Final Report
to the
American Lung Association – Sacramento Emigrant Trails
Health Effects Task Force

The Sacramento/Interstate -5 Aerosol Transect Study

December, 2002 – January, 2003

Prof. Thomas A. Cahill, P.I., Dr. M. Roumie (Fulbright Fellow, Lebanon), Lee Portnoff, Victor Ray, Jeanette Martin, Prof. Roger Miller (Dept. of Physics, CSU Stanislaus), Dr. Steven S. Cliff, Prof. Kevin D. Perry, (Dept. Meteorology, Univ. of Utah), and intern Chinyere Williams, the DELTA Group, University of California, Davis,
http://delta.ucdavis.edu,
and
volunteers of the ALASET HETF, especially Betty Turner and
Earl Withycombe.

Abstract: Fine aerosol mass was measured every 3 hours along a 9 site transect from west of Davis to Shingle Springs during the period December 12, 2002, through January 16, 2003. The fine $PM_{2.5}$ aerosols were size segregated into either 3 or 6 size modes above 0.09 μm diameter, with coarser aerosol available at 5 sites. While no violations of the 24 hr federal $PM_{2.5}$ standard were observed, the highest mass levels observed were associated with winds coming to Sacramento up the San Joaquin Valley under the typical inversion. The direct impact of Interstate 5 on near downwind sites was evident in all weather conditions, while Watt Avenue had a similar impact on Arden Middle School. On many days, aerosol mass values were similar across the entire network, but with an enhancement at the Crocker Art Museum site down wind of I-5 and lesser values at Shingle Springs, which was often above the inversion. Compositional and optical data were generated at Crocker Art Museum and Arden Middle School sites to help identify the sources of the observed aerosols. Size and compositional evidence of the impact of diesel and smoking car exhaust was strongly seen at both sites, but wood smoke was usually only a minor factor. A large PM_{10} event seen on the Del Paso Manor TEOM was shown to be sea salt from the California coast northwest of Sacramento, while the New Year's Eve fireworks on the Tower Bridge provided distinctive signatures in very fine aerosols at Crocker Art Museum site and even more strongly at Arden Middle School.

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HYSPLIT Trajectory analysis - January 2 – January 6, 2003
Note: For Pacific Standard Time, subtract 8 hr

Executive Summary:

With the essential and enthusiastic assistance of ALASET HETF volunteers, we have collected aerosol samples at 9 sites on a rough line from northwest Davis across Sacramento, including sites near I-5 and Watt Avenue, to Shingle Springs, in the period December 12, 2002, through January 16, 2003. Collection was accomplished continuously on lightly greased Mylar strips by rotating drum impactors with either 3 stages (2.5 to 1.15, 1.15 to 0.34, 0.34 to circa 0.15 µm diameter) or 8 stages (circa 12 to 5.0, 5.0 to 2.5, 2.5 to 1.15, 1.15 to 0.75, 0.75 to 0.56, 0.56 to 0.34, 0.34 to 0.26, 0.26 to 0.09 µm diameter). Analyses were performed on all samples for mass (soft beta ray attenuation) and optical transmission (350 – 850 nm) in 3 hr increments. All samples at Arden Middle School and the very fine particles ($0.26 > D_p > 0.09$ µm) from the Crocker Art Museum site were in addition analyzed by synchrotron x-ray fluorescence (S-XRF) for 32 elements sodium through molybdenum, plus lead. Detailed quality control and quality assurance tests were conducted on all collection and analysis protocols and are summarized in the report (Appendix A and Appendix B) and fully presented in the DRUM Quality Assurance Protocols ver 8/02 (2002) presented as part of this study.

The weather was typical for the period, with strong rainstorms in December and periods of hazy stagnation around Christmas week and in most of January. The results show $PM_{2.5}$ aerosol masses never violated 24 hr federal standards. During many periods, concentrations across the entire network were similar, although the aerosol enhancement caused by Interstate 5 was always evident. Much of this mass was in very fine particles that, near I-5, during periods of stagnation approached values seen in Fresno at the First Street EPA Super-site (Cahill et al, 2002). The estimated impact of diesel/smoking car exhaust from I-5 was about a quarter of the $PM_{2.5}$ mass seen nearby. There was direct influence of Watt Avenue on the Arden Middle School that was comparable to that of I-5 on the Crocker Art Museum site. This impact was successfully modeled using prior roadway studies in California and explained by the very short distance and flat terrain between the heavily traveled road and the school buildings..

Trajectory analysis through use of NOAA's ARL HYSPLIT model has allowed specific features of the aerosols to be tracked to source regions. The elevated levels of pollutants seen starting Jan 2, 2003, were associated with stagnant conditions, with haze and "dry" and saturated fogs seen repeatedly. Highest aerosol concentrations were seen on winds from the south during periods of inversion, winds that blew along the freeways from the San Joaquin Valley. Heavy biomass smoke signature was also seen on these trajectories that started in down slope winds from the Sierra Nevada, a site of heavy wood burning.

While we present working hypotheses and conclusions in this report, this enormous data set can provide the base for a great deal of future analysis.

Interpretation

1. The ALASET Health Effects Task Force Sacramento/Interstate 5 Transect Study was an operational success due to the heavy involvement of ALASET HETF volunteers, the efforts of the UC Davis DELTA Group, and modest but vital financial assistance.
    - **a.** The study was a size, time, and compositionally resolved transect of a major urban area, and opens a new approach to urban air quality studies.
2. No violations of the federal 24 hr $PM_{2.5}$ standards were measured.
3. There were extensive periods during which the transect showed spatial uniformity across the region, with rural Davis, Sacramento River, and Orangevale having very similar concentrations of $PM_{2.5}$ particles.
    - **a.** The Crocker Art Museum site next to I-5 was almost always elevated in $PM_{2.5}$ concentrations, and the Shingle Springs site, which was often above the inversion, usually had lower $PM_{2.5}$ concentrations.
4. The highest levels of $PM_{2.5}$ at all sites were generally associated with the typical slow winter drainage winds coming up from the San Joaquin Valley, (Appendix B), winds that moved parallel to Interstate 5 and Highway 99.
5. During periods of low winds, low inversions, and haze/dry fog, sharp increases in $PM_{2.5}$ concentration were seen as one went from immediately upwind to immediately downwind of I-5.
    - **a.** From the high point downwind of I-5, with 11 ± 5 $\mu g/m^3$ of added mass, concentrations fell off relatively smoothly as one moved to the east. On Jan 5 – 6, HYSPLIT isentropic trajectories showed that the wind came from the east, making the Crocker Art Museum site upwind of I-5 but downwind of the rest of Sacramento, including Hwy 99. Concentrations of $PM_{2.5}$ and all species fell to low levels, while the now down wind Sacramento River site had high concentrations.
6. Very fine particles ($0.26 > D_p > 0.09$ µm) were compositionally associated with diesel and smoking light duty gasoline powered vehicle exhaust through size, color, and the elements sulfur, phosphorus, and zinc at the Crocker Art Museum site, adding roughly 4.5 ($\pm$ 1.5) $\mu g/m^3$ of downwind mass based upon laboratory derived diesel ratios keyed to zinc. About ½ of this mass is from smoking cars.
7. The Arden Middle School site had a strong local source of mass in the sub-µm size mode that was most likely local in origin. On the average in the stable periods, Arden's concentrations fell between those of the ARB at 13 and T Street (not immediately downwind of a freeway) and Orangevale (suburban).
    - **a.** The direct effect of Watt Avenue was not immediately available in $PM_{2.5}$ mass profiles due to the lack of an immediate up-wind site.
    - **b.** The finest mode, $0.34 > D_p >$ circa 0.15 µm, showed both the effect of the New Years Eve fireworks on the Tower Bridge and a persistent elevated level of typical diesel/smoking car tracers - sulfur, phosphorus, and zinc.
    - **c.** The level of diesel/smoking gasoline vehicle impacts was larger at Arden Middle School than that at the Crocker Museum site despite lower traffic flows, a result consistent with model predictions including the proximity of the school to Watt Avenue and lack of barriers to air motion.

Introduction

While summer ozone health impacts in the Central Valley of California are a continuing and serious problem, winter impacts of atmospheric aerosols, liquid and/or solid particles suspended in the atmosphere, are a source in increasing concern. Routine violations of state and federal PM_{10} standards occur often, along with widespread and persistent violations of the new US EPA $PM_{2.5}$ standard.

There is overwhelming evidence from long term statistically based health effects studies of the effects of atmospheric aerosols on illness and death in humans. There has been for years a proven connection between health impacts and toxic metals such as cadmium, mercury, and lead, usually transported in aerosols, and major progress has been made in removing these from the atmosphere. Yet health impacts persist. In a recent presentation, (Devlin, 2002) the EPA summarized some of the components of the fine aerosols, those with sizes less then 2.5 μm in diameter ($PM_{2.5}$), that are most likely the causal factors in the currently observed health impacts, but there are certainly other factors as yet unidentified:

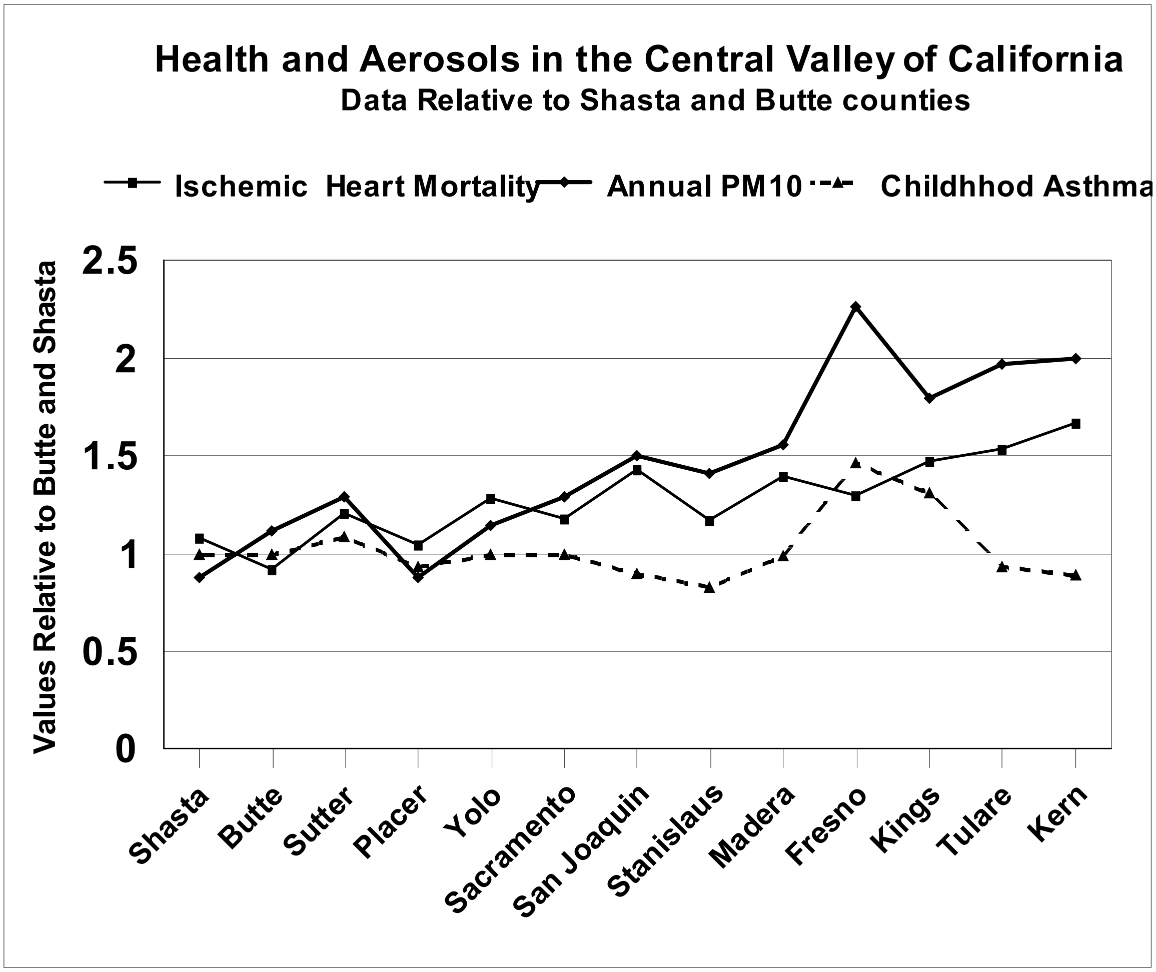
Insoluble very fine particles, < 0.1 μm diameter
Transition metals such as iron
High temperature organic matter from combustion
Acidic species (although the evidence is getting weaker)
Biological agents in the aerosols.

All of these components are abundantly present in the winter aerosols of the San Joaquin Valley.

While it is not the purpose of this report to detail potential health impacts of these particles, both long term and short term impacts have been documented in the Central Valley of California. Two examples are the association between PM_{10} particles and ischemic heart disease mortality documented in a prior Health Effects Task Force study (Cahill et al, ALASET HETF 1996), based on data from 1989 through 1992, and high rates for asthma shown in a survey of reported asthma cases by UCLA in 2002 (UCLA 2002) (shown below in Figure 1).

The association between ischemic heart disease, an illness that takes many years to develop, and PM_{10} aerosols in the Central Valley is statistically robust. Note that the meteorology of the northern Sacramento Valley, the land use, population mix, and even rates of cigarette smoking are essentially identical with those of the southern San Joaquin Valley. What is different is the air pollution. Weaker but still significant associations were found between ischemic heart disease and two different metrics of ozone. No association was found between carbon monoxide and ischemic heart disease. No association between any of these pollutants and strokes deaths was found.

Unlike ischemic heart disease, asthma is immediate. Thus, it responds on a very short time scale with pollutants, along with other factors. It too shows elevated levels, especially in parts of the San Joaquin Valley.



It is for these reasons that large scale studies are under way studying aerosols in the San Joaquin Valley, including an EPA Super-site at Fresno. Prior studies at Fresno (ARB-FACES) found a high level of very fine (0.26 > Dp > 0.09 micrometer) aerosols, including transition metals, present in winter months (DELTA Group FACES Final Report, CARB, 2003), similar to two of the factors mentioned by Devlin (2002).

Fewer studies have been done in the Sacramento Valley, with the important exception of the rice burning studies. In one study relevant to the present work, an effort was made to identify wood smoke. Profiles were made at Davis on Dec 23, 1994, and showed that the $PM_{2.5}$ aerosols during stagnation periods were spatially uniform across the city (Cahill and Gearhart, 1995) despite heavy use of wood burning fireplaces.

We attempted in this study to contribute to the resolution of these questions by joining a regional study and a local study of aerosol mass versus size and time for a period often characterized by persistent hazes, mid December to mid January

Purpose: To investigate the aerosols by size present near-upwind and near-downwind of Highway Interstate 5 in Sacramento and put these aerosols into time of day and regional context via a transect from northwest Davis to the Sierra Nevada foothills.

Work plan:

1. Prepare 9 rotating drum samplers (5 - DELTA 8-DRUMs, 4 - DELTA 3-DRUMs) with lightly greased Mylar substrates. Calibrate flows (critical orifice), prepare protection for the pumps. (Responsibility: DELTA Group http://delta.ucdavis.edu)
2. Choose 9 sampling sites on a roughly east-west profile. The sites were:

a. Upwind	8 DRUM	Northwest Davis, 1813 Amador Ave
b Upwind	3 DRUM	East Davis, USFS Chiles Rd, S I-80
c. Near upwind Interstate 5	8 DRUM	Sacramento River site, on levee
d. Near downwind	8 DRUM	Crocker Art Gallery, roof
e. Sacramento regional Watt Avenue	3 DRUM	ARB roof at 13th and T
f. Sacramento local traffic	3 DRUM	Arden Middle School roof
g. Sacramento - downwind	8 DRUM	Aerojet at Rancho Cordova
h. Sacramento – downwind	3 DRUM	Orangevale residence
i. Foothills – downwind	3 DRUM	Shingle Springs residence

(Responsibility: Joint with ALA-SET HE Task Force, volunteers)

Schedule:

1. On December 12, 2002, we set up 9 sampling sites by driving the transect, west to east, and meeting people at each site. The set up typically took < 30 minutes, including on site flow check.
   (Responsibility: DELTA Group and site volunteers)
2. Each week, checks were made sampler (is it running?) and phone to UCD
   (Responsibility: Site volunteers)
3. On January 16, 2003, we folded up the network, making final flow checks.
   (Responsibility: DELTA Group, site volunteers)
4. In late January, DELTA Group, UC Davis measured mass by soft beta ray technology. A quality assurance report is prepared.
   (Responsibility: DELTA Group)
5. In February, DELTA Group, UC Davis used S-XRF to measure elements every 3 hr at the Arden Middle School site (almost 1,000 measurements, 32,000 results) and in May the Crocker site (250 measurements, 8000 values)
   (Responsibility: DELTA Group) (Bench et al, 2002)
6. In March, optics are measured at Arden Middle School
   (Responsibility: DELTA Group)
7. In March, these data are combined with metrology.
   (Responsibility: TA Cahill)
8. In March
   1. Quality Assurance Documentation, and
   2. The Final Report Executive Summary is prepared for ALA-SET HETF (Responsibility: TA Cahill)

9. April 4 - Review by Health Effects task Force, ALA/SET; extensive comments noted and the report was modified. (HETF and T. A. Cahill)
10. June 20 – Copying and publication of draft Final Report to HETF. (Responsibility, UCD DELTA Group)
11. June 27 – Draft Final Report delivered to the Health Effects Task Force.
12. July 28 - Draft Final Report delivered to ALA/SET
13. September 5 - Comments received from ARB
14. September 25 – Report to and comments received from SMAQMD
14. November 21 – Review of ARB comments and suggested changes by HETF
15. December 3 – Final Report to ALA/SET

The data were analyzed (> 13, 000 values) for mass, combined with meteorology, and presented to the ALA-SET Health Effects task Force in March, 2003. Compositional analyses were later done for elements sodium through molybdenum plus lead by synchrotron x-ray fluorescence (S-XRF) at the Advanced Light Source, Lawrence Berkeley NL, for all three sub-$PM_{2.5}$ stages at the Arden Middle School and for the very fine ($0.26 > D_p > 0.09$ μm) particles at the Crocker Art Museum site.

On behalf of the entire DELTA Group and the ALA/SET Health Effects Task Force, we want to acknowledge all the volunteers for what turned out to be a pioneering study of winter aerosols around Sacramento. Thanks to your efforts, we were able to set up and operate an array 60 km long with 36 days of sampling, 288 – 3 hour periods, day and night, and achieve a greater than 90% capture rate for a total of over 27,000 samples.

The enormous amount of data generated in this study will require a great deal more analysis than is possible in this short time frame, 10 ½ months from last sample collection to final report. We anticipate the generation of peer reviewed publications on several aspects of this program with more extensive and detailed conclusions

Other informational resources

Important resources are local meteorology (various sources, from the Sacramento Bee, www.weatherunderground.com, and the US Weather Service.

Trajectory analysis was performed with the NOAA ARL program HYSPLIT, http://www.arl.noaa.gov/ready/hysplit4.html.

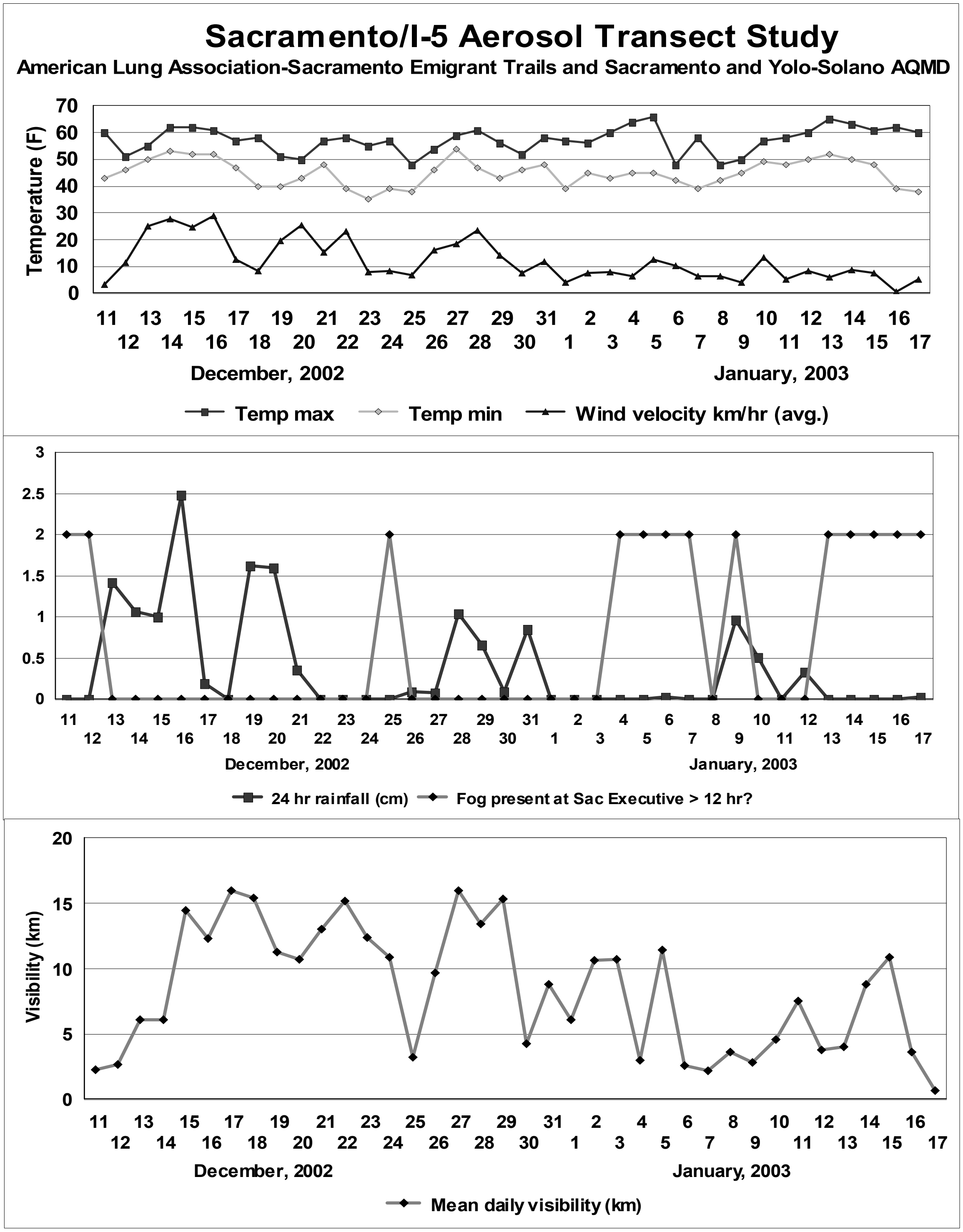
Air quality data are available from the California Air Resources Board, including the excellent ADAM site http://www.arb.ca.gov/adam/welcome.html.

Local traffic counts are available from http://www.sacdot.com/ and state wide from www.caltrans.ca.gov/.

The data from this study will be posted on the UC Davis DELTA Group web site http://delta.ucdavis.edu

Results – Meteorology and other supporting data

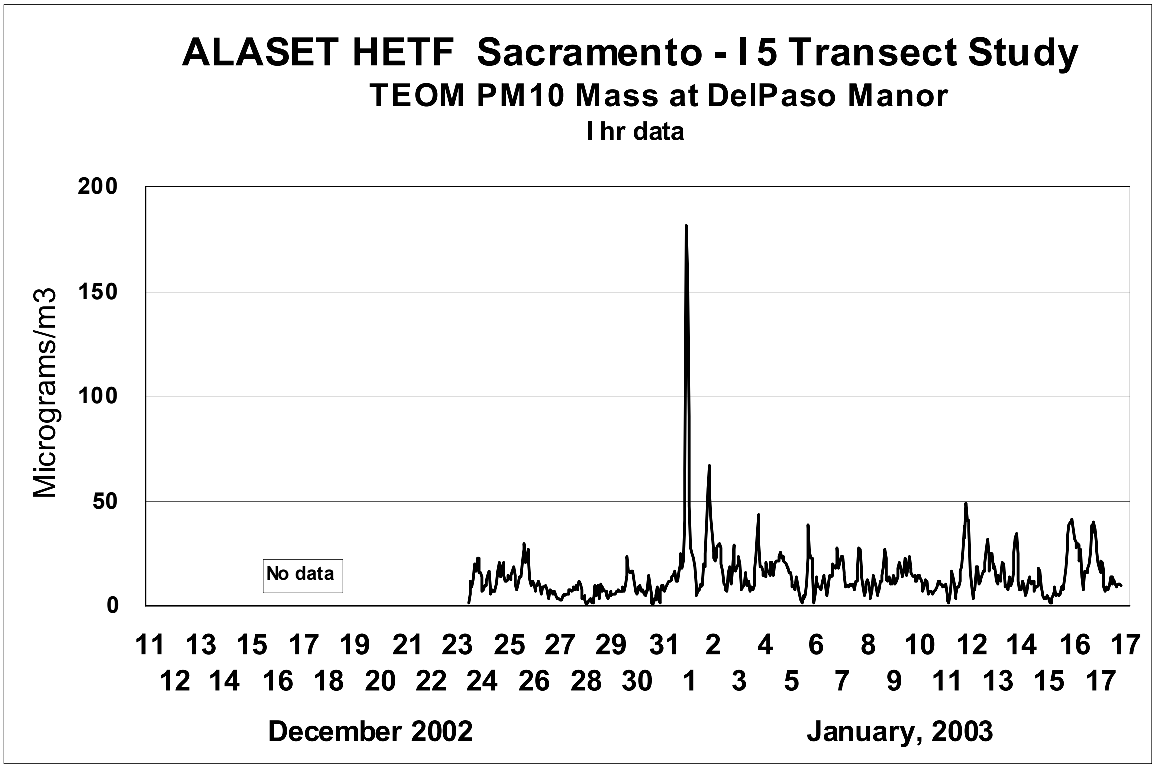
We were fortunate to have weather that ran from very clean, almost monsoonal rain conditions to typical valley wet and dry fogs. Data are shown in Figures 2 a) temperatures, wind, 2b) rain and observed fog > 12 hr, and 2c) mean daily visibility.



Note that the strong rain events of December were accompanied by increased wind velocities, while the weak rains of January in a foggy period were not. This usually occurs when a rain event is so weak that the rain falls through an inversion, scavenging large particles but not replacing the air mass on the valley floor.

Of all the air quality resources available to the study, the ARB's ADAM and AQMIS Preliminary Data stand out as being especially informative. One example is shown below in Figure 3, a TEOM (Tapered Element Oscillating Mass) PM_{10} aerosol sampler was operating at Del Paso Manor during much of the study. It provides PM_{10} mass data hourly, and is thus a major asset in a time resolved study. Further, the AQMIS data are available quickly from ARB, in time for inclusion is this report.

Figure 3 One hour PM_{10} data at Del Paso Manor from a TEOM sampler.



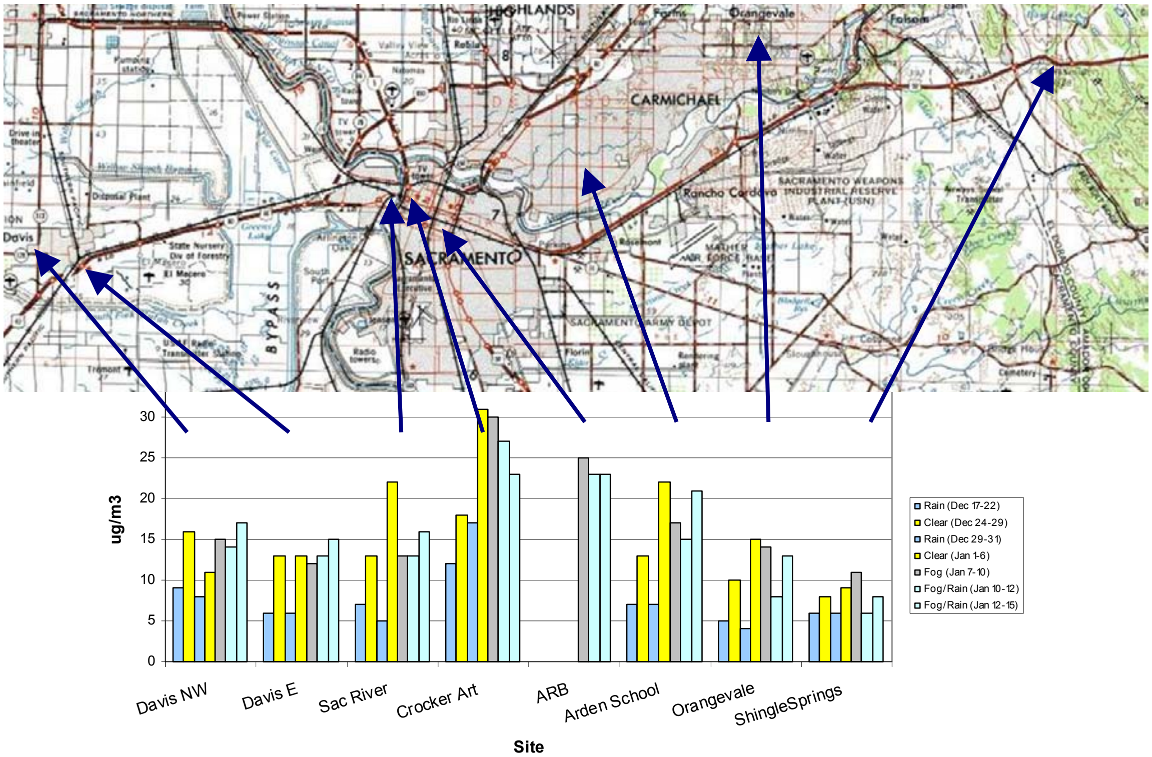
This TEOM plot indicates both the strengths and weakness of this approach. First, it measures only the size mode PM_{10} . We are more interested in $PM_{2.5}$ and its sub-components, especially the very fine fraction, $0.26 > D_p > 0.09$ μm diameter. Second, it contains no compositional data, so we have no way to tell whether the peaks represent natural or man made substances. In this case, we will later show that the large peak on Jan. 1, 2003, is likely sea salt in the size mode $10 > Dp > 2.5$ μm from the North Pacific, while the smaller peak right next to it on Jan 2 is an infusion of San Joaquin Valley air with fine and very fine anthropogenic components.

Results – Sacramento - Interstate 5 transect aerosol data

Mass

PM$_{2.5}$ mass data from DRUM samplers and soft beta ray attenuation analysis are presented below coordinated to our site map. We have aggregated the data in Figure 4 for mean multi-day averages of PM$_{2.5}$ mass for five periods: Dec 17 – 21 rain; Dec 24 – 29 clear; Dec 29 – 31 rain; Jan 1 – 6 clear; Jan 7-10 fog; Jan 10-12, fog/light rain; Jan 12-16 fog, some drizzle. Note that ultra-fine particles < 0.09 µm were not sampled by any of the DRUM samplers, and that while relative mass values are precise, a single 24 hr PM$_{2.5}$ value from an 8 DRUM sampler requires the averaging and summing of between 48 and 96 individual measurements, increasing absolute uncertainties to roughly $\pm$ 5 µg/m^3.

Figure 4 Site Map and PM$_{2.5}$ aggregated data



The pattern is extremely revealing. First, during periods of rain, PM2.5 at all the sites except The Crocker Art site are essentially identical, even Shingle Springs. We return to this later as we discuss the inability of rain to remove diesel particles. Note that Davis East (next to I 80) and Orangevale (residential) are almost identical in amount and time behavior of PM$_{2.5}$ aerosols, showing a regional pattern. We found a major enhancement of particles near I-5 that, while not a violation of the federal 65 µg/m^3 24 hr standard, is clearly far greater than our more remote sites. On one occasion, we found very fine (< 0.34 µm) particles in concentrations previously seen in Fresno (Bench et al, Aerosols Science and Technology, 2002), but whereas Fresno had 6 such peaks in 3 weeks, we saw just one in the 3 weeks of January (non-rainy) sampling.

Figure 5 PM$_{2.5}$ mass in two rainy periods.

