and construction equipment - a consequence of the heavy traffic on major north-south valley transportation corridors south of the Delta.

The key role for wood smoke in the Sacramento County inventories is shown below in Table 1. On average, wood smoke dominated all residential fuels and represents about 1/3 of all $PM_{2.5}$ mass in Sacramento.

	CO	NOx	PM2.5
ARB Data 2009			
Summary for Sacramento County			
Residential Fuel (all types)	**37.9**	**2.97**	**4.93**
Fraction residential fuels (%)	**11.2**	**3.9**	**35.7**
	11.2 %	**3.9 %**	**35.7 %**
Stationary sources			
Fuel Combustion (non-residential)	3.73	3.62	0.41
Waste Disposal	0.05	0.05	0.01
Cleaning and surfaces	0	0.00	0.00
Petroleum production and marketing	0.01	0.00	0.00
Total Industrial Processes	0.27	0.23	0.47
Total Stationary Sources	**4.06**	**3.90**	**0.90**
Area sources			
Solvent evaporation	0	0	0.01
Total Miscellaneous processes	**40.26**	**3.10**	**10.12**
Residential fuel (all types)	37.9	2.97	4.93
Mobile Sources			
On Road vehicles	209.32	44.06	1.45
Diesels	5.59	22.45	0.68
Other Mobile sources			
Off road, farm, and train diesels	86.01	24.91	1.34
Total Mobile sources	**295.33**	**68.98**	**2.79**
Total Sacramento County	**339.65**	**75.97**	**13.81**

Table 1. ARB Inventory for Sacramento County, 2009 (http://www.arb.ca.gov/app/emsinv/fcemssumcat2009.php)

Below is a regional gridded inventory of estimate smoke emissions (lbs/day). Note the high density and geographical extent of wood smoke emissions northeast of downtown Sacramento.

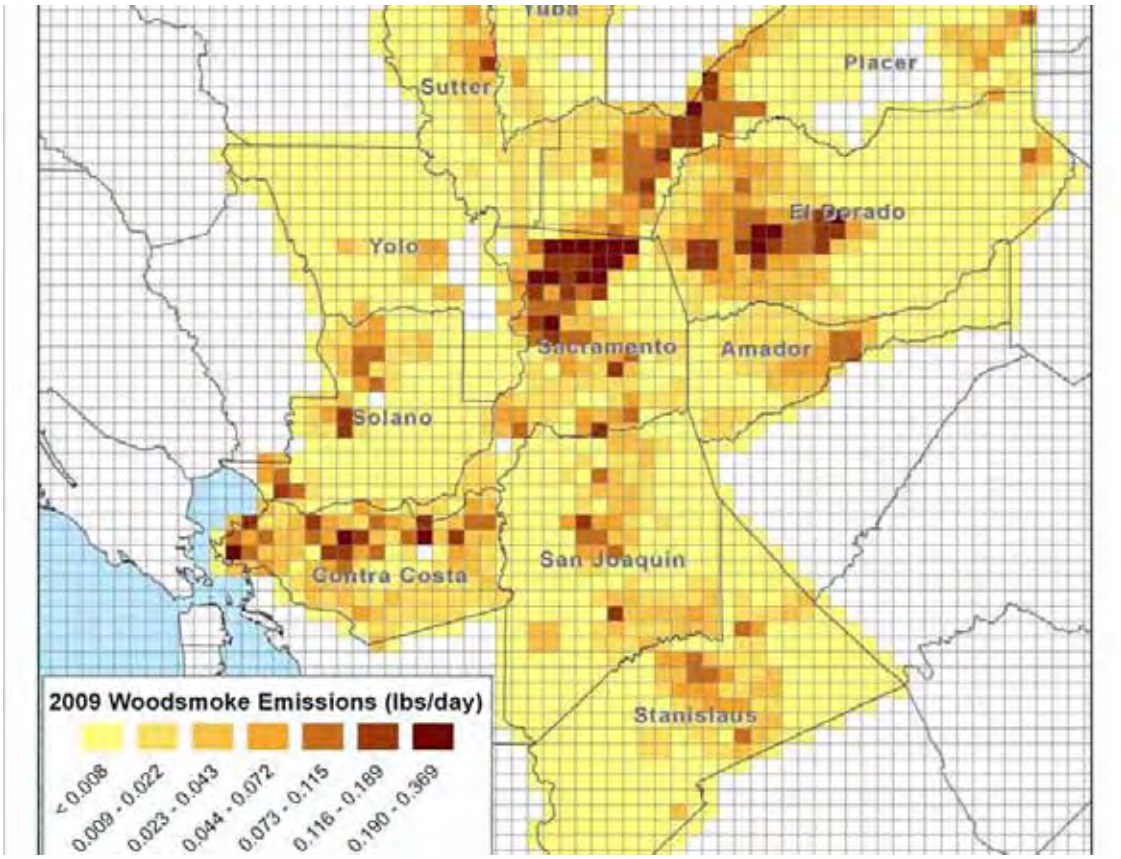

Figure 3.Gridded inventory of wood smoke emissions (lbs/day) (Barnes, 2010)

US EPA Publication AP-42 provides PM_{10} emission factors from various types of wood stoves and fireplaces (EPA 2010). It shows that these emissions from fireplaces and conventional wood stoves are much higher than for catalytic wood stoves, which in turn are much higher than from pellet stoves. Other data show that this is almost all $PM_{2.5}$.

The most complete US EPA analysis of open fireplaces and stoves is in “Residential Wood Combustion Technological Review” (Houck JE, and Tiegs PE, 1998), which can be supplemented by papers in the refereed literature in the past 10 years. Some of the most useful are cited and included in the references.

EPA AP-42 also summarizes emission factors for particulate matter reduction potential per mass of dry wood burned. Factoring in burning rates, fireplace combustion of western hardwoods emits somewhat less PM than fireplace combustion of softwoods such as pine.

This report (Houck and Tiegs, 1998), also distinguished between homes that use open hearth fireplaces for heating, <5% of all open hearths nationwide, and the vast majority who use them for aesthetic and social purposes. The latter have very few fires each winter, generally of short duration, while users of wood stoves tend to use them for home heating with a far greater number of hours of wood combustion.

Of three aerosol sampling sites around Sacramento County (13th & T Street, Del Paso Manor, and Roseville – N. Sunrise), the Del Paso Manor site typically records the largest number of exceedances of the 35 µg/m^3 federal 24-hour $PM_{2.5}$ mass standard in winter (November through February). Residential wood combustion has been established as a major driver of these winter peaks, about 42 percent of $PM_{2.5}$ emissions in Sacramento County, which is nearly four times the next largest source. The Sacramento Metropolitan Air Quality Management District (SMAQMD) has made great strides in controlling residential wood smoke pollution by restricting burning on days when atmospheric dispersion is inadequate to deal with the added emissions. Although winter $PM_{2.5}$ concentrations have been significantly reduced, occasional high concentrations still occur.

The difficulty of diagnosing the exact causes of the remaining rare high concentration events lies in the variability of source activity over any given 24-hour sample period, with motor vehicle activity dominating daytime emissions and residential emissions rising at night, coupled with the diurnal variation of winds and atmospheric mixing. Routine speciated $PM_{2.5}$ samples collected over 24 hours composite the materials from the various sources and the effects of changing atmospheric conditions into a single sample, and thus do not facilitate parsing the history of a particular peak event.

One of the primary goals of this study was to examine the synergy of wood smoke and other emission sources of winter pollution by using the hourly time resolution of a specially collected DRUM data set, combined with the routine hour-resolved gas and particle measurements and meteorological data taken by the District, to improve understanding of the dynamics of high $PM_{2.5}$ concentration events.

Between December 1, 2009 and February 28, 2010, only one exceedance was recorded in the region – at Del Paso Manor - on December 24: 49.3 µg/m^3. This event was associated with very unfavorable meteorology:

- Zero mean wind velocity
- High dew point caused fog to form Christmas night (recorded at Sacramento International Airport), with increased mass of hydrophilic air pollutants such as wood smoke.
- Cold down-slope air from the Sierras each evening, causing a very shallow inversion layer
- Christmas holiday favors fireplace use.
- Dec. 24 was a “Legal to Burn” day.

The results show that on most days, the three sampling sites had similar mass concentrations. On these days, mass concentrations in winter were driven largely by

ammonium nitrate, derived from NOx emitted primarily from vehicular sources, especially diesel trucks and locomotives.

While only one Del Paso Manor $PM_{2.5}$ measurement exceeded EPA's 35 $\mu g/m^3$ standard on the one-day-in-three Federal Reference Method (FRM) protocol, December 24, 2009, five additional values above the standard occurred when 24-hour values, based on hourly data, were recorded. Three of these occurred on "Burning Discouraged – Voluntary" days, and two (including 71 $\mu g/m^3$ on December 25, 2009) occurred during Stage 2 "All Burning Prohibited" days.

A detailed statistical and trajectory analysis was made of the period around Christmas. On December 24, the hourly gas data showed high levels (values greater than 1/2 of the peak value) from midnight to 9 AM, and from 6 PM to midnight. Similar values were observed on December 25, from midnight to 8 AM, and from 6 PM to midnight.

The exceedances at Del Paso Manor in 2009-2010 were caused by wood smoke added to the regional background, contained in a very shallow inversion layer, and the December 24 exceedance occurred during a "Legal to Burn" burn day on Christmas Eve. Some of this wood smoke persisted into the early hours of Christmas Day, which was an "All Burning Prohibited" day.

Based on the aerosol and gas data obtained during the December episodes, $PM_{2.5}$ was measured hourly at Del Paso Manor, and at Roseville – N. Sunrise - which was upwind of Del Paso Manor. The integrated Del Paso Manor level for 24 hours on December 25 was 71 $\mu g/m^3$. $PM_{2.5}$ potassium was measured from a 1-hour time resolution 8 DRUM sampler, including ultrafine aerosols. At the peak of the mass, wood smoke was only about 1/6 of the fine mass. Also, the carbon monoxide to nitric oxide ratio (CO/NO) from the emission inventory of Sacramento County was roughly 12.5 to 1, but the ratio on the evening of December 24 was unusually rich in CO (22.5 to 1).

A HYSPLIT wind trajectory analyses on December 24 showed that winds came from the northeast, down I-80 and across Roseville, before reaching Del Paso Manor, which mixed local CO from the wood smoke with vehicular oxides of nitrogen from the Roseville rail-yard and the I-80 freeway. Thus, the source of the wood smoke December 24 - 25 appears to be northeast of the Del Paso Manor site.

A long series of Stage 2 "All Burning Prohibited" days in early January, associated with low wind velocity and night fog, had significant $PM_{2.5}$ levels but relatively low amounts of wood smoke. The smoke that was present was well-aged smoke from the northeast quadrant, which implied that the SMAQMD "All Burning Prohibited" days were being observed in neighborhoods near and just northeast of Del Paso Manor.

Regional impacts on the Del Paso Manor site were likely, including I-80 and the Roseville rail-yard in the December 25 episode, a Bay Area incursion around January 8 including sea salt, and an industrial/vehicular source north and northwest of Del Paso Manor January 13 - 16, also toward the rail-yard.

The large data set, over 64,000 individual values in the 12 day intensive period around Christmas and New Year, lent itself to a statistical analysis. A 9-component factor analysis technique was applied to the entire data set of gases and aerosols, as a function of particle size and composition.

This analysis was able to separate the contribution of finer 'brake/tire dust' from local road dust, showing that 'brake/tire dust' roughly matched the pattern of the Christmas period mass exceedances. This result is in accord with a trajectory analysis showing winds on December 24-25 coming down parallel to I-80 in Roseville, and picking up the roadway aerosol signatures, before impacting Del Paso Manor. However, the brake/tire dust was a small fraction of the fine mass, which was dominated by wood smoke in these periods.

An hourly source allocation analysis was developed for a 12-day period (Dec. 22, 2009 - Jan. 2, 2010). During this period, on December 24, Del Paso Manor recorded its peak 24-hour $PM_{2.5}$ value. The strong late-evening peak recorded in the hourly $PM_{2.5}$ data from the Del Paso Station's beta attenuation monitor (BAM) sampler strongly supports an initial hypothesis that residential wood burning was a major contributor to the peak concentration. That hypothesis was tested in analyses that are discussed in Appendix 2.

Using fine temporal and chemical resolution available with positive matrix factorization (PMF) analysis of a hybrid data set composed of hourly size-resolved aerosol and gas data, it was possible to diagnose the causes of individual high $PM_{2.5}$ events in the Del Paso Manor area. The inclusion of hourly $PM_{2.5}$ data collected on-site in the analysis allowed statistical allocation of mass to nine observed elemental and gas "profiles" that appear to represent real components of the urban aerosol mass. The final $PM_{2.5}$ allocation explained the variation of observed mass to a high degree, and plots of the hourly allocation facilitated visualization of the dynamic variation of aerosol composition and concentration at the Del Paso Manor site over the study period.

A significant finding from this analysis is that the highest peak $PM_{2.5}$ concentration during the study, occurring over the Christmas holiday, was driven by unusually fresh emissions from residential wood combustion, and, based on its temporal pattern, not primarily for heat. This finding should be of value to the SMAQMD, since its control strategy for winter $PM_{2.5}$ includes managing use of wood for residential heating through a public information program and declaring "burn" and "no burn" periods based on meteorology. It seems likely from these data that this program has been successful, and that the unique events of Christmas 2009 were due to atypical behavior by residents who engage in infrequent burning for social reasons.

The 2009-2010 Del Paso Manor Winter $PM_{2.5}$ study was conceived to demonstrate the utility of extremely high temporal and compositional resolution sampling as a means to unravel the various source contributions to elevated 24-hour $PM_{2.5}$ concentrations. In that it has succeeded, with successful collection of samples with limited staff time invested at the sampling site, and a successful analytical program that has produced findings that are both scientifically novel and applicable to the needs of the SMAQMD.

SUGGESTED FUTURE RESEARCH

At Del Paso Manor, two markers of wood smoke were detected. Levoglucosan (a marker for general wood combustion) was present at much finer size than dehydroabietic acid (a marker for softwood combustion). Because it takes time for the initially fine emissions to accumulate into larger size modes, this indicates that the emissions from softwood combustion tended to come from sources relatively distant to Del Paso Manor.

Reducing emissions of the PAHs such as benzo[a]pyrene (BaP) associated with softwood combustion could be a health benefit. PAHs cause cancer and appear to promote allergic responses and asthma. Smoke from burning softwood tends to contain far more PAH per mass than smoke from burning hardwoods (Ancelet, 2011).

We suggest research to compare the emissions from softwood and hardwood, and their possible differences in toxicity. The results could lend support for a public outreach campaign to educate residents on wood selection to be burnt on legally allowable burn days.

Such an analysis could be studied in connection with the speciation information and tools contained in Appendix 2. We also suggest a study of the types of wood purchased by local residents in order to determine what types of wood are being burned.

Appendix 1: Further Research on $PM_{2.5}$ Aerosols in Sacramento

by

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Sacramento, Winter, 2009-2010

Monitoring data

The winter period is set from November 1 through February 28, with the HETF/UC Davis effort in the period December 22 through February 1.

This HETF/UC Davis intensive study was strongly supported by informational resources and measurements in and around Sacramento, as well as national data sources:

1. SMAQMD/ARB sites
   a. Del Paso Manor, Sacramento Metropolitan AQMD
   b. Roseville – N Sunrise
   c. ARB site 13th at T Street

2. US EPA Speciation Trends Network (STN)
   a) 13th and T Street
   b) Del Paso Manor

3. ARB Emission Inventories

4. Caltrans traffic counts

5. NOAA Sacramento International Airport data, including haze

Each of these sites has a variety of information available, either on the ARB's ADAM summaries or US EPA AIRS. One unusual source of information was the SMAQMD aethalometer at Del Paso Manor, designed to detect carbon soot.

Finally, national resources can be brought to bear, especially the NOAA READY trajectory tracking program HYSPLIT, weather from sources such as weatherunderground.com, and Google Earth.

The HETF/UC Davis intensive study operated from December 22, 2009 until January 18, 2010, with the primary site at Del Paso Manor. There were two intensive sampling periods with 1 hour time resolution, December 22 – Jan 4, and Jan 4 to Jan 18, 2010. Measurements and equipment at the HETF/UCD Del Paso Manor intensive site included:

a) DELTA Group continuously sampling 8 DRUM sampler, 1 hr resolution 9 size modes including ultra-fines, for mass, elements, and optical spectroscopy, 350 nm to 820 nm (Cahill et al, 1985, Raabe et al, 1989, Bench et al, 2002, Cahill et al, 2009)

b) DELTA Group continuously sampling 8 DRUM sampler, 3 hr resolution 8 size modes including ultra-fines, for mass, elements, and optical spectroscopy, 350 nm to 820 nm.

c) DELTA Group integrated sampling 8 DRUM sampler, 9 size modes, 5 week average, including ultra-fines, for organics (PAHs, sugars, organic acids, alkanes) (Cahill, T.M., 2010, Mazzolini et al, 2007)

Sacramento, Winter, 2009-2010

Monitoring Results

The main sampling sites are shown below in Figure 4.

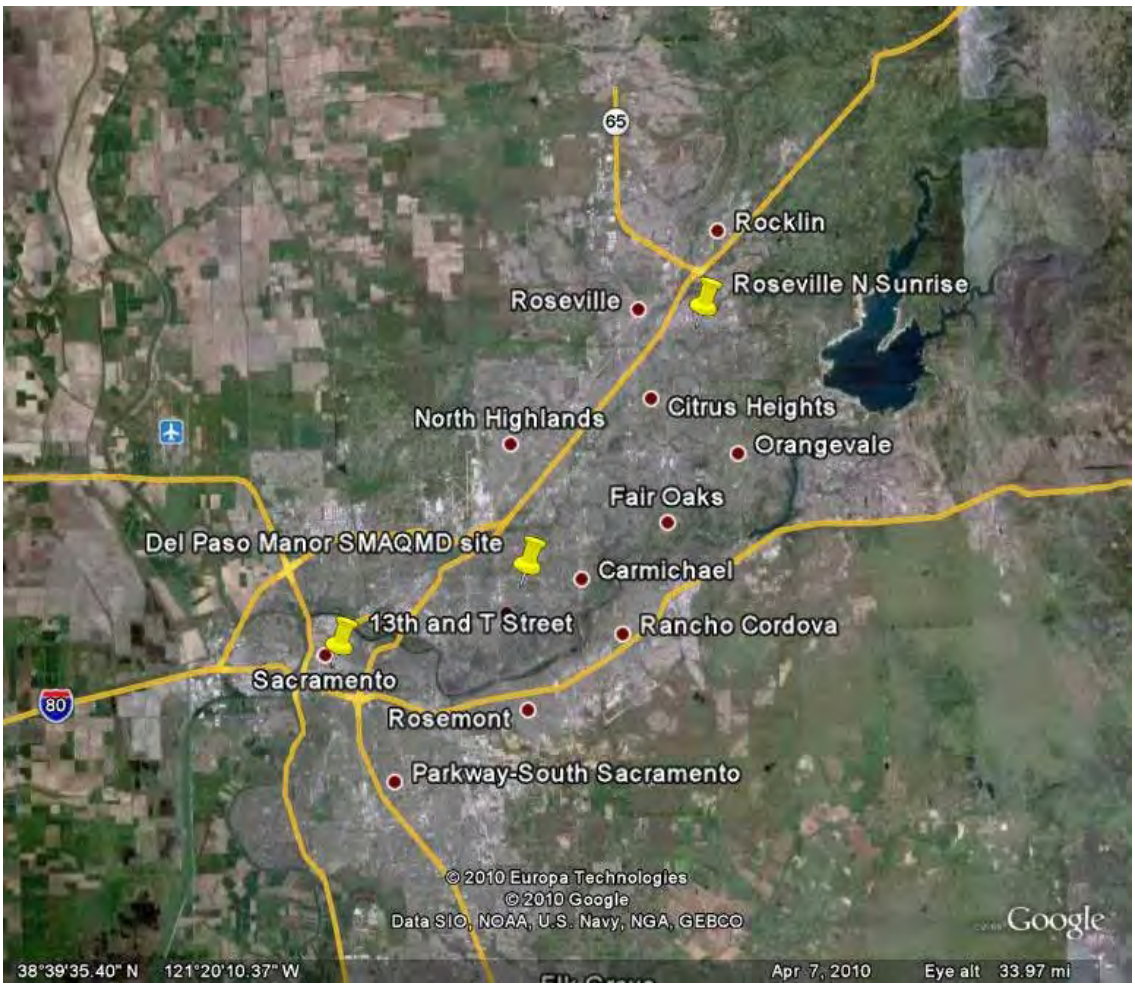


Figure 4 Google Earth picture of the study region

Meteorology for the period was fairly dry until late January, when heavy rain set in.

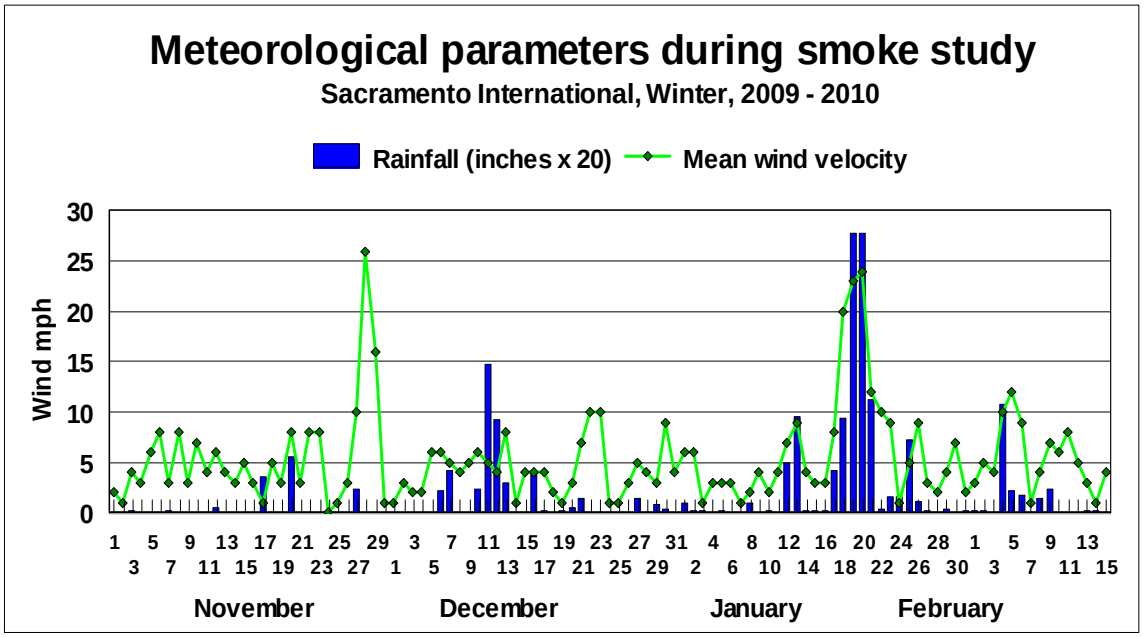


Figure 5 Meteorology at the Sacramento International Airport.

Rain and wind lead to lower levels of particulate matter. Rain washes out particulate matter (wet deposition), and higher wind velocities disperse particulate matter. Higher levels of particulate pollution are associated with the presence of temperature inversions in the lower levels of the atmosphere, and higher wind velocity tends to break up these inversions, thereby allowing greater mixing of pollutants in a larger volume of air (Australian Bureau of Meteorology). These factors lead to lower levels of particulate pollution.

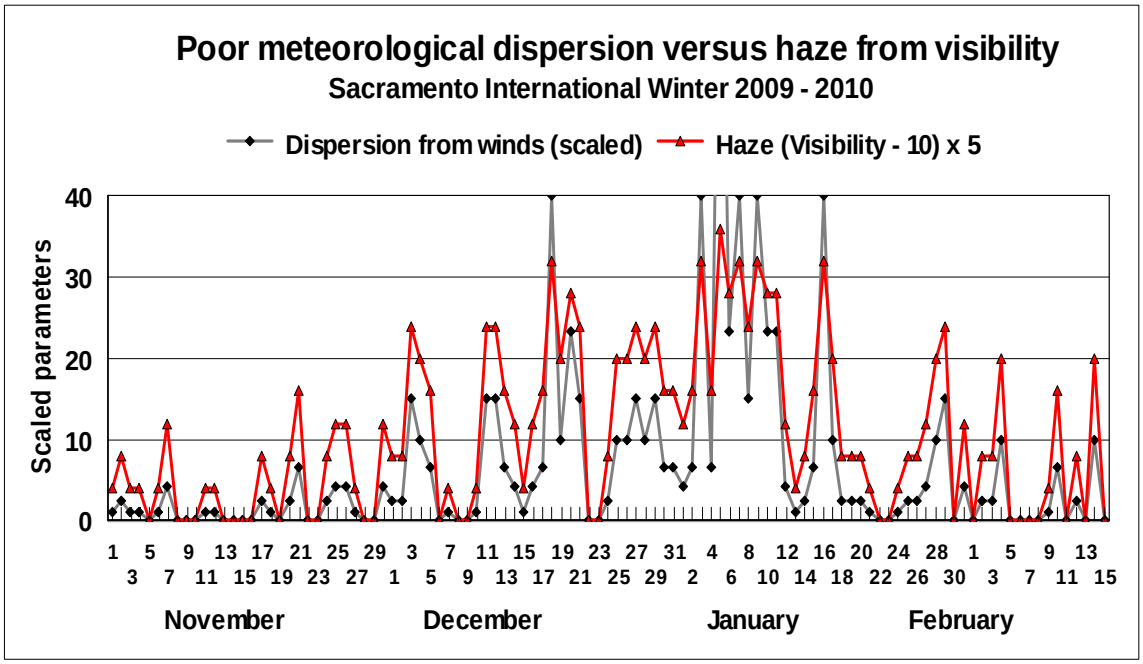


Figure 6. Dispersion potential, based on wind velocity, and haze measured at SMF.

Wood burning emits carbon monoxide, shown below for winter, 2009 – 2010.

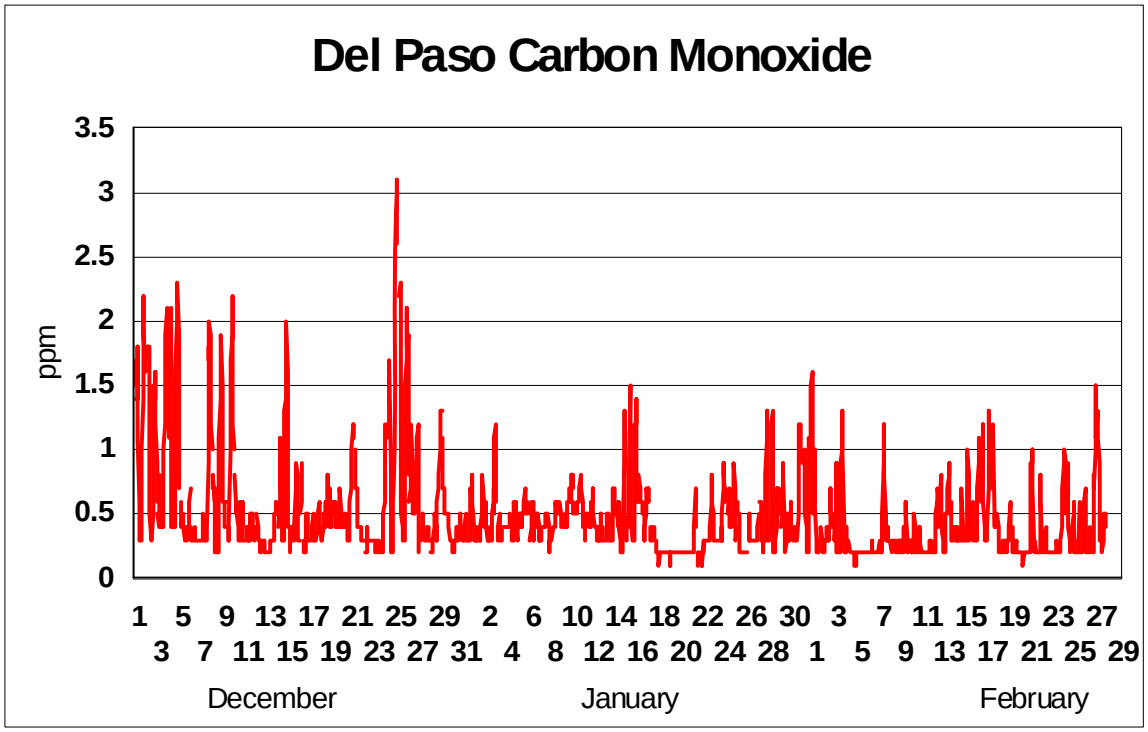


Figure 7. Hourly carbon monoxide at Del Paso Manor site

On the other hand, the low temperature wood fires are only a small source of NO.

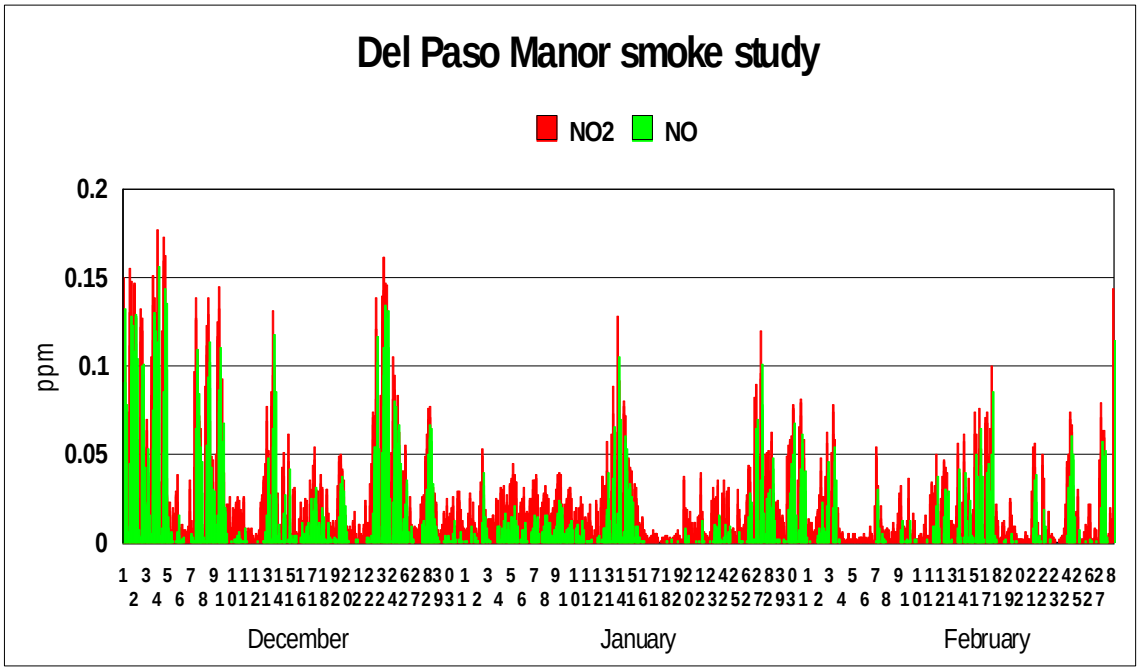
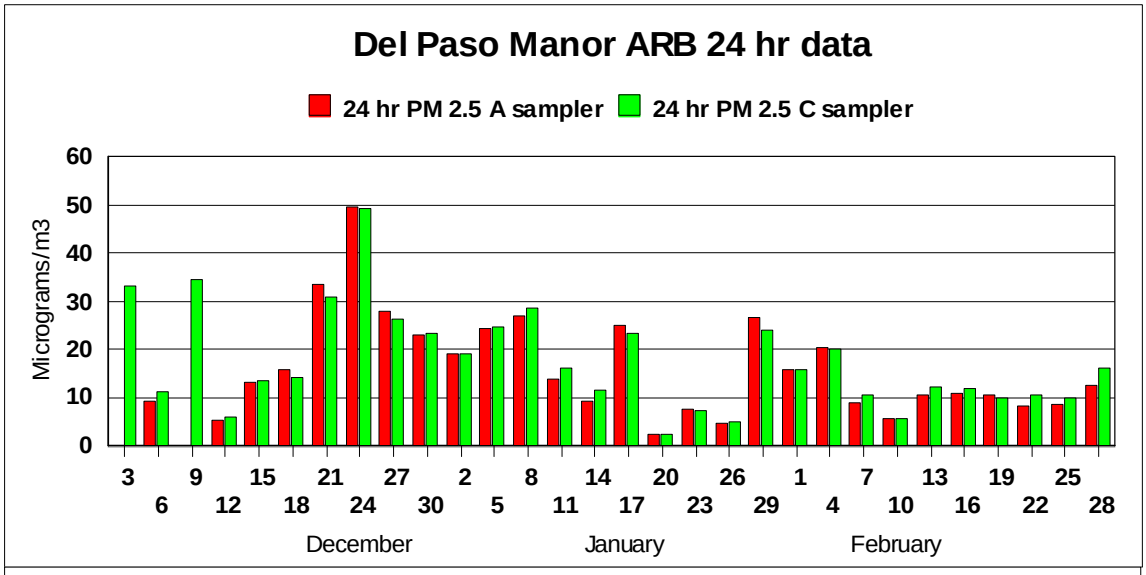


Figure 8. Hourly oxides of nitrogen at the Del Paso Manor site



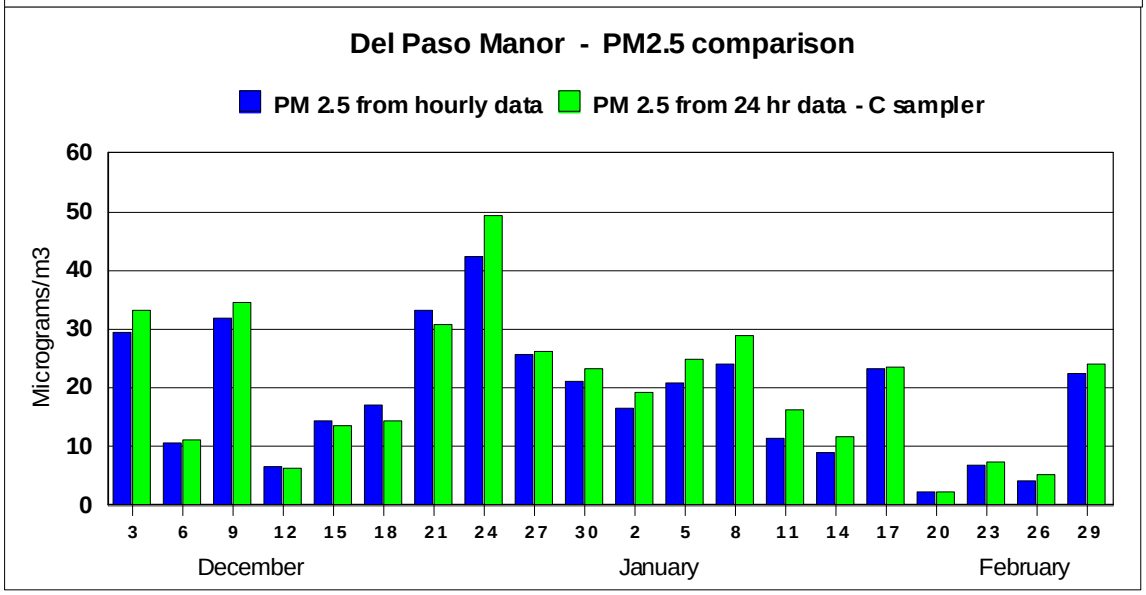


Figure 9 a, b. ARB duplicate 24 hr $PM_{2.5}$ mass samplers at Del Paso Manor (top), 24 hr and hourly $PM_{2.5}$ mass data averaged to get 24 hr data (bottom)

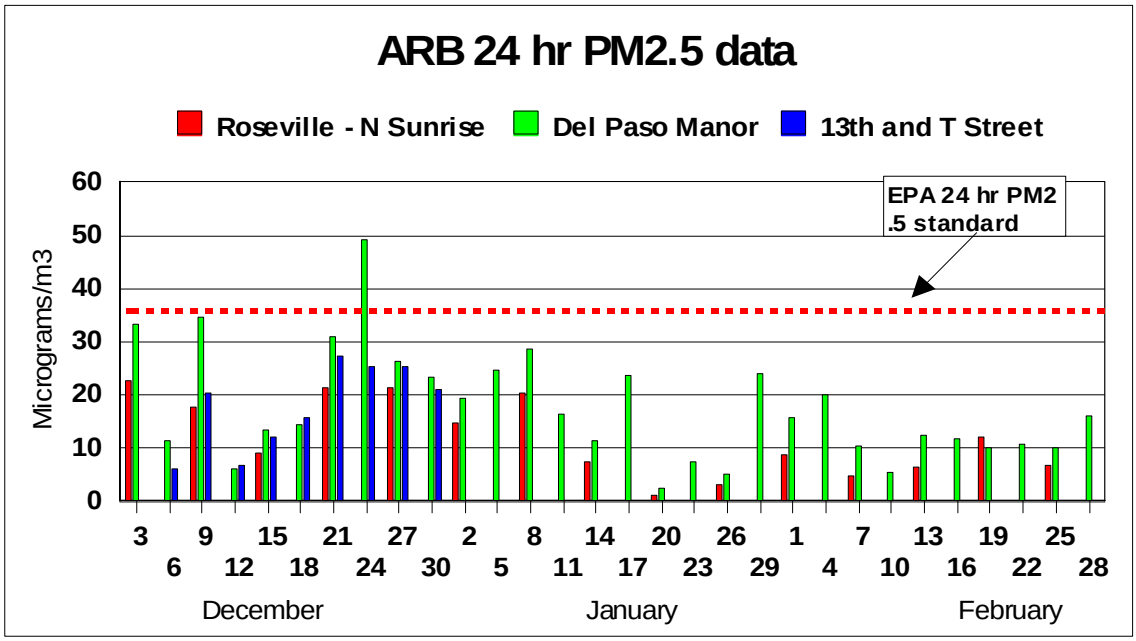


Figure 10. 24-hr $PM_{2.5}$ mass data from Del Paso Manor, 13th and T Street, and Roseville – N. Sunrise

During the entire winter period, there were 12 Stage 2 “All Burning Prohibited” days, 9 Stage 1 “No Burn – Unless Exempt” days, 33 “Burning Discouraged –Voluntary” days, and 67 “Legal to Burn” days.

Date	Forecast	Actual	Burn Control
11/9	32 to 35	25.3	Stage 1
11/10	32 to 35	20.6	Stage 1
11/15	32 to 35	23.1	Stage 1
11/16	**> 35**	**39.0**	**Stage 2**
11/17	32 to 35	14.9	Stage 1
11/25	**32 to 35**	**35.5**	**Stage 1**
11/26	**> 35**	**34.5**	**Stage 2**
12/01	**> 35**	**38.7**	**Stage 2**
12/02	> 35	31.6	Stage 2
12/03	32 to 35	31.2	Stage 1
12/04	**25 to 32**	**39.1**	**Voluntary no Burn**
12/09	32 to 35	24.1	Stage 1
12/10	25 to 32	37.1	**Voluntary No Burn**
12/19	32 to 35	17.7	Stage 1
12/20	**32 to 35**	**38**	**Voluntary No Burn**
12/24	**<25**	**42.3**	**Legal to Burn**
12/25	**> 35**	**71.3**	**Stage 2**
12/26	**> 35**	**37.1**	**Stage 2**
1/03	32 to 35	22.1	Stage 1
1/05	> 35	32.3	Stage 2
1/06	**> 35**	**37.0**	**Stage 2**
1/07	**> 35**	**38.2**	**Stage 2**
1/08	**> 35**	**38.0**	**Stage 2**
1/09	> 35	19.4	Stage 2
1/28	32 to 35	22.1	Stage 1

Table 2. No-burn days, Sacramento, winter, 2009 – 2010. Values are in $\mu g/m^3$ for BAM $PM_{2.5}$ mass. **PM2.5 exceedances at Del Paso are shaded and formatted in bold.**

Composition of $PM_{2.5}$ mass

STN speciation

The US EPA Speciation Trends Network (STN), capable of speciating fine mass, has three sites in the Sacramento Valley – Del Paso Manor, 13th and T Street, and in Chico. The data from this network were available up to Dec. 31, 2009, and provide a uniquely detailed analysis of the major fine mass components. One of the characteristics of the STN (and IMPROVE from which it is descended [Malm, et al., 1994]) is mass closure – gravimetric mass equaling the sum of species: soils, sulfates, nitrates, organic carbon, elemental carbon, and miscellaneous elements (below).

