NIPOMO MESA PARTICULATE STUDY
2007

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EXECUTIVE SUMMARY

Air quality monitoring on the Nipomo Mesa over the past 20 years has shown that the particulate concentrations on the Mesa are significantly higher than other areas of San Luis Obispo County [(11)]. Over the past decade the San Luis Obispo County Air Pollution Control District (District) has performed supplemental monitoring and data analysis projects to better understand this problem. While these past efforts have helped to increase our understanding, they did not provide a definitive explanation of the source and scope of elevated particulate levels on the Mesa.

A year long particulate monitoring study was initiated by the District from April 2004 through March 2005 to better delineate the nature and extent of the particulate problem observed on the Mesa. Comprehensive sampling of both fine (PM2.5) and coarse (PM10) particulate matter was conducted across the Mesa with extensive chemical analysis of the filter media to provide a more complete understanding of the sources and conditions responsible for the high particulate concentrations observed in that area.

The study was supported by the California Air Resources Board (CARB) and the United States Environmental Protection Agency (EPA) with loans of sampling equipment, chemical analysis of the filters, and a federal grant of $25,000. District staff designed and coordinated the study and performed the year long sampling program. Substantial efforts were made by District staff to ensure that all data from the over 10,000 data values collected and used in the study met stringent data quality requirements.

The results of the study document a serious particulate problem on the Nipomo Mesa, with exceedances of five of the six state and federal health standards for fine and coarse particulates recorded over the study period. Exceedances of the state 24 hour PM10 standard were measured on over one quarter of the sample days.

The study data clearly demonstrates that the single largest contributor to the particulate problem is high northwesterly wind events entraining crustal particles upwind from the Mesa and transporting them to the Mesa area; particulate concentrations dropped off substantially at the farther inland location of the Mesa. The farther the winds extended inland, the farther inland the high particulate concentrations extend. One exception to this pattern was the observation of localized areas of higher concentration that occurred near dirt roads composed of fine sandy particles.

This study also attempted to evaluate the potential impacts from offroad vehicle activities at the Oceano Dunes State Vehicle Recreational Area (SVRA) on the elevated particulate levels seen on the Mesa. The SVRA is located upwind of the Mesa in the area shown by the study data to be the major source of particulates when high PM concentrations are measured on the Mesa. An analysis of average weekend and weekday particulate measurements taken on the Mesa over the past 12 years was conducted to determine if there were higher PM levels on the weekends relative to the typically higher weekend offroad vehicle activity at the SVRA. The analysis found

higher weekend concentrations at one monitoring station, but the data were not conclusive. Secondary impacts from the offroad activities, such as denuding vegetation, may also play a role by destabilizing the dune structure, allowing winds to entrain fine particles and carry them downwind. Determining the potential secondary impacts of the offroad activities is beyond the scope of this report, but deserves further study.

Regardless of whether human activities or natural sources are responsible, the study documents the frequent occurrence of unhealthful particulate levels on the Mesa. It is important to note that simply because the composition of the particulates is mostly natural crustal particles, the health implications are not lessened. All fine airborne particulate matter, regardless of composition, can cause respiratory distress when inhaled, especially to the very young, the elderly and those with compromised respiratory systems. In addition, sand particles are high in crystalline silica, a known carcinogen with a high risk factor (14,15).

The study results also demonstrated that sulfate concentrations on the Mesa are well within the California state sulfate standard, although higher sulfate concentrations were found on the Mesa than measured at other rural coastal areas of California. On days with light winds, the study data showed monitoring locations downwind from the ConocoPhillips Refinery complex with significantly higher sulfate concentrations than sites located upwind from the refinery.

As a result of this study, it is recommended that the District install a federal reference method (FRM) PM2.5 sampler and a real-time tapered element oscillating microbalance (TEOM) PM10 analyzer in the more populated area of the Mesa. The FRM PM2.5 sampler will confirm the representativeness of the study PM2.5 measurements made with non-certified samplers. The TEOM analyzer will provide hourly PM10 measurements 24 hours a day. This real time PM10 data can be examined with real time wind data to allow for further understanding of the wind events that are causing the unhealthful particulate concentrations. The continuous TEOM data will also provide a much larger PM10 database, which may allow a more conclusive weekend/weekday analysis of the PM10 data.

To reduce the elevated PM concentrations observed in localized areas near dirt roads, it is recommended that the District move forward with the proposed PM control strategies adopted by the Board as part of the 2005 Particulate Matter Report to meet the requirements of SB 656. This includes a control strategy to reduce emissions from high volume unpaved roads by working with County Public Works, County Planning and Building Department, South County Advisory Council and developers to evaluate and implement measures such as speed limit reductions, application of dust suppressants or paving new and existing unpaved roads in areas of higher population where exposure is greatest.

Finally, the District should work with the South County Advisory Council, State Parks, County Public Works and County Planning and Building Departments to further investigate the effects of off-road vehicle use at the SVRA in contributing to the elevated PM levels measured on the Mesa, and what mitigation efforts are reasonable and feasible to reduce that impact.

STUDY BACKGROUND AND DESCRIPTION

Particulate concentrations in the Nipomo Mesa area are significantly higher than other locations in San Luis Obispo County [11]. Federal and state health standards have been established for both PM10 (coarse) and PM2.5 (fine) particulates (see Table 1). Numerous violations of the state 24 hour PM10 standard and one violation of the federal 24 hour PM10 standard have been recorded at one or more of the monitoring stations in the Nipomo Mesa area. In the other areas of San Luis Obispo County, the state 24 hour PM10 standard is violated only occasionally, and has never come close to the higher federal 24 hour PM10 standard. Table 2, summarizing PM10 measurements for 2004, demonstrate this pattern of particulate concentrations in San Luis Obispo County [11].

Table 1. California and Federal Particulate Health Standards

Pollutant	Averaging Time	California Standard	Federal Standard
PM10	24 hours	50 ug/m3	150 ug/m3
	Annual Average	20 ug/m3	No standard
PM2.5	24 hours	No Standard*	35 ug/m3
	Annual Average	12 ug/m3	15 ug/m3

*The state 24 hour PM2.5 standard of 25 ug/m3 was proposed and withdrawn just prior to board approval. It is expected that this standard will be proposed again in the near future.

Table 2. Summary of 2004 PM10 Measurements in San Luis Obispo County

Monitoring Station	Percent of Samples that Exceed State Health Standard	Maximum Measured 24 hour Concentration
San Luis Obispo	0%	35 ug/m3
Morro Bay	0%	43 ug/m3
Atascadero	0%	41 ug/m3
Paso Robles	0%	43 ug/m3
Nipomo Regional Park	3%	64 ug/m3
Mesa 2	17%	131 ug/m3

In order to better understand these higher particulate concentrations measured on the Nipomo Mesa additional monitoring and data analysis projects have been performed over the past decade. Table 3 presents a summary of the routine and additional particulate monitoring that has been performed in the Nipomo Mesa.

Table 3. Summary of Routine and Special Particulate Monitoring in the Mesa Area

Site Name	Begin Date	End Date	Particulates Measured
Old Town Nipomo	1975	1990	Total Suspended Particulate (TSP)
Old Town Nipomo	1990	1996	PM10
Nipomo Regional Park	11/1998	Present	PM10
Eucalyptus Road	1989	5/1991	PM10
Mesa 2 (UCD1)	5/1991	Present	PM10
Ralcoa Way	1990	11/2002	PM10
Ralcoa Way	9/1995	11/1995	PM10 and PM2.5 with elemental analysis
Black Lake	9/1995	11/1995	PM10
CDF Station	5/2002	8/2002	PM10

The location of these historical monitoring sites is presented below in Figure 1.

Figure 1. Nipomo Mesa Area Historical Monitoring Stations

ln 2003, the District performed a detailed review of all available PM data from the Nipomo Mesa. This review strongly suggested that the predominant source of high coarse particulate concentrations (PM10) is wind blown crustal material. While not conclusive, the data also suggests that the source of the majority of crustal material is the dune fields of the Oceano Dunes State Vehicle Recreation Area directly upwind between the coast and the Nipomo Mesa area. Additionally, the data showed that overall, the PM10 concentrations decline as one moves further inland. One exception to this overall pattern was found at the Ralcoa Way monitoring location which measured significantly higher PM10 concentrations than the CDF monitoring station, located much closer to the coast. The data further showed that the Ralcoa Way monitoring location measured significantly higher PM10 concentrations than any other measurement location on the Mesa.

In the 2003 data review, only 13 fine particulate (PM2.5) measurements had been made in the Nipomo Mesa area, at the Ralcoa Way monitoring site. Though very limited, these data suggest that the area may also experience higher PM2.5 concentrations than elsewhere in San Luis Obispo County. Additionally, elemental analysis of these 13 samples suggests that there may, at times, be higher than expected concentrations of sulfate in the area.

The 2003 review of data provided some insight into the particulate problem on the Nipomo Mesa, but also raised some questions that need to be answered before definitive conclusions can be reached on the cause, extent and potential solutions to this problem. Some of the outstanding issues include:

- What source or sources are responsible for the relatively high PM10 concentrations measured at the Ralcoa Way monitoring station?
- How large of an area is represented by the elevated PM10 concentrations measured at the Ralcoa monitoring site?
- Are the average weekend PM10 concentrations on the Mesa higher than weekday concentrations?
- Is the predominant source of crustal material that appears to be driving the high PM10 concentrations in the Nipomo Mesa area the result of a natural dune/wind process?
- What role might off-road vehicle use at the Oceano Dunes play in contributing to the observed higher concentrations of particulates in this area?
- Are the PM2.5 measurements made at Ralcoa representative of a larger region, or localized to the Ralcoa area?
- Are the PM2.5 concentrations on the Nipomo Mesa higher than elsewhere in the county, and do they violate state and/or national standards?
- Are the sulfur measurements made at Ralcoa indications of a sulfate problem in the Nipomo Mesa area? If so, what are the source(s) of the sulfur?

In an effort to answer these questions and provide a more complete understanding of the PM issues on the Nipomo Mesa, the District initiated a major particulate study for the Nipomo Mesa area.

STUDY DESIGN

A one year study was initiated in early 2004 to gather coarse and fine particulate mass concentrations as well as chemical speciation data from a variety of locations. The study collected this data from April 2004 through March 2005. To assist the District with this study, the California Air Resources Board (CARB) provided: PM10 filter anion analysis (SO4, Cl, and NO3), two additional PM10 hi-volume samplers, eight PM2.5 mini-vol samplers, and PM2.5 elemental/organic carbon filter analysis. CARB was unable to provide PM2.5 filter x-ray fluorescence (XRF) elemental analysis due to the loss of key staff and budget constraints. The U.S. Environmental Protection Agency (USEPA) agreed to cover the cost of PM2.5 filter XRF and mass analysis (to be performed by Desert Research Institute) with a federal grant of $25,000.

The eight PM2.5 mini-vol samplers provided by CARB (See Figure 2 below) offer the benefit of portability, battery operation, and simple operation. However, they have not been designated by the USEPA as an approved equivalent monitoring method for PM2.5; thus, data from these samplers can not be used to determine compliance with health standards. CARB and other organizations have performed comparisons of the mini-vol samplers to the USEPA approved PM2.5 Federal Reference Method (FRM) samplers with good general agreement [5]. Based on these comparisons, the District decided to proceed with the use of the mini-vol samplers for PM2.5 sampling as a way to improve our understanding of the PM2.5 concentrations and chemical composition. Should the study results indicate the possibility that PM2.5 concentrations on the Nipomo Mesa exceeded health standards or were higher than elsewhere in San Luis Obispo County, a PM2.5 FRM sampler would need to be installed on the Mesa to collect data that could be used to determine compliance with any state and/or federal health standards.

Figure 2. PM2.5 Mini-Vol Sample Example

Various sampling locations on the Mesa were evaluated for the study. Locations were selected to provide measurements in populated areas and areas immediately downwind from expected major sources of coarse particulates and sulfur emissions. Weighing these monitoring needs with power availability, EPA siting criteria and site availability determined the final site selections. It should be noted that the Ralcoa Way monitoring location, where the highest PM concentrations on the Mesa have historically been measured, was not selected for this study due to this site no longer meeting EPA siting criteria. The final study design is presented in Table 4 and Figure 3 presents the location of study sites.

Table 4. Final Study Design

Monitoring Station	**Parameters Measured**
CDF	• PM10 mass, sulfate, nitrate, and chloride • Directional PM10 mass, sulfate, nitrate, chloride • Wind Speed and Direction
Bendita	• PM10 mass, sulfate, nitrate, and chloride • PM2.5 mass, elements by XRF, elemental/organic carbon
Hillview	• PM10 mass, sulfate, nitrate, and chloride
Nipomo Regional Park	• PM10 mass*, sulfate, nitrate, and chloride
Mesa 2	• PM10 mass*, sulfate, nitrate, and chloride • Collocated PM10 mass* for quality assurance • PM2.5 mass, elements by XRF, elemental/organic carbon • Collocated PM2.5 mass for quality assurance
Oso	• PM2.5 mass, elements by XRF, elemental/organic carbon
Atascadero/Santa Maria (Quality Assurance only)	• PM2.5 mass for quality assurance comparison to PM2.5 FRM sampler

*existing measurements from the District monitoring network

This study design generated almost 10,000 particulate and chemical species data points to improve our understanding of the particulate problem on the Nipomo Mesa.

All PM10 measurements were made with US EPA equivalent method hi-volume samplers utilizing quartz fiber filter media following District standard operating procedures. PM2.5 measurements were made with mini-vol samplers. Because quartz fiber filters must be used for elemental carbon and organic carbon (EC/OC) analysis and Teflon filter media is typically used for mass and XRF analysis, two separate mini-vol samplers were utilized at each site when EC/OC as well as mass and XRF analysis were performed.

Enormous effort was taken to ensure that the data collected for this study would be of the highest quality. Quality control procedures were implemented to directly control and document numerous variables in the measurement process. Additional quality assurance procedures were implemented to measure the effectiveness of the quality control tasks in controlling the data quality. Data from these quality control and quality assurance tasks were used to validate the entire study data set. A detailed discussion of data validation and quality assurance results and procedures is provided in Appendix A.

Figure 3. 2004 Nipomo PM Study Monitoring Site Locations

PM10 DATA PRESENTATION AND SUMMARY

PM10 measurements were made at Nipomo Regional Park, Mesa 2, Hillview, Bendita, and the CDF station. These measurements follow the national PM10 schedule where a sample is collected every 6 days. The data are collected for a 24 hour integrated average, from midnight to midnight of the sample day.

In addition to the 24 hour average measurements, an additional directional PM10 sampler was located at the CDF station (collocated with a standard PM10 sampler). The directional sampler was a modified PM10 sampler configured to be started and stopped by the CDF data logger used to record the wind parameters at the CDF monitoring site. The CDF data logger was programmed to evaluate the wind conditions every five minutes. If the previous five minute average recorded a wind speed greater than five miles per hour and a wind direction between 260 and 330 degrees, the directional PM10 sampler was turned on (if it was a sample day). This allowed the directional PM10 sampler to operate only during those meteorological conditions that would be conducive to the entrainment and transport of particulates to the CDF station from the Oceano Dunes State Vehicle Recreation Area (SVRA).

Each PM10 filter was analyzed for total mass as well as the anions sulfate (SO4), nitrate (NO3), and chloride (Cl). This study assumed that all sulfate is in the form of ammonium sulfate ((NH4)2SO4), that all nitrate is in the form of ammonium nitrate (NH4NO3), and that all chloride is in the form of sea salt (NaCl). The "other" category includes all particulates other than sulfate, nitrate, and sea salt, and was determined by subtracting the sum of ammonium sulfate, ammonium nitrate, and sea salt from the total mass of the sample. The largest component of the "other" category for PM10 would typically be crustal material, but could also include elemental/organic carbon and other minor components.

The annual average of all valid samples over the study period for each site is presented below in Figure 4.

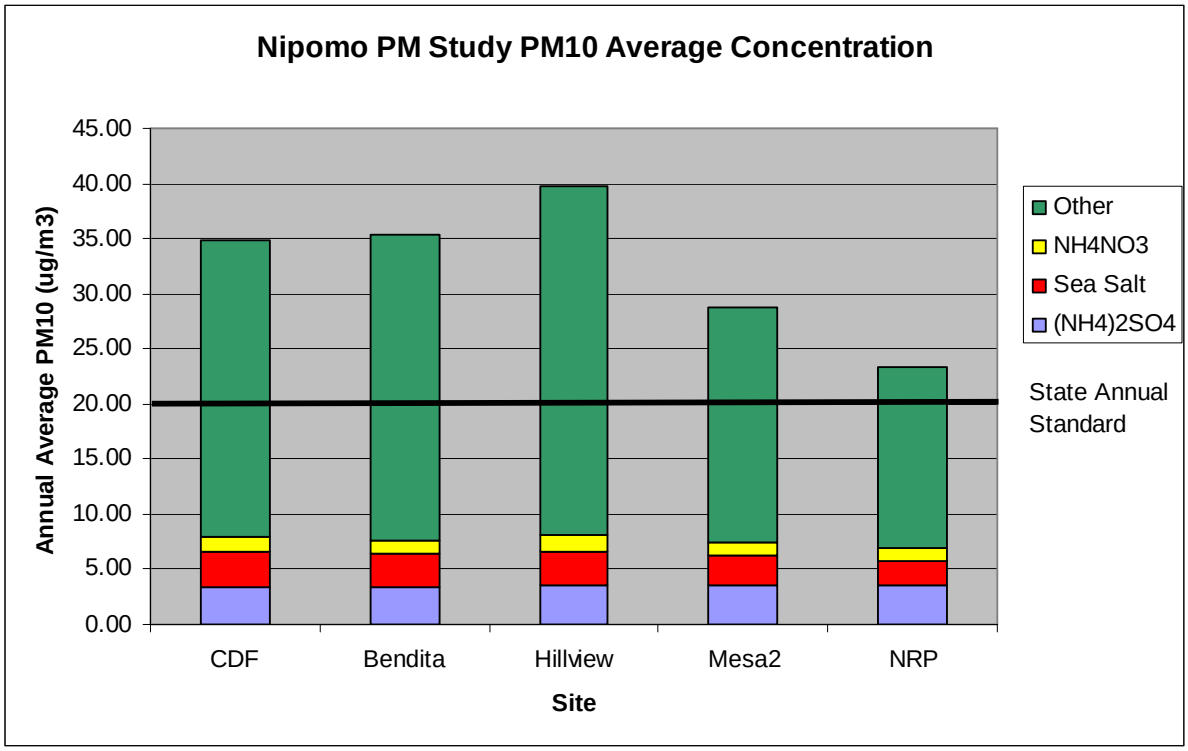

Figure 4. 2004 Nipomo PM Study Annual Average PM10 Concentrations

Figure 4 shows that the annual average concentration for each site exceeds the state annual PM10 health standard of 20 ug/m3. Historically, PM10 data on the Nipomo Mesa has exhibited the same pattern as seen in the study data. The sites closest to the ocean tend to be the highest, with the concentration dropping further inland.

The one anomaly to this pattern is Hillview. Hillview is located farther inland than CDF or Bendita, but shows a higher annual average concentration. This deviation from the typical pattern is very similar to historical data showing the Ralcoa Way monitoring station PM10 values being higher than other sites on the Mesa.

Analysis of the annual average sulfate and nitrate concentrations showed similarities among all sites. The sea salt concentrations decrease the farther from the coast as one would expect. The largest difference from site to site is the "other" category that accounts for the drop in concentration as one moves inland as well as the higher concentration observed at the Hillview site.

Data for each valid 24 hour sample is presented for each site in figures 5-9 below.