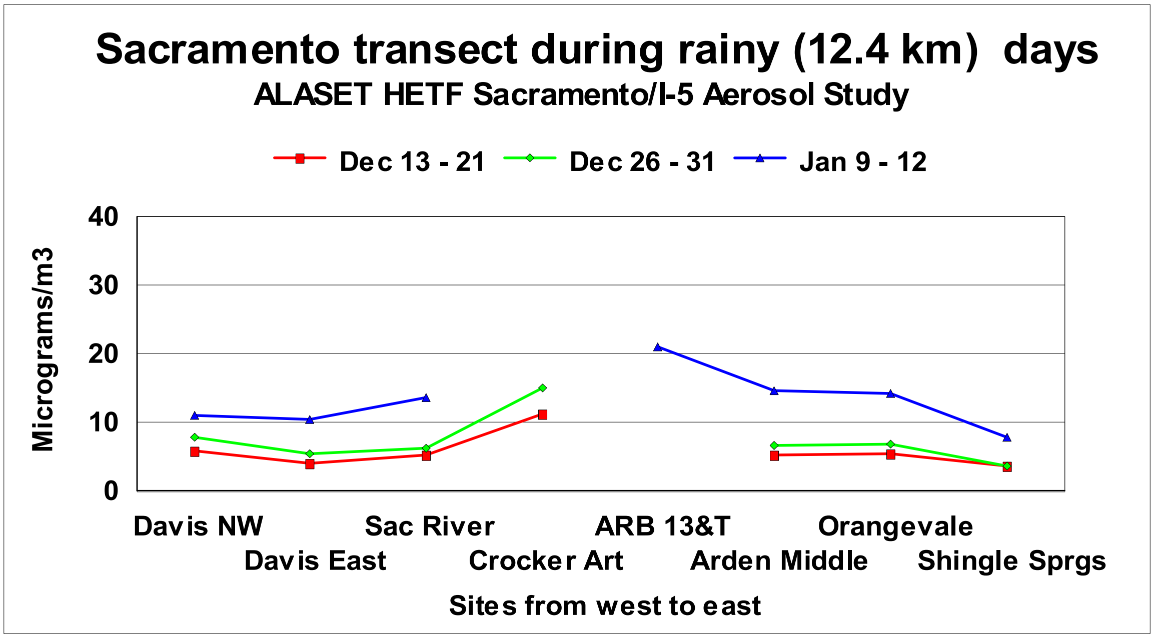
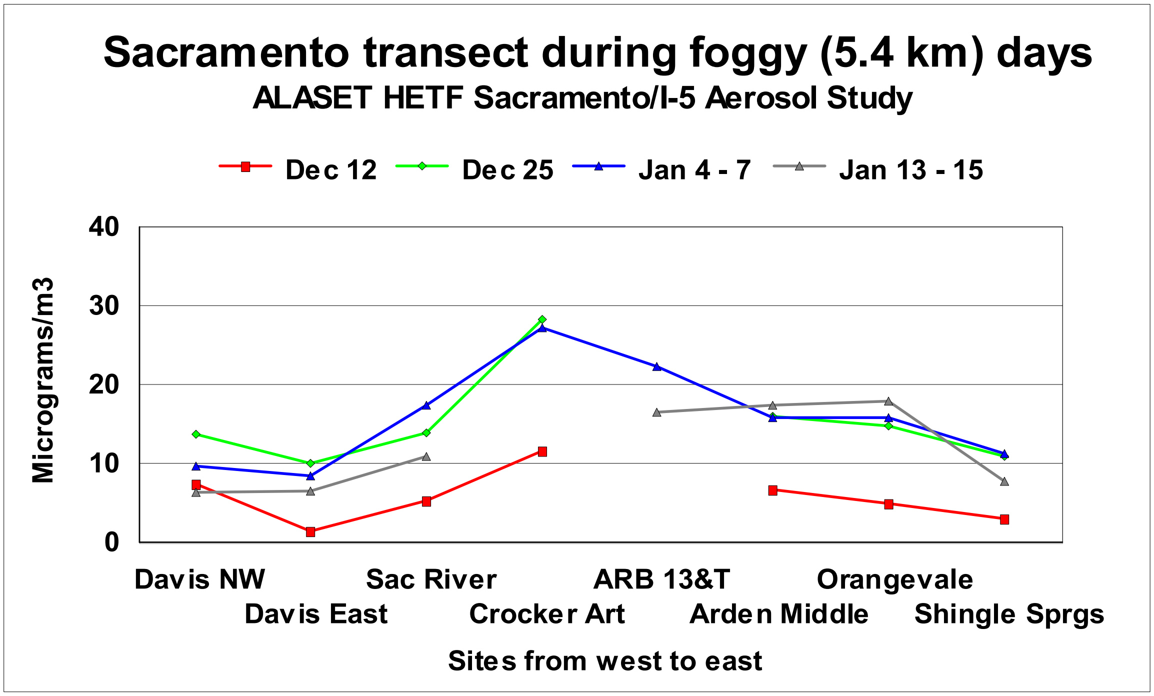


Figure 6 PM$_{2.5}$ mass in hazy/foggy periods



The days marked “clear” are especially interesting (Figure 7). Generally, these were typical periods of haze with 9.9 km (6 mi) mean visibility and low wind velocities, generally around 5 mi/hr. These are periods of strong inversions, and resulted in the highest levels of PM$_{2.5}$ mass seen and the greatest difference between the cleanest sites

(Davis NW, Davis E, Shingle Springs) and the most impacted sites. The rapid drop off between the Crocker Art Museum site and the ARB at 13&T on Jan. 3 is striking, indicating a localized plume of aerosols very near I-5 (and Watt Avenue) which persisted in the weak winds.

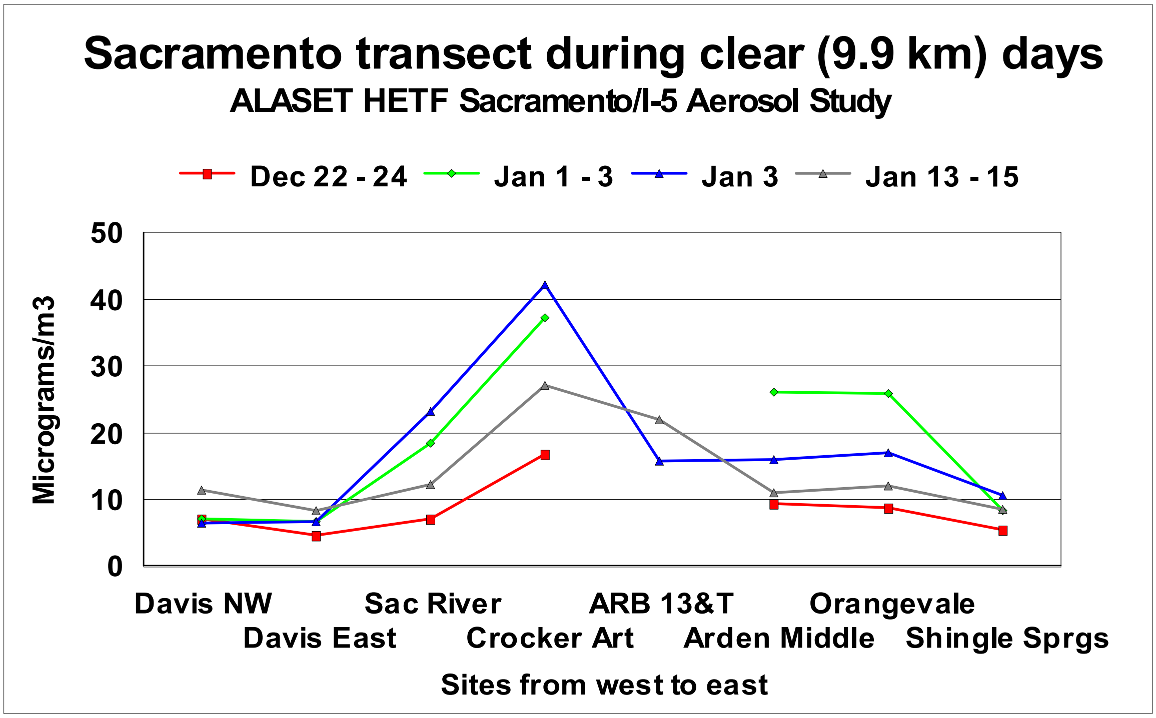


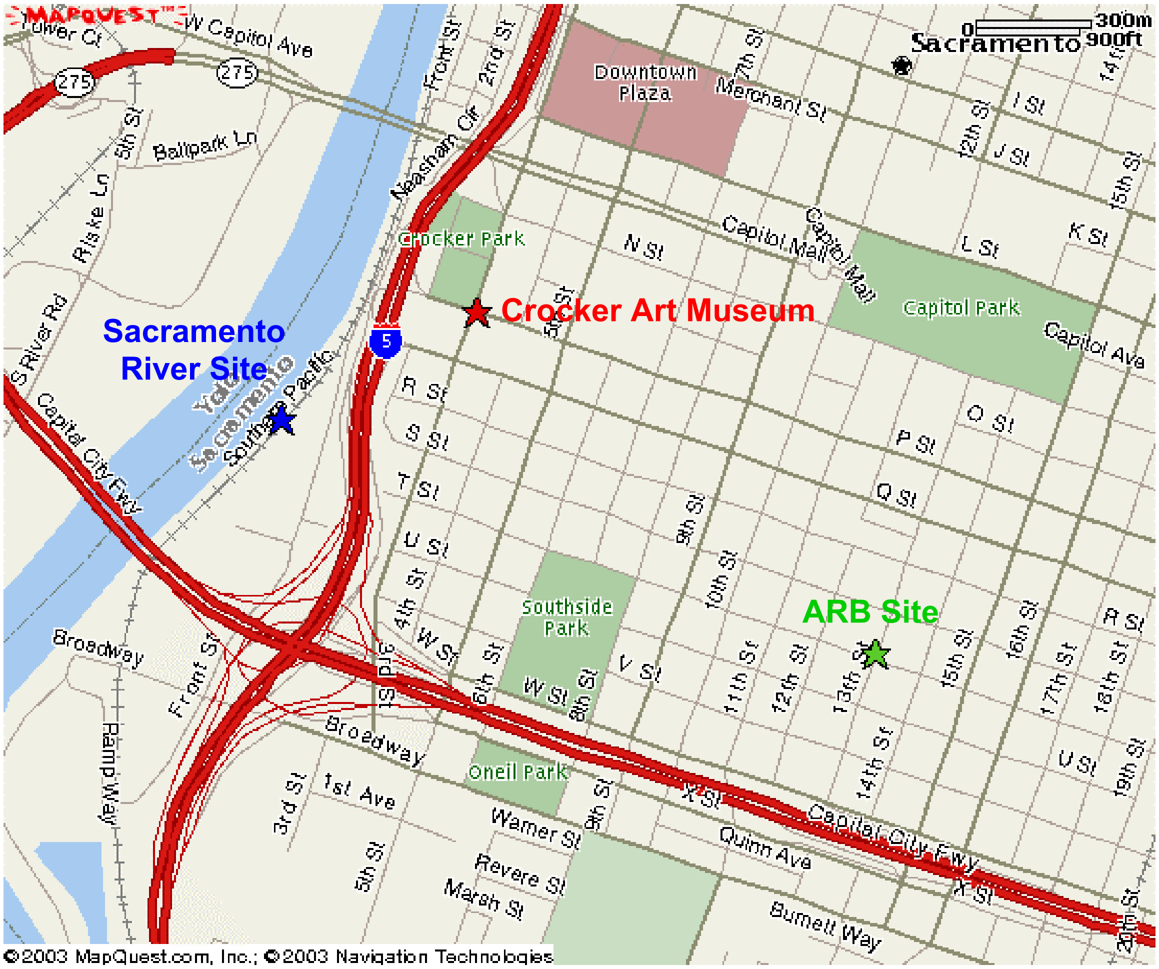
Figure 7 $PM_{2.5}$ mass in clear periods

The very sharp rise in mass across I-5 involves sampling sites that are only a few hundred meters apart, clearly identifying I-5 as the source. The fall of as one goes east from the freeway incorporates additional strong sources such as Hwy 99. Nevertheless, the levels never reach those directly downwind of I-5.

Site Intensive: Sacramento River/Crocker Art Museum sites

In the figures below, we plot $PM_{2.5}$ mass and its components, 2.5 to 1.15, 1.15 to 0.34, and 0.34 to 0.09 µm, derived from aggregating the 6 finest stages of 8 DRUM samplers, at the Sacramento River and Crocker Art Museum sites. These sites are separated by only a few hundred meters, which include however Interstate 5. These two sites were chosen directly west and east of I-5 in Sacramento which would generally be in the upwind and downwind vectors of the depressed freeway (see map, Figure 5). They were also north of the Pioneer Bridge on Hwy 50, and thus represent one of the most traffic intensive regions of the area. While no traffic counts are yet available for these freeways during the study, I-5 averages 285,000 vehicles/day, roughly 10% of which are

Figure 8 Map of Downtown Sacramento sites.



©2003 MapQuest.com, Inc.; ©2003 Navigation Technologies heavy trucks, while Hwy 50 averages 348,000 vehicles/day, of which roughly 5% is heavy truck traffic (www.caltrans.ca.gov, traffic counts by route and truck traffic, 2002).

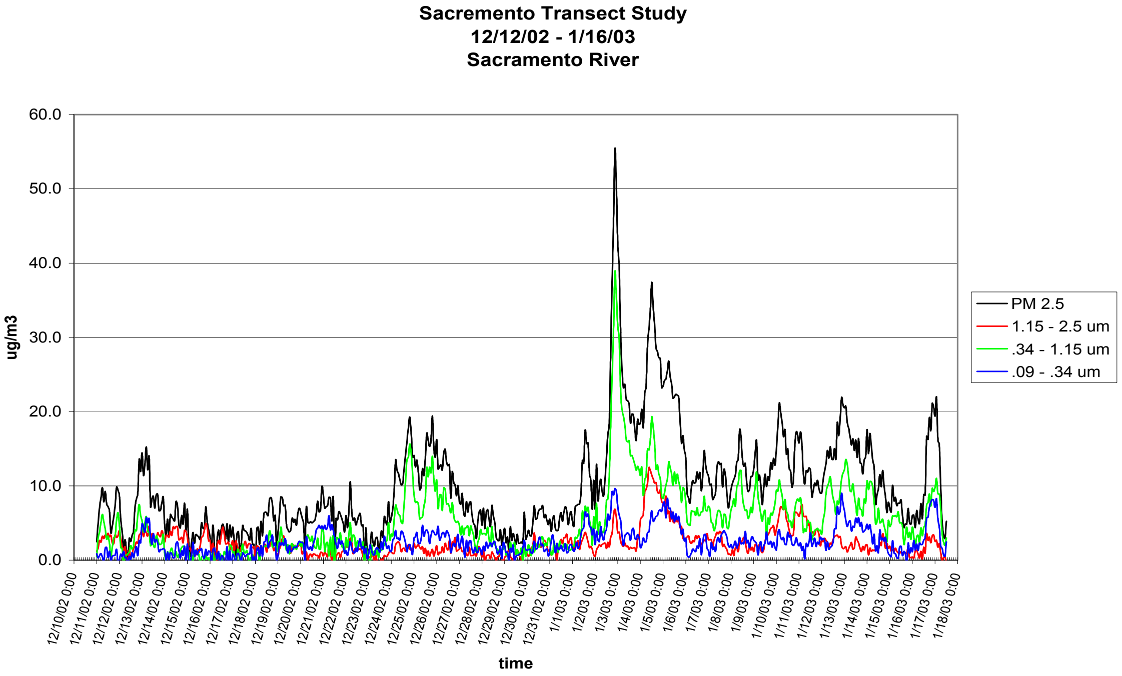


Figure 9 Sacramento River site mass in 3 components of $PM_{2.5}$

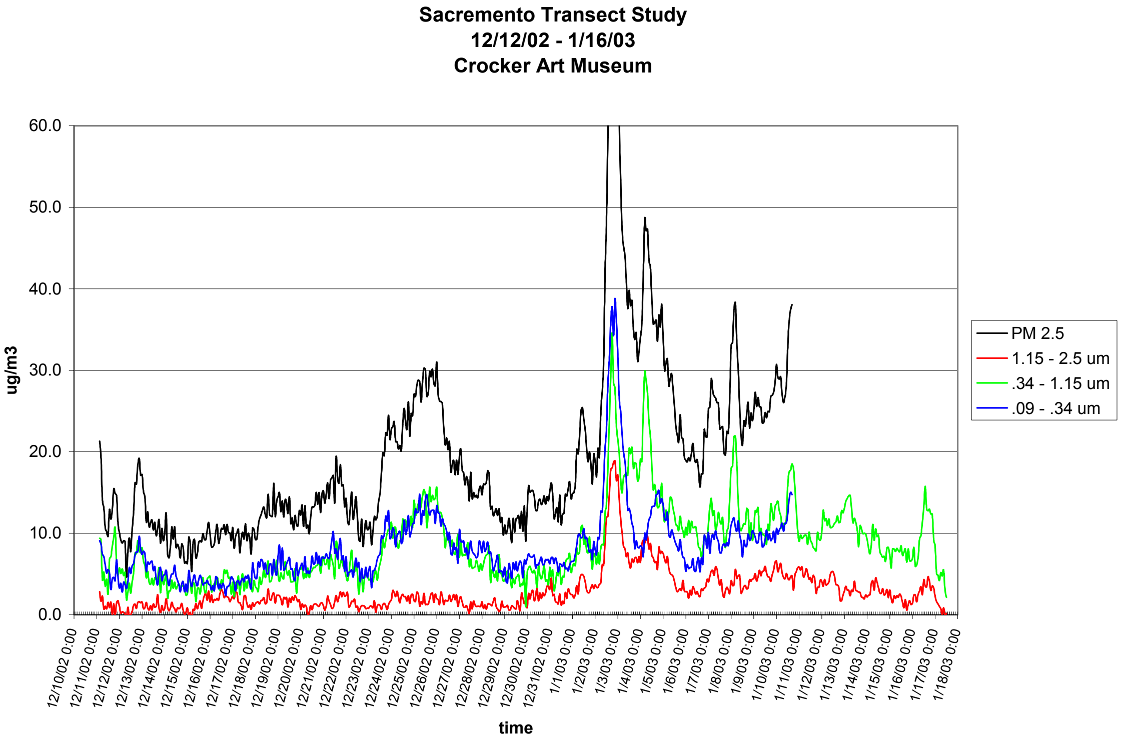


Figure 10 Crocker Art Museum site mass in 3 components of $PM_{2.5}$

The Sacramento River sampler (Fig.7) was located close to ground level, on the levee at the river and about 10 m above water level, but the Crocker Art Museum site was on the roof of the southern Annex of the building, at an estimated height of about 25 m. Each site shared operationally identical DELTA Group 8 stage slotted DRUM impactors.

Trajectory analysis can be used to help identify sources of aerosols. We applied the HYSPLIT hybrid single particle Lagrangian model of NOAA's ARL division to identify where the air that reached the sampling site came from. We ran the model in the backward isentropic mode that allows one to follow the vertical motion of the air parcel. We used standard above ground level elevations of 500 m, 1000 m and 2000 m, with the elevations characterizing air under, at the top of, and above the strong ground level inversions in the California Central Valley. The lowest elevation, 500m, should be most indicative of the air actually sampled by a ground level site. The next 6 figures, T-1 through T-6, show the results for 4 periods, each calculated at 8 AM Pacific standard time:

T-1	The rain event of Dec 29- Dec 30,
T-2, T-3	The December stagnation periods, Dec. 25 and Dec 27,
T-4	The high concentration stagnation event of Jan 3 and
T-5	The rain and poor visibility period of Jan 10, and
T-6	The very clean period at the Crocker Museum site..

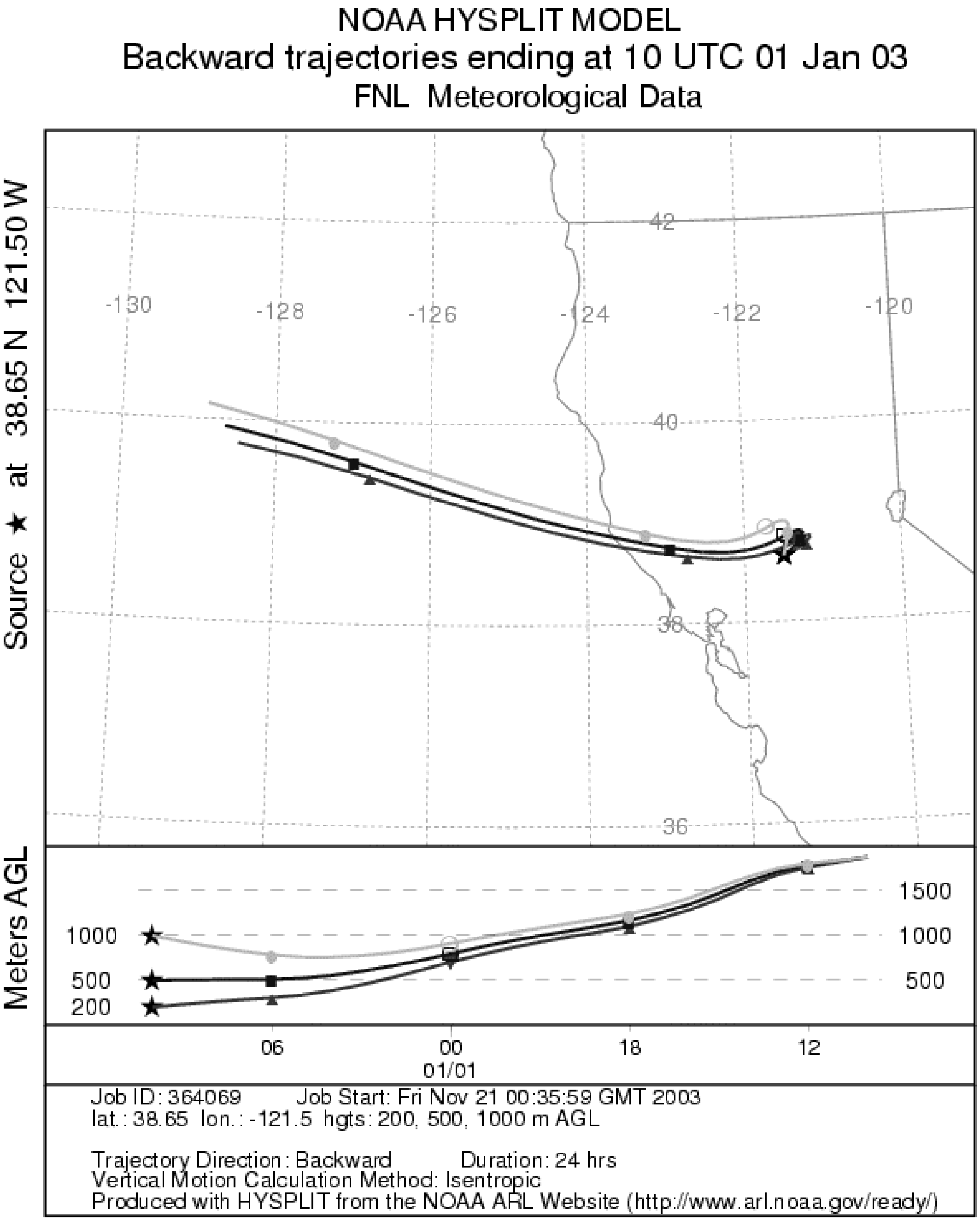
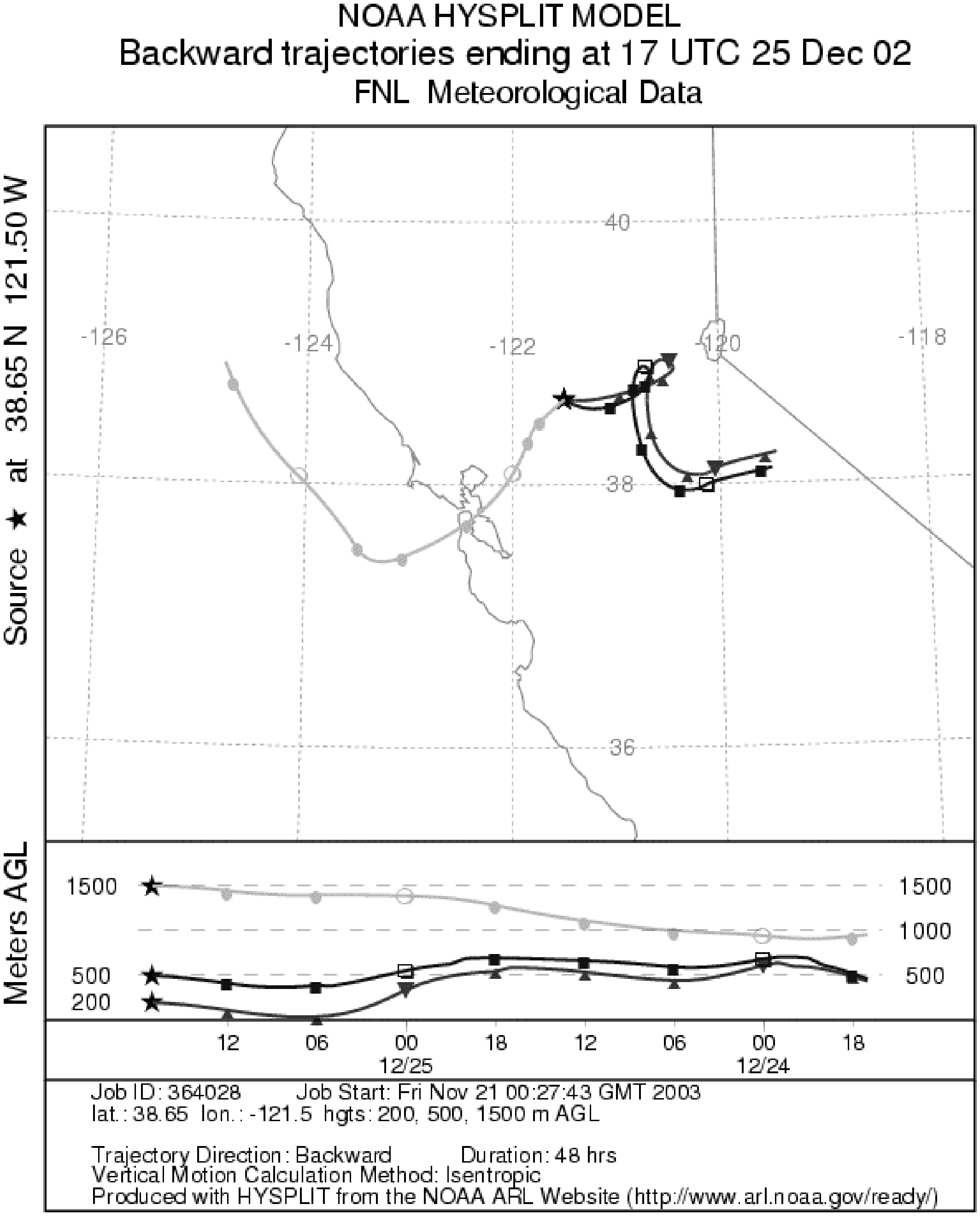


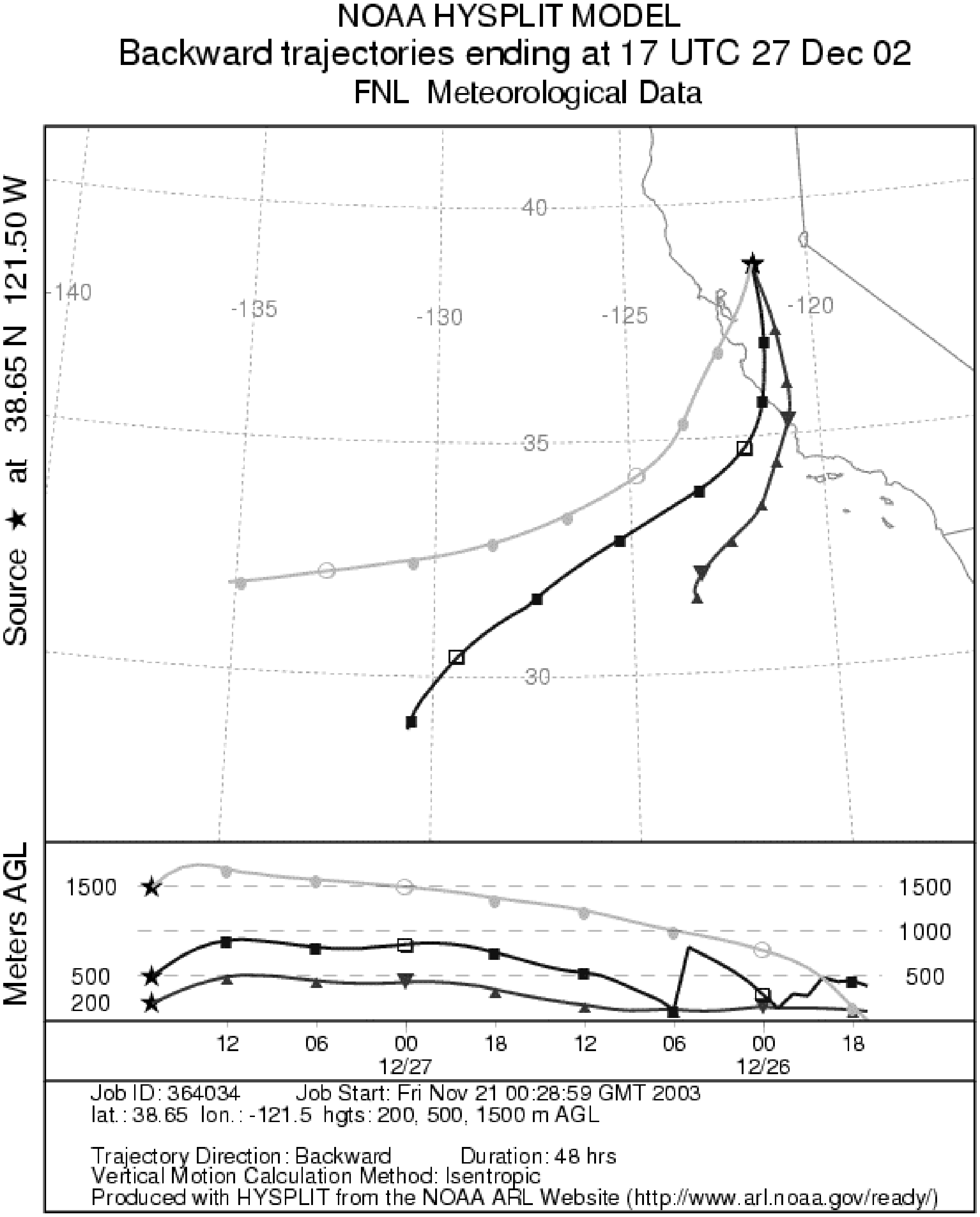
Figure T-1

The rain events of early December and the rain events of late December were characterized by clean air masses that came in from the Pacific, carrying with them sea salt that we will see later at the Arden Middle School site. Figure T-1 shows an example of this trajectory.



Figures T-2, T-3

The stagnation around Christmas week is examined via trajectories for December 25 and December 27. The trajectories cover 48 hr, with each tick mark being 6 hr back in time. T-2 on Dec. 25 shows the 500 m trajectory coming on the nighttime down slope wind or the Sierra, then moving up the San Joaquin Valley under the inversion, circling over Sacramento and then arriving at the sites. Recall that in this period the valley had a rather flat aerosol gradient, indicating a well mixed aerosol, with the usual exception of the I-5 enhancement at the Crocker Art Museum site.



T-3 of Dec. 27 is an even simpler pattern with San Joaquin Valley air dominating the 500 m trajectory.