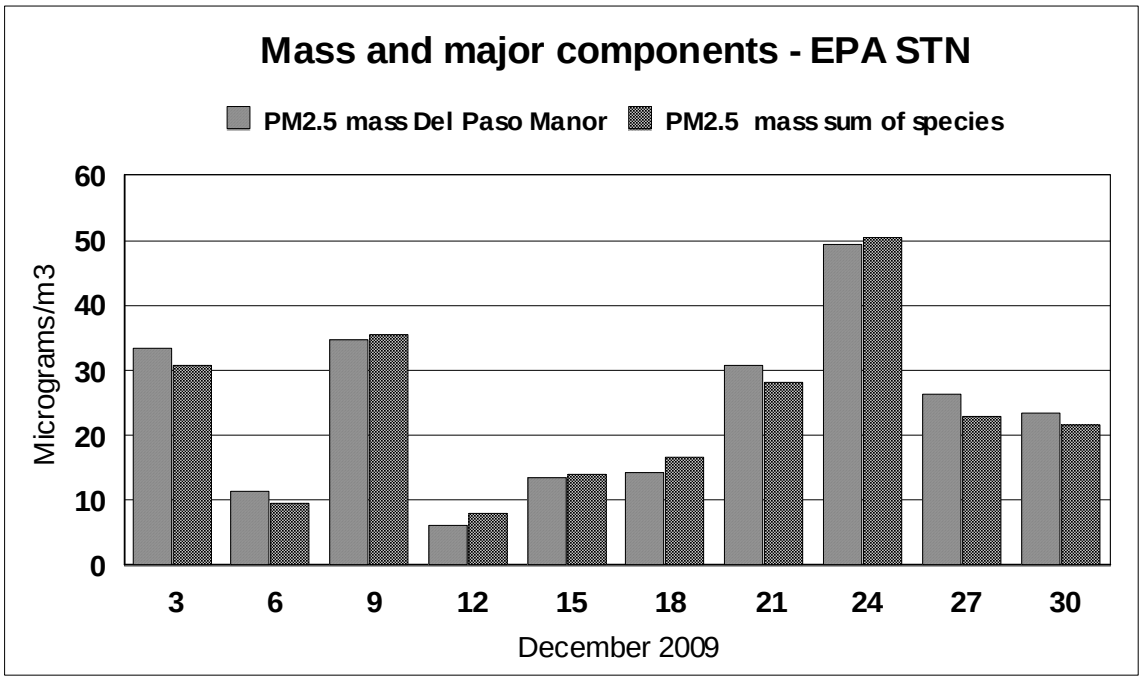


Figure 11. STN mass closure at Del Paso Manor

The comparison between Del Paso Manor and 13th and T Street shows slightly higher values on the average, circa 10% ± 16%, at Del Paso Manor on the four days when both were sampled.

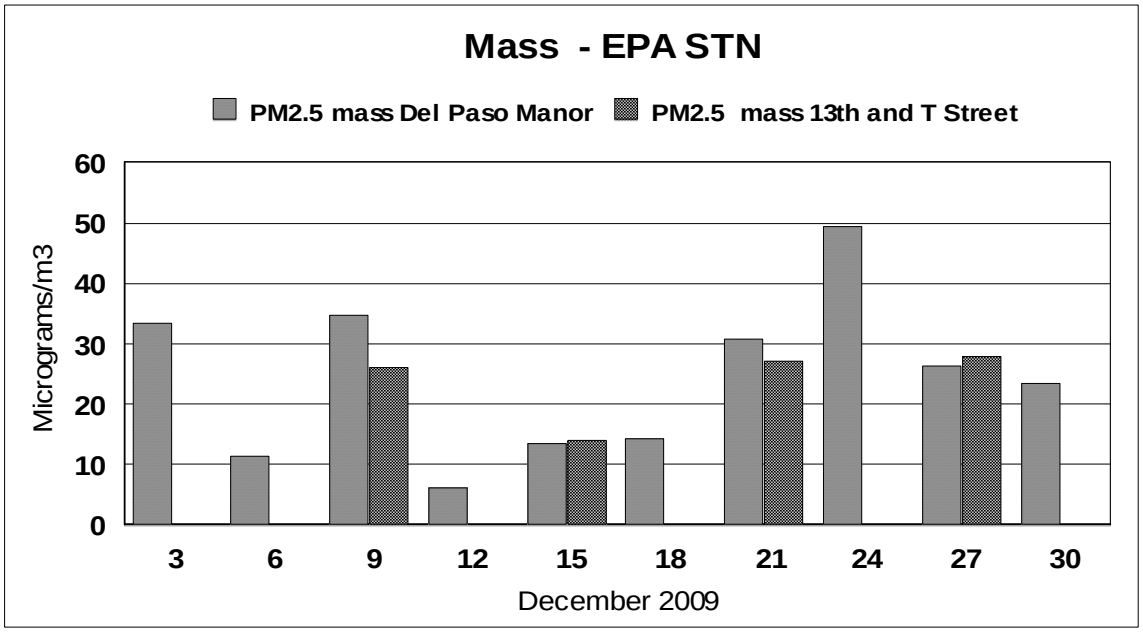


Figure 12a. Comparison of fine mass: Del Paso Manor and 13th& T Street

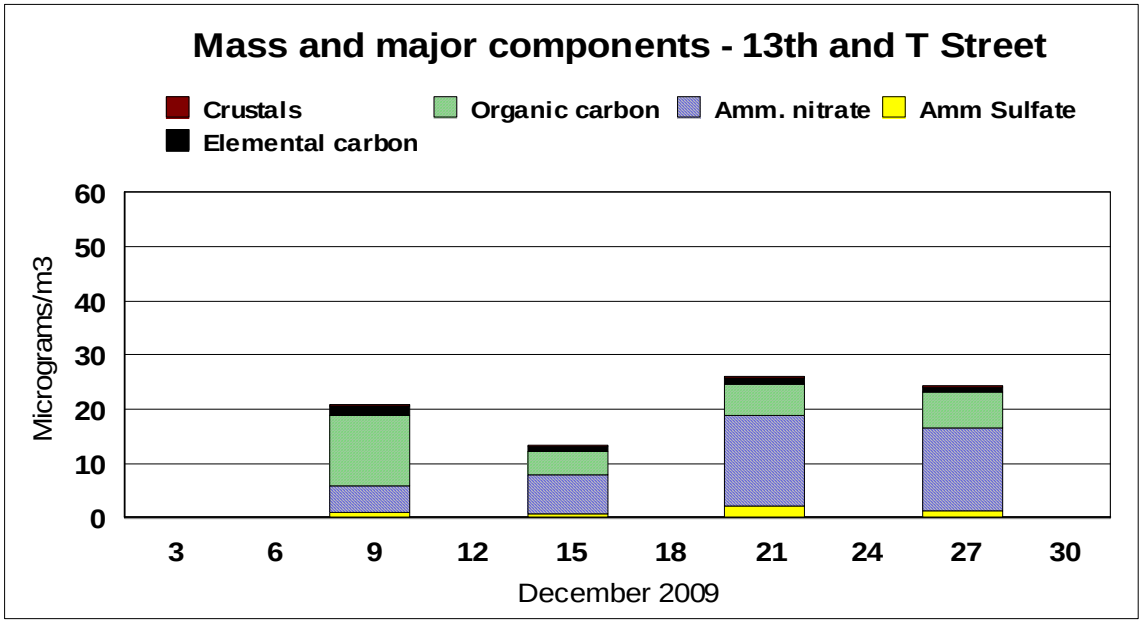


Figure 12b. Speciated fine mass at 13th and T Street, on the same scale as Del Paso Manor.

However, on 3 days, large excesses of organic matter are seen, which correlate well with fine potassium, a tracer of wood smoke.

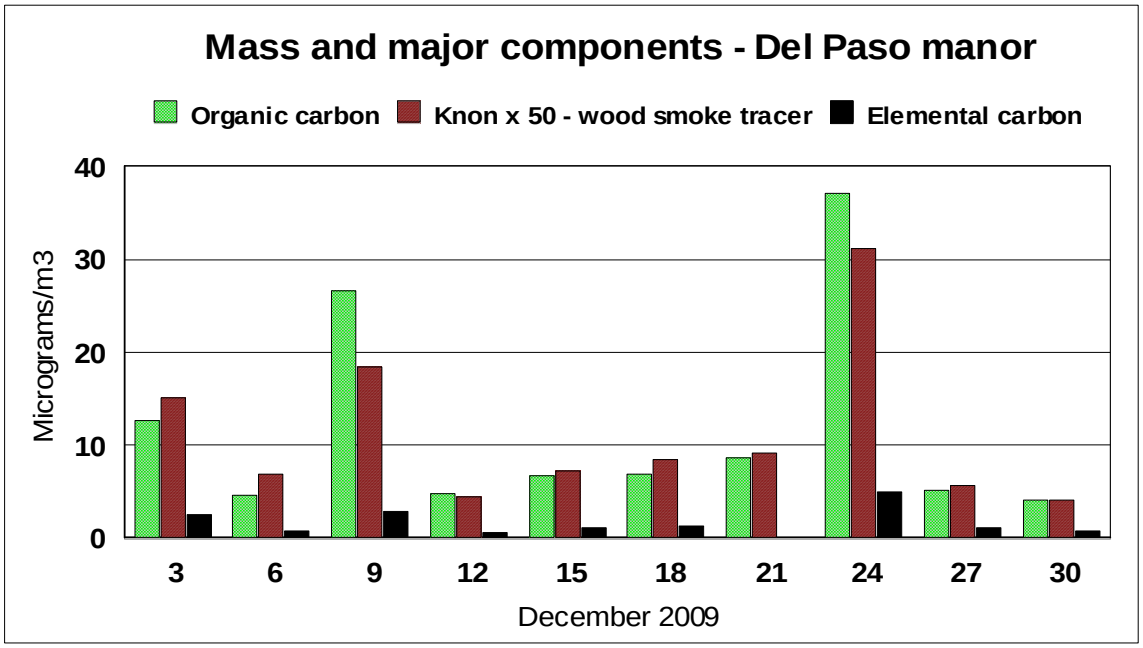


Figure 13. Comparison of the fine potassium smoke tracer x 50, to approximate mass in $\mu g/m^3$, to STN organic carbon and elemental carbon.

Thus, on 3 out of 10 days in December, Del Paso Manor was impacted by wood smoke.

Sacramento site inter-comparisons – mass and gaseous species

The Del Paso Manor site is well served by a variety of air monitoring instrumentation.

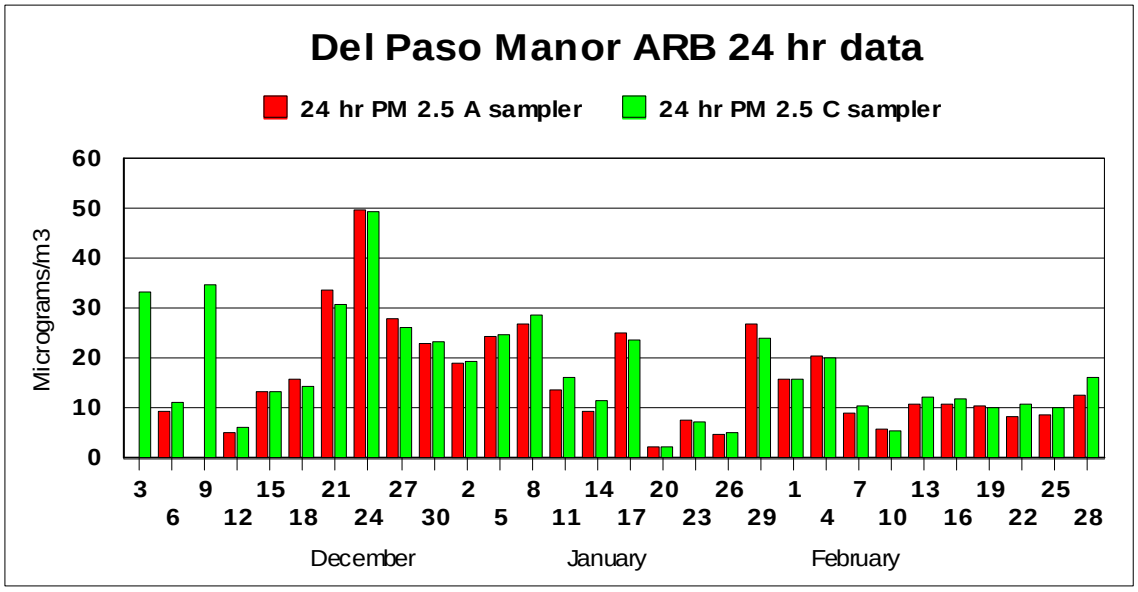


Figure 14. Comparison of paired $PM_{2.5}$ samplers at Del Paso Manor.

Excellent precision was exhibited by the paired 24-hr $PM_{2.5}$ samplers at Del Paso Manor, A being the primary FRM, C the co-located FRM.

In addition, data are available for $PM_{2.5}$ mass hourly, allowing direct comparisons with hourly data on gaseous pollutants.

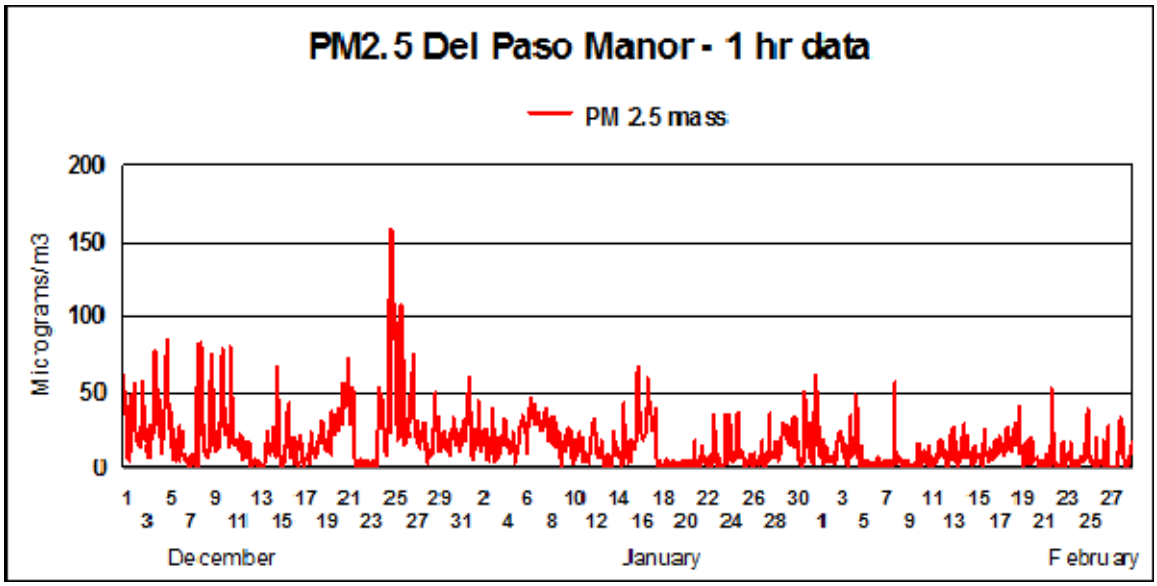


Figure 15. Hourly $PM_{2.5}$ mass at Del Paso Manor.

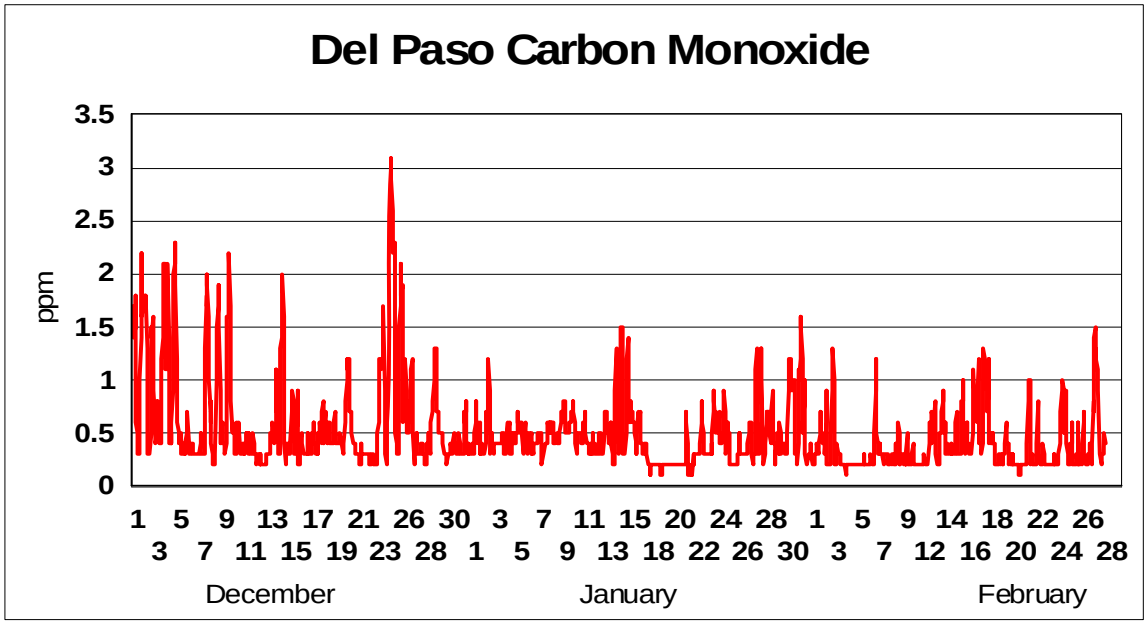


Figure16. Hourly carbon monoxide at Del Paso Manor

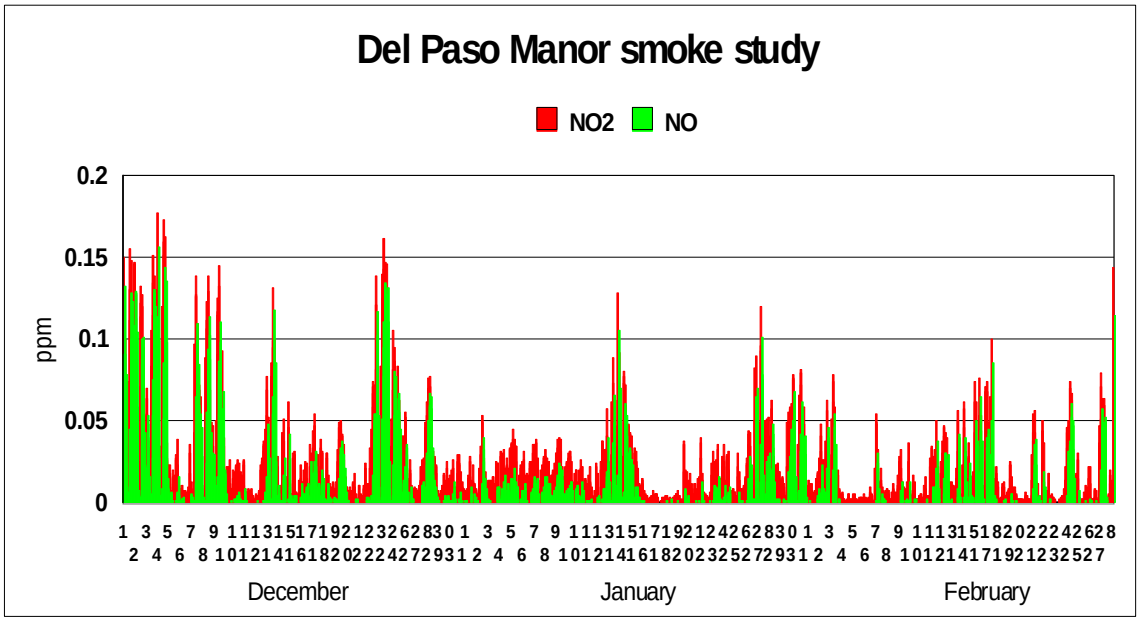


Figure 17. Hourly oxides of nitrogen (NO, NO_2) at Del Paso Manor

The availability of 1-hr $PM_{2.5}$ mass data at Del Paso Manor, 13th and T Street, and Roseville-N. Sunrise allows detailed tracking of mass events. Below we show 1-hr mass data converted into 24-hr data so as to compare with 24-hr FRM protocol samplers.

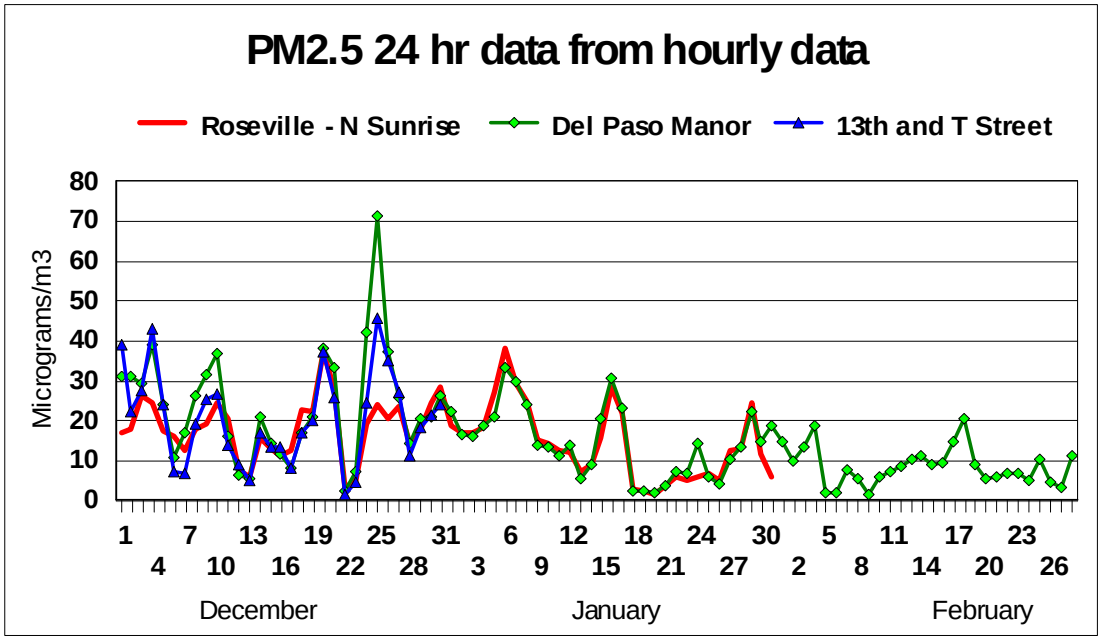


Figure 18. Comparison of $PM_{2.5}$ mass values at Del Paso Manor, 13th& T Street, and Roseville – N Sunrise as derived from hourly $PM_{2.5}$ data.

An additional data resource was the aethalometer at Del Paso Manor. Aethalometers measure the blackness of a filter and convert the optical absorption into equivalent black carbon mass.

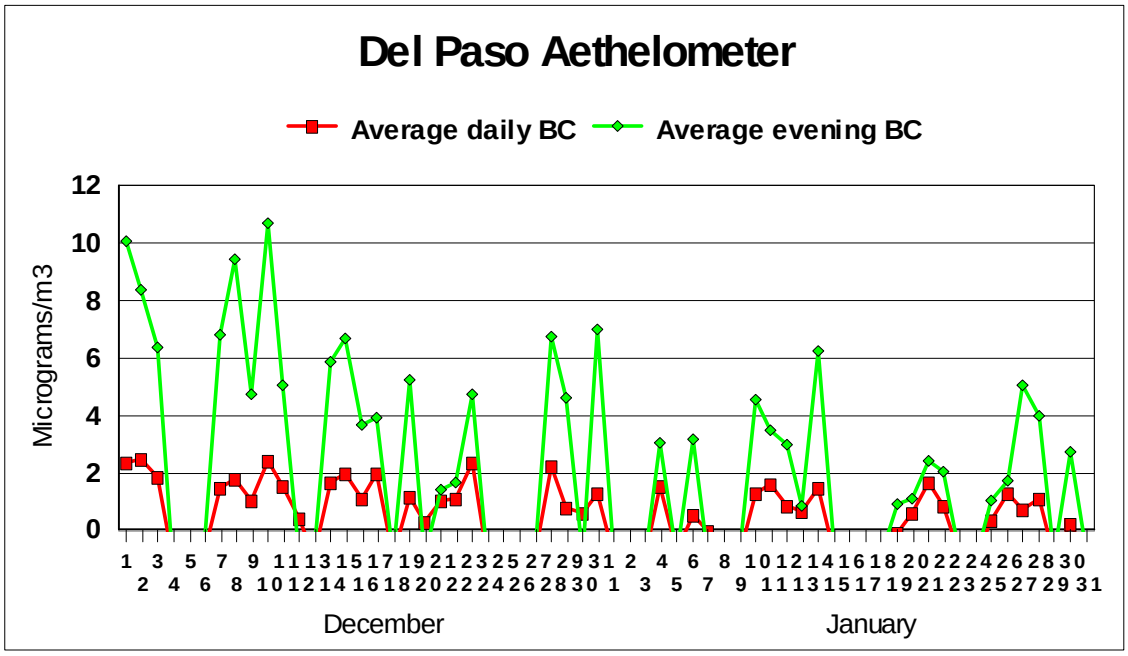


Figure 19. Aethalometer data from Del Paso Manor. The data from December 24 through December 27 are missing.

Del Paso Manor Study –

Winter intensive – Phase 1, December 22, 2009 – January 4, 2010

DRUM mass and elements, 9 size modes

Sampling began at noon on December 22, after a power loss had prevented a start of December 21. The previous 3 days had strong winds and clean conditions (Figure 23, below). The Christmas Eve – Christmas day smoke impact at Del Paso manor is seen as the darkest band in the 0.09 to 0.56 μm size modes. Note the wind velocity, measured at Sacramento Metropolitan Airport, was <1 mph during that period, but local subsidence winds (HYSPLIT analysis, Figure 34) were slightly higher.

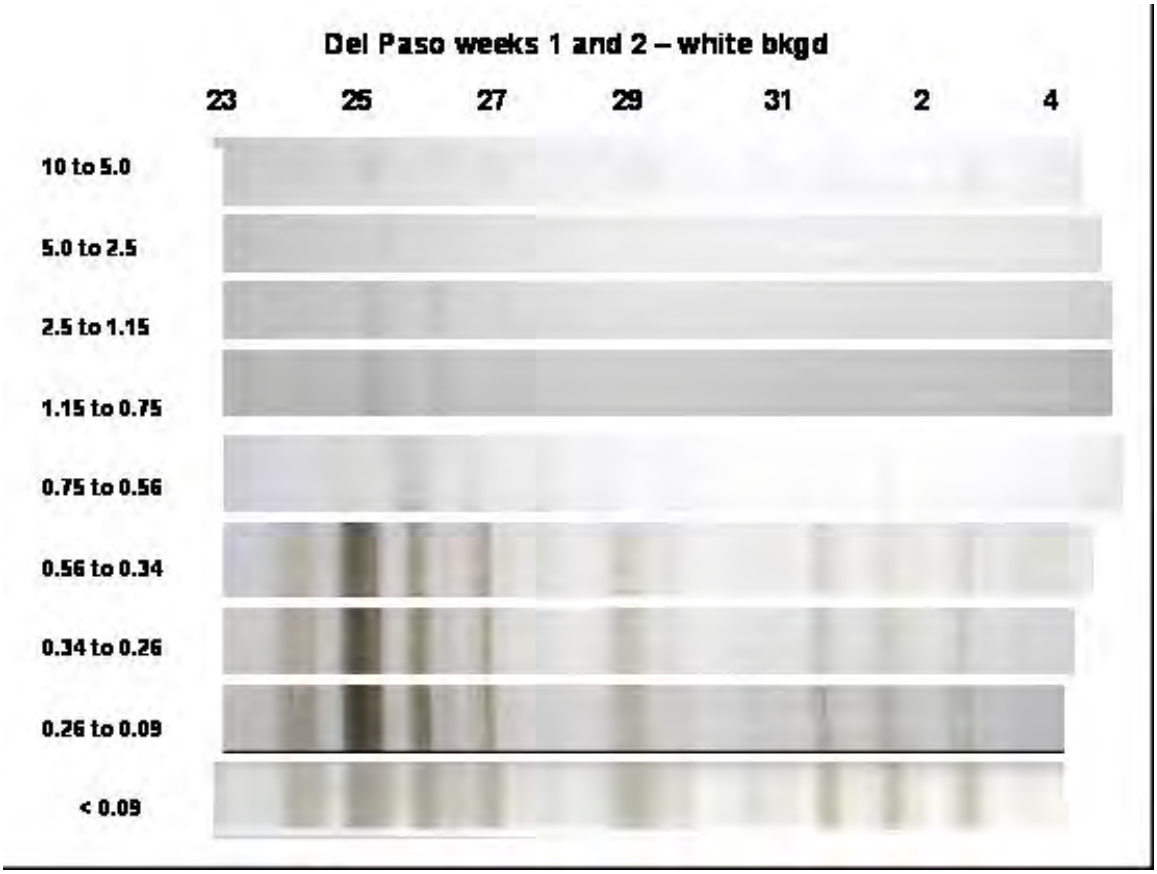


Figure 20. Photographs of DRUM sampler impaction strips in true color.

Photographs are for the December 22, 2009 – January 4, 2010 winter intensive, Phase 1. The intense black deposit starts in the evening on December 24 and continues until the morning of December 25.

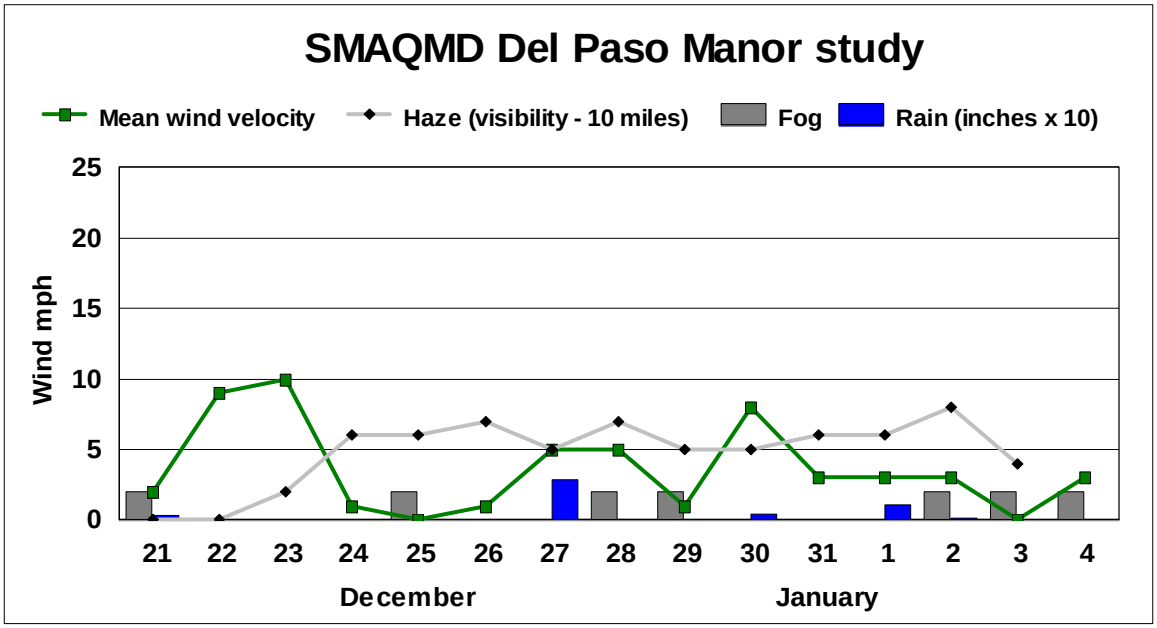


Figure 21. Meteorology during the Phase I intensive, December 22, 2009 – January 4, 2010, as measured at Sacramento International Airport (KSMF). Since this airport is near the valley floor (27 feet elevation), it will not likely experience subsidence winds. Del Paso Manor (84 feet elevation) lies on a slope down from the foothills, and likely experiences light nocturnal downslope winds from the Sierras.

One hour $PM_{2.5}$ data give details of the mass event. It is interesting to note that while on most occasions 13th and T Street tracks Del Paso Manor, on Dec. 24 at 13th and T Street the $PM_{2.5}$ level was only 24.3 $\mu g/m^3$, which would have been within the Permissive Burn category, <25 $\mu g/m^3$.

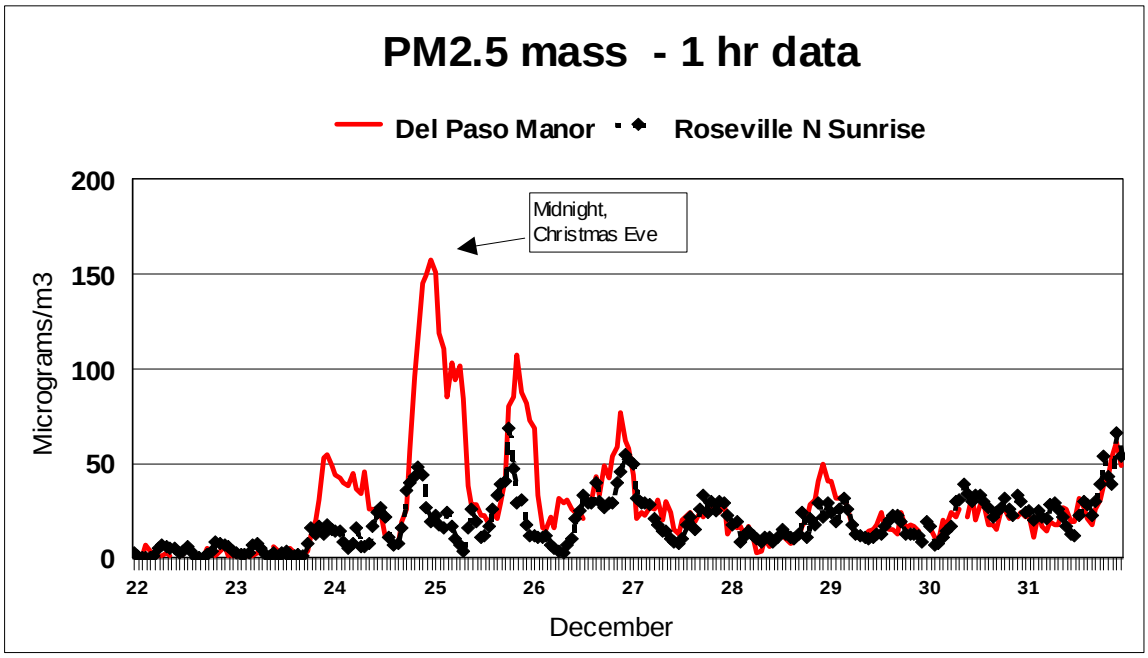


Figure 22. Hourly $PM_{2.5}$ mass at Del Paso Manor and Roseville-N. Sunrise during the Phase I intensive

Both carbon monoxide and oxides of nitrogen are generated during wood burning, although many other sources exist for both species. In terms of the emission estimates, wood burning contributes 11.3% of all carbon monoxide, 3.9% of NO, versus 35.7% of $PM_{2.5}$ mass (www.arb.ca.gov).

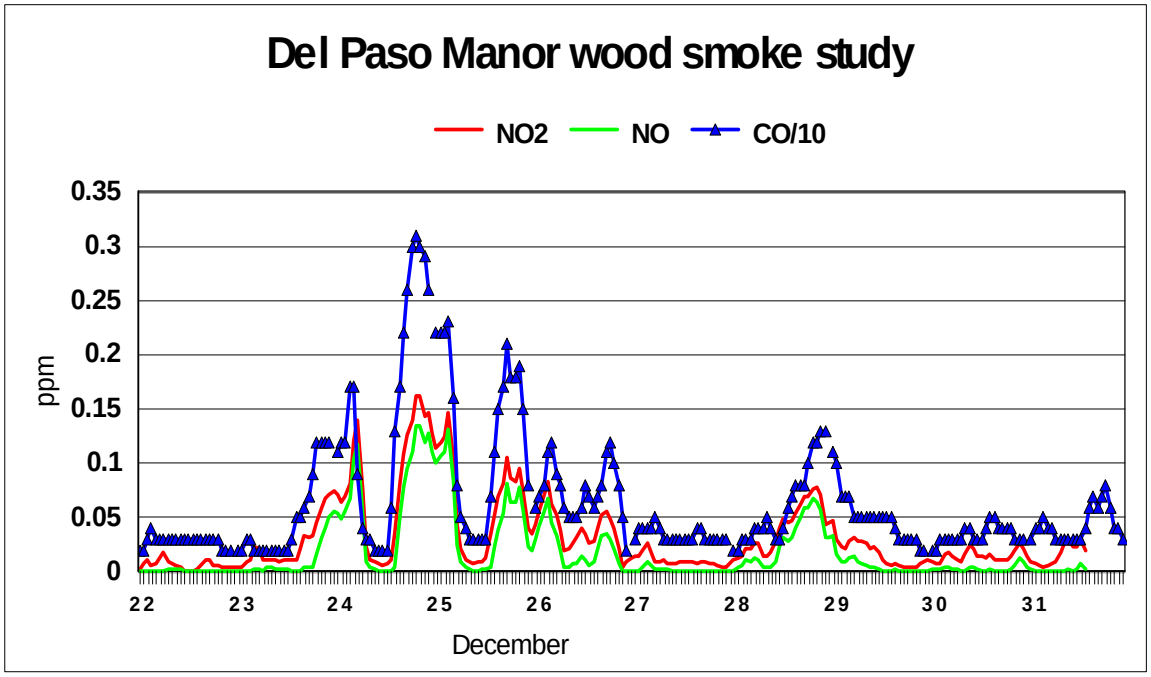


Figure 23. Comparison of carbon monoxide, divided by 10, and oxides of nitrogen seen at Del Paso Manor during the Phase I intensive.

The CO to NO ratio from the emission inventory of Sacramento County is roughly 12.5 to 1 (Table 1), so the ratio on the evening of December 24, 22.5 to 1, is CO rich. This may be a reflection of the trajectory analysis (below) that shows that the trajectories on December 24 came from the northeast, down I-80 and across Roseville, before reaching Del Paso Manor.

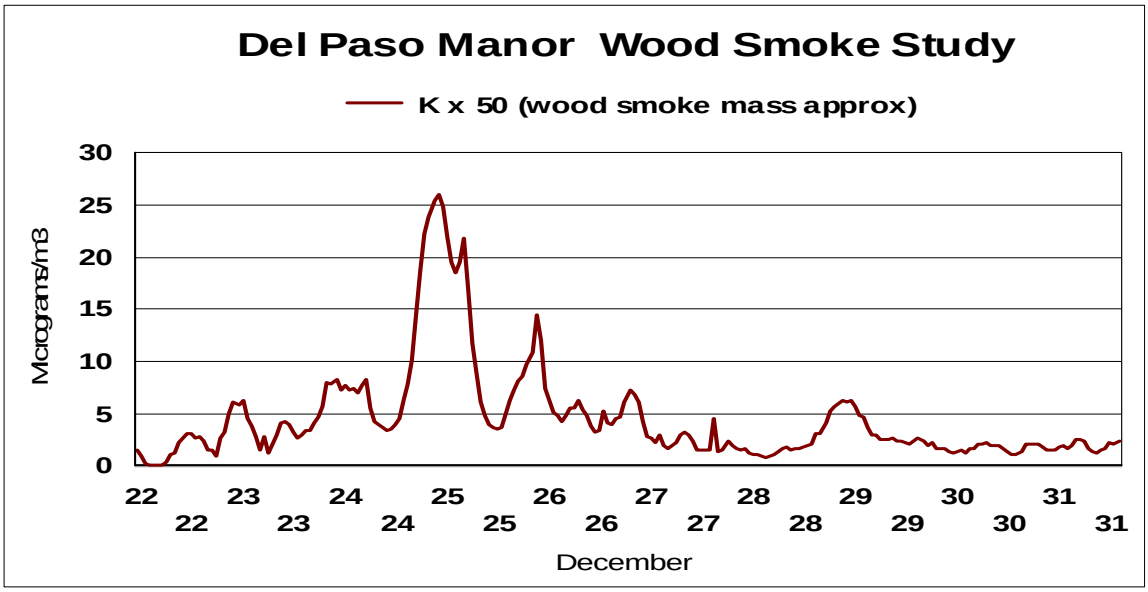


Figure 24. The fine potassium wood tracer at Del Paso Manor, using the same 50 to 1 scaling factor to fine mass from the STN data (Figure 15). Note that the wood smoke was only about 16% of the total mass at midnight, Christmas Eve.