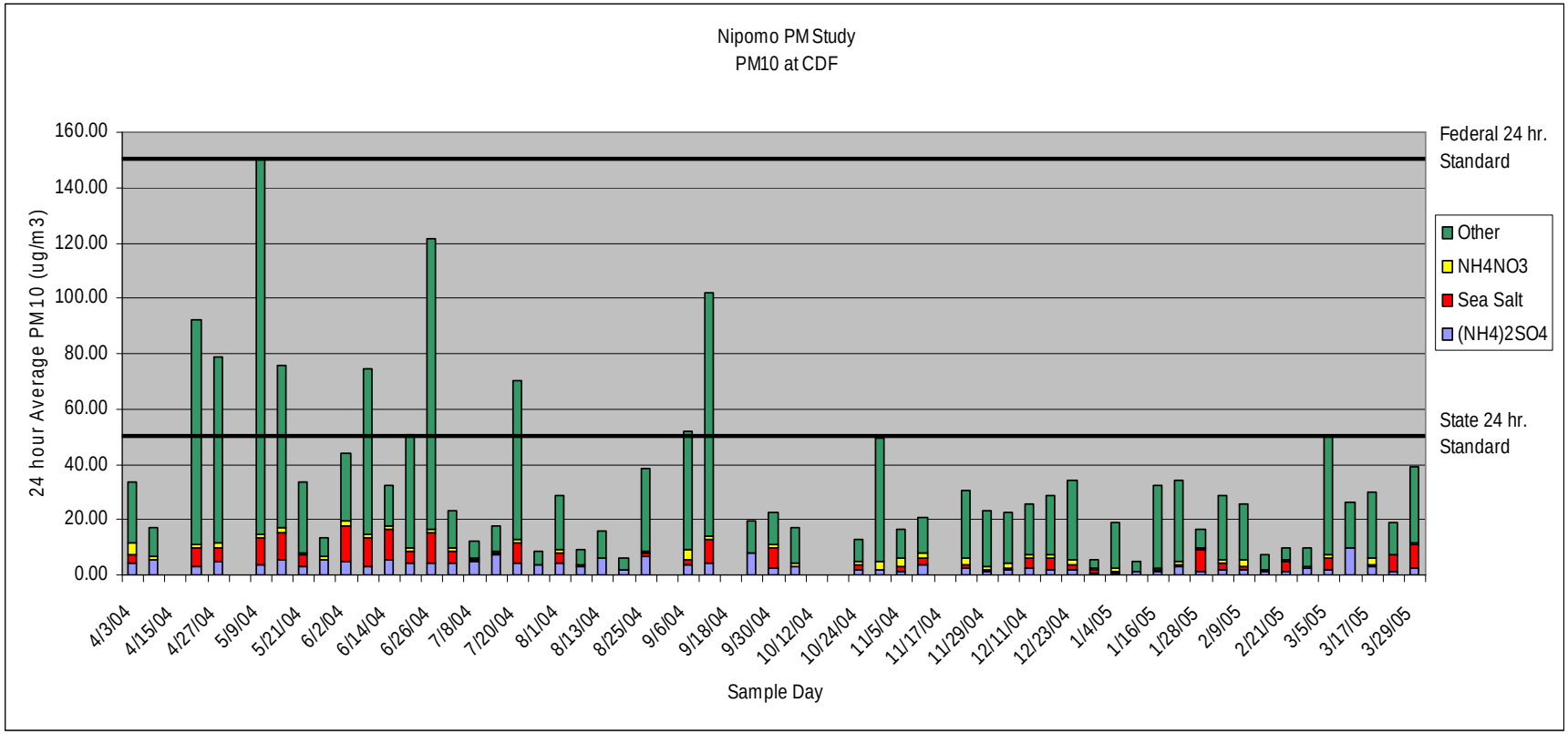

Figure 5. PM10 at CDF

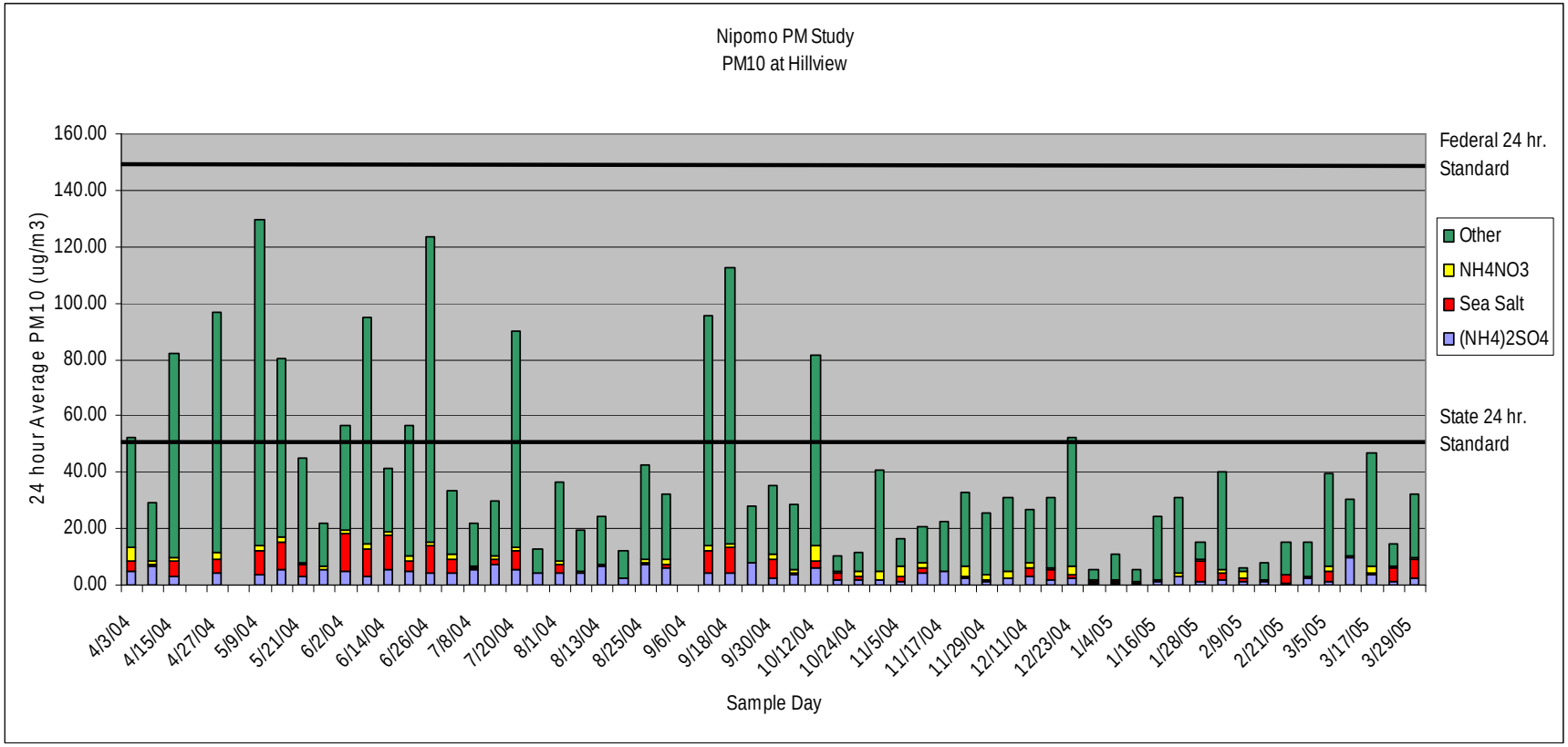

Figure 6. PM10 at Hillview

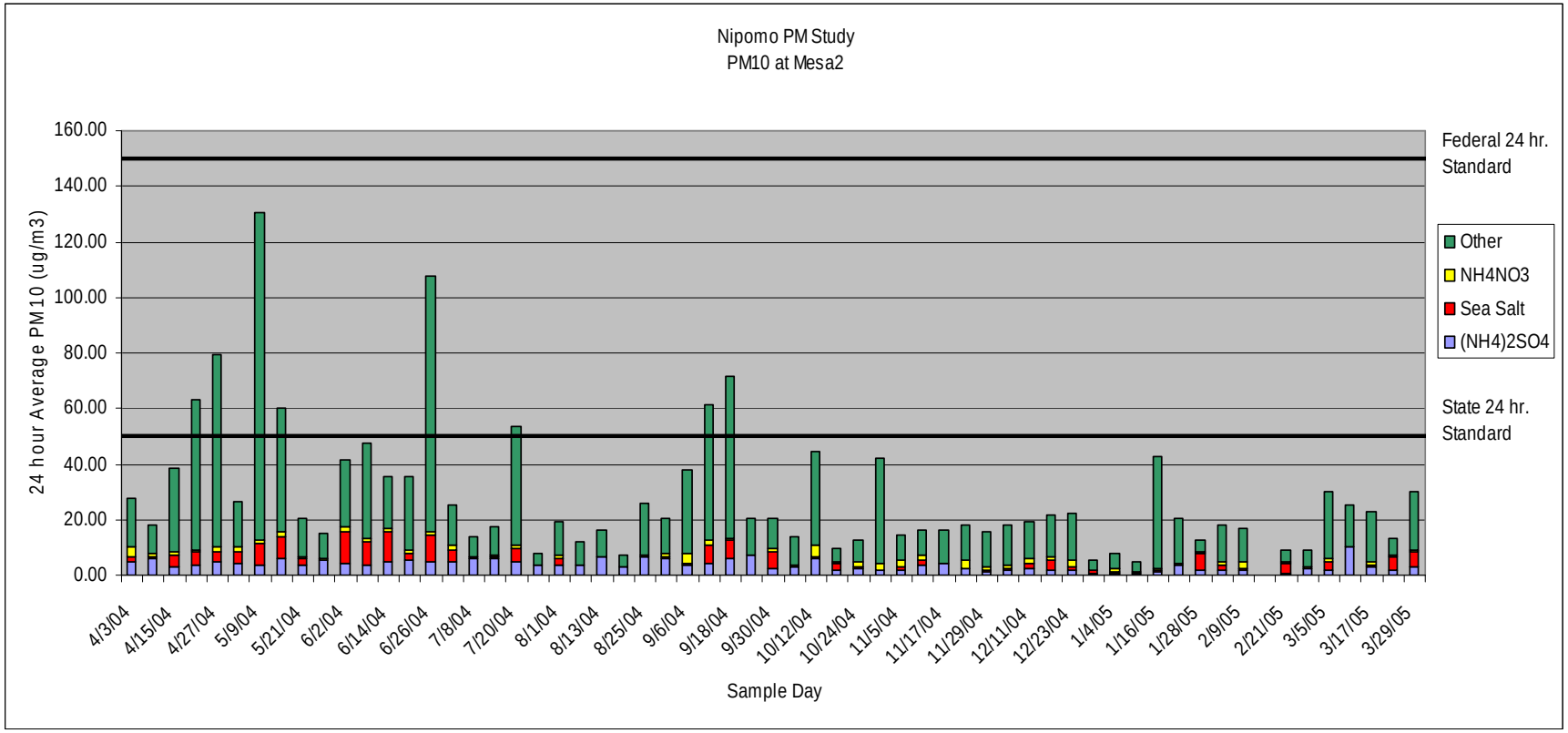

Figure 7. PM10 at Mesa 2

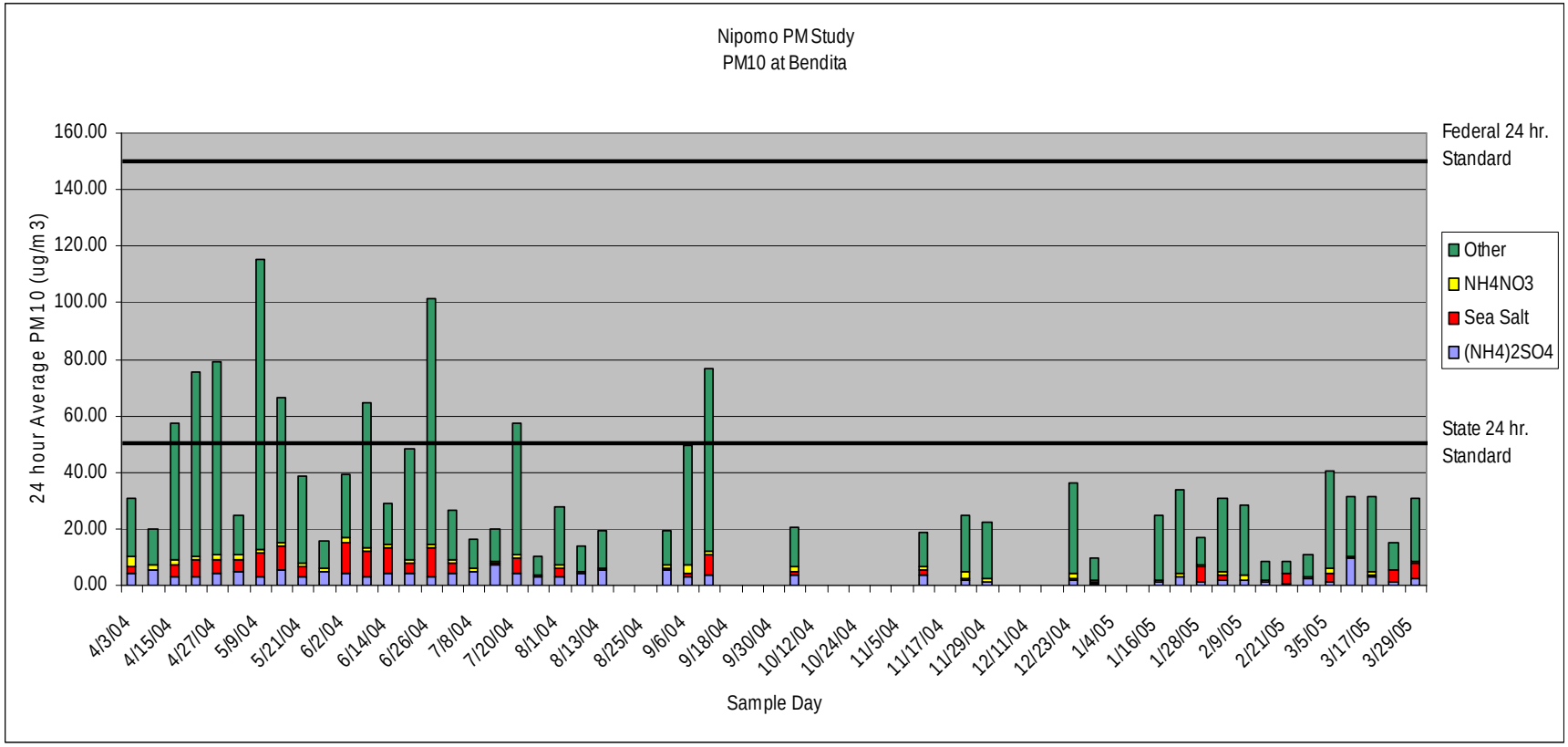

Figure 8. PM10 at Bendita

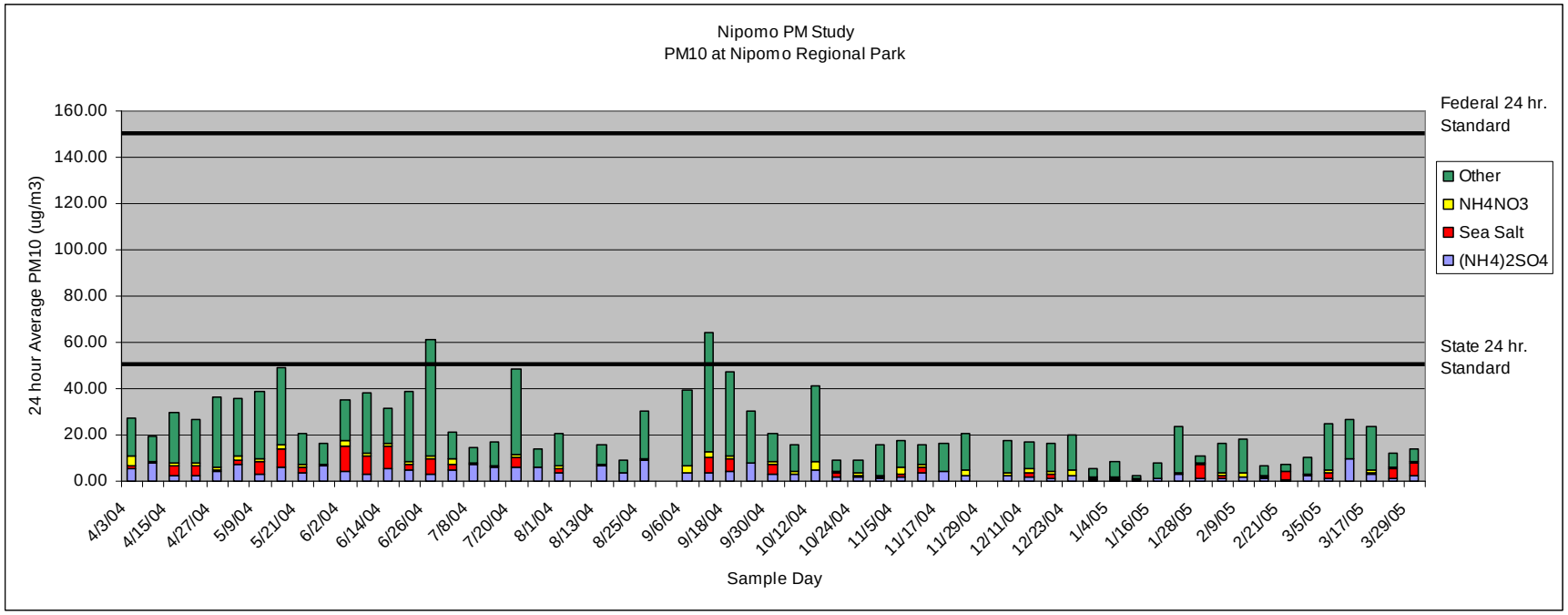

Figure 9. PM10 at Nipomo Regional Park

A review of the individual 24 hour concentrations from the study sites shows numerous violations of the state PM10 standard at all sites, and one violation of the federal PM10 standard at the CDF monitoring site. As was observed in the annual summary of PM10 data, the PM10 concentrations tend to be the highest near the coast and decreasing inland. Also, the "other" category is the most variable and the main component of the highest overall PM10 concentrations. PM10 concentrations at all sites were highest in the spring and early fall and decreased dramatically during the wet winter season.

The directional sampler at the CDF station was designed to sample only the air mass passing over the Oceano Dunes SVRA with sufficient speed to pick up and transport particulates to the CDF location. Comparisons between the standard PM10 sampler and the directional PM10 sampler at CDF allow for estimates of the contribution to the measured PM10 at the CDF monitoring station from the Oceano Dunes SVRA. The mass collected on the directional sampler is subtracted from the mass collected on the standard sampler to estimate the "non-dune" contribution to the CDF PM10 measurements. Figure 10 presents this data. From this data presentation, it is clear that the higher concentration sample days are caused by large contributions from the dunes. It is interesting to note that the highest measured PM10 concentration at CDF (5/9/04) resulted entirely from the dunes contribution. Without the contribution from the dunes, the PM10 measured at CDF would be more typical of PM10 measurements elsewhere in San Luis Obispo County.

The most common source of sulfate aerosol is from the atmospheric reactions of the combustion of fuels containing sulfur. However, it has been observed that the natural wave action in the coastal zone can produce natural "marine sulfate". The wave action creates natural particulates in the coastal zone. The composition of these particulates roughly resembles the elemental composition of ocean water, with salt compromising the vast majority of marine particulates. A small component of marine particulates is sulfate, due to the naturally occurring sulfur present in ocean water. The amount of this marine sulfate can be estimated by applying the approximate ratio of chlorine (from sea salt) to sulfur in ocean water. This relationship has been refined by research performed by Dr. Thomas Cahill of the University of California at Davis (4,7). It is also important to note that sulfate aerosol that results from burning sulfur containing fuels is always in the fine particulate fraction (particulate diameters less than 2.5 micron), where the marine aerosol is more often in the coarse fraction (diameters greater than 2.5 micron) (4,9). Figure 11 presents average PM10 marine and anthropogenic sulfate from the study sites using the chlorine/sulfur relationship identified by Dr. Cahill.

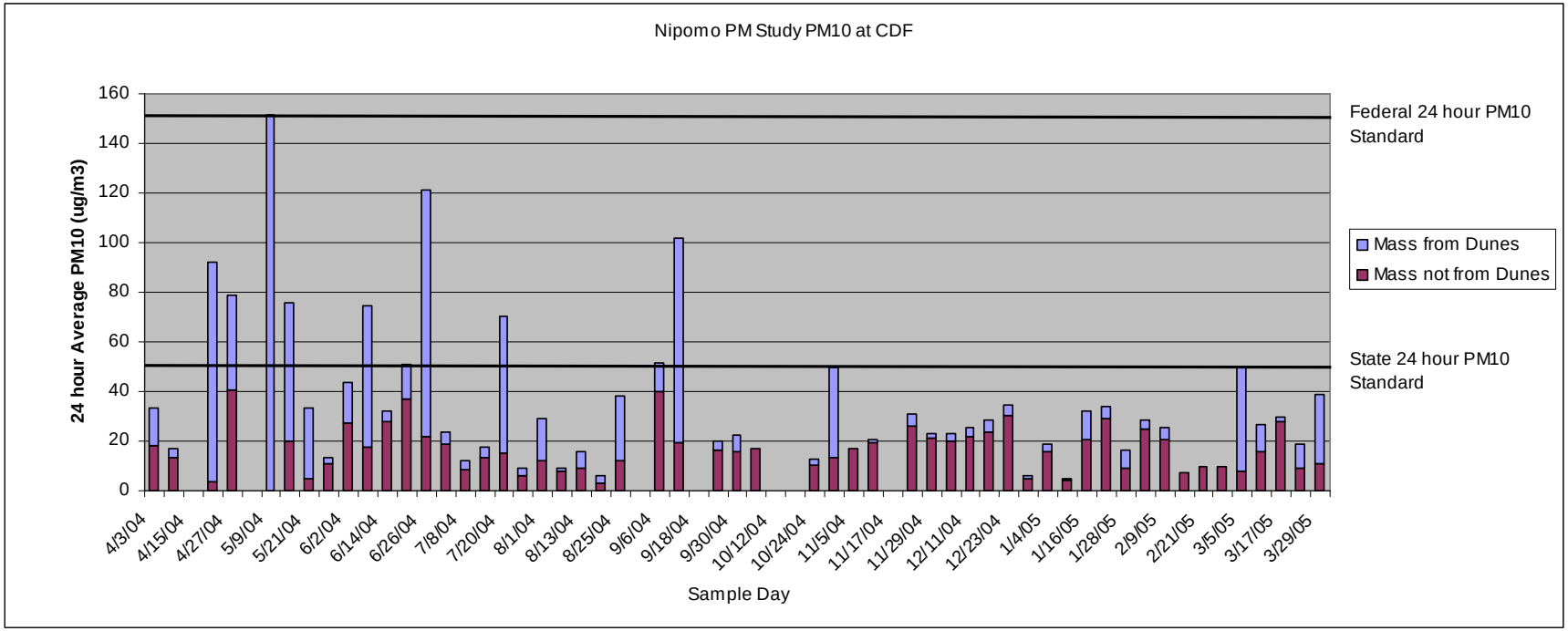

Figure 10. PM10 Concentrations at CDF Attributed to Dunes and Non-Dunes

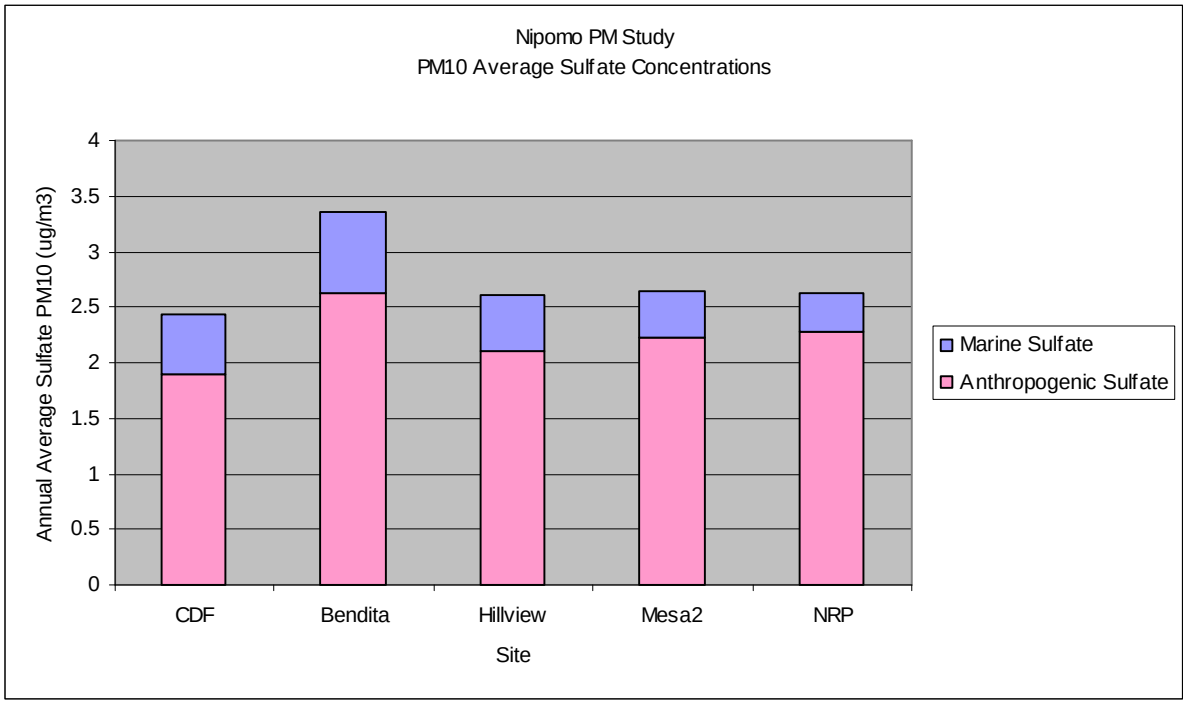

Figure 11. Average PM10 Sulfate Values

As Figure 11 shows, the average sulfate values for four of the five sites show a consistent trend. Anthropogenic sulfate is lowest on the coast and increases as one moves inland. Marine sulfate is highest on the coast and decreases at the inland sites. Overall sulfate increases as one moves inland. These trends in the average sulfate values are quite consistent with expectations. Emissions of sulfur dioxide from offshore marine vessels will convert to sulfate aerosols as they move to the coast. This sulfate combines with any background sulfate. Sulfur dioxide emissions from the ConocoPhillips Refinery are added to the air mass at the coast. These sulfur emissions will also convert to sulfate as the air mass moves inland and add to the sulfate concentration. It is important to note that the rate of conversion from sulfur dioxide to sulfate aerosol is extremely variable. The conversion can take days to occur in very dry air, and can occur quite rapidly in air with water droplets present. Other variables such as metallic particles and high ozone concentrations in the atmosphere also increase the reaction rate of sulfur dioxide gas to sulfate aerosol [(9)].

The Bendita average sulfate values are quite different from the other sites. This appears to be due to significant periods of invalidated data due to sampler malfunctions (see Appendix A). The period of invalidated Bendita data is when sulfate values measured elsewhere were low, resulting is a positive bias to the average Bendita PM10 sulfate values.

PM2.5 DATA PRESENTATION AND SUMMARY

PM2.5 measurements were made at the Bendita, Mesa 2, and Oso monitoring sites. As noted in a previous section, prior to this study only 13 fine particulate measurements have ever been performed on the Nipomo Mesa. These sites were selected to provide data to assess the fine particulate concentrations across the Mesa as well as attempting to understand the particulate sources impacting this area.

These measurements were made on the same national particulate sampling schedule as the PM10 measurements. Each monitoring site utilized two PM2.5 samplers. One sampler utilized a Teflon membrane filter with the other sampler using a quartz fiber filter. The Teflon filters were analyzed for total mass and various elements by x-ray fluorescence (XRF). The quartz filter was analyzed for elemental/organic carbon (EC/OC). The XRF and EC/OC analysis was performed to allow a more complete chemical speciation of the samples. Additional PM2.5 measurements were made outside the study area (Atascadero and Santa Maria) in order to compare the samplers utilized in the study with Federal Reference Method PM2.5 samplers. (See Appendix A for a detailed discussion of this quality assurance aspect of the study.)

In addition to the above listed analysis, Teflon filters for eight sample days from all sites were analyzed for the following ions: Sulfate (SO4), Ammonium (NH4), Nitrate (NO3), Sodium (Na), and Potassium (K). These eight sample days were selected to provide one or two examples of a particular type of day. The eight days were selected for the following reasons:

Sample Day Selected	Reason Selected
4/9/04	Low mass, but high sulfur
5/9/04	Highest mass, and very high crustal contribution
6/2/04	Low crustal, but high sea salt
8/13/04	Low mass but high sulfur
9/24/04	Low mass but high sulfur
11/17/04	One of the highest mass samples without significant crustal contribution.
1/22/05	Low winter sample
3/11/05	Highest sulfur measured in study, almost highest mass in study

To best utilize the extensive chemical analysis of the PM2.5 samples, the overall mass concentration was segmented into typical categories of PM2.5 particulates. These categories were calculated from the chemical analysis performed on all of the PM2.5 measurements using accepted USEPA algorithms. Table 5 lists how each particulate category was calculated (8,10).

Table 5. Algorithms Used to Calculate PM2.5 Categories

Category	Algorithm	Explanation
Crustal	(Al*2.2)+(Si*2.49)+(Ca*1.63)+(Fe*2.42)+(Ti*1.94)	The mass of the most common elements in crustal material is adjusted to add the mass of the other elements composing the compounds found in crustal material.
Sea Salt	Cl*1.642	The mass of chlorine is adjusted by ratio of atomic weights of sodium and chloride.
Organic Carbon	(Organic Carbon-blank value)*1.4	The measured mass of carbon is first blank corrected (see Appendix A) then adjusted to account for the other elements in typical carbon containing particulates.
Ammonium Sulfate (NH4)2SO4	S*4.125	The measured sulfur mass is adjusted by the ratio of atomic weights of sulfur to the other atoms in ammonium sulfate.
Ammonium Nitrate NH4SO4 and Other	Total Mass – (Crustal+Sea Salt+Organic Carbon +Ammonium Sulfate)	The above categories are subtracted from the total measured mass.

Figure 12 presents the annual average PM2.5 concentrations and compositions measured during the study.

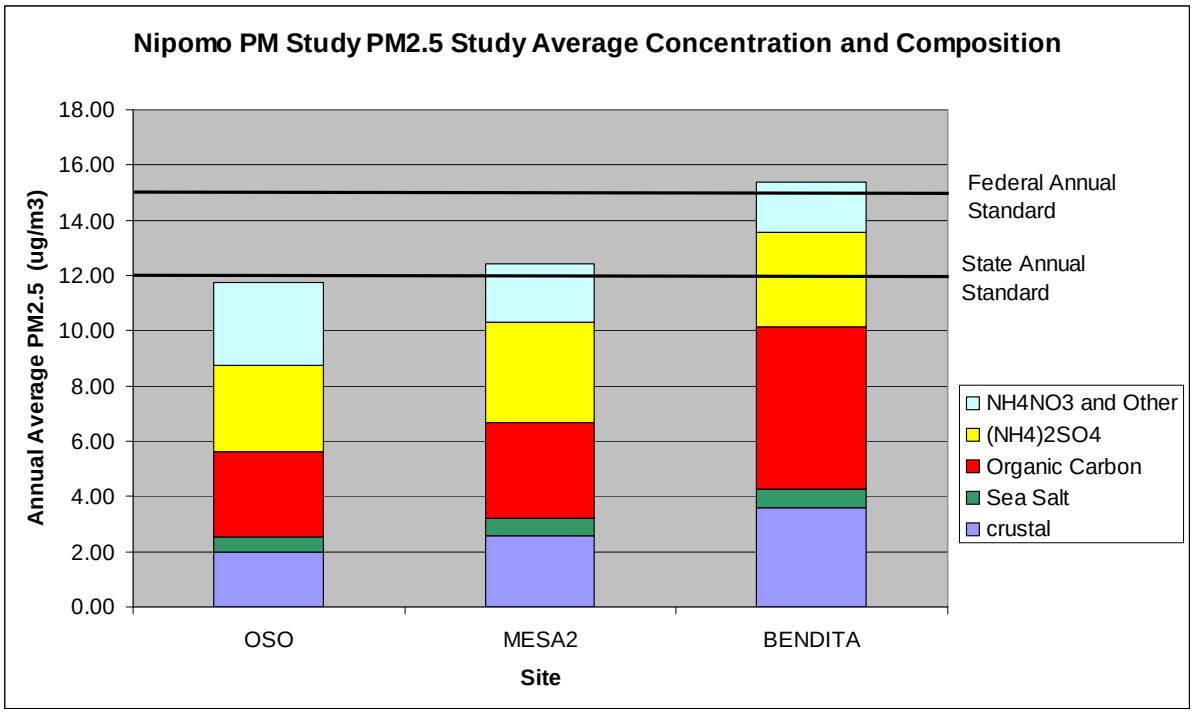

Figure 12. 2004 Nipomo Mesa Study PM2.5 Average Concentrations and Compositions

The state annual PM2.5 standard (12 ug/m3) was exceeded at both the Mesa 2 and Bendita sites. In addition, the federal PM2.5 annual standard (15 ug/m3) was exceeded at the Bendita site. These measurements were not made with USEPA reference samplers and therefore alone can not be used to demonstrate attainment/non-attainment of the PM2.5 standard, but can be used as a general indication of the PM2.5 levels in the study area. See Appendix A for a detailed discussion of PM2.5 sampler comparisons performed for quality assurance purposes.

The data from Mesa 2 and Oso stations are quite similar, with slightly more crustal and sulfate particulates at Mesa 2 and slightly more ammonium nitrate/other at the Oso monitoring station. The Bendita data shows a significantly greater portion of crustal and organic carbon than the other two sites. The Bendita monitoring site is located in the center of a small neighborhood. One possibility why the Bendita crustal and organic carbon concentrations are higher than the other two sites is that this location (unlike the other two) is in a neighborhood with significant human activities. The higher organic carbon at Bendita appears to be at least partially due to wood burning based on a non-soil potassium (tracer for wood smoke) analysis [8]. The higher crustal fraction at Bendita could also be due to human activities. Bendita is a paved road, but there are numerous unpaved roads in the neighborhood. If the human activities in the Bendita neighborhood are the cause of the higher carbon and crustal particulate values, one can expect the particulate concentrations in less populated areas (like Mesa 2) to increase if those areas become more populated.

PM 2.5 organic carbon and elemental carbon (EC/OC) measurements were performed at the study sites, and the study annual averages for organic carbon are presented above. However, 24 hour sample data for EC/OC is not presented in the figures 13 through 16 due to contamination of the filter media used for EC/OC analysis prior to sampling. See Appendix A for a detailed discussion of this issue. Corrections to the data for this contamination was possible for study averages by subtracting average blank values, but was not possible for individual samples due to the large variability of the level of contamination from one filter to another. Elemental carbon was not detected above the detection limit of 1.0 ug/m3 on any sample. It is not unusual for the elemental carbon concentration to be below this detection limit. Only a very small percentage of samples statewide exceed the detection limit for elemental carbon [(6)].

PM2.5 measurements were taken for quality assurance purposes at the CARB monitoring site in Santa Maria. These measurements were made in order to compare the PM2.5 data values from the mini-vol sampler that was used for study PM2.5 measurements to a PM2.5 federal reference sampler. See Appendix A for a detailed discussion of this issue. PM2.5 data from Santa Maria is presented in figure 16 for comparison purposes only.

Figures 13 – 16 present 24 hour average PM2.5 samples from the study sites as well as data from the CARB Santa Maria monitoring station where sampler comparisons for quality assurance purposes were performed.

Review of this data shows very similar data patterns from all study sites. The most variable particulate categories are crustal and sea salt. High crustal values are associated with high sea salt values. This suggests that the days with high crustal concentrations are associated with a strong sea breeze that contributes to higher sea salt concentrations. Ammonium sulfate is also quite variable with the lowest values occurring in the winter months. Sulfate concentrations are generally higher on non-winter days with little to no crustal component. Sample days with light winds and less atmospheric dispersion had little to no crustal particles, while allowing more time for sulfur dioxide emissions from the ConocoPhillips facility and any other sulfur dioxide sources to convert to sulfate aerosol.