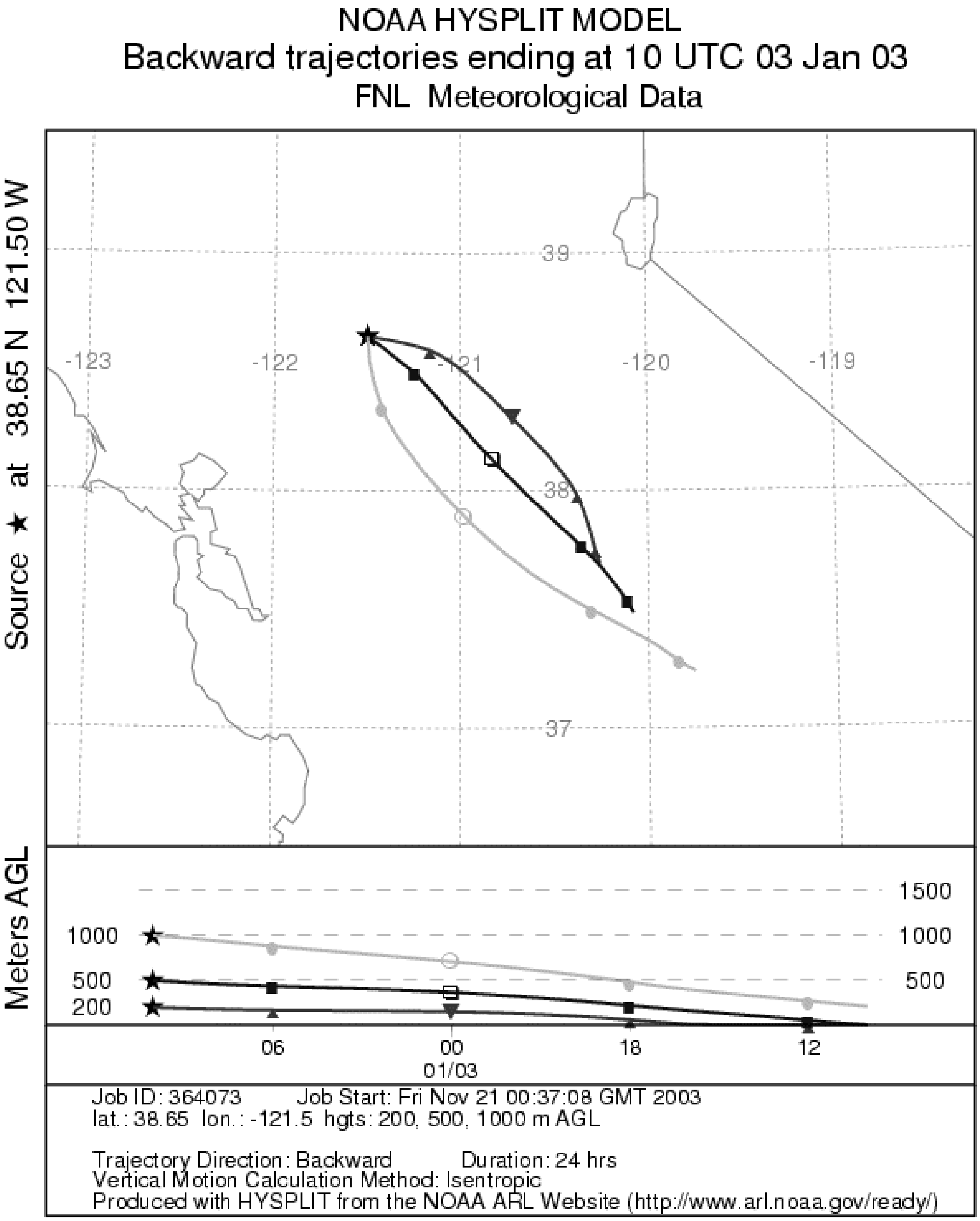
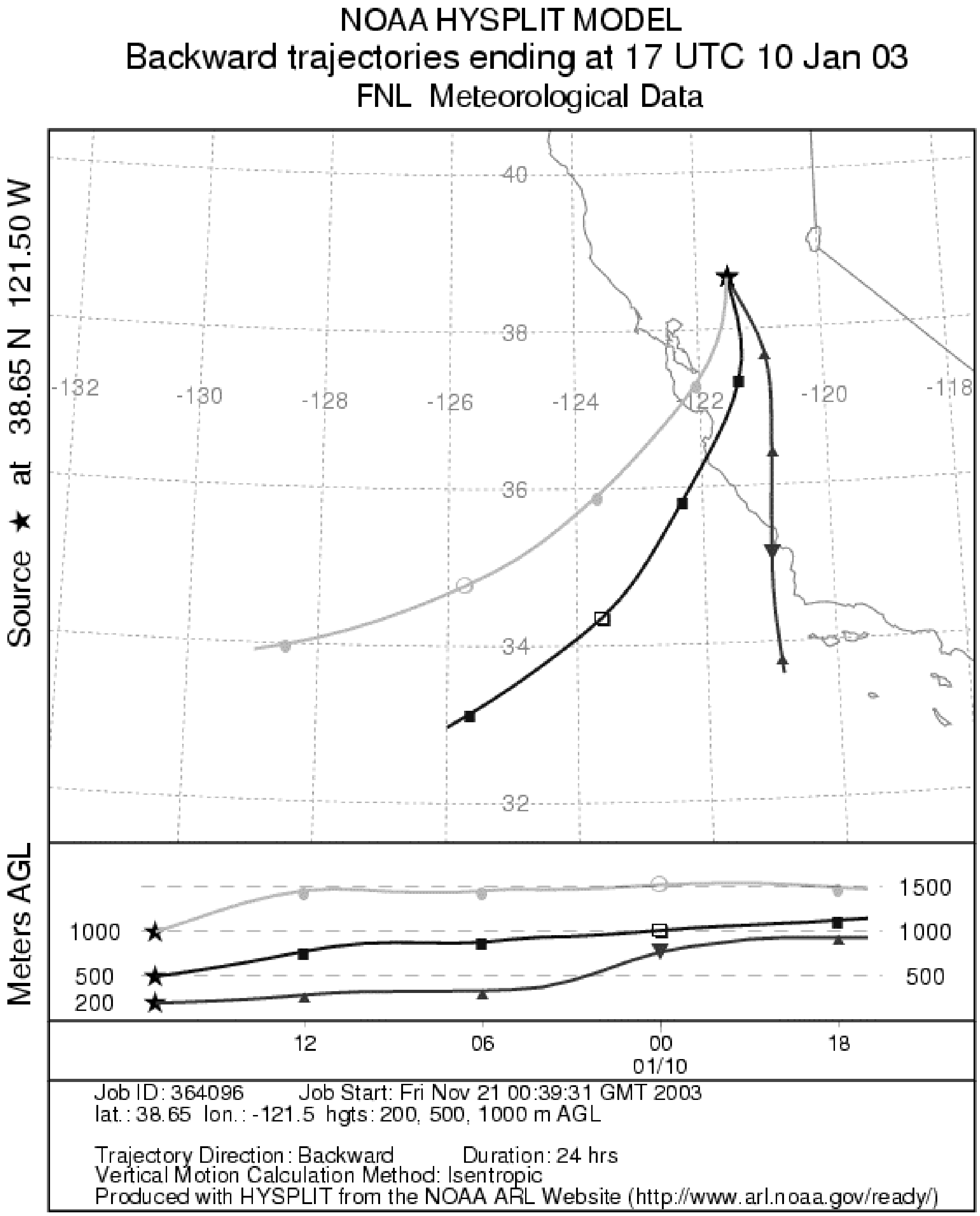
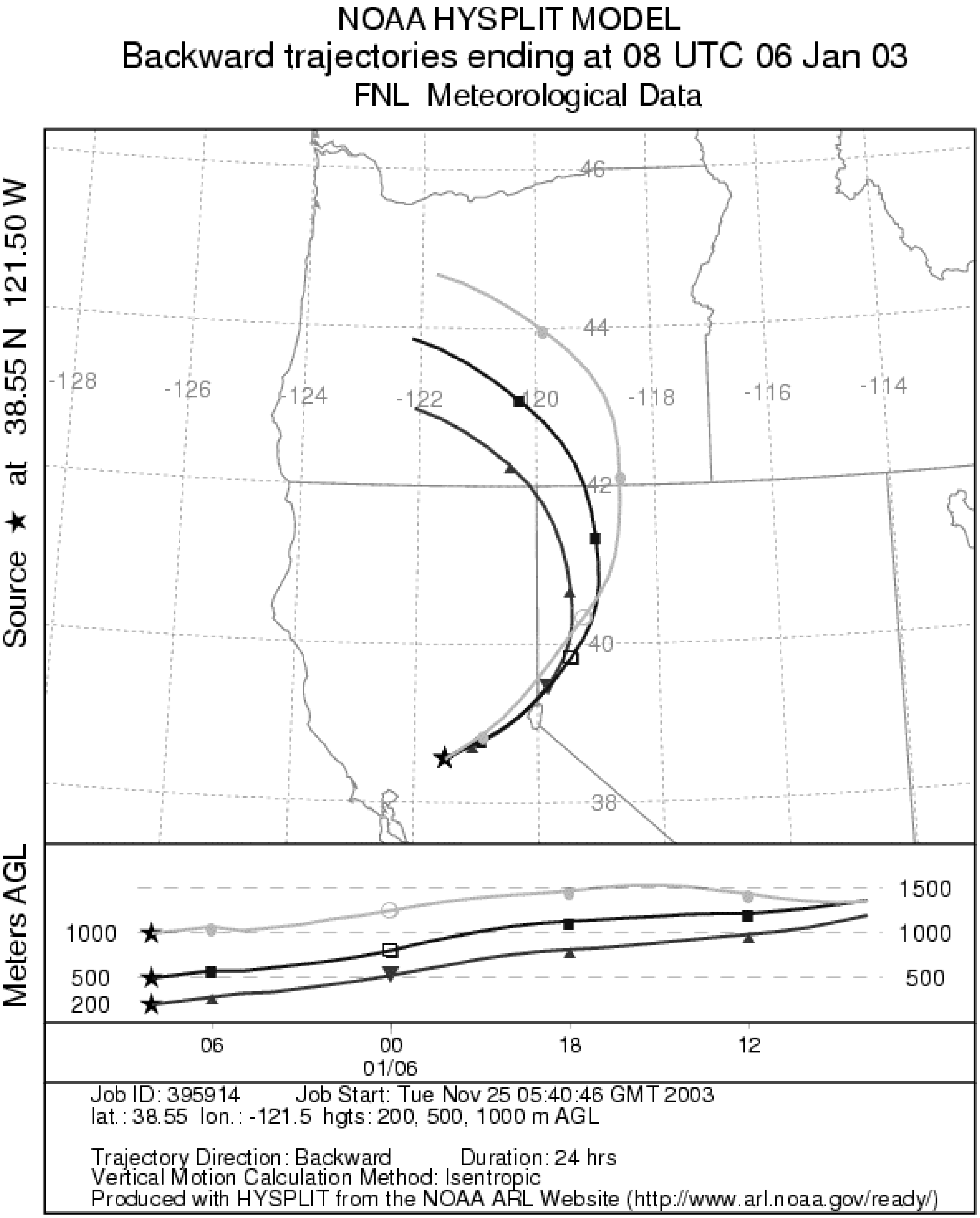


Figure T-4, T-5

Figure T-4 on Jan 3 represents the highest concentration seen at all sites in the study. The 500 m trajectory has low wind velocities and remains entirely constrained to the inversion in the San Joaquin Valley for (at least) 48 hr. Over it lays a layer of Bay Area air, but it is not near the ground. The conclusion is that on those days, Sacramento is breathing air typical of Fresno. Figure T-5 on Jan 10 resembles Figure T-2 in the December stagnation, and again has significant San Joaquin Valley air at 500 m.


NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 10 Jan 03
FNL Meteorological Data
Source ★ at 38.65 N 121.50 W
40
38
36
34
32
-132
-130
-128
-126
-124
-122
-120
-118
Meters AGL
1000
500
200
1500
1000
500
12
06
00
18
01/10
Job ID: 364096 Job Start: Fri Nov 21 00:39:31 GMT 2003
lat.: 38.65 lon.: -121.5 hgts: 200, 500, 1000 m AGL
Trajectory Direction: Backward Duration: 24 hrs
Vertical Motion Calculation Method: Isentropic
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)



Job ID: 395914 Job Start: Tue Nov 25 05:40:46 GMT 2003
lat.: 38.55 lon.: -121.5 hgts: 200, 500, 1000 m AGL

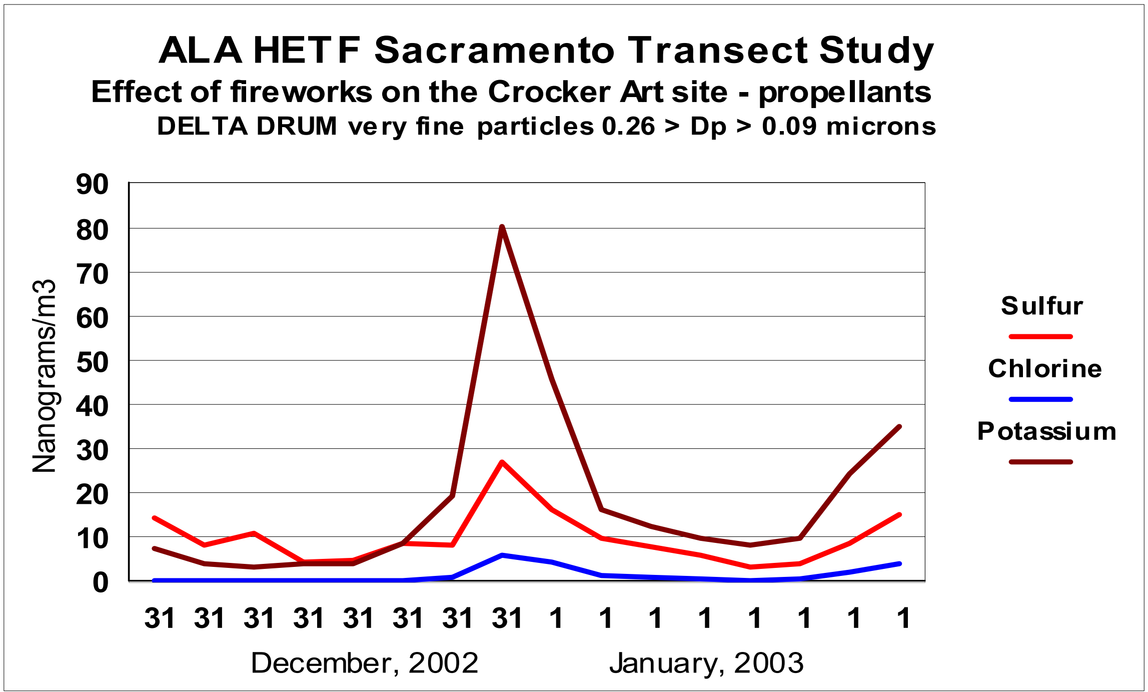
Trajectory Direction: Backward Duration: 24 hrs
Vertical Motion Calculation Method: Isentropic
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

Figure T-6

The mass data, and later the elemental data at the Crocker Art Museum site, shows sharply cleaner air on Jan 5 – 6. This was examined in Figure T-6, which shows air coming in from the pacific, circling over Nevada, and arriving at the Crocker Art Museum site from the east. The Sacramento River site shows a sharp increase in concentration, as it is now in the downwind direction.

Thus, especially for the very finest particles, $0.26 > D_p > 0.09$ µm, Sacramento city and all sites east of I-5 are a much smaller source of these particles than I-5 all by itself. Later we will show that the characteristic diesel/smoking car signature (S, P, and Zn) essentially disappears on Jan 5 and 6, confirming our association of these particles with I-5.

While of only modest interest in health effects studies, the effect of the fireworks on the Tower Bridge on New Year's Eve, December 31, 2002, is useful both as a marker of absolute time and because the impact was also seen at the Arden Middle School site. Thus, it serves as a tracer of air transport and dilution. The propellants are mostly black powder, while colorants are used to give the display its spectrum of colors. (Perry, 1999; Dutcher et al 1999). Similar elements are seen in the air of Fresno on the 4th (and 5th) of July, and on Cinco de Mayo (Cahill et al, Final Report, CA Air Resources Board 2003).



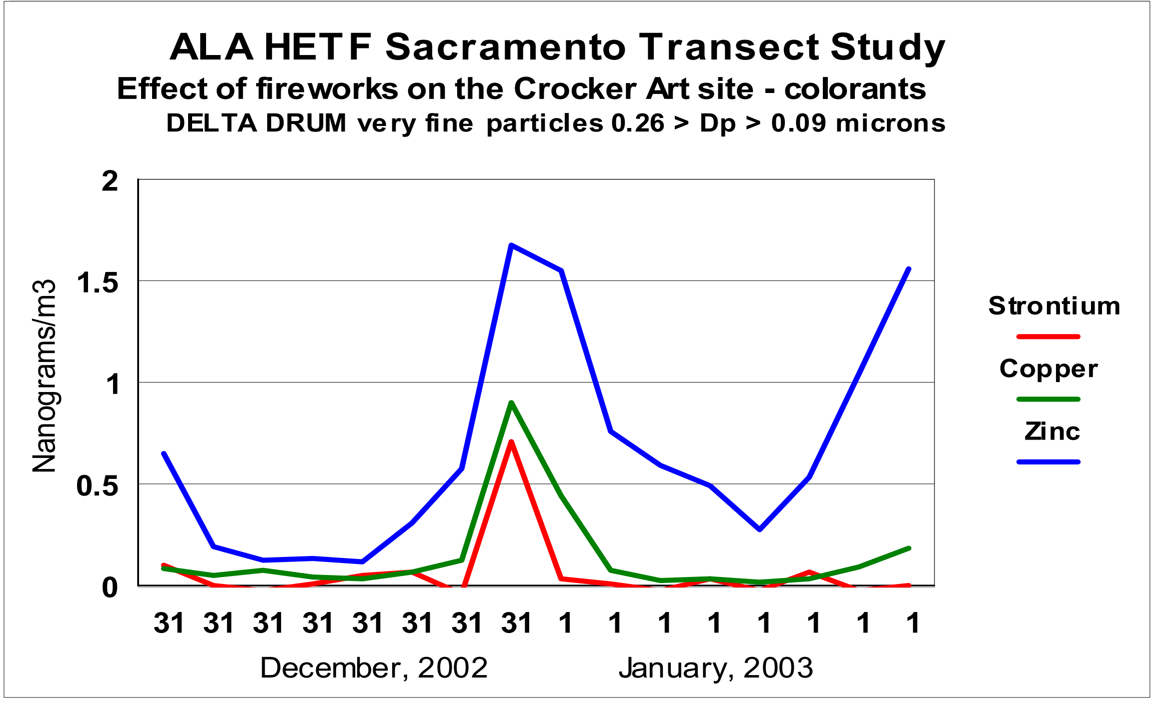


Figure 11 Firework aerosols at the Crocker Art Museum site

Identification of Highway Influence - Diesel and smoking trucks and cars

The impact of roadways on adjacent neighborhoods has been a long standing problem in California, first raised to serious concerns by the work on airborne lead in the 1970s. Concerns continue to be raised today by the impact of emissions of aerosols from diesels, and most specifically diesel soot, a Prop 65 toxic, but also including similar materials from gasoline powered vehicles, especially gross emitting and smoking light duty vehicles. Because of the similarities of these aerosols, and because typically diesels are usually a minor fraction of total vehicular traffic, the two sources in their ensemble can be considered as a tracer of highway impact with aerosols distinct in size, shape, composition, and probably health impacts from typical ambient aerosols of the region.

A recent review article (Cadle et al, 2003) and a set of studies of the Tuscarora Tunnel (Gertler et al, 2002) summarize on-road vehicle tests that are a way of both supplementing and averaging over the high degree of variability in individual vehicles and laboratory scale studies. The extensive report of Gertler et al (2002) was, however, in Pennsylvania, and thus can differ from California. For example, California was unique among the states in reducing the sulfur in gasoline to low levels 25 years ago. Second, the data were taken from a flat, free flowing rural freeway and thus represents probably the lowest emission rates for on-road vehicles.

However, the tunnel cycled between domination by light duty largely gasoline powered vehicles in the day and heavy trucks at night (83%), allowing Gertler and coworkers to extract the emission factors of each. From the regression of vehicle type to emissions, Gertler obtained the ratio of heavy duty to light duty vehicles gasoline powered emission rates. The results of the 20 individual tests with their variances are given below in Table 1.

Table 1 Comparison to heavy duty and light duty PM_{10} and $PM_{2.5}$ emission rates form the Gertler at al 2002 Tuscarora Tunnel studies and other studies.

Parameter			Heavy duty (mg/km)	Light duty (mg/km)	Mixed (mg/km)
PM_{10} mass	Gertler 2002	Tuscarora	181 ± 13	10 ± 11	87 ± 54
$PM_{2.5}$ mass	Gertler 2002	Tuscarora	135 ± 18	14 ± 13	62 ± 42
PM_{10} mass	Gillies 2001	Sepulveda	na	Na	69 ± 30
$PM_{2.5}$ mass	Gillies 2001	Sepulveda	na	Na	53 ± 27
$PM_{2.5}$ mass	Norbeck 1998	In-use (med)		18 ± 9	
$PM_{2.5}$ mass	Norbeck 1998	In-use (high)		185 ± 50	
PM_{10} mass	Sagebiel 1997	High CO, HC		346 smoke	
PM_{10} mass	Sagebiel 1997	High CO, HC		32 no smoke	

From these results, we see that diesel is about 18 times worse than light duty vehicles for PM_{10} emissions and 10 times worse than light duty vehicles for $PM_{2.5}$ emissions, and that the worst case smoking car is about the same as the average diesel. Incidentally, these emission values are sharply lower than occurred only a decade ago.

For identification of highway aerosol impacts, one must move beyond mass values and into the size and composition of the aerosols. Yet one of the most challenging tasks in ambient air quality studies is the identification of the contribution of diesel exhaust to fine ($PM_{2.5}$) particle mass. A great deal of research is in progress looking at specific chemical markers, such as PAHs in diesel exhaust. Without diesel specific organic markers, other methods must be used to get a likely or probable result. In this effort, we are aided by the fact that diesel has a unique combustion process not seen in other vehicles. The essential characteristics are high temperature combustion, high enough to fix NO and thus most NO from highway processes is from diesels, and high compression, requiring close tolerances at the cylinder wall, which must be kept relatively cool to avoid damage. If these tolerances are not maintained, lubricating oil enters the combustion process. In addition diesel fuel has a relatively high molecular weight, often with considerable sulfur content.

This problem can be approached from both the tunnel studies and laboratory studies. Individual species were also measured in the Gertler study using the same protocols as for mass to separate heavy duty (HD) from light duty (LD) vehicles. Table 2 presents these data.

Table 2. Light duty and heavy duty $PM_{2.5}$ emission rates for numerous particulate species as taken from the Tuscarora Tunnel studies (Gertler et al, 2002).

Vehicle	Light duty avg	Light duty SE	Heavy duty avg	Heavy duty SE	Ratio, HD/LD
$PM_{2.5}$ rate	(mg/mi)	(mg/mi)	(mg/mi)	(mg/mi)	
Species					
Org. Carbon	4.5	1.7	179.8	69.1	40.0
Elem. Carbon	5.3	1.9	296.2	106.5	55.9
NH_3	55.1	28.2	42.6	22.6	0.77
Silicon	1.2	1.2	1.4	1.4	1.17
Sulfur	1.9	1.1	0.43	0.24	0.23
	(µg/mi)	(µg/mi)	(µg/mi)	(µg/mi)	
Manganese	644	200	4454	1387	6.9
Iron	335	145	3194	1386	9.5
Copper	23.7	29.6	141.6	176.7	6.0
Zinc	73,2	49.1	219.6	147.3	3.0
Mercury	2.7	0.7	18.0	4.7	6.7
Lead	17.7	12.3	59.7	41.3	3.4
Gasses	grams/mi	grams/mi	grams/mi	Grams/mi	grams/mi
CO_2	249	24	1197	117	4.8
CO	3.1	1.1	< 1	na	< 0.3
NO (as NO_2)	0.68	0.11	19.1	3.1	28.1
THC	0.65	0.34	2.4	1.3	3.7

Most PAHs are also elevated in diesel exhaust by large factors, 100 or more. Naphthalene had the largest emission rate of the 48 PAHs surveyed at 4 mg/mi, 10 times that of light duty vehicles.

Finally, the sizes of particles were measured in the Gertler study down to and including ultra-fine particles ($D_p < 0.1$ μm). Sulfur was seen to peak in the ultra-fine mode for both LD and HD vehicles, while most other elements (including organic matter and zinc) peaked in both the very fine mode, $0.26 > D_p > 0.09$ μm and a coarser mode between 0.5 and 1.0 μm. The latter mode overlapped the abundant fine soil modes and thus was hard to ascribe to vehicles alone, despite the use of upwind subtraction.

Another series of tests were conducted of heavy diesels in laboratory conditions The result of these tests also showed very fine aerosols, an example of which is shown in Figure 11, taken from the final report to the National Renewable Energy Laboratory (NREL), Golden, CO. (Cahill et al., 2003) In this plot, a MOUDI sampler was operated in the diluted exhaust from a truck using California (low sulfur) fuel. Almost all the mass of diesel exhaust falls in the range between about 0.1 and 0.3 μm diameter (MOUDI Stages 8, 9, and 10). Further, the exhaust was black, indicting incomplete combustion. Sulfur (from the fuel) and the correlated elements phosphorus and zinc are seen (from the stabilizing agent in lubrication oil, zinc thiophosphate). Normal automobiles with well tuned engines and low sulfur California fuel do not have these characteristics, but some of these characteristics may be present in smoking gasoline power vehicles (gross emitters). We are in the process of making detailed spectroscopic examinations of diesel exhaust to find optical characteristics, and our early work indicates that the absorption in the 350 – 400 nm band, due to PAHs, may provide such a signature in the near future. Inadequate data exists at this time, however, to make this distinction in a routine manner. Note also that many elements (notably manganese, iron, and copper) seen in the very fine mode in the Tuscarora Tunnel studies were not seen in the laboratory studies.

Thus, based upon the Minnesota/NREL results, we will look for very fine mass (DELTA 8 DRUM Stage 8, $0.26 > D_p > 0.09$ μm diameter) with sulfur, correlated P and Zn, and a black color.

Given these parameters, we can also then propose to use the Minnesota/NREL results to estimate diesel mass contributions to both very fine particles and $PM_{2.5}$ mass. However, the presence of roughly equal contributions from smoking gasoline powered cars and trucks with an unknown mass to tracer ratio makes the calculation only an estimate.

The ambient concentration of diesel/smoking light duty vehicle roadway emissions will depend both upon the mass contribution per unit time, the volume of air into which it is mixed, and the removal rate. We are unable to find information on the removal rate of size segregated diesel particles, but modeling indicates that this rate could be substantially lower than the very short residence times associated with ultra-fine and very-fine particles. The particles are too fine to ever settle. Thus the removal rate must involve growth of the particles into larger sizes either by absorbing moisture, coagulation particle to particle, or interception by rain drops. However, the presence of unburned oil in these particles will make them hydrophobic, while their small size makes interception by rain very inefficient. Thus, diesel particles could have an anomalously long lifetime in the air, much longer than smoke, dust, or hydrophilic particles such as nitrate and sulfate.

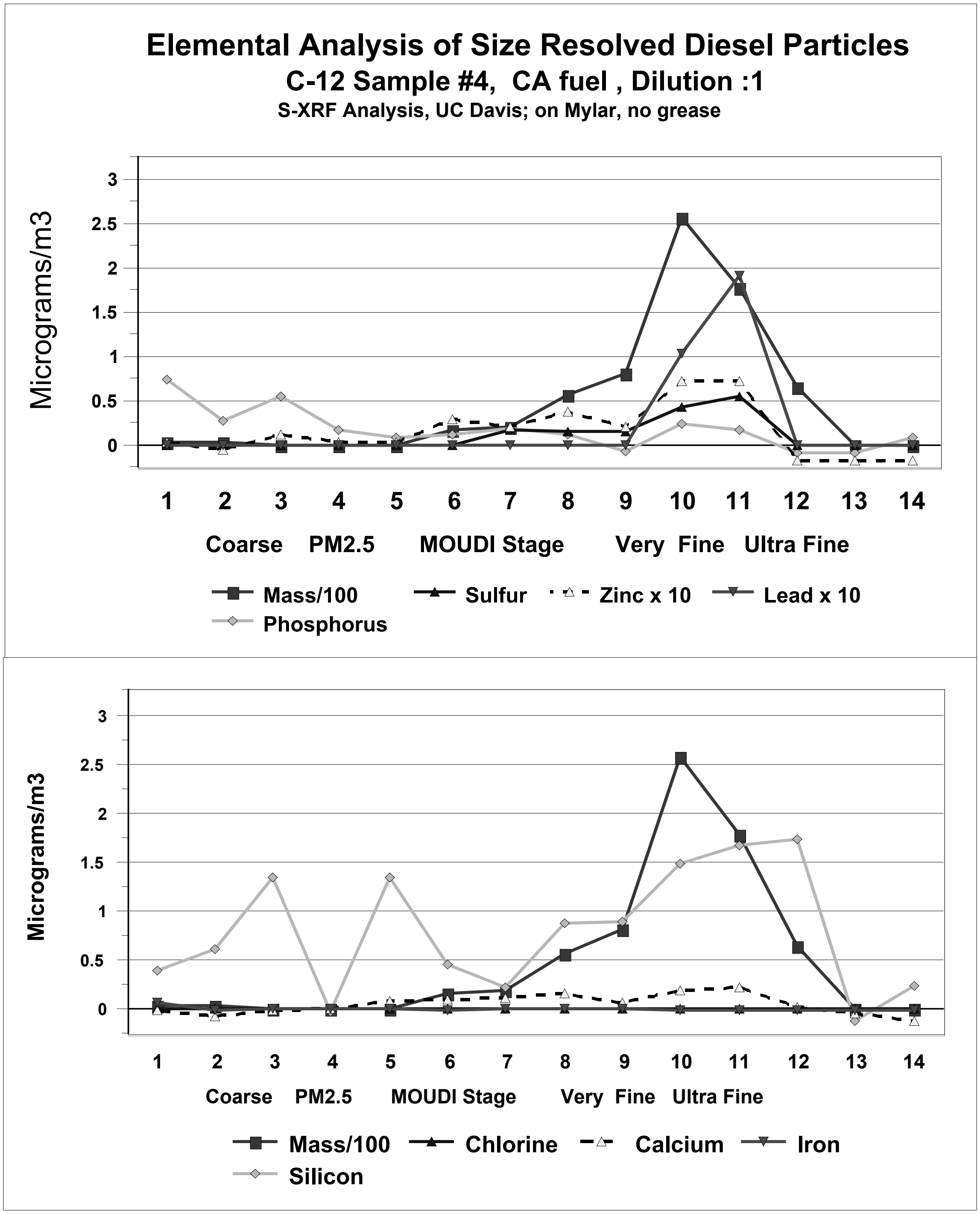


Figure 12 Elemental analysis of size resolved diesel particles

In order to apply these results to the present study, first we examine the data for evidence of very fine particulate mass (Figure 12). The mass concentrations listed are for those periods when all sites were operational in early January. The enhancement of very fine particulate mass at the Crocker Art Museum site is striking, especially in the major episode starting on Jan. 3 that reaches levels seen earlier in Fresno (Bench et al, 2002). The association of these particles from the nearby freeway is established by the low values at the nearby Sacramento River site. Note that the upwind Davis NW and the ARB 13th and T sites are essentially equal in this period, and in fact Davis sees some very fine mass throughout the study.

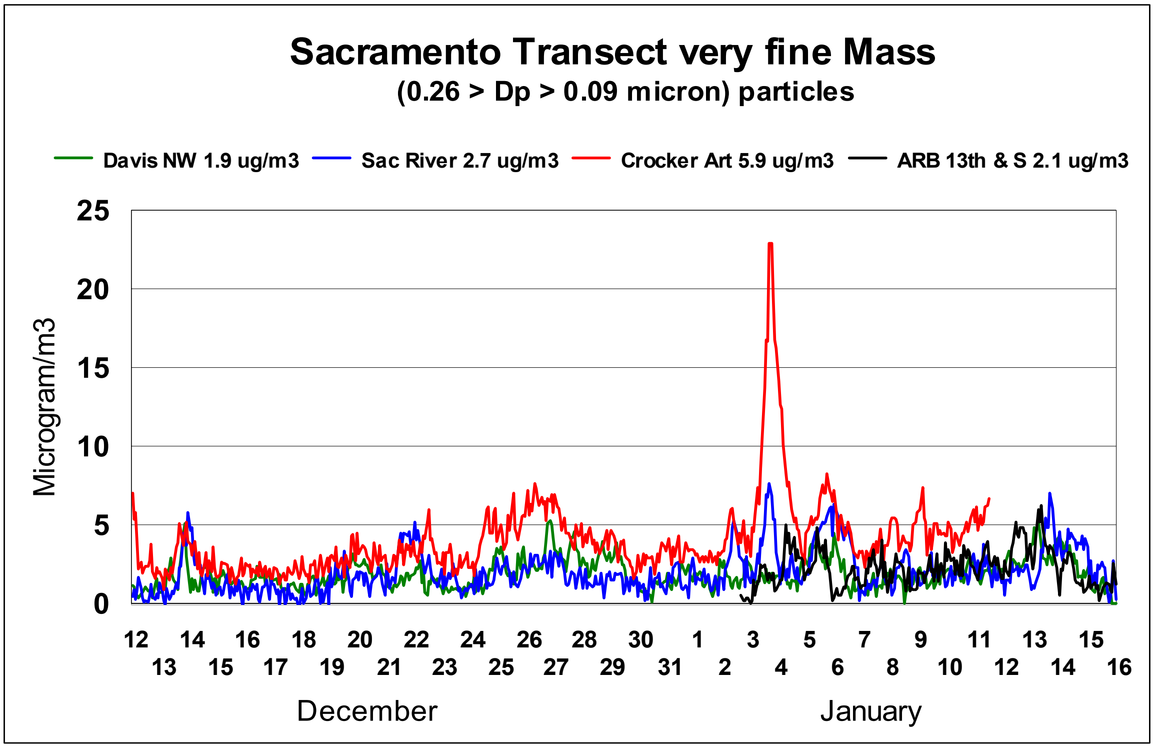


Figure 13 Transect of very fine (0.26 > Dp > 0.09 µm) particulate mass.

The presence of some very fine mass across the transect would require a component of the very fine particle mode with a long lifetime in addition to a dominant mode with the very short lifetimes predicted by theory, but additional studies are required to test this hypothesis. Thus, even though mass contributions are relatively minor, we hypothesize that the persistence of diesel/smoking light duty gasoline powered vehicle particles could result in a long lifetime in Central Valley conditions and thus a disproportionately large component in fine particle mass

In the Figure 13 below, we present the several known tracers of diesel exhaust – very black particles in the very fine (0.26 > D_p > 0.09 µm) mode with correlated sulfur (from the fuel, phosphorus and zinc from the lubricating oil). We must include the impact of smoking, oil burning gasoline powered vehicles in this plot, although evidence is that some of these emissions are in a somewhat larger size mode (Gertler, 2002).

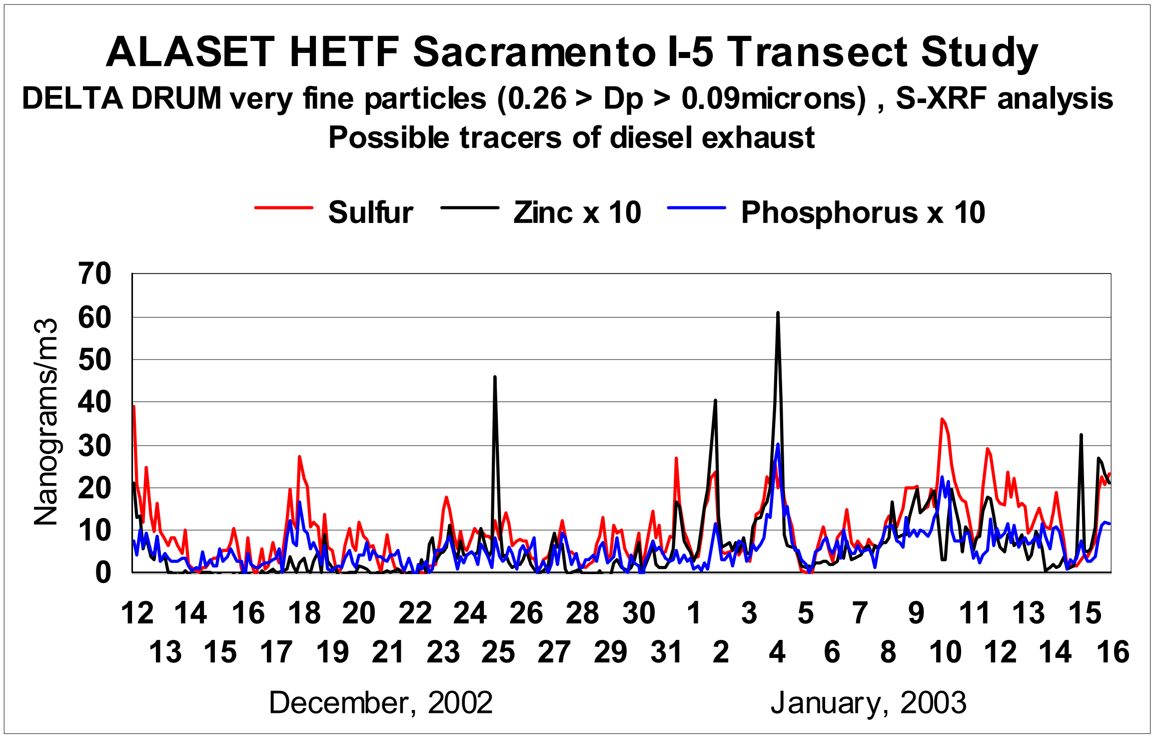


Figure 14 Diesel/smoking car signatures in very fine particles at the Crocker Art Museum site

There are a number of interesting points about this graph. First, it has less dynamic range than that shown by larger particles. Even in heavy rain storms of early December, these materials are generally present. Note that the fireworks on Dec 31 had sulfur and zinc, but not phosphorus. As such, it is a good test for the lack of these species in standard Sacramento city air. The zinc/phosphorus ratio is about what was seen in the NREL tests, and from these tests, some of which used California fuel, we can estimate the total contribution of diesel exhaust to mass.