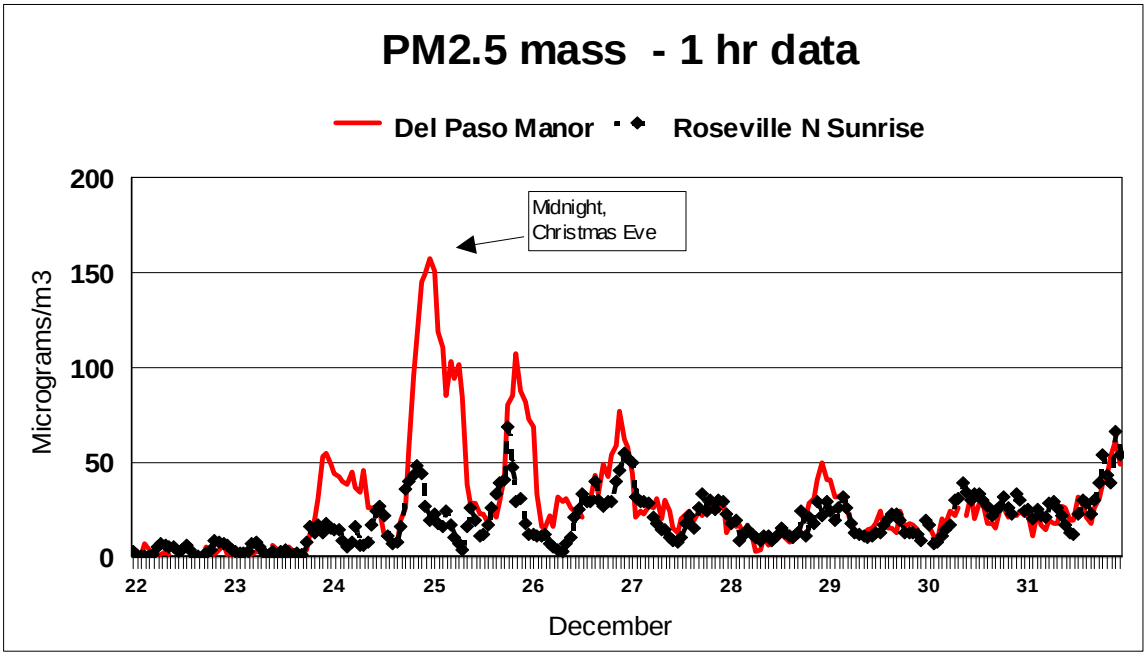


Figure 25. PM2.5 mass (1-hr data)

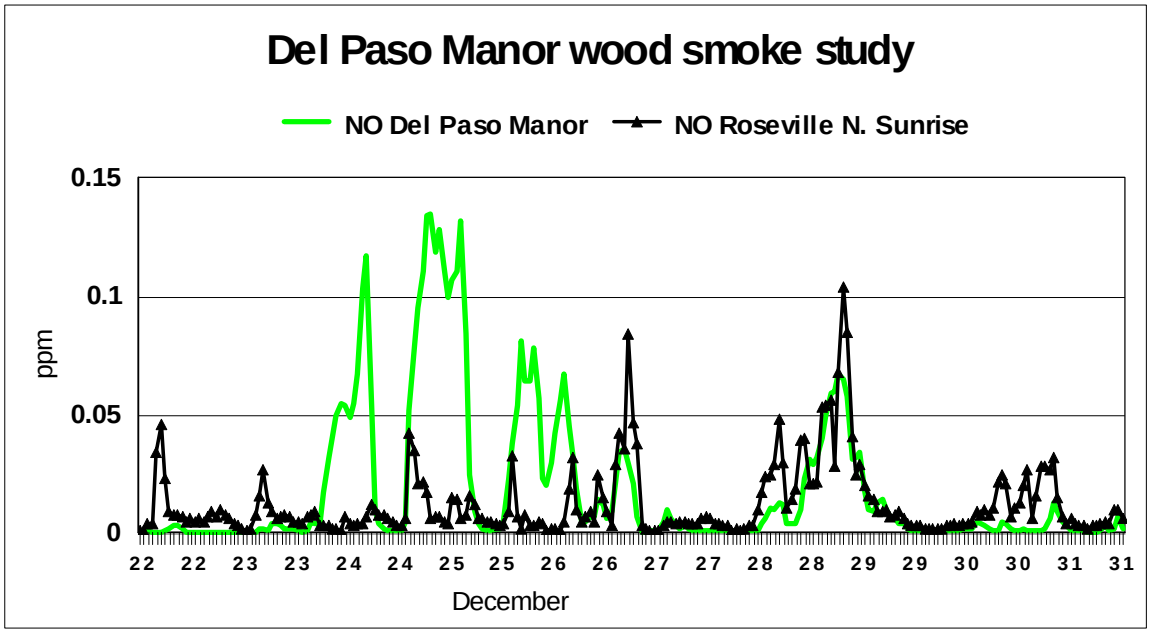
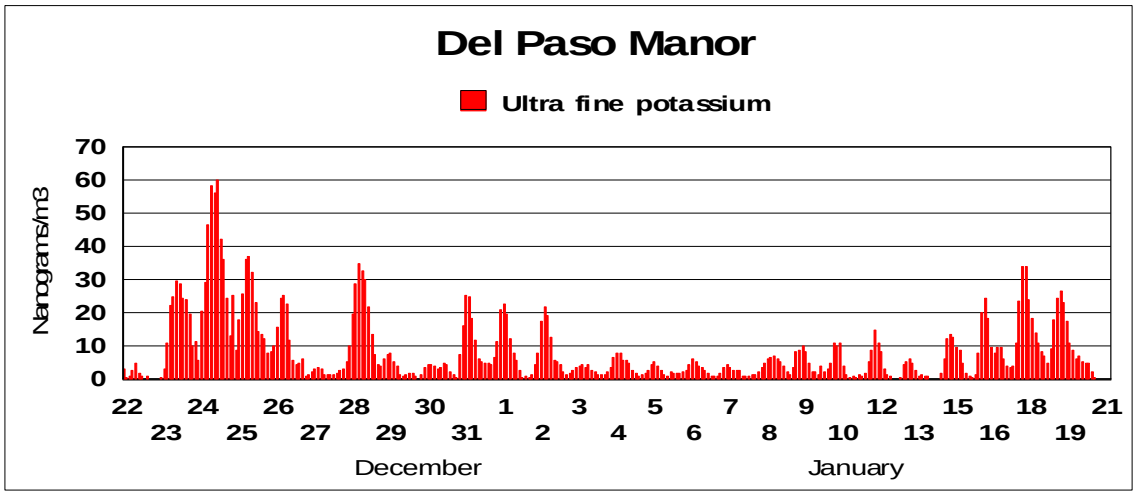
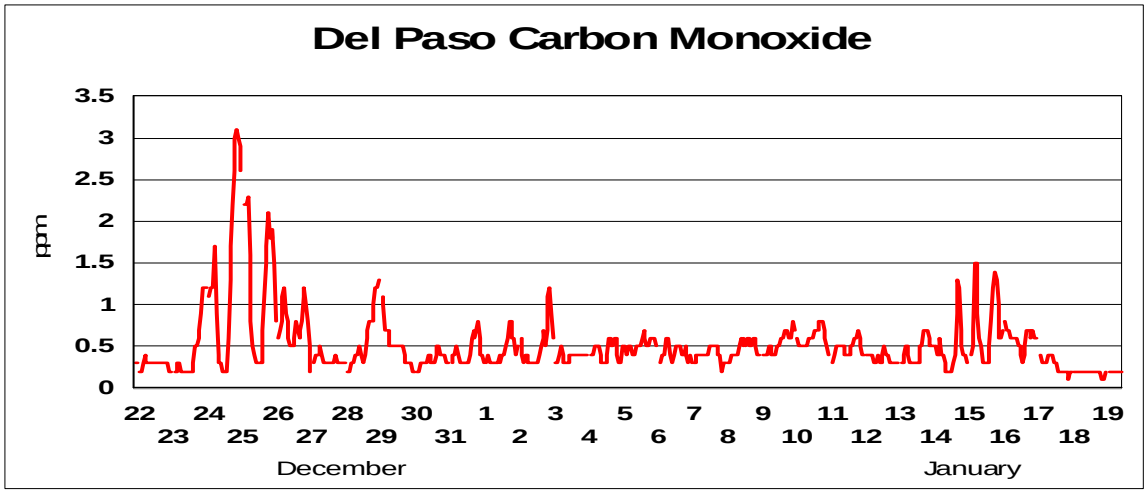


Figure 26. $PM_{2.5}$ mass, plus NO comparisons, Del Paso Manor versus Roseville

The ability of the DELTA Group to do mass and elemental composition of ultra-fine particles added a unique aspect to the study. Ultrafine hydrophilic particles are very short lived in the atmosphere, so that ultrafine potassium smoke tracer must originate from nearby sources – a few hundred meters at most (Zhu et al. 2002).





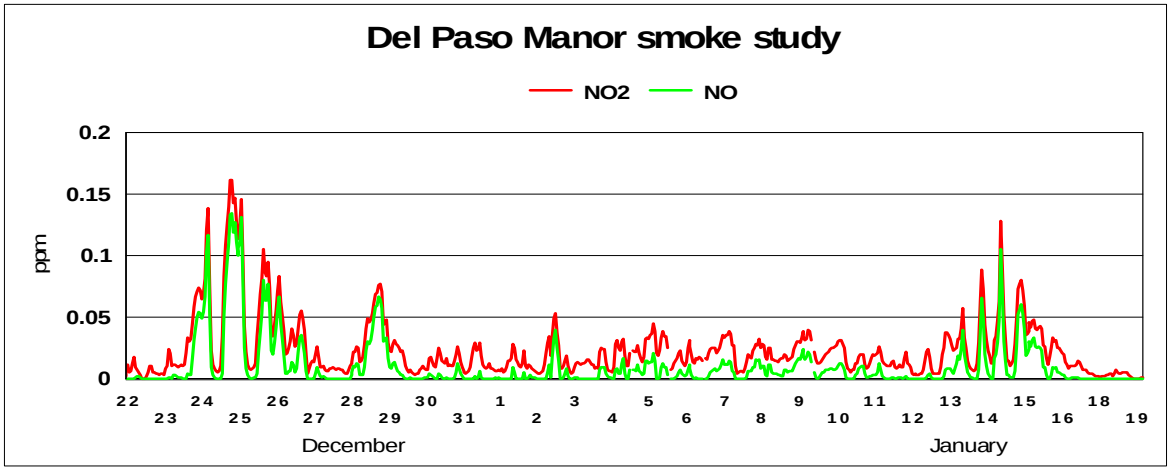
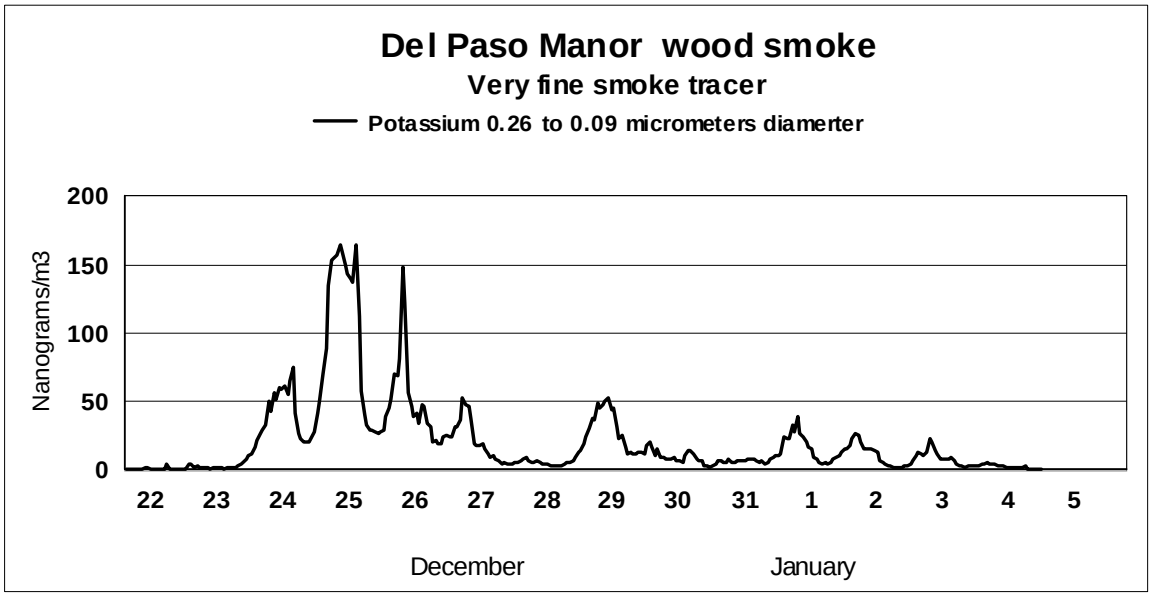


Figure 27 a,b,c. Ultrafine aerosols (true color, top strip) versus potassium (3-hr integration), plus hourly CO, NO, and NO_x



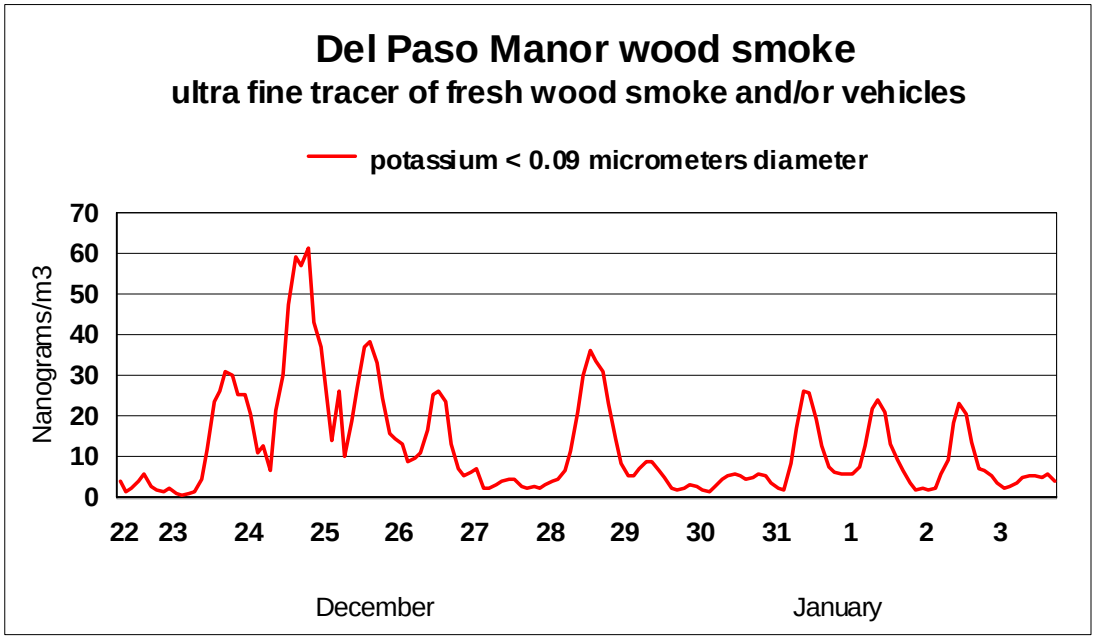


Figure 28 a, b. Very fine (0.26 to 0.09 μm, top) and ultrafine (< 0.09 μm, bottom) potassium, the latter a tracer of nearby smoke and/or vehicles.

The close association of ultrafine and very fine potassium, mass, and soot indicates sources near the Del Paso Manor site during this event. Larger particles tend to deposit and not travel as far (Bonanno, 2008).

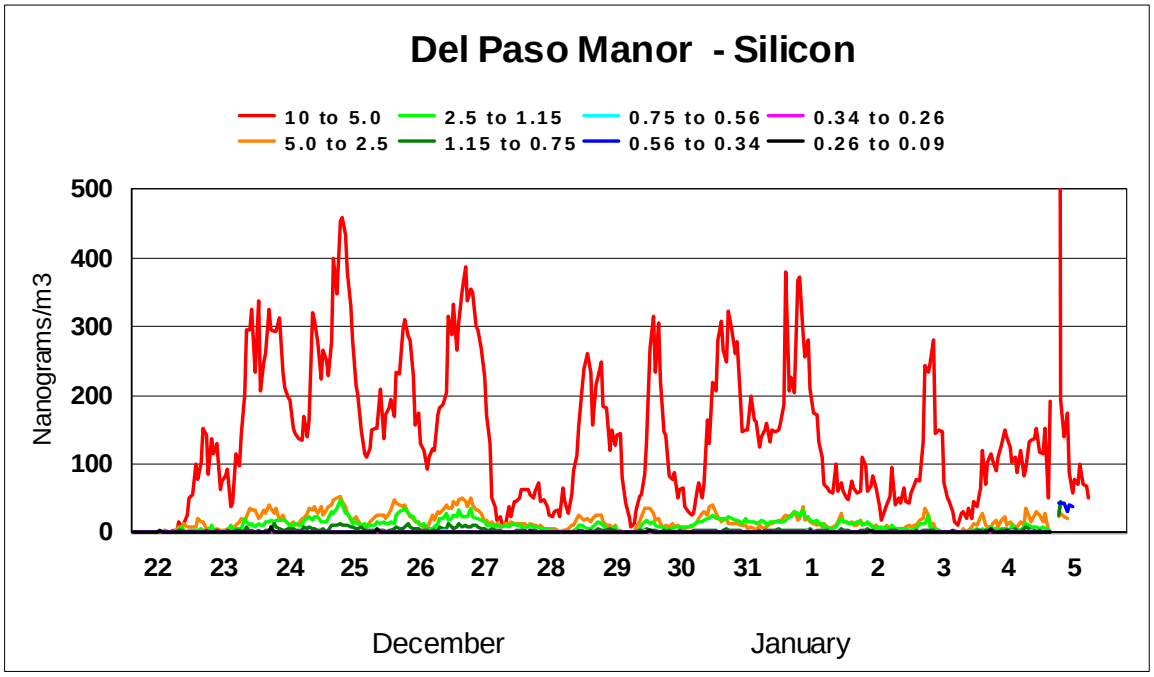


Figure 29. Silicon from soil at the Del Paso Manor site.

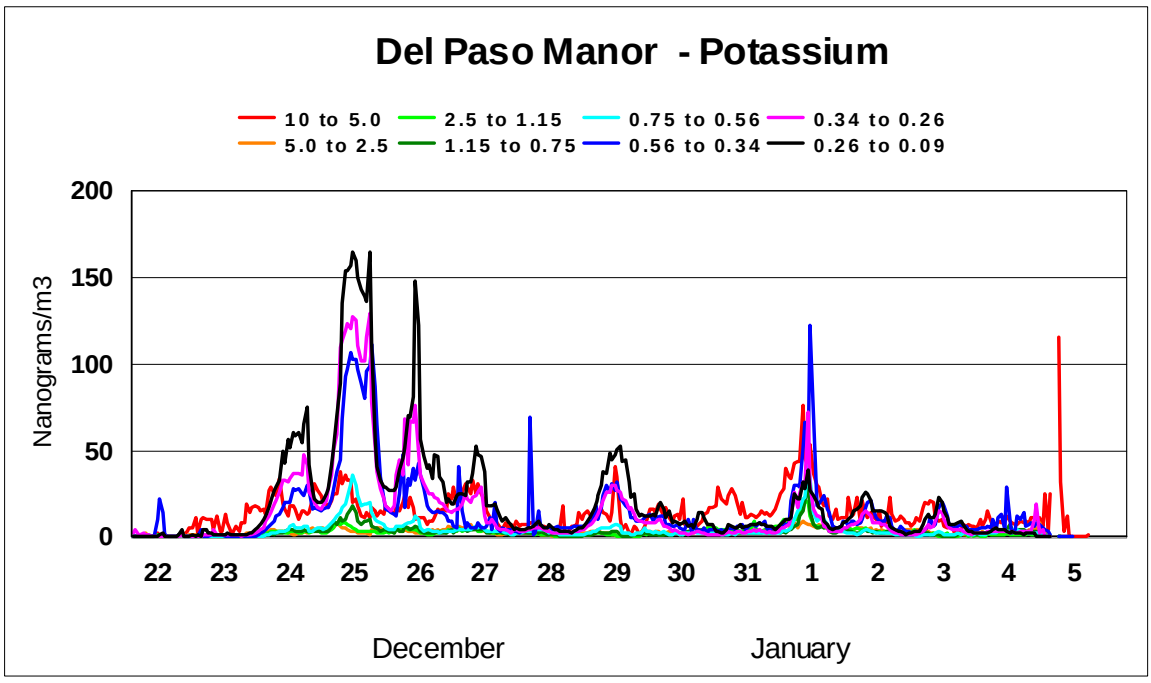


Figure 30. All potassium size modes, showing that interferences with fine soil (Figure 30), common in summer, are not important in the winter Phase I intensive.

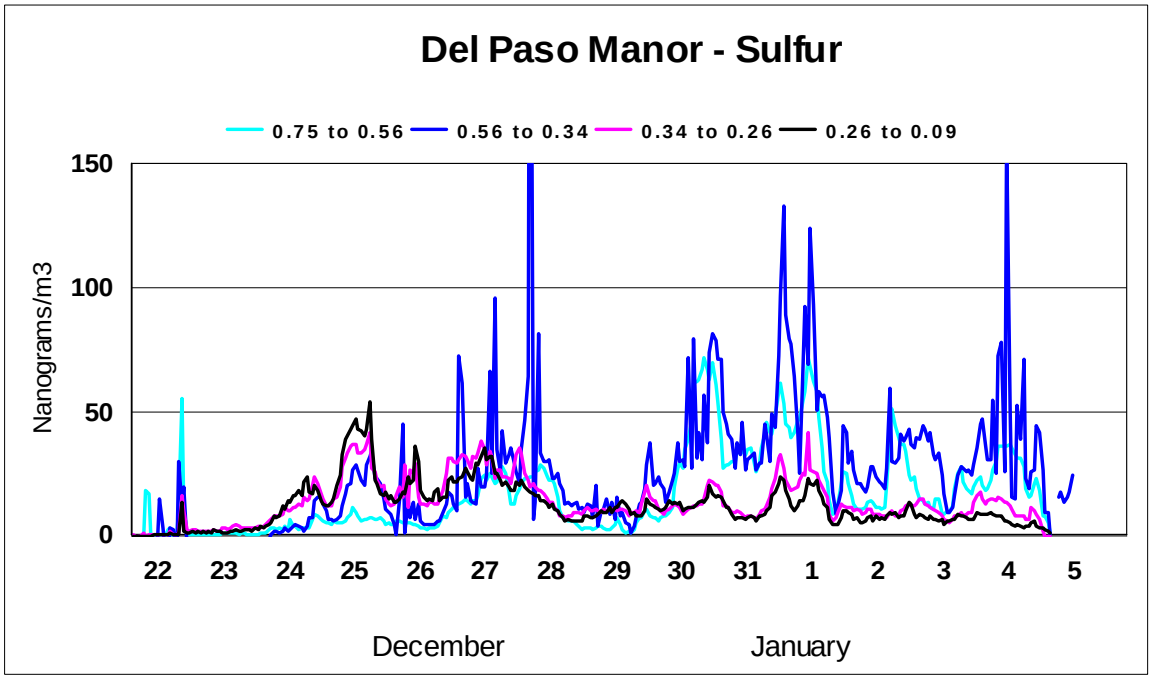


Figure 31. Sulfur was not a major component of the mass. The winter sulfur can have a Bay Area origin (high-sulfur ship fuel and refineries – see figure 53), as shown by the chlorine (Figure 36). For example, 70% of the emissions of sulfur dioxide in the South Coast Air Basin's port area come from ships (McCarthy, 2009). Ocean-going ships burn high-sulfur fuel oil at cruise, thereby emitting a relatively large amount of sulfur dioxide (ARB, 2011).

HYSPLIT trajectory analysis of pollution events

In order to identify the origins of the aerosols at Del Paso Manor, we used the NOAA READY trajectory model HYSPLIT (Draxler et al, 2010, Rolph, 2010). We ran the model in the backward mode with the Del Paso Manor site as the end point of the trajectories. We used isentropic trajectories based on the potential temperature to allow us to model vertical displacement.

The results are shown below in Figure 32, 33, 34, and 35, showing the direction and speed of the winds arriving at Del Paso Manor for December 24, 10 AM, 4 PM and 7 PM, and December 25, 2009, 4 AM. In the first 2, which correspond to relatively clean periods during the daylight hours on December 24, we modeled at a 500 m height.

The trajectories all came in from the northeast at moderate wind velocities. Each mark on the trajectory is 6 hr.

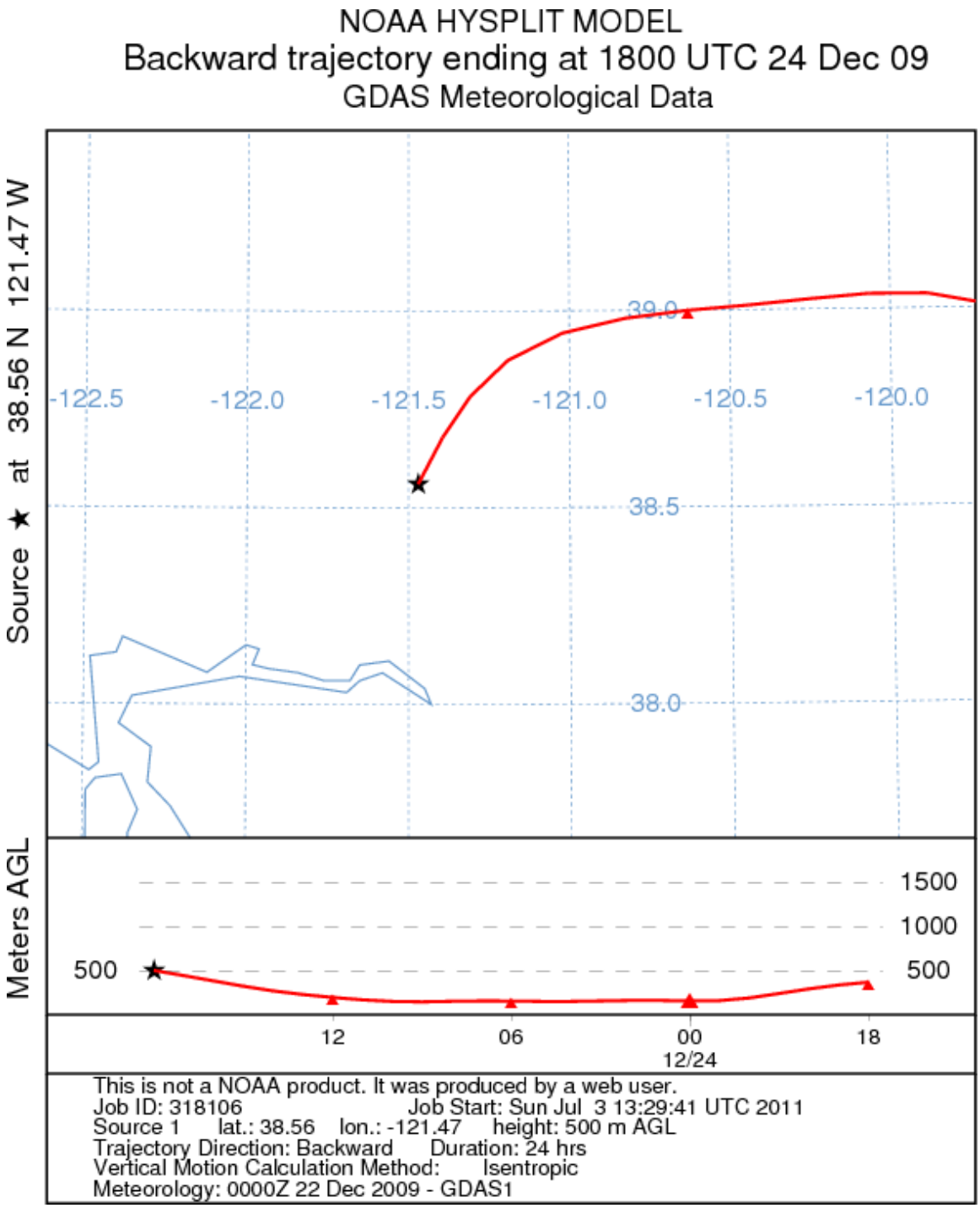


Figure 32. Trajectory analysis by HYSPLIT shows the direction of the winds arriving at Del Paso Manor for December 24, 10 AM

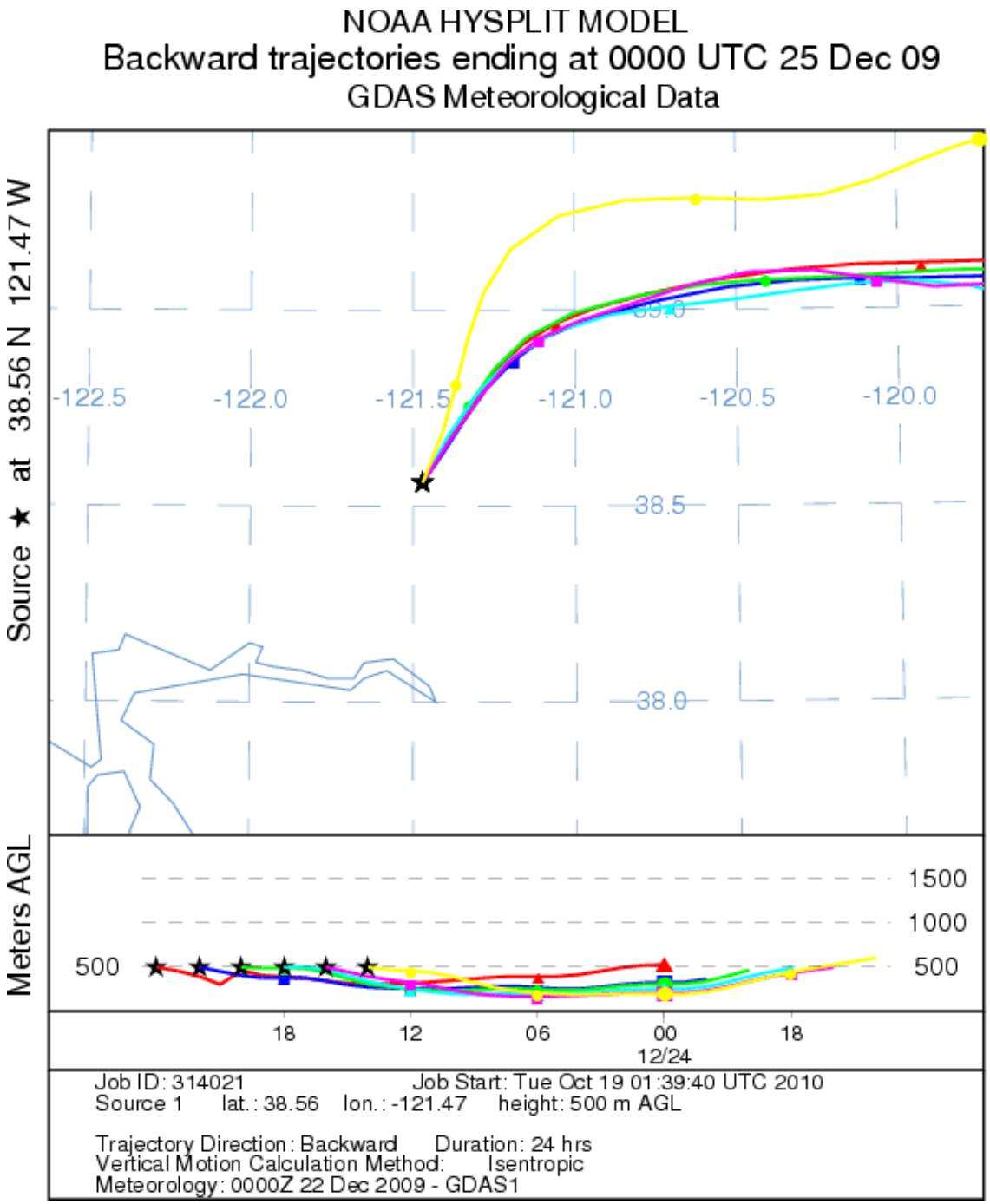


Figure 33. 4 PM December 24, and then every hour for 6 hours until 10 PM. The colors represent trajectories arriving at Del Paso Manor. The colors represent start times each displaced by 6 hr.

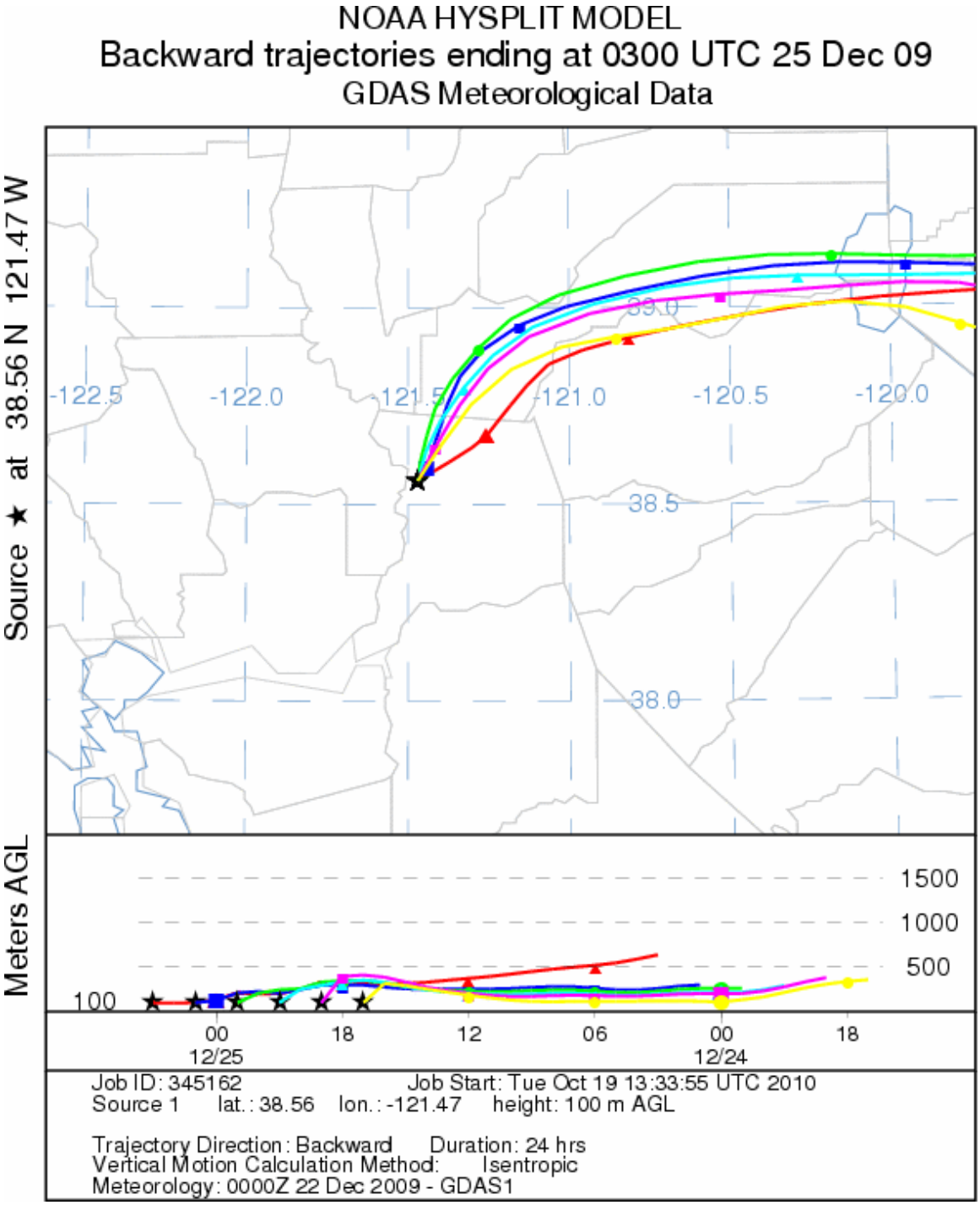


Figure 34. 7 PM December 24

At 7 PM, during a period of high mass loadings, the trajectories, now modeled at 100m height, show descending air masses and inversion conditions, as well as an abrupt reduction in wind velocity. The direction, however, remains from the northeast.

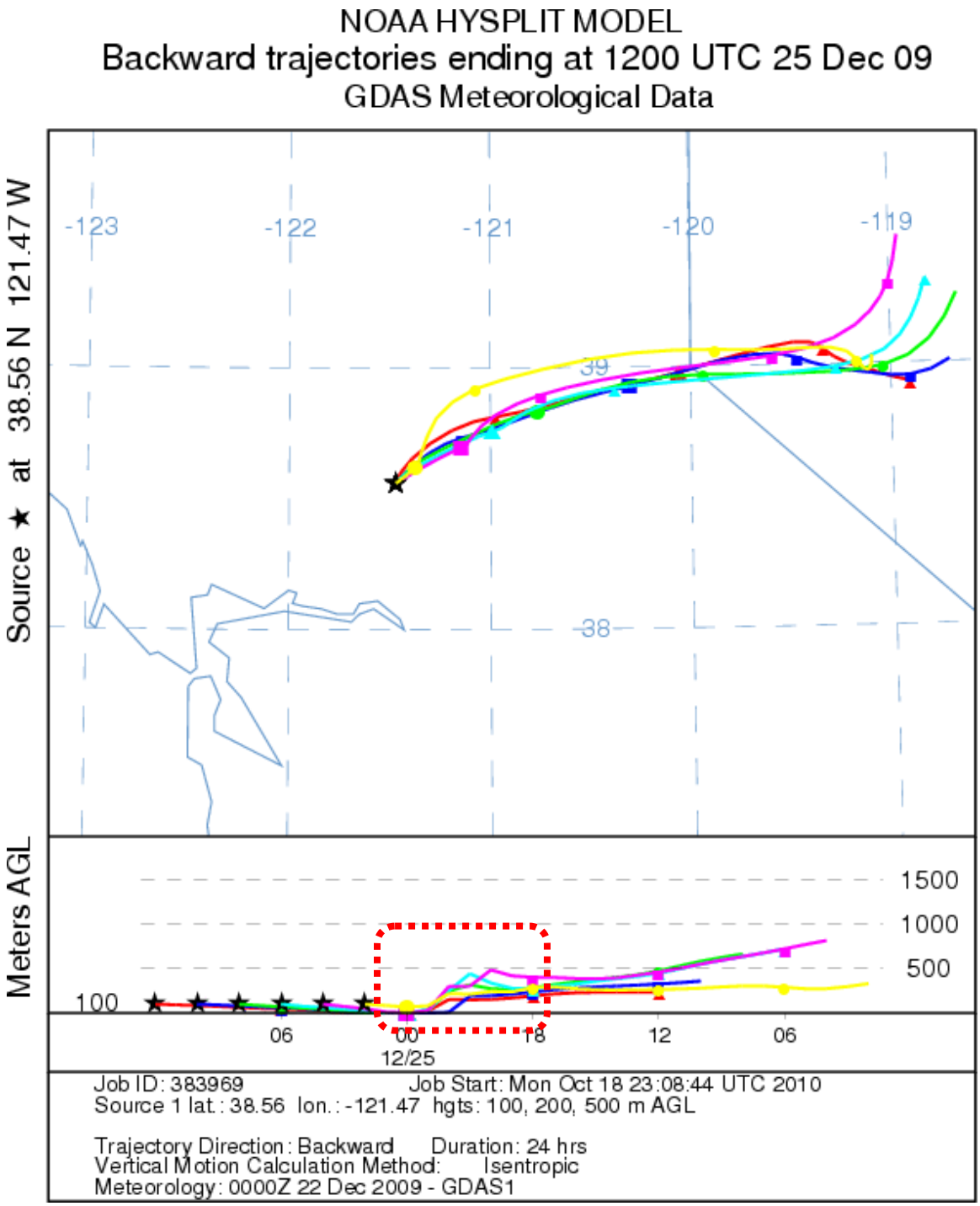


Figure 35. 4 AM December 25, 2009, during high mass loadings, again showing descending air masses and low wind velocities, on the order of a few miles per hour.