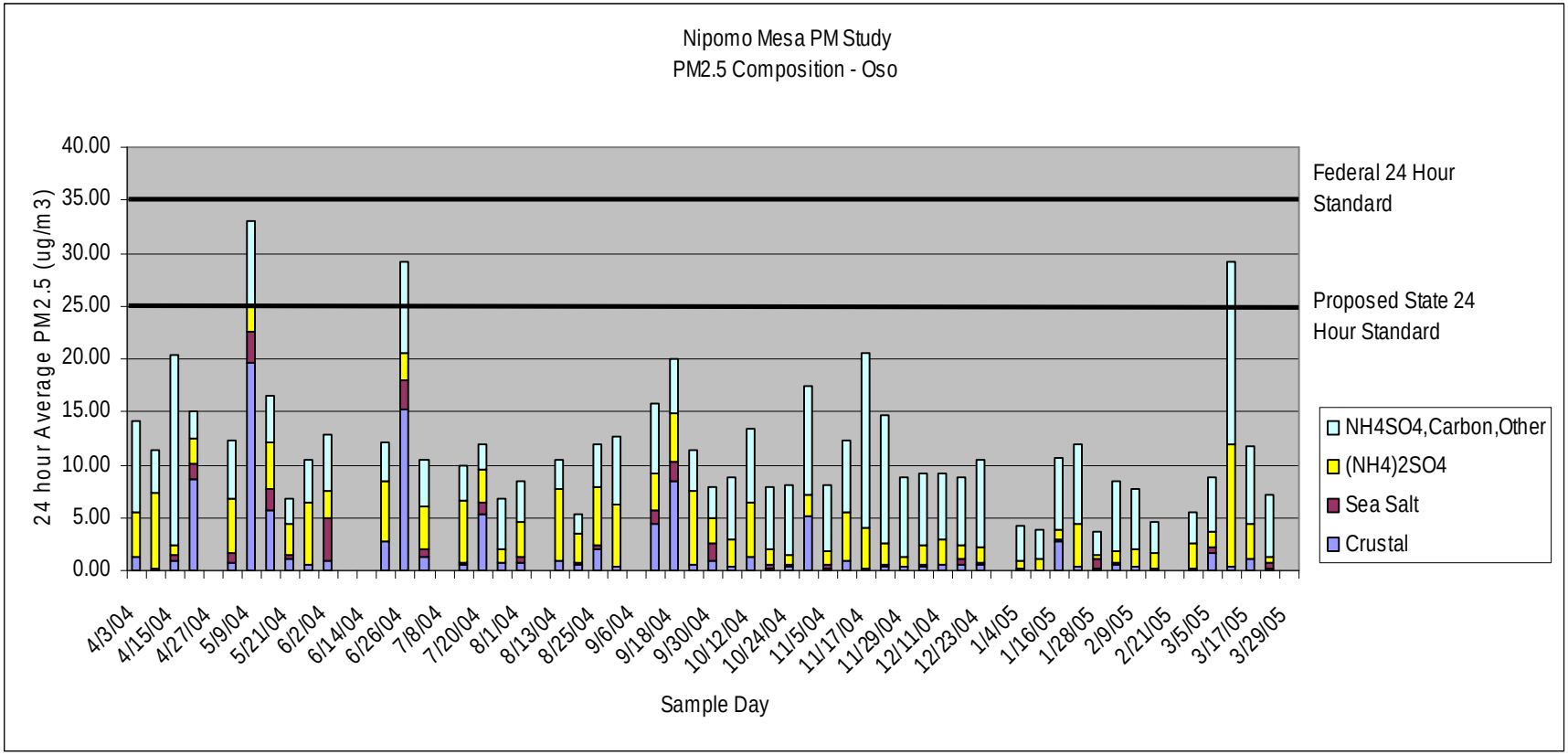

Figure 13. PM2.5 at Osos

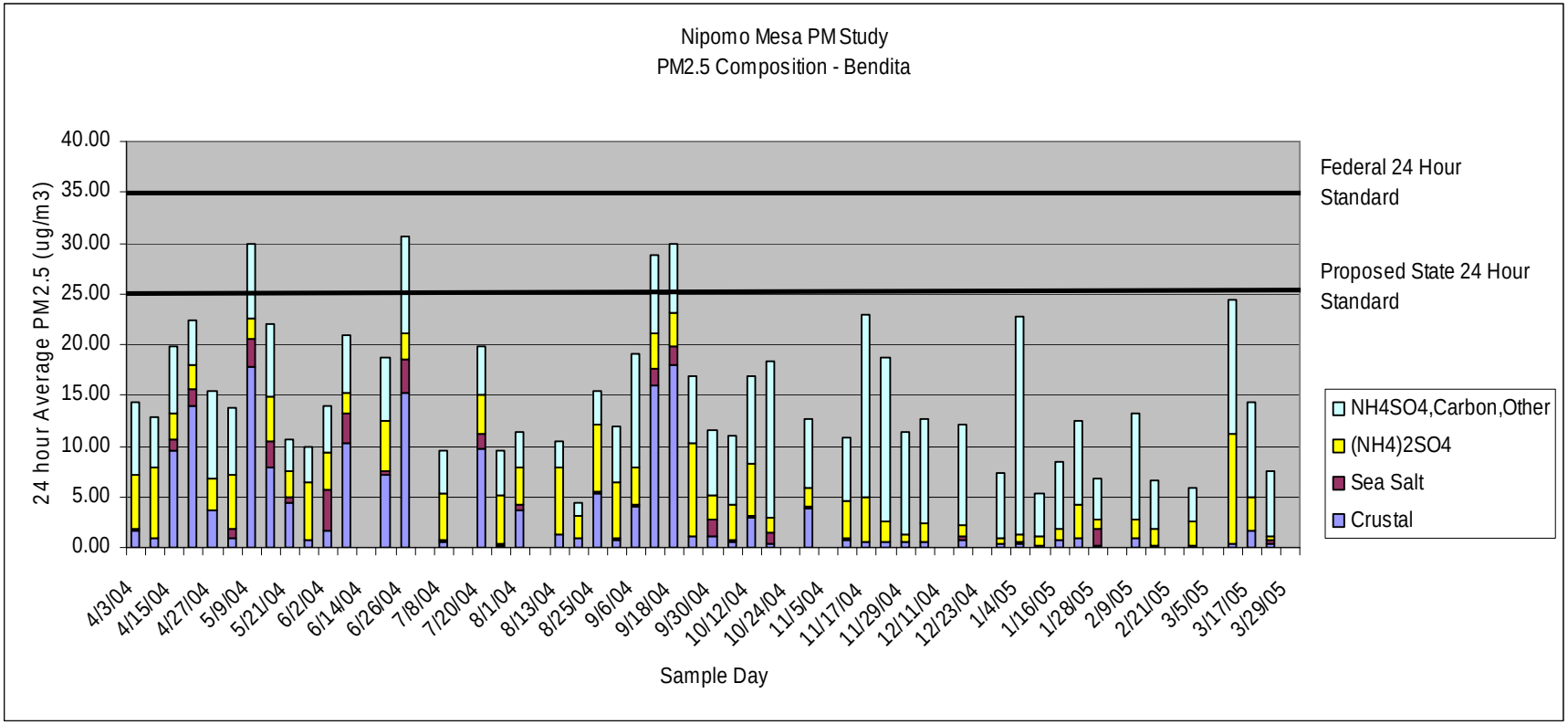

Figure 14. PM2.5 at Bendita

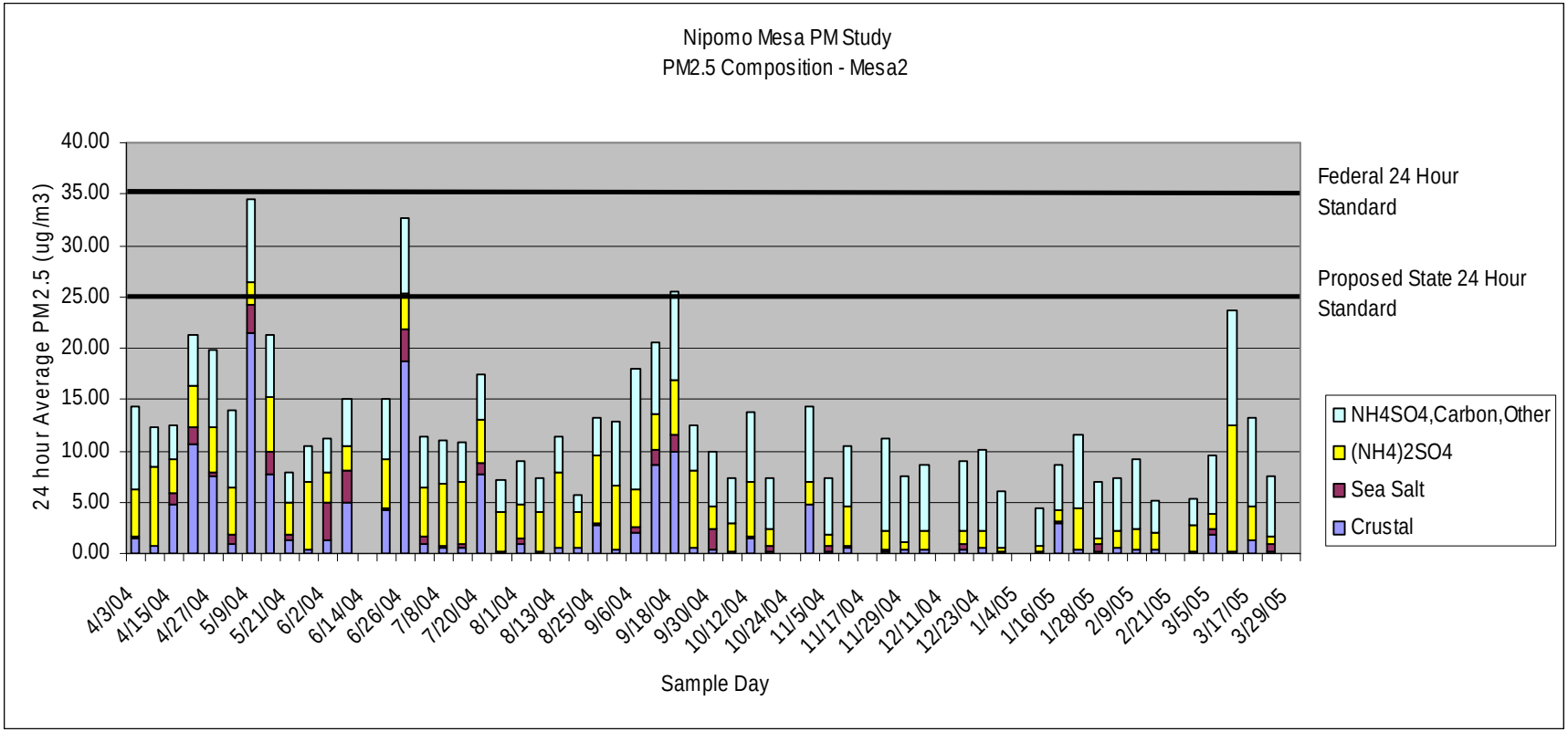

Figure 15. PM2.5 at Mesa 2

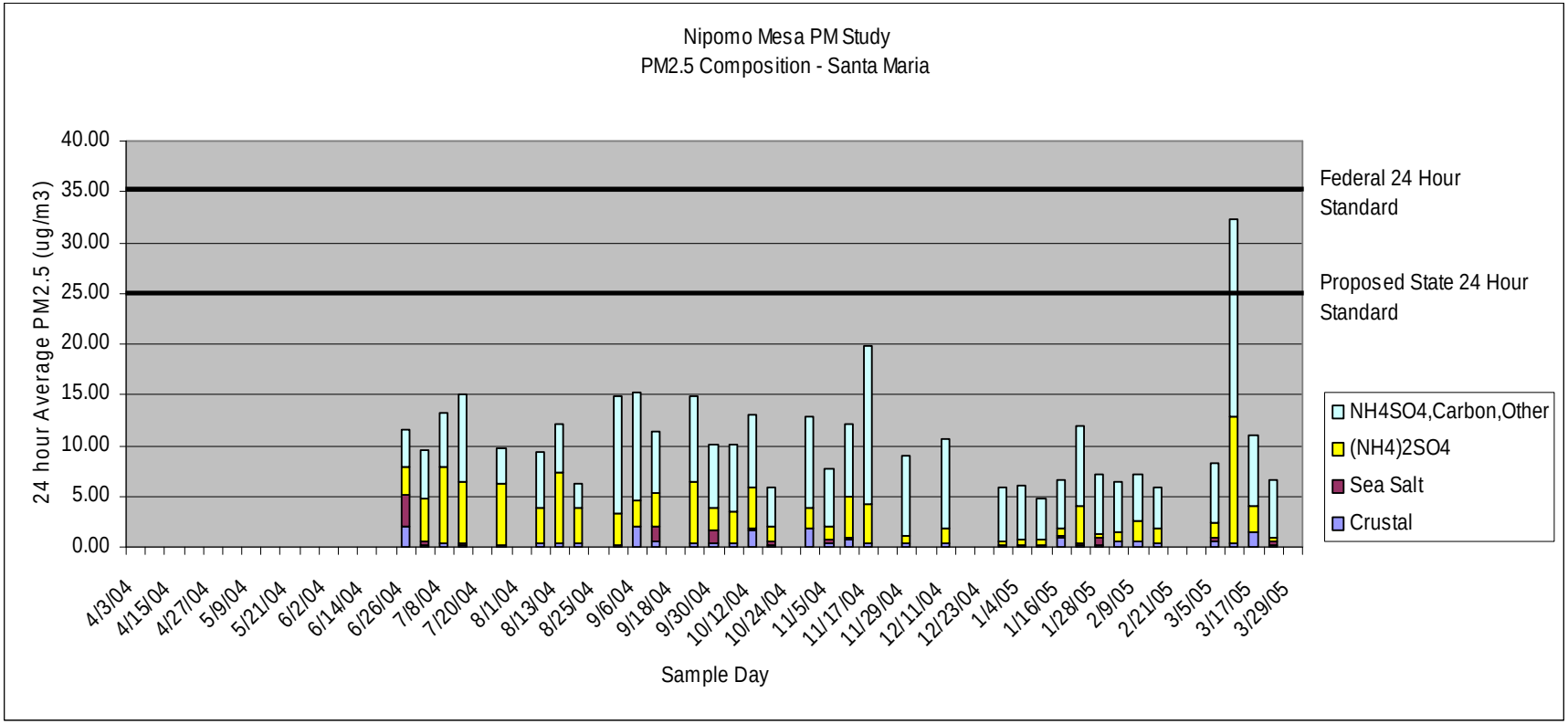

Figure 16. PM2.5 at Santa Maria

The Santa Maria data set shows significantly less crustal contribution than any of the study sites, resulting is lower overall PM2.5 concentrations.

Winter samples from Bendita exhibit significantly higher overall PM2.5 concentrations than the Mesa 2 and Oso monitoring sites for the same period. Examination of this data shows that the higher Bendita PM2.5 concentrations are due to higher organic carbon values. In addition to the higher organic carbon values, non-soil potassium, a qualitative tracer for wood smoke, was also high on a number of these same sample days. These higher organic carbon values and associated non-soil potassium in the winter months indicate that the higher Bendita PM2.5 concentrations are likely due to neighborhood backyard burning, home fires, and heating with wood stoves [(8)].

Following mass and XRF analysis on the PM2.5 Teflon filters, eight sample days were selected for full ion analysis. The full ion analysis, used in conjunction with the previous XRF and EC/OC analysis of these filters, provides the most complete and accurate assessment of the particulate mix. This more complete analysis provides direct measurement sulfate rather than calculating sulfate from elemental sulfur and direct measurement of nitrate that was not measured on other samples.

Figures 17 – 20 present this "fully speciated" analysis. Note that there were no EC/OC measurements made at Santa Maria, and EC/OC data is not presented on the first four sample days for the other sites due to problems with contaminated filters (See Appendix A). In these cases, where no organic carbon data is presented, the organic carbon portion is contained in the "other" category. Elemental carbon was never detected above the detection limit of 1 ug/m3 in any sample.

Review of samples from these eight fully speciated days shows that the sulfate values calculated from the XRF sulfur measurements agree well with the measured sulfate on these eight sample days. This indicates that the sulfur measured by XRF is in the form of sulfate, and not elemental sulfur particulates or some other sulfur compound. The fully speciated samples are the only samples with any nitrate measurement. These samples show that nitrate makes up a very small fraction of the fine particulate mix on the Mesa.

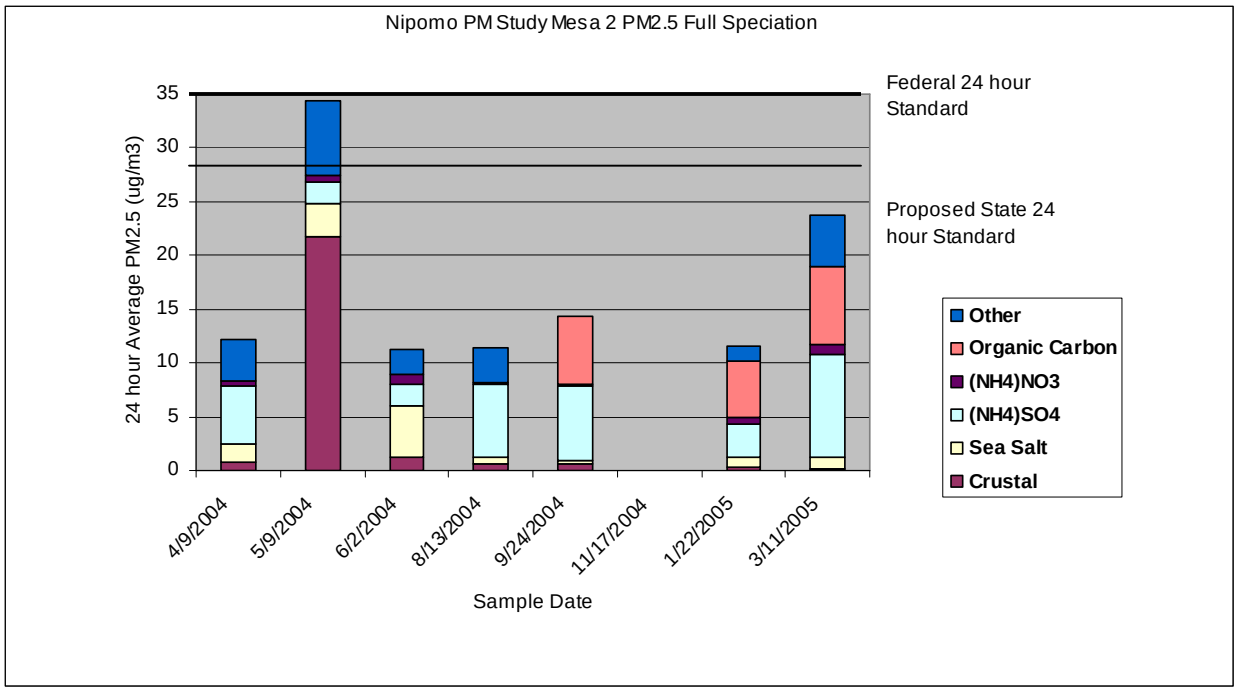

Figure 17. Mesa 2 Fully Speciated PM2.5 Samples

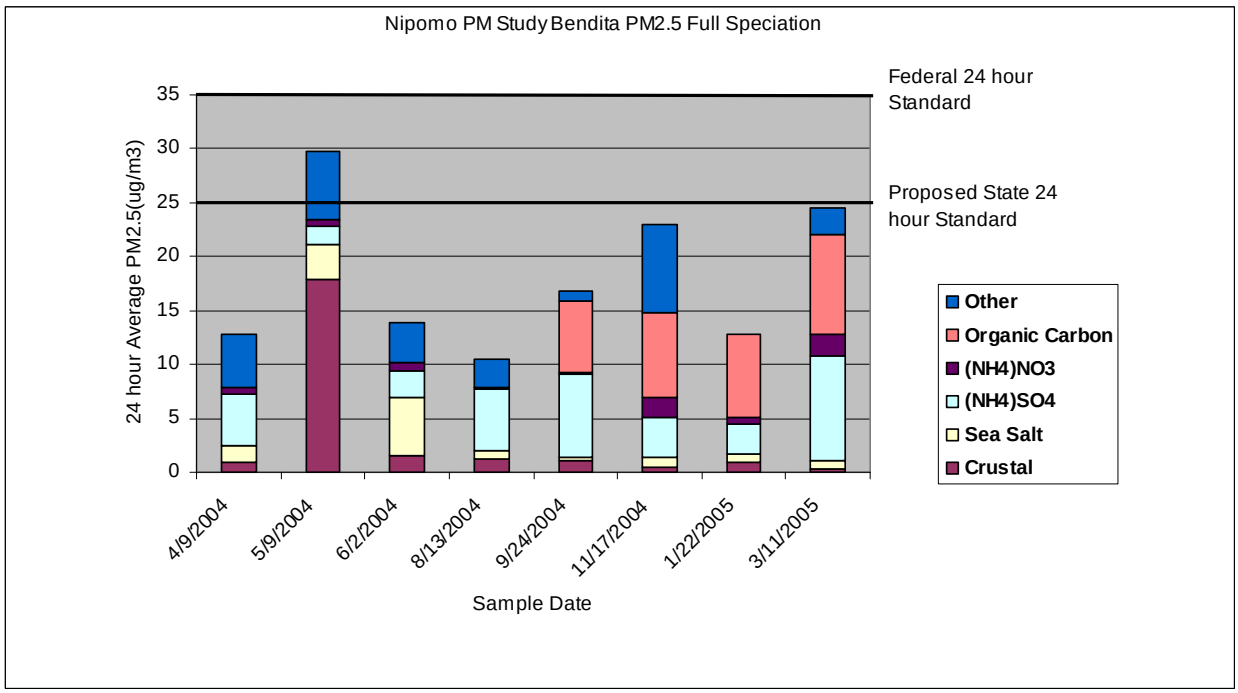

Figure 18. Bendita Fully Speciated PM2.5 Samples

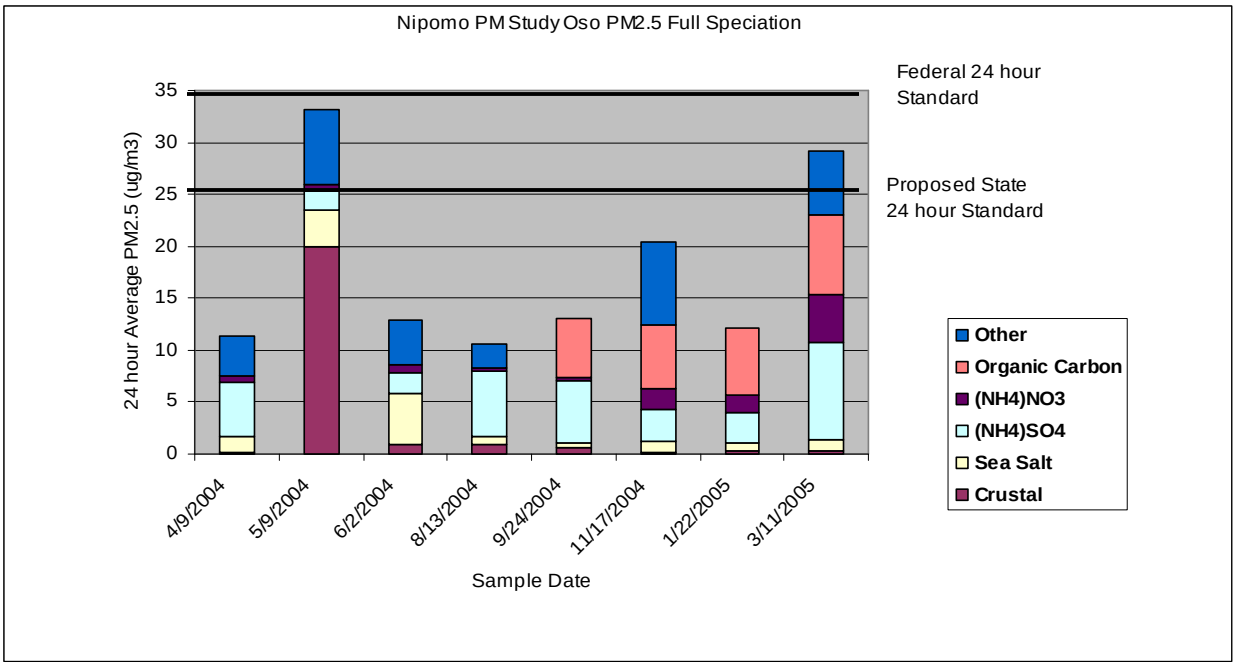

Figure 19. Oso Fully Speciated PM2.5 Samples

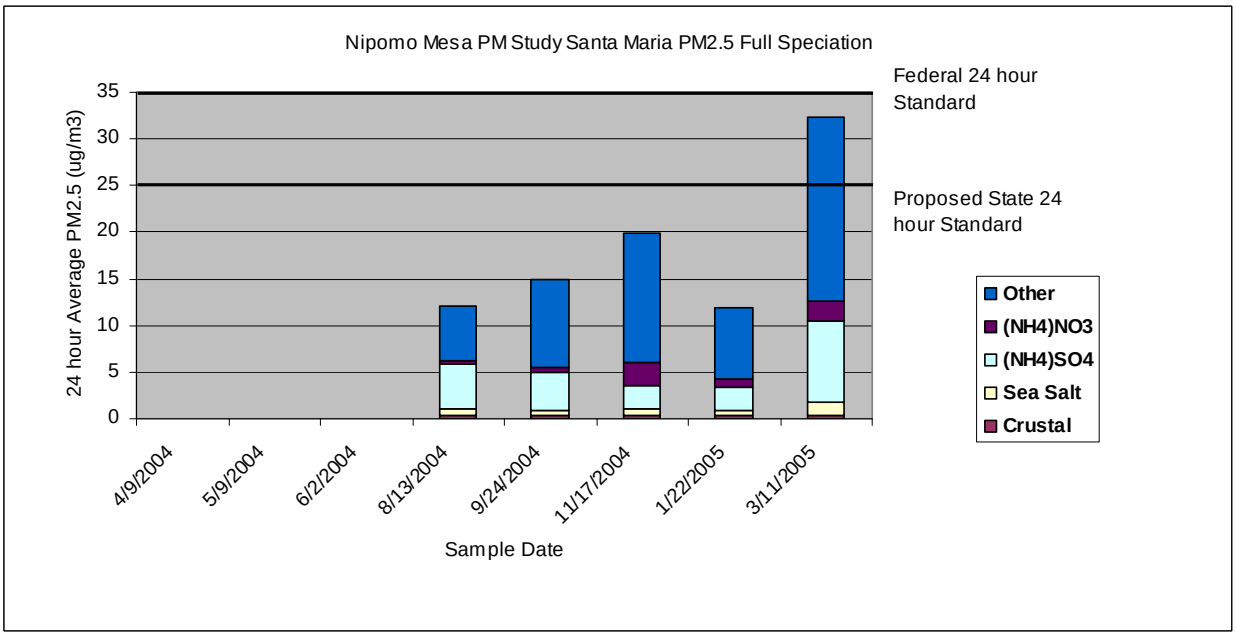

Figure 20. Santa Maria Fully Speciated PM2.5 Samples

INTEGRATED DATA ANALYSIS

Integrating all available data sources can provide additional insight and understanding of the characteristics of the particulate mix present in the study area. Understanding these characteristics is essential in understanding the particulate sources and processes that lead to high particulate concentrations.

Analysis of the size distribution of particulates from a given measurement helps in determining their origin. In general, combustion sources produce fine particulates (<2.5 micron in diameter), while crustal particles entrained by wind or marine particles tend to be coarse particles (>2.5 micron in diameter) (6,9).

Figure 21 presents the PM10 data from the Mesa 2 station allocating the contribution of the coarse fraction and fine fraction of particles. This graph demonstrates that while there is some variation in the fine fraction, the high PM10 days are a result of huge increases in the coarse fraction.

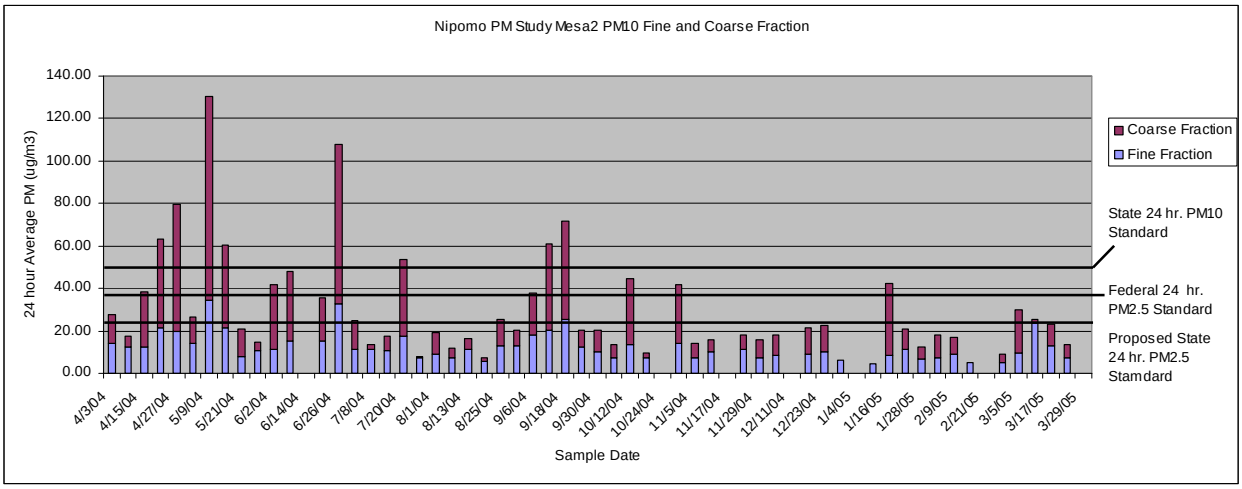

Figure 21. Mesa 2 Coarse/Fine Particulate Fraction

Eleven days were selected where either the PM10 or PM2.5 concentrations exceed standards or the sulfate measurements were significantly higher than the average day. These "episode" days are studied and discussed in detail to provide a more complete understanding of the conditions that lead to standards exceedances or high sulfate levels. Table 6 lists the episode days and the reason for selection. A PM10 threshold of 80 ug/m3 rather than the state 24 hour PM10 standard of 50 ug/m3 for selection of these episode days was used to limit the number of days analyzed to a manageable number.

Appendix B presents graphical data summaries of all data from all sites for each "episode" sample day. Each individual sample day summary presents graphical summaries of data from each site on a map of the study area. These graphical summaries from each site present the data in spatial context, allowing a more complete understanding of the mechanisms involved in

particulate formation and transport. Please refer to the graphical summaries in Appendix B for each episode day in order to fully understand the following discussion of episode days.

Table 6. "Episode" Days

Sample Date	PM10>80 ug/m3	PM2.5>25 ug/m3	High Sulfate
4/9/04			X
5/3/04			X
4/21/04	X		
4/27/04	X		
5/9/04	X	X	
6/26/04	X	X	
7/8/04			X
8/25/04			X
9/12/04	X	X	
9/18/04	X	X	
3/11/05		X	X

High PM10 and PM2.5 Sample Days

Sample days with high PM10 measurements also recorded high PM2.5 concentrations. The meteorological conditions on these days all show strong northwesterly winds. The stronger and more persistent the winds, the higher the particulate concentrations. On days where persistent winds extended inland, PM10 concentrations at the Nipomo Regional Park (NRP) site were also elevated. However, on days with strong winds on the coast, but more variable winds inland, PM10 concentrations at NRP were not elevated.

On all days with high PM concentrations, except 4/27/04, over 80% of the PM10 mass measured at the CDF station was from the dune area. The highest measured PM10 concentration (151 ug/m3) for the study, measured at CDF on 5/9/04, was 100% from the dune area.

Analysis of PM2.5 samples for these days show that all samples were composed of an atypical high percentage of crustal particulates. The crustal fraction of PM2.5 samples is usually a very minor component (6,9). Sea salt concentrations in these samples were also elevated. Sulfate concentrations were quite low, with a higher than average natural marine sulfate fraction.

The high PM concentrations on these "episode" days are clearly caused by northwesterly wind events. Data from the CDF directional PM10 sampler shows that the vast majority of the PM10 mass at CDF is transported from the dune area. The farther inland the wind event, the farther inland the elevated PM concentrations will be seen. The high crustal fraction of the PM2.5 samples further supports the observation that wind driven crustal particles from the dunes are responsible for the high PM observed on the Nipomo Mesa.

The data for sample day 4/27/04 is different from the other high PM "episode" days. While there are some strong northwesterly winds on this day, the winds are much more variable than other high PM "episode" days. The winds at CDF were from the dunes for only 25% of the sample day, but about half of the mass at CDF was from the dunes. Review of PM10 data from the San

Luis Obispo and Morro Bay sites show that this day was one of the highest of the year for these sites, indicating that the background concentration in our region was higher than normal. It appears that this day's PM10 concentrations on the Mesa were elevated due to a brief wind event combined with higher than normal background PM concentrations.

High Sulfate Sample Days

The meteorological conditions on the high sulfate days were quite different from the high PM days. Winds on the high sulfate days were quite calm, rarely exceeding 8 miles per hour. Winds were variable, with little to no wind from the northwest. The most common wind direction for these days was due west, followed by west-southwest.

The coarse PM fraction on these days is significantly lower than most days in the study. The fine PM fraction concentration was average for the study. Approximately half of the fine fraction on these days is composed of ammonium sulfate. The sulfate concentration on these days was significantly higher at the most inland site, Nipomo Regional Park (NRP). For these high sulfate days, the sulfate concentration measured at NRP was 35% to 70% greater than the sulfate measured on the coast.

The data show high sulfate concentrations are associated with light winds from the west to west-southwest, at stations downwind of the ConocoPhillips Refinery. These light winds allow sufficient time for sulfur dioxide emissions from the ConocoPhillips Refinery to convert to sulfate. In addition, the light winds provide little dispersion of pollutants, resulting in higher concentrations.

Regional Episode Day

High PM2.5 measurements and the highest sulfate measurements of the study were recorded from all study sites on 3/11/05. PM and sulfate concentrations on this day were homogeneous across the study sites. The winds were out of the northwest all day, rarely exceeding 7 mph and while the fine PM fraction was quite elevated, there was almost no coarse fraction measured at any study site. About half of the mass of the PM2.5 samples were ammonium sulfate, with almost no crustal or sea salt fraction present in the samples.

Other PM measurements on the central and south coast of California recorded elevated PM2.5 concentrations with little to no coarse fraction. This pattern of measurements was recorded at the San Luis Obispo and Santa Barbara monitoring stations. In addition to the regional elevated PM2.5 measurements, high concentrations of ozone (85 ppb hourly average) were recorded at the Grover Beach monitoring station on this day.

The homogenous elevated PM2.5 and sulfate measurements over such a wide area on the central coast strongly suggest that these high concentrations are a result of long range transport of a polluted air mass. The high ozone readings observed at the Grover Beach monitoring station further support this hypothesis.