Thus we conclude that we have identified a highly probably tracer for highway emissions by the presence of diesel/smoking car particles which form a major source of $PM_{2.5}$ particulate mass at the Crocker Art Museum site.

Using the values measured in the NREL study, it appears that an average of about 4.5 $\mu g/m^3$ of $PM_{2.5}$ directly downwind of I-5 can be tied to diesels and smoking cars, (18 $\mu g/m^3$ on the peak day). This can be compared to the 11 $\pm$ 5 $\mu g/m^3$ of roadway $PM_{2.5}$ enhancement observed in the study based on subtraction from the upwind Sacramento River site (Figures 5, 6, and 7). Recall that about 10% of all vehicles are trucks on the section, or about 28,000/day. Further, as predominantly long haul trucks, they probably match the Minnesota/NREL profile.). Thus, from the heavy duty diesel to total vehicular traffic, the contribution from gasoline powered smoking cars and trucks is about the same as that from heavy duty diesels.

The lack of this diesel/smoking car signature on Jan 5 and 6 occurs during a very sharp drop in temperature. We have performed trajectory analysis on this period using the NOAA ARL HYSPLIT trajectory program (Figure T-6). This program allows one to go back from 6 hr to 10 days to see where the air came from that was sampled at the receptor site. Sources along the trajectory can contribute to the concentrations seen. This technique is an excellent complement to continuous sampling techniques. Thus, we established that the dip in concentrations was associated with winds from the northeast that did not pass over I-5, but did cross the entire City of Sacramento.

The key point to make of this result is that the air mass moved across the entire width of Sacramento before arriving at the Crocker Art Museum site, yet even so, and despite the presence of Hwy 99 and numerous surface streets, the concentration still dropped, especially in the very finest stages. Thus, I-5 is a far more intense source of very fine particles than miles of Sacramento proper. Supporting this conclusion is the fact that the Sacramento River site, which is downwind of I-5 in this period, showed a sharp increase in $PM_{2.5}$ and very fine mass.

Site Intensive: Arden Middle School site

This site was chosen because of the previous concerns about the proximity of Arden Middle School to traffic on Watt Avenue and its use in a prior ARB study. The site (see map, Figure 16) was on the roof of a 1 story maintenance building in about the center of the school complex, roughly 5 m above ground level. Traffic on Watt Avenue averaged 62,000 vehicles/day (August, 2002).

Measurements of mass made at Arden Middle School show a pattern seen at no other site (Figure 15). Twice each day, there is a short but intense spike of fine particle mass, peaking in the 0.34 to 1.15 µm size mode but still very evident in particles below 0.34 µm size. We strongly suspect but can not yet prove that this source is extremely close to the sampler itself, most likely on the school grounds, possibly a water heater that is on an automatic timer. Whatever their source, these fine mass spikes do represent an increase of particulate mass that may impact students.

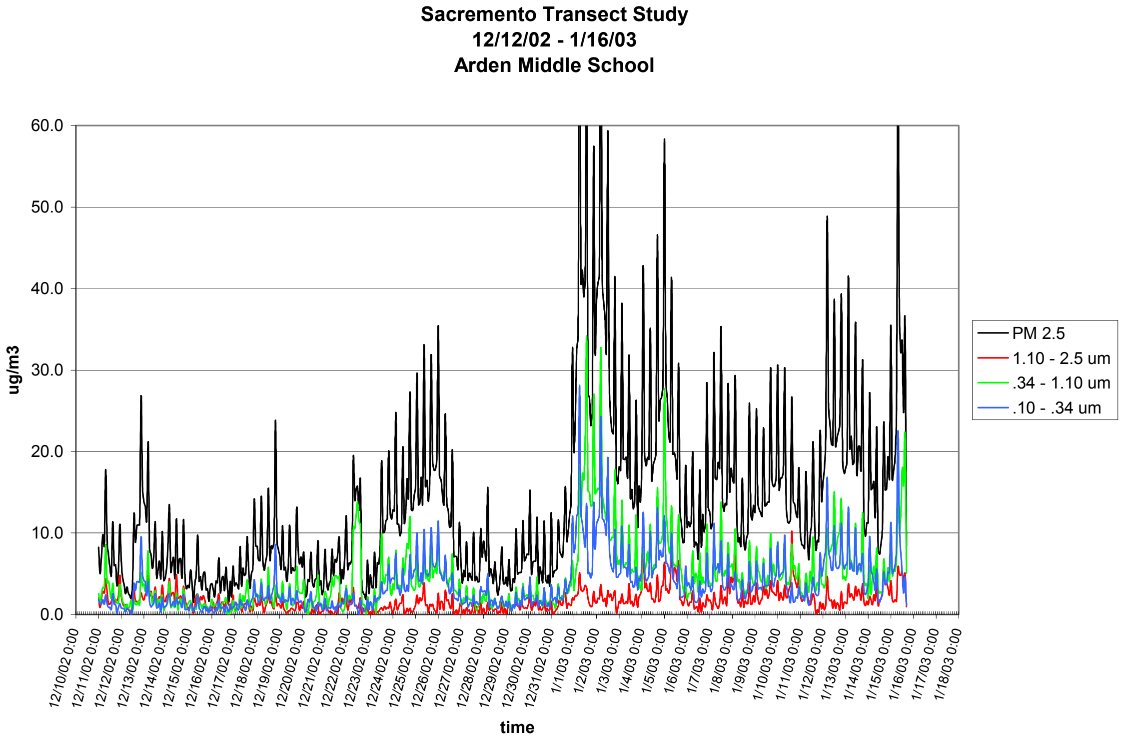


Figure 15 PM$_{2.5}$ mass and 3 sub components, Arden Middle School site

Since these local spikes are not seen at other sites, they were removed to allow comparison of the data from Arden Middle School to other sites in the array. When this is done, Arden Middle School is similar to other nearby sites.

The Del Paso Manor PM$_{10}$ TEOM has some siting similarities to the Arden Middle School site, although it lacks the nearby presence of a heavily traveled roadway. We have taken the data from the site and smoothed the 1 hr TEOM data to better match the 6 hr DRUM data, and these are presented together below in Figures 17 and 18.

Figure 16 Map of the Arden Middle School site

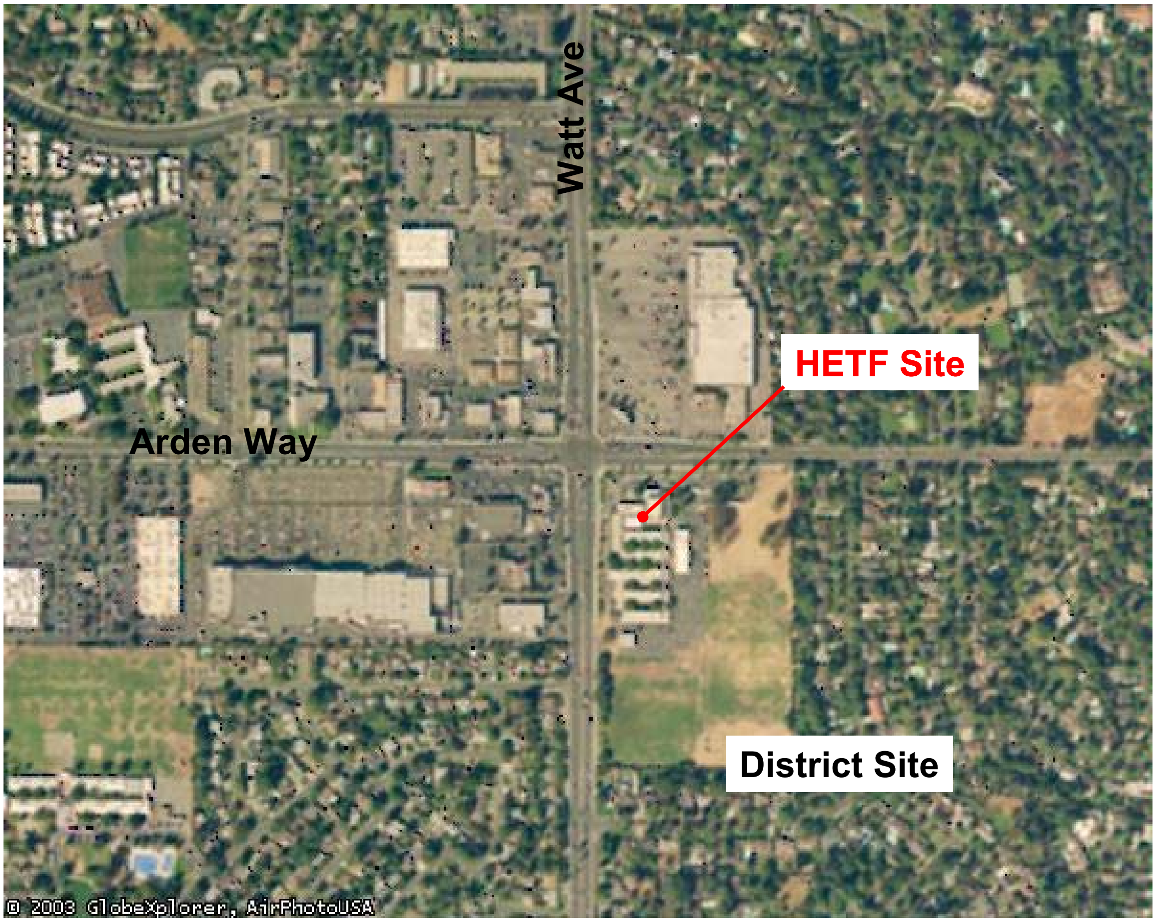
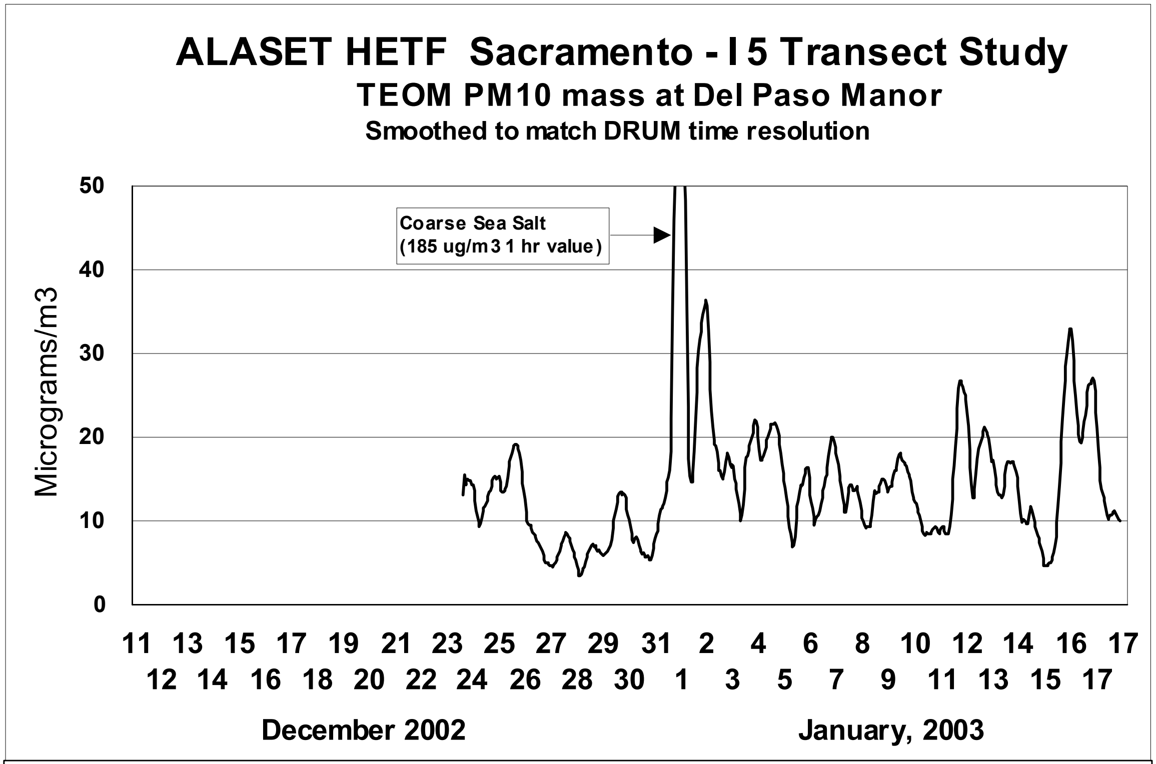
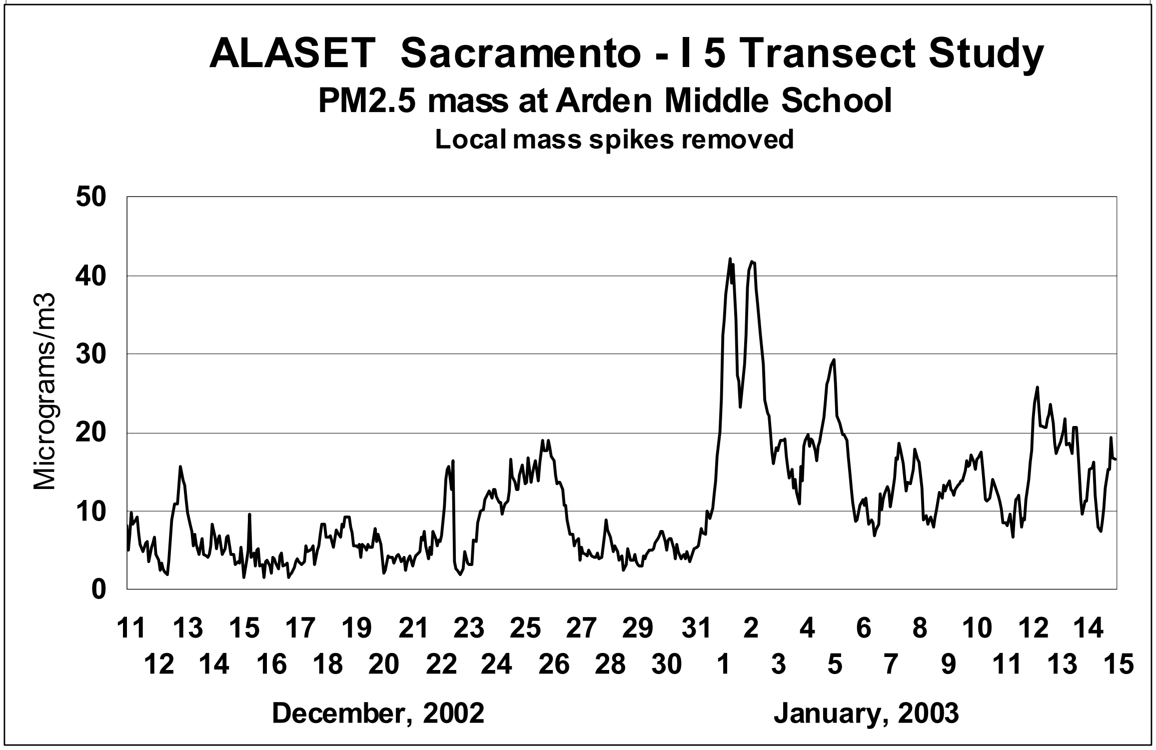


Figure 17 and Figure 18 – Comparison of Del Paso Manor TEOM (smoothed) with Arden Middle School DRUM. The compositional data and the HYSPLIT trajectories identify the large peak on January 1 as sea salt. Winter valley PM_{10} aerosols are usually overwhelmingly $PM_{2.5}$ (circa 90%) so rough agreement is expected, especially in regional aerosol such as those around Christmas.





We also provide information on the Arden site from district CO data (below, Figure 19). The data are taken just beyond the far south east corner of the school yard and are thus much farther from Watt Avenue than the aerosol data, but should still represent the diurnal pattern. Note that the data are from 2002. . The rough equality between nighttime CO values and daytime CO values occurs because the intense nighttime inversion traps pollutants and magnifies the effect of the far lower number of vehicles/hr at night.

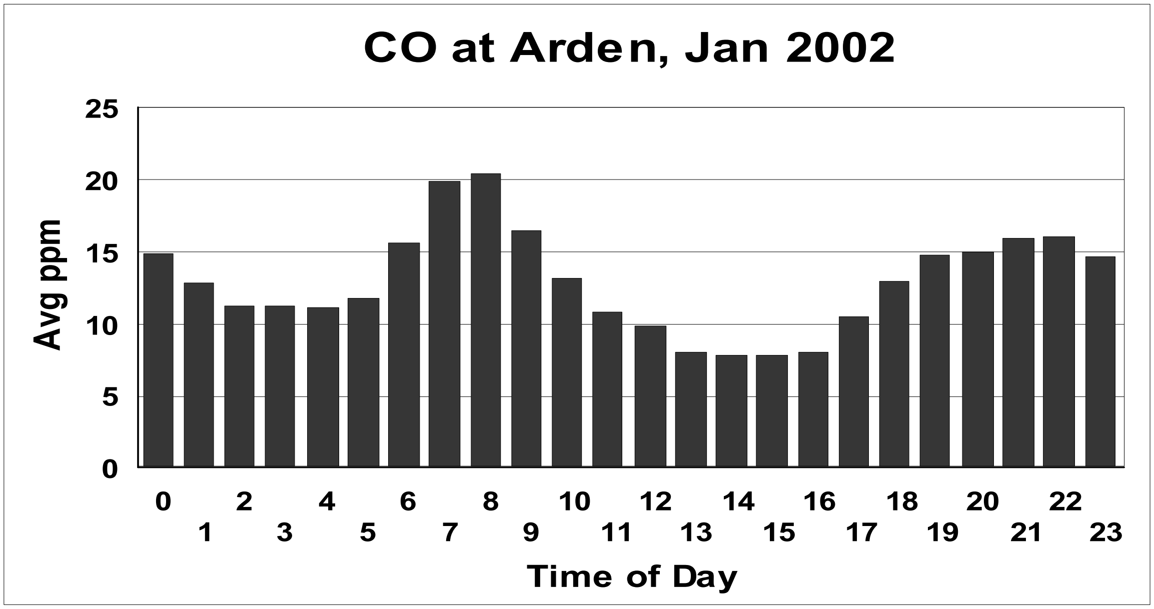


Figure 19 CO data from the district sampling site nearest Arden Middle School but several hundred feet east of Watt Avenue, data taken from the previous year,

Compositional analysis was made of these samples by synchrotron x-ray fluorescence (S-XRF) at the Advanced Light Source, Lawrence Berkeley NL. The data are presented here from the largest stage to the finest stage for some of the major elements (Fig. 20).

There is a lot of information in these three plots, more than we can explain in this short report.

Starting with the top plot, the coarse particles (but still part of $PM_{2.5}$), the sea salt signature (sodium is also seen in about the correct ratio) during and near the rain events is a consequence of strong winds off the Pacific, shown by the inferred velocities in Figure T-1. This provides the explanation for the very large TEOM peak on Jan 1 (185 $\mu g/m^3$) since the PM_{10} TEOM would see coarse sea salt in the range between 2.5 and 10 μm not sampled by the $PM_{2.5}$ DRUM. Sea salt aerosols are also seen at Davis in summer on strong Bay Breezes (Cahill et al, 1986). Little soil is seen (calcium) until very late in the sampling period after about a week with no rain. Sulfur is seen in a coarse mode, most likely from Bay Area sources that have entered the valley as SO_2 from Benecia, converted to sulfate, and picked up water in the fogs.

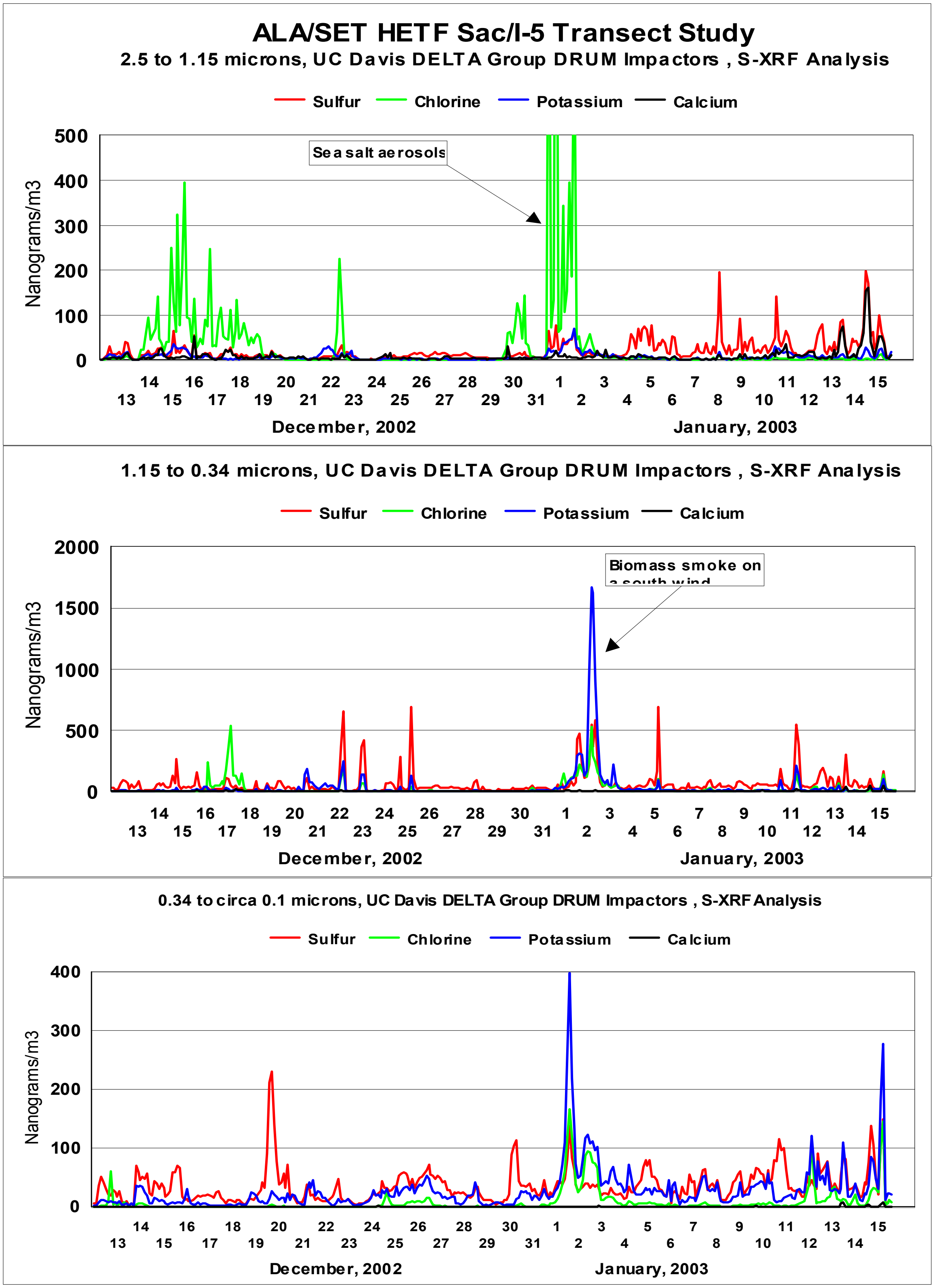
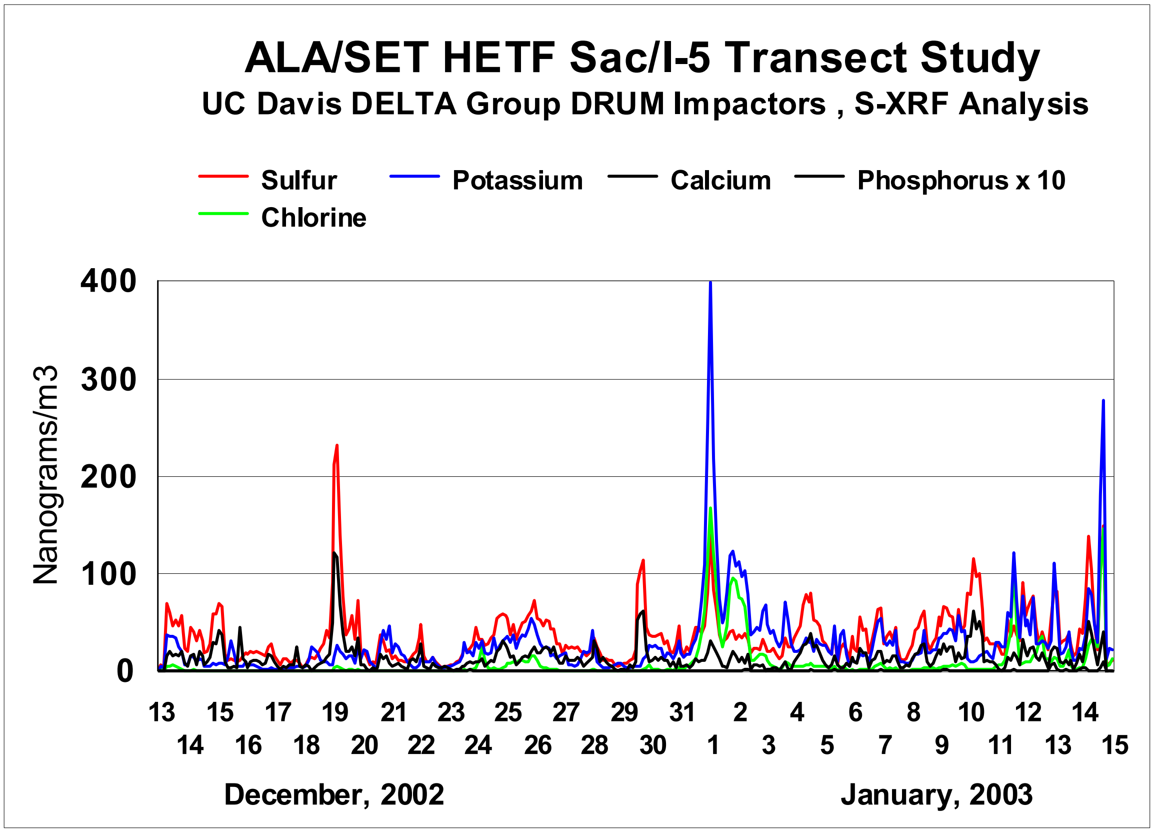


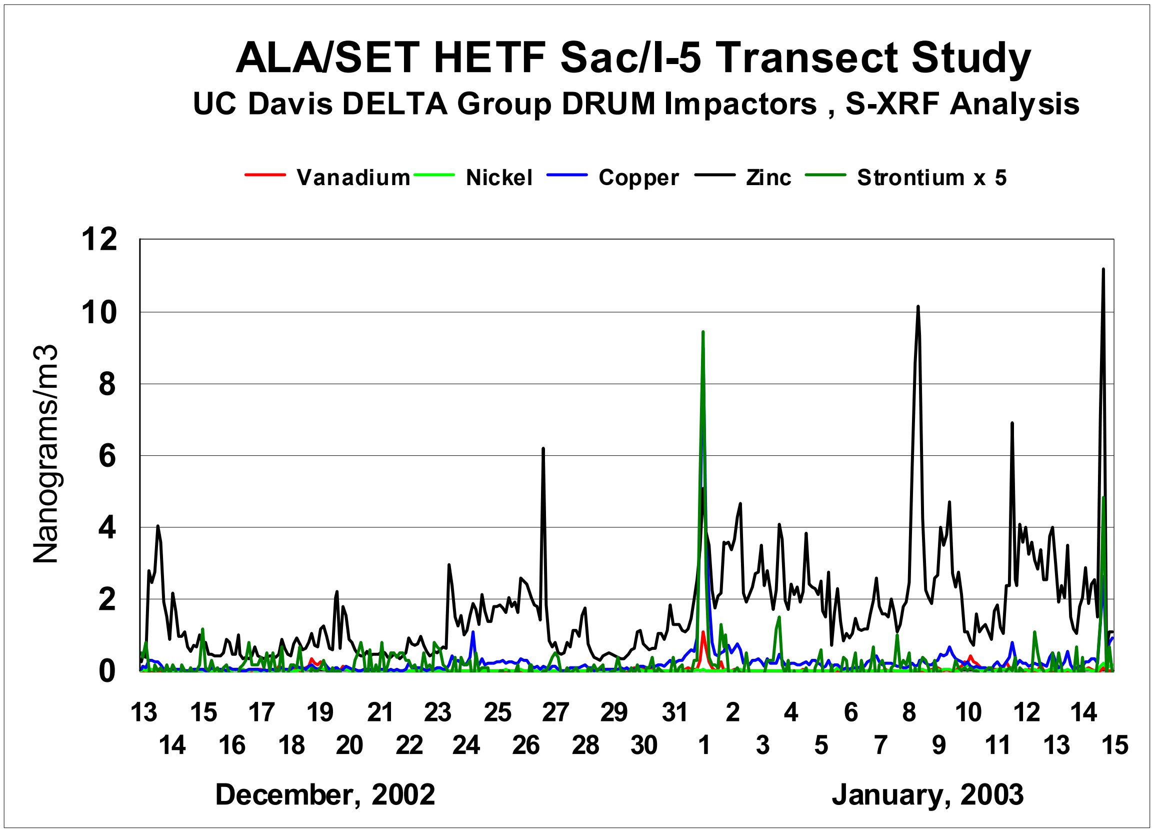
Figure 20 S-XRF elemental data, Arden Middle School, for 3 components of $PM_{2.5}$.

The intermediate size particles are dominated by a large potassium peak on Jan 3. Normally potassium in this size mode is associated with biomass smoke. The trajectory started in the Sierra foothills and moved downslope into the valley before moving north to Sacramento (Figure T-2). There is also an association with chlorine, which we have not seen before. The sulfur is now seen in short spikes, almost always with potassium. The source of this is also unknown. If we assume that the intense potassium peak is from biomass smoke, the question then arises – where is the rest of the biomass smoke on the other days? If fireplaces are a major factor, there should have been a lot of potassium in this size mode, especially in the stagnation period between Christmas and New Year.

Examining the finest mode in more detail, we see that phosphorus is associated with the sulfur in this size mode, as was seen near I-5 at the Crocker Art Museum site.

Figures 21, 22 Very fine ($0.34 > D_p >$ circa 0.15 μm) aerosols at Arden Middle School.





The finest mode has many of the same elements as the intermediate mode, but note how the pattern has changed. The peak concentrations are much lower than on the intermediate stage. There is a sulfate peak around Dec. 20 with no phosphorus but potassium, and the largest peak now occurs on Jan 2. The persistent zinc in the finest mode, often with sulfur and phosphorus, indicates diesel/smoking gasoline vehicle impacts at the Arden Middle School. Comparing the Arden Middle school zinc with that at the Crocker Art Museum site, we find that they are often comparable.

Fireworks elements are seen on the finest stage on Dec 31 (Figure 11), roughly the same elements as see at the Crocker Art Museum site, and surprisingly about the same concentration.

Comparison of Roadway Influence – Interstate-5 vs. Watt Avenue

We and others have previously done studies of the influence of roadways on downwind neighborhoods (Cahill et al, 1974, Feeney et al, 1975, Courtney et al, 1978)**.** In these early studies, lead was used as the fine particle marker of traffic, since the amount burned and emitted in automobiles was known with precision. In Table 3, we show the results normalized to 5,000 vehicles/hr for winds transverse or across the road way. The perfect agreement between the measured versus calculated value at 27 m for the "At Grade" section was based on first principles and was not scaled. The calculation is valid for non-reactive gasses and very fine particles. The actual lead numbers are now, thankfully, immaterial, but merely serve as a fine particle tracer from the past.

Table 3 Effect of roadway distance and configuration on downwind concentrations of lead [1].

Roadway	**Distance**	**27 m**	**40 m**	**100 m**	**160 m**
At grade	*Calculated*	*4.0*	*3.4*	*1.4*	*0.41*
At grade	Measured	4.0	**3.1**	1.4	0.35
			Arden		
Depressed	Measured	4.5	1.7	**0.26**	
				Crocker	
Elevated	Measured	4.8	2.3	3.1	(3.5)

Thus, the relative effect of I-5 on the Crocker Art Museum site versus Watt Avenue on Arden Middle School site is governed by both distance and roadway configuration, a ratio of 3.1/0.26 = 12, and by traffic volume, which is 4.5 times greater on I-5 than Watt Avenue. This gives a net effect of 12/4.5 = 2.6, with the Arden Middle School site higher than the Crocker Art Museum site despite the higher traffic volume on I-5. This calculation, while only approximate, assumes non-reactive gasses and very fine particles with sizes similar to lead, including diesel/smoking car particles, which transport like a gas.

Very fine zinc is of a similar size and acts as a tracer for combustion of lubricating oil containing zinc thiophosphate, seen in diesel exhaust (Fig. 12) and predicted to occur also in oil burning smoking cars. These species were observed both at the Crocker Art Museum site (Fig. 14) and Arden Middle School (Fig. 21, 22). While there is no upwind compositional data to allow correction for non-highway zinc, the observed zinc provides a semi-quantitative support for this calculation. The approximate diesel/smoking car ratio is calculated from the 1.3 ng/m^3 of zinc at Crocker and 3 ng/m^3 of zinc at Arden in hazy periods in January, for a ratio of 2.3, versus the predicted 2.6. However, there are so many assumptions and potential sources (Highway 99) involved that the numerical values should not be taken too seriously.