The collapse of the trajectories to the ground in the previous evening is shown in the dashed box, resulting in a very thin surface based inversion into which all emissions are trapped and enhanced, traffic, rail-yard, wood smoke, and others.

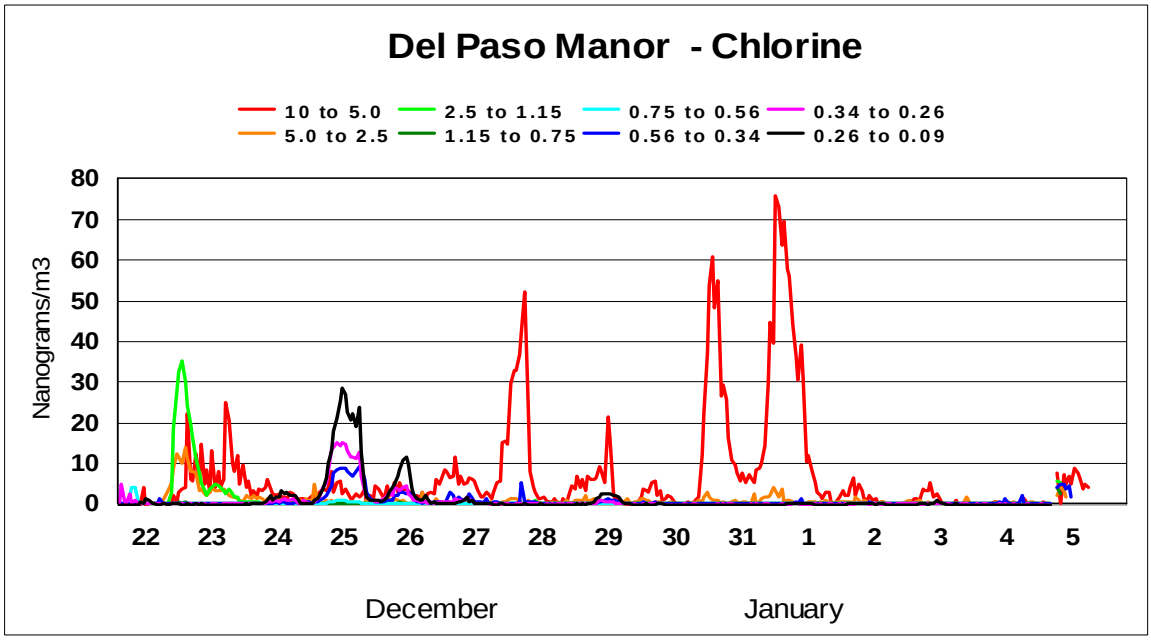


Figure 36. Chlorine during the winter intensive.

Coarse chlorine is usually associated with transported sea salt. Fine chlorine is a component of wood smoke, and tracks the smoke mass on the nights of Dec. 24, Dec. 25, and Dec. 26.

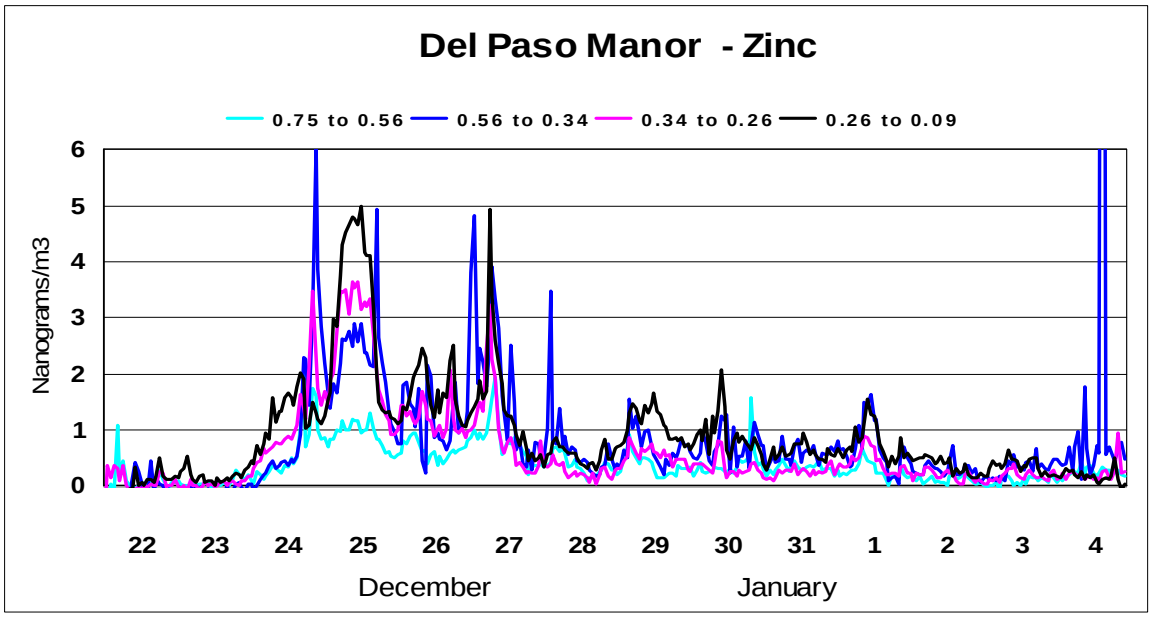


Figure 37. Fine zinc during the winter intensive

Fine zinc is usually associated with traffic due to the zinc thiophosphate additive in lubricating oils (Fujita, 2007). However, there are many other sources, and incinerators are a major source if uncontrolled.

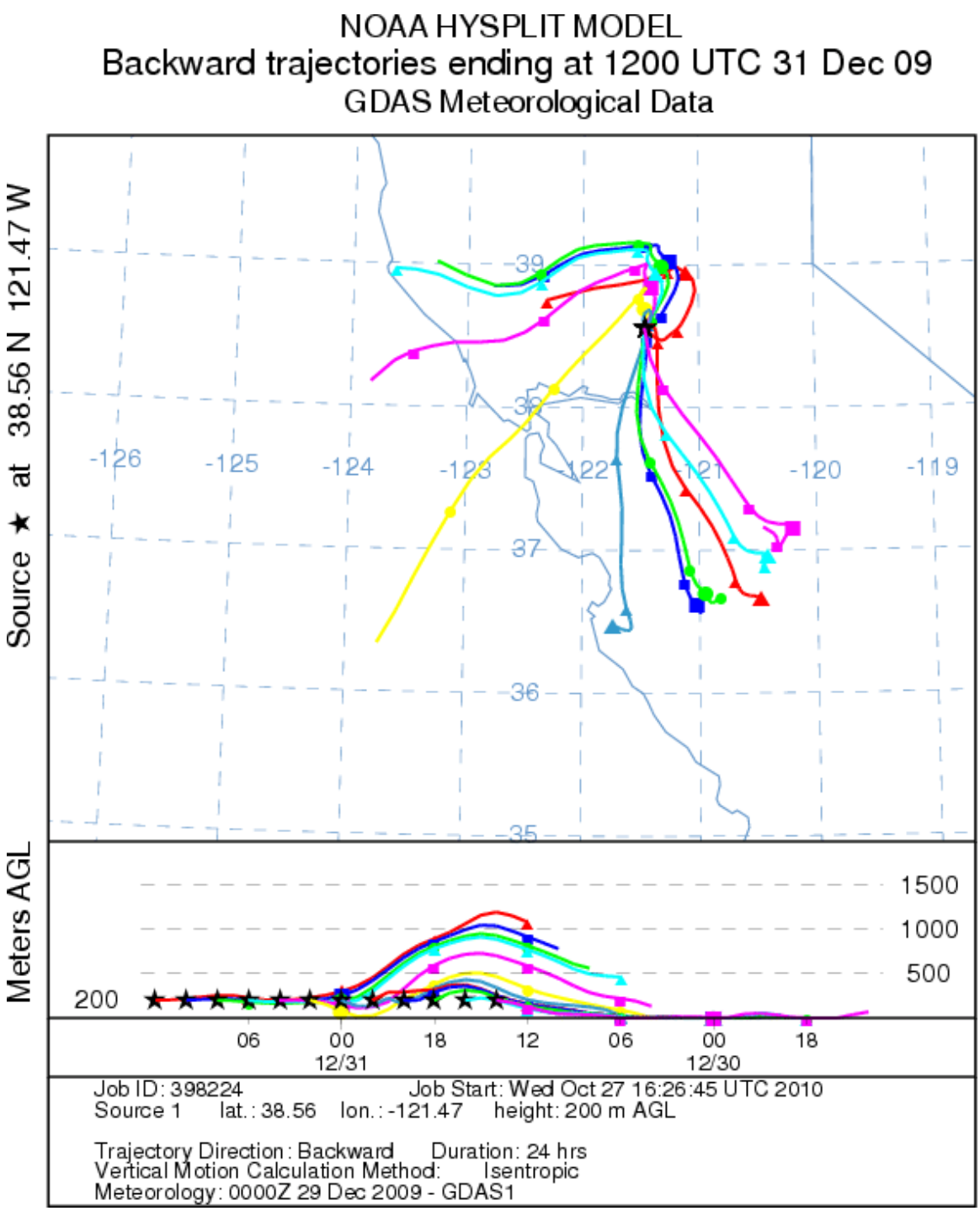


Figure 38. Trajectory analysis during the chlorine impact events, showing oceanic influences. 1200 UTC is 0400 Pacific Standard Time.

Note that on this day there was slight rainfall and no fog present in the Sacramento Valley.

Below we compare the other ultra-fine materials found at Del Paso Manor with prior work at non-near roadway impacted sites in Sacramento in winter.

Major	**µg/m3**	**µg/m3**	**µg/m3**		**ng/m3**	**ng/m3**	**ng/m3**	**ng/m3**
	Del Paso Manor	**Watt - 0.5 km**	**Sac. Center**		**Del Paso Manor**	**Watt – 0.5 km**	**Watt + 15 m**	**Sac. Center**
		filter	**filter**	**P**	0.2	1.1	**1.0**	2.4
Mass (gr.)	na	na	2.04	V	0.00	0.06	0.18	0.15
Mass (rec.)	na	na	2.15	Cr	0.01	2.2	1.3	0.45
Elemental	na	na	na	**Fe (n-s)**	**0.5**	**5.2**	**34.9**	**17.0**
H (org.)	na	na	1.72	**Ni**	**0.04**	**0.3**	**16.3**	**3.5**
Diesel	na	na	na	**Cu**	**0.05**	**0.1**	**9.8**	**8.3**
Ammon. Sulfate	0.045	0.09	0.34	**Zn**	**0.45**	**1.2**	**17.3**	**11.5**
Salt	0.00	0.00	0.04	As	0.03	0.16	0.46	0.6
Soil	0.054	0.04	0.048	Se	0.13	0.10	0.13	0.3
K (n-s)	0.009	0.011	0.053	Br	1.3	0.8	1.1	3.7

Table 3. Measured and reconstructed ultra-fine mass and elemental components in 2 studies in Sacramento, 2007. “Watt - 0.5 km” is a residential area with heavy wood smoke. The bold values represent verified traffic derived aerosols near a stop light. In this size mode, the non-soil potassium has many potential sources, including vehicles and very fresh wood smoke.

“Watt - 0.5 km” is 500 m upwind, “Watt + 15 m” is downwind from the road edge. “Sac. Center” is the ARB 13th and T Street site. Iron (ns) is non-soil iron corrected via known soil components. There are no elemental carbon data, so the reconstructed mass is incomplete. The Del Paso Manor results show low levels of metallic aerosols from vehicular aerosols (noted by the bold numbers) as might be expected from a site so far from major roadways.

The aethalometer data shows a strong enhancement of soot every evening, but the low levels after midnight are not in accord with other optical data.

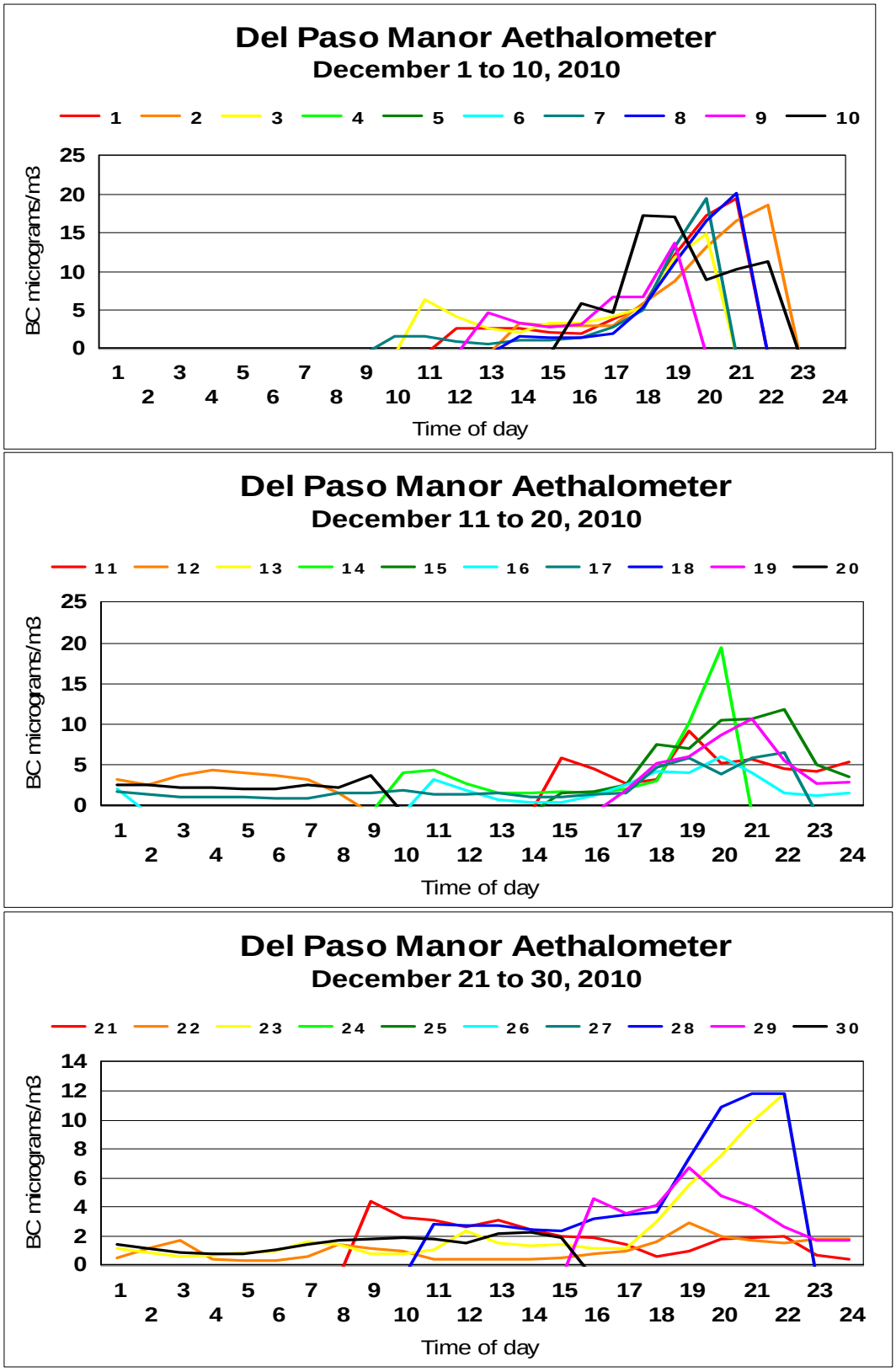


Figure 39 a, b, and c. Aethalometer data on optical absorption converted to black carbon (BC) mass. Data from December 24 through December 27 are absent from the record.

Optical analysis by optical spectroscopy

The 1-hour time resolution DRUM strips collected at Del Paso Manor (December 22, 2009-January 4, 2010) were analyzed using transmission spectrometry. Attenuation measurements were made by placing the Mylar strips between a tungsten-halogen-deuterium light source and a CCD spectrometer. The light from the lamp is directed onto the surface of the sample by a bare 0.3 mm optical fiber. The transmitted light is collected by a collimating lens that is attached to a second fiber. This fiber brings the light to the entrance slit of the spectrometer. The spectrometer separates the light into 2048 bins between 190 nm and 900 nm. The system has a usable spectral range from about 350 nm to 800 nm. Each strip was processed twice, once using the halogen lamp and once using the deuterium lamp. This allows optimization of the light intensity in different regions of the spectrum. The precision of these measurements was estimated to be 2%-5% by comparing the attenuation measurements by the two lamps in regions that both lamps produce significant flux.

The attenuation coefficient is defined by the formula:

$$\alpha(\lambda) = -\log_{10}\frac{I(\lambda)}{I_0(\lambda)},$$

where α is the attenuation coefficient, λ is the wavelengths, I is the intensity of the light through the sample, and I_0 is the intensity of the light through clean Mylar. Note that as defined the coefficient is dimensionless. It will ultimately have dimensions of m^{-1} when related to a physical quantity.

The relative attenuation of the light is caused by scattering and absorption by the sample. At 880 nm, black carbon is about 10,000 times more absorptive than any other species commonly found in aerosols. In the visible spectral region some minerals, in particular hematite, can contribute measurably to the absorption, and in the ultraviolet region some organic compounds can also affect the measured absorption. In general, black carbon dominates the optical attenuation when present in the sample, and spectral differences between samples indicate changes in the chemical composition of the collected particles.

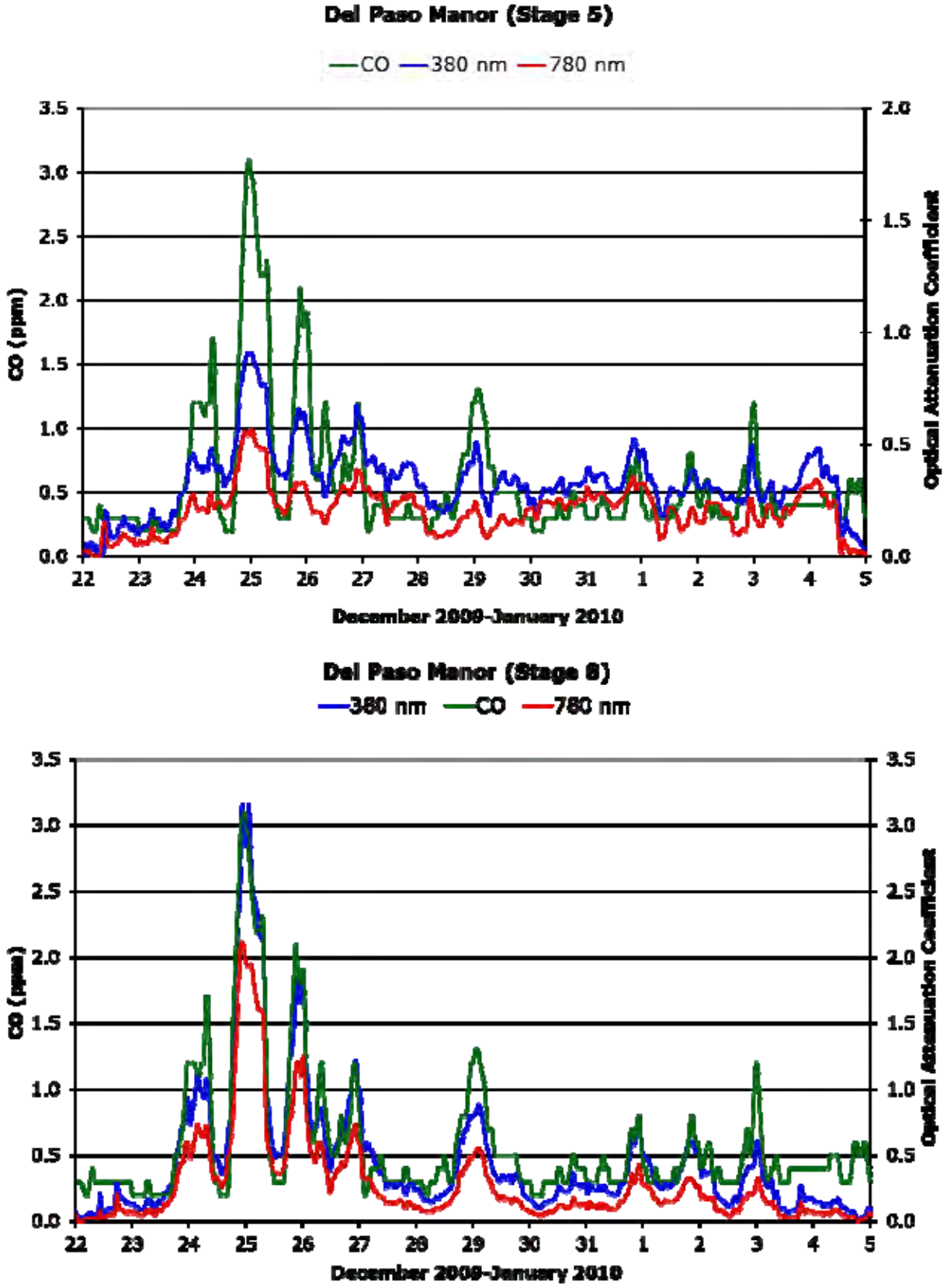


Figure 40 a,b. Relative optical attenuation at 380 nm and 780 nm for stages 5 and 8 compared with the concentration of carbon monoxide. The 380 nm data reflect wood and diesel sources, while the 780 nm data is mostly diesel exhaust. (Cahill et al, 2011 c)

As can be seen in Figure 40, the optical attenuation for stages 5 and 8 has a strong correlation with the concentration of carbon monoxide. Differences in relative heights of the CO and attenuation curves on the 25th, 26th and 29th, when compared to 27th and 3rd are strong indications of different source profiles.

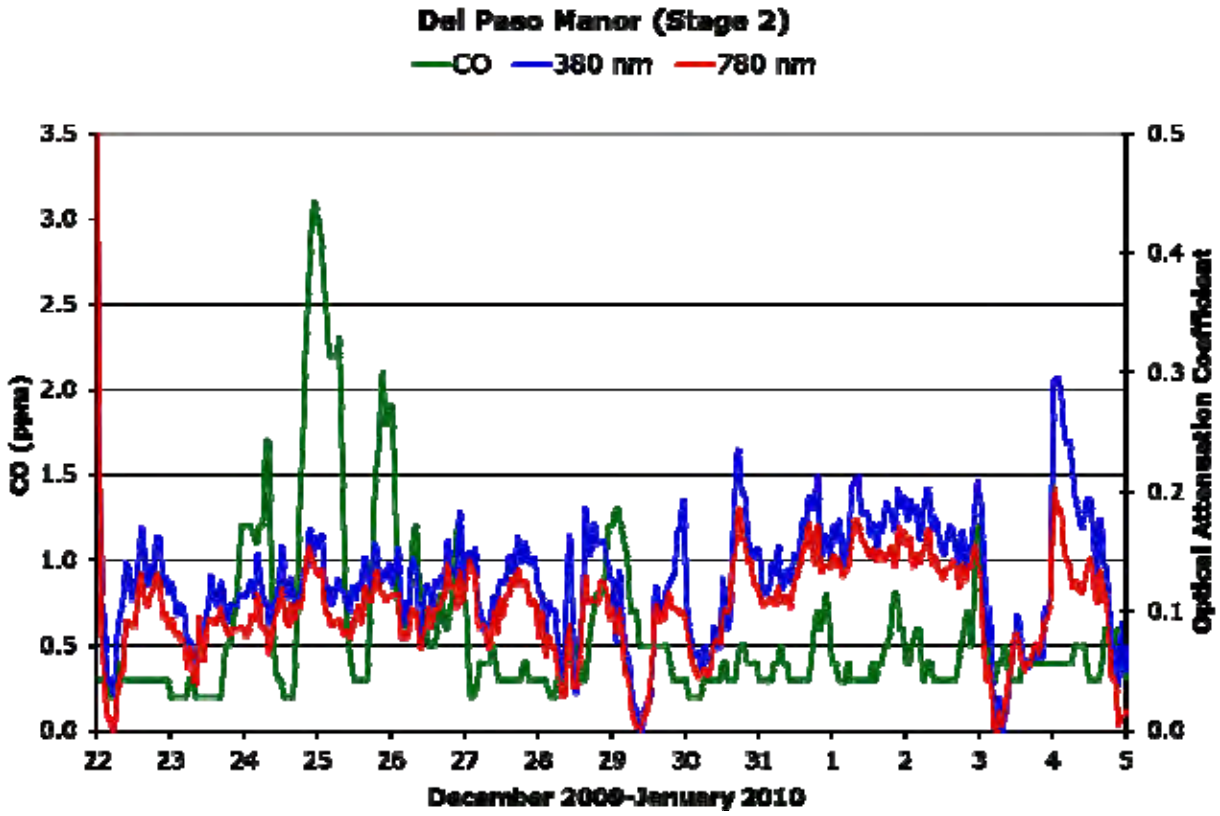


Figure 41. Relative optical attenuation at 380 nm and 780 nm for stage 2 compared with the concentration of carbon monoxide.

It is useful to compare the specific attenuation (attenuation per unit mass) of particles on different stages. As can be seen in Figure 42, the highest mass loading on stage 8 is approximately 35 $\mu g/m^3$. This compares with the highest mass loading on stage 4 of 14 $\mu g/m^3$, a factor of 2.5 less. Making a similar comparison of the attenuation coefficients we find the highest value for stage 8 is about 3.5, and the highest value for stage 4 is about 0.5, which translates to 1000 times greater attenuation on stage 8 than stage 4. Combustion products have been found primarily on stages 6-8 and the after-filter (Zielinska et al, 2003). This is not surprising, since black carbon (a major combustion product) is several orders of magnitude more absorptive than any other species commonly found in aerosols.

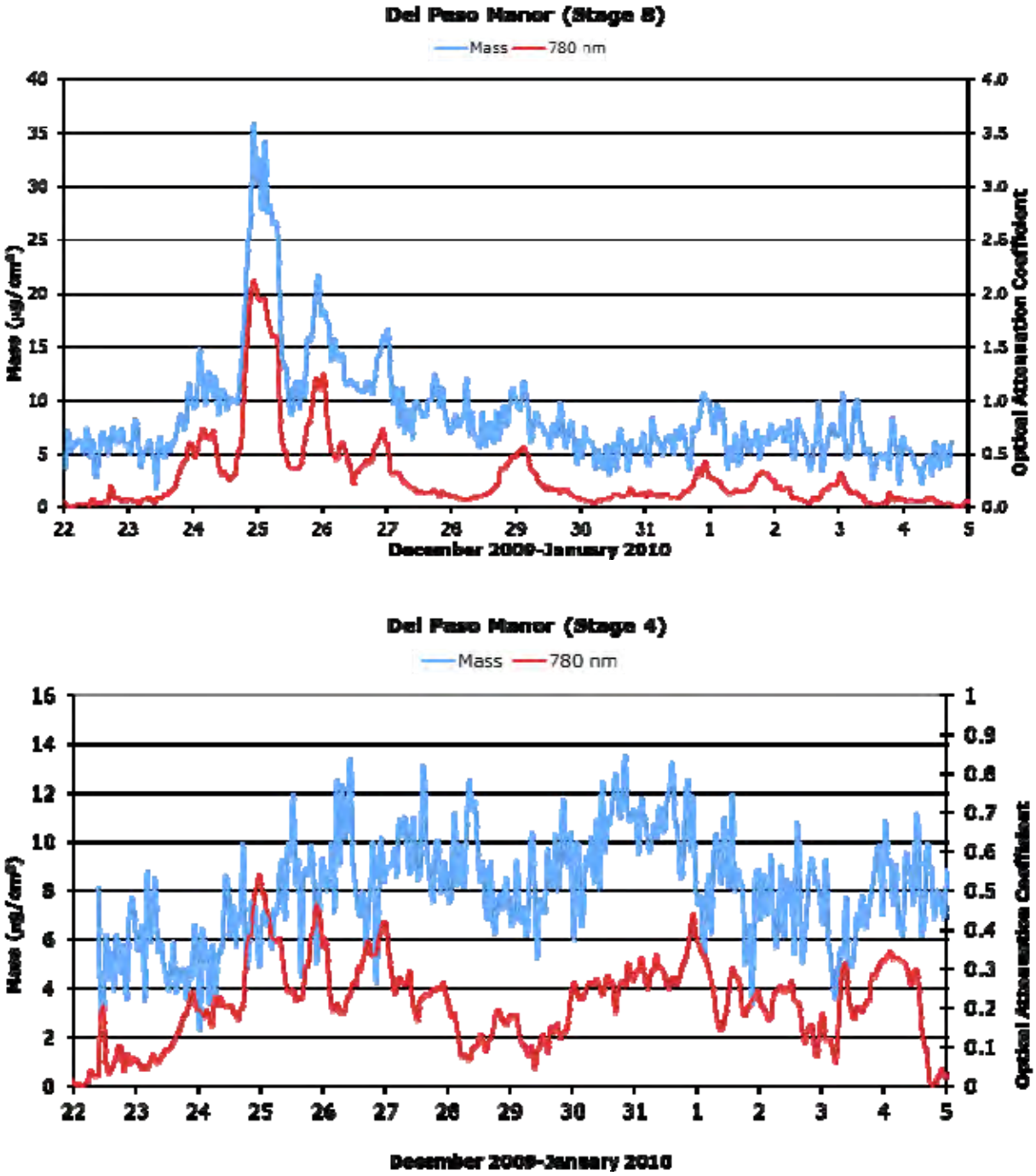


Figure 42 a,b. Mass and the attenuation coefficient at 780 nm are shown for stages 4 and 8. A comparison shows a much higher specific attenuation for the EC dominated stage 8 than for stage 4.

To further explore how well the optical attenuation coefficient tracks the black carbon we compared the EC measurements by thermal optical reflectance (TOR) to our measured optical absorption coefficients for the same days. Twenty-four hour integrated samples of elemental carbon were measured on December 24, 27 and 31. Since most of the EC should be in the size modes collected on stages 5-8, and the optical attenuation coefficients should be additive, we summed the coefficients for the 24 1-hour period on each of these dates and made a scatter graph of them with the EC-TOR measurements (figure 43). The three points generated a line with an R^2 of 0.996.

This is suggestive that the attenuation coefficient will be able to be used as a surrogate for EC measurements. However, we need to collect significantly more data at multiple types of sites before a strong conclusion can be made or a calibration curve can be generated.

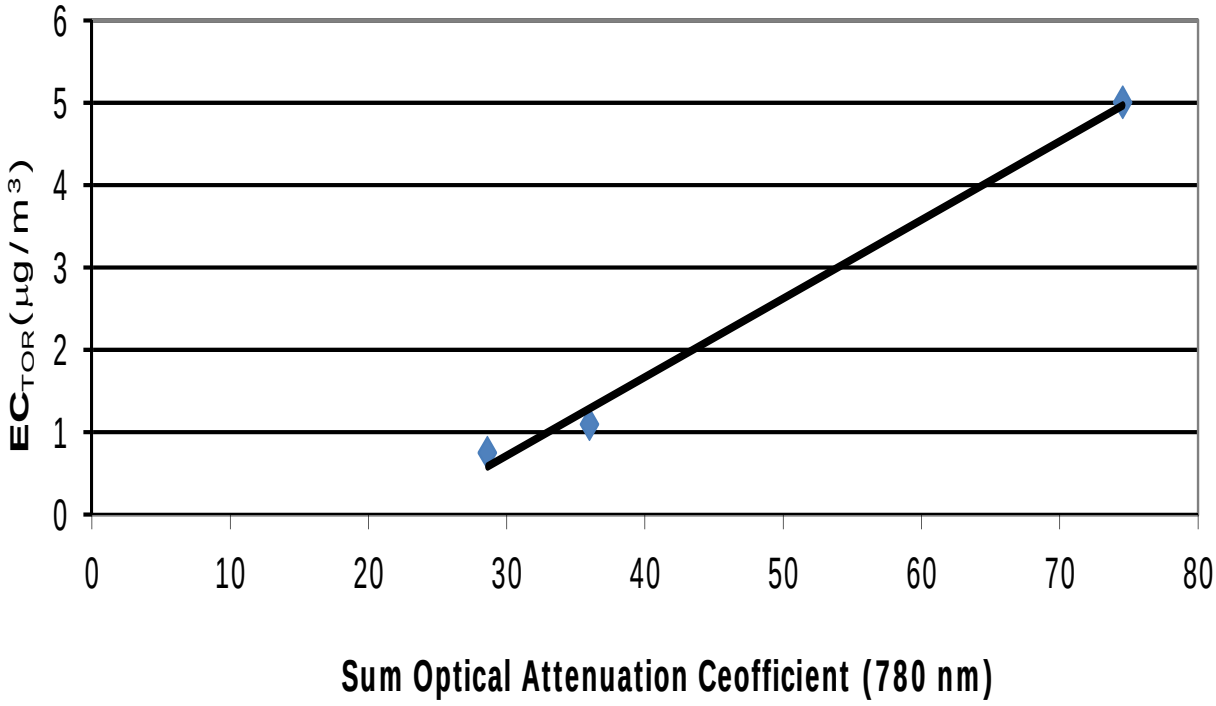


Figure 43. Comparison of the integrated elemental carbon and attenuation coefficients for 24 hour periods on December 24, 27 and 30.

It should be noted that there appears to be a systematic error shifting the attenuation measurements to the right. This is likely caused by attenuation due to scattering causing a higher level of attenuation that would be accounted for from absorption by black carbon.

Del Paso manor – winter intensive – Phase 2

January 4, 2010 – January 19, 2010

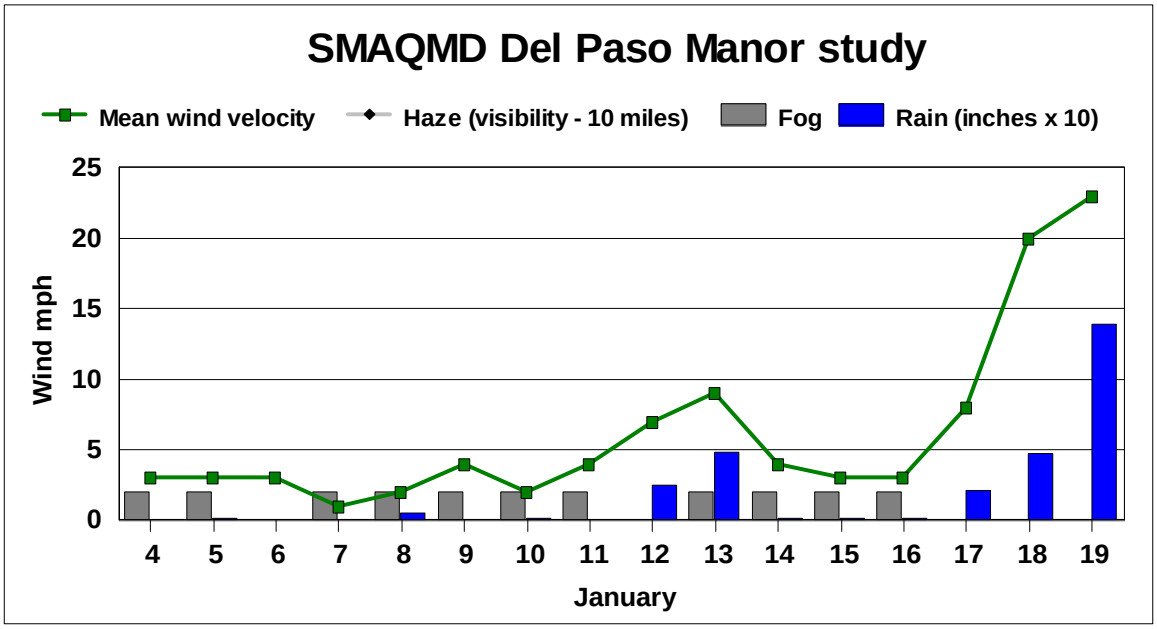


Figure 44. Meteorology at KSMF for January, 2010. Phase II was terminated on January 19 at the start of a heavy rain event.

The period from January 3, Stage 1, “No Burning unless Exempt”, and January 4 through 9, Stage 2, “All Burning Prohibited”, was characterized by low wind velocities and nightly fog events.

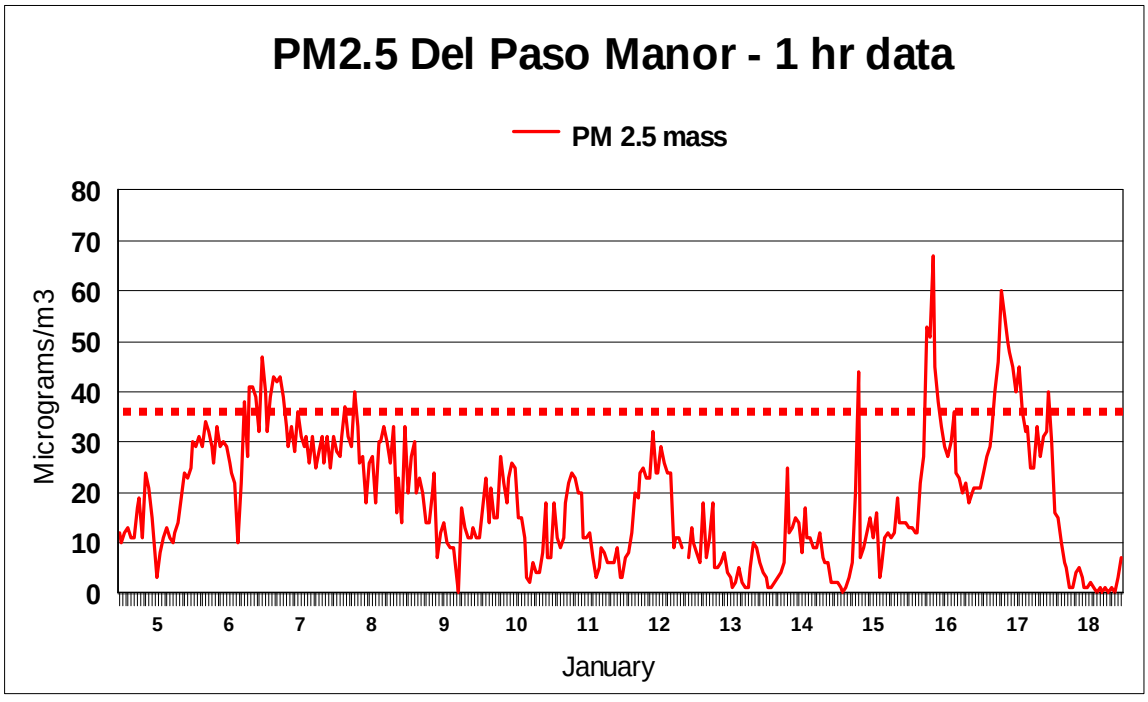


Figure 45. Hourly $PM_{2.5}$ mass values during the Phase II intensive

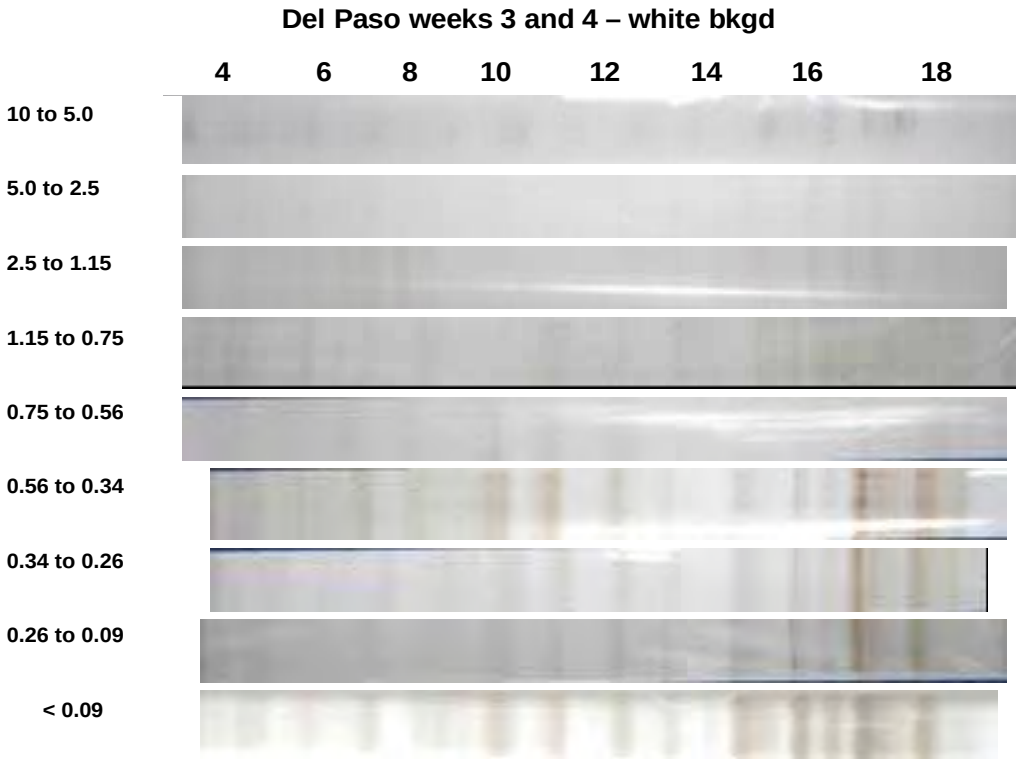


Figure 46. True color pictures of aerosols deposited in the 2nd 2 week intensive.