ADDRESSING STUDY QUESTIONS

The Nipomo Mesa PM study was conducted to gain a more complete understanding of the particulate levels and sources on the Nipomo Mesa as well as answer specific questions that the previously collected particulate data could not clearly answer. Questions that the study attempted to answer included the following:

1. What source or sources are responsible for the relatively high PM10 concentrations measured at the Ralcoa Way monitoring station?
2. How large of an area is represented by the elevated PM10 concentrations measured at the Ralcoa monitoring site?
3. Why were the average Ralcoa weekend PM10 concentrations higher than weekday concentrations?
4. Is the predominant source of crustal material that appears to be driving the high PM10 concentrations in the Nipomo Mesa area the result of a natural dune/wind process?
5. What role might off-road vehicle use at the Oceano Dunes play in contributing to the observed higher concentrations of particulates in this area?
6. Are the PM2.5 measurements made at Ralcoa representative a larger region, or localized to the Ralcoa area?
7. Are the PM2.5 concentrations on the Nipomo Mesa higher than elsewhere in the county, and do they violate state and/or national standards?
8. Are the sulfur measurements made at Ralcoa indications of a sulfate problem in the Nipomo Mesa area? If so, what are the source(s) of the sulfur?

Question #1:
What source or sources are responsible for the local positive bias in the Ralcoa PM10 Data?

Review of historical data from the Nipomo Mesa prior to this study showed a consistent pattern of PM10 concentrations being highest near the coast and declining at sites farther inland. One exception to this pattern was the Ralcoa Site which consistently measured higher PM10 levels than the other PM10 monitoring sites on the mesa, as shown in Figure 22 below. Figure 22 presents data from a small PM10 study performed in the spring and summer of 2002. In this study, the PM10 concentrations measured at Ralcoa showed a consistent positive bias of about 30 ug/m3 as compared to the other Nipomo Mesa sampling locations, even the Nipomo CDF (NCDF) site that is significantly closer to the coast that the Ralcoa Site.

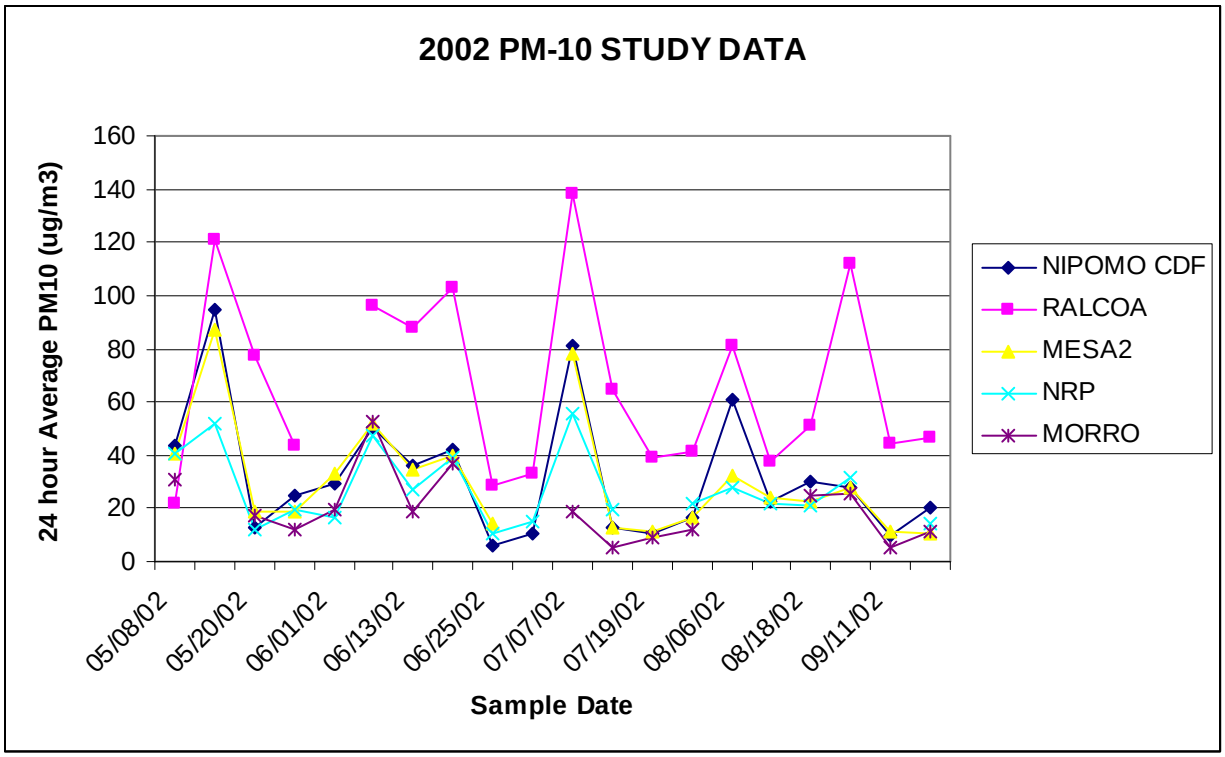

Figure 22. 24 hour PM10 Measurements Made in 2002

The Ralcoa monitoring site was located in an industrial area surrounded by a wide variety of potential sources that could account for this observed positive bias in the Ralcoa data. These local sources include a concrete crushing operation, numerous auto wrecking operations, and dirt roads. The Ralcoa site was also surrounded by large eucalyptus trees that over the years had grown to the point where the site no longer met siting criteria for the various parameters measured there. As a result, the site was shut down in late 2002.

The higher Ralcoa data is of concern because there are small residential areas nearby that could be exposed to the higher PM concentrations. Determining the source or sources that caused the higher concentrations is essential in understanding this phenomenon and its implications.

The Hillview site measured consistently higher PM10 values as compared to the other PM10 site locations on the Mesa (see Figure 4). This pattern at Hillview is very similar to the pattern observed at Ralcoa. Hillview, like Ralcoa is located near dirt roads. It is likely that the localized higher PM10 readings at both Hillview and Ralcoa are due to there proximity to dirt roads. Technicians changing the PM10 filter at Hillview often observed cars travel along these dirt roads (composed of very fine sand particles) resulting in a large plume of particulates that would drift from the roadway to the sampler location.

Question #2:
How large of an area is represented by the elevated PM10 concentrations measured at the Ralcoa monitoring site?

This study as well as previous studies clearly show that the elevated concentrations observed at Ralcoa and now at Hillview are very localized areas of elevated PM10 concentrations. The study data demonstrates that the Hillview PM10 values are consistently higher than the Bendita site that is in very close proximity to the Hillview site. The previous 2002 study also showed that the higher Ralcoa PM10 concentrations were not present at the nearby Nipomo CDF monitoring station. One can conclude that these higher PM10 concentrations are limited to small areas on the Mesa near regularly traveled dirt roads. One should expect other areas on the Mesa with dirt roads to also experience higher PM10 concentrations.

Question #3
Are the average weekend PM10 concentrations on the Mesa higher than weekday concentrations?

Comparison of weekend verses weekday concentrations can be help identify potential sources contributing to measured concentrations. If activities that are more prevalent on either weekends or weekdays are making a significant contribution to the measured concentration, one would expect the average weekend or weekday concentrations to show a positive bias on those days of the week. This analysis could be used to determine if off road activities (mostly on summer weekends) at the Oceano Dunes State Park are creating direct particulate emissions (from both fuel combustion and crustal particulate disturbed by the offroad activities) that would significantly impact the Mesa area. Attendance data from the Park show that on average there is about a 50% greater use on weekends verses weekdays [(3)]. If there is a direct impact from this activity on particulate concentrations, the weekend average particulate concentrations should be higher than the weekday averages. This analysis does not address secondary effects of offroad vehicle use such as denuding natural vegetation which results in less stable dune structure, allowing winds to entrain particulates easier.

In the 2003 review of PM data from the Mesa, a weekend verses weekday analysis of PM10 data was performed. In this analysis an average concentration for weekdays was calculated and compared to an average concentration for weekends. This analysis was performed on data from the year 2000 and showed that Ralcoa had a significantly higher weekend average PM10 concentration than the average weekday average.

In this study, weekend/weekday analysis was performed on the study data. While performing this analysis it became apparent that even one full year of data (a total of 60 samples, approx. 17 weekend and 43 weekday) is too small a sample size to account for normal data variations that can result from cyclical weather patterns or other phenomena that affect particulate concentrations. It became apparent that a five to ten year data set is necessary to calculate average weekend/weekday concentrations without the natural variability of the data causing a bias to the averages. The larger the data set, the less effect other variables, such as meteorological conditions have on the calculated average values.

Average weekend and weekday averages were calculated for all sites where a five to ten year data set was available (Ralcoa Way, Mesa 2, Nipomo Regional Park, Atascadero, and Morro Bay). The averages were calculated for the three sites on the Mesa and other District operated sites elsewhere in the county. The analysis of data from locations elsewhere in the county was

performed as a control to evaluate the significance of the data from locations on the Mesa. Figure 23 presents the average weekend/weekday concentrations from selected sites for all data available for the period 1995 through October 2006.

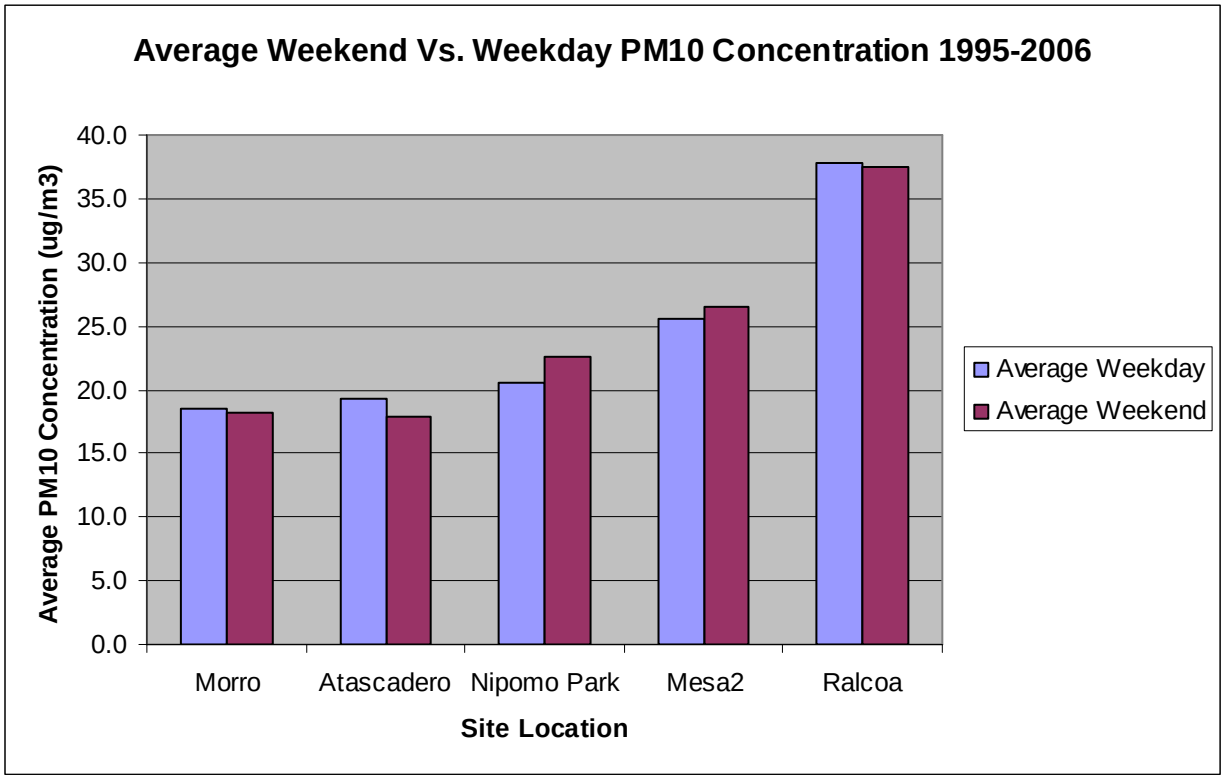

Figure 23. Average Weekend Vs. Weekday PM10 Concentrations

Figure 23 shows some interesting differences in average weekend verses weekday PM10 concentrations in the Nipomo area compared to other locations in the county. Mesa 2 and Nipomo Regional Park in particular have slightly higher average weekend concentrations, while Morro Bay and Atascadero show slightly lower weekend concentrations compared to weekday PM10 levels. Interestingly, with the larger data set, Ralcoa no longer shows a higher weekend average concentration.

In an attempt to provide a more complete analysis of the data, weekend/weekday averages were calculated for both the summer (June-September) and non-summer periods. Activity in the summer months, both in attendance as well as vehicle usage in the Park is almost twice the activity as for non-summer months [(3)]. If there is an impact from these activities, one would expect the data to show a greater weekend bias for the summer months than the non-summer period. Figures 24 and 25 below present the weekend/weekday particulate averages for both the summer and non-summer months. While this analysis is intended to suggest whether there is a significant direct impact from the Oceano Dunes State Park, any other activity with PM emissions that occurs primarily on weekdays or weekends will also influence its outcome.

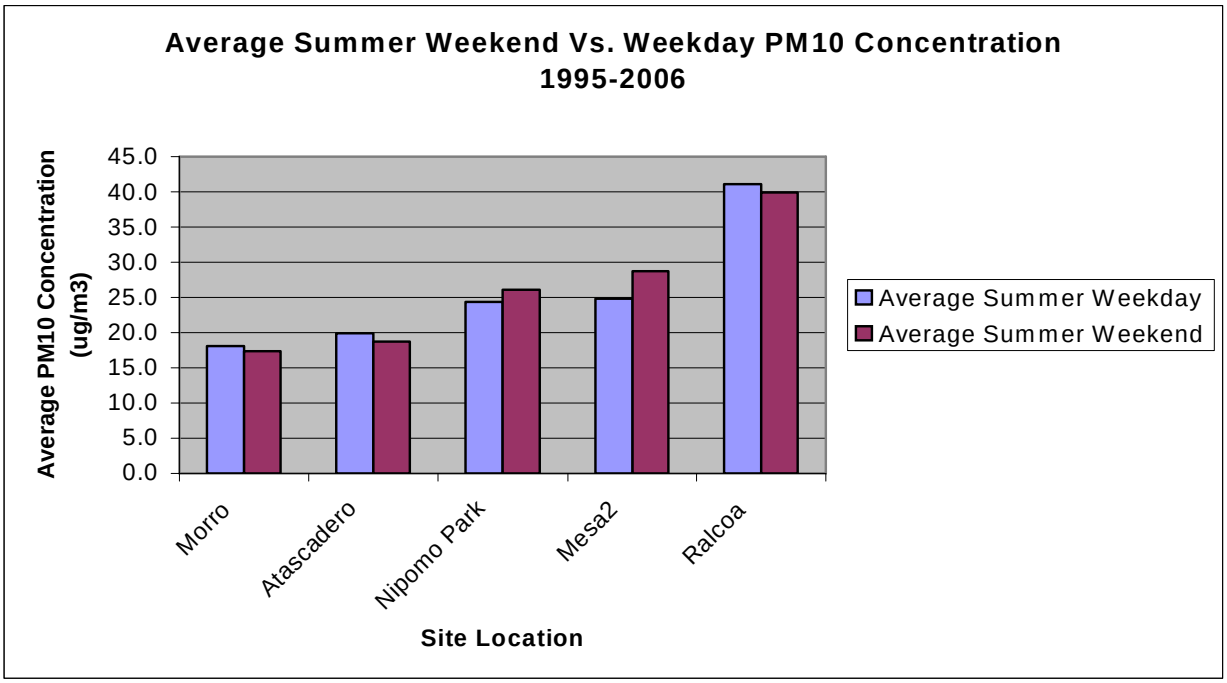

Figure 24. Average Summer Weekend vs Weekday PM10 Concentration

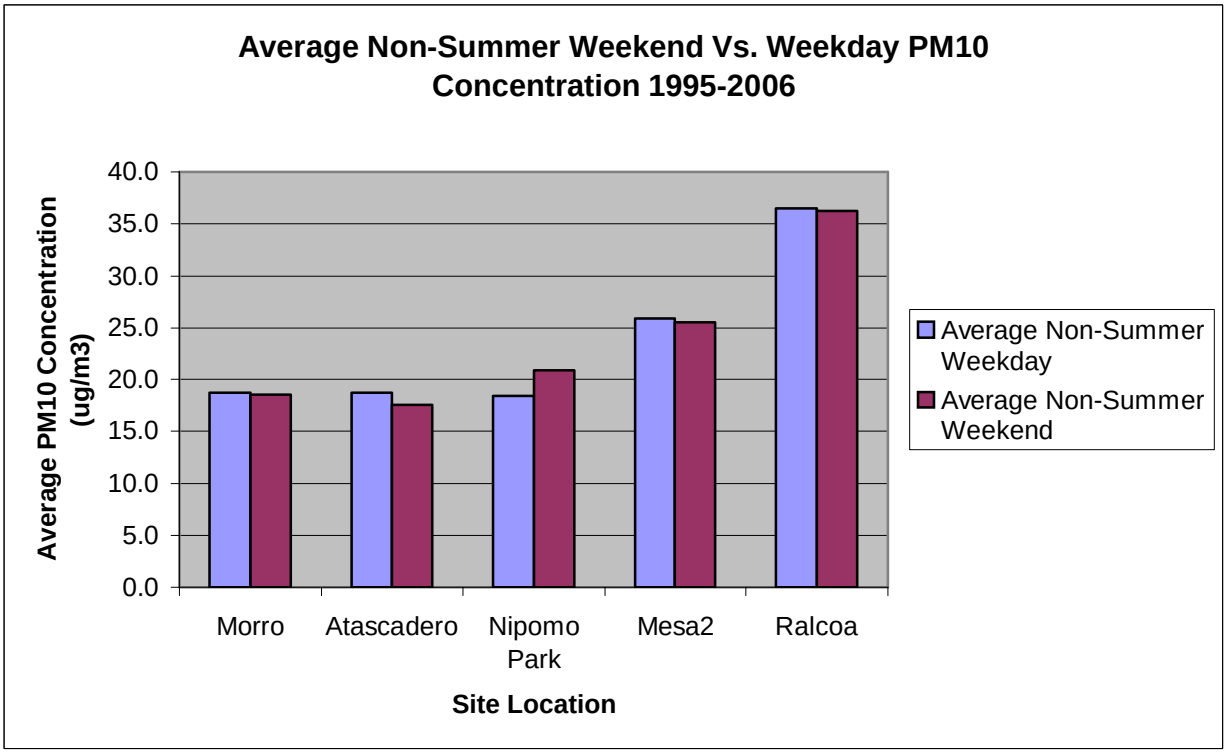

Figure 25. Average Non-Summer Weekend vs Weekday

Morro Bay and Ralcoa show somewhat insignificant weekend/weekday differences for both seasons. Atascadero has significantly lower weekend readings for both seasons. Nipomo Regional Park shows significantly higher average weekend concentrations for both seasons. The Mesa 2 analysis shows a significantly higher (15%) weekend bias for the summer months and an insignificant bias for the non-summer months.

The Atascadero monitoring station is located next to a school yard, in an area that could be considered the central business district; the data indicate significantly more activity on the weekdays verses the weekends in the area of this monitoring station, as expected. The Nipomo Regional Park monitoring station is located adjacent to a large community park, which receives significantly more activity on the weekends compared to weekdays. It is difficult to explain why the bias is greater for the non-summer months, as the park is more active in the summer than the non-summer period. It is possible that the meteorological conditions in the non-summer months are less conducive to disperse local emissions.

The Mesa 2 site is located in an area with no apparent local activities that are more prevalent on the weekends. The Mesa 2 data analysis results suggest that the off road activities upwind at the dunes are impacting air quality in the Mesa.

If this is indeed the case, however, it is unclear why the Ralcoa analysis does not show a similar long-term weekend bias. One possible explanation, as noted in the discussion of Question #1 above is that the heavy influence of local sources at the Ralcoa site cancels out the potential weekend effect of the dunes suggested at Mesa 2.

This analysis indicates that activity at the Oceano Dunes Park could be causing measurable air quality impacts on the Mesa. However, the conflicting data from Ralcoa, as well as the possibility that other weekend/weekday activity patterns may be influencing this analysis, make this conclusion quite tentative. Further study will be needed to provide a more definitive answer.

Question #4
Is the predominant source of crustal material that appears to be driving the high PM10 concentrations in the Nipomo Mesa area the result of a natural dune/wind process?

This study provides very strong evidence that crustal material from the dune complex upwind of the Mesa is driving the highest PM10 concentrations measured on the Mesa. The measurements made at the CDF site location with a directional PM10 sampler (programmed to only sample when the wind is blowing from the dune area) provides the most compelling evidence of the impact from the dune area. Figure 26 presents the PM10 from CDF, separated between mass from the dune area and mass from all other areas. Figure 27 presents the PM10 data from the Mesa 2 site separating the fine and coarse fraction of the total PM10 concentration. Looking at both figures together, it is clear that the highest concentration days are due to significant mass contributions from the dunes and that on those same days the coarse fraction becomes the dominate fraction of the PM10. These two factors are compelling evidence that coarse

particulate from the dune area is causing the highest PM10 measurements on the Nipomo Mesa. While there was no elemental analysis performed on the PM10 samples, it is generally accepted in the scientific community that the coarse PM10 fraction is composed mostly of crustal elements.

Further evidence that crustal materials from the dune area are the major contributor to the highest PM10 concentrations is presented in Figures 28 and 29. Figure 26 presents the relationship between the square of the average wind speed and the PM10 concentration at Mesa 2 in 2001 (for sample days without the influence of rain). Figure 29 presents the relationship between the percent of time the wind is blowing from the dune area with a speed greater than 5MPH at the CDF site and the PM10 concentration measured at the CDF site. While this data demonstrates a relationship between wind speed and PM10 contribution from the dune area, as one would expect, there are factors other than wind speed influencing the PM10 concentration.

The wind driven crustal particulate deposition is also visible from aerial photographs. Figure 3 in an earlier section shows depositional land forms along the clearly defined prevailing northwest daytime wind flow.

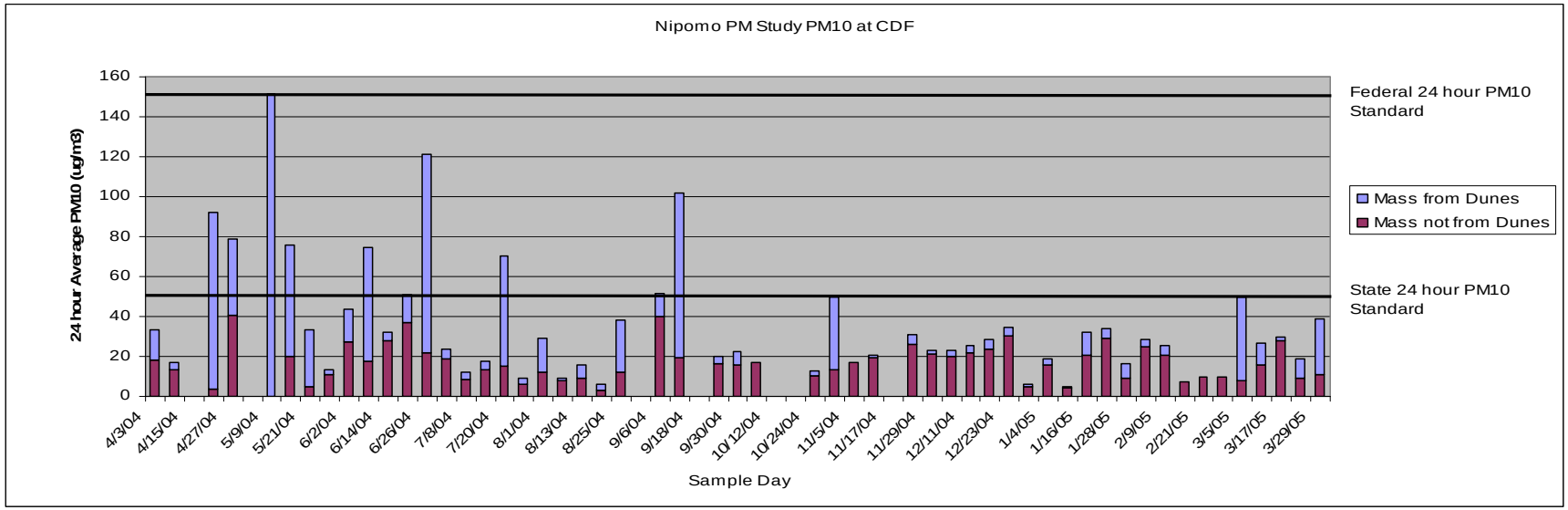

Figure 26. CDF PM10 Dune/Non-Dune Contributions

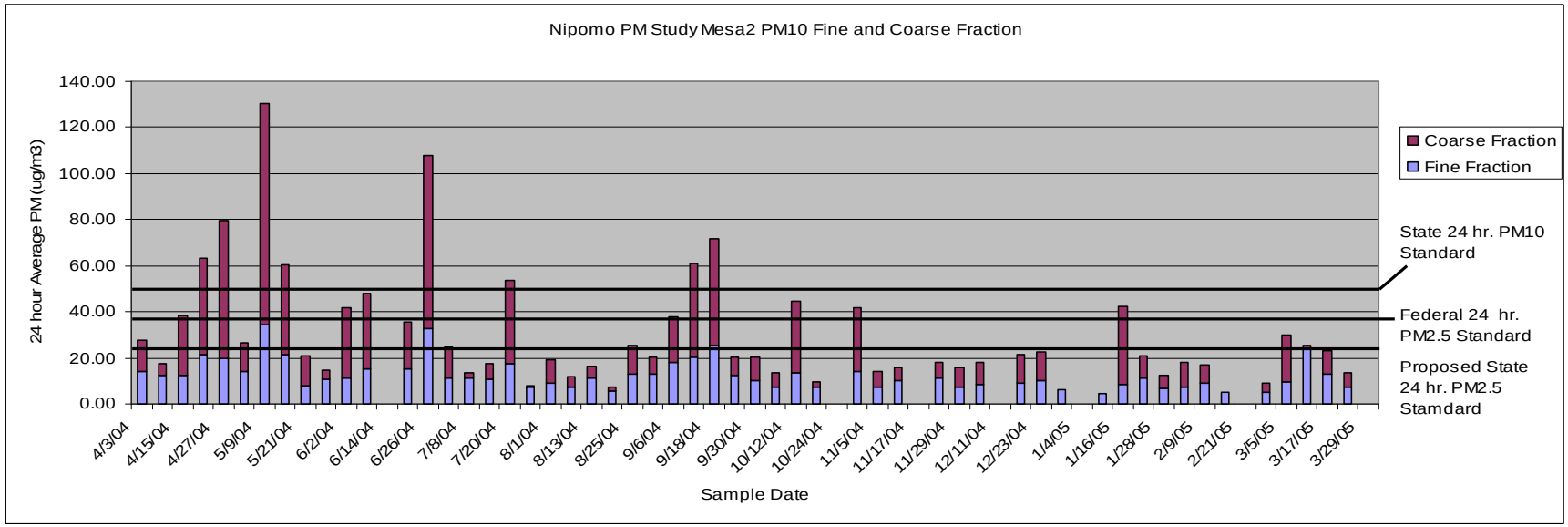

Figure 27. Mesa 2 Coarse and Fine Fraction PM

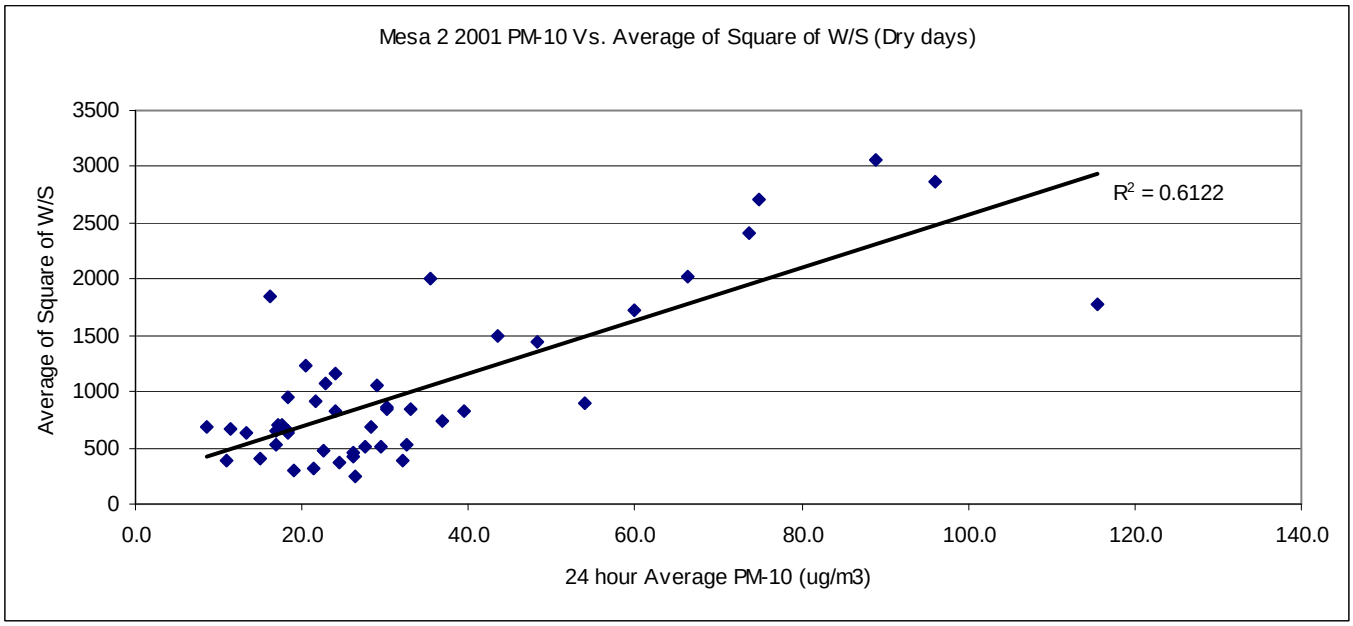

Figure 28. Mesa 2 Wind Speed/PM10 Concentration Relationship

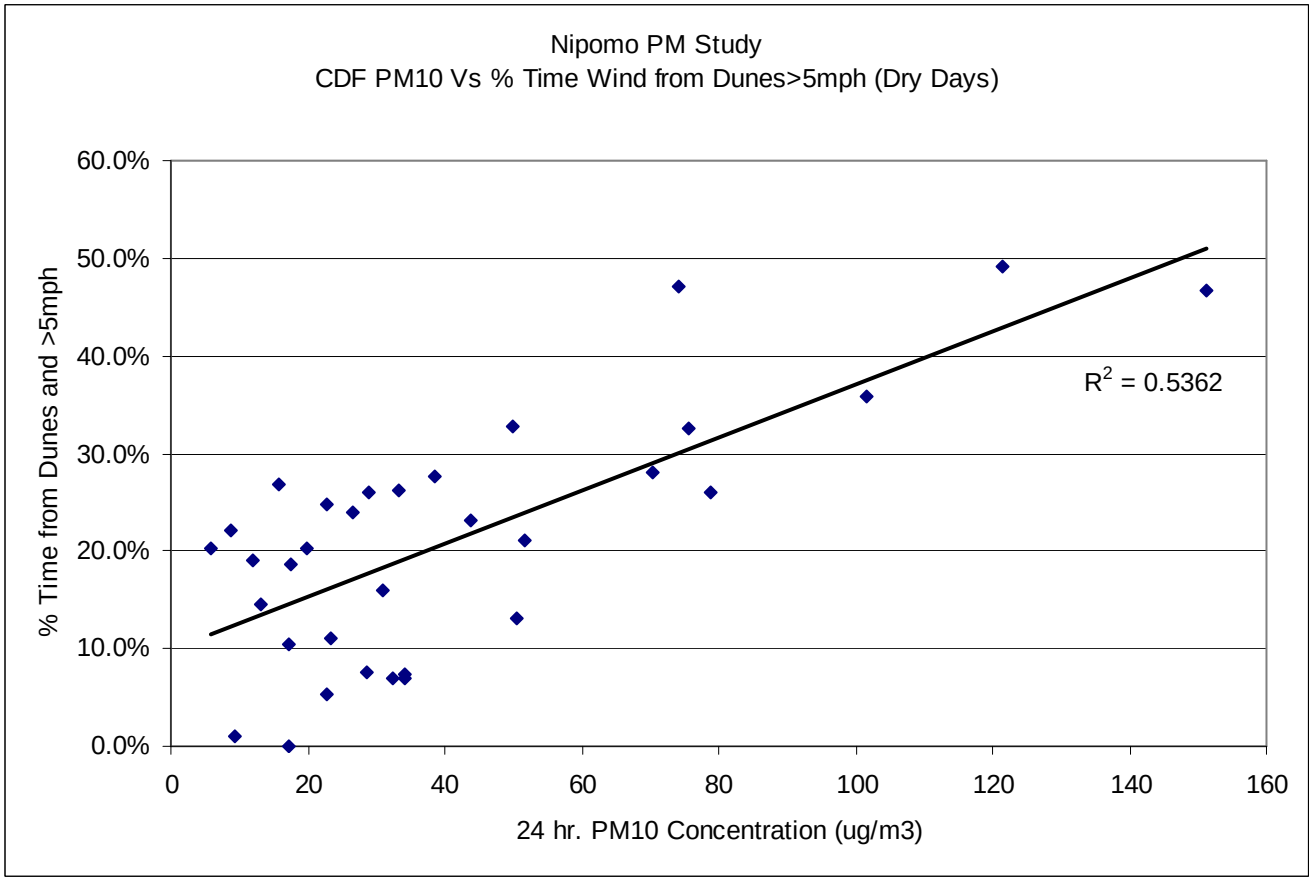

Figure 29. CDF Winds From Dune Area/PM10 Concentration Relationship

The data from the study clearly demonstrates that the highest PM10 concentrations measured on the Mesa are largely due to wind driven crustal material from the upwind dune area. The data does not show however, whether this is a "natural" event, or one that is exacerbated by human activities.