In this regard, we might also mention the fact that the New Year's Eve fireworks on the Tower Bridge were seen strongly at Arden Middle School. Unlike the freeway emissions, the fireworks were an elevated source of very fine particles and thus able transport efficiently downwind, in qualitative agreement with the "Elevated" freeway results of Table 1, especially when combined with the typical low inversions of Sacramento in winter.

Using the zinc/mass ratio from the NREL data (Figure 12) we predict 4.5 μg/m^3 of diesel/smoking car mass at the Crocker Art Museum site and a few μg/m^3 at the Arden Middle School, although we have no laboratory data for the typical short haul truck traffic characteristic of Watt Avenue and no upwind mass or elemental data on Watt Avenue.

Mitigation at Arden Middle School

While this study recorded no violations of state or federal ambient air standards, the efficient transport of pollutants from heavily traveled Watt Avenue into the Arden Middle School is not a good idea, especially with the documented presence of diesel and/or smoking automobile pollutants, some of which are toxic.

The typical westerly winds push Watt Avenue emissions into Arden Middle School during much of the year. The problem is that there is no barrier to air flow from Watt Avenue into the school grounds, a problem which was probably exacerbated sometime in the past when Watt Avenue was widened and a school buffer of distance and vegetation lost while traffic volumes increased. However, some mitigation is still possible.

The following suggestions are being proposed as worthy of further study and potential implementation:

1. Sound wall. A sound wall on Watt Avenue would prevent straight line transport of pollutants from Watt to the classrooms, forcing the air up and over, mixing the roadway pollutants with cleaner air above.
2. Trees. A line of closely spaced redwood trees directly behind the sound wall would continue the barrier to roadway effluents, while adding particle removal to the foliage. It also would provide afternoon shade.
3. Mysterious mass spikes. These are large, and efforts should be made to understand the source, since it may be so local as not to impact the children. If it is serious, locate the source and remove or control it.
4. Furnace Air Filters. If they are not in use already, high efficiency electrostatic furnace filters would reduce classroom concentrations when outdoor air is used.
5. Ventilation Establish where it is that the air in the classrooms comes from, and make sure it is not directly impacted by Watt Avenue.
6. Trees on site. Always a good idea, especially if they have a dense foliage and are not deciduous.

Suggested School Project

On of the greatest uncertainties is the vehicle mix on Watt Avenue. Students could make it a project to count vehicles by type during selected daytime hours. An inventory of the number and type of vehicles with visible smoke would also be useful.

Analysis of an Episode – Jan 1 – Jan 6, 2003

The ending of the rains in late December, 2002 and the strong northwest winds on January 1 ushered in a period of low wind velocities and fogs with elevated levels of $PM_{2.5}$, decreased visibility, and fog, Jan. 3 through Jan. 8. The Air Resources Board recorded a 24 hr $PM_{2.5}$ mass of 50 µg/m^3 at 13th & T Street on Jan 3. In this section, we examine the causes for these elevated levels.

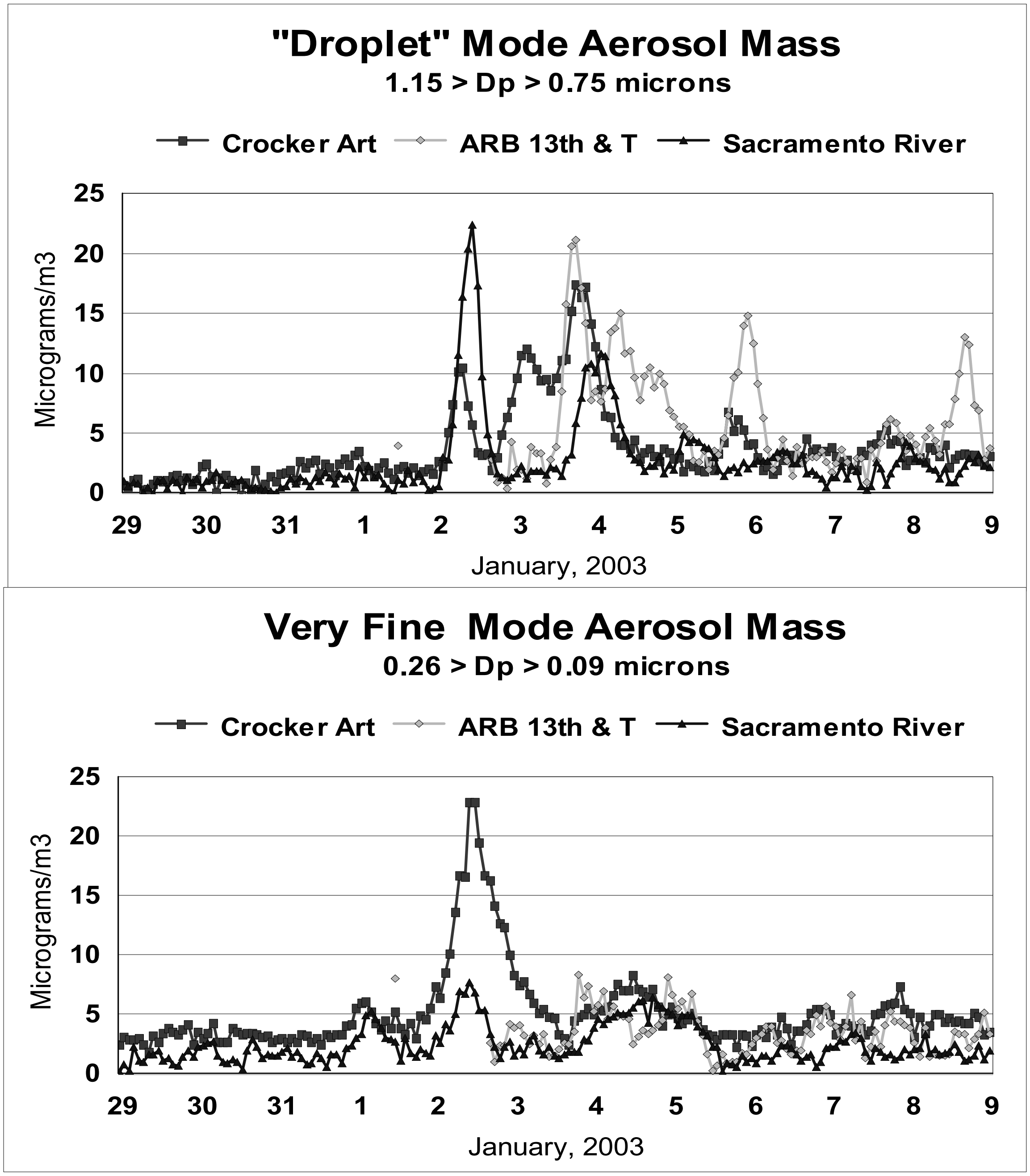


Figure 23 "Droplet" mode and "very fine" mode aerosols, Dec. 29 to Jan. 9, 2003, at the central Sacramento sites.

Figure 24 shows two mass components of $PM_{2.5}$ in this period, the "droplet " mode of $1.15 > D_p > 0.75$ µm and the very fine mode $0.26 > D_p > 0.09$ µm. The "droplet' mode is often associated with the growth of hygroscopic aerosols in humid conditions, while the very fine mode is often closely tied to local high temperature combustion.

The first point to note is that the two modes seem totally uncorrelated in time. The second point to note is that often they are often uncorrelated even though 13th and T Street is only about 1.8 km (1.1 mi) ESE from the Sacramento River and Crocker Art Museum site. However, 13th and T is also only about 0.5 km north of the heavily traveled "W-X" section of Business 80/Highway 50 Capital City Freeway, with close to 330,000 vehicles/day. Thus, it is clear that a single air sampling station misses a great many local influences from specific sources, in this case highways.

We have argued that the very fine mode particles seen strongly at the Crocker Art Museum site are from I-5 both on the basis of particulate size and chemistry. It is interesting that no equivalent impacts of the "W-X" section seen to be evident at 13th and T. The "droplet" mode, which often dominates the total $PM_{2.5}$ mass in this period, has clearly a different behavior and doubtless different sources. However, as shown in Figure 13, the very fine component of the Jan. 3 episode has the highest levels of diesel/smoking car aerosols, while at Arden Middle School, we saw high levels of accumulation mode potassium on Jan 3, a signature of biomass smoke. Trajectory T-4 showed these aerosols arriving on very slow winds coming up the valley from the direction of Stockton and Fresno, parallel to Highway 99 and parts of I-5. Are the observed aerosol consistent with San Joaquin Valley air, and/or are other sources also implicated? Certainly aerosol concentrations rise as one goes south from Sacramento (Figure 25). We also broke up this profile as a function of the weather types used above (Figure 26). Note that on one occasion, the north end of the valley had higher $PM_{2.5}$ than areas further south, but this was the exception.

We next will examine the transport patters to find potential source areas for the aerosols. In order to understand this event, we ran HYSPLIT isentropic backward trajectories every 6 hr from Jan 2 00 UTC (Universal Time, the old Zulu or Greenwich, which is 8 hr earlier, or 4 PM on Jan 1) until Jan 6 06 UTC (10 PM, Jan 5). We used elevations above ground level of 200 m, 500 m, and 1000m, with the latter generally above the valley inversion. We ran isentropic trajectories so that we could see when the air parcels were touching or near the ground (T-7 through T-23).

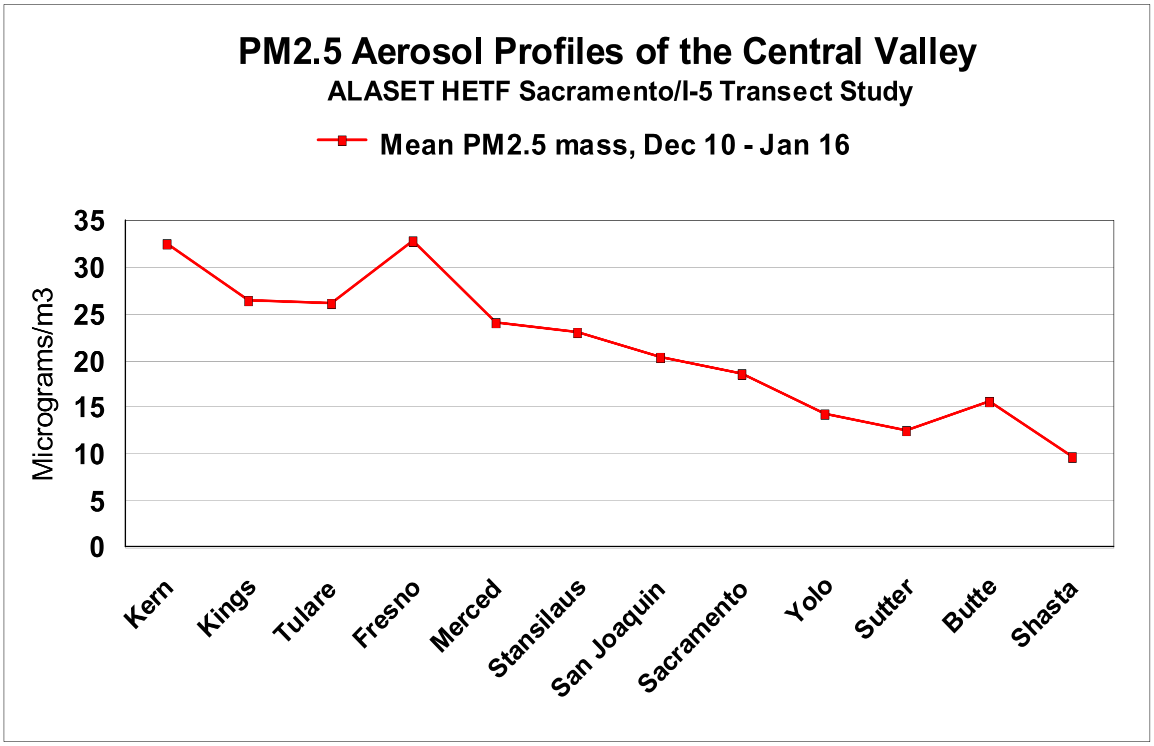


Figure 24 Mean $PM_{2.5}$ concentrations in the Central Valley during the study period.

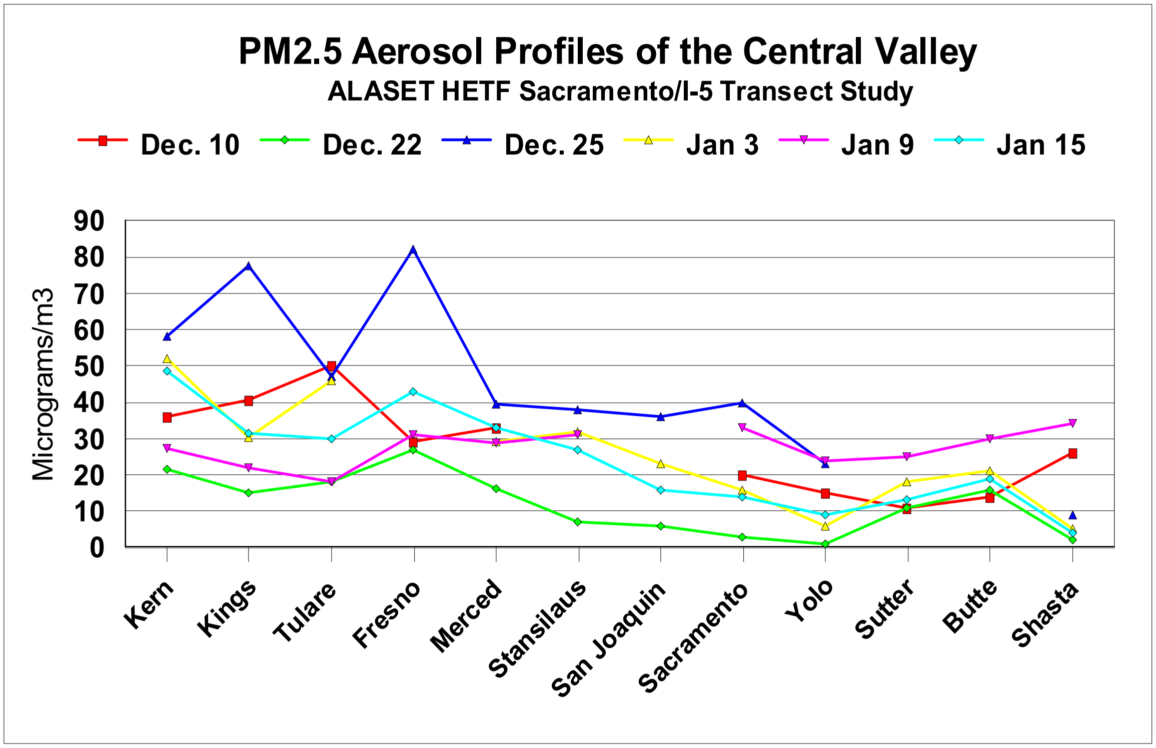
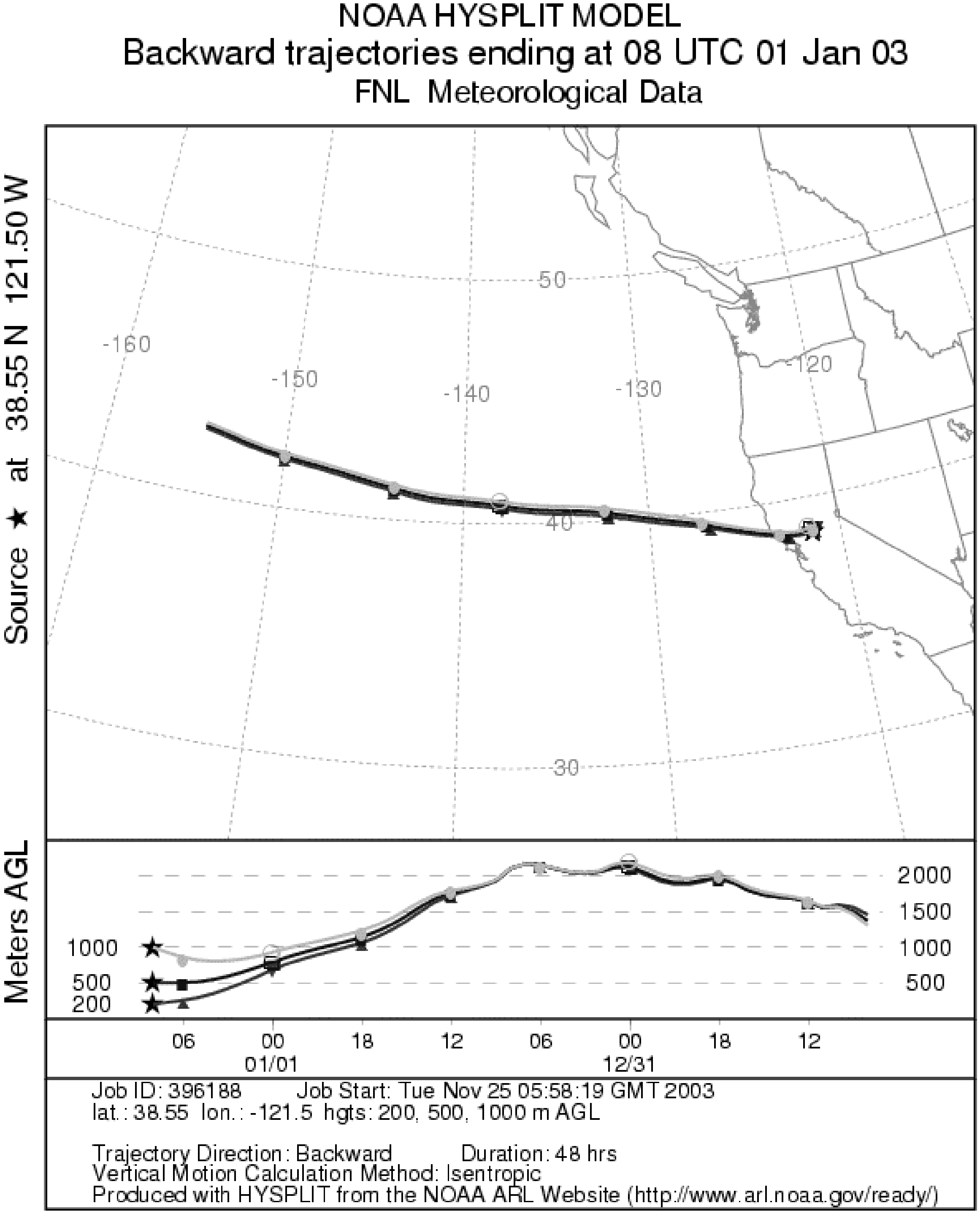


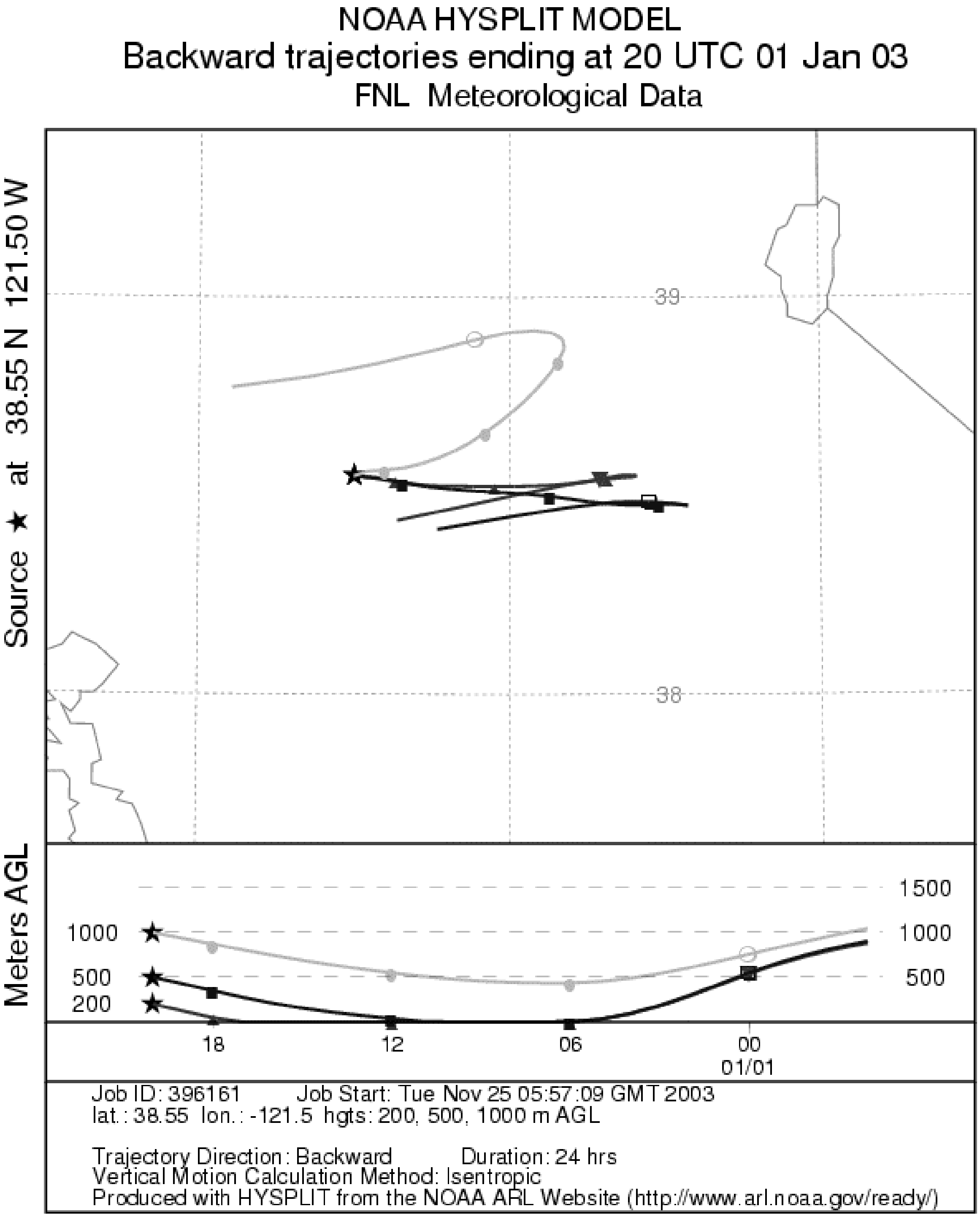
Figure 25 $PM_{2.5}$ profiles as a function of weather-based groups in the Central Valley during the study period.



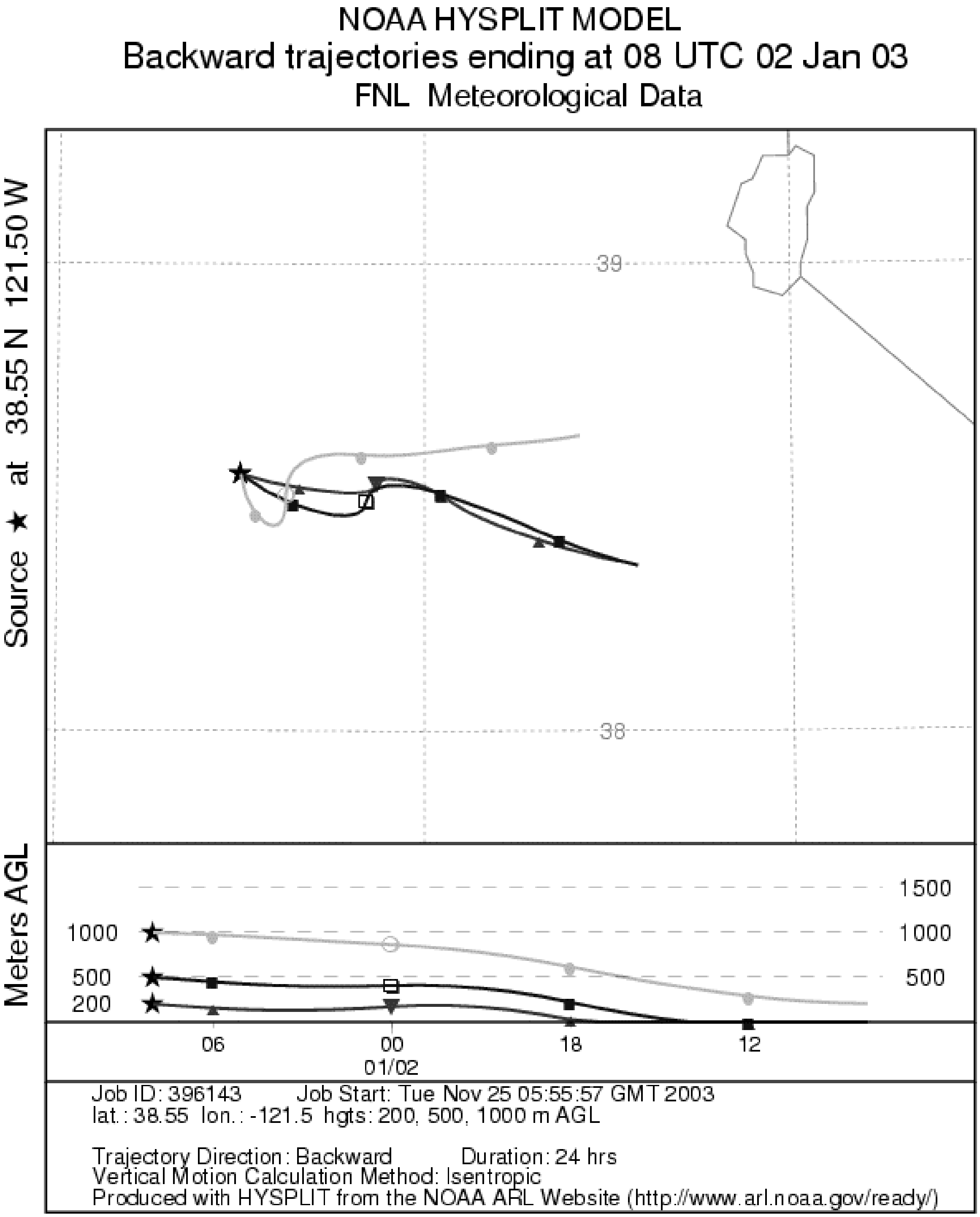
Job ID: 396188 Job Start: Tue Nov 25 05:58:19 GMT 2003
lat.: 38.55 lon.: -121.5 hgts: 200, 500, 1000 m AGL

Trajectory Direction: Backward Duration: 48 hrs
Vertical Motion Calculation Method: Isentropic
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

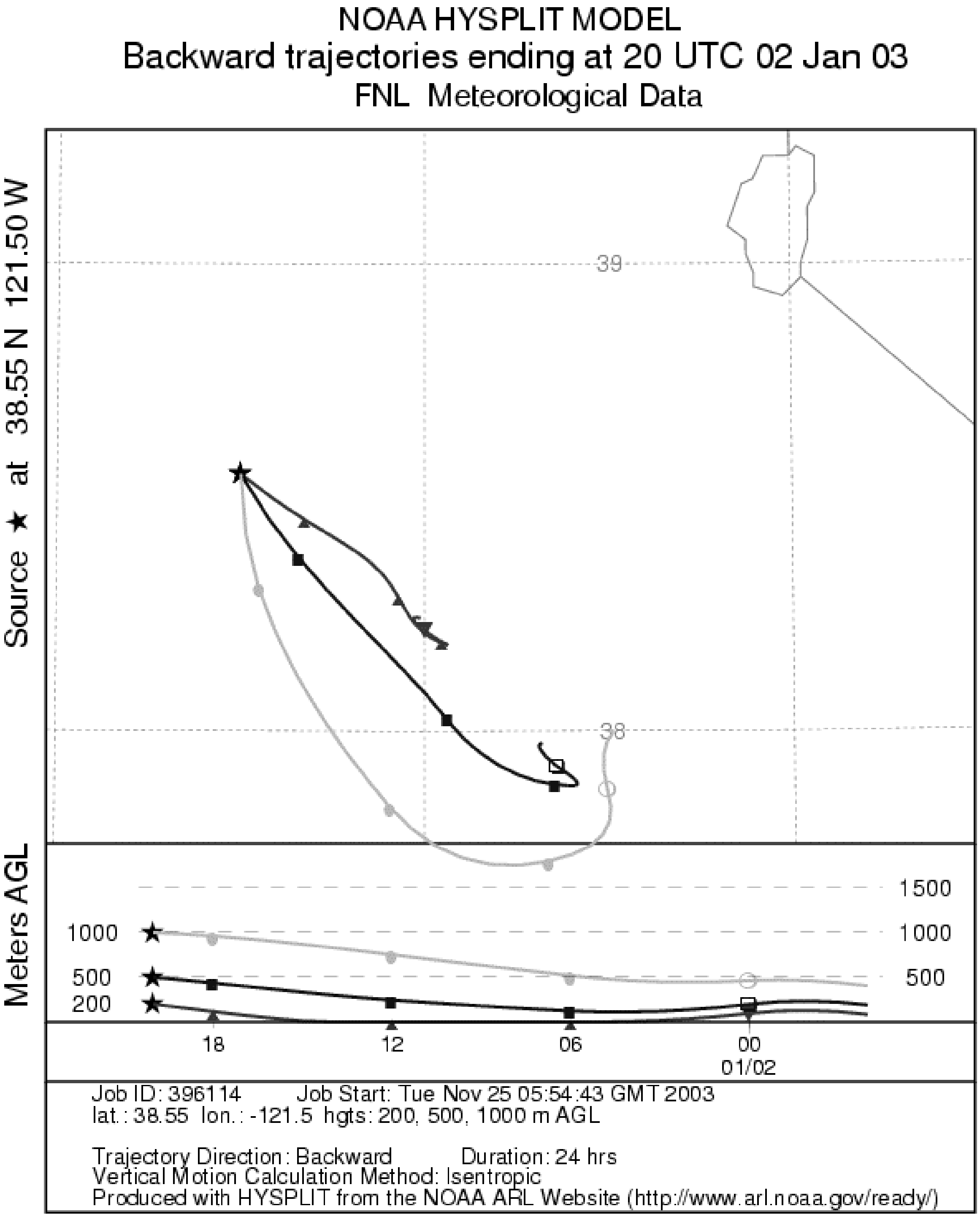
T-7 On Dec 31 at midnight (0000 hr), we still had strong oceanic trajectories, with a sea-salt signature in 2.5 to 1.15 µm particles at Arden Middle School and the fireworks from Tower Bridge.



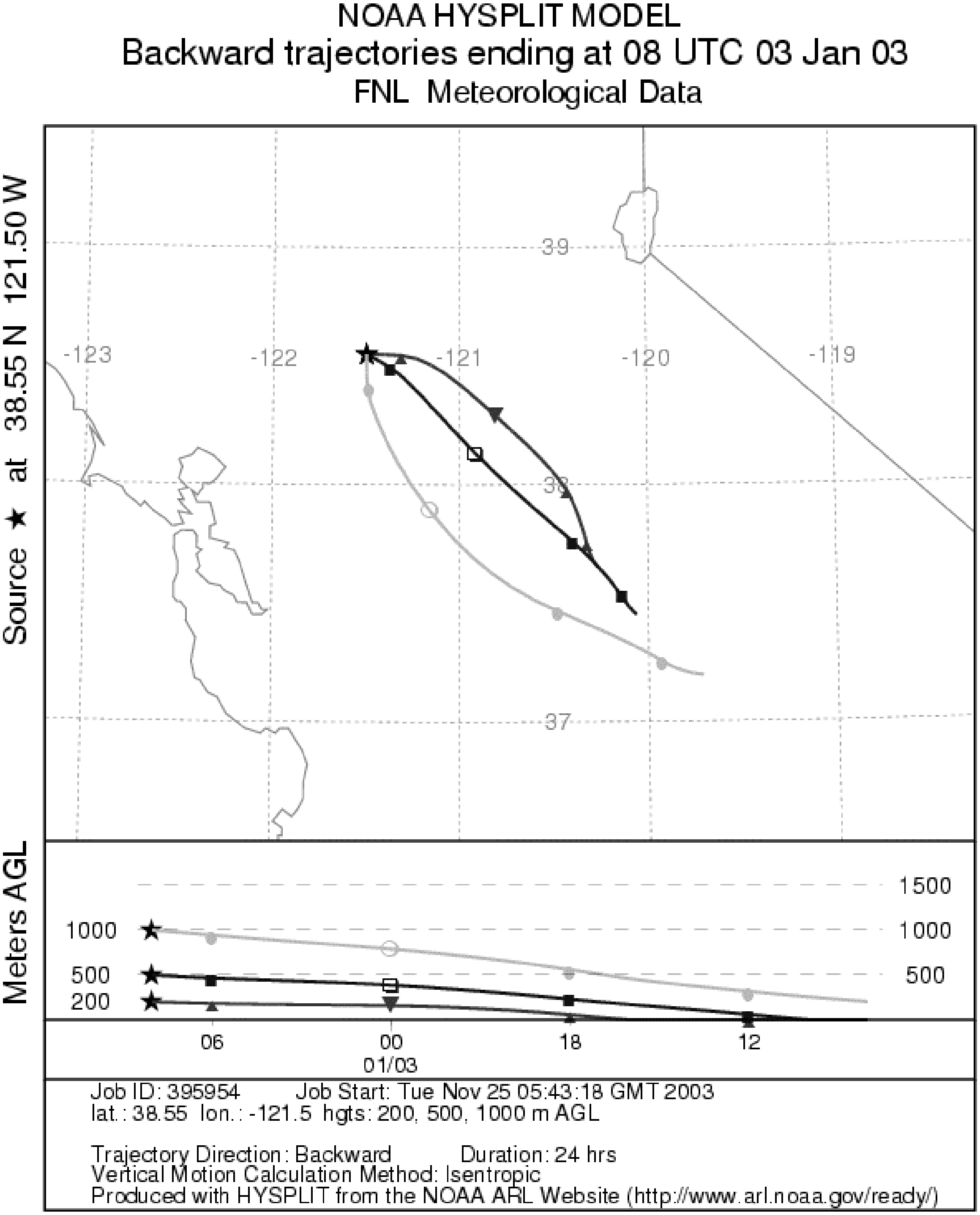
T-8 By noon on New Year's Day, the trajectories are slowing down and now represent air masses arriving on the west slope of the Sierra Nevada and then sliding westward down to Sacramento.