However, despite the unfavorable meteorology, the $PM_{2.5}$ mass levels are much less than during the Phase I intensive. Further, unlike Phase I, the close association of mass with gaseous pollutants is largely absent for the first half of the Phase II intensive.

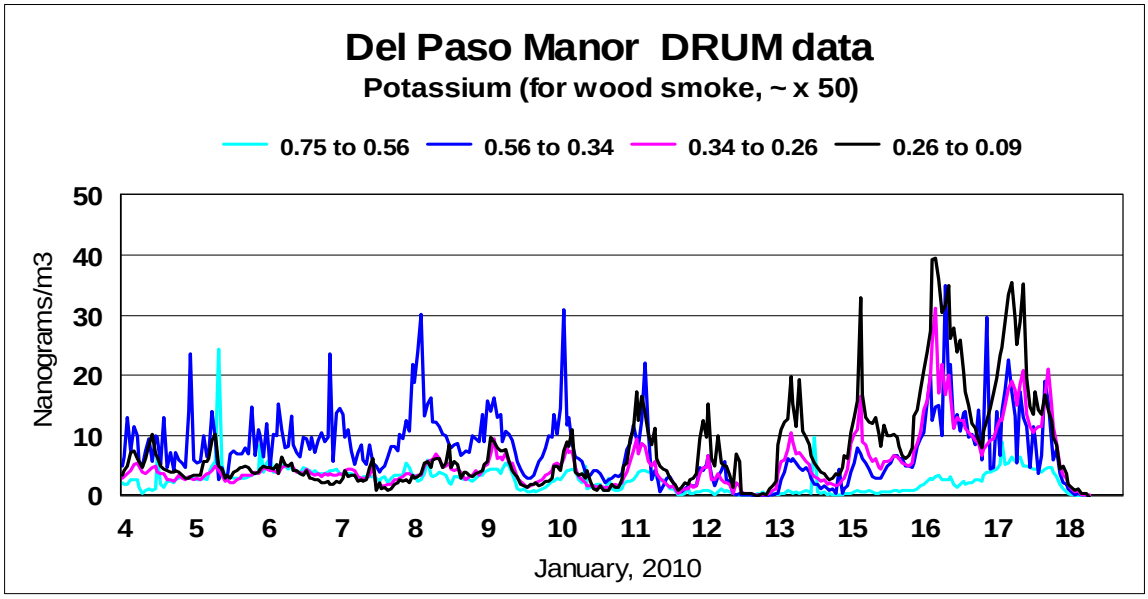


Figure 47. Potassium in the fine mode, a wood smoke tracer.

However, the color seen on the aerosol samples correlates well with the peaks the fine potassium wood smoke signatures and in the gaseous pollutants.

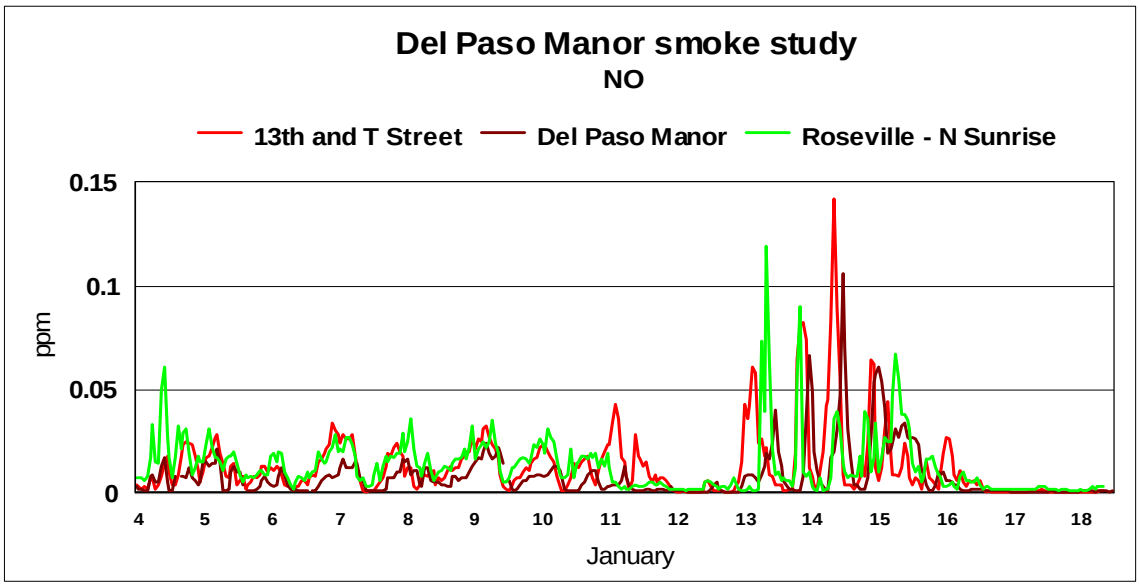


Figure 48. Oxides of nitrogen at Del Paso Manor during the Phase II intensive

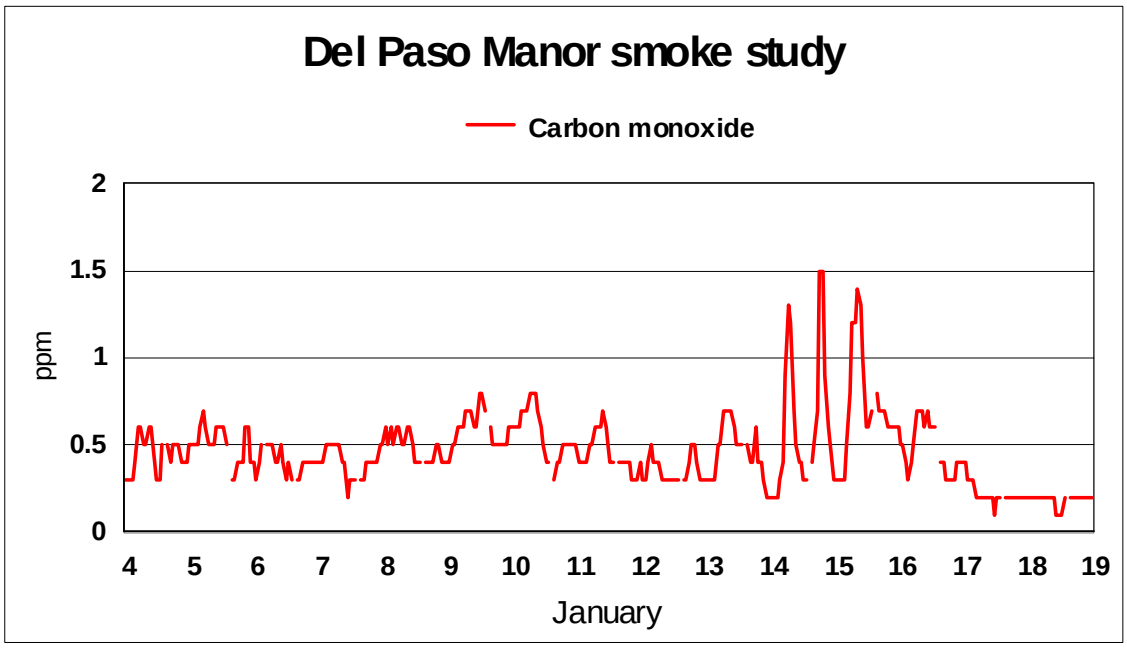


Figure 49. Carbon monoxide at Del Paso Manor during the Phase II intensive.

The mass and gaseous pollutant association re-appears during the last half of the intensive. However, in this case, the HYSPLIT trajectory analysis indicates winds from clean coastal areas north of the San Francisco metropolitan area that then came in from the northwest to Del Paso Manor.

Further, the ratio of oxides of nitrogen to $PM_{2.5}$ mass was then higher than in the December wood smoke event, indicating a non-wood smoke source. The relatively low carbon monoxide levels make the most likely diesel emissions source from trucks and/or trains. The largest source of NO in the Placer County area from which the trajectories come is the Roseville rail-yard.

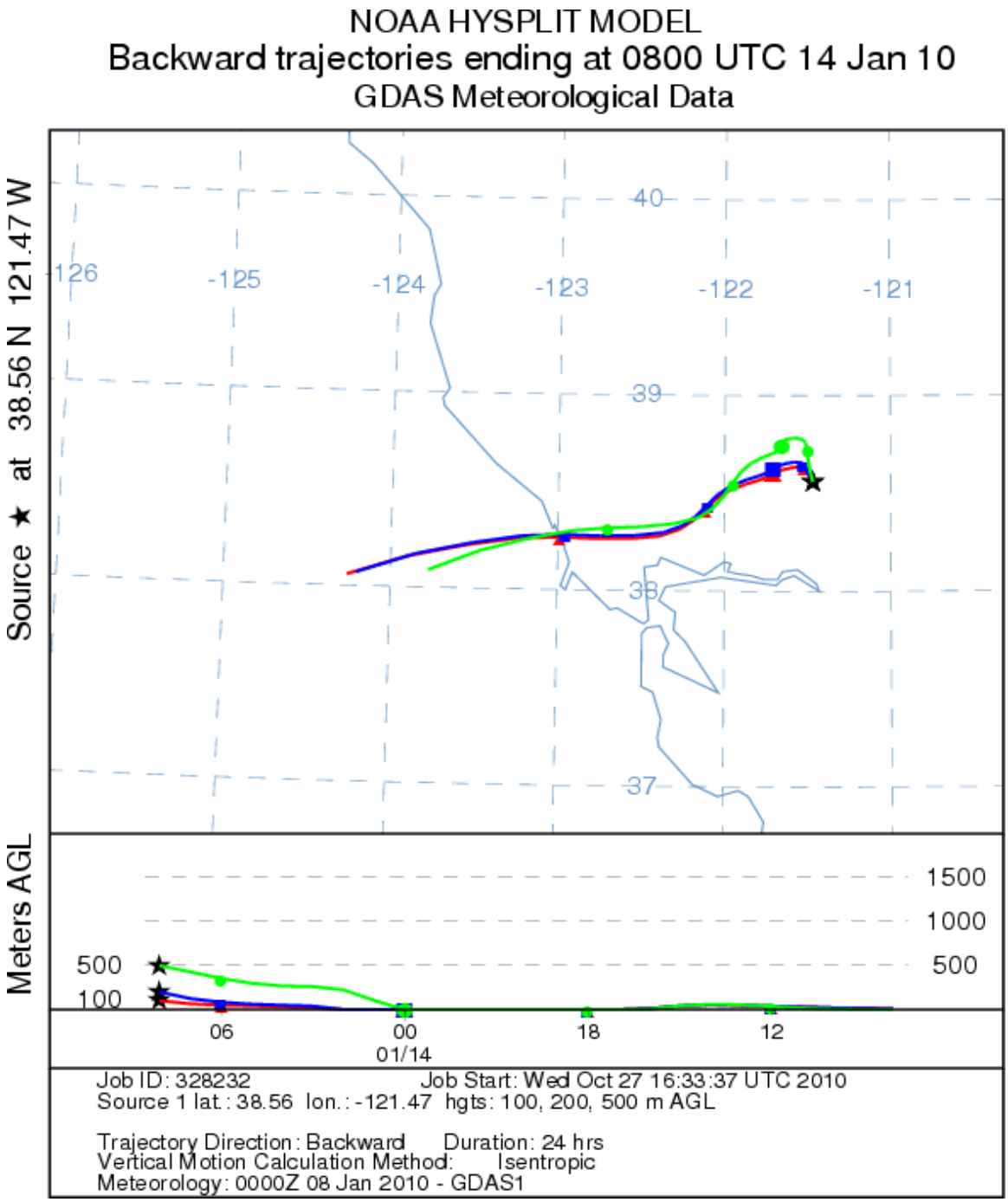


Figure 50. HYSPLIT trajectories for midnight, January 13, 2010.

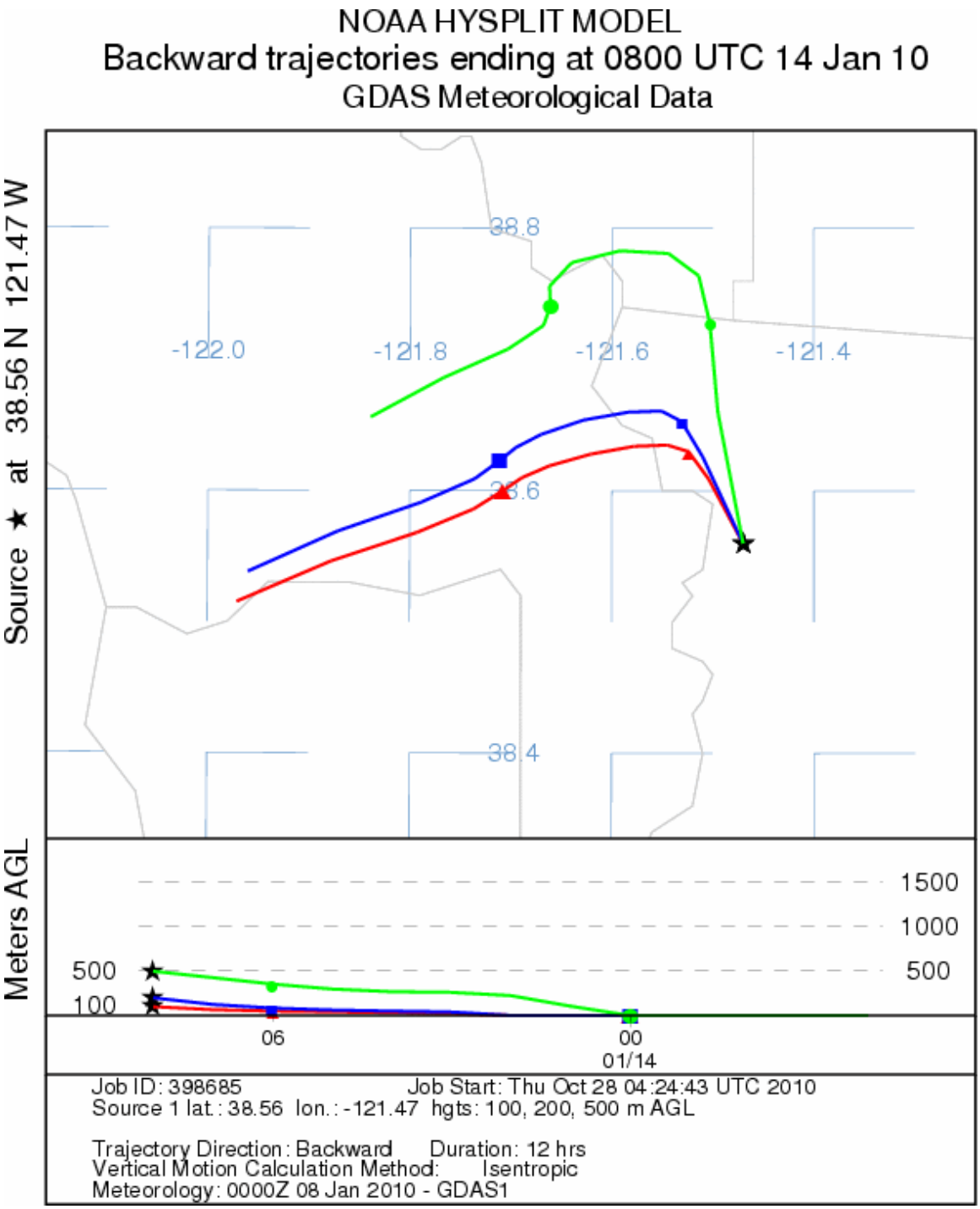


Figure 51. HYSPLIT trajectories for midnight, January 13, 2010. The time scale is reduced to 6 hrs and county boundaries are shown.

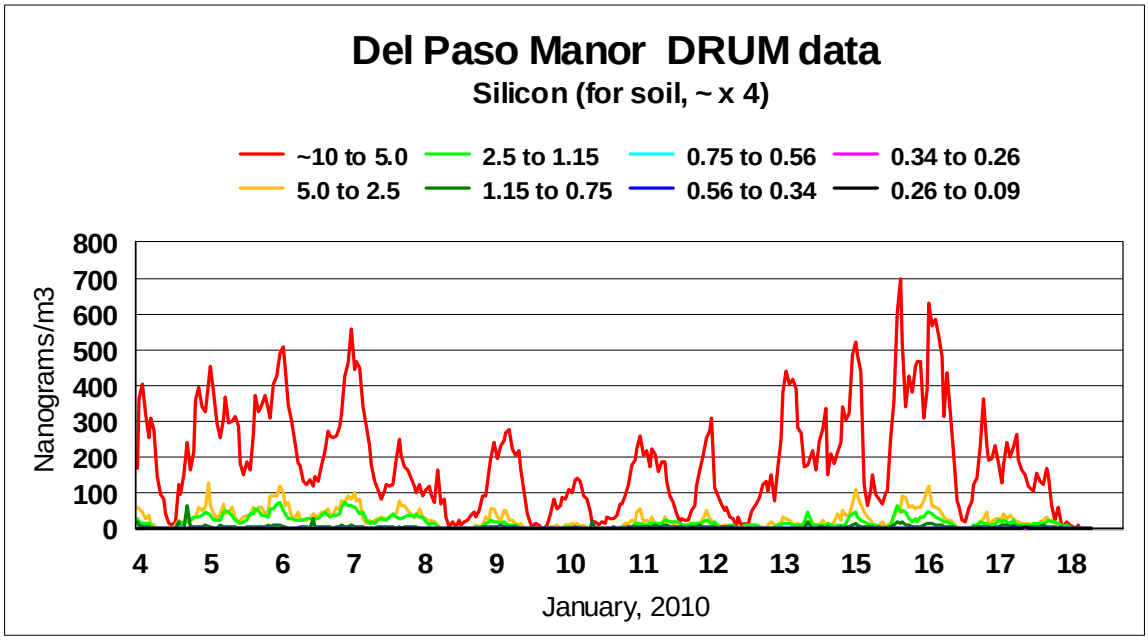


Figure 52. Silicon, a soil tracer, showing an enhancement during the NO/NO_x episodes.

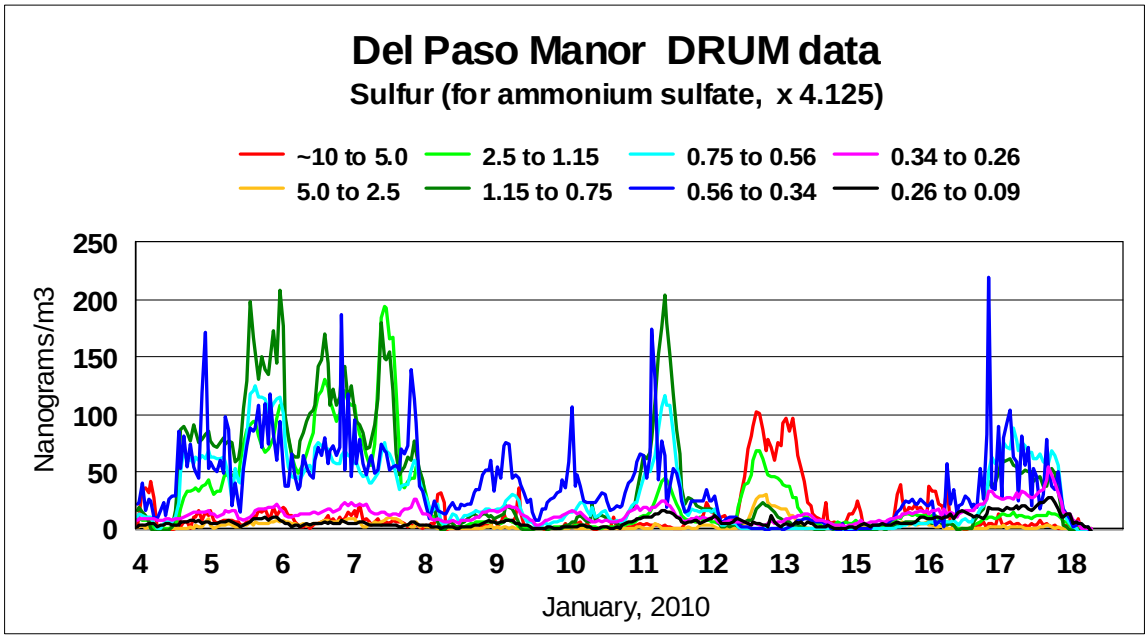


Figure 53. Sulfur, with the coarse sulfur episode on January 13 from a trajectory that crossed the Bay Area with sources including ocean-going ships, oil refineries.

The coarse sulfur is usually associated with sea salt.

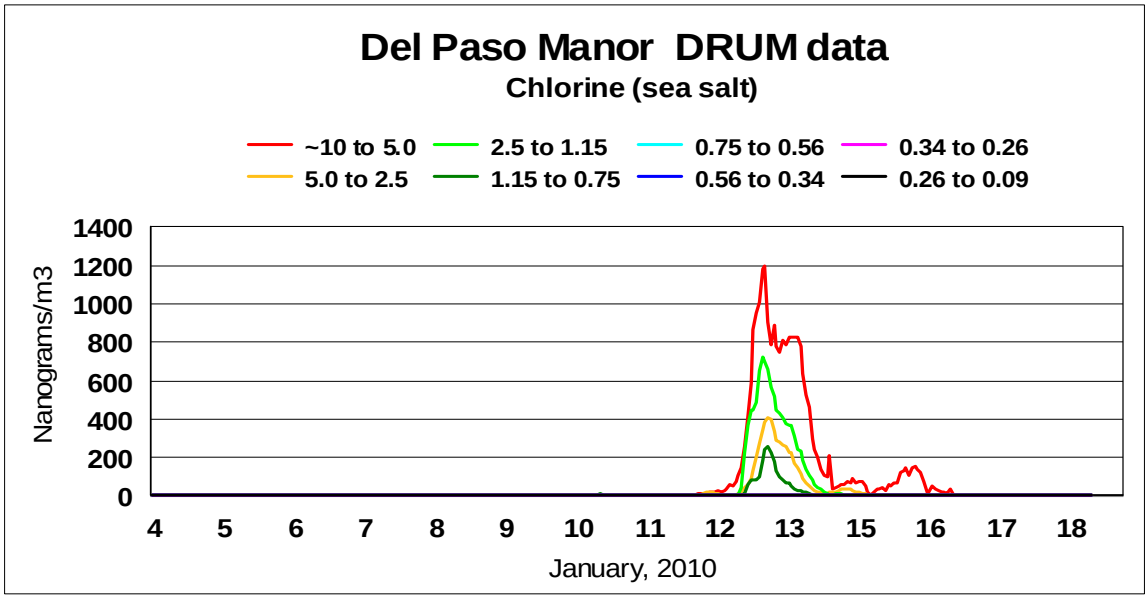


Figure 54. Chlorine in the coarse mode, which confirms the source of coarse sulfur as sea salt on January 13 in Figure 53.

During the pollution event and Stage 2, “All Burning Prohibited” period, the size distribution of the wood smoke shows a well-aged smoke with relatively small local additions. (Figure 55)

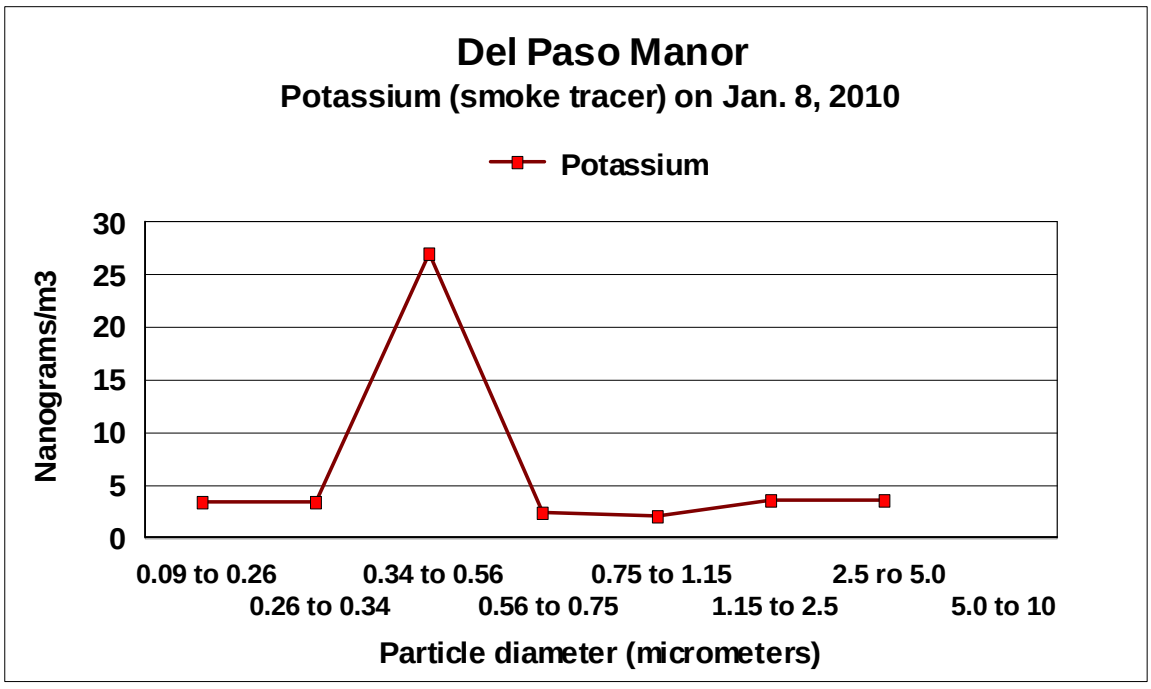


Figure 55. Size distribution of wood smoke during the wood smoke peak on January 8, during the Stage 2 prohibition on all burning.

HYSPLIT analysis of the trajectories during this period January 3 - January 8 typically showed slow air movement from the north.

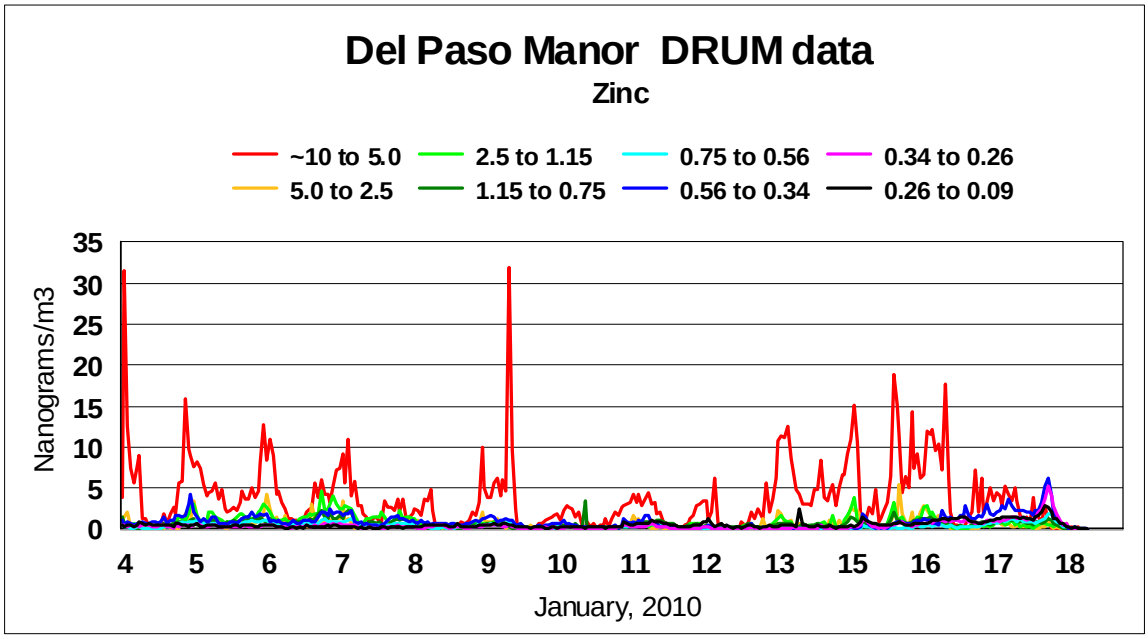


Figure 56. Zinc shows enhancements around the same time that the NO levels are elevated, indicating a high temperature source, transportation or industrial. (Zinc thiophosphate is an additive in lubricating oils.)

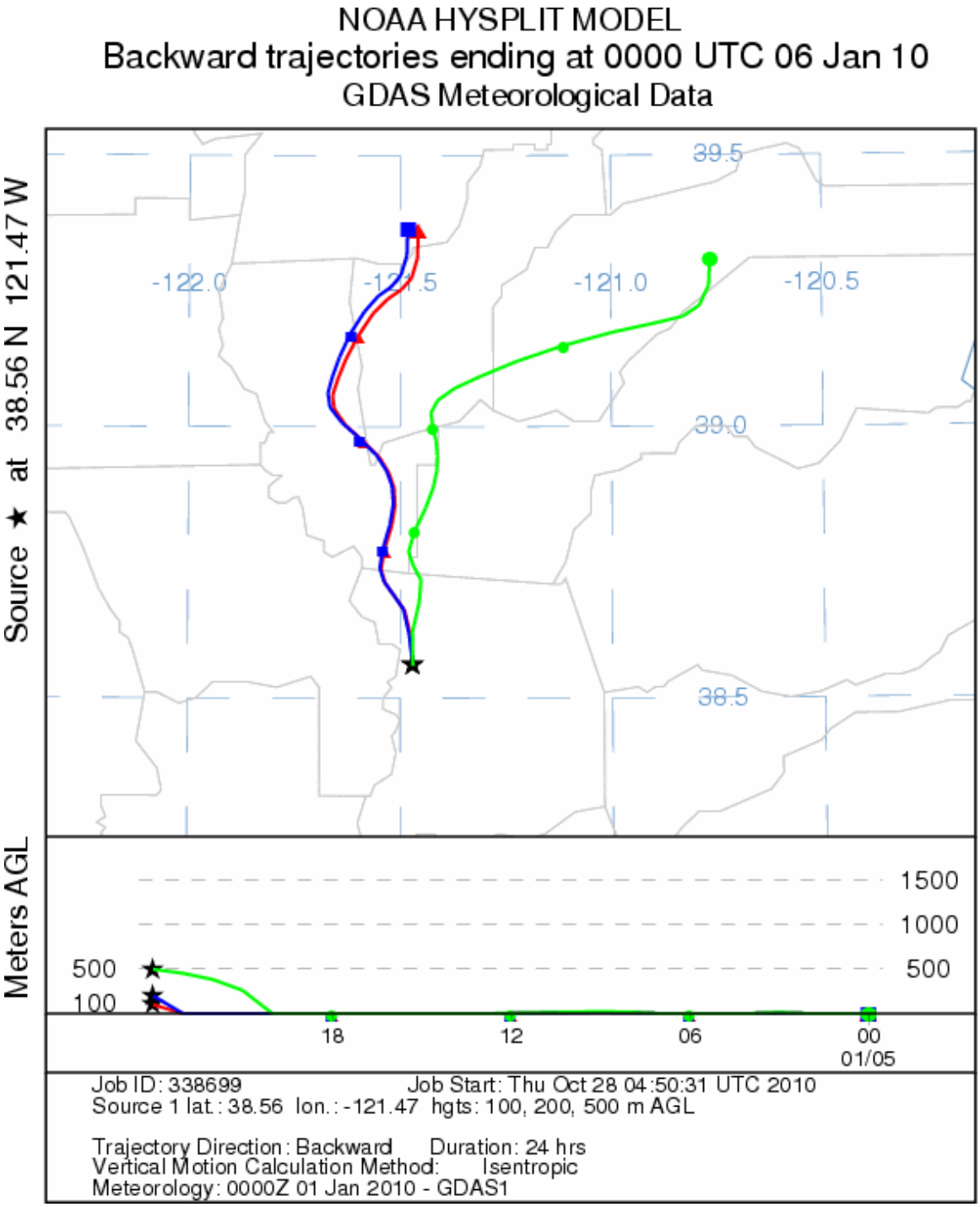


Figure 57. HYSPLIT trajectory during the Stage 2 “All Burning Prohibited” period in early January.

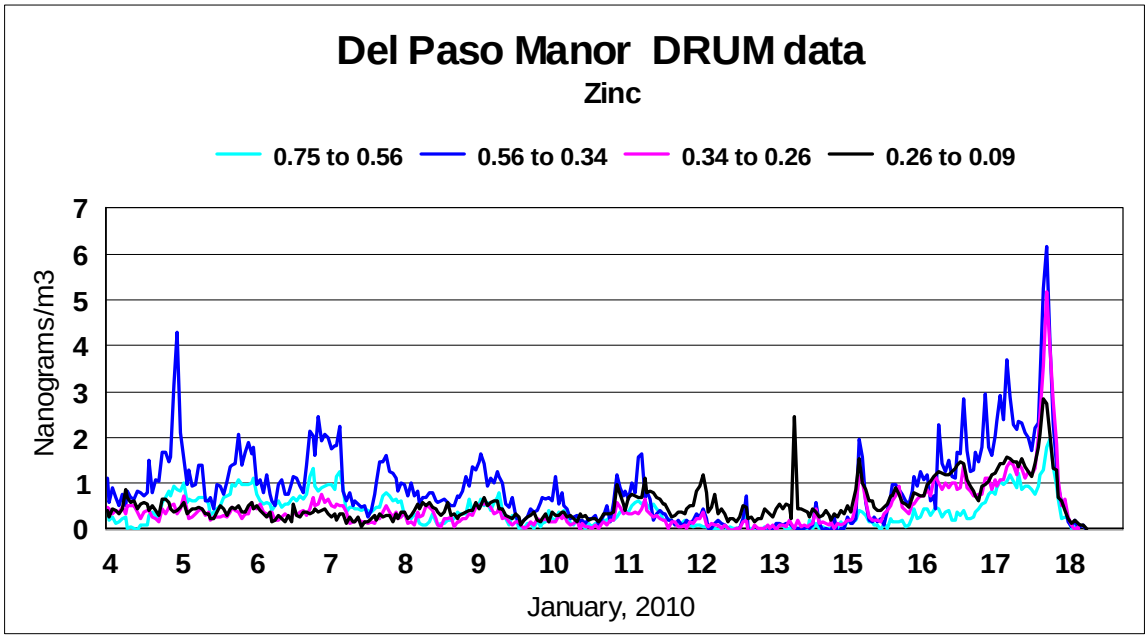


Figure 58. Fine zinc: Stages 5 through 7; very fine zinc: Stage 8

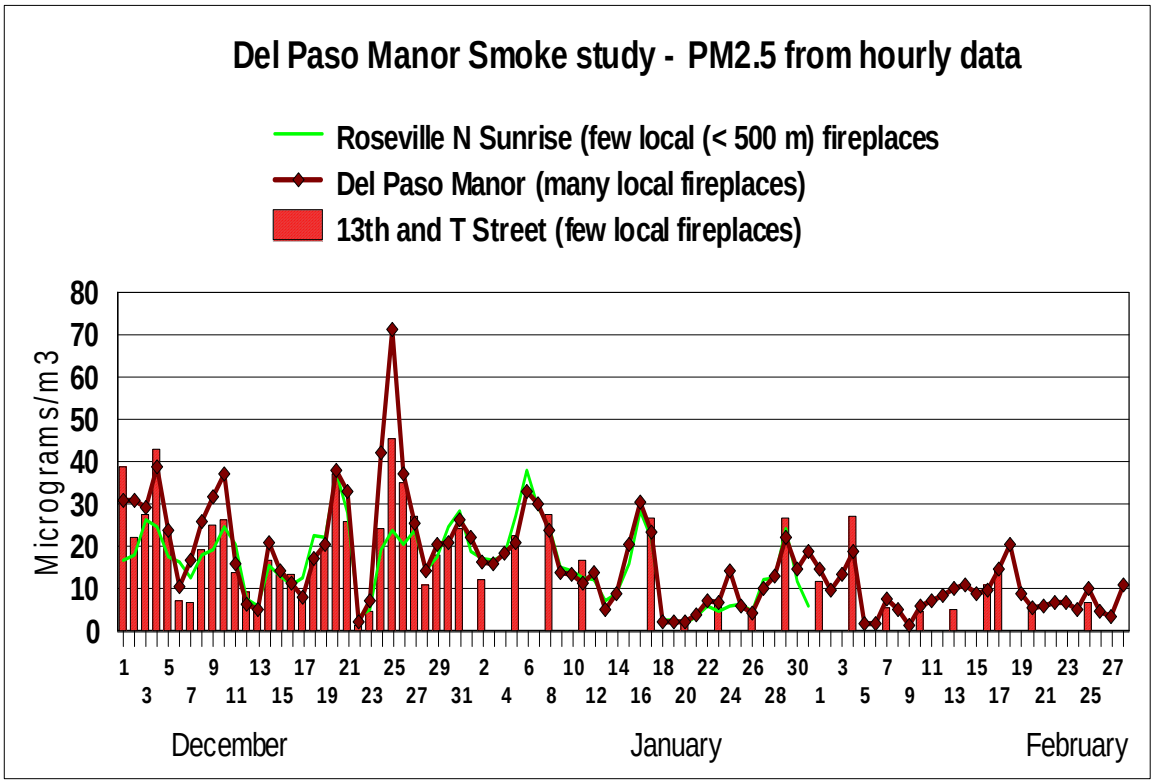


Figure 59. $PM_{2.5}$ 24 hr data from Roseville-N Sunrise, Del Paso Manor, and 13th & T St.

Note that during the mass episodes around January 13 to January 17, Roseville and Del Paso Manor had exactly the same mass levels.

Discussion

The data set addressed in this study is one of the most extensive ever gathered at a single site for any extended period of time. The Del Paso Manor site includes a rich suite of SMAQMD measurements, enhanced with instrumentation such as a soot-detecting aethalometer, as well as the local STN network site. To this we added a combination of highly time- (1-hour) and size-resolved mass, S-XRF elemental data, including speciated ultrafine particles, optical spectroscopy as a function of size and time, and full organic speciation as a function of size. Information was added from nearby sites in the SMAQMD territory, and from recent Central Valley studies.