Wind blown crustal particulates become entrained in an air mass as part of "natural" processes. In areas of loose sandy soil it is common for high wind events to cause natural dust storms. This is essentially what is happening on the coastal dune complex, with the dust storm plume extending inland to the Mesa area. However, there are substantial human activities on the dunes that could be contributing to this problem. Data presented above in question #3 suggests the possibility that summer weekend activities are creating a 15% higher average PM10 concentration at Mesa 2 from only primary vehicular impacts. In addition to these primary impacts, the off road activities on the dunes have the secondary affect of denuding the dunes of natural vegetation. The loss of this natural vegetation may cause degradation of the dune structure, allowing easier entrainment of particles during a wind event.

While the study data suggests some level of impact from the off road activities, determining the extent of that impact is beyond the scope of the study. Nonetheless, it is important to remember that the health impacts are the same, regardless of how much is caused by human activities verses natural processes.

Question #5
What role might off-road vehicle use at the Oceano Dunes play in contributing to the observed higher concentrations of particulates in this area?

The role of off road vehicles at the Oceano Dunes is discussed above in Question #4.

Question #6
Are the PM2.5 measurements made at Ralcoa representative of a larger region, or localized to the Ralcoa area?

The PM2.5 measurements referred to in this question are 13 measurements at the Ralcoa location made in September through November 1995. Prior to this study, these were to only PM2.5 measurements made on the Mesa. These limited measurements ranged between 27ug/m3 and 9 ug/m3 and were made between September and November 1995. Because these measurements were made at only one location, it was not clear if these measurements were representative of the entire Mesa area, or just that one location.

The extensive PM2.5 sampling from this study clearly shows homogeneous concentrations over the western Mesa area in most cases. Somewhat higher concentrations were measured at the Bendita monitoring location in the winter, and appear to be due to wood burning. The range of concentrations measured in1995 is in line with the concentration ranges measured in this study (see figures 12-15).

Question #7
Are the PM2.5 concentrations on the Nipomo Mesa higher than elsewhere in the county, and do they violate state and/or national standards?

As described previously, the extensive PM2.5 measurements demonstrate that the PM2.5 concentrations on the Mesa are higher than elsewhere in the county. The study data also suggest that the PM2.5 concentrations on the Mesa violate the state annual standard, the proposed state 24 hour standard and the federal annual standard; one sample came very close to violating the federal 24 hour standard. It should be noted that the PM2.5 study data was collected using non-Federal reference samplers, so it can not be used officially to demonstrate attainment or non-attainment of any standard. Nonetheless, the data strongly suggests that at least some of these standards are being violated on the Nipomo Mesa.

Question #8
Are the sulfur measurements made at Ralcoa indications of a sulfate problem in the Nipomo Mesa area, and what is the source of the sulfur?

This question refers to the 13 fine particulate measurements from the Ralcoa site in 1995 discussed above. These samples were analyzed for various elements (including sulfur) by XRF. The sulfur concentration of these samples was higher than expected for a rural coastal area, with the highest sample representing about 9ug/m3 sulfate. Unfortunately, the limited sample size was insufficient to determine if they represent the typical range of sulfate concentrations for that area. In addition, the analysis did not differentiate between ammonium sulfate and elemental sulfur, which is stored in large quantities at the ConocoPhillips Facility. The extensive PM10 sulfate analysis, PM2.5 sulfur and sulfate analysis performed on samples taken from various locations on the Mesa during this study provides a sufficient data set to evaluate these questions.

The highest sulfate measurement during this study was about 1/3 of the state sulfate standard; thus, by that measure, there is not a “sulfate problem” on the Mesa. There currently is no area of California that is in violation of the state sulfate standard.

The sulfate concentrations measured on the Mesa however are higher than those measured from other rural coastal areas. Figure 30 presents the average sulfate concentrations for the study period from other coastal areas of California where sulfate is measured.

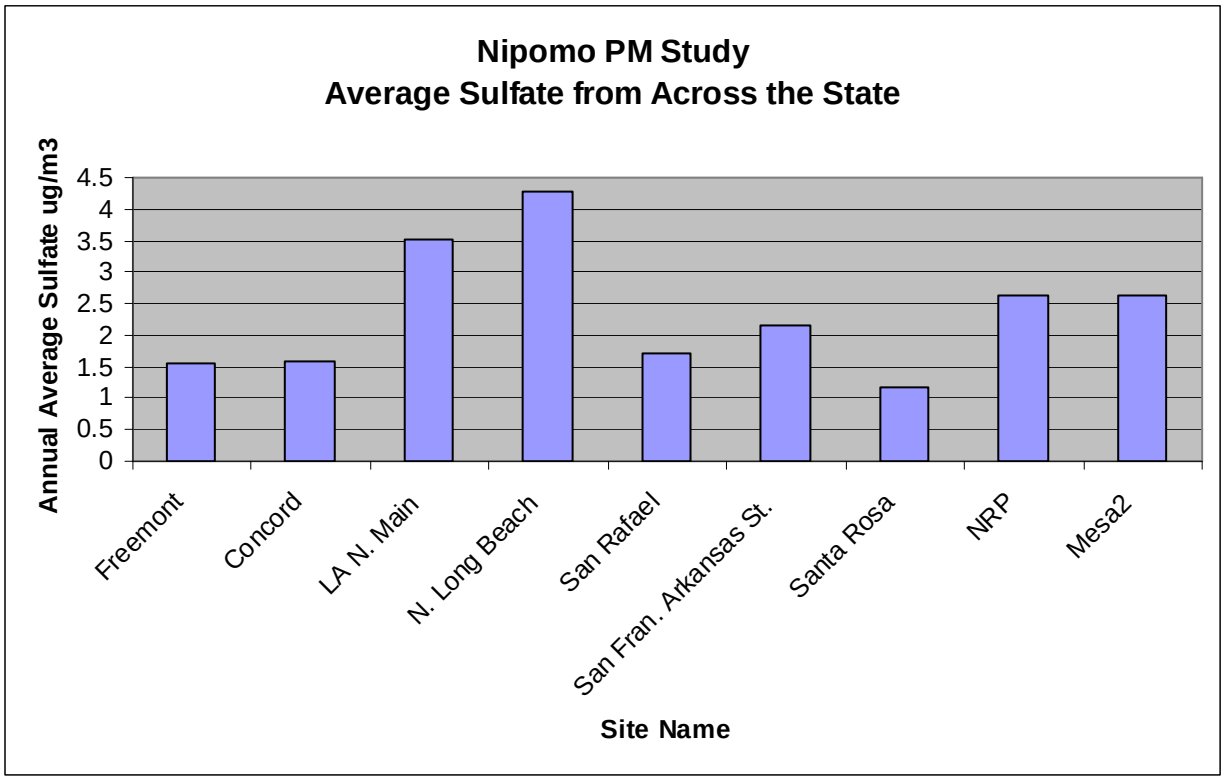

Figure 30. Average Sulfate Concentrations

The only other coastal areas to measure higher average sulfate values are the heavily industrialized areas of Los Angeles and Long Beach Harbor. Marine vessels are substantial sources of sulfur dioxide emissions and associated sulfate formation, so this is not surprising.

Data from this study also shows that the sulfur measured by XRF is almost entirely in the form of sulfate, and not elemental sulfur (or other sulfur compounds). Figures A-10 through A-12 demonstrate the strong correlation between sulfate concentrations calculated from elemental sulfur measurements and sulfate measured by ion chromatography. This strong correlation shows that the sulfur measured on the Nipomo Mesa is in the form of sulfate, and not elemental sulfur as some had theorized.

The sources of sulfate on the Mesa are very difficult to determine. Like most pollutants, there can be many different sources that contribute to the ambient concentrations. As described earlier, it has been established that "marine sulfate" resulting from wave action is one contributor to sulfate levels in most coastal areas. This report documents that the "marine sulfate" portion of the total measured sulfate can be calculated by using the ratio of chlorine to sulfur in the sample following the procedure established by Dr. Cahill of U.C. Davis (4,7).

Figure 31 presents the marine and anthropogenic fractions of the total sulfate measured at the Mesa 2 site. Analysis of meteorological conditions on sample days where there is significant marine fraction show the presence of a strong sea breeze; days with no marine fraction have a much calmer sea breeze and less atmospheric dispersion.

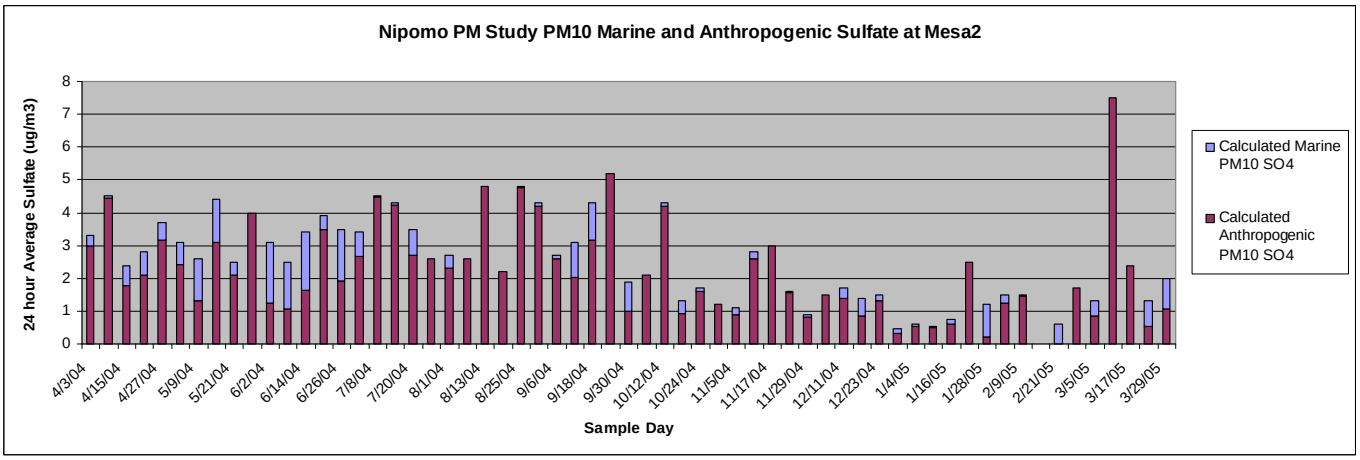

Figure 31. Mesa 2 PM10 Marine and Anthropogenic Sulfate

The largest source of sulfur dioxide (SO2) in the county is the ConocoPhillips refinery. This facility emitted over 2700 tons of SO2 in 2005. This represents over 99% of the SO2 emissions from all stationary sources in the county and about half of the total sulfur dioxide emissions from all sources countywide; emissions from marine vessels are the other significant source (43% of total emissions) [(13)]. Given the magnitude of these emissions, it is highly likely that the ConocoPhillips facility is a significant contributor to sulfate levels in southern San Luis Obispo and northern Santa Barbara Counties.

Attempting to apportion the sulfate measured in any particular sample to one single source is very difficult. Wind direction fluctuations over the 24 hour sample period can limit the portion of the total sample potentially collected from one particular source. Other meteorological variables, variations in other local sources, and variations in overall background concentrations can also complicate apportioning a measured concentration to one particular source. In addition, the rate of conversion from SO2 to sulfate can range from a few minutes to many hours depending on several atmospheric variables, including the presence of water droplets, certain metallic particulates, and ozone concentration [(9)]. If the distance downwind from the source where the sampling is performed is too close for the atmospheric conditions at the time, the majority of sulfur dioxide may have not yet converted to sulfate. The farther downwind from the source, the more likely the SO2 to sulfate conversion has occurred, but also the more dispersion of the emissions, resulting in less measurable impact.

Figure 32 presents the PM10 sulfate measurements from all study sites. This graph also shows a seasonal variation in sulfate concentrations, with the wet winter months being the lowest. For many of the sample days, all of the study sites measured very similar concentrations, indicating little direct impact from a local source. However, there are a number of sample days where the Nipomo Regional Park (NRP) sulfate value is significantly higher than the other study sites. Review of the meteorological conditions for these sample days shows light winds from the direction of the COP facility for a substantial portion of the day. See Appendix B for graphical data summaries demonstrating these conditions.

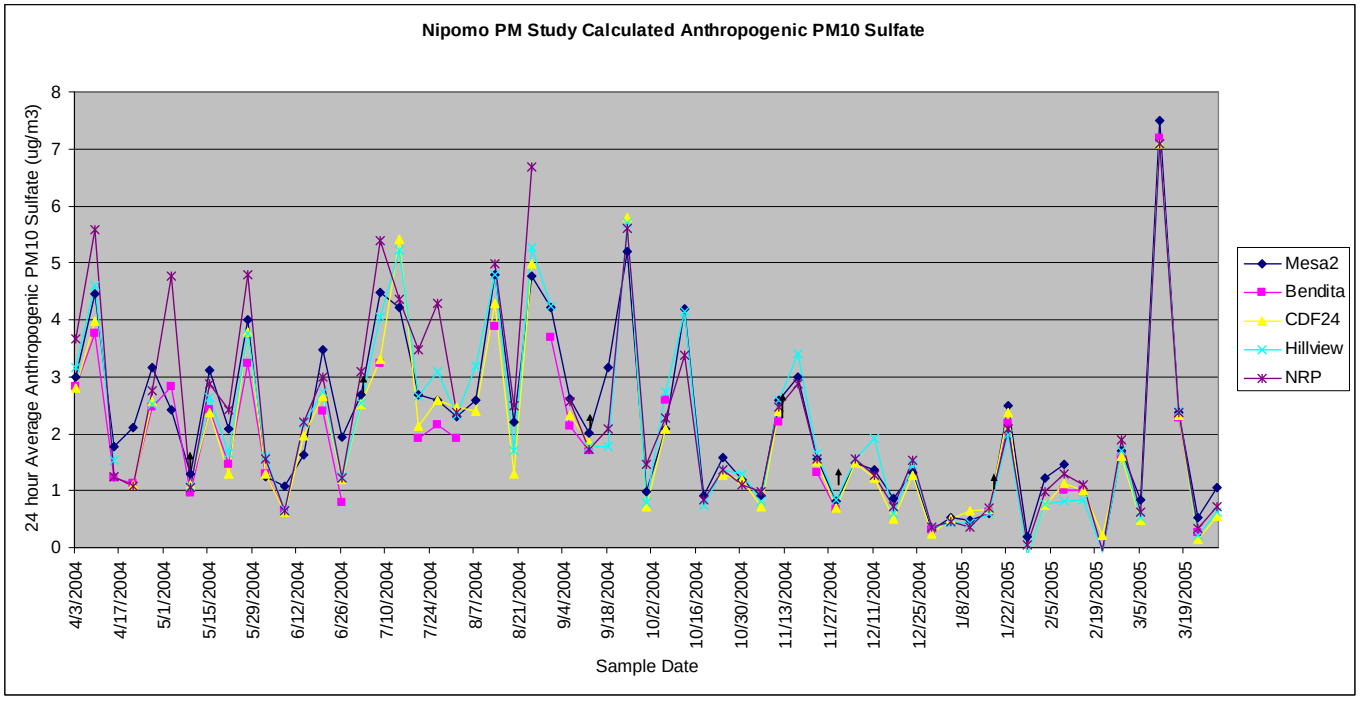

Figure 32. PM10 Sulfate Measurements

This could indicate that the other study sites are too close to the COP facility for the SO2 emissions to have time to convert to sulfate. The NRP site location, being farther downwind, may have allowed more time for this conversion to occur, resulting in a higher sulfate measurement. With no other sources in the county other than marine vessels emitting anything close to the SO2 emissions from COP facility, it is unlikely that another source nearby the NRP monitoring station caused the higher sulfate measurements at NRP.

CONCLUSIONS

This year long study clearly documents a serious particulate pollution problem on the Nipomo Mesa. Numerous exceedances of both state and federal health standards were measured as shown below:

1. The state 24 hour PM10 standard of 50 ug/m3 was exceeded at one or more monitoring station on 17 out of the 61 sample days (28%).
2. The federal 24 hour PM10 standard of 150 ug/m3 was exceeded at the CDF station on one day out of the 60 sample days.
3. The state annual PM10 standard of 20 ug/m3 was exceeded at all five PM10 sampling locations in the study.
4. The state annual PM2.5 standard of 12 ug/m3 was exceeded at two of three PM2.5 sampling locations in the study.
5. The federal annual PM2.5 standard of 15 ug/m3 was exceeded at one of the three PM2.5 sampling locations in the study.
6. The anticipated state 24 hour PM2.5 standard of 25 ug/m3 was exceeded at one or more of the sampling stations on 5 out of the 61 sample days (8%).

The study results clearly identify wind blown crustal particles as the single largest cause of the high particulate concentrations measured on the Mesa. Meteorological data shows wind events entraining crustal particulate from the dune fields upwind of the Mesa area as the likely cause; data from the directional PM10 sampler at the CDF station strongly supports this conclusion. Elemental analysis of the PM2.5 samples further confirm that on these high particulate days, the largest fraction of particles are composed of the crustal elements of silicon, iron, aluminum, and calcium. Thus, the data clearly implicates wind events entraining crustal particulates from the dune fields on the coast and transporting them inland as the primary cause of the PM10 and PM2.5 levels measured on the Mesa.

The study results also show that as the winds progress inland and begin to decrease, the particulate concentration also decreases dramatically. The data from the Nipomo Regional Park monitoring station measured the lowest PM levels in the study due to being farther inland than the other monitoring site locations. Localized areas of elevated concentration, where the particulate concentrations were even higher than most areas of the Mesa were also identified. Dirt roads with fine sandy soil were seen to add an additional particulate load to the air in their vicinity, contributing to some of the highest particulate measurements.

This study does not definitively identify the impact to particulate concentrations on the Mesa from off road vehicle use at the Oceano Dunes State Park Offroad Vehicle Area. A weekend/weekday analysis of long term PM data was performed to see if any direct impact to particulate concentrations from the offroad activities was apparent; while the analysis did show higher average weekend concentrations at the Mesa 2 monitoring site, the results were not conclusive. Secondary impacts from the vehicle activity, such as denuding the natural vegetation, may also play a role in destabilizing the dunes and allowing the winds to pick up the fine particles and carry them downwind. However, this is a question of geologic processes outside the scope of this study.

Regardless of whether human activities or natural sources are responsible, the study documents the frequent occurrence of unhealthful particulate levels on the Mesa. It is important to note that simply because the composition of the particulates is mostly natural crustal particles, the health implications are not lessened. All fine airborne particulate matter, regardless of composition, can cause respiratory distress when inhaled, especially to the very young, the elderly and those with compromised respiratory systems. In addition, sand particles are high in crystalline silica, a known carcinogen with a high risk factor (14,15).

The study data demonstrated that sulfate concentrations on the Nipomo Mesa are well below the California state sulfate standard, though the levels seen there are higher than other rural coastal areas. On days with light winds, the study data showed monitoring locations downwind from the ConocoPhillips Refinery complex with significantly higher sulfate concentrations than sites located upwind from the refinery.

RECOMMENDATIONS

As a result of this study, it is recommended that the District install a federal reference method (FRM) PM2.5 sampler and a real-time tapered element oscillating microbalance (TEOM) PM10 analyzer in the more populated area of the Mesa. The FRM PM2.5 sampler will confirm the representativeness of the study PM2.5 measurements made with non-certified samplers. The TEOM analyzer will provide hourly PM10 measurements 24 hours a day. This real time PM10 data can be examined with real time wind data to allow for further understanding of the wind events that are causing the unhealthful particulate concentrations. The continuous TEOM data will also provide a much larger PM10 database, which may allow a more conclusive weekend/weekday analysis of the PM10 data.

To reduce the elevated PM concentrations observed in localized areas near dirt roads, it is recommended that the District move forward with the proposed PM control strategies adopted by the Board as part of the 2005 Particulate Matter Report to meet the requirements of SB 656. This includes a control strategy to reduce emissions from high volume unpaved roads by working with County Public Works, County Planning and Building Department, South County Advisory Council and developers to evaluate and implement measures such as speed limit reductions, application of dust suppressants or paving new and existing unpaved roads in areas of higher population where exposure is greatest.

Finally, the District should work with the South County Advisory Council, State Parks, County Public Works and County Planning and Building Departments to further investigate the effects of off-road vehicle use at the SVRA in contributing to the elevated PM levels measured on the Mesa, and what mitigation efforts are reasonable and feasible to reduce that impact.

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NIPOMO PARTICULATE STUDY

APPENDIX A - DATA VALIDATION AND QUALITY ASSURANCE

Table of Contents:

STUDY OVERVIEW

The Nipomo Mesa PM study was designed to answer numerous questions concerning the historical measurement of high concentrations of particulate matter on the Nipomo Mesa. A detailed review of historical PM data from the Nipomo Mesa area performed in late 2003 generated a variety of questions that could not be adequately answered with the data gathered to date

In order to gather the data necessary to answer these questions, a year long particulate measurement study was designed for the Nipomo Mesa area consisting of the following measurements:

- What source or sources are responsible for the relatively high PM10 concentrations measured at the Ralcoa Way monitoring station?
- How large of an area is represented by the elevated PM10 concentrations measured at the Ralcoa monitoring site?
- Are the average weekend PM10 concentrations on the Mesa higher than weekday concentrations?
- Is the predominant source of crustal material that appears to be driving the high PM10 concentrations in the Nipomo Mesa area the result of a natural dune/wind process?
- What role might off-road vehicle use at the Oceano Dunes play in contributing to the observed higher concentrations of particulates in this area?
- Are the PM2.5 measurements made at Ralcoa representative a larger region, or localized to the Ralcoa area?
- Are the PM2.5 concentrations on the Nipomo Mesa higher than elsewhere in the county, and do they violate state and/or national standards?
- Are the sulfur measurements made at Ralcoa indications of a sulfate problem in the Nipomo Mesa area? If so, what are the source(s) of the sulfur?.

These measurements were performed on the schedule noted above from April 2004 through the end of March 2005.

The following sections present specific quality data, data validation criteria utilized, as well as a discussion of observed strengths and weakness of each measurement method.

PM10 MEASUREMENTS

PM10 was measured with hi-volume samplers followed by gravimetric analysis and ion chromatography of all valid filters. Procedures for calibration, sampling, and weighing followed the District Standard Operating Procedure [12].

Co-located samplers were operated at the Mesa 2 monitoring station to access precision of these measurements. As can be seen in Figure A-1, the collocated measurements demonstrate very good measurement precision.

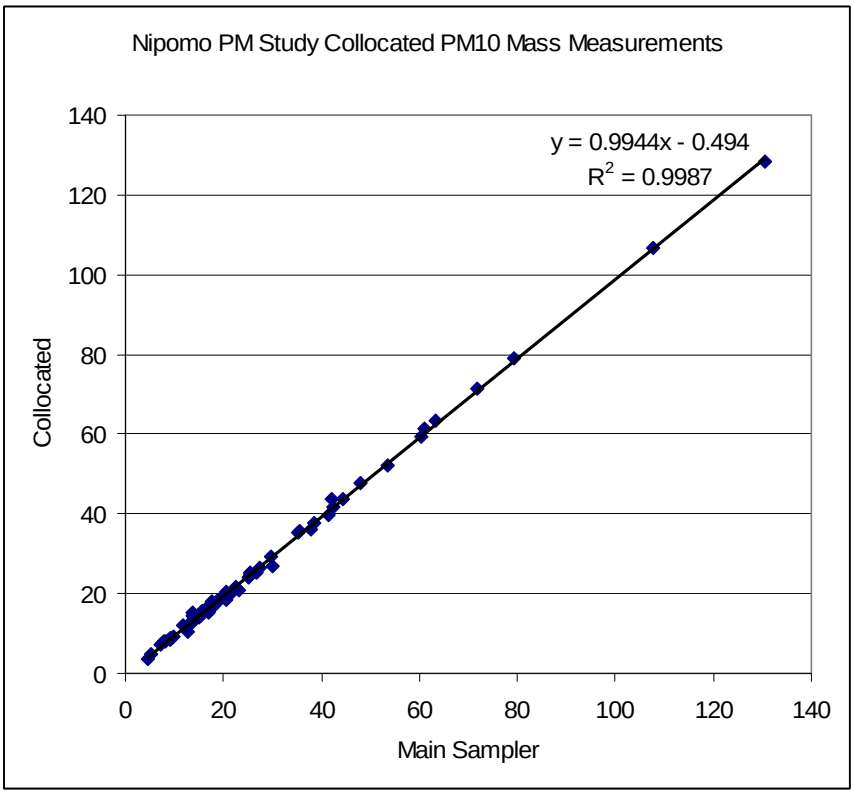


Figure A-1. PM10 Collocated Measurements

The overall upper and lower 95% probability limits for PM10 from the study data set are +9.5% and -4.8% respectively. EPA specifies that 95% probability limits be calculated excluding all values where either the main or collocated value is lower than 20 ug/m3 (40CFR58 Appendix A) to provide a more representative value. Excluding values lower than 20 ug/m3 from the study data, the upper and lower 95% probability limits are +6% and -2.7%.

The San Luis Obispo County APCD PM10 weighing lab is audited by California Air Resources Board (CARB) each year. The weighing lab was last audited on April 28, 2005 passing on all criteria.

The validation criteria used for the study is the same criteria used for other District PM10 sampling [12]. Table A-1 summarizes the data validation criteria.

PARAMETER	MEASURED BY	VALIDATION CRITERIA
Sampler Flowrate	calibrated flow recording device on sampler	36-44 cfm
Sample Duration	elapse time meter on sampler	24 hrs +/- 1 hr
Filter Inspection	Visual inspection	no tears, pinholes, obvious foreign material

Table A-1. PM 10 Data Validation Criteria

Directional PM10 sampling was performed at the CDF monitoring site. The CDF directional sampler was a modified PM10 sampler configured to be started and stopped by the CDF data logger that was used to record the wind parameters at the CDF monitoring site. The data logger was programmed to allow the sampler to operate only when the wind was blowing at sufficient speed to pick up dirt or sand particles and was blowing from the coastal dune complex of the Oceano Dunes State Vehicle Recreational Area. The data logger evaluates the wind conditions every 5 minutes, turning the sampler on whenever the previous 5 minute average showed a wind speed greater than 5 mph and a wind direction between 260 and 330 degrees.

The overall data completeness for PM10 was 92%. Most data loss was from the Bendita monitoring site where mass flow controller malfunctions caused numerous samples to be invalidated due to an out of tolerance sampler flowrate. The mass flow controller was replaced with a volumetric flow controller in mid January 2005 to solve this problem.

As is typical with PM10 filters, they were not refrigerated prior to anion analysis by CARB. The lack of refrigeration should have no affect on sulfate and chloride ion measurements, but nitrate is known to volatize as the temperature increases, so the nitrate ion measurements may be biased low due to volatilization [(2)].