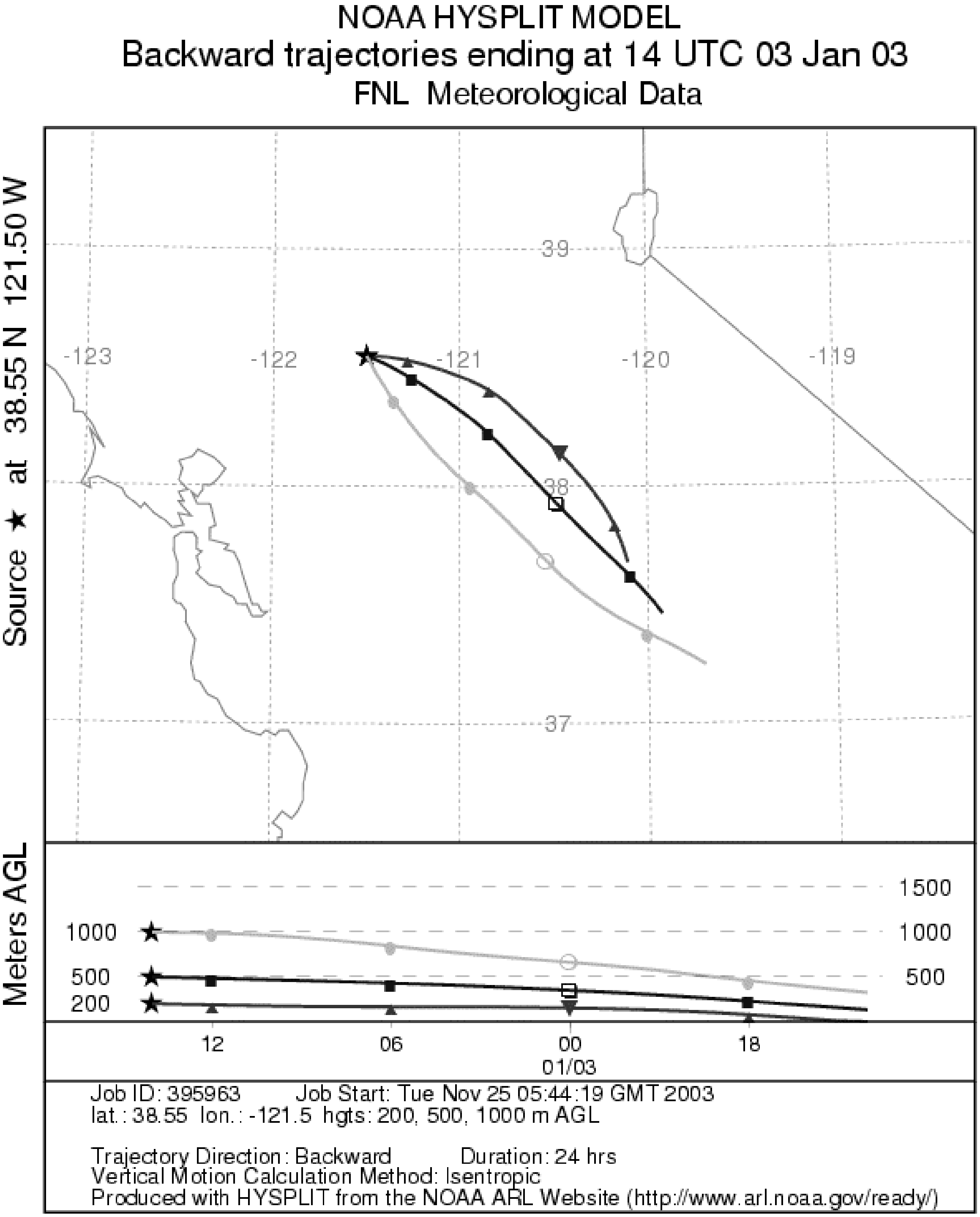
T – 9 This pattern continues, with slow trajectories downslope to Sacramento from the west slope of the Sierra Nevada at all elevations. Clearly, any wood smoke wood from that region would drift down to Sacramento on very slow winds (roughly 1 mi/hr).



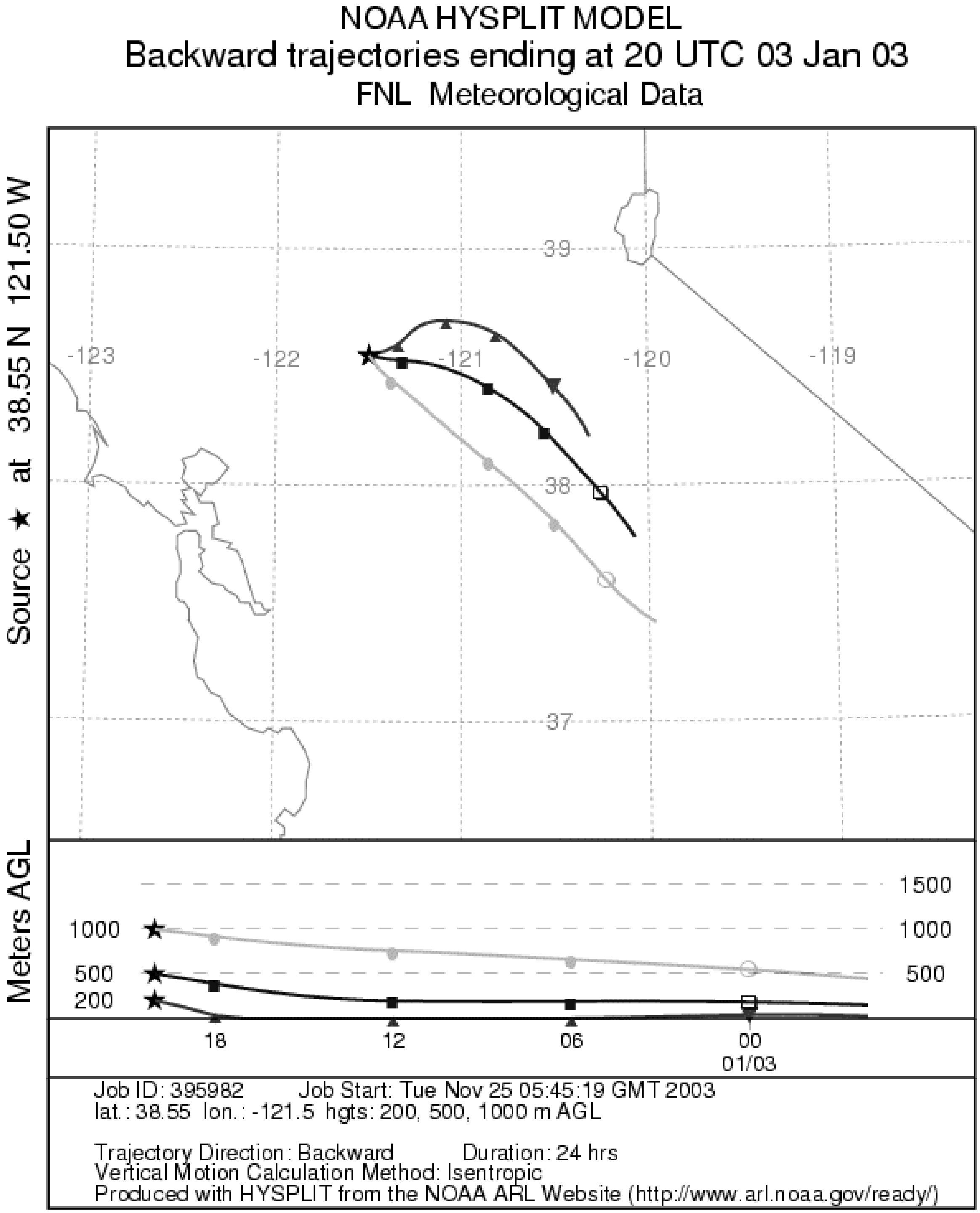
T-10 By noon on Jan 2, the air mass continues to slide downslope, but reaches the Valley floor well south of Sacramento and then moves northwest to Sacramento, again with very low velocities, , a classic winter pattern. These trajectories are parallel to and overlay Highway 99 and the part of I-5 between Sacramento and Stockton. By now, the air parcels have lingered almost 24 hr on the valley floor south of Sacramento



T-11 This pattern continues on midnight, Jan 3, with the 200 m trajectory reaching about Merced and the 1000 m trajectory reaching Fresno. These trajectories parallel Hwy 99 and parts of I-5, so that as they move, the pollutants are continually injected into the air mass.



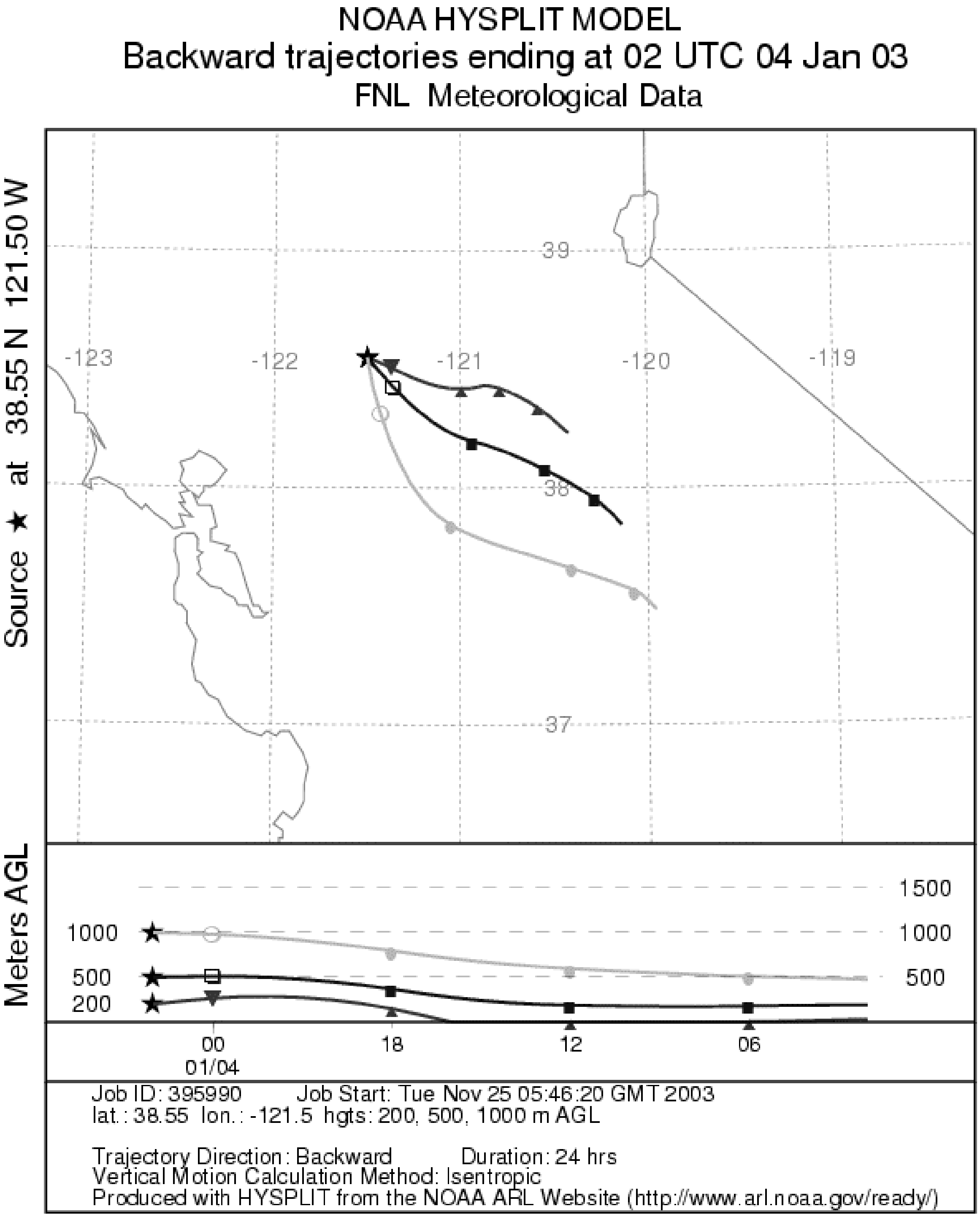
T-12 The pattern of transport from the northern San Joaquin Valley continues at 6 AM.



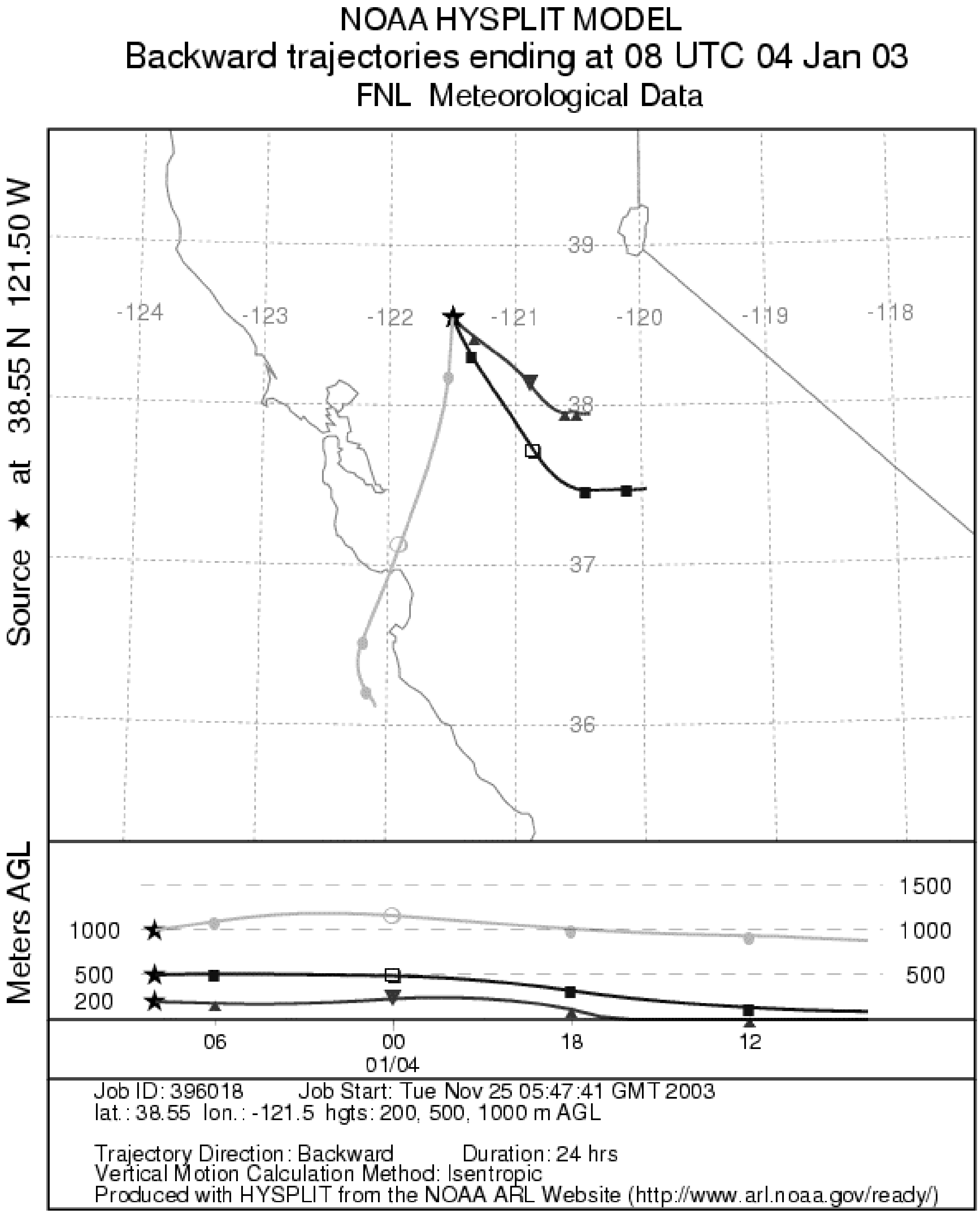
Job ID: 395982 Job Start: Tue Nov 25 05:45:19 GMT 2003
lat.: 38.55 lon.: -121.5 hgts: 200, 500, 1000 m AGL

Trajectory Direction: Backward Duration: 24 hrs
Vertical Motion Calculation Method: Isentropic
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

T-13 By noon, the 200 m trajectory lies in the Sierra foothills before descending to Sacramento.

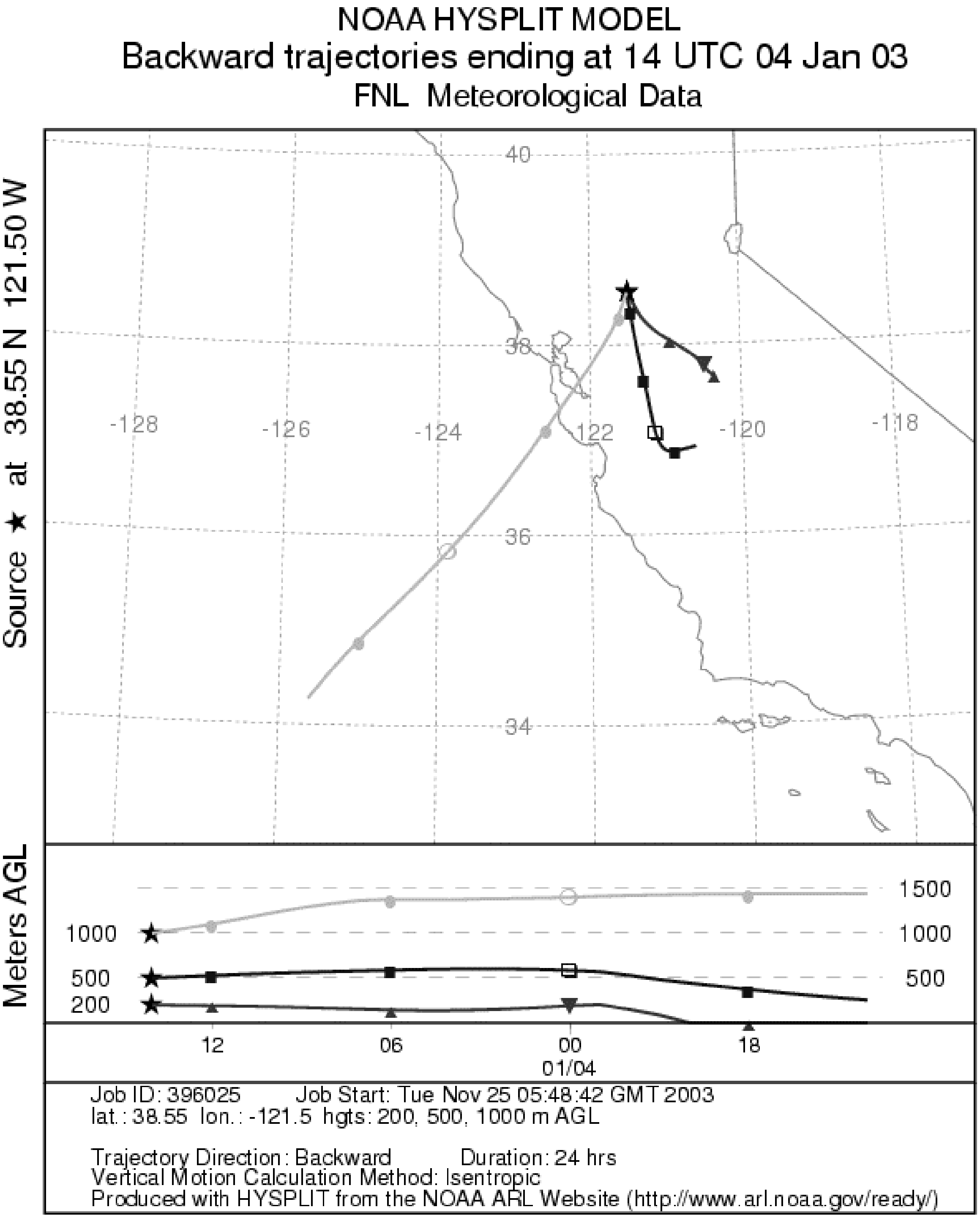


T-14, T-15, T-16, and T-17 Slow transport from the northern San Joaquin Valley continues for Jan 4.


NOAA HYSPLIT MODEL
Backward trajectories ending at 08 UTC 04 Jan 03
FNL Meteorological Data

Job ID: 396018 Job Start: Tue Nov 25 05:47:41 GMT 2003
lat.: 38.55 lon.: -121.5 hgts: 200, 500, 1000 m AGL

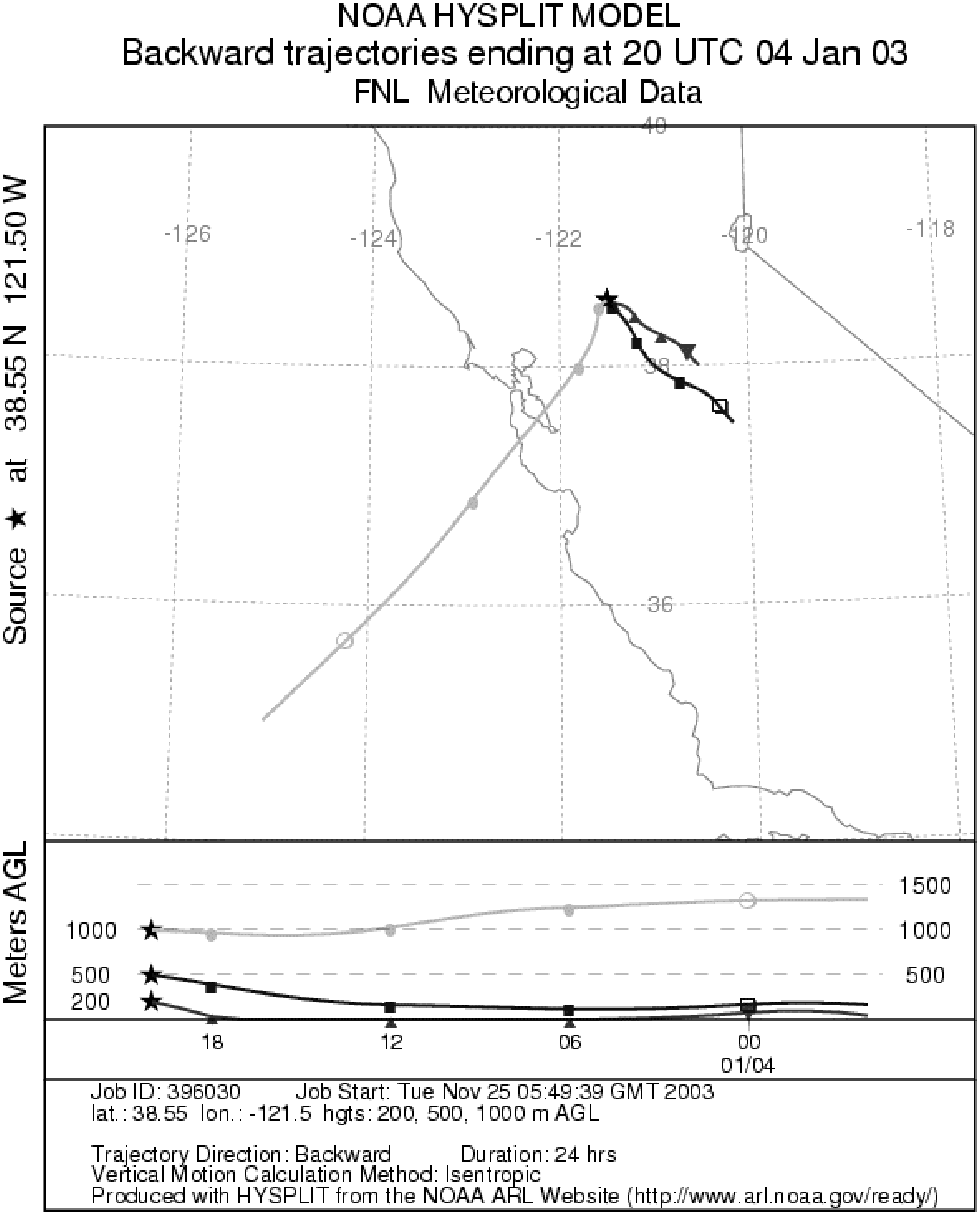
Trajectory Direction: Backward Duration: 24 hrs
Vertical Motion Calculation Method: Isentropic
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

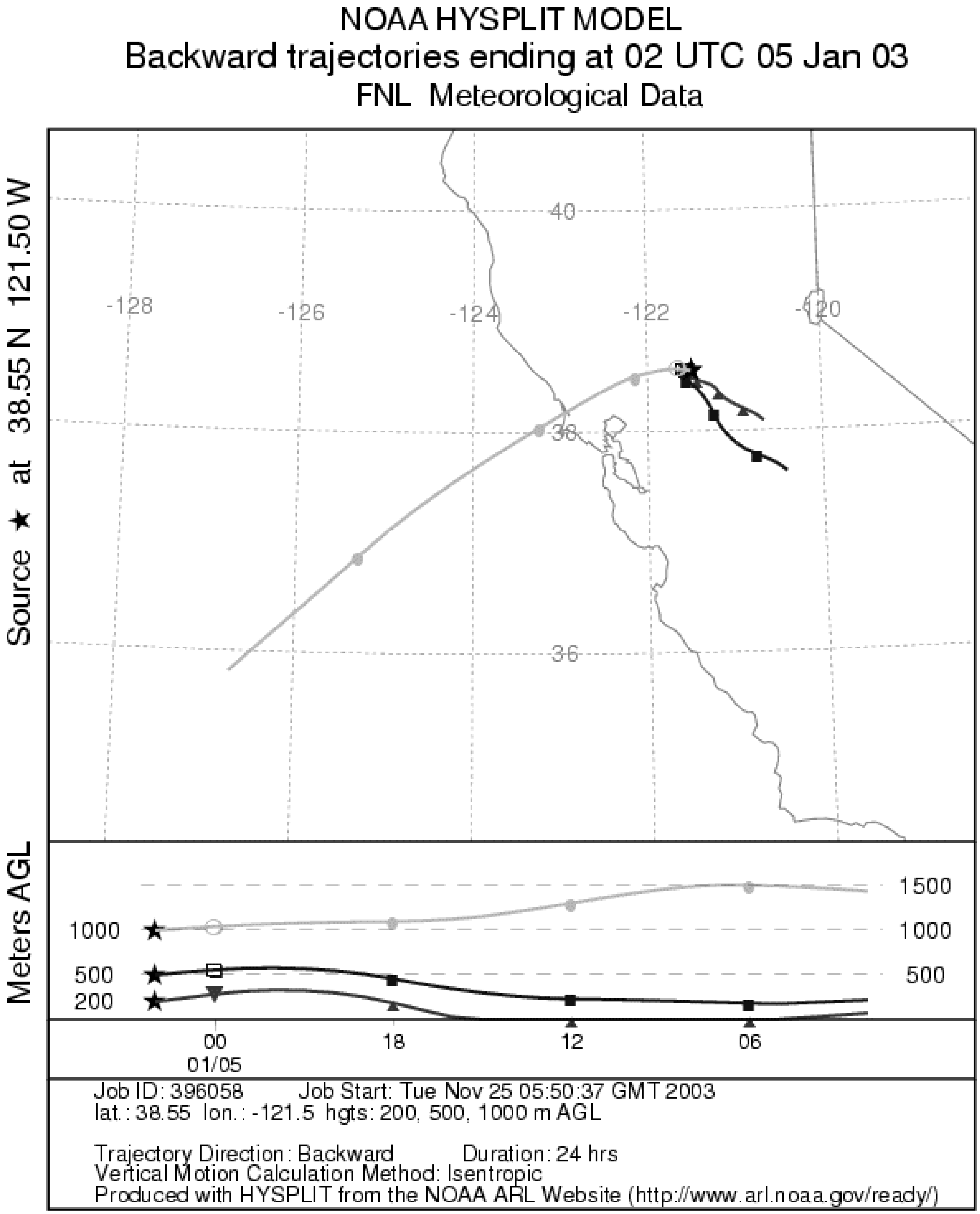


NOAA HYSPLIT MODEL
Backward trajectories ending at 14 UTC 04 Jan 03
FNL Meteorological Data

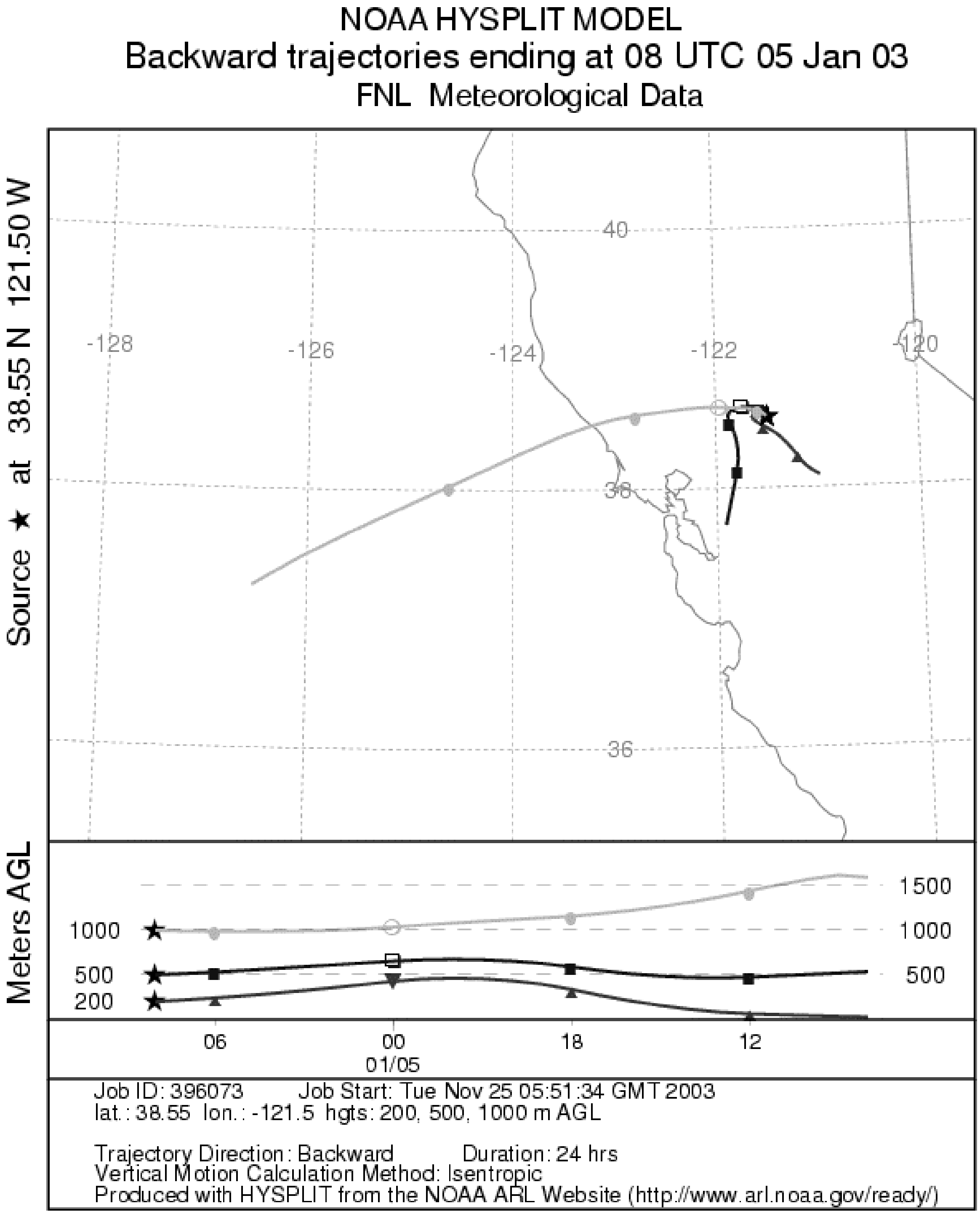
Job ID: 396025 Job Start: Tue Nov 25 05:48:42 GMT 2003
lat.: 38.55 lon.: -121.5 hgts: 200, 500, 1000 m AGL

Trajectory Direction: Backward Duration: 24 hrs
Vertical Motion Calculation Method: Isentropic
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)


NOAA HYSPLIT MODEL
Backward trajectories ending at 20 UTC 04 Jan 03
FNL Meteorological Data
Source ★ at 38.55 N 121.50 W
40
-126
-124
-122
-120
-118
38
36
Meters AGL
1500
1000
500
200
18
12
06
00
01/04
Job ID: 396030 Job Start: Tue Nov 25 05:49:39 GMT 2003
lat.: 38.55 lon.: -121.5 hgts: 200, 500, 1000 m AGL
Trajectory Direction: Backward Duration: 24 hrs
Vertical Motion Calculation Method: Isentropic
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)



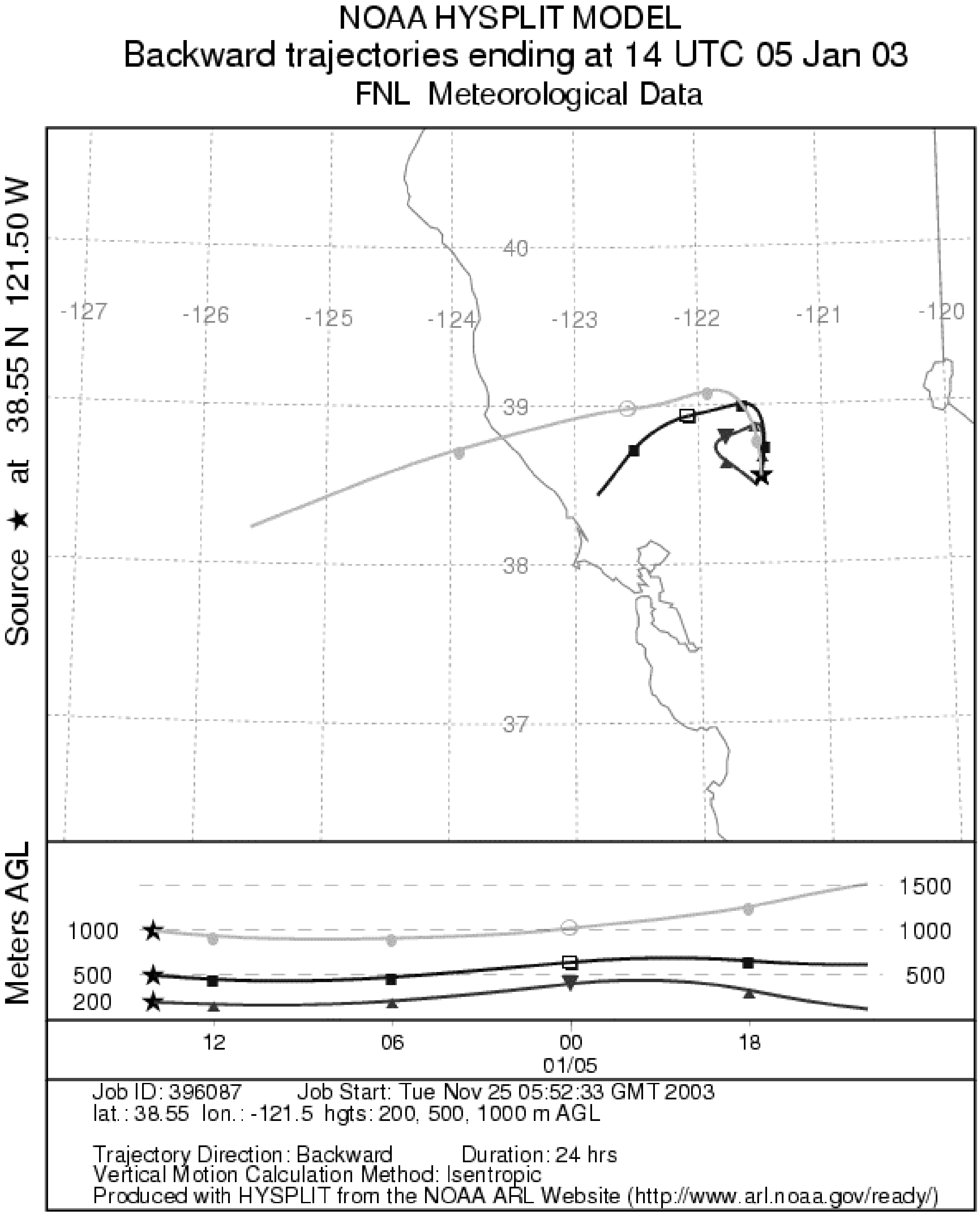
T-18 A strong upper wind flow from the southwest is seen at 6 PM on Jan 4, while the lower level trajectories continue San Joaquin Valley transport to Sacramento.