Del Paso Manor – winter intensive – Phase 1 and Phase 2

December 22, 2009 – January 18, 2010

Time integrated organic aerosols

Organic aerosols were collected on two co-located DELTA 8 DRUMs and integrated over the entire 4 week study. The two time-integrated organic data (from Arizona State University) from paired organic DRUM samplers (fired aluminum impaction, Teflon ultrafine after-filters) for benzo[*a*]pyrene (BaP) compare reasonably well, except for an error in the slot dimensions of Stage 4 in Sampler B.

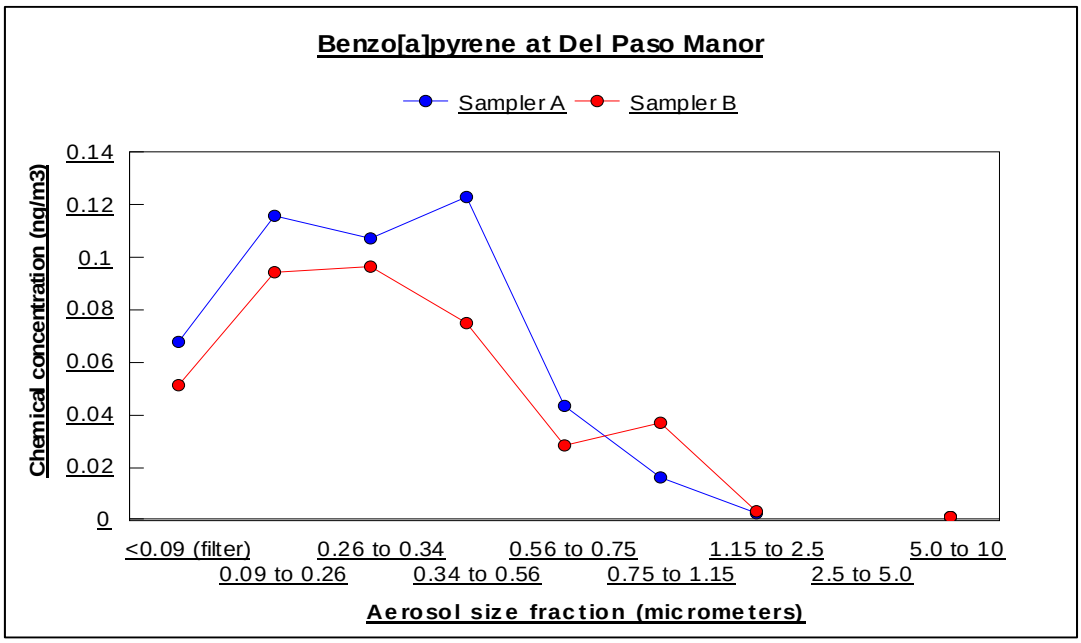


Figure 60. Comparison of paired organic samplers. The notch in DRUM B was later found to be an incorrect impactor slot.

There are three tracers for wood smoke (Simoneit et al, 1999; Fine et al, 2001; Cahill TM 2010):

1) levoglucosan, from the combustion of cellulose,

2) dehydroabietic acid, from the combustion of softwood resin, and

3) non-soil potassium, from the combustion of biomass such as wood.

Below we show the size distributions of the first two. The pattern between 0.56 and 1.15 μm was an error in the sampler slots of Sampler B and not from the aerosol distribution which was smooth.

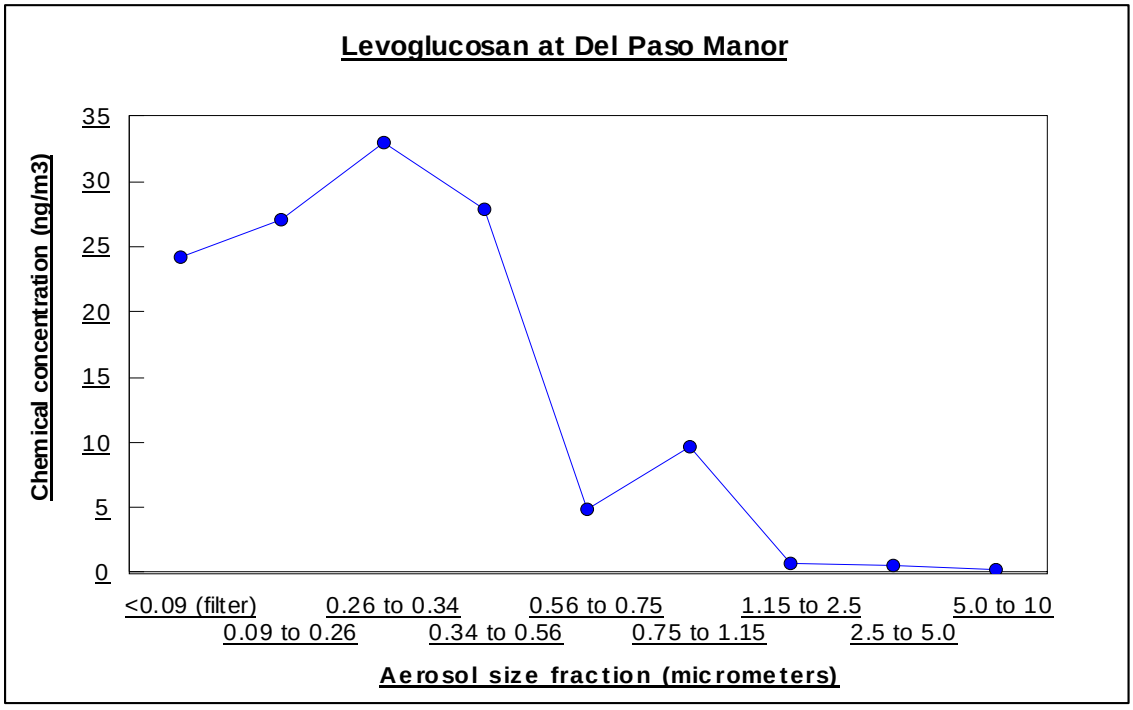


Figure 61. Size distribution of levoglucosan

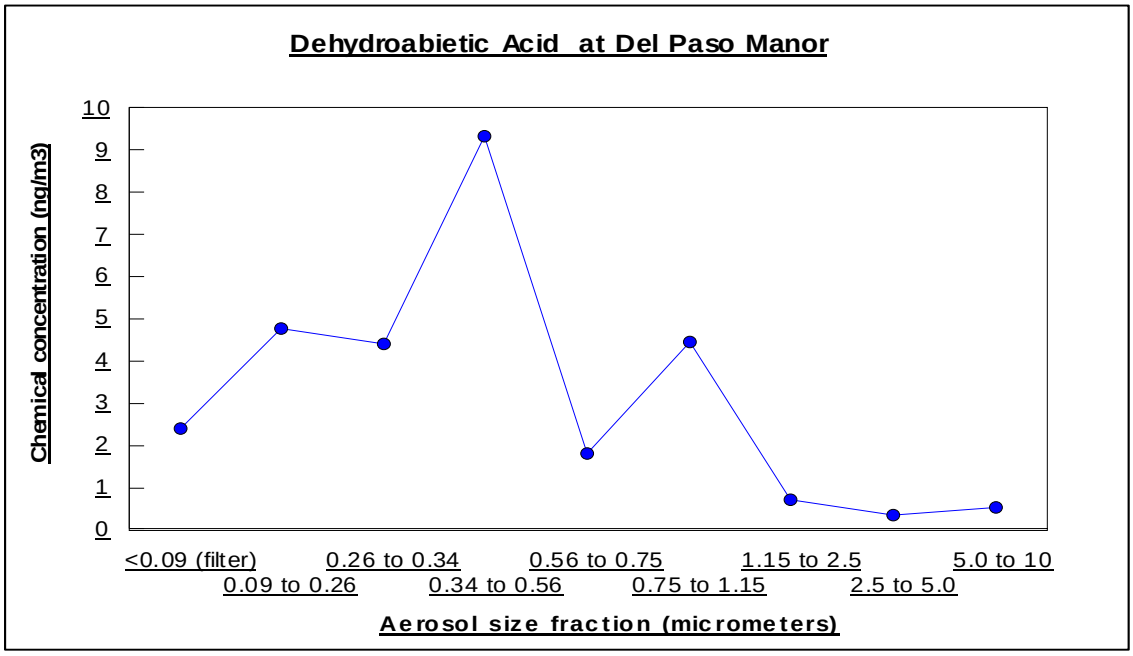


Figure 62. The size distribution for dehydroabietic acid, a tracer of the burning of resinous woods such as pine, fir, and spruce (softwood).

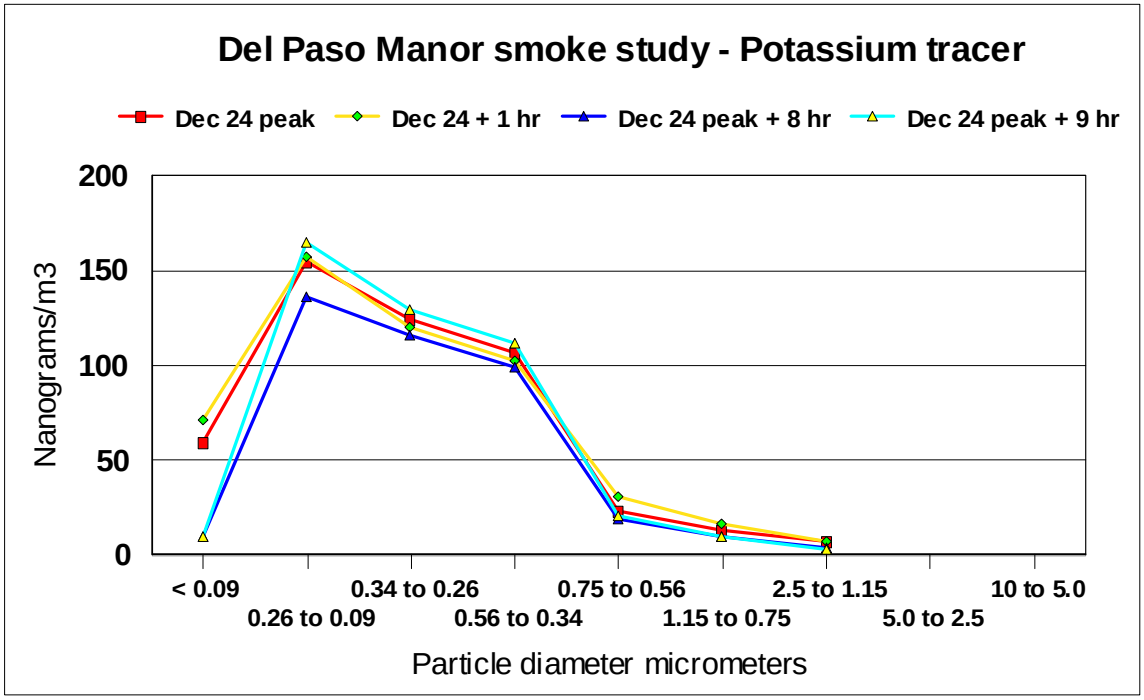


Figure 63. Wood smoke tracer fine potassium for Dec 14 and Dec 25, 2009.

Since the DRUM sampler elements allow high resolution time as well as size, we can examine the potassium distribution at the beginning of the smoke episode (December 24) and 9 hours later (Christmas day). The ultrafine potassium levels on December 24 were far higher than 9 hours later, indicating that the smoke on Christmas Day was aged wood smoke. Christmas day was a Stage 2 “All Burning Prohibited” day, with very light winds. Therefore it is plausible that the “All Burning Prohibited” day was generally observed, and what was seen on Christmas day was largely older wood smoke from the previous “Legal to Burn” day. Note also that the softwood smoke (dehydroabietic acid tracer) was also aged smoke, so that what was observed could have been wood smoke from well northeast of the Del Paso Manor site that had a higher fraction of burned softwood.

The lack of ultrafine organics indicates that the sources of benzo[a]pyrene (BaP) are not very close to the Del Paso Manor site, in agreement with the tracer of softwood combustion. Hardwoods yield far less BaP per unit smoke mass as softwoods (Ancelet, 2011 provides a factor of 1/6). This supports a hypothesis that Sacramento’s relatively low level of ultrafine organics is due to a relatively high fraction of burned hardwoods. A similar result was observed in the Watt Avenue transect (below).

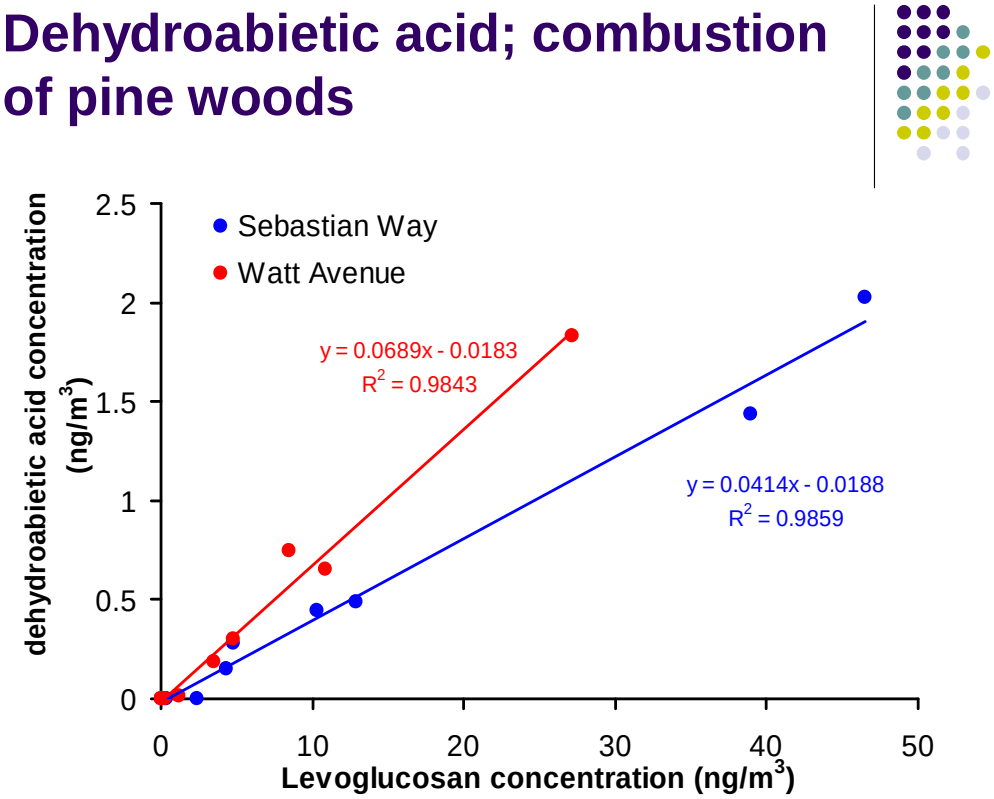


Figure 64. Correlations of levoglucosan to dehydroabietic acid from a site well away from fireplaces (Watt Avenue), and one surrounded by fireplaces (Sebastian Way) (Cahill et al, 2007)

Levels of levoglucosan (tracer of wood smoke) and dehydroabietic acid (tracer of softwood smoke) in the ultrafine mode tended to be lower in Sacramento than at other Central Valley locations (below), indicating less softwood smoke in Sacramento. This is also consistent with the lower levels of benzo[a]pyrene observed.

	Levoglucosan	Benzo[a]pyrene	Indeno[123-cd]pyrene	Coronene
Redding	213	0.19	0.04	0.13
Chico	497	1.77	1.59	0.66
Del Paso Manor	**127**	**0.43**	**0.53**	**0.26**
Sac'to 13 & T	255	0.31	0.43	0.41
Fresno	407	0.76	0.95	0.58
Bakersfield	130	0.26	0.37	0.36

Table 4. Average PAHs in organic matter, December 22, 2009 to January 19, 2010. Cahill TM (2010) provides levels of benzo(a)pyrene, wood smoke, and softwood smoke for five Central Valley sites in winter 2009; this also included a period of low winds.

Analysis of the near-Christmas elevated mass values

When did the high mass levels (and CO, NO, NO_2, soot, ...) occur?

From the time-resolved gas data for mass, CO, NO, NO_2, we can establish that when the high pollution levels occurred. While all metrics are roughly equivalent in timing, for CO < 1 ppm,

For Dec. 23, 11 PM,

For Dec. 24, from midnight to 8 AM and 6 PM to midnight,

For Dec. 25, midnight to 8 AM and 6 PM to midnight, and

For Dec. 26, midnight, 1 AM, 7 and 8 AM, 9 PM to 11 PM.

Below we show a plot of the CO_2, NO_2, and NO data for the period. The data are highly synchronized in time. The NO is usually associated with high temperature combustion, not fireplaces.

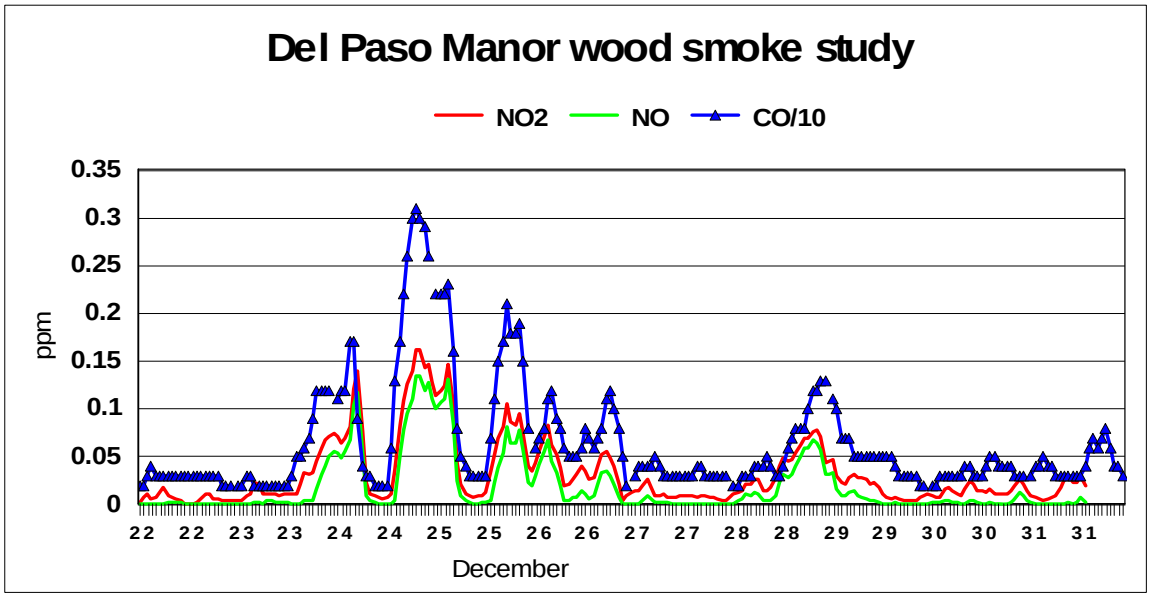


Figure 65. NO, NO_2 and CO/10 during the Phase 1 winter intensive

Where did the air mass come from?

All of the HYSPLIT trajectories come from the northeast, roughly parallel to I-80, and then turn south to impact the Del Paso Manor site. This is the same on both night and day in this 4-day period.

However, a major difference occurred at roughly 6 PM each night, when cold air regularly slid slowly down the Sierra Nevada foothills. The resulting temperature inversion pinned this cold air close to the ground, giving a very small air volume into which ground-based pollutants can disperse. This pattern continued until roughly 8 AM.

The Hysplit data (see figure 66 below) show that two very different sources of $PM_{2.5}$ mass occurred during the Intensive Phase II period:

1) A period with well-aged wood smoke during slow north winds that included considerable sulfates from industrial and/or transportation sources.

2) Later in the month, there was an NO-rich episode with correlated mass during periods when burning was allowed, or, on one day, discouraged but voluntary. This source lay to the northwest of Del Paso Manor.

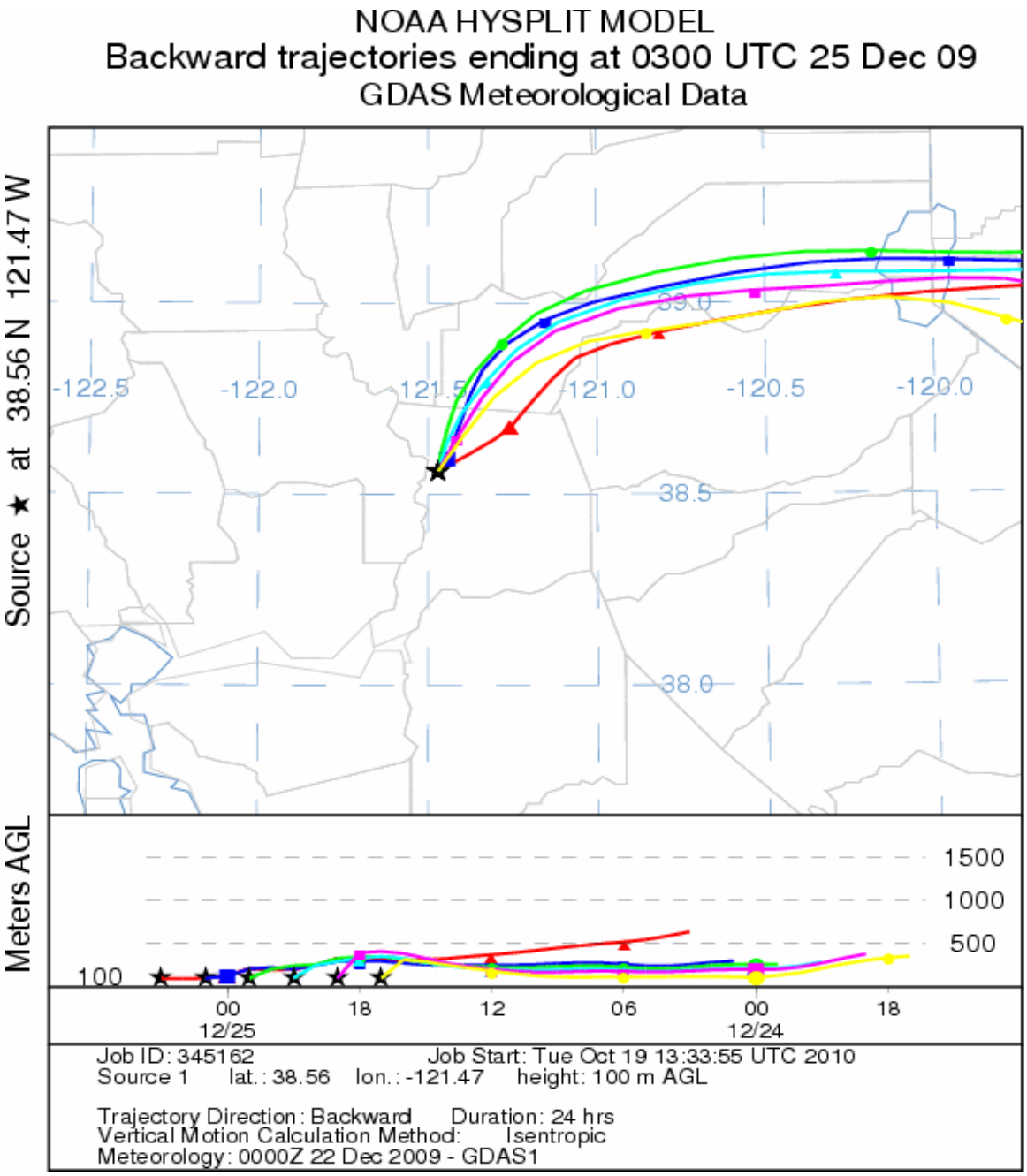


Figure 66. 7 PM December 24, and every three hours until 10 AM.

What is the nature of the $PM_{2.5}$ mass?

From the elemental data, the presence of potassium is a signature of wood smoke. This study used the newly developed continuous mass and elemental data from the DELTA Group's continuous ultrafine sampler. It reveals the presence of very fine and ultrafine potassium, which indicates nearby sources of wood smoke.

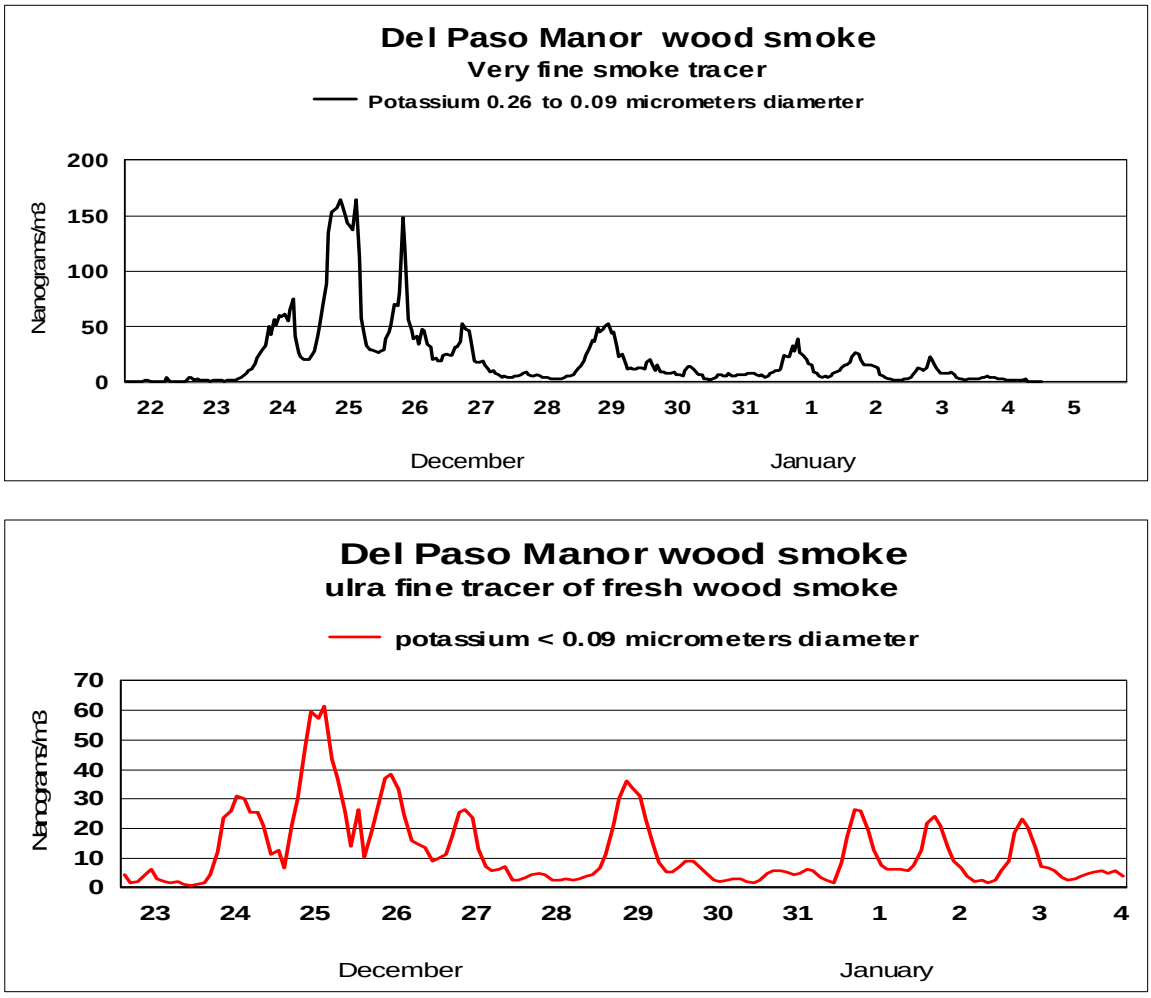


Figure 67 a,b. Very fine (0.26 to 0.09 μm, top) and ultrafine (< 0.09 μm, bottom) potassium, the latter a tracer of nearby smoke.

Given time, the hydrophilic very fine and ultrafine particles take up water and grow in size to the typical wood smoke mode closer to 1 μm diameter (Naeher, 2007).

The fine mass values on Dec. 24, 25, and 26 represent more than half of the mass seen in the first winter intensive. Therefore, we used the time-integrated organic data. The data on size distributions and chemistry are consistent with the following:

1. The smoke on Christmas Eve was fresh wood smoke with significant ultrafine fraction (note that the wood smoke tracer levoglucosan data are consistent with the potassium data).

2. The smoke on Christmas day was larger in size, consistent with a more aged wood smoke that originated from relatively distant sources, and

3. The dehydroabietic acid (also hydrophilic) peaked in the accumulation mode (0.34 to 0.56 μm), consistent with the smoke from softwood combustion originating from more distant sources compared to the general wood smoke.

The persistence of wood smoke at periods when open hearth fireplaces are not expected to be as active (early morning hours - EPA AP 42) may indicate that much of the smoke arises from wood-burning stoves. A significant fraction of levoglucosan mass was below 0.26 μm; and much was below 0.09 μm. This indicates the presence of a cellulose combustion source close to the Del Paso Manor site, as otherwise the hydrophilic sugar would have had time to grow to the accumulation mode (above 0.26 μm). On the other hand, dehydroabietic acid (also hydrophilic) levels peaked in the accumulation mode (0.34 to 0.56 μm), indicating that the source of smoke from softwood combustion was farther away than the general wood smoke.

US EPA Publication AP-42 (EPA 2010) provides PM_{10} emission factors from various types of wood stoves and fireplaces. It shows that emissions from fireplaces and conventional wood stoves are much higher than from catalytic wood stoves, which in turn are much higher than from pellet stoves. Other data show that this is almost all $PM_{2.5}$. Thus, with the relatively modest differences in emission rates, between 2.5 (more recent studies) and 1.7 (EPA AP 42) emissions per mass of wood burned, we can now turn to the duration during which the wood was burned. The vast majority of open hearth fireplaces (EPA estimate: 95%) are used for aesthetic reasons, with fires of short duration. This compares to wood-burning stoves used for space heating, which tend to be in more continuous use during cold weather. Also, these stoves are expected to burn cooler than open hearth fireplaces, which would make their smoke less buoyant.

Based on the aging of the wood smoke, it appears that there was considerable compliance with the restrictions on burning for Christmas day. This was also noted in early January, during a long string of no-burn days. The December 23rd through 25th period included the Dec. 24 “Legal to Burn” day, and the Christmas holiday favors fireplace use. This period had very unfavorable meteorology:

- Winds were calm.
- High dew point caused fog to form Christmas night (at least as recorded at Sacramento International Airport), with increased mass of hydrophilic air pollutants such as wood smoke.
- Cold down-slope air from the Sierras each evening, causing a very shallow inversion layer.

Acknowledgments

This study could not have been performed without the encouragement, guidance, and financial support of the Sacramento Metropolitan AQMD.

The authors gratefully recognize BrigetteTollstrup and the staff of the Sacramento Metropolitan AQMD for support in setting up and maintaining the Del Paso Manor site during the intensives, and providing access to the extensive and high quality SMAQMD data.

We appreciate Mike Redgrave of the ARB staff for getting special and timely access to air monitoring data not yet posted in ADAM.

We recognize and appreciate the data reduction and analysis by S-SRF that was performed by Steve Cliff, Yongjing Zhao, and Kevin Perry.

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.php) used in this publication.

Finally, the advice and guidance of the members of the Health Effects Task Force of Breathe California of Sacramento-Emigrant Trails were critical in all aspects of this study.

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Attachment

Quality Assurance (from "DRUM Quality Assurance Protocol")

DELTA* Group DRUM samplers

January, 2009 Version. (DQAP 1/09)

Tom Cahill and DELTA* Group staff: Steve S. Cliff, Kevin D. Perry (Meteorology, Univ. Utah), David E. Barnes, Lee Portnoff (DRUMAir)

*Detection and Evaluation of Long-range Transport of Aerosols

1. Final report to the California Air Resources Board, **Comparison of Fine Mass, UC Davis DRUM versus FRM, at the ARB 13th and T Street Site**, Thomas A. Cahill and David E. Barnes, UC Davis DELTA Group, and the Breathe California of Sacramento-Emigrant Trails' Health Effects Task Force, April 25, 2009

2. Final Report, **Drum Sampler Demonstration of PM Mass and XRF Elements** Final Report to the US EPA ORD, March 14, 2009, Thomas A. Cahill, David E. Barnes and Jonathan Lawton, University of California, Davis, with Thomas M. Cahill, Arizona State University, May, 2009

3. **Organic and Elemental Aerosols near Watt Avenue, Late Winter – Spring, 2007,** Draft prepared for Breathe California of Sacramento-Emigrants Trails' Health Effects Task Force, and the Sacramento Metropolitan Air Quality Management District, June 26, 2009

The first two are available electronically from BC/SET and the UC Davis DELTA Group.

Appendix 2
Further Research on $PM_{2.5}$ Aerosols in Part 2 – Source Characterization and Hourly $PM_{2.5}$ Apportionment
September 30, 2011

Final Report to

The Health Effects Task Force,
Breathe California of Sacramento-Emigrant Trails,

Jananne Sharpless, Chair

by

Tony VanCuren[1, 3]

Measurements provided by:
Thomas A. Cahill[1, 2], David E. Barnes[2], Nicholas Spada[2], Jonathan Lawton[2], and Roger E. Miller[2],
and
Sacramento Metropolitan Air Quality Management District

[1] Health Effects Task Force,
Breathe California of Sacramento-Emigrant Trails,
[2] DELTA Group, UC Davis, CA
[3]Air Quality Research Center, UC Davis, CA

for

The Sacramento Metropolitan AQMD
Larry Greene, APCO

Part 2 – Source Characterization and $PM_{2.5}$ Apportionment

The Problem of Explaining Individual 24-hr $PM_{2.5}$ Exceedances

The Del Paso Manor site has recorded the highest winter $PM_{2.5}$ concentrations in the Sacramento Metropolitan Air Quality Management District (SMAQMD) in recent years, and residential wood combustion has been established by District and EPA analyses (SMAQMD, 2009) to be a major driver of these winter peaks. In fact, residential wood smoke is estimated to be 42 percent of $PM_{2.5}$ emissions in the District, nearly four times the fraction of the next largest source (SMAQMD, 2009). SMAQMD has made great strides in controlling residential wood smoke pollution by restricting burning on days when atmospheric dispersion is inadequate to deal with the added emissions. Although winter $PM_{2.5}$ concentrations have been significantly reduced, occasional high concentrations still occur.

The difficulty of diagnosing the exact causes of the remaining rare high concentration events lies in the variation of source activity over any given 24-hr sample period, with motor vehicle activity dominating daytime emissions and residential emissions rising at night, coupled with the diurnal variation of winds and atmospheric mixing. Routine speciated $PM_{2.5}$ samples collected over 24 hours composite the materials from the various sources and the effects of changing atmospheric conditions into a single sample, and thus do not facilitate breaking down the history of a particular peak event.

One of the primary goals of this study was to examine the synergy of wood smoke and other emission sources of winter pollution by using the hourly time resolution of a specially collected DRUM data set (described in detail in Part 1 of this report), combined with the routine hour-resolved gas and particle measurements and meteorological data taken by the District, to improve understanding of the dynamics of high $PM_{2.5}$ concentration events.

To this end, we developed an hourly source allocation analysis for a 12-day period beginning before Christmas and running through the New Year's holiday (Dec. 22, 2009 through Jan. 2, 2010). During this time Del Paso Manor recorded a peak 24-hour $PM_{2.5}$ value of 49.3 $\mu g/m^3$ on December 24.

The peak event occurred on a "Legal to Burn" day, and the strong late-evening peak recorded in the hourly $PM_{2.5}$ mass data from the Del Paso Station's BAM sampler strongly supports an initial hypothesis that residential wood burning was a major contributor to the peak concentration. Our analysis tests that hypothesis.

Analytical Approach Building a Unified Data Set

The analysis requires a "data matrix" consisting of a time series of sets of simultaneously-measured values for particle and gas pollutants, with no missing values, and an identically structured "error matrix" with uncertainty values for each "data" measurement.

The raw S-XRF DRUM results cover 27 elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pb) plus a light absorption measurement, all reported for each of 9 size bins, for a total of 252 size-resolved aerosol measurements for each hour. The routine instruments at the Del Paso Manor monitoring site produce hourly data for fine particle mass (BAM- $PM_{2.5}$), "Black Carbon" (measured as total

light absorption by aethalometer), vapor-phase non-methane volatile organic compounds (NMOC), three criteria pollutant gases (CO, O_3, NO_2), and 4 meteorological variables (wind speed, direction, temperature, and humidity) – another 10 measurements. Thus the full data set for the 12 days includes over 150,000 values (75456 "data" and 75456 "error" values).

In order to reduce unnecessary calculation and to reduce statistical "noise" in the results, measurements were screened for their quality (signal to noise ratio) and relevance to identifying common pollutant types, loosely following the guidance of Paatero and Hopke (2003). The meteorological data were separated out for later analysis against the "source" pollutant data, since meteorology is not an inherent component of emissions. The aethalometer data were deleted due to a large number of missing values during the period of interest, but its loss is compensated by the size-resolved light absorption measurements. Finally, eleven elements in the S-XRF data were eliminated based on low signal-to-noise ratio or lack of any known useful source associations. This reduced the data matrix to 158 variables per hour, or 45504 data/error pairs over 12 days. The "error" values for the S-XRF data come directly from the AXIL data reduction software; "error" values for the routine data were estimated based on published instrument specifications, or, if no published values were available, a default ± 10 percent of the mean was used. These matrices will be provided to SMAQMD electronically along with this report.

PMF Analysis

Since such a large data set is impractical to visualize, we used Positive Matrix Factorization (PMF) as a tool to compress the data to a reduced set of variables, termed "factors." Each factor is a group of variables that are correlated in time, and their internal relative abundances are interpreted as a factor or source "profile."

PMF has been regularly applied as a source allocation tool for speciated particle measurements for a decade or so. The basic concept was described by Paatero and Tapper (1994), and its utility has been demonstrated in a number of settings from urban sites to the remote Arctic. The value of PMF is recognized by USEPA, who now provide free software to facilitate its use (USEPA, 2010). USEPA's PMF-3 is the software employed in this analysis.

PMF produces three types of outputs, (1) a set of factor profiles, (2) time series of the contributions of the profiles, and (3) statistics showing how well each variable is reproduced by the PMF statistical model. From these it is possible to both identify source types represented by the factors and reconstruct their relative contributions at each time step in the original data set.

Implementing PMF for the Del Paso Manor winter study

PMF is fundamentally a tool to find temporal correlations among measurements, and the computation is not inherently bound to any single type of input data. The unusual mixed mode data set created in this experiment combines particle, optical, and gas pollutant measurements. Exploiting this diverse information calls for applying the statistical power of PMF in a more abstract way than the simple mass-allocation approach for strictly particle data developed and popularized by Paatero, Hopke and others.

Normalized, Mixed-Mode PMF Analysis

The EPA PMF-3 software provides outputs that describe each factor in three forms, assigning each variable its fraction of the mean mass of the factor, its fraction of the mass of the variable overall, and as the variable's concentration within the factor. In order to be able to combine disparate data types without inadvertently giving one data type more weight in the analysis than any other, we selected the output showing the fraction of each variable assigned to a factor. In this view, variables are transformed to have a mean of 1, computed by dividing each measurement by the mean of all measurements for that variable. This balances all the variables without modifying any peculiarities in their distributions, thus not modifying the internal correlation structure of the data. The great virtue of this is that species comprising the bulk of sample mass, low concentration trace species, and measurements in disparate units all get equal representation in the factors' compositional profiles generated by the analysis, which makes it easier for the human interpreter to see the correlations among variables in the profiles. Final validation of interpretations is done by examining the actual mass values to confirm the profiles' similarity to known sources.

Unlike data from the USEPA STN speciated PM network, in this particular data set the sum of all measurements is not equal to the particle mass: S-XRF provides only a subset of the particle composition, notably lacking masses for hydrogen, oxygen, carbon and nitrogen; moreover, optical measurements are only loosely tied to mass, and gases are not part of the particle mass at all. As a result, the profiles produced in this analysis represent source abstractions which convey a broad spectrum of information about the source, such as trace contaminants in fuel, unburned fuel vapor (NMOC), and NO_2 emissions correlated with the source. In application, these mixed mode profiles provide a fuller picture of source behavior, without losing any of the utility of a conventional speciated particle mass PMF analysis, although some additional manipulation is needed to retrieve profiles which can be compared to particle emission source profiles such as those in the USEPA SPECIATE data base (USEPA, 2009).