PM2.5 MEASUREMENTS

PM2.5 measurements were made with mini-vol samplers which utilized 47 mm quartz or Teflon filter media. Filter analysis included: gravimetric analysis, thermal/optical elemental/organic carbon (EC/OC) analysis, x-ray fluorescence (XRF), and ion chromatography for selected filters. Because different filter media are needed for mass/XRF and carbon analysis, two separate samplers were used at each location to allow the simultaneous sampling with both Teflon and quartz filter media.

PM2.5 Precision Measurements:

Collocated samplers with Teflon filter media were located at the Mesa 2 monitoring station to assess the precision of the mini-vol measurements. As demonstrated by Figure A-2, the precision is good, especially considering the simple nature of the mini-vol samplers. The mini-vol sample flowrate of 5 l/m is extremely low compared to other PM2.5 samplers (Federal Reference PM2.5 samplers flowrate is 16.7 l/m). The low flowrate utilized by the mini-vol samplers magnifies the bias caused by sample handling, weighing inaccuracies and other such artifacts.

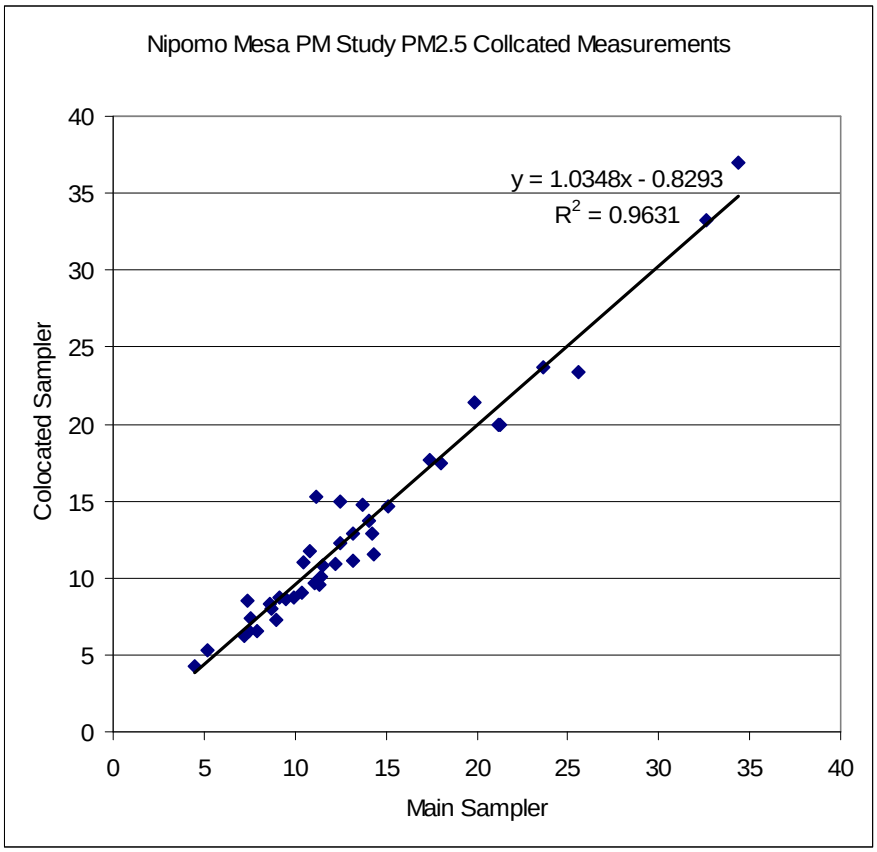


Figure A-2. PM2.5 Collocated Measurements

PM2.5 Sample Validation and Completeness:
The PM2.5 validation criteria used for the study are listed below in Table A-2.

Parameter	Measured by	Criteria
Sample Flowrate	Certified Mass Flowmeter before and after sampling	5 l/m +/- 10%
Run Time	Sampler Elapse Time Meter	24 hours +/- 30 min.
Filter Inspection	Visual inspection upon recovery from sampler	Damaged filter, insects, water droplets.
Filter Inspection	Microscopic inspection following analysis (Teflon Only)	Evidence of water or other obvious debris on filter
Exposed Filters Chilled		

Table A-2. PM2.5 Data Validation Criteria

Overall data completeness for PM2.5 measurements was 84%. Table A-3 lists the data completeness for each PM2.5 mini-vol sampler:

SITE/SAMPLER	Valid samples	% Completeness
Mesa 2 main Teflon	54	88.5%
Mesa 2 colo Teflon	42	68.9%
Mesa 2 Quartz	55	90.2%
Bendita Teflon	49	80.3%
Bendita Quartz	53	86.9%
Oso Teflon	52	85.2%
Oso Quartz	56	91.8%
Sm/Atas – Teflon	49	80.3%
Average		84.0%

Table A-3. PM2.5 Data Completeness

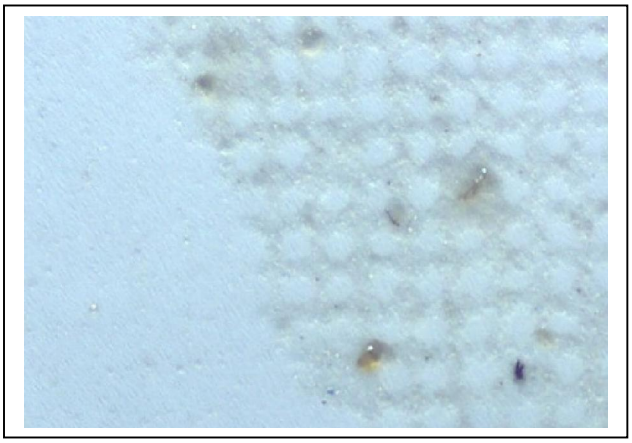
A high percentage of data from the PM2.5 samplers was invalidated for timer malfunctions causing the run time to be outside of validation criteria. It was determined that most of the "timer malfunctions" were caused by the AA battery in the sampler to momentarily "jiggle" out of the battery holder causing a short interruption of power to the sampler's timer. This short interruption would cause the timer to enter an unusual mode where it would often not shut off. An inexpensive battery holder that employs a spring to ensure tight connections of the battery could eliminate this problem.

Another significant cause of data loss was water somehow entering the sampler inlet and dripping down on the filter. During the especially wet winter period of the study, water was discovered inside the inlet and on the filter on a few samples when the filter was recovered following the sample run. Due to this observation, all Teflon filters were inspected with a x60 microscope following gravimetric and/or XRF analysis. In this microscopic inspection, numerous filters had clear evidence of evaporated water droplets and residue from the evaporated water being present on the filter media. In addition to the evidence of water on the filter, a few other obvious contaminants were found on the filter media. All filters with evidence of water or other contamination were invalidated. The photographs in figure A-3 below demonstrate these observations:

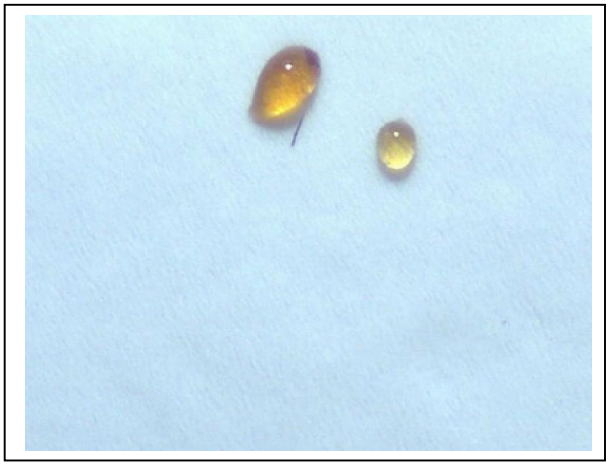
Blank Filter (X60)

Heavily Loaded Filter (X60)

Filter jcpft209 with evidence of water (X10)



Filter jcpft209 with evidence of water (X60)



Filter jcpft138 with evidence of contamination (X60)

Filter jcpft261 with evidence of contamination (X60)

Figure A-3. Microscopic Photographs of PM2.5 Filters

It is not understood how the water was able to enter the mini-vol sampler inlets, as the inlet is equipped with a "rain cap" to prevent water from entering the inlet. The Teflon filters that somehow had water droplets deposited on them showed a characteristic "grid" pattern (see photo above). This "grid" pattern resulted from the water droplet on the filter causing the smooth texture of the membrane filter to deform in the pattern of the gridded stainless steel support that the filter rests on in the sampler. This "grid" pattern allowed easy identification of Teflon membrane filters that somehow had water drip down the inlet and land on the filter.

Following the inspection of all Teflon study filters, all quartz study filters were also inspected with the use of a microscope. There was no evidence of water droplets observed on any quartz filters. It is highly unlikely that we detected about 6% of the Teflon filters with evidence of water, and no quartz filters that had water contamination. It is more likely that the nature of the quartz filter media does not show evidence of water contamination as easily at the Teflon media does.

To determine for sure if water droplets on the quartz filter media would leave any visible evidence, a water droplet was placed on a quartz filter and allowed to sample (at the same sample flowrate) until the droplet dried. The filter was then examined with the microscope and no evidence of water was detected. This test confirms that the quartz filter media reacts differently than Teflon filter media and does not leave any visible evidence of water contamination.

Because water contamination of quartz filters could not be detected, it is highly likely that some the quartz filters that have been validated were contaminated with water. As a result, the elemental/organic carbon (EC/OC) data likely will have some data values that were affected by water dripping on the sample filters. It should be noted that in the EC/OC analysis, only a small punch of the quartz filter is analyzed, so for water contamination to actually bias the data value of a particular sample, the water droplet must have landed on the portion of the filter where the punch was later taken. There is no way to determine which filters may have been affected, so the use of elemental/organic carbon data must be used with this caution. It should also be noted, that the water problem only occurred in the wet winter period of the study, where most data values were generally low.

Another important validation parameter for the PM2.5 mini-vol samplers is sample flowrate. Accurate sample flowrate is important both in ensuring the inlet "cut point" is maintained at 2.5 microns as well as accurately determining the total volume of air sampled. In designing the mini-vol sampling procedures, the sampler flowrate was set prior to each run to 5 l/m using a certified mass flow meter (MFM), then measured again following the sampling period with the MFM. The results of the pre and post flowrate measurements were used to calculate average sampler flowrate for the run as well as ensuring the sample flowrate (and inlet cut point) validation criteria were met. This procedure was used, in spite of it greatly increasing the study workload, due to concerns that the mini-vol samplers could not be trusted to maintain the nominal 5 l/m sample flowrate. It appears that much of this procedure was unnecessary for our study. Out of the 488 mini-vol runs in the study, there was never an instance that the sampler's flowrate drifted enough to trigger the sampler flowrate validation criteria. As can be seen in figure A-4, the drift was generally so low that the drift would not have a significant affect on the average sample flowrate used to calculate concentrations. In situations with greater sample loading than was experienced in our study the sample flowrate drift may be greater.

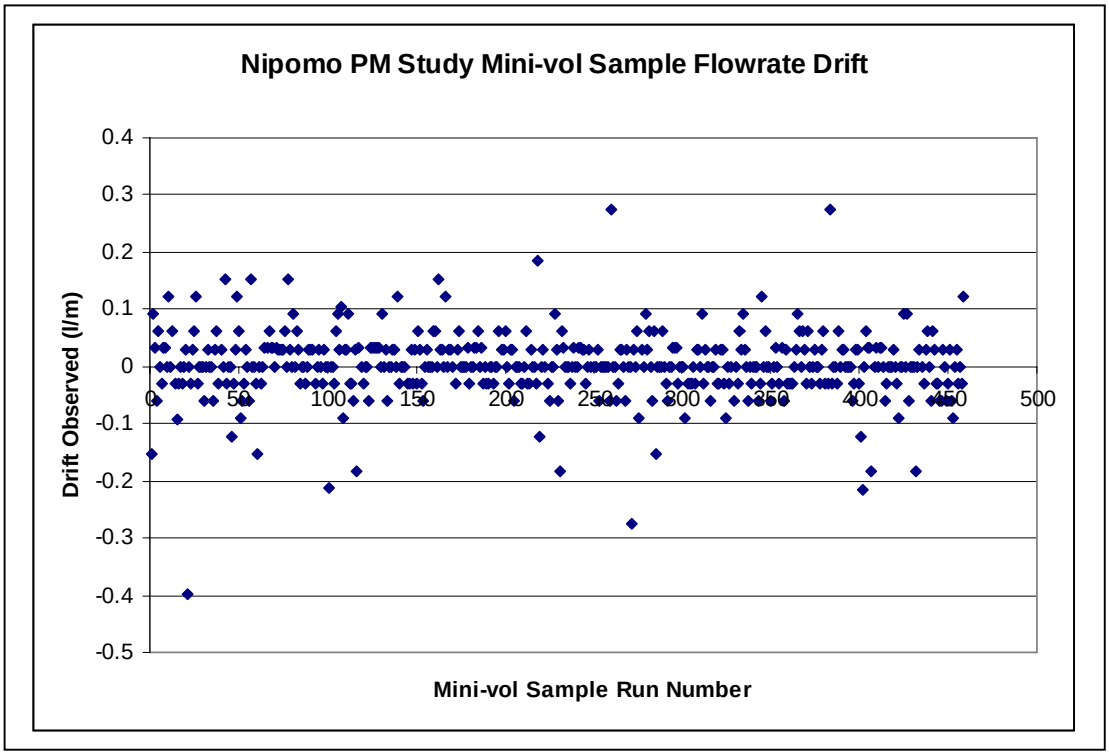


Figure A-4. PM2.5 Sampler Flowrate Drift

PM2.5 Teflon Filter Media Field and Trip Blank Measurements:
Field and trip blanks were taken throughout the study to ensure filter handling was not significantly biasing the PM2.5 measurements. Trip blanks were collected by selecting an unexposed filter at random and submitting the filter for analysis. Field blanks were collected by selecting an unexposed filter at random, then loading into a spare mini-vol inlet, transporting to the field with the next runs mini-vol samplers, strapping the "field blank inlet" to an actual mini-vol sampler, recovering the field blank filter with the normal mini-vol sample filters, and submitting for analysis. This field blank procedure is much more representative of any actual bias that may occur to actual sample filters than the typical field blank procedure of simply installing a filter in the sampler, then immediately removing the filter, and submitting for analysis.

As previously noted, one disadvantage of mini-vol samplers is the low sample flowrate. This low sample flowrate will magnify any bias measured by field or trip blanks. For example, the same change in mass of a blank filter will have over three times the resulting blank concentration with a mini-vol than with a Federal Reference Method PM2.5 sampler, due to the difference in sampler flowrate.

Table A-4 presents the results of trip and field blanks with Teflon filters:

	Trip Blanks		Field Blanks	
Average Blank Value	-0.3	ug/m3	1.4	ug/m3
Minimum Blank Value	-1.1	ug/m3	0.4	ug/m3
Maximum Blank Value	1.0	ug/m3	2.4	ug/m3

Table A-4. PM2.5 Mass Blank Values

The trip blanks show no significant overall bias. The field blank results do show a slight positive bias, again being magnified due to the low sample flowrate of the mini-vol samplers. The slight positive bias from the field blanks must be noted in evaluating the data from this study, but is not significant considering that the weighing uncertainty alone for these filters is approximately 0.7 ug/m3. Blank values were not applied to adjust any data from Teflon filters.

PM2.5 Quartz Filter Media Field and Trip Blank Measurements:

Field and trip blanks for quartz filter media were taken in the same manner as described above for the Teflon filter media. Blank measurements for elemental/organic carbon (EC/OC) measurements are especially important because with the ubiquitous nature of organic carbon compounds and the filter media's natural affinity for many of these organic compounds, contamination with trace organic carbon compounds is a very common problem with EC/OC measurements.

EC/OC Blank results from the first two months of sampling were received from the CARB laboratory in early August 2004. These results showed excessively high organic carbon blank values. An investigation with the help of CARB staff was immediately initiated. Trip blanks as well as Field Blanks showed similar high OC values. This indicates that the contamination of the blanks was not associated with District staff's handling of the filters, but likely was to storage of the filters. After evaluating possible sources of contamination, it was concluded that the likely source was the plastic bags that CARB shipped the filters in. At room temperature, plastic bags can outgas organic carbon vapors, which the quartz filter media has an affinity for. CARB's decision to use plastic bags to store the filter media in was largely influenced by the lack of availability other containers that would be compatible with our program.

An easy solution to this problem was to keep the filter media (and plastic bags) refrigerated before sampling. The filters and plastic bags had always been refrigerated following sampling to prevent volatilization of organic carbon from the filter media. Keeping the filters and plastic bags refrigerated at all times would greatly reduced the "out gassing" of organic vapors from the bags, thereby hopefully eliminating the contamination of the filter media.

In early September 2004 fresh quartz filters were provided by CARB that were contained in refrigerated plastic bags. The filters and bags were kept refrigerated until just prior to sampling, and then following sampling were immediately refrigerated until analysis. This change in procedure dramatically reduced the OC blank values. Table A-5 below presents the blank data before and after the procedure change was implemented:

	Trip Blanks		Field Blanks	
	Before	**After**	**Before**	**After**
Average OC ug/m3	5.1	1.2	4.9	2.3
Minimum OC ug/m3	3.9	0.7	3.9	1.3
Maximum OC ug/m3	6.4	2.1	7.2	3.5

Table A-5. PM2.5 Organic Carbon Blank Values

The trip and field blank values measured after the procedure change are in line with blank values used by the USEPA IMPROVE and STN nationwide particulate speciation programs. These nationwide programs utilize a data handling protocol that subtracts a nationwide average blank value. The blank value used on these programs, when adjusted for differences in sampler flowrate is approximately 1.7 ug/m3 for mini-vol samplers [(8)]. As this USEPA blank value is in line with the blank values measured in the Nipomo PM Study, all OC data produced after the filter procedure change will be blank adjusted by subtracting 1.7 ug/m3 from the measured OC concentration. EC blank as well as ambient values never reached the detection limit of 1 ug/m3.

Great consideration has been focused on trying to utilize the OC data produced prior to the filter procedure change. One hope was that the blank data did not actually represent the true bias to the ambient data. The thinking was that the organic vapors that contaminated the filter media were not particulates trapped on the filter, rather they were vapors adsorbed by the filter media. Actual sample filters (that had adsorbed organic vapors from the plastic bags) were flushed with ambient air for 24 hours as part of the normal sampling process. The hope was that the sampling of ambient air had the effect of stripping the filters of the adsorbed organic vapors. So an experiment was devised to determine to what extent 24 hours of sampling ambient air would result in a decrease of the blank value.

A number of fresh uncontaminated quartz filters were stored in plastic bags at room temperature for 30 days to contaminate the filters with organic vapors. Six filters were installed in mini-vol samplers, allowed to sample humidified zero air for 24 hours, recovered from the samplers, and submitted for analysis. Six filters were treated as trip blanks for control. Results showed no reduction in OC concentration on the 6 filters that sampled humidified zero air. Unfortunately, the experiment demonstrated that the organic vapors from the plastic bags were not removed from the quartz filter media by the sample flowrate passing through the filters on a typical sample run.

The high blank OC values prior to the procedure change were quite variable. This makes subtraction of an average blank value from the sampled OC values for this period result in some samples with obvious low or even negative OC values, and other samples with OC values that are obviously too high (OC+crustal+(NH3)2SO4 greater than mass measurement). As a result, the use of individual OC data values from all study sites for the period 4/3/04 through 8/31/04, must be used with great caution. However, it is reasonable to utilize the average OC data for this period, corrected by the average blank value prior to the procedure change with much less caution. As a result, OC data for this period was blank corrected with an average blank value of 4 ug/m3. OC data from this period will only be used in calculating average species concentrations, not individual sample concentrations.

SAMPLING AND ANALYTICAL METHOD COMPARISONS

Different sampling and analytical methods for particulate matter are known to have different strengths and weaknesses. There is no single method that is known to perfectly represent the actual particulate concentration. Even simple filter methods have documented positive and negative artifact issues due to filter handling and conditioning environments. The sample inlets of different sampling methods are known to behave differently under a variety of conditions. Two methods can agree well when sampling a preponderance of a particular type of particulate and then show stark disagreement when sampling a preponderance of another type of particulate. Even though no method produces a "true" representation of particulate concentration under all conditions, specific methods have been designated by the USEPA as reference methods that are used to compare to state and federal health standards.

Intercomparison of methods is a useful tool in validating and gaining confidence in the data from the various methods. In this study, comparison of the mini-vol PM2.5 samplers to Federal Reference Method PM2.5 samplers is helpful in evaluating the data from the mini-vol samplers in terms of the state and federal PM2.5 health standards. Performing other methods comparisons is also helpful in validating data and providing the data users a greater understanding of the level of confidence and applicability of the data.

PM2.5 Mini-vol Sampler Comparisons to PM2.5 Federal Reference Method (FRM) Samplers:
The mini-vol samplers used for PM2.5 sampling, while known to be reasonably accurate, do not have federal reference or equivalent method certification, and therefore can not be used to demonstrate state or federal air quality standard compliance or violation. In planning the Nipomo PM study, District staff evaluated various PM2.5 samplers for use in the study. Weighing all the pros and cons, mini-vol samplers were selected for their greater portability and economy, knowing that they might produce data somewhat different from data that would have been produced with FRM samplers. The approach was to use the min-vol study data to get a general understanding of PM2.5 levels and composition in the Nipomo Mesa area, and then if the study data indicated, install a permanent PM2.5 FRM sampler to provide data for record that could be used to demonstrate standard compliance or violation.

Various studies have indicated that PM2.5 data from mini-vol samplers compare favorably to data from FRM samplers. CARB performed comparisons between PM2.5 mini-vols and PM2.5 FRM samplers in Bakersfield, California in the winter of 1998 that showed a close agreement between the PM2.5 mini-vol and FRM samplers. Other studies have shown approximately a 10% difference between PM2.5 mini-vol and FRM sampler data [(5)].

Prior to the beginning of the Nipomo PM study a pilot study for the month of December 2003 was performed at the District's Atascadero monitoring station. The purpose of the pilot study was to better understand the various procedures for operating the mini-vol samplers as well as gain confidence that there is some general agreement between the mini-vol and FRM samplers prior to initiation of the Nipomo PM study.

The study consisted of collocated measurements on five sample days between two FRM samplers, two mini-vols operated by the procedure recommended by CARB, and one mini-vol operated by a procedure utilized by Desert Research Institute (DRI). The main difference

between the CARB and DRI procedure is that with the CARB procedure the mini-vol sampler flowrate is set with a MFM prior to each run, and measured with the MFM following each run. The DRI procedure is to mark on the mini-vol sampler's rotameter at 5 l/m (using a certified MFM) and simply set the sampler's flowrate to the marking on the sampler's rotameter prior to each run. The DRI procedure assumes that the flow stayed at the 5 l/m setting throughout the run, where the CARB procedure actually measures the flow when the filter is installed prior to the run, and again measured when the filter is recovered following the run.

The results of the study are presented in the figures A-5 and A-6 below:

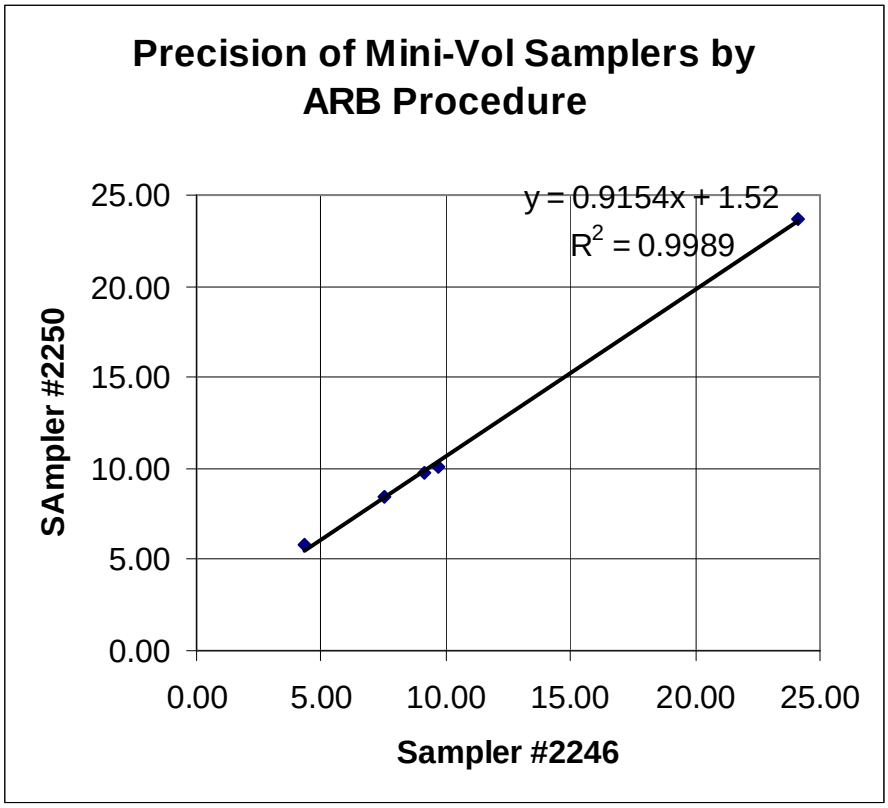


Figure A-5. Pre-Study PM2.5 Mini-vol Sampler Precision

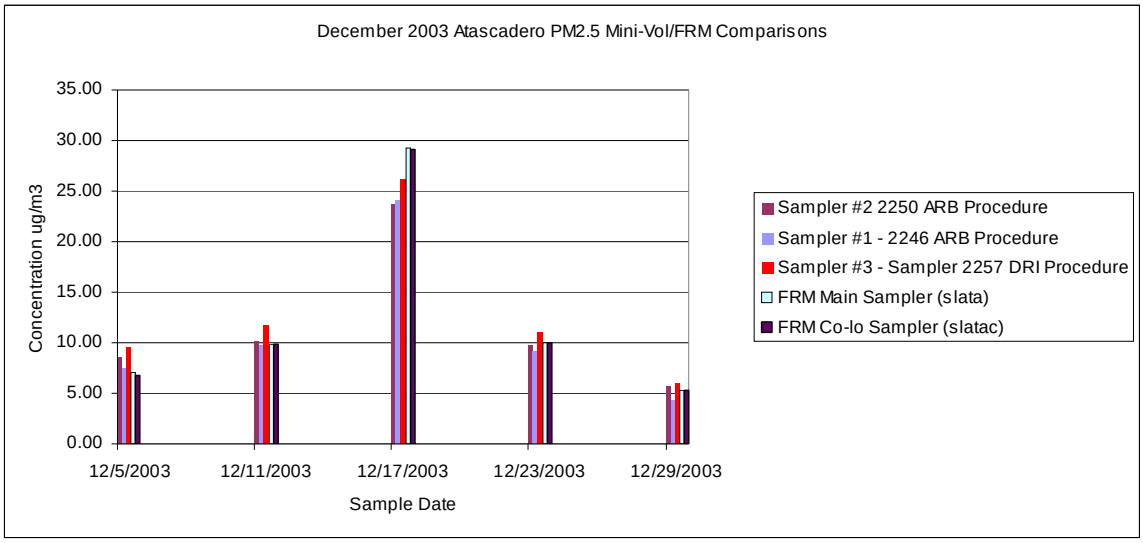


Figure A-6. Pre-Study FRM/Mini-vol Comparison

These results showed little variation between the DRI and CARB methods of mini-vol operation. Additionally, there was generally good agreement between the mini-vol samplers and the FRM samplers. The 12/17/03 sample was the highest value and did show the mini-vol sampler measuring a somewhat lower value than the FRM. These comparisons between the FRM and mini-vol samplers were similar to results obtained in other studies. Based on the pilot study, the District decided to use the mini-vol samplers with the CARB procedure for PM2.5 measurements.

As part of the main Nipomo PM study, in order to assess the comparability of mini-vol PM2.5 data to FRM PM2.5 data, a mini-vol sampler was collocated with a nearby existing FRM PM2.5 sampler for each sample day. For the first part of the study, the mini-vol was collocated with the District PM2.5 FRM sampler in Atascadero (4/3/04 – 6/20/04), but was moved to the CARB monitoring site in Santa Maria for the remainder of the study (6/26/04 – 3/29/05). The collocated measurement was moved from Atascadero to Santa Maria because the levels at Atascadero were much lower than the levels measured in the study area, and because it is believed the particulate composition in Santa Maria would be closer to the particle composition being measured in the Nipomo Mesa study area.