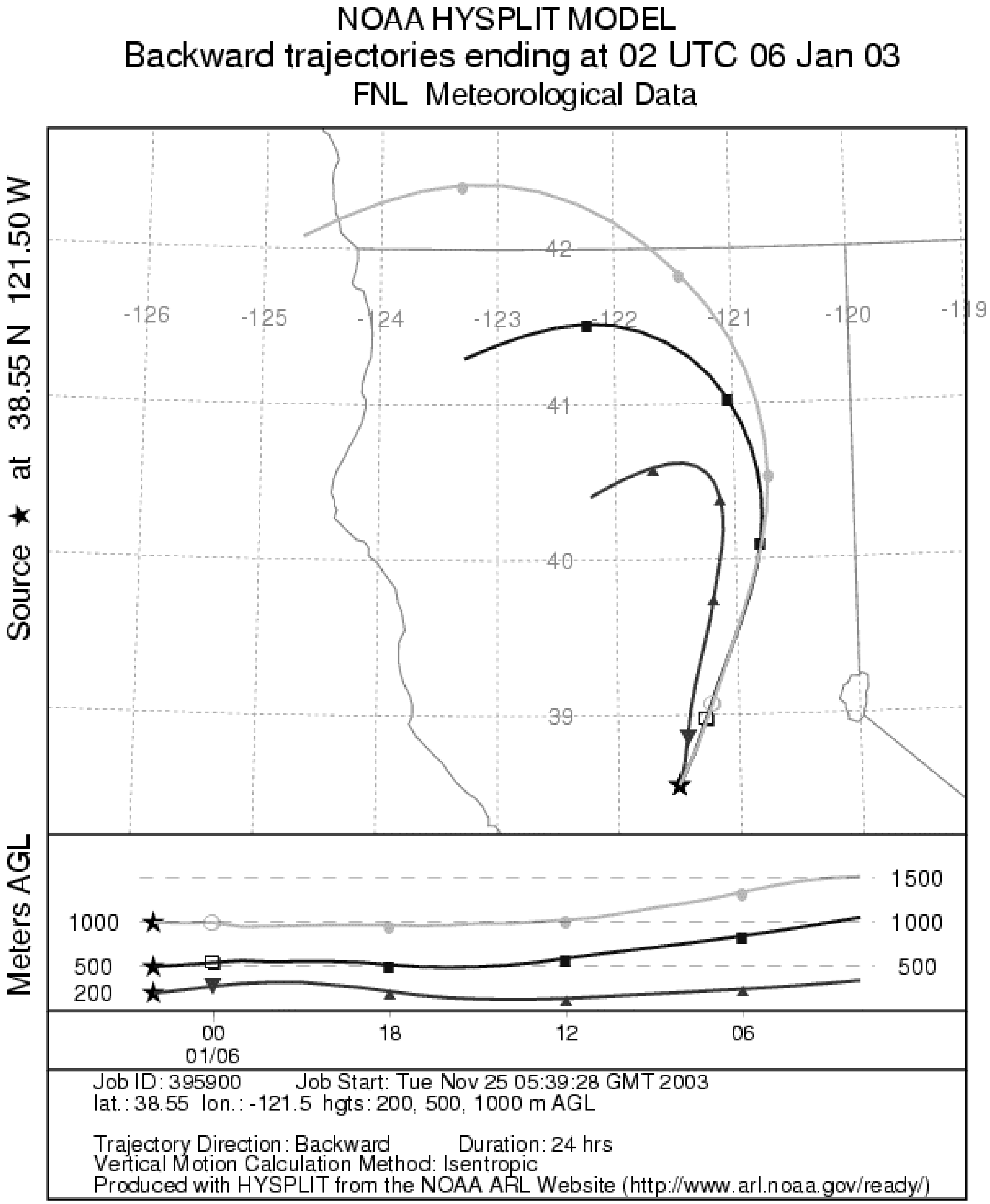
Job ID: 396073 Job Start: Tue Nov 25 05:51:34 GMT 2003
lat.: 38.55 lon.: -121.5 hgts: 200, 500, 1000 m AGL

Trajectory Direction: Backward Duration: 24 hrs
Vertical Motion Calculation Method: Isentropic
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

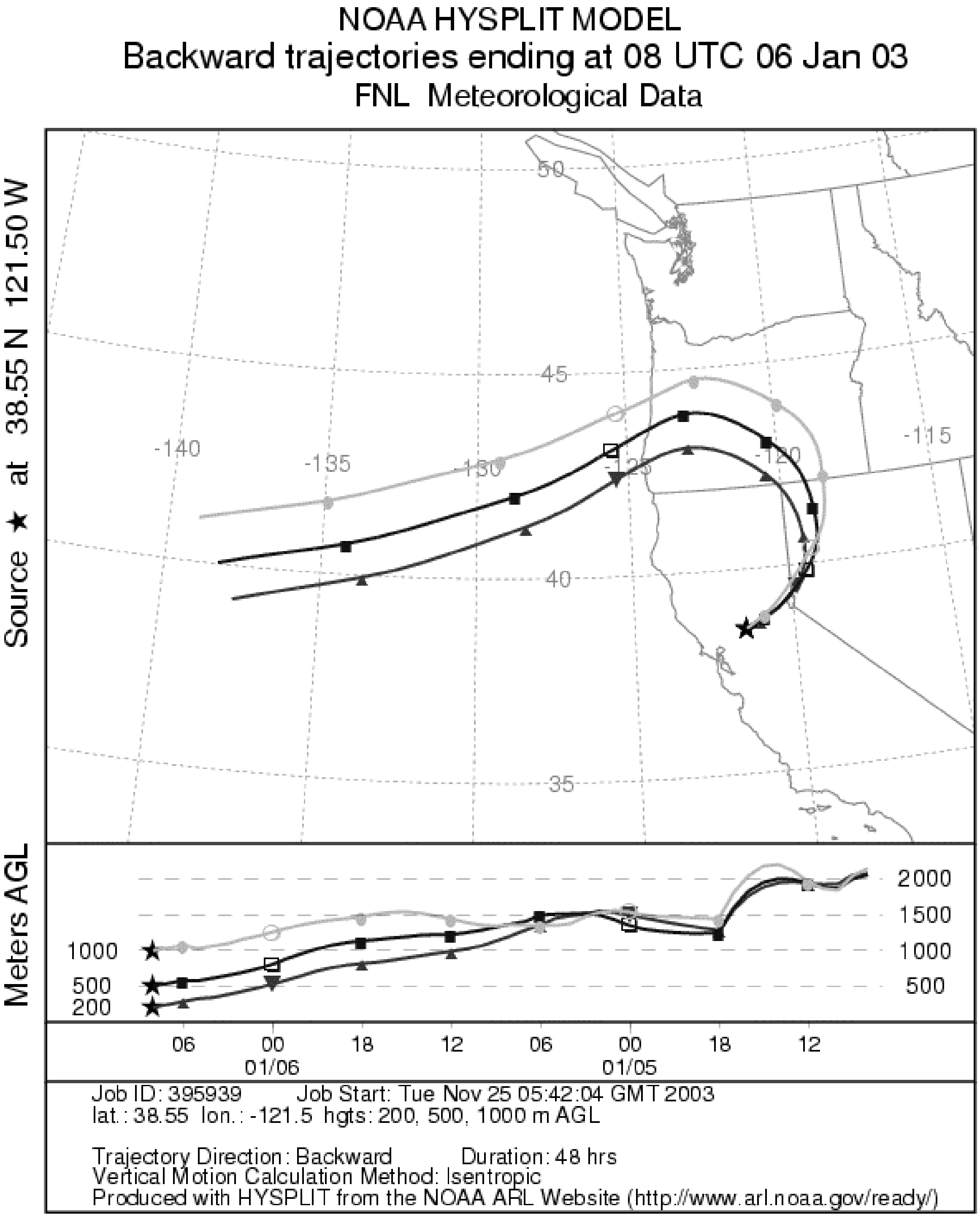
T-19 By midnight on Jan 5, only the lowest level trajectory continues the slow flow from the San Joaquin, while both upper level trajectories are now responding to the southwesterly upper level winds.



T-20 By 6 AM, Jan 5, the air now comes into Sacramento from the north, although the lowest level trajectory was in the northern San Joaquin Valley two days before.



T-21 By 6 PM Jan 5, the wind is now entirely northerly for the previous 24 hr.



Job ID: 395939 Job Start: Tue Nov 25 05:42:04 GMT 2003
lat.: 38.55 lon.: -121.5 hgts: 200, 500, 1000 m AGL

Trajectory Direction: Backward Duration: 48 hrs
Vertical Motion Calculation Method: Isentropic
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

T-22 By midnight, Jan 6, the wind comes into Sacramento from the east after following a looping trajectory that has it pass over Lake Tahoe and northern Nevada before doubling back to the ocean off southern Oregon 24 hours earlier. Valley pollutants are cleared out by the strong clean northeast winds starting at about 10 PM, Jan 5.

Conclusions

1. The ALASET Health Effects Task Force Sacramento/Interstate 5 Transect Study was an operational success due to the heavy involvement of ALASET HETF volunteers, the efforts of the UC Davis DELTA Group, and modest but vital financial assistance.
2. The study was a size, time, and compositionally resolved transect of a major urban area, and opens a new approach to urban air quality studies.
3. No violations of the federal 24 hr $PM_{2.5}$ standards were measured.
4. There were extensive periods during which the transect showed spatial uniformity across the region, with rural Davis, Sacramento River, and Orangevale having very similar concentrations of $PM_{2.5}$ particles.
5. The Crocker Art Museum site next to I-5 was almost always elevated in $PM_{2.5}$ concentrations, and the Shingle Springs site, which was often above the inversion, usually had lower $PM_{2.5}$ concentrations.
6. The highest levels of $PM_{2.5}$ at all sites were generally associated with the typical slow winter drainage winds coming up from the San Joaquin Valley, (Appendix B), winds that moved parallel to Interstate 5 and Highway 99.
7. During periods of low winds, low inversions, and haze/dry fog, sharp increases in $PM_{2.5}$ concentration were seen as one went from immediately upwind to immediately downwind of I-5.
8. From the high point downwind of I-5, with 11 ± 5 $\mu g/m^3$ of added mass, concentrations fell off relatively smoothly as one moved to the east.
    a. On Jan 5 – 6, HYSPLIT isentropic trajectories showed that the wind came from the east, making the Crocker Art Museum site upwind of I-5 but downwind of the rest of Sacramento, including Hwy 99. Concentrations of $PM_{2.5}$ and all species fell to low levels, while the now down wind Sacramento River site had high concentrations.
9. Very fine particles ($0.26 > D_p > 0.09$ µm) were compositionally associated with diesel and smoking light duty gasoline powered vehicle exhaust through size, color, and the elements sulfur, phosphorus, and zinc at the Crocker Art Museum site, adding roughly 4.5 (± 1.5) $\mu g/m^3$ of downwind mass based upon laboratory derived diesel ratios keyed to zinc. About ½ of this mass is from smoking cars.
10. The Arden Middle School site had a strong local source of mass in the sub-µm size mode that was most likely local in origin. On the average in the stable periods, Arden's concentrations fell between those of the ARB at 13 and T Street (not immediately downwind of a freeway) and Orangevale (suburban).
11. The direct effect of Watt Avenue was not immediately available in $PM_{2.5}$ mass profiles due to the lack of an immediate up-wind site.
12. The finest mode, $0.34 > D_p >$ circa 0.15 µm, showed both the effect of the New Years Eve fireworks on the Tower Bridge and a persistent elevated level of typical diesel/smoking car tracers - sulfur, phosphorus, and zinc.
13. The level of diesel/smoking gasoline vehicle impacts was larger at Arden Middle School than that at the Crocker Museum site despite lower traffic flows, a result consistent with model predictions including the proximity of the school to Watt Avenue and lack of barriers to air motion.

Acknowledgements

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We would like to recognize the teams that set up and took down the sites and the volunteers who supported sampler sites, including Earl Withycombe, Nancy Ray, Ralph Propper, Lynn Jacoby, David Turner, Carolyn Craig, Norm Covell, and Stew Wilson.

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Appendix A

Limitations and Advantages of DRUM sampling protocols

The HETF of ALASET used DRUM sampling protocols for the Sacramento/I-5 Transect Study in preference to filter sampling protocols. This choice presented both advantages and limitations in regard to more standard filter based techniques, which we will summarize in this Appendix. Detailed comparisons are found in the DRUM Quality Assurance Protocols ver. 9/02, which is an integral part of the study.

The key reason for our choice was the well recognized inadequacies of filter based techniques for research in aerosol source identification and impacts on health and welfare. These include:

1. Integration over particle sizes, originally 35 µm to 0 µm (TSP), then 10 µm to 0 µm (PM_{10}), and now 2.5 µm to 0 µm ($PM_{2.5}$). Both visibility (Mie Theory) and human health research indicate that portions of these size ranges are far more important than the integrated range (EPA PM Criteria Document 600-P, 1996, Devlin, 2002).
2. Integration over time, with massive diurnal changes and sharp episodes of mass hidden in the daily average. This is even more of a problem when a one-day-in-three or other such limitation is imposed on sampling frequency.
3. Integration over composition to get mass. Both federal and state regulations for aerosols are based on mass data generated from filter based technology, when all evidence shows that health effects are compositionally dependent. For this reason, first IMPROVE under UC Davis and now the US EPA have instituted compositional measurements on a national grid.

There are additional problems with filters, including artifact mass loss, mass gain, and compositional changes, problems that become more acute as one moves away from mass and into compositionally segregated data. In addition, infrastructure requirements and analytical coasts/.filter make large filter based studies costly. These limitations are so severe that in one recent review article (Watson, AWMA 2002) a prediction was made that in the not to distant future filter methods would be almost entirely supplanted by continuous methods. Many groups, including both UC Davis and the ARB, are moving to newer continuously sampling protocols.

The UC Davis DELTA Group approach to continuous sampling is through DRUM (Davis Rotating-drum Unit for Monitoring) protocols which consist of three components:

1. Particle size separation by inertial impaction and collection onto slightly sticky substrates,
2. Slow translation of impaction surfaces on a drum, and
3. Non-destructive mass and compositional techniques designed for the small amounts of mass collected on the substrates.

Inertial impaction. Particle size separation for the UC Davis DRUMS follows the well established theory and validations of Marple, Rao, and co-workers at the University of Minnesota, (1974 – 1981) and the theory and validations for the UC Davis DRUM sampler of Cahill et al (1985), Raabe et al, (1989) and Cahill et al (1992), the latter as part of the ARB MSAM Project. The important point is that for the two configurations used at UC Davis, the single circular orifice and the semi-infinite slot, the theory is simply basic aerodynamics and can be solved analytically and exactly. Thus, calibrations merely confirm the theory, unlike samplers such as the U. Minnesota MOUDI where every stage must be studied separately as it can not be solved analytically. Note that the sampler only is 18" high, weighs 20 lbs, and uses only 350 watts, allowing easy siting in back yards and roof tops.

Impaction results in a difference from filters in that the impactor cuts are much sharper than the typically softer cut points of filter samplers, so that if much mass lies around a given cut point (say, $PM_{2.5}$) the impactor will give a different value that a filter based system. This was the reason that the US EPA went to the sharper double-cut WINS well impactor for the national $PM_{2.5}$ sampler. A final limitation of the present DRUM is that we are unable to continuously sample particles smaller than 0.09 µm, which are either not sampled (the present study) or collected on manually-changed filters (DELTA Group current practice), which then requires additional costs and labor.

Slow translation. The slowly moving substrate of the DRUM sampler allows continuous sampling, typically for 6 weeks at a time (4 mm/day). The advantage of this protocol is that one can later establish any desired time resolution (down to about 1 hr) any time within the 6 week period. The limitation is that the small amount of stretch in the thin Mylar substrate results in a time error, typically 1 mm/6 weeks, which turns into 6 hrs. Thus, what is simple with a filter (say, midnight to midnight, ± 1 second) is impossible for the DRUM, which can do no better than about ± 1 hr in a 6 week sample, even using our new timing protocols, since the impactor slot is about 1 hr wide.

DRUM analyses. The rotating drum impactor was first designed by Lundgren in 1967, yet has been used only sparingly and in research modes for the past 35 years (key exceptions: ARB, 1973-1977, and US EPA, 1977 -1979). This was mostly because analytical protocols were inadequate to give mass and composition from the miniscule deposits delivered by a rotating drum impactor. This limitation is inherent, for one can not put too much mass on an impaction surface without risking miss-sizing by particle bounce (hence the sticky substrates used by UC Davis). The early rotating drum analyses were almost entirely done by particle induced x-ray emission (PIXE) which required an accelerator and was thus of limited availability and quite expensive.

The UC Davis DELTA Group was formed in 1997 with an explicit goal to further develop DRUM protocols, sampling and analysis, to achieve higher accuracy and precision and improved compositional analytical capabilities, including mass which heretofore was not done with DRUM samplers.

For mass measurements, the problem is compounded by the nature of continuous size resolved sampling. For example, to match a single 24 hr $PM_{2.5}$ filter mass measurement, a DRUM protocol has to make 8 measurements/day (3 hr time resolution) on each of the 6 sub-2.5 μm DRUM stages, or 48 individual mass measurements. The propagation of error requirements are thus extreme. However, there is one advantage because mass measurements on impactor samples on Mylar substrates are largely insensitive to relative humidity, a major problem with both discrete and continuous filter based mass measurements.

For compositional analysis, a good XRF measurement of 30 elements costs commercially somewhere between \$50./sample and \$200./sample, depending on the sensitivity desired. Even using the lowest cost, a single 24 hr day of 3 hr time resolved composition by commercial XRF from a DRUM sampler would cost roughly \$2,500., even if they could achieve the sensitivity of DELTA Group S-XRF (which they can not). Thus, cost reduction was a major goal that had to be achieved for continuous size resolved compositional analysis could become widely useable.

The present DELTA Group protocols include: (see DQAP ver. 9/02)

Mass by soft beta attenuation (β-mass)	(Portnoff et al, in prep, 2003)
Mass by scanning transmission ion microscopy (STIM) and	
Hydrogen by proton elastic scattering analysis (PESA)	(Bench et al, 2002)
Elements by synchrotron-x-ray fluorescence (S-XRF)	(Cliff et al, prep. 2003)
Optical attenuation versus wavelength (λ-optical)	(R. Miller, thesis, 2003)
Single particle analysis (SEM, TEM)	(Shackelford et al, 2003 in prep)

Most of these were featured in just published articles on the large NSF ACE-Asia Study (Seinfeld et al, 2003) and the World Trade Center aerosols study (Cahill et al, 2004), which also included other techniques, including organic matter (GC/MS and LDIOTPF/MS) that are under development. Users of DELTA Group DRUM protocols in the most recent 3 years includes US EPA (2 programs), NPS (2 programs), USFS, NASA, NOAA (2 programs), DOE (2 programs), and DOD (3 programs), multi-state organizations LADCO, NESCAUM, and TRPA, plus California and Alaska.

Detailed comparisons of S-XRF DRUM results with filter based analyses (IMPROVE, ARB, …) in blind tests are included in DQAP ver. 9/02, showing excellent agreement (average ratio, 3 extensive recent comparisons, 1.08 ± 0.10) with the most accepted standard protocols and higher sensitivity than any alternative method. Earlier results with prior versions of the DRUM sampler also showed good agreement with IMPROVE (Cahill et al, ARB Final Report, 1992, Cahill and Wakabayashi, 1996, and ARB Bakersfield Study 1996), typically within 10% of unity despite the limitations of a single jet impactor and PIXE analyses, which had a precision of only ± 15%. In the ARB Bakersfield comparison of 1996, the prototype slotted DRUM using the PIXE analyses agreed with filter based measurements for sulfur within 10% while providing the only continuous measurements of sulfur, soils, and smoke tracers. However, precision and sensitivity were only fair, which helped accelerate the development of S-XRF analysis.

The cost of analysis on a per-day basis (β-mass, λ-optical, STIM, PESA, S-XRF) for a single day of < $PM_{2.5}$ DRUM sampling (6 Stages, 8 measurements/day) giving in excess of 4500 data/day (48 mass, 96 STM, 96 PESA, 2000 elements, 2,500 optical attenuations) is $42.

The HETF ALASET Sacramento/I-5 Transect Study has shown the wisdom in these choices:

- The very fine ($0.26\ \mu m > D_p > 0.09\ \mu m$) spikes as high as 23 $\mu g/m^3$ downwind of I-5,
- Valley wide coherence across the 80 km array for most periods,
- Previously unanticipated mass spikes, most likely from a local source, at Arden Middle School,
- Dramatic compositional changes versus time, with the very fine mode having great similarities to previously published diesel aerosol data (and presumably smoking cars),
- Probable identification of a large PM_{10} mass peak at the Del Paso TEOM site with sea salt from the California coast near Mendocino.
- Detailed analysis of transport into Sacramento from the San Joaquin Valley.

Finally, there is no way that any other than UC Davis DELTA Group DRUM technology and our volunteers could have delivered even 1% of the data of the HETF ALASET Sacrameto/I-5 Transect Study within the total costs allocated, $4,800.

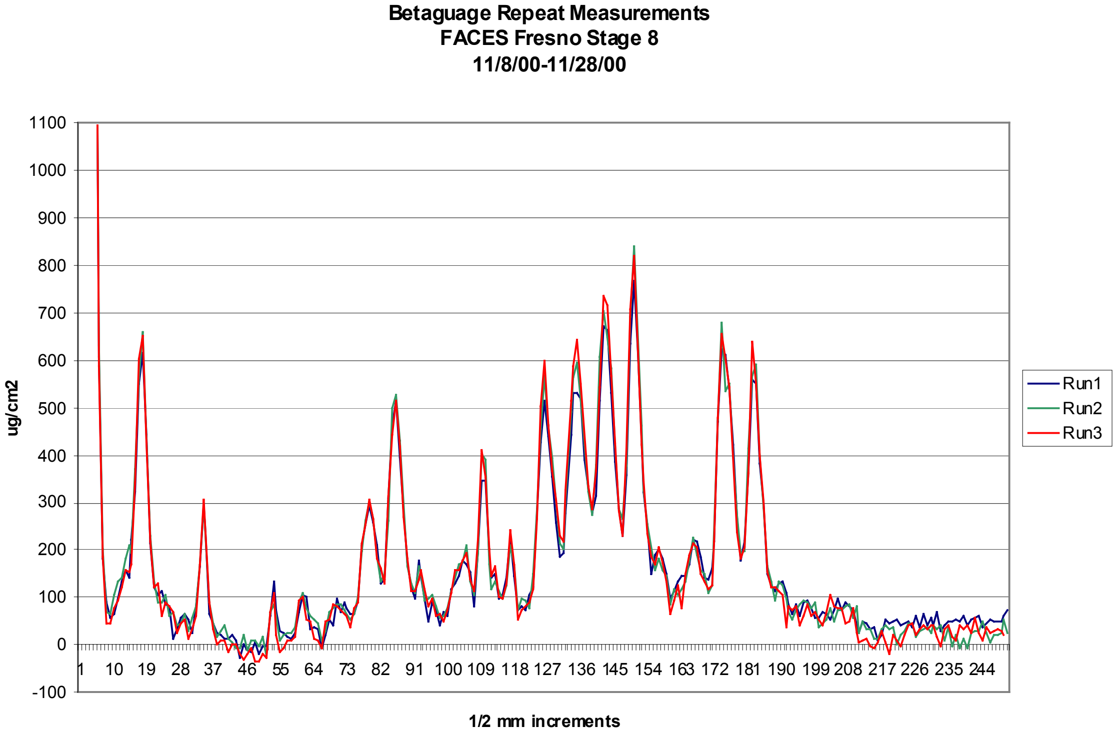
Appendix B

Quality Assurance and Documentation

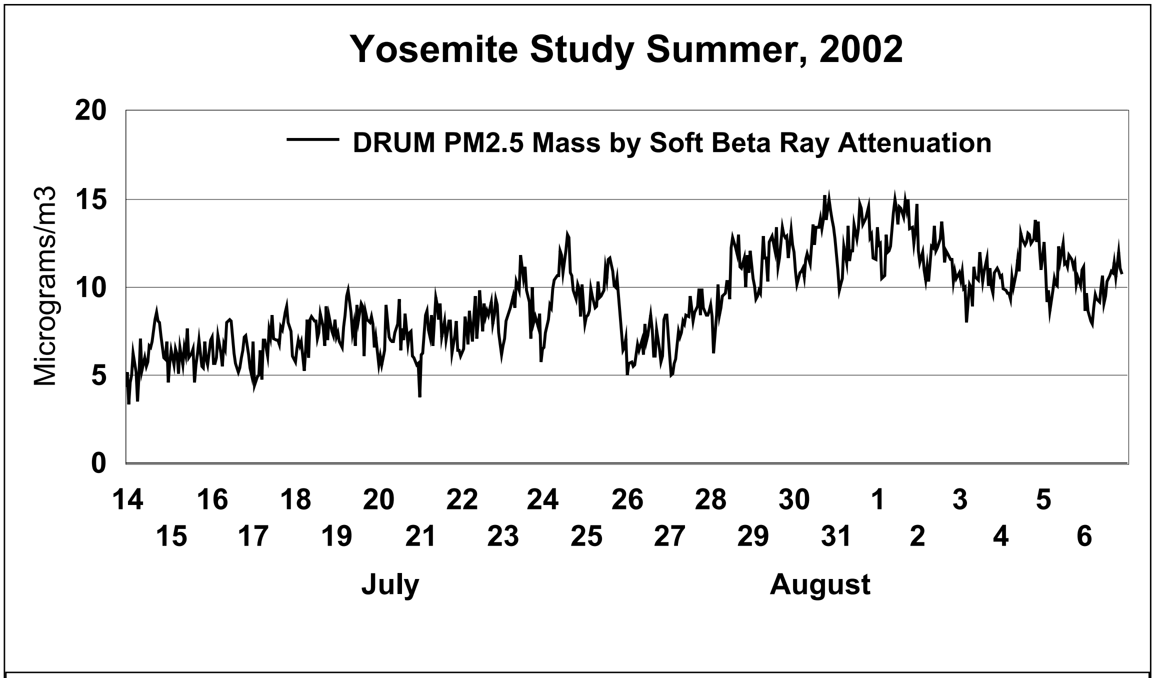
All data on sampler operation and analytical protocols are contained in DELTA Group DRUM Quality Assurance Protocols ver. 9.02, (DQAP ver 9.02) one copy of which will be transmitted to ALASET. A few relevant pages are given below.

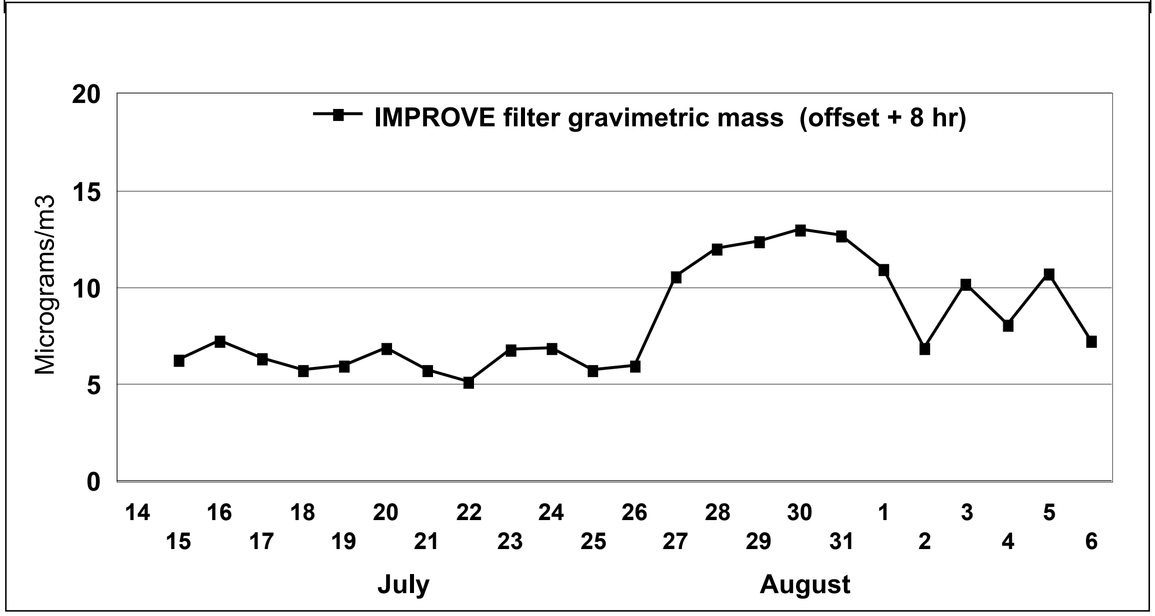
Mass by soft beta ray transmission

The accuracy and precision of mass by soft beta ray transmission are shown below. These samples are from the very fine mode of the DELTA 8 DRUM, the same configuration used for the ARB 13 & T site and reported in Bench et al 2002 as part of pre-study test for FACES, November, 2000. The masses were highly correlated with the STIM data. The largest peak at location 150 is equivalent to approximately 18 μg/m^3. The off-scale reading at the far left is from a timing marker.

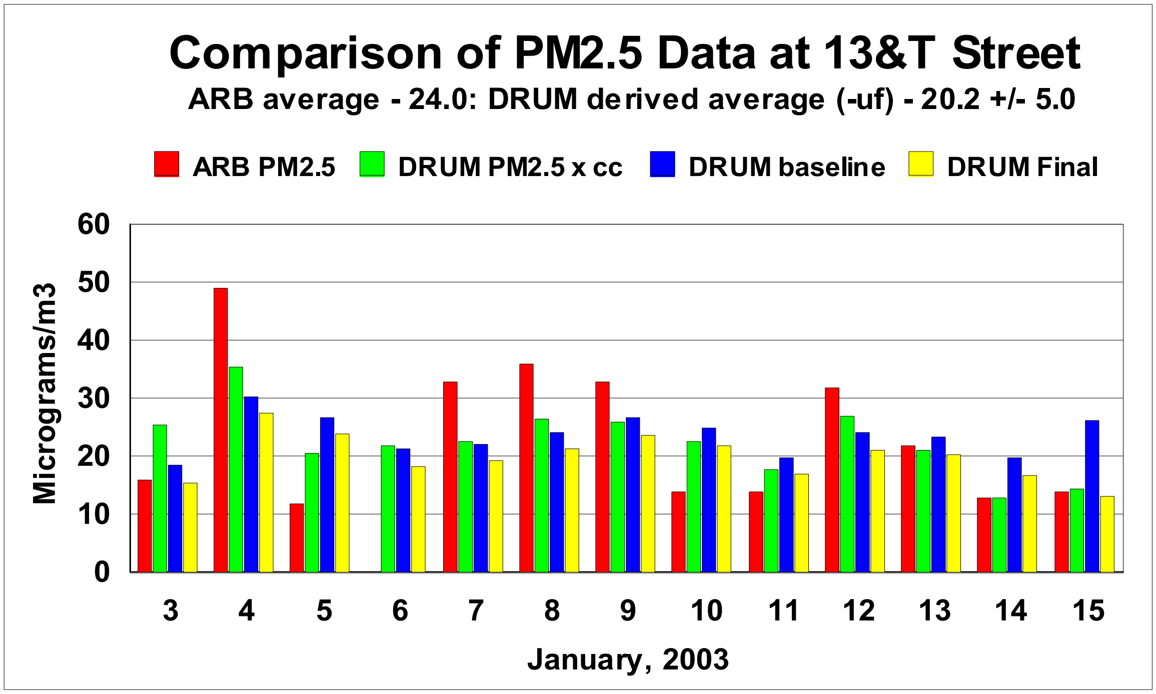


A recent comparison of mass by IMPROVE and mass by soft beta ray transmission (β – mass) from an 8 DRUM sampler was performed at Yosemite NP, summer, 2002. Note that it took 96 individual mass measurements from the DRUM (6 stages below PM2.5 times 16 measurements/day) to equal a single measurement from IMPROVE, which would emphasize any off-set error in the β – mass values. Note also that the total masses were quite low at the Turtleback Dome IMPROVE site around 6,000 ft elevation.