Results

Factor Numbers

Mathematically, a PMF analysis does not have a single solution; rather, its application needs to be guided by a human observer who has some *a priori* expectations of what the factor profiles should be. In practice, the best way to approach it is to estimate the number of likely distinct factors ("sources") to be found, and then run PMF solutions for a range of factor numbers spanning the initial estimate. Using too few factors creates profiles that lump together similar sources in an uninformative way, while too many factors may subdivide a source type inappropriately. For example, only differentiating to three factors in an urban environment would produce factors for dust, combustion, and secondary PM (*e.g.* sulfates); this would not improve understanding beyond what can be gleaned from simply examining the raw data. Alternatively, too many factors produces sets of similar factors that vary only in ways driven by the variation in the data unrelated to source type (for example, separate factors for the same material differentiated by the size shift of humid vs. dry conditions), and thus may also be

uninformative, or even confusing. The best solution for any particular data set is found by comparing multiple solutions and selecting the one that seems most reasonable for the hypothesis under examination – in this case, discerning particle mass due to residential wood burning from similar material due to other combustion, such as motor vehicle exhaust, forest fire smoke, or aged pollution transported into the study area.

For this analysis, solutions were run for 8 to 12 factors, with the 9-factor solution producing a set of physically reasonable profiles that are neither too broad nor obviously based on "noise" in the data. The 9-factor solution is not ideal, as it produces one factor that is somewhat ambiguous as to its physical counterpart and is likely a product of diurnal meteorological patterns, but that factor is wholly uncorrelated with $PM_{2.5}$ mass, so the impact on the overall study is minor.

Reading the "Source Profiles"

The factor ("source") profiles derived from the PMF analysis are presented here as three-dimensional correlograms. The arrangement of the elements in the plots is explained by the generic example shown in Figure 2-1. Interpretation of these plots relies on recognizing expected associations among elements, and, in the extended aerosol and gas data from this experiment, associations with varying amounts of NOx, CO, and VOCs. The reader should bear in mind that the 3-D plots and time series are based on normalized data, not mass. Only the reconstructed $PM_{2.5}$ data (Figure 2-15) is mass-scaled.

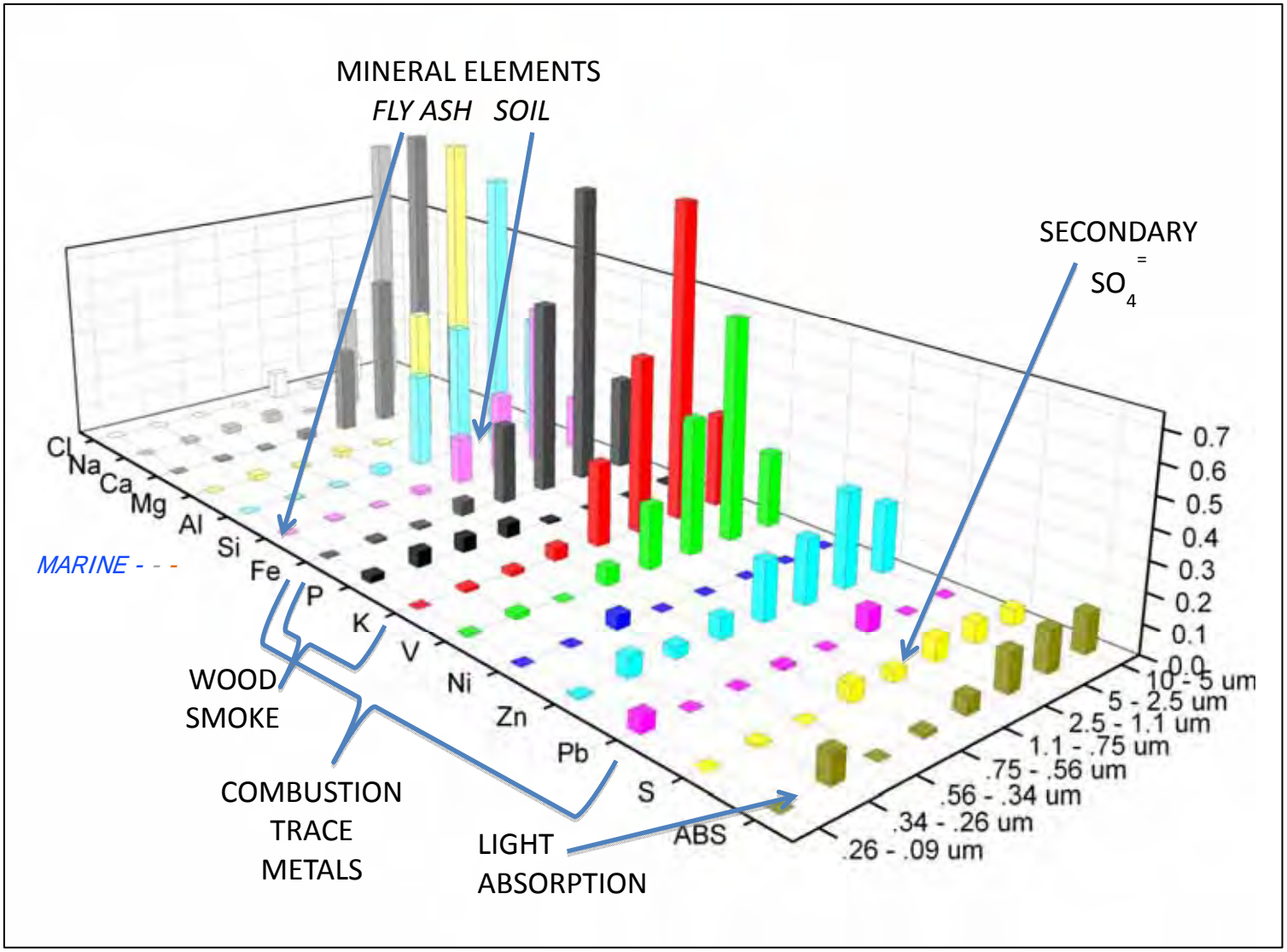


Figure 2- 1. Guide to interpretation of the size-resolved species correlograms. The S-XRF measurements are arranged along the long axis according to common chemical associations, beginning with marine (primarily sea salt), and grading through soil dust, biomass burning tracers, fossil fuel tracers, and ending with secondary pollutants. Size often aids in source recognition; for example, Si in mineral dust is usually larger than 1 µm, while Si in ash in combustion exhaust is usually well below .5 µm.

Note on Comparing PMF Factors with Source-Test Profiles

The profiles produced by PMF are based on the time-varying composition of ambient air, which will always contain material from multiple sources. When multiple sources are located in the same direction from the sampling site, and especially if these sources operate on similar temporal patterns, some "blurring" of the PMF profiles can occur due to co-linearity and/or temporal auto-correlation among sources. This can result in small signals for unexpected species showing up in certain profiles, for example, a small road dust signal is usually found in PMF profiles assigned to tailpipe emissions, while a weak exhaust signal may show up in a profile dominated by road dust. In addition, sources vary in emissions due to many factors, so that published source-test profiles are not necessarily accurate for the actual sources impacting a monitoring site. For these reasons, comparisons between published source profiles and PMF profiles are not rigidly quantitative, and minor discrepancies need to be seen in the context of the individual sampling program.

The 9 Source Profiles from the Del Paso Manor Winter Study

The nine mixed-mode normalized factor profiles identified for the Christmas-New Year's period at Del Paso Manor are shown in Figure 2-2. The correllograms for this study are expanded from the model in Figure 2-1 to also show the BAM and gas data as well. The profiles are discussed in groups of similar composition in the following sections.

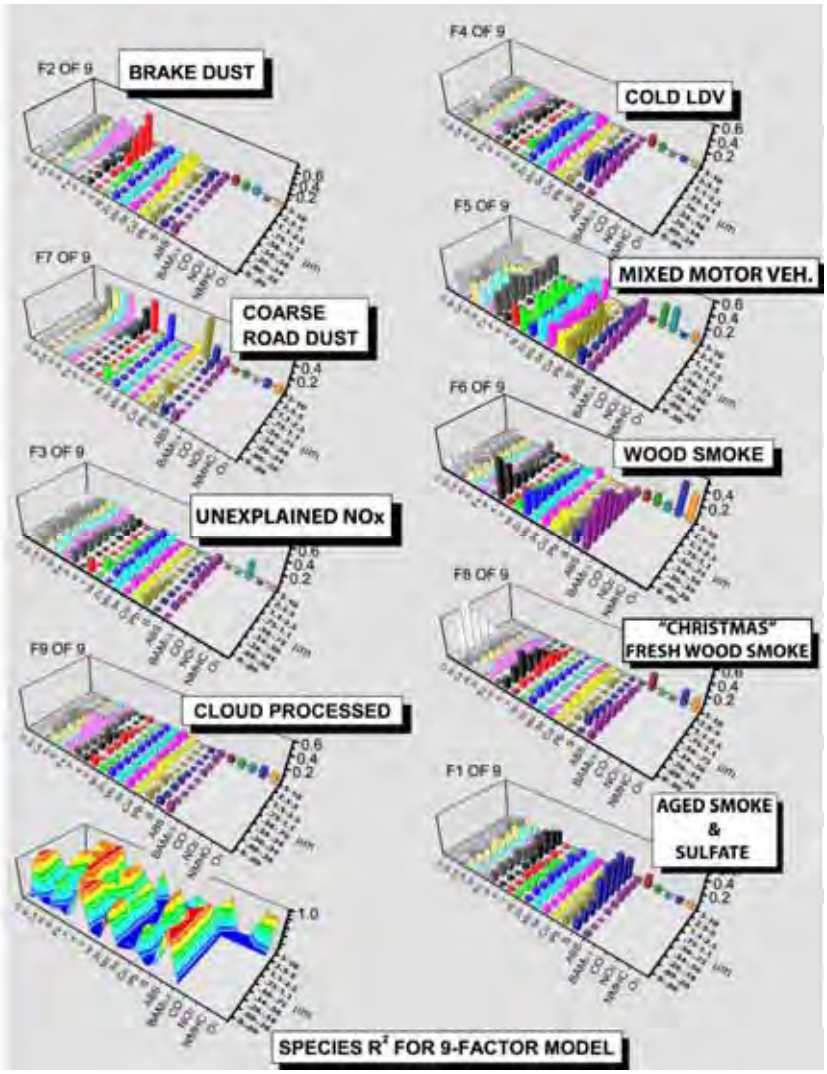


Figure 2- 2. Correlograms for the nine factors identified in this study. The bottom left diagram shows the R^2 values for the fit of the 9-factor linear model to the reported measurements.

Group 1 – Fugitive Particulate Emissions

Fugitive particulate emissions are materials that are not released from a defined vent or exhaust stream, and usually consist of loose material lofted by wind or surface disturbance, or generated by human activities like construction, farming, and material handling. Two fugitive aerosol types are identified in the Del Paso Manor data, Coarse Road Dust (Figure 2-3, top) and Brake Dust (Figure 2-3, bottom).

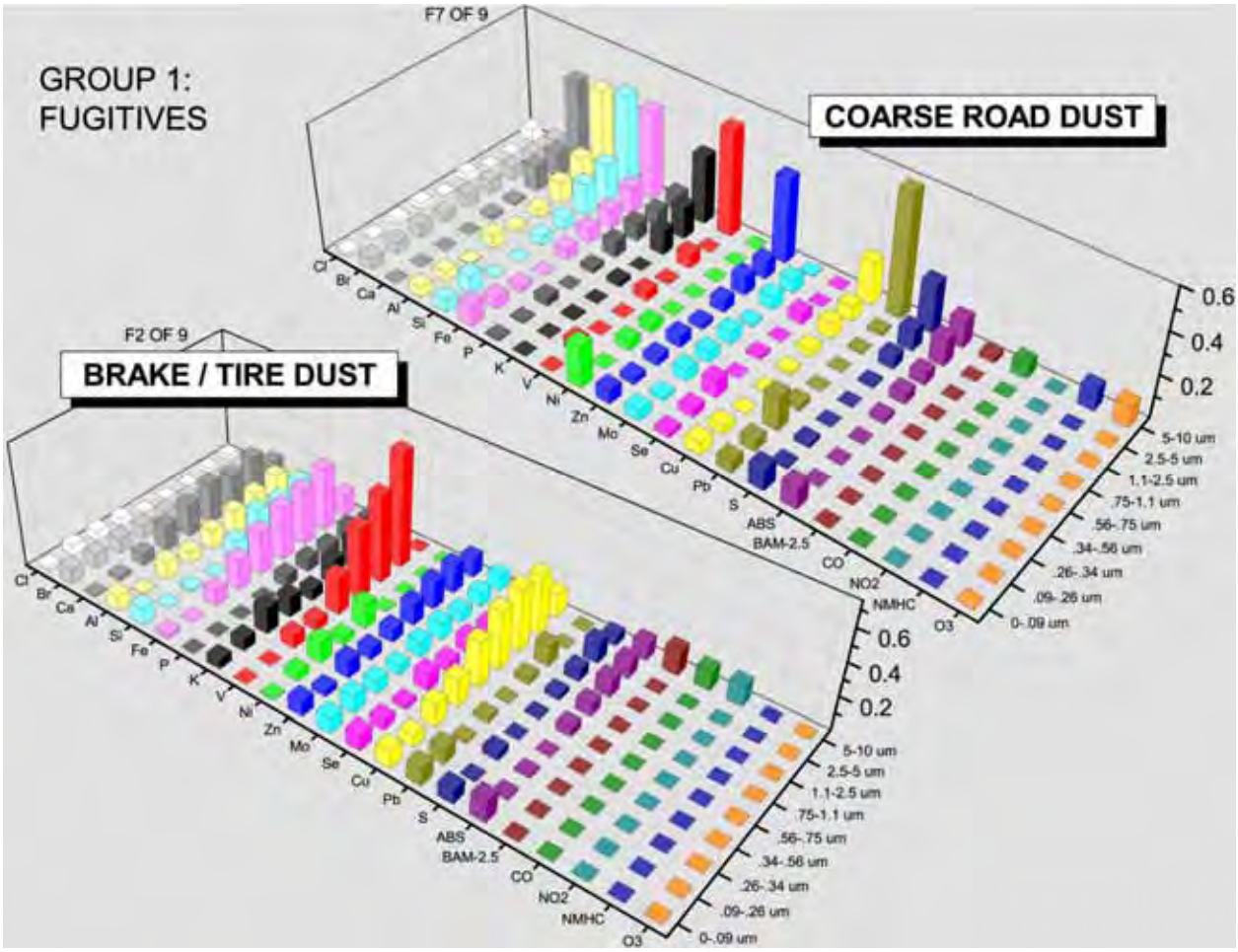


Figure 2- 3. Fugitive aerosol types in winter at Del Paso Manor. The road association for the coarse dust is based on the presence of Pb and evidence of rubber granules, as suggested by light absorption, S, Zn, and Cu.

Coarse Dust. In winter in suburban Sacramento, frequent rains and the growth of annual grasses on open ground tend to reduce dust emissions from windblown soil, leaf blowers, construction sites, and similar sources, leaving dust lofted from hard, dry surfaces, such as roadways, as the dominant provider of large particles to the atmosphere. The Coarse Road Dust profile (Figure 2-3a) reflects this with a mix of typical soil components, such as Al, Fe, Si, and Ca occurring in the largest size bins of the DRUM samples, with elements indicative of roadways, such Pb, which is present in road shoulder dust due to long term accumulation dating to the era of leaded gasoline (Young *et al*., 2002), tire dust as suggested by light absorption, S, Zn, and Cu (Adachi and Tainosho, 2004), and coarse S, which may be due to both tires and

heterogeneous oxidation and capture of motor fuel sulfur emissions on the surface of roadway particles.

Brake Dust. The second fugitive type is identified as brake dust (Figure 2-3b). This is identified by the large Fe, V, and Cu content and the distinctive size distribution (Sanders *et al*., 2003). For comparison, the size distributions of brake dust reported by Sanders *et al*. (2003) are

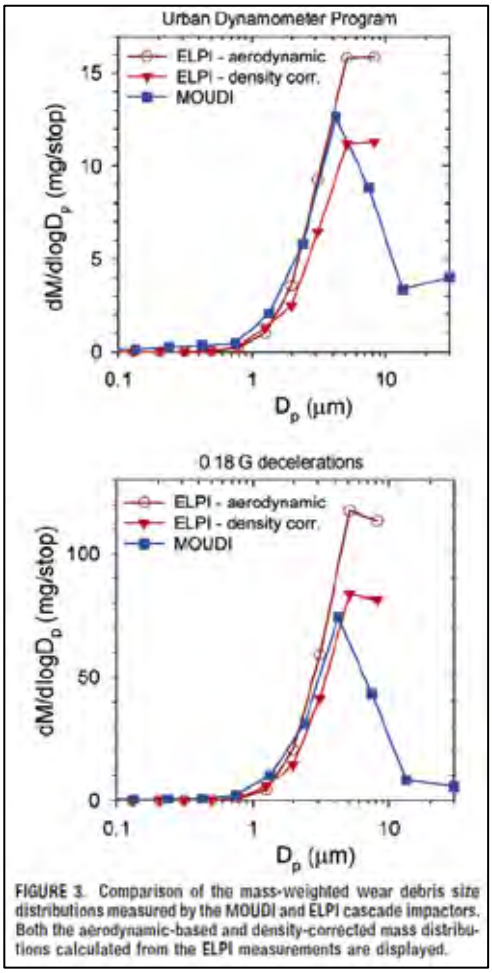


Figure 2- 4. Size distributions for light duty vehicle brake dust by multiple measurements. Reproduced from Sanders *et al*. (2003).

shown in Figure 2-4. The distributions in Figure 2-4 are nicely reproduced by the shapes of the normalized elemental data in Figure 2-3 (lower). This particular result highlights the additional source discrimination ability provided by size-resolved sampling.

The time-series data for the fugitive aerosol types are shown in Figure 2-5. The timing of the concentration variation strongly reflects the diurnal patterns of vehicle traffic, including the morning and evening peaks (especially in the brake dust data) and the low traffic activity on

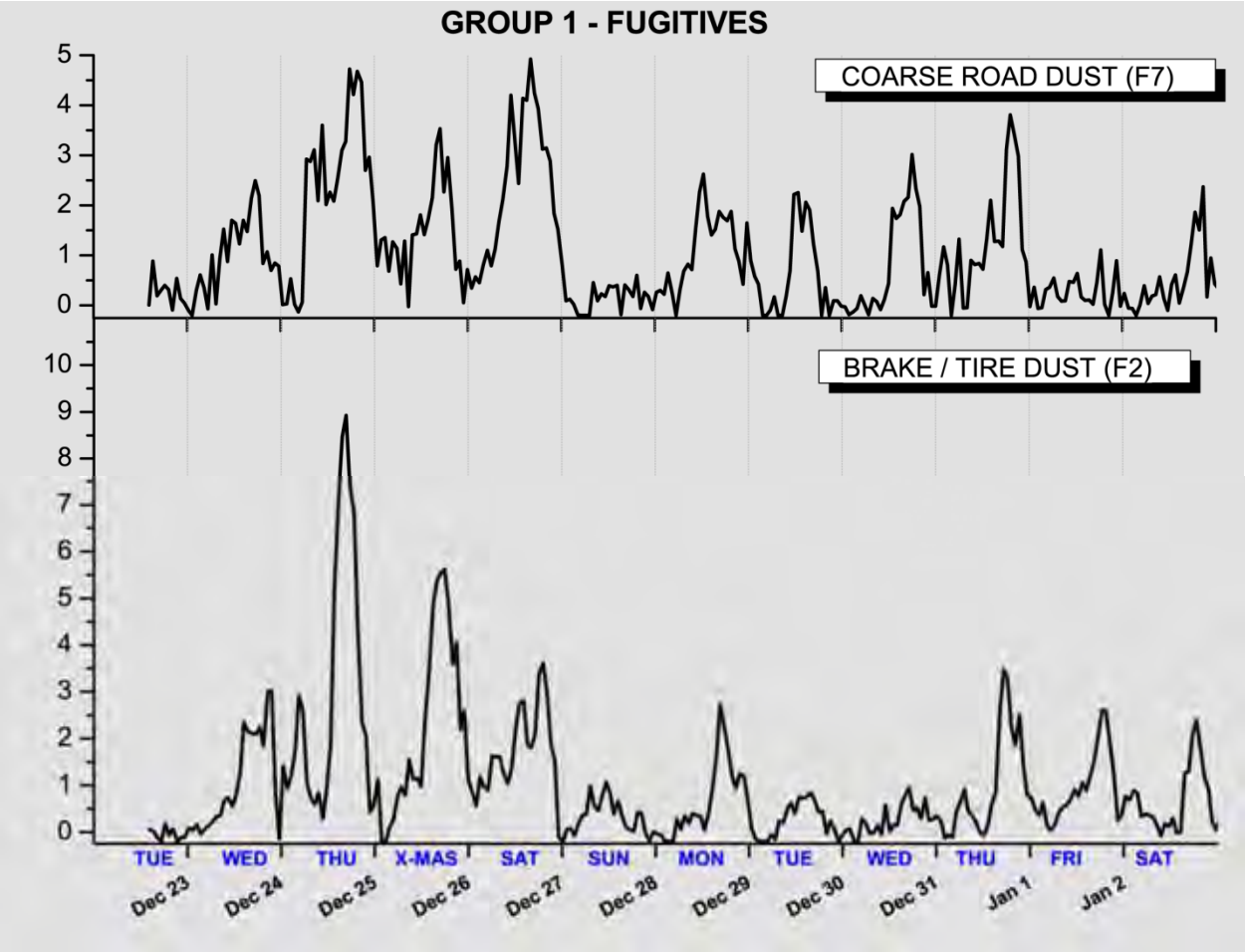


Figure 2- 5. Temporal patterns for fugitive emissions produced by the PMF 9-factor solution. The strong diurnal cycles and the Sunday lulls in vehicle traffic are clearly visible in the plots.

Sunday. The day-to-day variation in the heights of the road dust peaks also strongly reflects the effects of rain on 12/28 (about .3 inches, sufficient to strongly suppress road dust) and light rain on 12/31 and 1/2.

Group 2 – Regional Aerosols

Regional aerosols are those that are widespread and cannot be ascribed to individual sources, usually because they are formed, at least in part, by atmospheric conversion of precursor emissions, because the material has been chemically and physically aged in the air, or because they are a mix of material from multiple sources transported from a distant source area, such as urban air from another city.

The PMF analysis identified two such aerosol mixtures, one consisting of aged, chemically transformed urban air from the San Francisco Bay area (Figure 2-6, top), and the other consisting of presumably local urban air modified by interaction with water droplets, primarily fog, but including light rain.

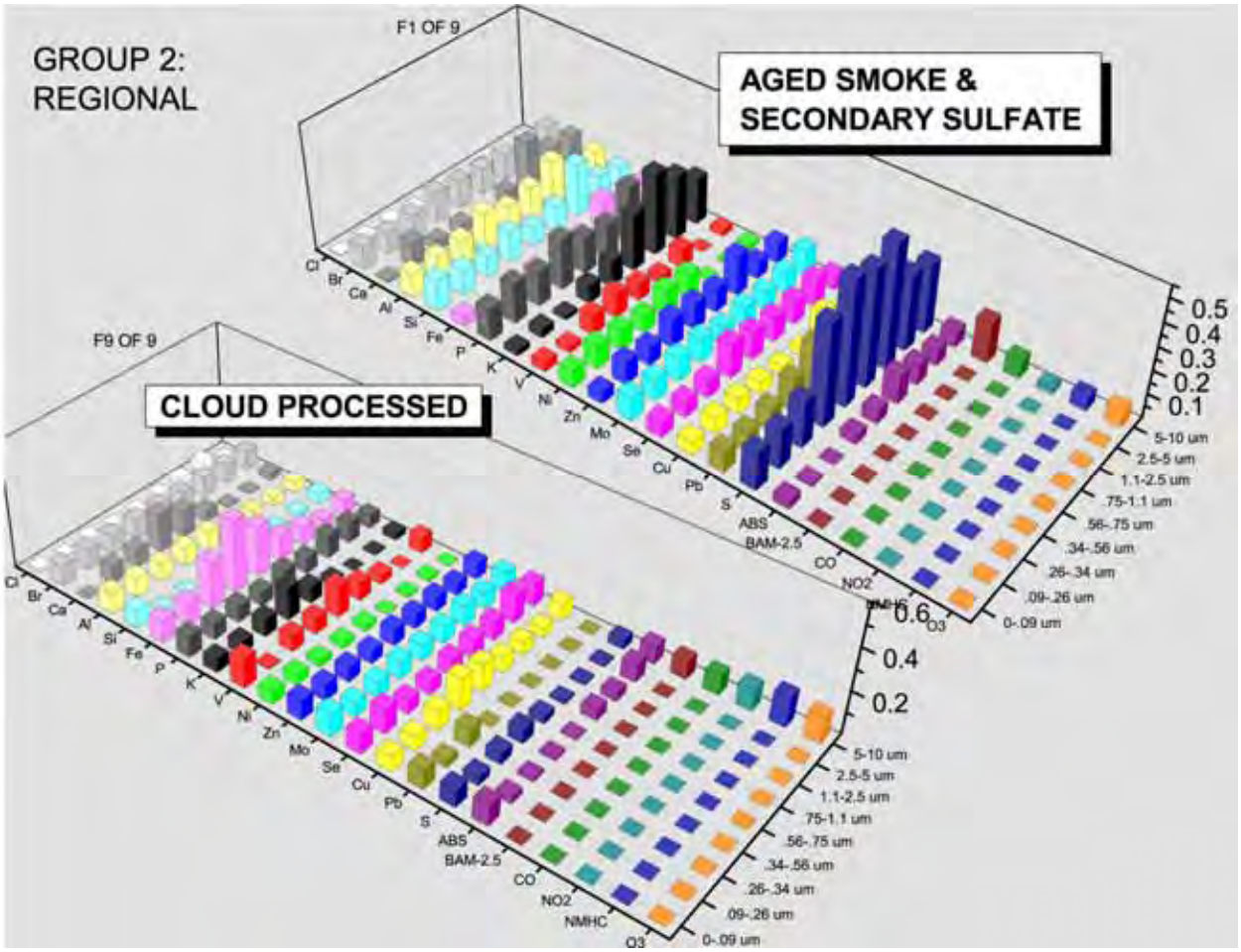


Figure 2- 6. Regional aerosol types in winter at Del Paso Manor. Two distinct types were identified, one transported from the San Francisco Bay area, and the other strongly modified by interaction with water droplets (fog and rain).

Aged Smoke and Secondary Sulfate is readily recognized as aged material by two characteristics. First, elemental combustion markers are present, but with only weak signals for their original fine sizes as emitted, suggesting long aging that permits aerosol coagulation.

Second, the broad and robust sulfur signature, peaking over the size span of about 0.5-2 μm diameter, is a classic characteristic for secondary sulfate, whose growth involves oxidation of gaseous SO_2 to SO_4, its incorporation into particle sulfate, and then significant particle coagulation and accumulation of water on the particles to produce the particle size distribution shown in Figure 2-6 (top) - a process that takes several to many hours.

Cloud Processed aerosols are particles that exist in between droplets in fog or rain. They consist of both materials that have low affinity for water (low water solubility) and particles produced by evaporation of droplets (such as the remnants of evaporated virga). The former are dominated by fresh combustion emissions, which show up as the metals from V to Pb and fine light absorption in the correlograms for this factor (bottom of Figures 2-6 and 2-7). The latter are recognized by their size distribution as an important diagnostic characteristic: they exhibit low "deposition velocity", meaning they are neither so large that their inertia prevents them from being pushed aside by the air in front of falling droplets (large particles are scavenged by falling droplets), nor so small that they are readily captured by surface attraction to droplets or other particles. This is illustrated in Figure 2-7.

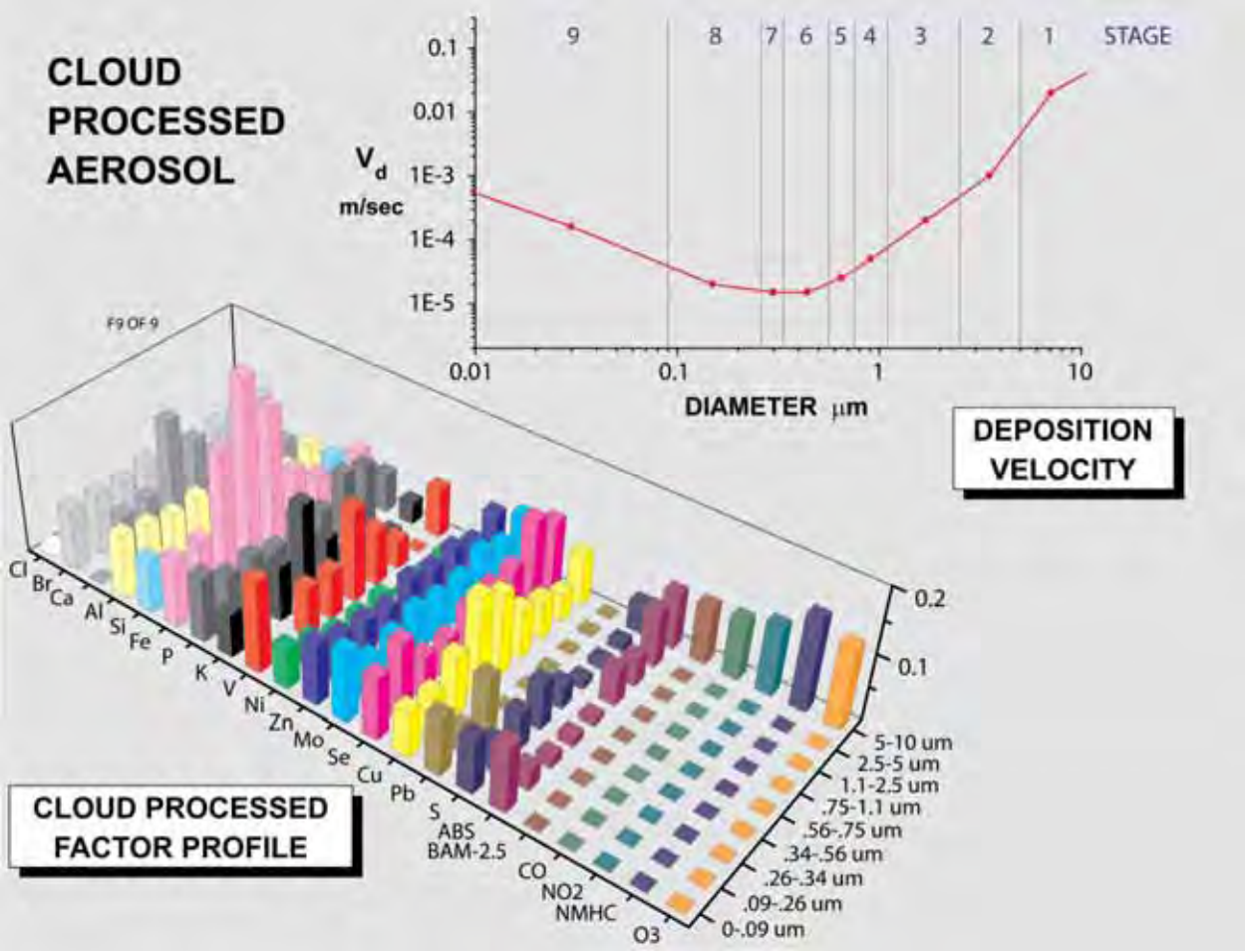


Figure 2- 7. The size distribution of cloud processed aerosols peaks at about .3 - .8 μm, which represents a minimum in the tendency of particles to either be inertially scavenged by collisions with droplets or diffusionally collected on to the surface of droplets or other particles. The size relationship with particle deposition velocity as computed by Piskunov (2009) is shown at the top. The correlogram is the same as in Figure 2-6, but drawn with an enhanced z-axis.

The time series data for the regional factors reflect their origins (Figure 2-7). The temporal patterns of the aged aerosol shows its association with the strong air flow from the west which accompanied the cold front rain event of Dec. 28, and then the persistent onshore flow after Dec. 30.

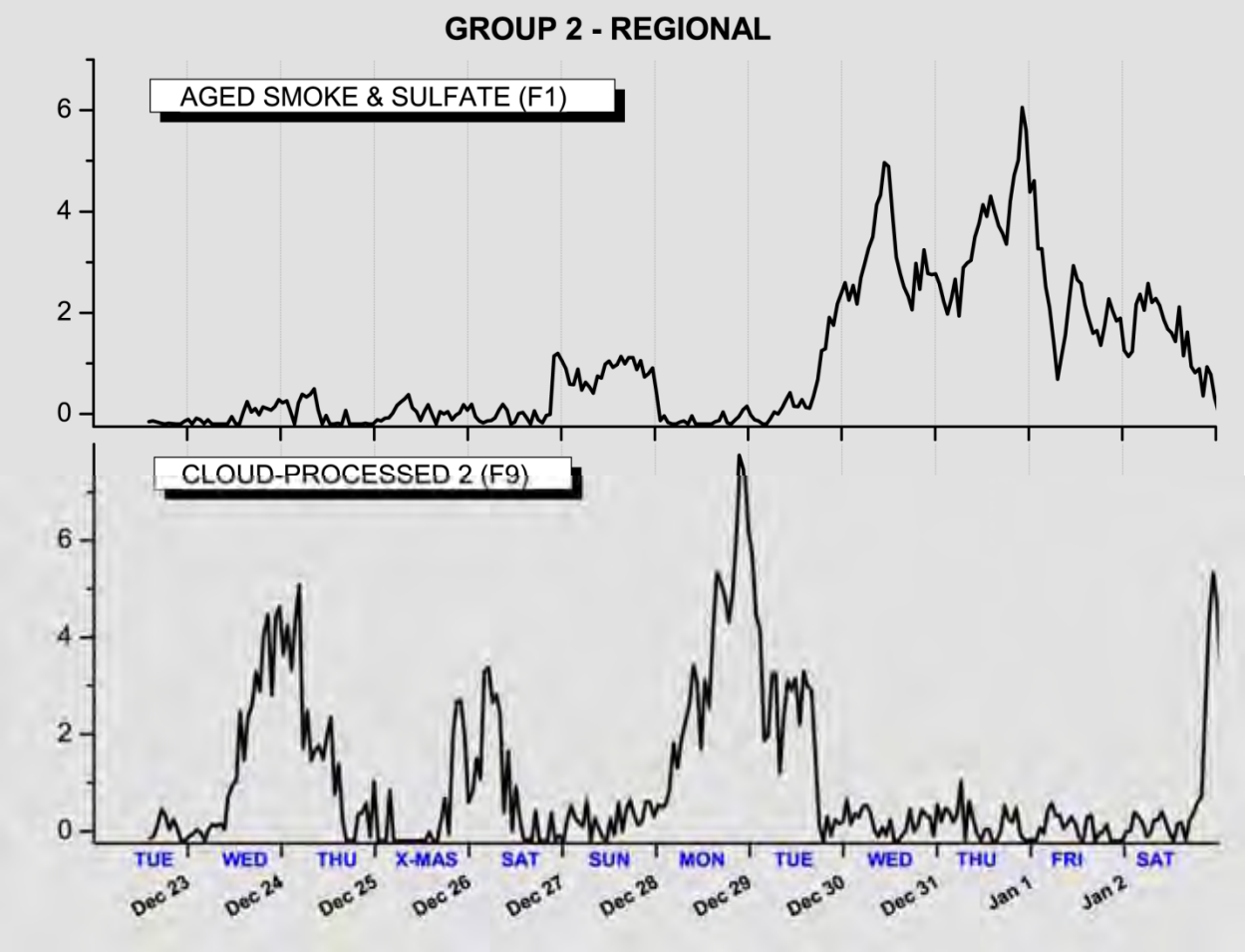


Figure 2- 8. Timeseries for the regional aerosol types. The "Aged Smoke and Sulfate" shows the changeover from local to transported materials that occurred after Dec. 30, when westerly wind diluted local emissions and brought aged San Francisco Bay Area air into Sacramento. The "Cloud Processed" material peaked in the presence of fog or rain (see Figure 2-9).

The association between moisture and the "Cloud Processed" factor is shown in Figure 2-9, which plots relative humidity, fog, and precipitation data for the study period along with the timeseries score for the factor and the total $PM_{2.5}$ load as recorded by the BAM sampler. The peaks of this factor (red curve in Figure 2-9) tend to coincide with overnight high humidity and fog periods, and the factor is absent during periods of wind (when the transported Bay Area material shows up in Figure 2-10).