The comparison of data from the PM2.5 mini-vol and the PM2.5 FRM sampler are presented in figures A-7 and A-8 in both time series and scatter graphs:

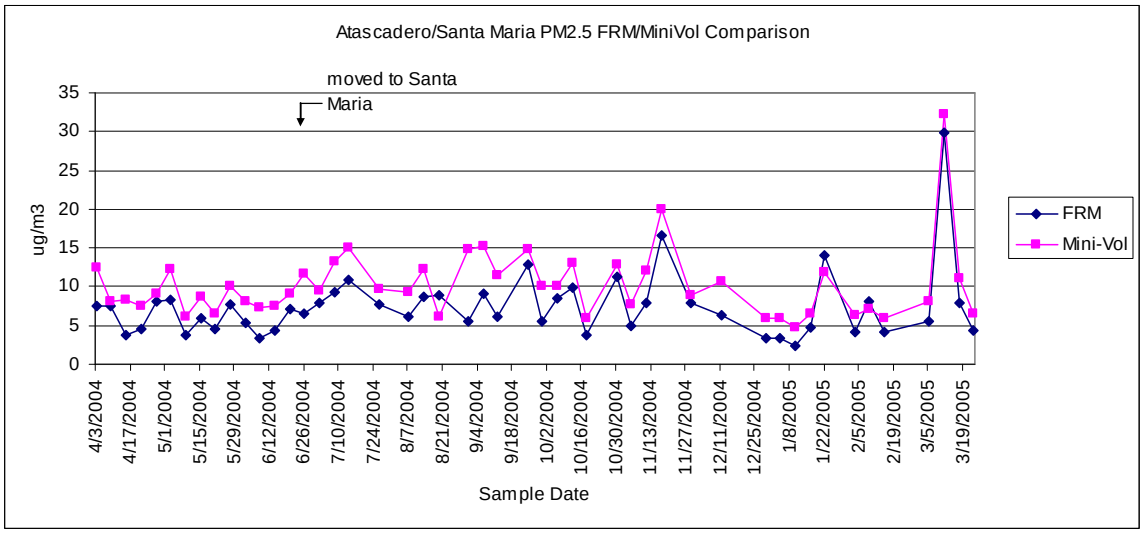


Figure A-7. PM2.5 FRM/Mini-vol Comparison

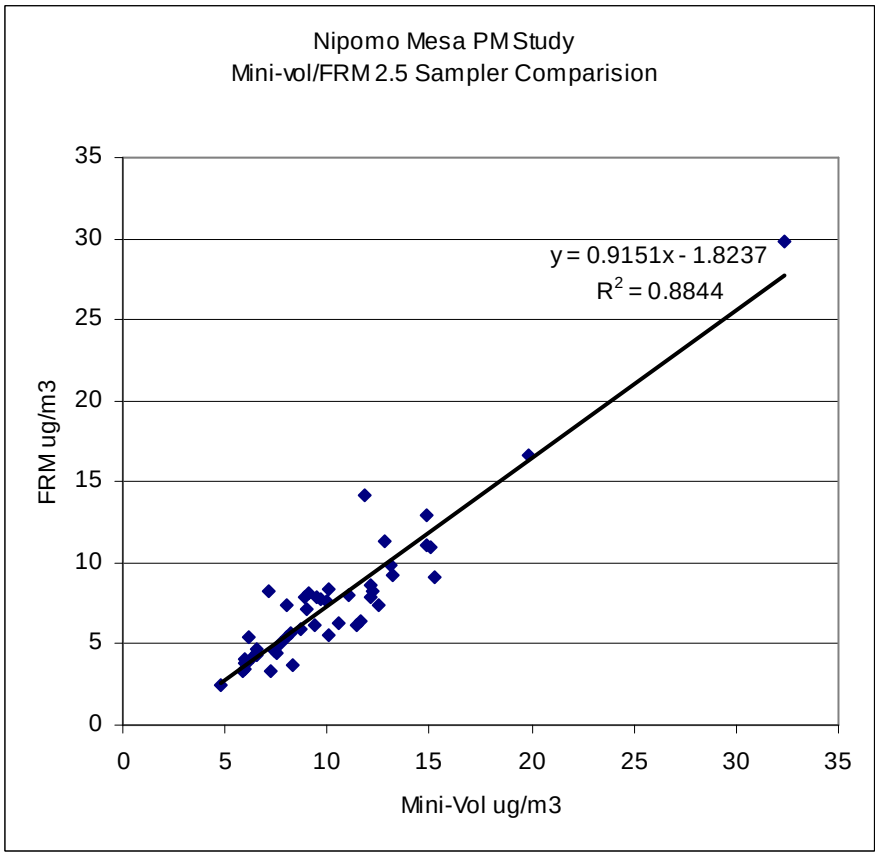


Figure A-8. PM2.5 FRM/Mini-vol Comparison

The mini-vol/FRM sampler comparisons show general agreement between the two sampling methodologies. The majority of the comparisons showed the mini-vol value higher than the FRM sampler's value. However, there are some data points where the mini-vol sampler value was lower than the FRM sampler's value, as was the case in most of the comparisons made in the December pilot study. It was surprising that the majority of comparisons showed the mini-vol

data value higher in the District's December pilot study and the CARB 1998 Bakersfield study showed the opposite trend.

In order to better understand the results of the mini-vol/FRM comparisons the entire data set was reviewed. In this review, it became apparent that sample days where the mini-vol value was the same or even higher than the FRM sampler value were days where the particulate mix being sampled was mostly fine particulates (using the PM2.5/PM10 ratio to assess the size segregation of the particulates being sampled). On days where the particulate mix was predominately coarse, the mini-vol data value was greater than the FRM value.

The relationship of the discrepancy between the mini-vol and FRM methods to the particulate size segregation suggests that the difference in the two methods may be due to different characteristics of the two sampler's inlets. This relationship also helps to understand why closer agreement between the two methods was observed in the CARB Bakersfield Study in the winter of 1998 and the District December 2003 Pilot Study. These two studies were performed in the winter months in locations where the overwhelming predominate particulate size would be in the fine fraction.

The comparison of the two methods implies that the mini-vol PM2.5 data collected from the study sites may overestimate the PM2.5 concentrations that would have been measured by a FRM PM2.5 sampler. It is quite difficult to determine just how much the mini-vol overestimated the data values. A linear regression analysis of the comparison of all FRM to mini-vol data suggests on average, there is approximately a 10 – 20% overestimation by the mini-vol samplers, with the greatest overestimation on the lower concentration data values.

Manual PM2.5 Measurement Methods Compared to "Real Time" PM2.5 Measurement Methods

Another helpful comparison to provide perspective on the different PM2.5 measurement methods is the comparison of both the mini-vol and the FRM data values to other PM2.5 methods. For part of the study period, while collocated mini-vol/FRM measurements occurred at the CARB Santa Maria station, PM2.5 measurements were also made at the Santa Maria CARB site with a Met One PM2.5 Beta Attenuation Monitor (BAM). The results of the comparisons are presented in figure A-9.

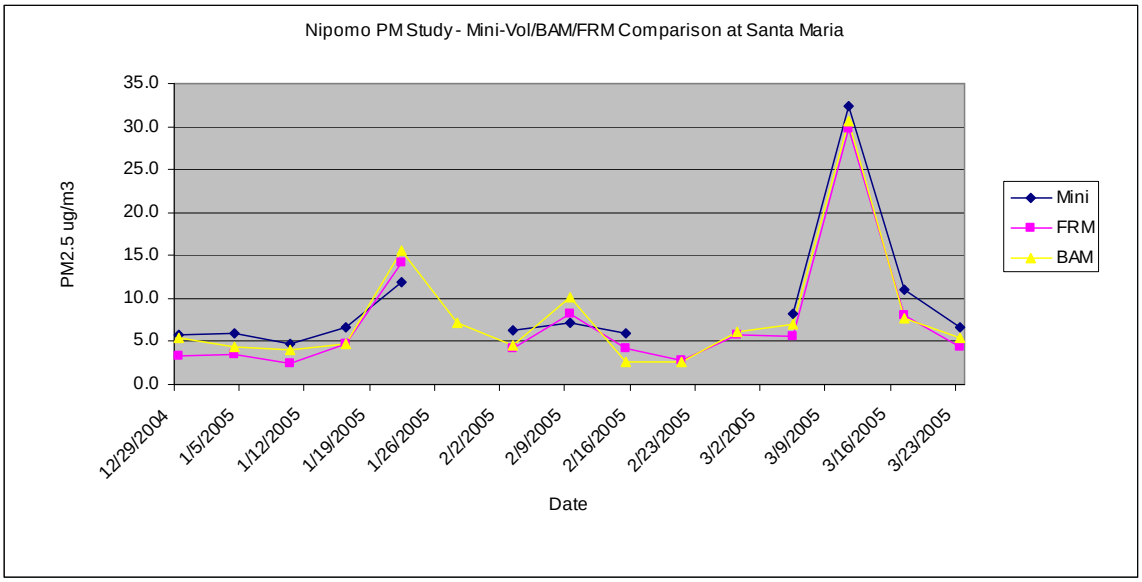


Figure A-9. PM2.5 FRM/Minivol/BAM Comparison

This comparison demonstrates that the measurement discrepancies between the FRM method and both the mini-vol and BAM methods are approximately the same magnitude.

Comparison of measured PM10 Sulfate to PM2.5 Sulfate calculated from Measured PM2.5 Sulfur

Sulfate concentration can be calculated from elemental sulfur measurements by applying the relative molecular weights of the atoms that compose the sulfate molecule. For this calculation to be valid, one must assume that all sulfur present in the sample is in the form of sulfate. In addition, anthropogenic sulfate is always in the fine fraction (<2.5 micron) [(9)]. Oceanic sulfate, that results from the natural churning and saltation of the ocean surface is most often in the coarse fraction (>2.5 micron). This naturally occurring oceanic sulfate can be estimated from the chlorine concentration in a sample by applying the approximate ratio of chlorine to sulfur in ocean water (4,7).

Using these relationships, one can perform a comparison between anthropogenic PM10 sulfate measured by ion chromatography of the PM10 filters and anthropogenic PM2.5 sulfate calculated from the XRF sulfur measurements. By excluding the only source of non-anthropogenic sulfate – oceanic sulfate – one would expect the PM10 sulfate value to be the same as the PM2.5 sulfate value in measurements made at the same time at the same location.

This comparison was made at both the Mesa 2 and Bendita study sites. The results of these comparisons are presented in figures A-10 and A-11.

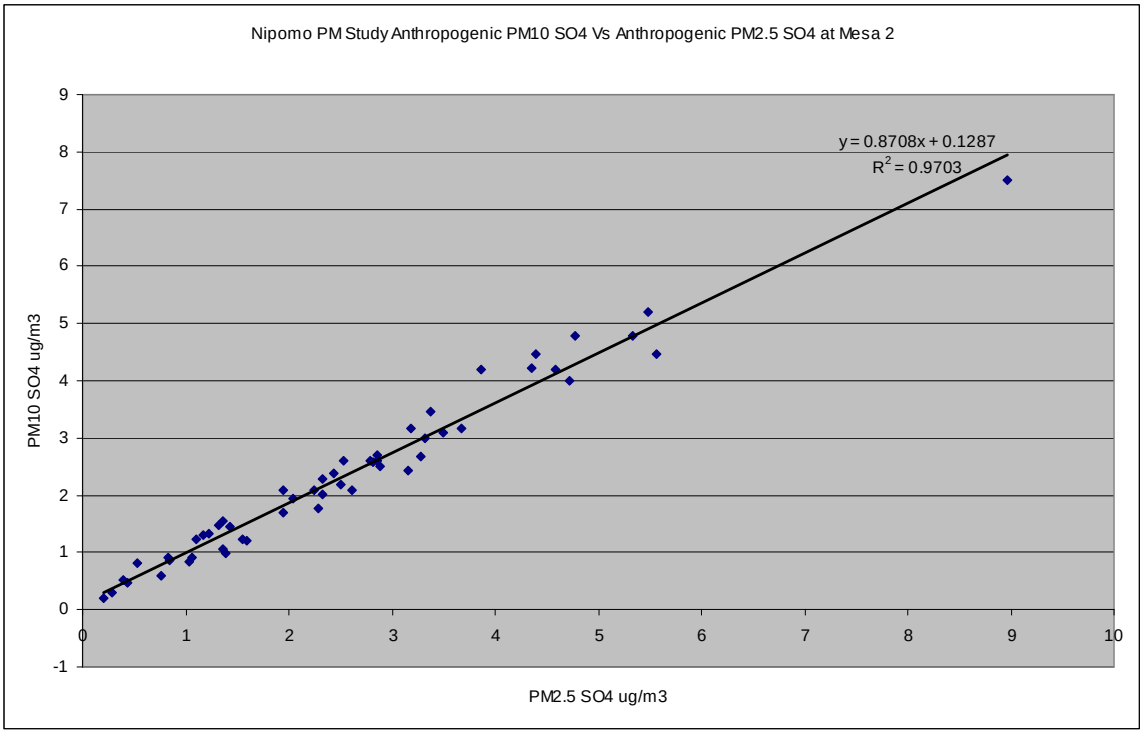


Figure A-10. Mesa 2 PM10 Measured Sulfate and PM2.5 Calculated Sulfate Relationship

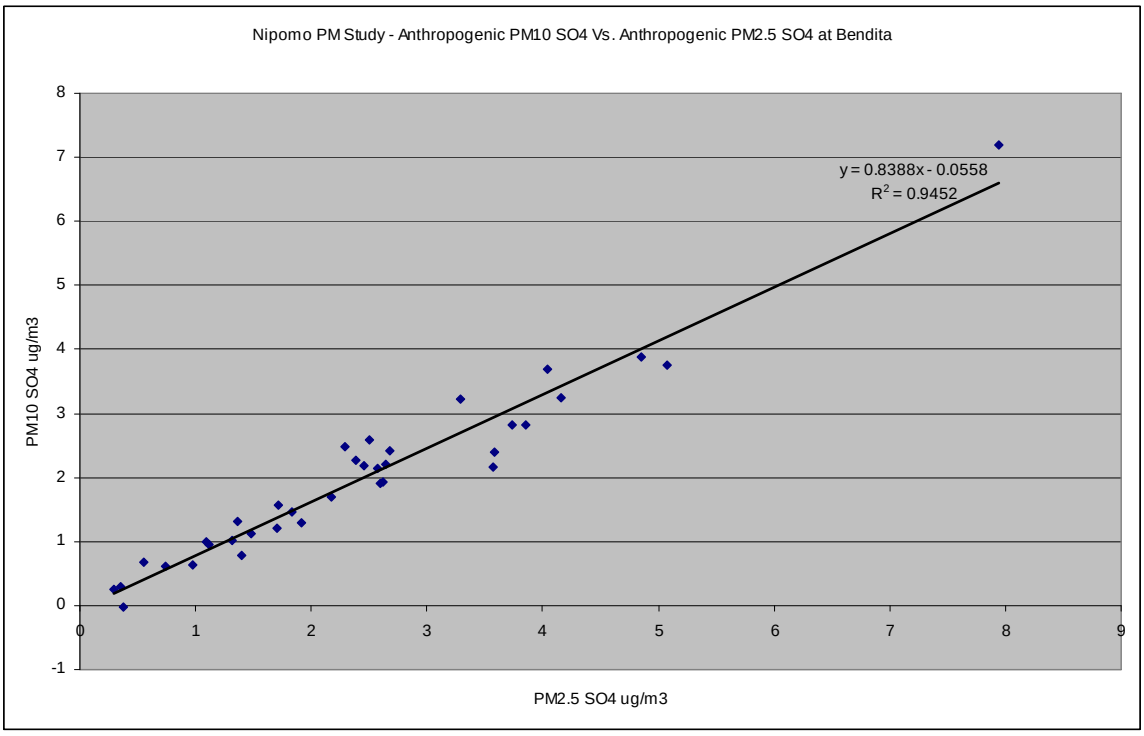


Figure A-11. Bendita PM10 Measured Sulfate and PM2.5 Calculated Sulfate Relationship

The results of these comparisons are quite good. Considering that the data came from completely different measurement methods, different filter media, and completely different analytical methods. These results assume that all the sulfur measured by XRF is in the form of

sulfate, and that the oceanic sulfate contribution has been correctly estimated. These comparisons provide further confidence in both the PM10 and PM2.5 measurements.

Comparison of measured PM2.5 Sulfate to PM2.5 Sulfate calculated from Measured PM2.5 Sulfur

A small number of PM2.5 Teflon filters were analyzed for sulfate (and other ions) following mass and XRF analysis. This provides another opportunity to compare calculated sulfate to measured sulfate, this time both values from the fine particulate fraction.

The comparison for all sites is figure A-12:

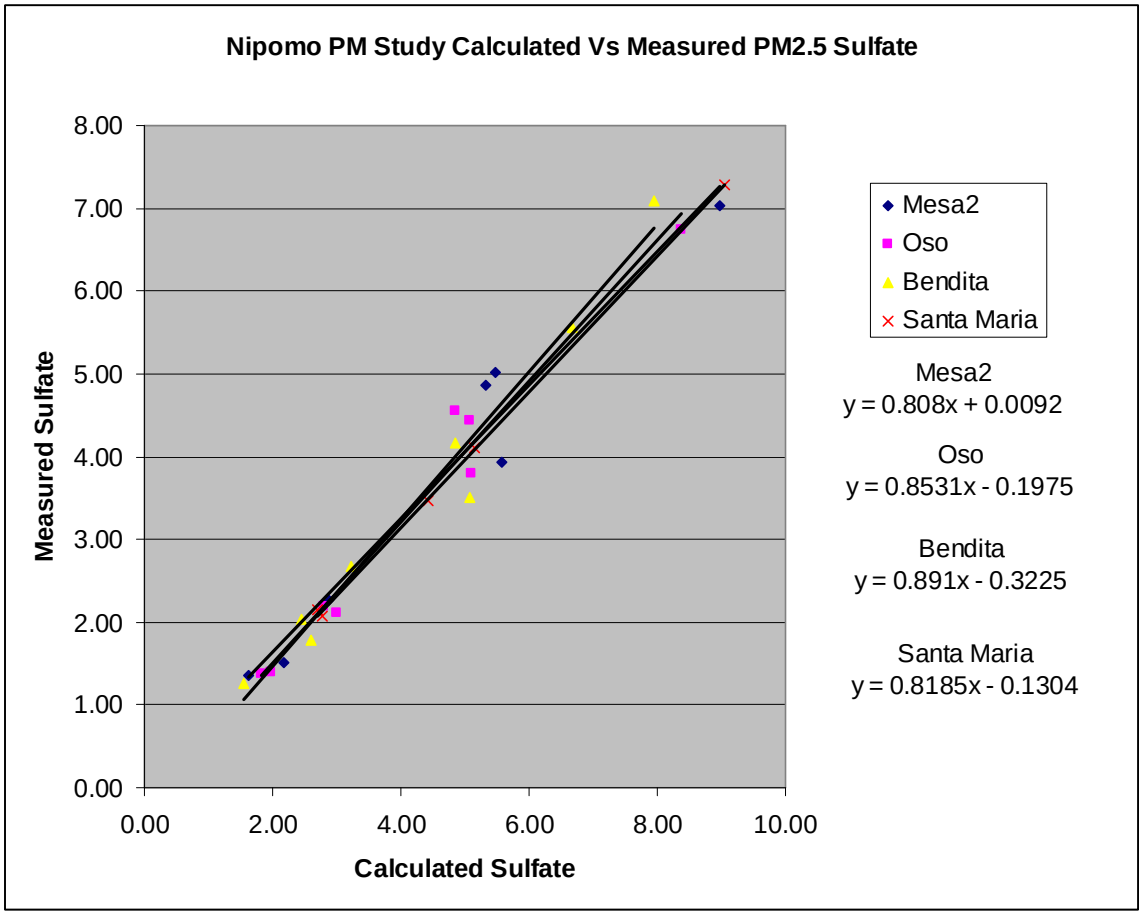


Figure A-12. PM2.5 Measured Sulfate and Calculated Sulfate Relationship

The linear regression results for this comparison are very similar to the PM10 to PM2.5 sulfate comparisons above. The slope of all of these comparisons of approximately 0.85 indicates about a 15% difference between the calculated sulfate and measured sulfate values. This 15% discrepancy is very typical between two different analytical methods.

OVERALL DATA QUALITY ASSESSMENT

Enormous effort in this study was placed on ensuring that the data quality would meet the study objectives. Quality control procedures were implemented to directly control and document numerous variables in the measurement process. Additional quality assurance procedures were implemented to measure the effectiveness of the quality control tasks in controlling the data quality.

Data from these quality control and quality assurance tasks were used to validate the entire study data set. In this validation process, a few observations were made. These observations include:

- Data loss from the PM2.5 mini-vols occurred due to loose internal "AA" battery holders. This could be avoided in the future by replacing the battery holders with holders utilizing a spring to keep tension on the battery. All data affected by this problem was identified by quality control procedures and invalidated.
- Significant data loss (~ 6%) from the PM2.5 mini-vols occurred due to water entering the sampler inlet and dripping down the inlet on to the sample filter. It is unclear how the water entered the inlet. All data, other than elemental/organic carbon (EC/OC) data affected by this problem was identified by microscopic analysis and invalidated. There was no way to identify EC/OC filter media that was affected by this problem. As a result there may be a small set of organic carbon data that was affected by this problem. However, the data that may have been affected would have been during the rain season, when the concentrations were generally very low.
- A large portion of the organic carbon data (4/3/04 – 8/31/04) was biased positive by the storage of unexposed filters in plastic bags at room temperature. This problem was detected by the use of trip and field blanks utilized as part of the study protocol. Organic carbon data for this period was corrected by subtracting average blank values. This blank corrected data for this period should not be used on an individual sample basis due to the large variations in the level of contamination from the plastic bags. However, average values from this period should be representative and can be utilized.
- The corrective action taken to eliminate the contamination of the EC/OC quartz filter media by the plastic bags was effective and the remainder of the organic carbon data set blank values is in line with organic carbon blank values obtained in two nationwide USEPA particulate speciation networks.
- Comparisons made between the PM2.5 mini-vol sampler used for all study PM2.5 sampling and a PM2.5 Federal Reference Method sampler demonstrated overall good agreement with an average 10-20% positive bias from the mini-vol sampler. And with the greatest discrepancy at the lower concentration data values.
- Comparisons between PM10 measured anthropogenic sulfate and calculated PM2.5 anthropogenic sulfate showed remarkable agreement between the two different measurement and analytical methods.

In conclusion, the resulting study data set can now be utilized with great confidence in the quest to understand the issues surrounding particulate pollution on the Nipomo Mesa.

NIPOMO PARTICULATE STUDY

APPENDIX B - INDIVIDUAL SAMPLE DAY GRAPHICAL DATA SUMMARIES

This appendix presents a study area map with graphical summaries of data for eleven sample days with high PM10, PM2.5, or sulfate. Sites that collected wind data are depicted with the wind rose for that sample day. The center of the wind rose is located at the site location on the map. Sites that did not collect wind data have their location depicted with an oval.

The graphical summary of particulate data for each site for that particular sample day is located nearby the site location on the map. The scale of each bar graph is the same from site for site for each parameter, but the scale of different parameters is different. The numerical data values and color code is listed above the map. Table B-1 explains how to read the graphical summaries.

Table B-1. Key to Graph

Graph	Sites	Explanation
PM10	CDF	Blue portion represents dunes contribution. Yellow portion represents non-dunes contribution. Blue plus Yellow portions represent total PM10 concentration.
PM10	Hillview and NRP	Blue represents total PM10 concentration.
2.5/10	Bendita and Mesa 2	Blue represents the coarse fraction (2.5-10 micron). Brown represents the fine fraction (<2.5 micron). Blue plus brown portions represent the total PM10 concentration. The scale of this graph is the same as the two PM10 graphs.
SO4	All Sites Present	Blue represents the anthropogenic portion of sulfate. Brown represents the marine portion of sulfate. Blue plus brown portions represent the total sulfate concentration. Note this is only the sulfate portion, not ammonium sulfate.
PM2.5	All Sites Present	Blue represents the crustal portion. Brown represents the sea salt portion. Yellow represents the ammonium sulfate portion. Light blue represents the other categories such as elemental/organic carbon. The total of each category represents the total PM2.5 concentration.

SAMPLE DAYS WITH HIGH PM10 AND PM2.5 CONCENTRATIONS

The following sample days were identified as having high PM10 and PM2.5 concentrations:

4/21/04
4/27/04
5/9/04
6/26/04
9/12/04
9/18/04

Graphical summaries for these days are presented in figures B-12 through B-6

SAMPLE DAYS WITH HIGH SULFATE CONCENTRATIONS

The following sample days were identified as having high sulfate concentrations:

4/9/04
5/3/04
7/8/04
8/25/04

Graphical Summaries for these days are presented in figures B- through B-10

REGIONAL EPISODE DAY

The sample day of 3/11/05 was identified as a regional episode day. The data from this day showed elevated PM2.5 and sulfate concentrations, but very low coarse PM fraction. The wide spatial extent of these measurements indicates that this was a regional episode. A graphical summary of this day is presented in Figure B-11.