Yosemite Study Summer, 2002
DRUM PM2.5 Mass by Soft Beta Ray Attenuation
Micrograms/m3
0
5
10
15
20
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
1
2
3
4
5
6
July
August


IMPROVE filter gravimetric mass (offset + 8 hr)
Micrograms/m3
0
5
10
15
20
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
1
2
3
4
5
6
July
August

Below were present the comparison of the mass derived from 8 DRUM data at the ARB 13th & T site, the only site where co-located sate were taken. Recall that each DRUM derived PM$_{2.5}$ mass is the sum of 16 individual measurements pre day of 1 ½ hr duration per stage, which with 6 stages gives a total 96 measurements that must be averaged and sum to give the single filter PM$_{2.5}$ mass. While the comparison of the absolute values is reasonable (especially considering that the DRUM does not collect ultra-fine mass collected by the ARB filter) the DRUM is consistently lower on the peak values. We performed a sensitivity analysis using the limits of conversion factor (CC) scaling (deposit area) and baseline choices (mass offset) but could still not reproduce the highest peaks. This was a period of fog, occasionally dense, and we believe that the DRUM, with its flat hydrophobic greased stages, could be handling moisture differently than the filters. This problem has plagued other mass devices in the Central Valley, such as the otherwise laudable TEOM.



Elemental analysis by synchrotron-x-ray fluorescence (S-XRF)

The IMPROVE/EPA BRAVO study in Texas provided opportunities for quality assurance. Below in Table 1 are two S-XRF analyses of the same DRUM strip.

Table 1 Comparison of Two S-XRF Analysis Runs on the Same DRUM Strip

UC Davis DELTA Group
Quality assurance tests - Tom Cahill, Steve Cliff, Michael Jimenez-Cruz, March 24, 2002

Synchrotron - XRF analysis of Fresno DRUM strips
March 10 – April 25, 2001, Stage 8 - 0.26 to 0.09 micrometers diameter

July 2001 S- XRF 160 measurements (6 hr steps); January 2002 S-XRF 320 measurements (3 hr steps)

Analysis Run	Na ng/m^3	Mg ng/m^3	Al ng/m^3	Si ng/m^3	P ng/m^3	S ng/m^3	Cl ng/m^3	K ng/m^3	Ca ng/m^3	Ti ng/m^3	V ng/m^3	Cr ng/m^3	Mn ng/m^3	Fe ng/m^3	Co ng/m^3	Ni ng/m^3	Cu ng/m^3	Zn ng/m^3	Ga ng/m^3	As ng/m^3	Se ng/m^3	Br ng/m^3	Rb ng/m^3	Sr ng/m^3	Y ng/m^3	Zr ng/m^3	Mo ng/m^3	Pb ng/m^3
July, 2001	3.87	0.11	4.42	6.45	4.39	56.57	1.25	10.05	1.15	0.05	0.08	0.08	0.07	1.14	0.02	0.05	0.07	1.02	0.03	0.05	0.08	0.27	0.00	0.01	0.03	0.06	0.25	0.17
January, 2002	3.42	0.07	2.42	6.56	4.02	54.70	1.15	10.65	0.67	0.05	0.09	0.07	0.09	1.52	0.01	0.04	0.09	1.60	0.00	0.11	0.12	0.31	0.01	0.03	0.04	0.08	0.29	0.30
average value	3.65	0.09	3.42	6.50	4.21	55.63	1.20	10.35	0.91	0.05	0.08	0.07	0.08	1.33	0.02	0.04	0.08	1.31	0.02	0.08	0.10	0.29	0.01	0.02	0.03	0.07	0.27	0.24
avg uncertainty in quadrature	2.17	1.02	1.04	1.31	1.10	8.06	0.26	1.49	0.58	0.07	0.06	0.03	0.03	0.24	0.02	0.03	0.03	0.24	0.02	0.17	0.08	0.18	0.10	0.13	0.13	0.15	0.31	1.07
Measures of Performance																												
1. chi-square	0.04	0.00	3.73	0.01	0.11	0.05	0.13	0.16	0.68	0.00	0.01	0.27	0.37	2.52	0.16	0.09	0.53	5.80	0.86	0.12	0.18	0.05	0.01	0.01	0.01	0.01	0.02	0.01
avg chi sqr	0.57																											
2. Mean error	12.30	39.49	58.41	-1.74	8.74	3.37	7.70	-5.74	52.28	-8.21	-5.35	17.92	-21.40	-29.11	50.70	18.85	-30.32	-43.67	136.92	-74.24	-33.49	-14.01	-99.78	-67.35	-36.78	-18.62	-16.53	-53.73
in percent	5.5 %																											

With the precision and accuracy established for DRUM strips, blind filter inter-comparisons were also performed versus the well established IMPROVE protocols. The agreement was generally excellent, as was summarized above in the report. Note also that S-XRF has much lower MDLs than the IMPROVE protocol analyses.

Table 2 Blind Filter Inter-Comparison with IMPROVE at the EPA BRAVO Study

Avg MDLs	Avg MDLs	Avg MDLs	Avg MDLs	BRAVO BR2, Oct 4			BRAVO BR4 Octr 22		
CNL	CNL MDL	DELTA	DELTA	CNL	DELTA	DELTA	CNL	DELTA	DELTA
PIXE+XRF	PIXE+XRF	S-XRF	S-XRF	PIXE + XRF	S-XRF average	error	PIXE+XRF	S-XRF average	Std
Element		**Element**			**16 points**			**10 points**	
(Switch at Fe)									
Pna	147.6	**Na**	**8.8**	2504	**979**	208.8	0	**18**	20
Pmg	84.9	**Mg**	**7.0**	0	**300**	141.4	0	**111**	35
Pal	47.8	**Al**	**3.1**	1675	**2050**	249.9	442	**580**	57
Psi	37.6	**Si**	**1.6**	4474	**4720**	500.5	1336	**1329**	106
Pp	34.1	**P**	**1.0**	0	**812**	79.6	0	**277**	15
Ps	33.4	**S**	**1.3**	14511	**15971**	1574	3955	**4316**	294
Pcl	32.4	**Cl**	**0.4**	0	**55**	12.8	0	**18**	2
Pk	22.4	**K**	**0.3**	711	**740**	85.0	268	**291**	20
Pca	17.5	**Ca**	**0.3**	2360	**2417**	240.5	872	**821**	103
Pti	17.1	**Ti**	**0.9**	146	**170**	28.9	34.7	**45.1**	7.5
Pv	0.3	**V**	**0.2**	10	**18**	7.3	0.5	**2.2**	2.9
Pcr	11.3	**Cr**	**0.1**	47	**2**	1.0	12.5	**0.6**	0.6
Pmn	11.5	**Mn**	**0.1**	30	**24**	10.1	17.9	**8.2**	4.4
Fe	2.0	**Fe**	**0.2**	1040.3	**994.7**	131.5	387.6	**472.4**	531.5
Co	na	**Co**	**0.2**	0	**6.5**	1.2	0	**4.2**	3.1
Ni	1.6	**Ni**	**0.2**	0	**50.0**	9.8	0	**4.1**	1.6
Cu	1.2	**Cu**	**0.3**	0	**12.0**	2.4	0	**2.8**	0.8
Zn	0.8	**Zn**	**0.2**	25.1	**29.8**	5.2	8.9	**9.9**	2.1
Ga	0.6	**Ga**	**0.2**	0	**0.2**	0.3	0	**0.3**	0.2
As	0.5	**As**	**0.4**	4.4	**2.0**	3.6	0	**1.1**	1.1
Se	0.6	**Se**	**0.3**	4.5	**2.1**	1.6	0	**1.2**	0.7
Br	0.6	**Br**	**0.4**	32.0	**12.6**	3.4	16.9	**7.7**	0.9
Rb	1.0	**Rb**	**0.6**	0	**1.3**	2.2	0	**1.3**	1.3
Sr	1.0	**Sr**	**0.7**	10.0	**5.3**	5.4	2.3	**0.9**	0.9
Y	1.2	**Y**	**0.9**	0	**2.0**	2.7	0	**0.5**	0.8
Zr	1.6	**Zr**	1.2	0	**2.9**	3.3	0	**1.5**	2.5
		Mo	1.5		**9.2**	8.5	0	**4.8**	7.5
Pb	1.1	**Pb**	1.7	4.2	**11.7**	15.9	0	**3.9**	4.8

Since that report, we have results from an extensive study at Yosemite NP including 2 months of IMPROVE filters and 1 month of DELTA Group 8-DRUM. The average of the ratio of DRUM $PM_{2.5}$, obtained by summing 72 separate measurements, and filter $PM_{2.5}$ was 0.93 ± 0.24 for all elements except soil elements, which were 1.76 ± 0.05. This result, seen earlier in Fresno, has been shown to be due to the sharp cut point of the DRUM (see Texas A&M analysis in DQAP v 9/02).

Comparisons of S-XRF to CARB XRF and RAAS data

As part of the CARB FACES study in Fresno, Dichot filters (Coarse and $PM_{2.5}$) and RAAS data ($PM_{2.5}$) were provided to insure inter-comparability of data versus S-XRF filter data

In summary, there was excellent agreement between ARB Dichot and DELTA S-XRF Dichot analyses:

> Ratio 1.02 ± 0.11, 16 measurements, with the minimum ratio 0.7 and the maximum ratio 1.7.

However, ARB Dichot and ARB RAAS data had much poorer inter-comparison,

> Ratio 1.29 ± 0.63, 16 measurements, with the minimum ratio 0.6 and the maximum 4.35.

as did the DELTA S-XRF Dichot and the ARB RAAS,

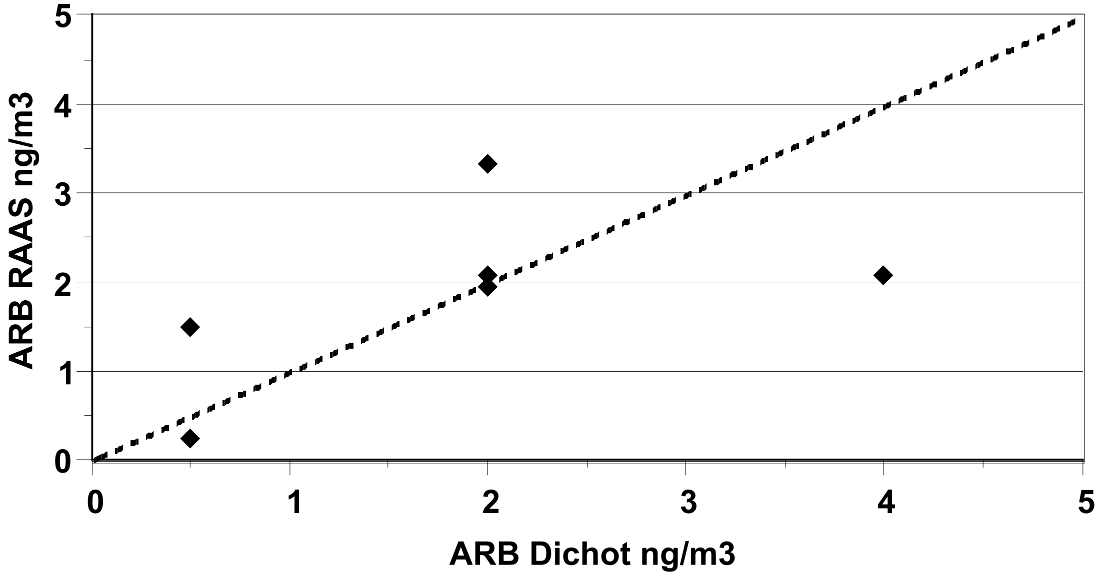
> Ratio 1.29 ± 0.58, 16 measurements, with the minimum ratio 0.42 and the maximum 3.86.

The comparison of ARB Dichot to ARB RAAS for lead was poor,

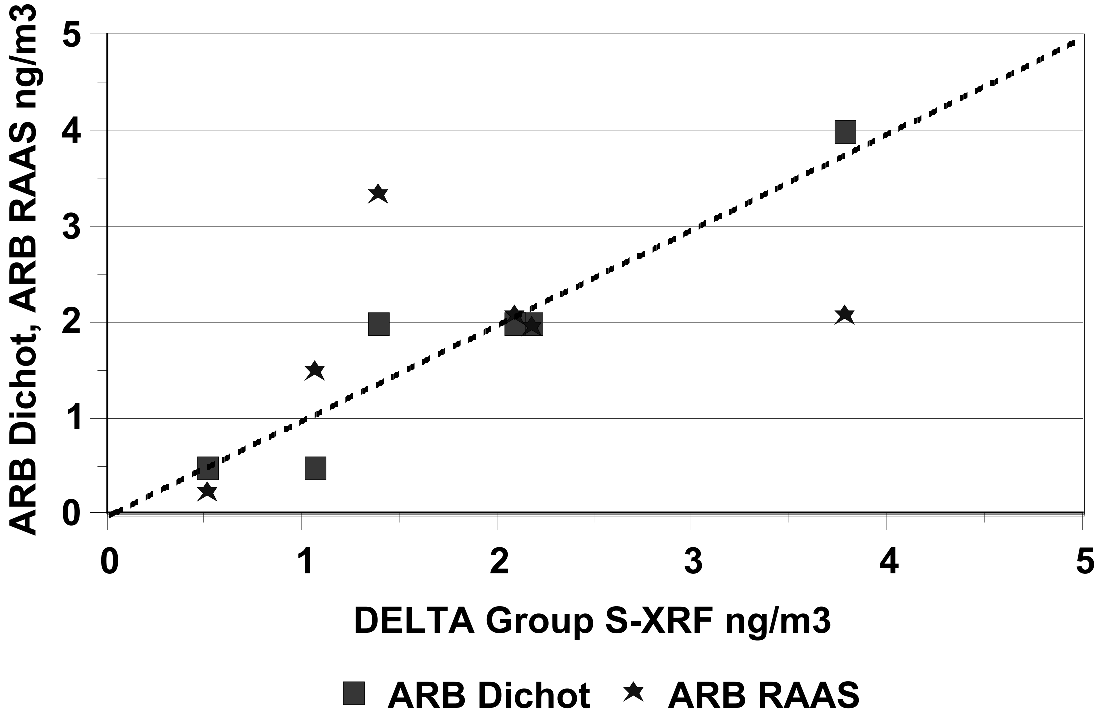
> Ratio 2.83 ± 1.37, 4 measurements, with the minimum ratio 1.16 and the maximum 4.94.

Examples of these data are plotted below. The one to one line is plotted in each case. It is not a fit to the data.

Fresno FACES Filter Intercomparison



ARB Dichot vs ARB RAAS
Manganese

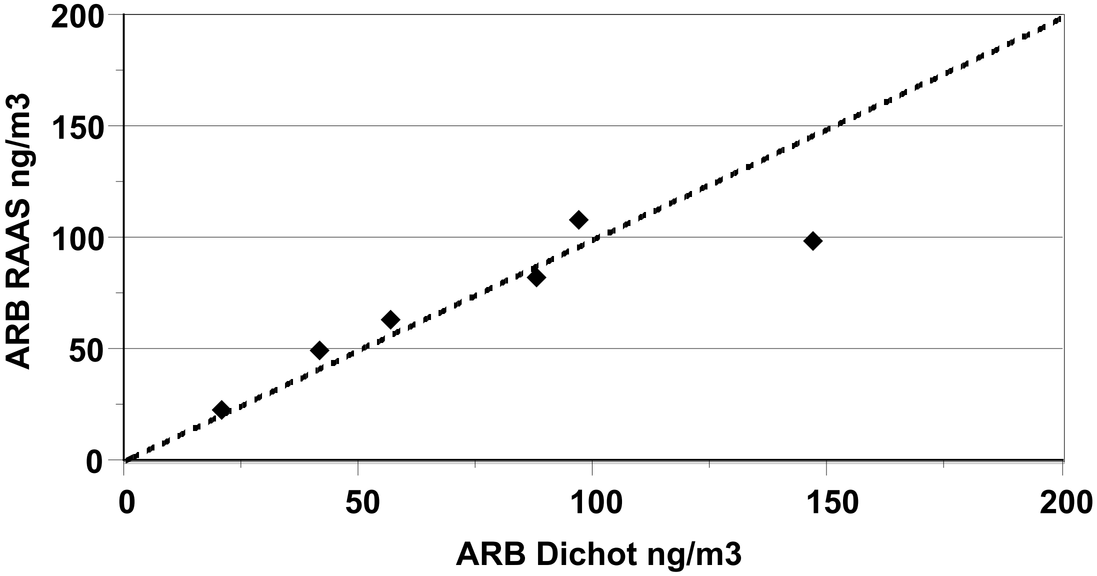


DELTA S-XRF vs ARB Dichot and ARB RAAS Filters
Manganese

Fresno FACES Filter Intercomparison

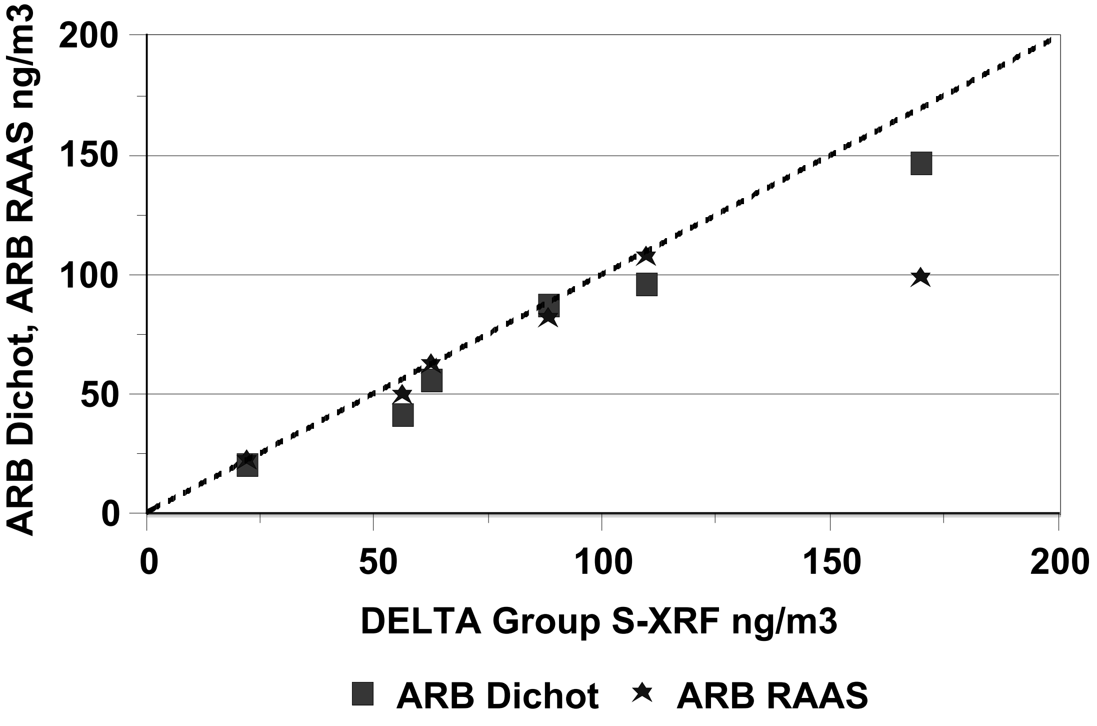
ARB Dichot vs ARB RAAS

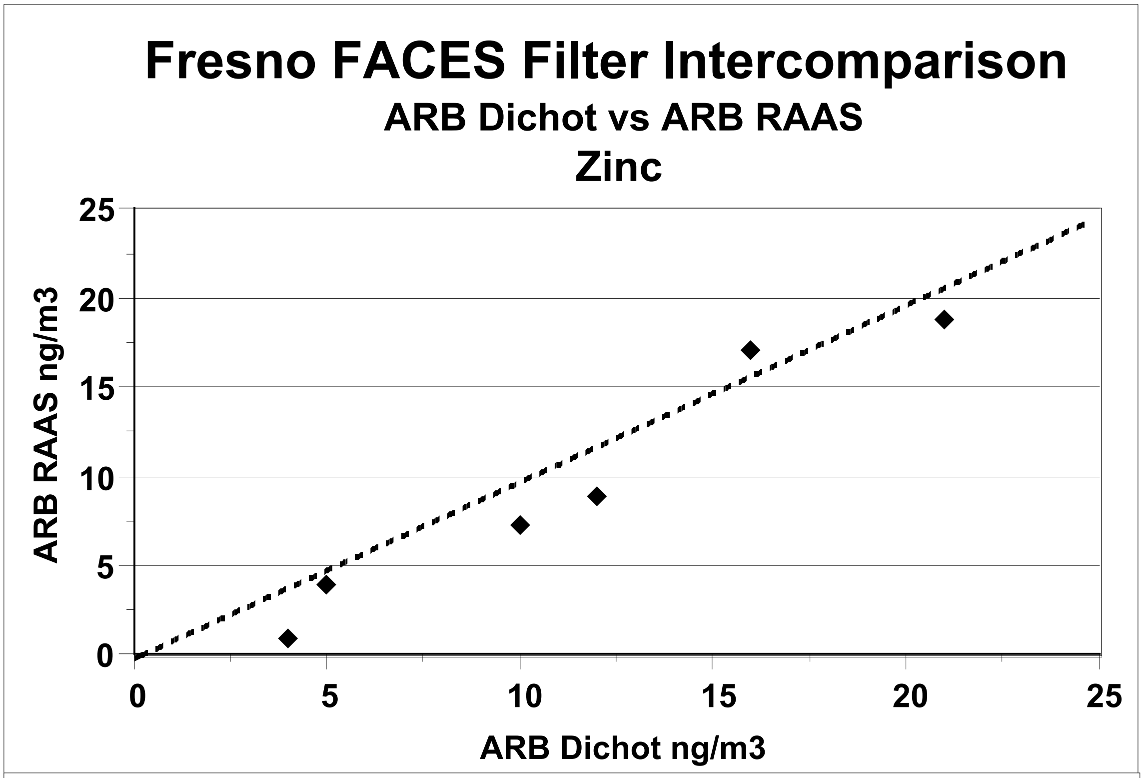
Iron

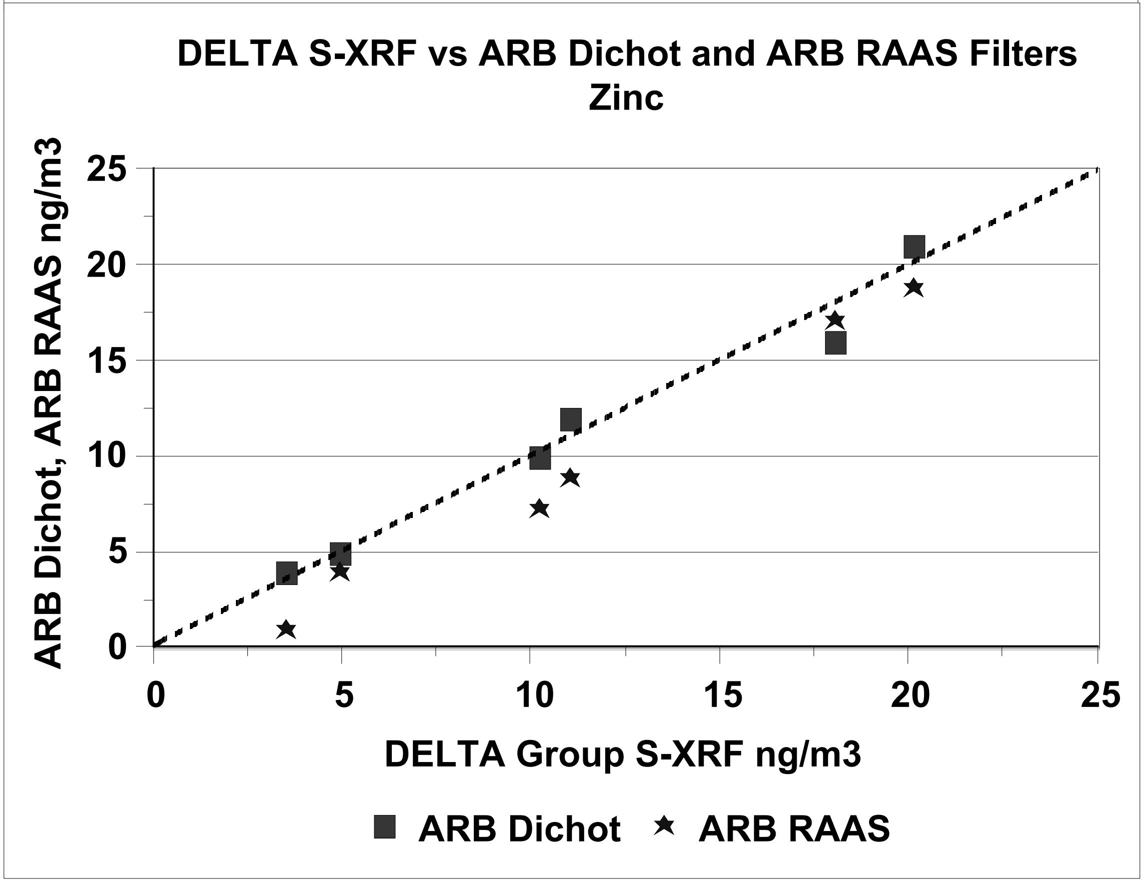


DELTA S-XRF vs ARB Dichot and ARB RAAS Filters

Iron

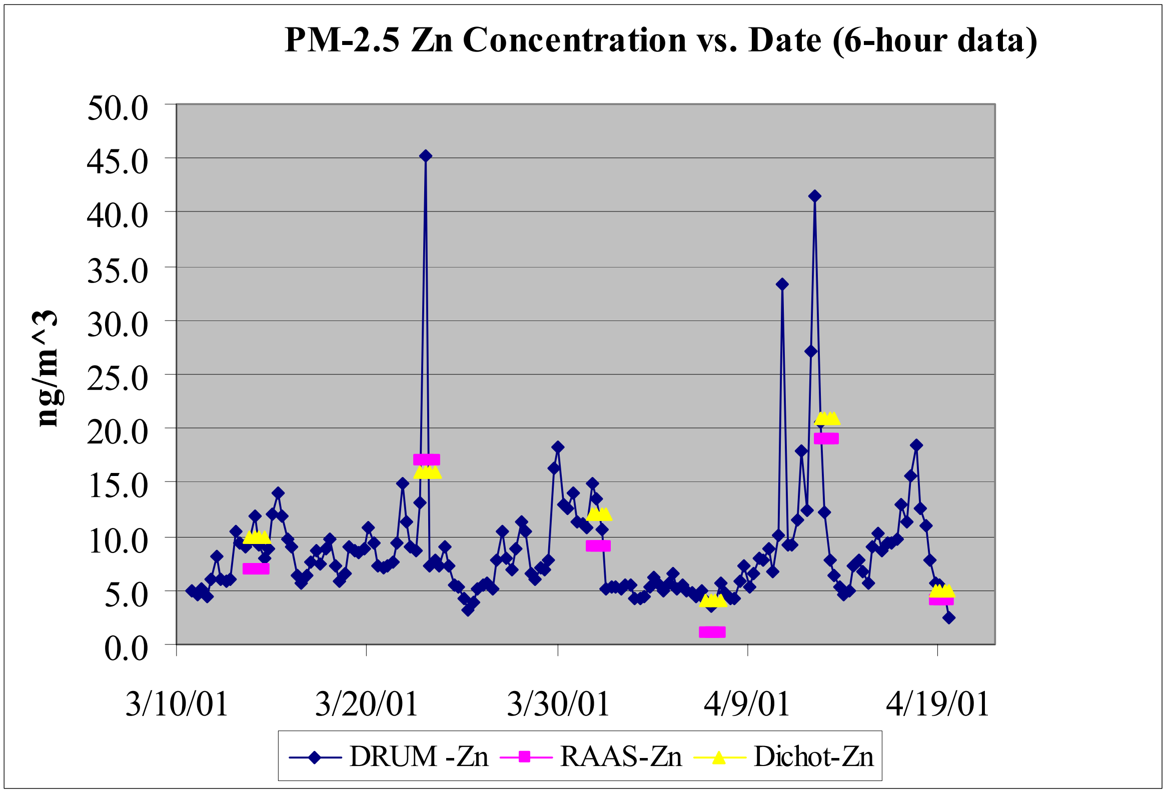



Fresno FACES Filter Intercomparison
ARB Dichot vs ARB RAAS
Zinc

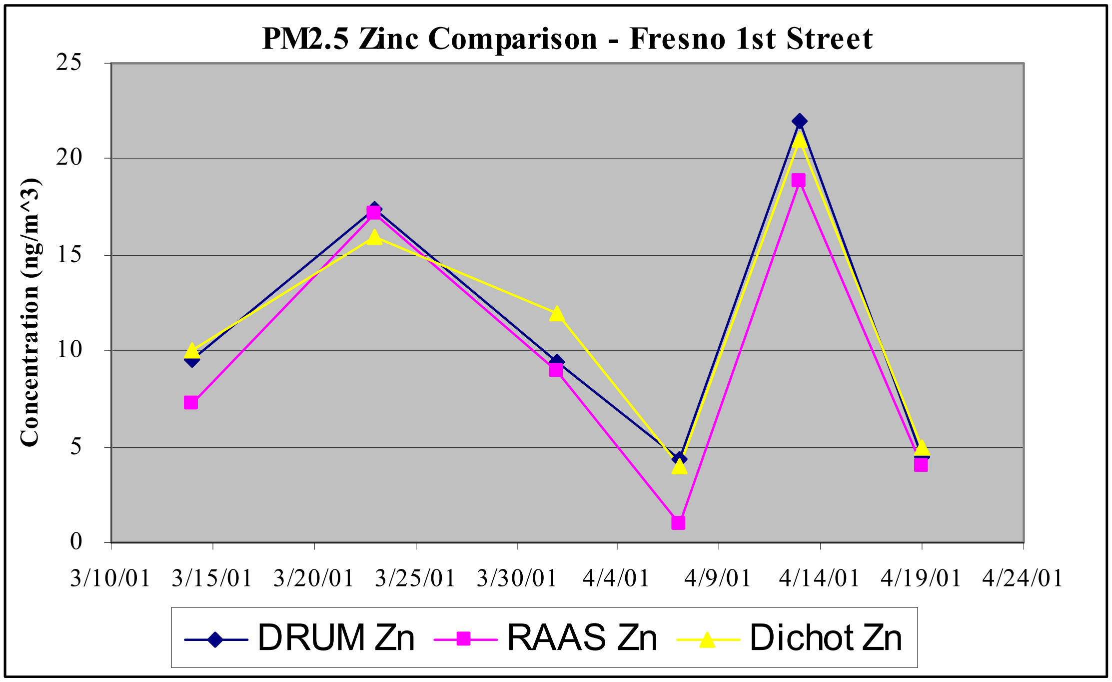

DELTA S-XRF vs ARB Dichot and ARB RAAS Filters
Zinc

The FACES program also provided a direct comparison of UC DELTA Group DRUM data with ARB Dichotomous sampler and RAAS data. We use for theis comparison zinc, since a) all analytical methods agreed for zinc, b) it had an extreme variability in time and was thus a severe test of timing for the DRUM, and c) it is an important tracer of diesels and smoking cars via the zinc thio-phosphate stabilizing agent in most lubricating oil.

Below we show a time series of $PM_{2.5}$ Zinc concentration. Note large spike of Zn of short duration on April 13, 2001. The 24 hour average concentration for 4/13/01 is approximately 20 ng/m^3 according to DRUM, RAAS, and Dichot data. The 24-hour filter data are superimposed for comparison. Originally, in the preliminary data, we had made an error of 6 hr in DRUM timing, which made a factor of 2 error in the DRUM concentration on April 13.



In the figure below, we show the time corrected PM2.5 comparison for zinc at Fresno site. Note similarity between 3 independent sampling methods.



For more details and many other examples, please consult DQAP ver 9.02.

Appendix C

California Surface Wind Climatology, maps of Summer, Fall, Winter and Spring wind flow patterns. California Air Resources Board Aerometric Data Division, 1984 (reprinted 1994)

Appendix D

Effect of Roadbed Configuration of Traffic Derived Aerosols, Feeney, P.J. T.A. Cahill, R.G. Flocchini, R.A Eldred, D.J. Shadoan, T. Dunn, Journal Air Pollution Control Assoc. 25, 1144- 1147 (1975)

Appendix E

Air Sickness: How microscopic dust particles cause subtle but serious harm, Science News 164, No. 5 pg 72 – 74 (2003)