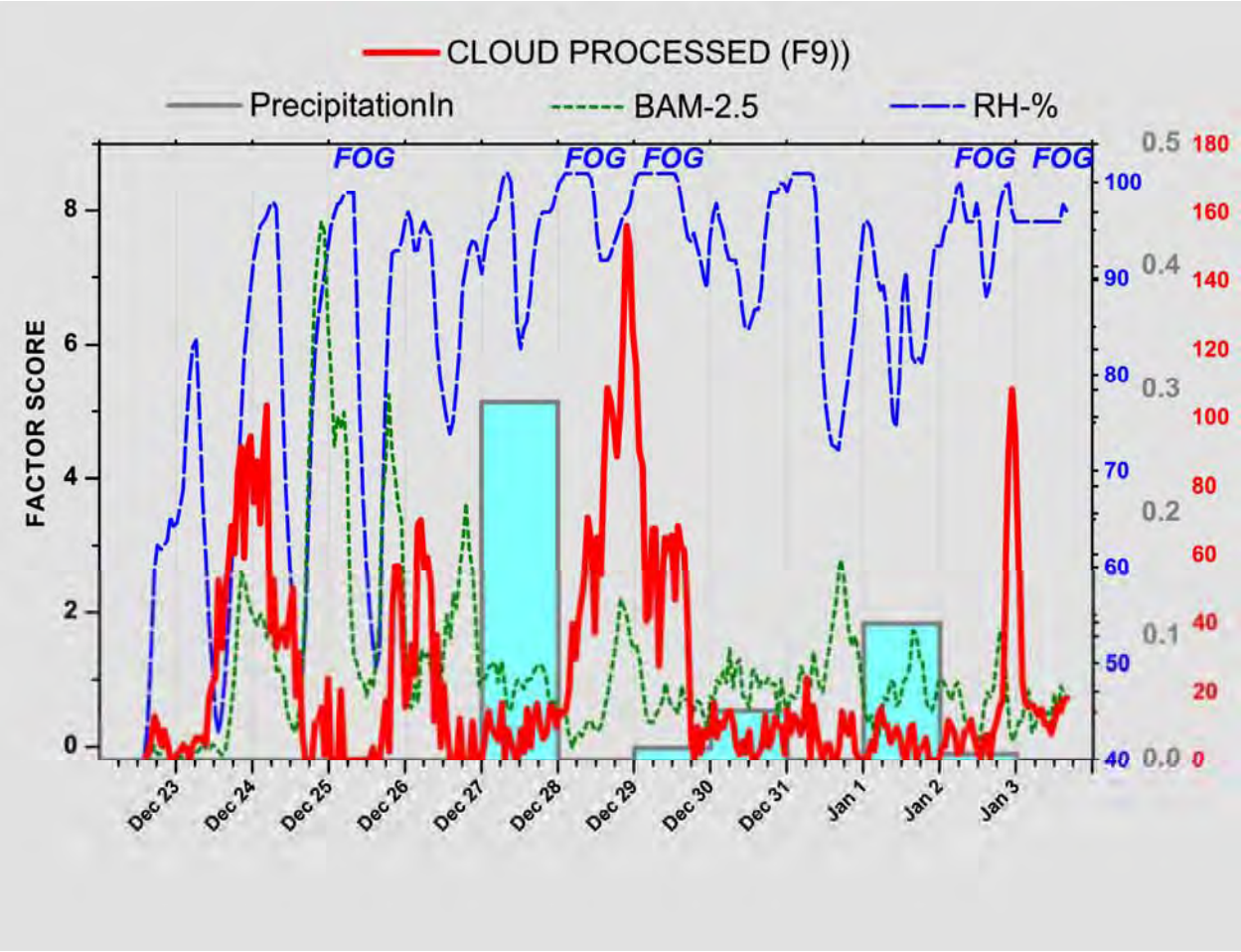


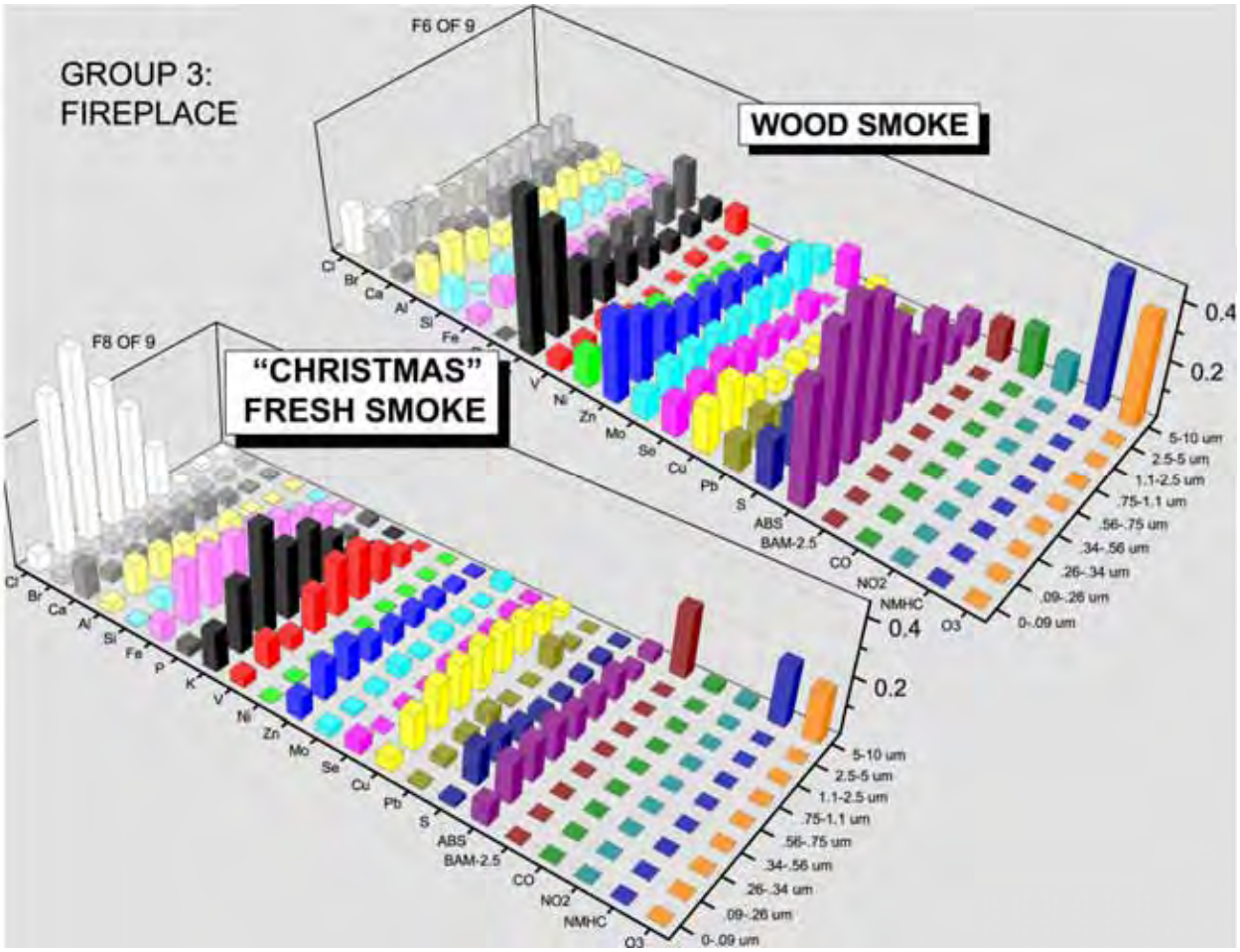
Figure 2- 9. Time traces of the "cloud Processed" factor (solid red), relative humidity (long dash blue), precipitation (grey with cyan fill), and total $PM_{2.5}$ from the BAM sampler (short dash green). Both the cloud processed and total aerosol drop during the sustained rain on Dec. 28.

Group 3 – Fireplace Emissions

Biomass combustion smoke was a major component of the particle load at Del Paso Manor during this experiment. The PMF identified two "flavors" of this smoke.

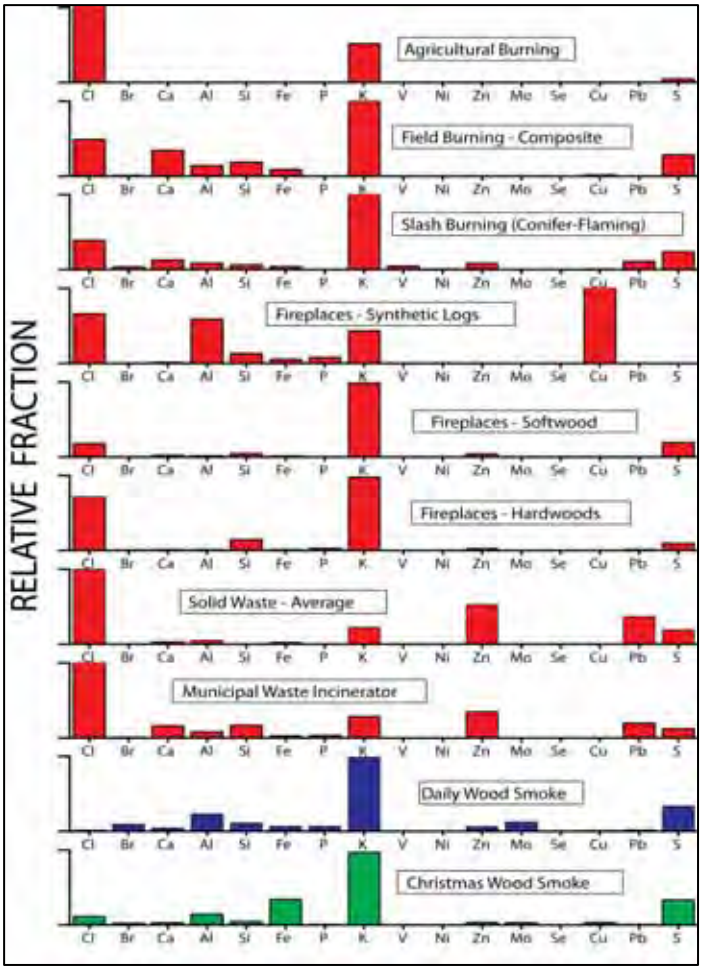
Figure 2- 10. Fireplace biomass smoke factor correlograms. The conventional "Wood Smoke" factor (top) is rich in potassium and "soot" (light absorbing particles), and also is a major source of non-methane hydrocarbons. The "Christmas" factor shows the expected potassium of biomass, but is strongly enriched in chlorine, and produces less hydrocarbon vapor.

Wood Smoke (Figure 2-10, top) was familiar from past winter studies in the region, consisting of the expected markers for wood combustion, especially potassium, strong light



absorption, and strong hydrocarbon vapor emissions, all consistent with wood smoke.

"Christmas" Wood Smoke (Figure 2-10, bottom) is a surprise in this data set. Although similar to the "Wood Smoke" factor in that it shows the expected potassium of biomass, its stronger peaks of Cl, Fe, and V clearly indicate a different type of smoke. This indicates a



source very close to the monitoring site, such that chlorine in the smoke has little time to be liberated by reactions with other pollutants such as nitric acid. The very strong pulse of this smoke results in a disproportionate Cl signature in the correlogram. Resolving the source of this material required constructing bulk chemical profiles for comparison with known emission sources recorded in the USEPA SPECIATE data base.

The top 8 profiles in Figure 2-11 were selected based on known Cl content and biomass associations. The PMF-derived $PM_{2.5}$ profiles (bottom two) were constructed by summing the mass-converted species factors for the relevant elements over the lower 7 of the nine size bins in the PMF output (0-2.5 μm). The plots are all scaled so that the largest constituent is the full height of the Y-axis. Comparing both PMF profiles to the source tests, what appeared initially to be an excess of Cl on 12/24-25 is more likely evidence of significant loss of Cl most nights as wood smoke ages.

The timeseries plots for the fireplace factors are shown in Figure 2-12. The Daily Wood Smoke factor is relatively consistent over the time period of the experiment, peaking after

Figure 2- 11. Comparison of the $PM_{2.5}$ portion of the "Christmas" Wood Smoke and Daily Wood Smoke PMF profiles to source-test based $PM_{2.5}$ profiles for a range of candidate sources (USEPA, 2009). Although not a perfect match, the peaks of Cl, Al, Fe, K, and S are strongly suggestive of a softwood combustion source.

midnight most nights. This tracks well with heating demand and reflects the longer burning of heating fires and a city-wide buildup leading to the late peak. In comparison, social fireplace use, as would be expected on a holiday is less likely to be sustained after midnight, and the timeseries plots support this interpretation.

Based on the lack of wind on the night of 12/24-25, it is assumed that the sources of the "Christmas" Smoke are very close to the monitoring site. It is likely, then, that the "Christmas" Smoke is much fresher than the smoke measured at this site most nights, and that may account for the much stronger Cl signal. Referring back to the PMF-derived profiles in Figure 2-11, there is a small enhancement of Zn and Mo in both that suggest some mixing with vehicle exhaust; the larger fraction in the Daily Smoke, although not impressive, does support the interpretation of greater aging in this factor.

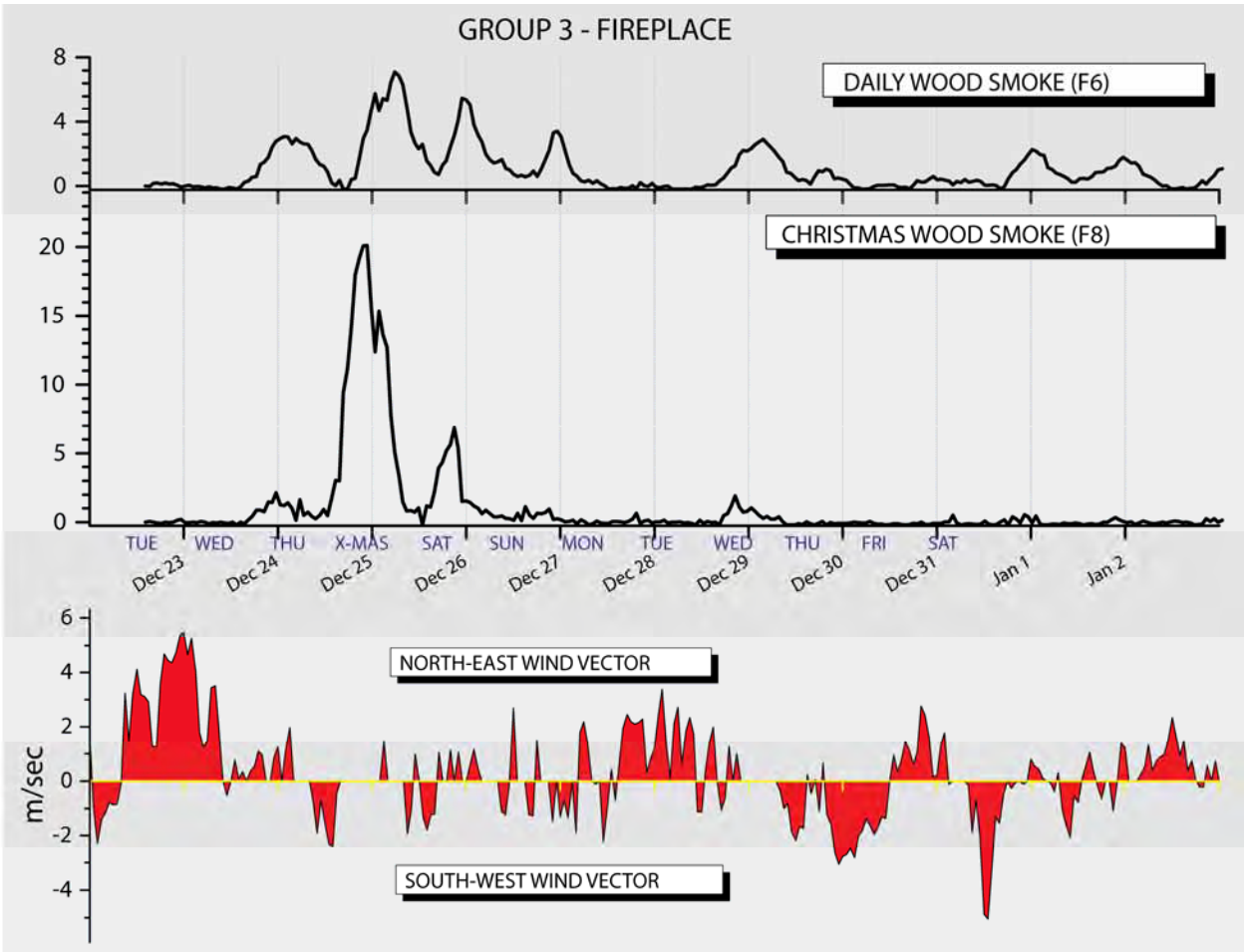


Figure 2- 12. Timeseries of the fireplace factors and computed "upslope-downslope" wind vectors (prevailing winds in this run back and forth NE and SW) The Daily Wood Smoke factor tracks the expected diurnal cycle of the demand for residential heat. The extreme confinement of the other factor to the Christmas holiday period suggests a different burning regime and the very low winds define this factor as very fresh emission.

Group 4 – Fossil Fuels

The factors in the final group all initially appear to be variations of internal combustion engine emissions, in that they all share markers for lubricating oil ash (Zn, P, and Mo). They differ in their association with sulfur, light absorption, NO_2, CO, hydrocarbons and $PM_{2.5}$ mass. The three profiles are shown in Figure 2-13.

Cold Gasoline Vehicle profile identification is based on the combination of sulfur (now more prevalent in gasoline than in diesel fuel), sooty particles (light absorption), and gaseous evidence of cool combustion conditions – low NO_2, and elevated CO and NMHC, consistent with minimal exhaust catalyst activity during cold starts.

Mixed Motor Vehicle is a profile showing the higher NO_2 to CO ratio expected of warmer combustion and presumed higher engine loads, as well as efficient control of NMHC, as expected for vehicles with effective (*i.e.* warmed up) exhaust catalysts. This profile dominates the correlation data for fossil fuels because warm running dominates the operation time of most

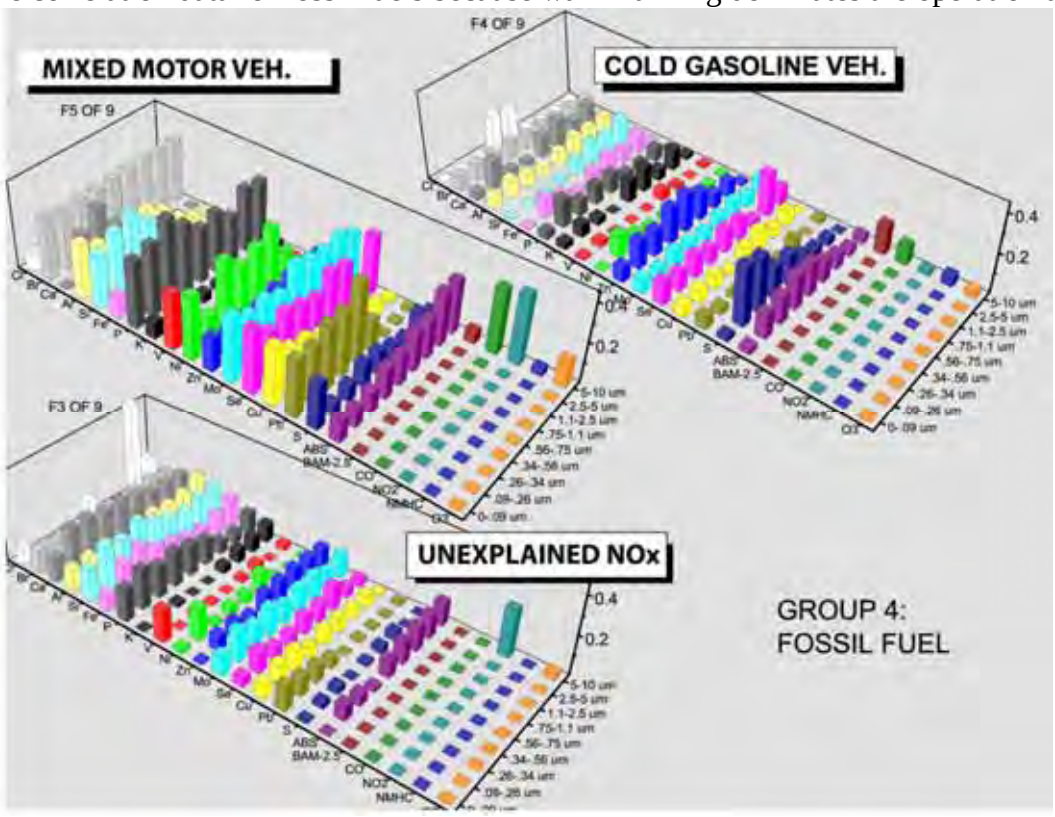


Figure 2- 13. Composition profiles for the three Fossil Fuel types. These have markers for lubricating oil ash in common, and are distinguished by their varying associations with sulfur, light absorption, NO_2, CO, hydrocarbons, and $PM_{2.5}$ mass. The "Unexplained NOx" factor has zero correlation with $PM_{2.5}$ mass.

vehicles. The midday dips in this factor (Dec. 29- Jan.1) are probably in part due to the diurnal wind cycle at Del Paso Manor (Figure 2-14, red plot at center), which would commonly carry emissions from the Interstate 80 corridor to the site at night, but reverse in midday. At this point, the PMF analysis does not permit finer distinctions regarding internal combustion engine (ICE) emissions. The ICE emissions in the region include not only light duty vehicles, but also medium and heavy duty trucks and significant rail operations; distinguishing among these sources would be a desirable PMF result, but apparently the sample period was not long enough to capture enough variation in ICE activity to permit such discrimination.

Unexplained NOx is a problematic profile. The source exhibits very clean combustion, based on the much lower CO and NMHC loading, essentially no sulfur, and has zero correlation with $PM_{2.5}$ mass (BAM). The correlation with coarse Cl (sea salt?) is inconsistent with motor vehicle fuel formulations, but may indicate that this profile is associated with deeper atmospheric mixing that could bring marine air through the delta to the Del Paso Manor site. Alternatively, this profile may represent the accumulated regional vehicle signature, but aged enough to be temporally de-coupled from accompanying aerosol.

The leading candidate explanation at this time is that this is, indeed, motor vehicle exhaust from fully warmed up, clean-running vehicles. Based on its temporal pattern, its appearance in midday is likely driven by the break-up of the nocturnal inversion over the city, causing a sudden change from local to more regional mixing. Since this factor makes no statistically recognizable contribution to $PM_{2.5}$ it does not need to be identified in order to explain the high $PM_{2.5}$ events that were the focus of this study.

The timeseries data for the fossil fuel factors is shown in Figure 2-14. These plots indicate that, as expected, during the Christmas holiday period there was more low speed local traffic in the suburban neighborhood surrounding the measurement site and less warm running (presumably commuter) traffic. There is an anomalous overnight period of sustained warm-running vehicle activity at the end of the holiday weekend (Dec. 28-29), which is tentatively explained as holiday-end traffic on Interstate 80.

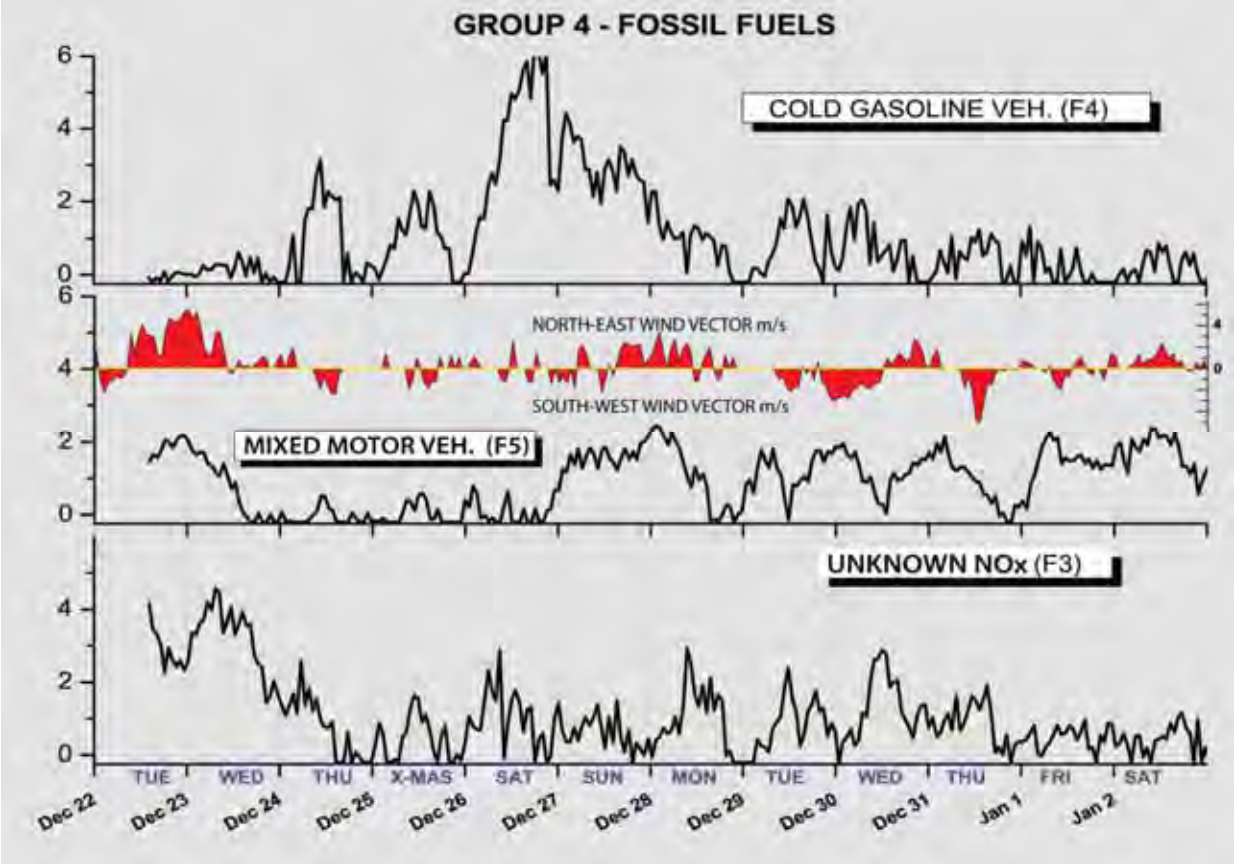


Figure 2- 14. Time series results for the fossil fuel factors. In the residential neighborhood location of the Del Paso Manor site, the local, cool-running emissions of local traffic dominate on the Christmas holiday weekend. The strong warm gasoline signature overnight on Dec. 28-29 may reflect unusually heavy holiday traffic on Interstate 80. The unknown NOx is probably a regional signature, but its nature is unclear.

Hourly Source Apportionment for the Study Period

A primary goal of this study was to understand $PM_{2.5}$ source contributions at an hourly level, thereby being able to examine the factors driving individual $PM_{2.5}$ peak days. By incorporating the BAM $PM_{2.5}$ hourly data into the PMF data matrix, the cross-correlations among the factors and that measurement were directly computed and individual factor's contributions to hourly $PM_{2.5}$ mass can be extracted directly from the PMF outputs. With these results it is possible to reconstruct hourly $PM_{2.5}$. Figure 2-15 presents these results as stacked curves. The regression line for this reconstruction has an intercept of 4.3 $\mu g/m^3$, a slope of .85, and an R^2 of .84, and is highly statistically significant.

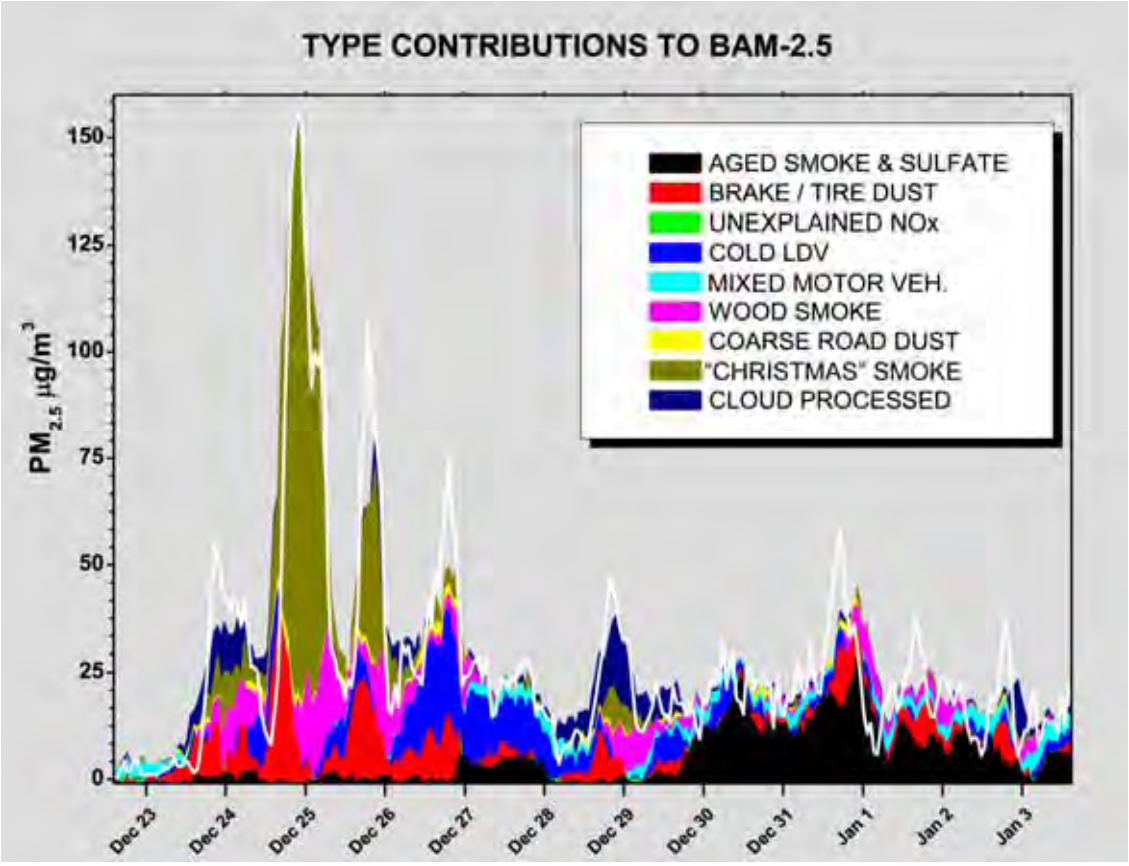


Figure 2- 15. Hourly contributions to $PM_{2.5}$ by each of the nine pollution types identified by the PMF analysis. The stacked curves total the reconstructed contributions to the $BAM_{2.5}$ data. The actual $BAM_{2.5}$ observations are plotted as a white line. The Christmas holiday period is notable for the very large contribution of the "Christmas" factor, tentatively identified as very fresh wood smoke. In the latter part of the period local emissions are significantly diluted, but total mass is little changed as imported aerosol, apparently from the San Francisco Bay Area, moves through Sacramento.

Discussion

The goal of this study was to utilize the fine temporal and chemical resolution available with PMF analysis of a hybrid data set composed of hourly size-resolved aerosol and gas data to diagnose the causes of individual high $PM_{2.5}$ events in suburban Sacramento. Although the speciated measurements did not span the entire range of aerosol components (specifically, the elements O, N, and C, usually significant fractions of the total mass), the inclusion of hourly $PM_{2.5}$ data collected on site (BAM $PM_{2.5}$) in the analysis allowed statistical allocation of mass to nine observed elemental and gas "profiles" that appear to represent real components of the urban aerosol mass. The final $PM_{2.5}$ allocation explained the variation of observed mass to a high degree, and plots of the hourly allocation facilitate visualization of the dynamic variation of aerosol composition and concentration at the Del Paso Manor site over the study period.

The most striking finding of this analysis is that the highest peak of $PM_{2.5}$ concentration during the study, occurring over the Christmas holiday, was driven by unusually fresh emissions from residential wood combustion, and, based on its temporal pattern, not primarily for heat.

This finding should be of significant value to the Sacramento Metropolitan Air Quality Management District, since its primary control strategy for winter $PM_{2.5}$ has been based on managing use of wood for residential heating through a public information program and declaring "burn" and "no burn" periods based on meteorology. It seems likely from these data that that program has been successful, and that the unique events of Christmas 2009 were not due to a failure of that program, but atypical behavior in residences which do not rely on wood for heat, but rather engage in infrequent burning for social reason. Managing this source would probably require a different approach to public outreach and education from that aimed at wood-heat users.

Conclusions

The 2009-10 Del Paso Manor Winter $PM_{2.5}$ study was conceived to demonstrate the utility of extremely high temporal and compositional resolution sampling as a means to unravel the various source contributions to elevated 24-hour $PM_{2.5}$ concentrations. In that it has succeeded, with successful collection of samples with limited staff time invested at the sampling site, and a successful analytical program that has produced findings that are both scientifically novel and directly applicable to the needs of the sponsors, the Sacramento Metropolitan Air Quality Management District.

We would like to thank the District for its indulgence of our intrusion on the Del Paso – Manor site during a busy season, and for their support in the pursuit of this research.

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Appendix 1.
Measuring Size-Resolved Light Absorption and Coordinating S-XRF Data

Light absorption for the samples was measured by digitally imaging each set of 9 strips against a white background (thus compensating for any effect of scattering aerosols), then using image processing to extract "blank" and sample deposit brightness data along each strip.

The initial image is created by scanning the strips along with a calibrated optical density standard ("density wedge") on the bed of a photographic quality scanner (HP 6280), Figure X-1.

Figure X-1. Digital scanned image of DRUM sample strips with calibration "density wedge" (right). Blue rectangle is image area shown in Figure X-2.

The scanner image is then converted to a 256-bit, 300 BPI panchromatic black-and white bitmap and the density wedge brighnesses are extracted and used to verify linear response of the scanner over the densities shown by the samples in the image.

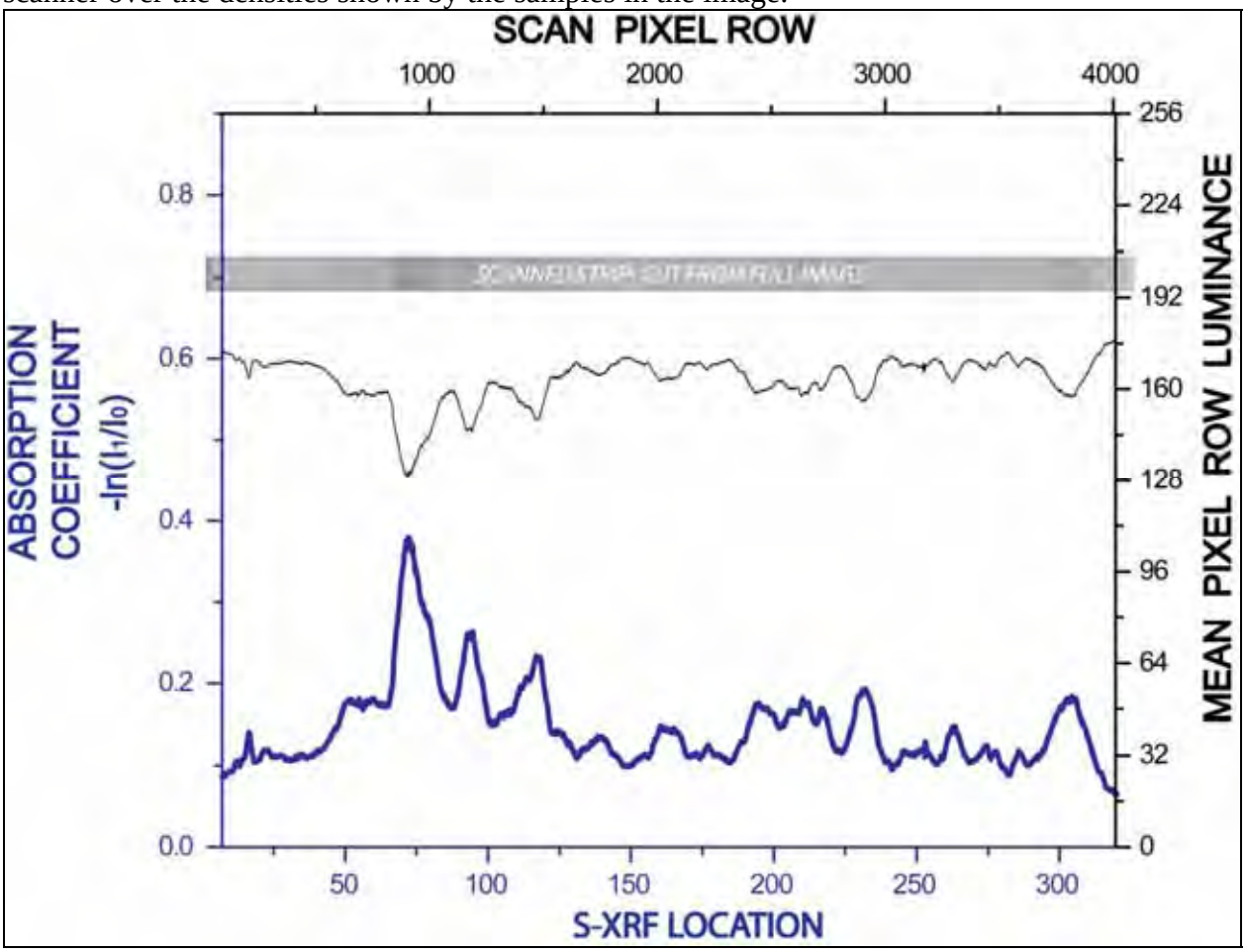

Figure X–2. Image segment from 256-bit grey scale is converted to absorption coefficient, and then scaled to match S-XRF data.

A sample strip of 30 or more pixels width is cut along the imaged deposit for each strip, and then converted to a numerical matrix of brightness values. Statistics are computed for each row of the matrix, providing a mean and an uncertainty value (1σ) for each pixel scan (row) along the strip (Figure X-2).

An array of light absorption coefficients along the sample deposit is computed by applying Beer's Law, using the mean of pixel luminances of an area of the strip without sample deposit as a field blank to compute I_0, and the luminances of each row of pixels from the deposit as replicates of I_1, then recorded as a mean and uncertainty (1σ) for each row. Since each S-XRF point covers about 6 optical scan lines, absorption data is then aggregated again to match the S-XRF data, carrying the pixel-level uncertainty (now 150+ pixels per XRF point) through into the final merged data set. For a normalized analysis, the deposit absorption coefficients are ready to use in the PMF.

If real atmospheric absorption is desired, size-specific absorption coefficients, b_{abs}, can be computed by dividing the deposit absorption coefficient by the effective ambient air optical path length, then summing all stages to get ambient absorption. For 1-hour resolved data with a nominal flow of 10 l/min, sample volume is 0.6 m^3 and the time step deposit area is .000005 m^2 (10 mm x .5 mm), giving an effective path length of 1200 m.

Figure X-3 shows a comparison of absorption measured by this method with IMPROVE "elemental carbon" (EC) data and absorption derived from an aethalometer.

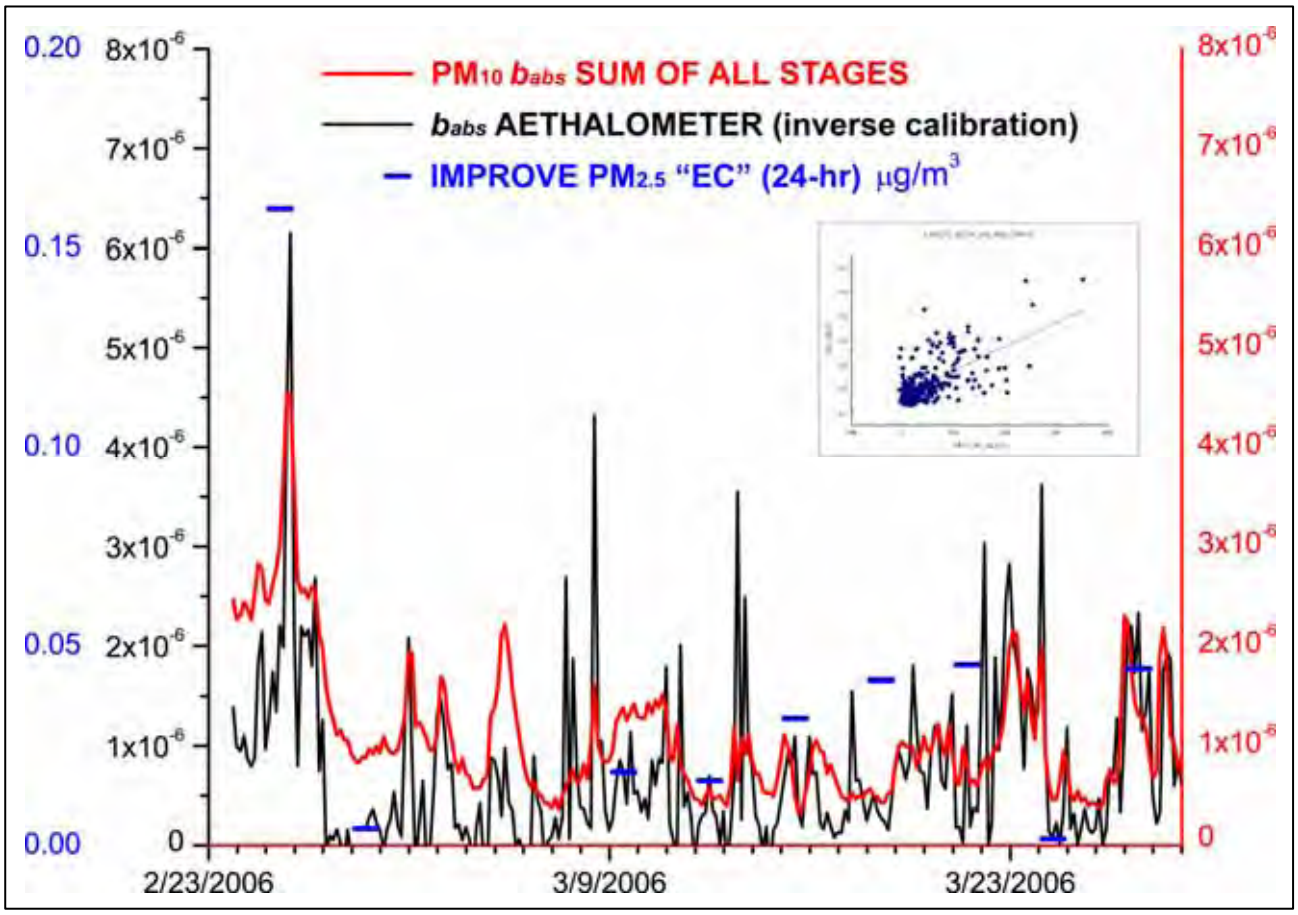

Figure X-3. Comparative time series of aerosol light absorption measurements from drum samples (red), an aethalometer (black – inferred by reverse calibration of reported BC mass), and IMPROVE 24-hr EC mass (blue). The EC mass scale (blue, left Y-axis) is adjusted to match the aethalometer calibration factor. Inset is a scattergram of the DRUM absorption vs. the aethalometer absorption. In this case, the aethalometer repeatedly reported 0 when the DRUM indicates aerosols were present, thus, it appears that the DRUM is more sensitive under clean conditions than is the aethalometer.