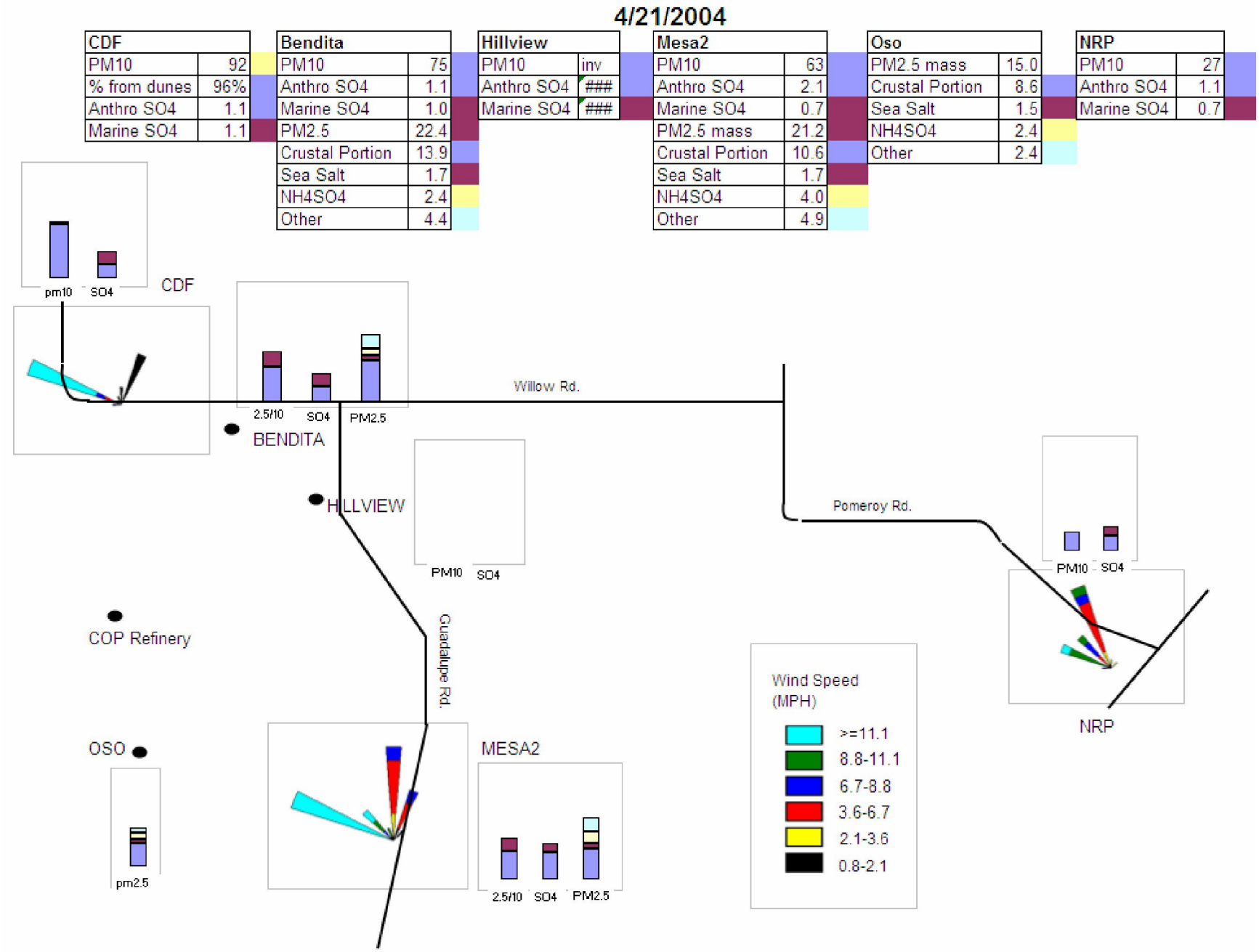


Figure B-1. 4/21/04

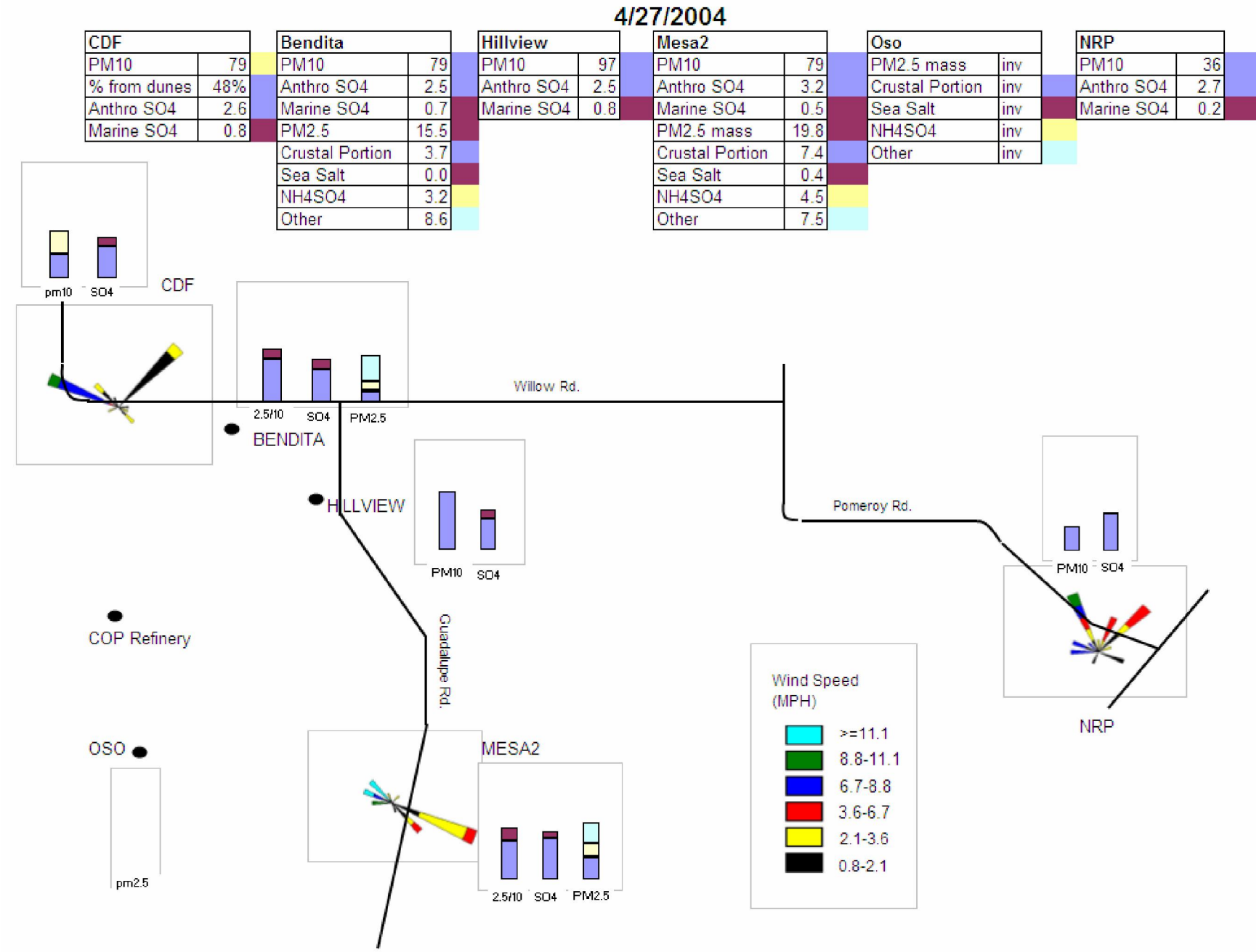


Figure B-2. 4/27/04

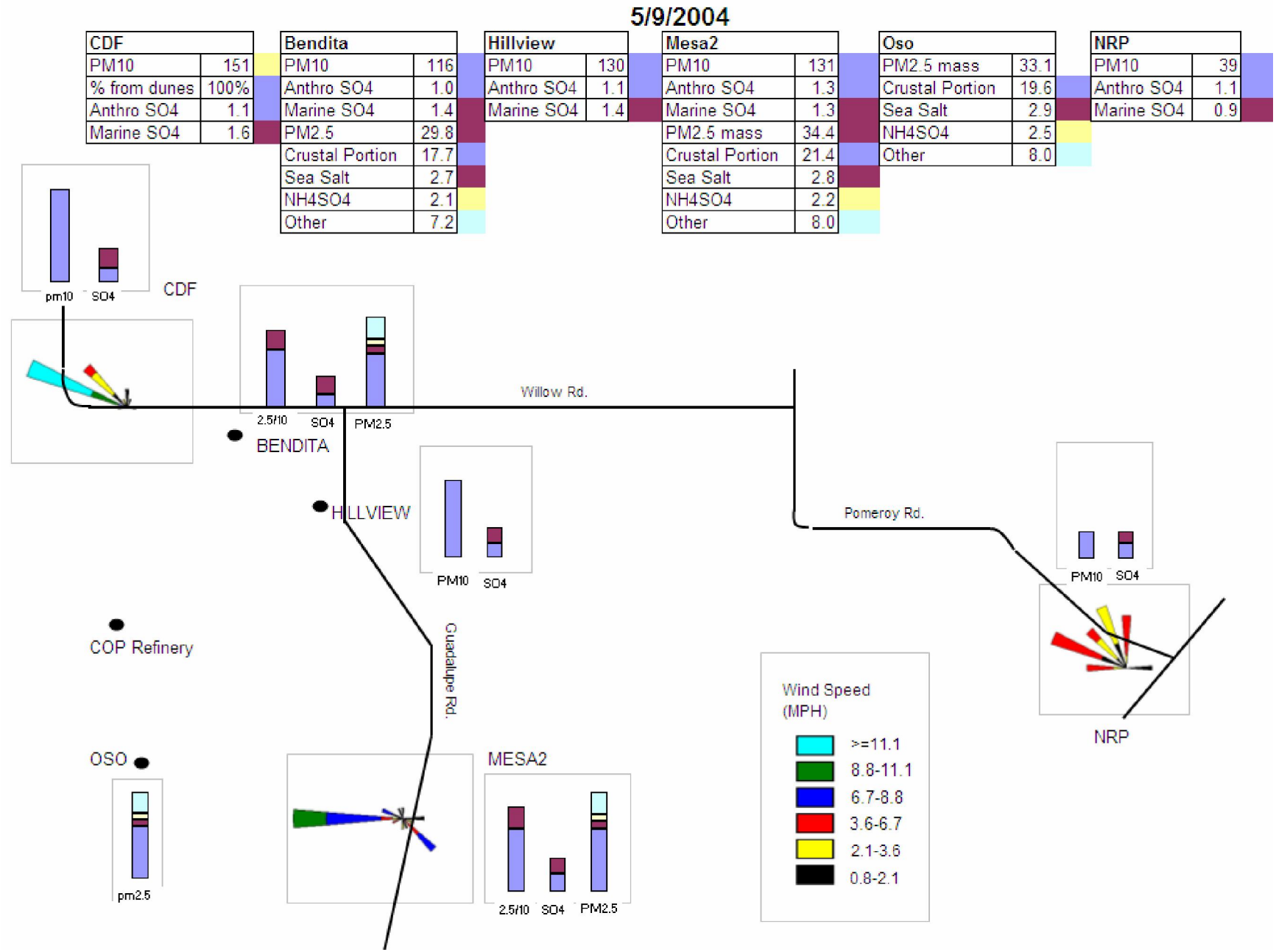


Figure B-3. 4/27/05

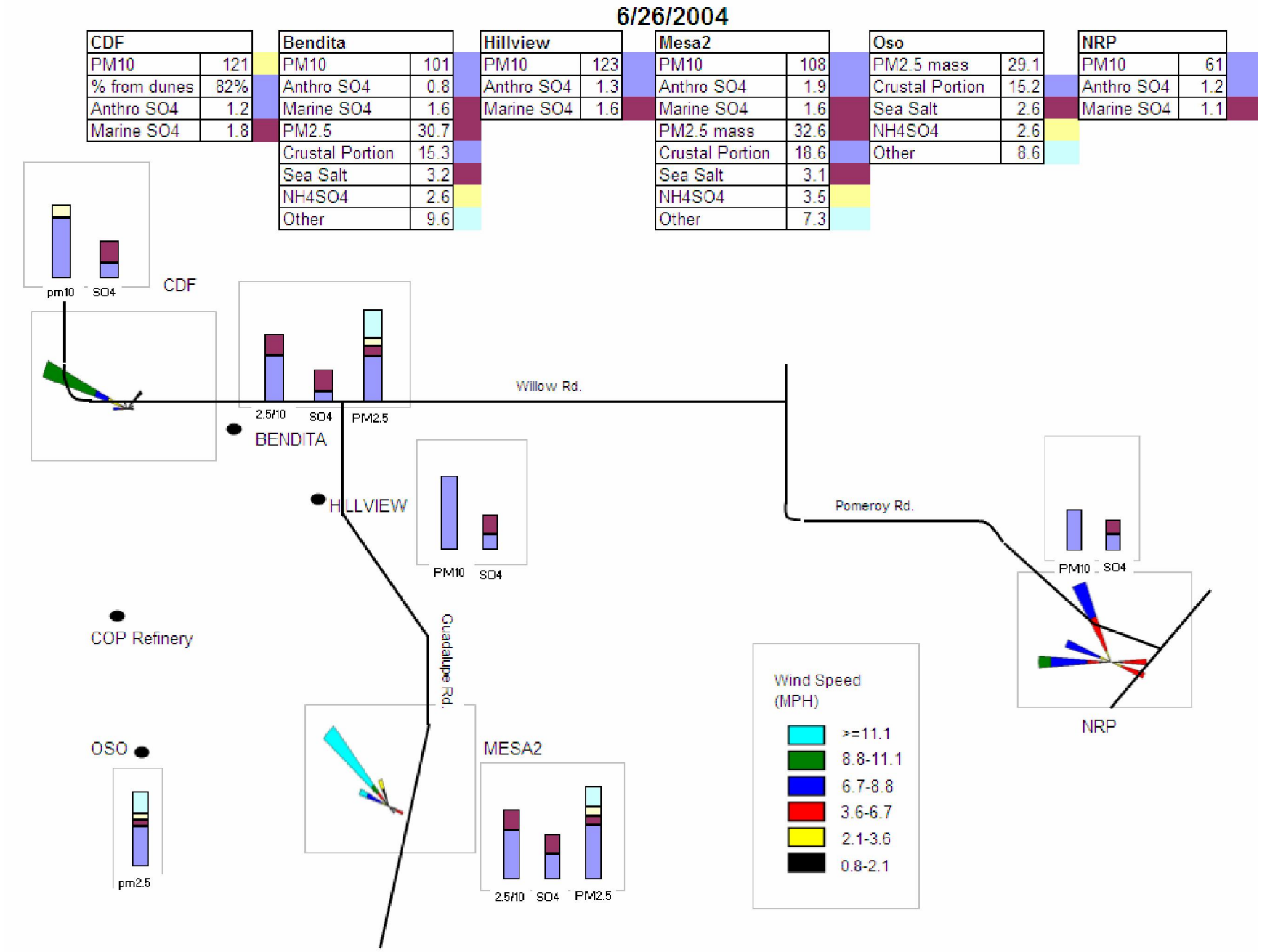


Figure B-4. 6/26/04

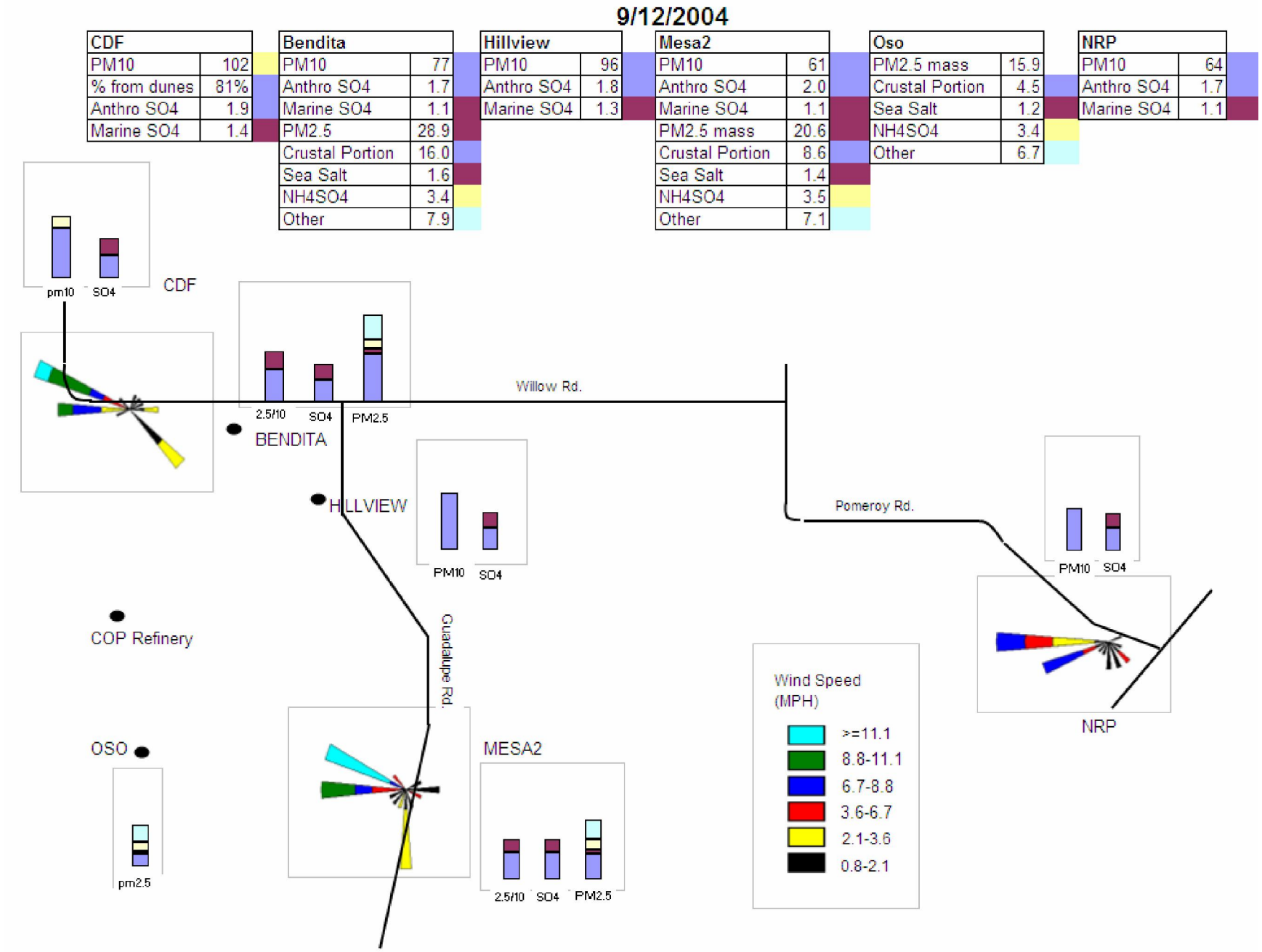


Figure B-5. 9/12/04

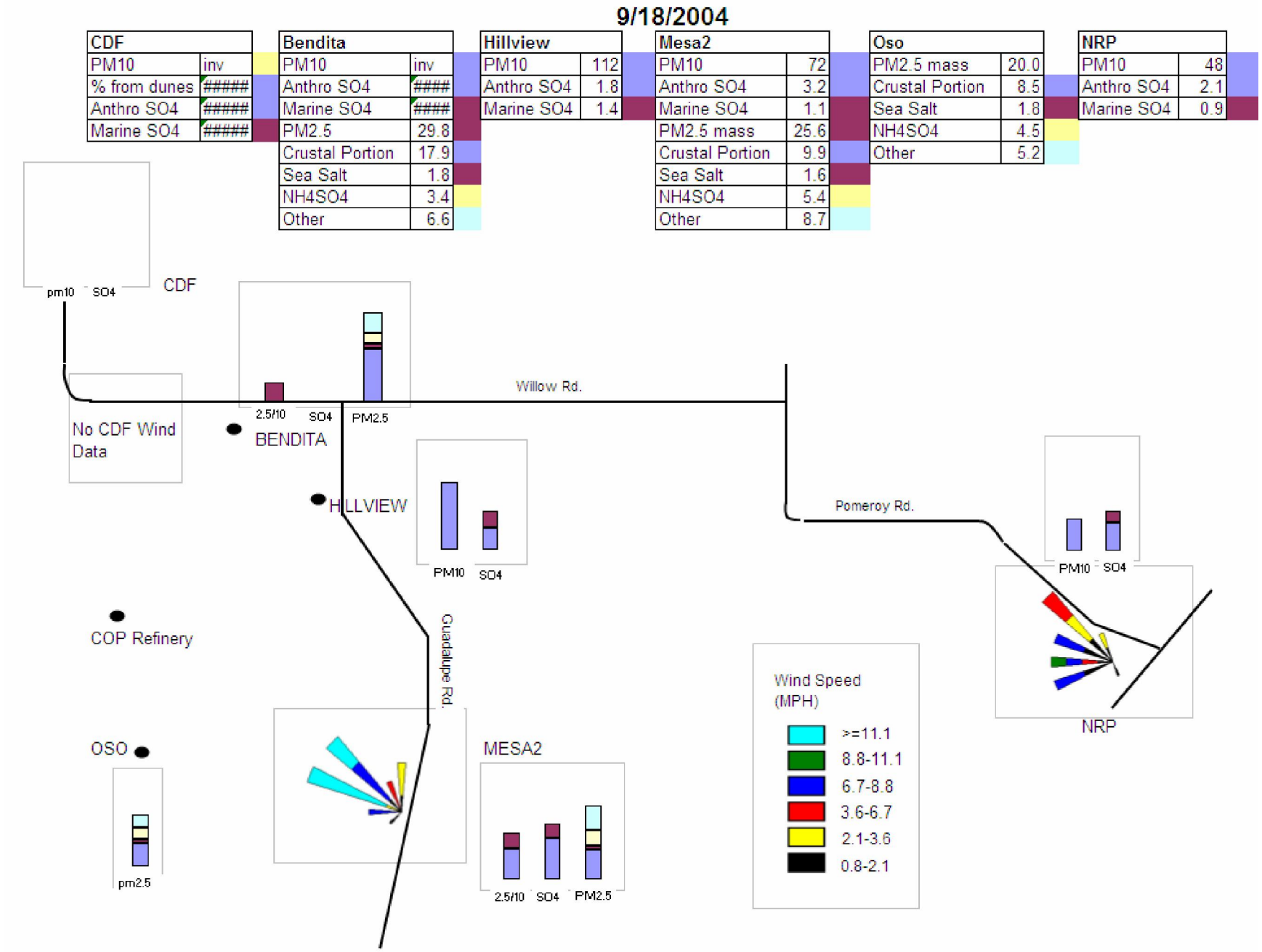


Figure B-6. 9/18/04

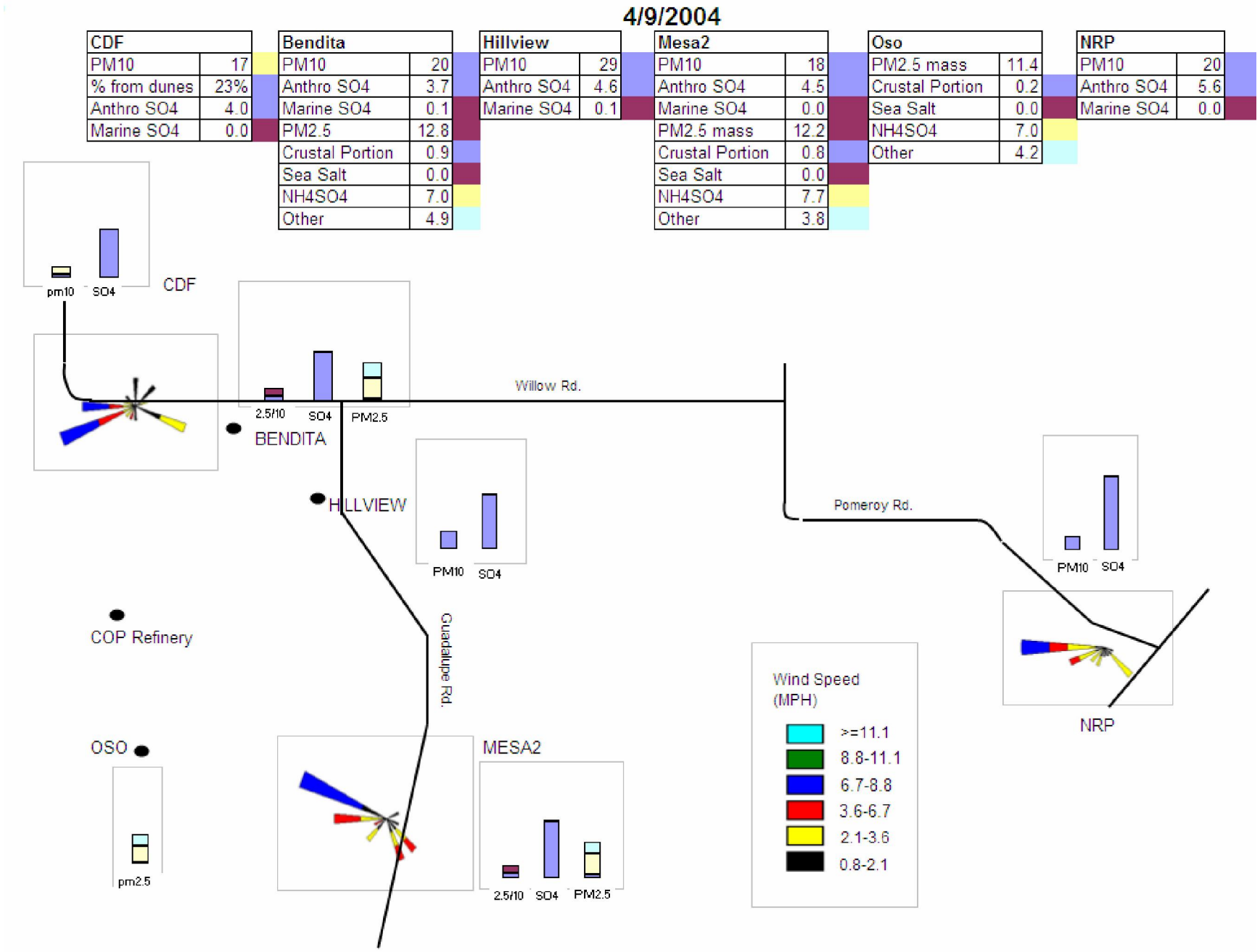


Figure B-7. 4/9/04

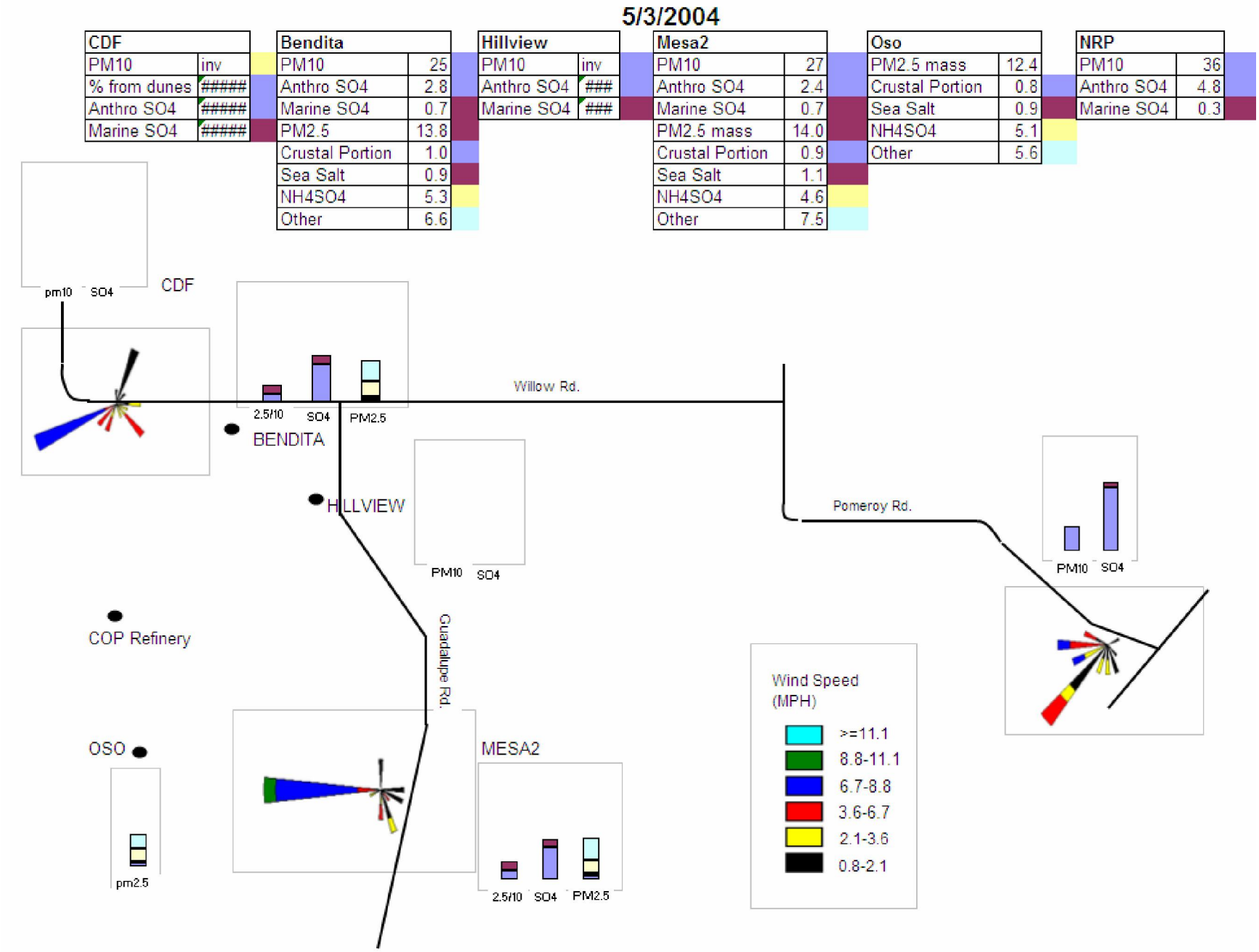


Figure B-8. 5/3/04

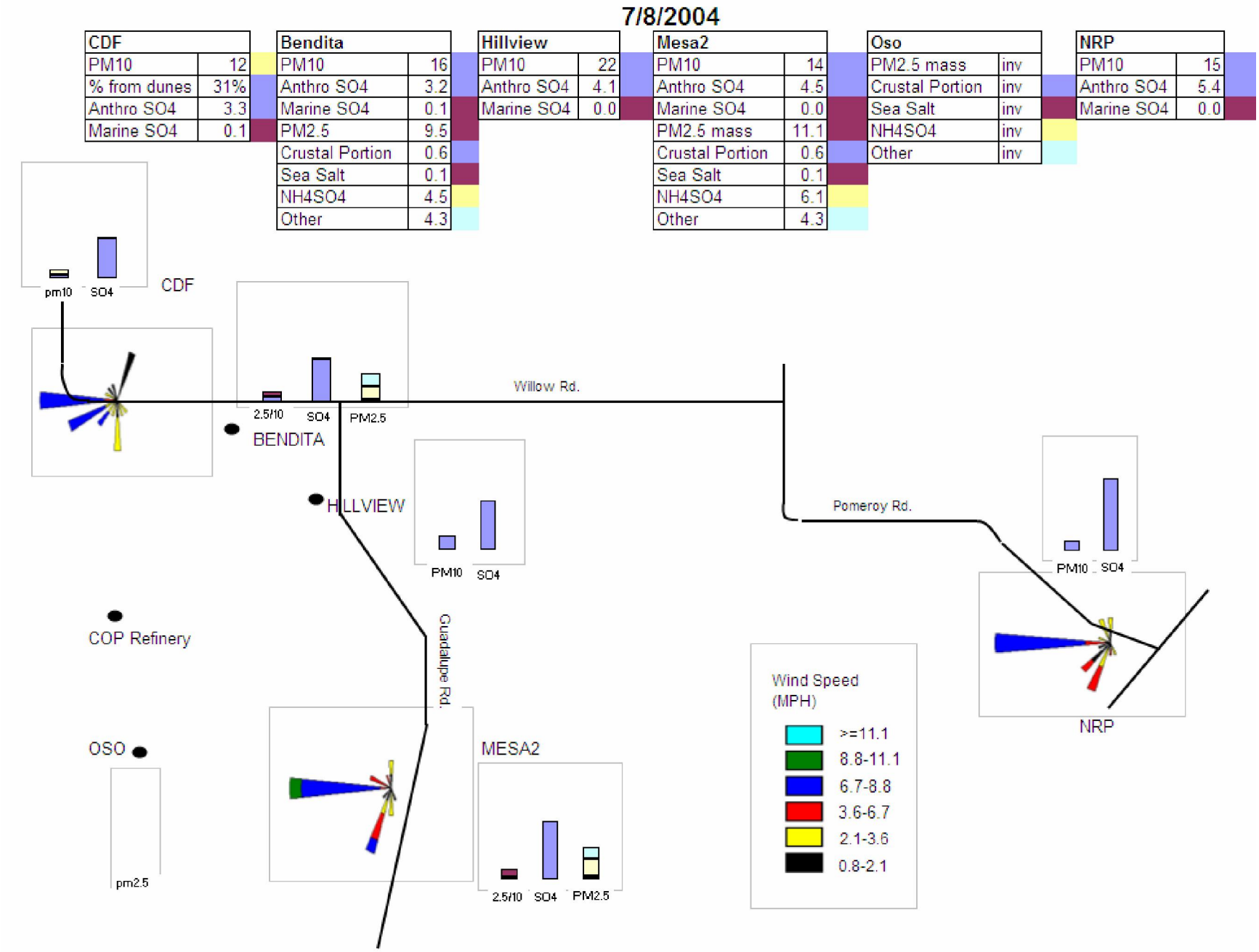


Figure B-9. 7/8/04

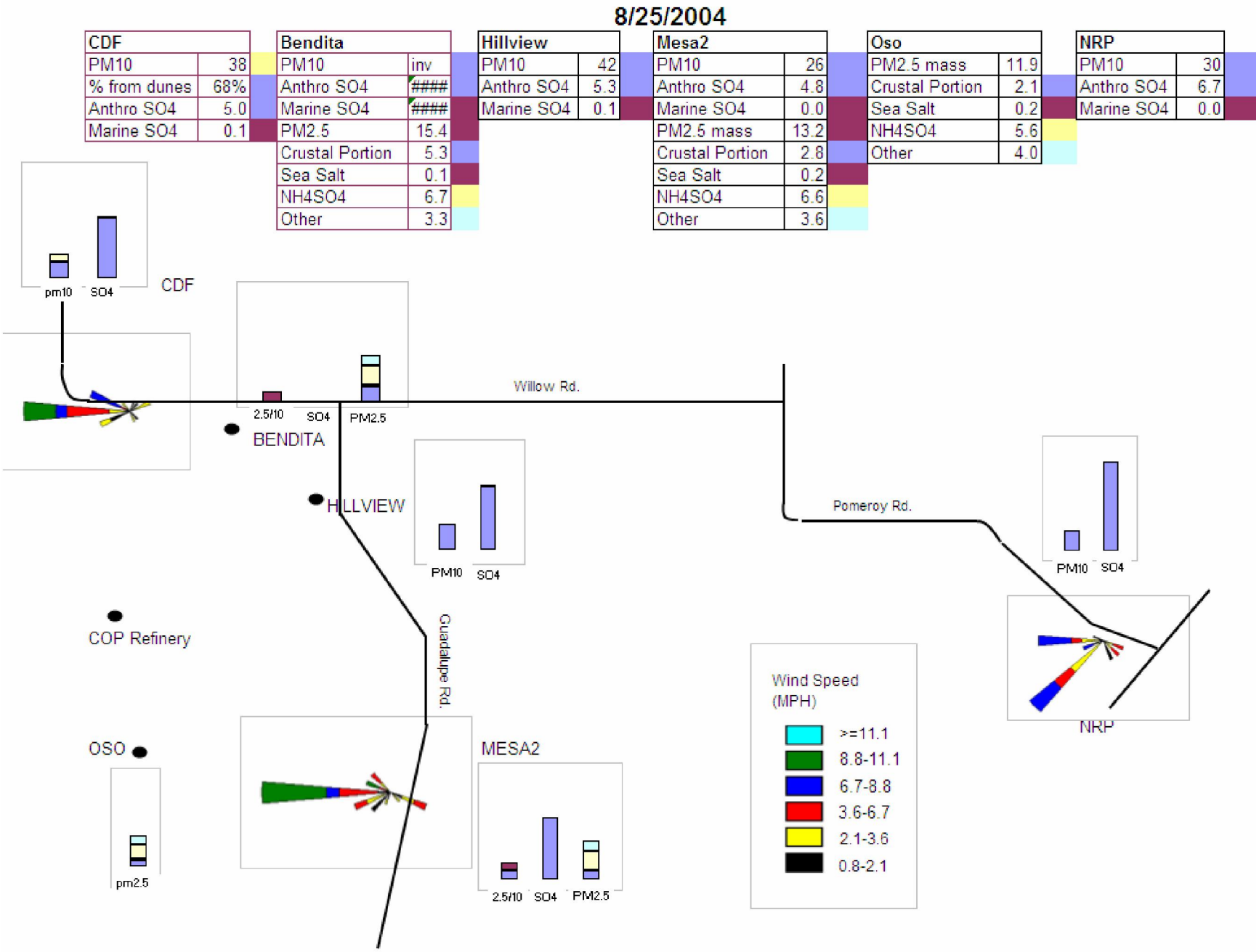


Figure B-10. 8/25/04

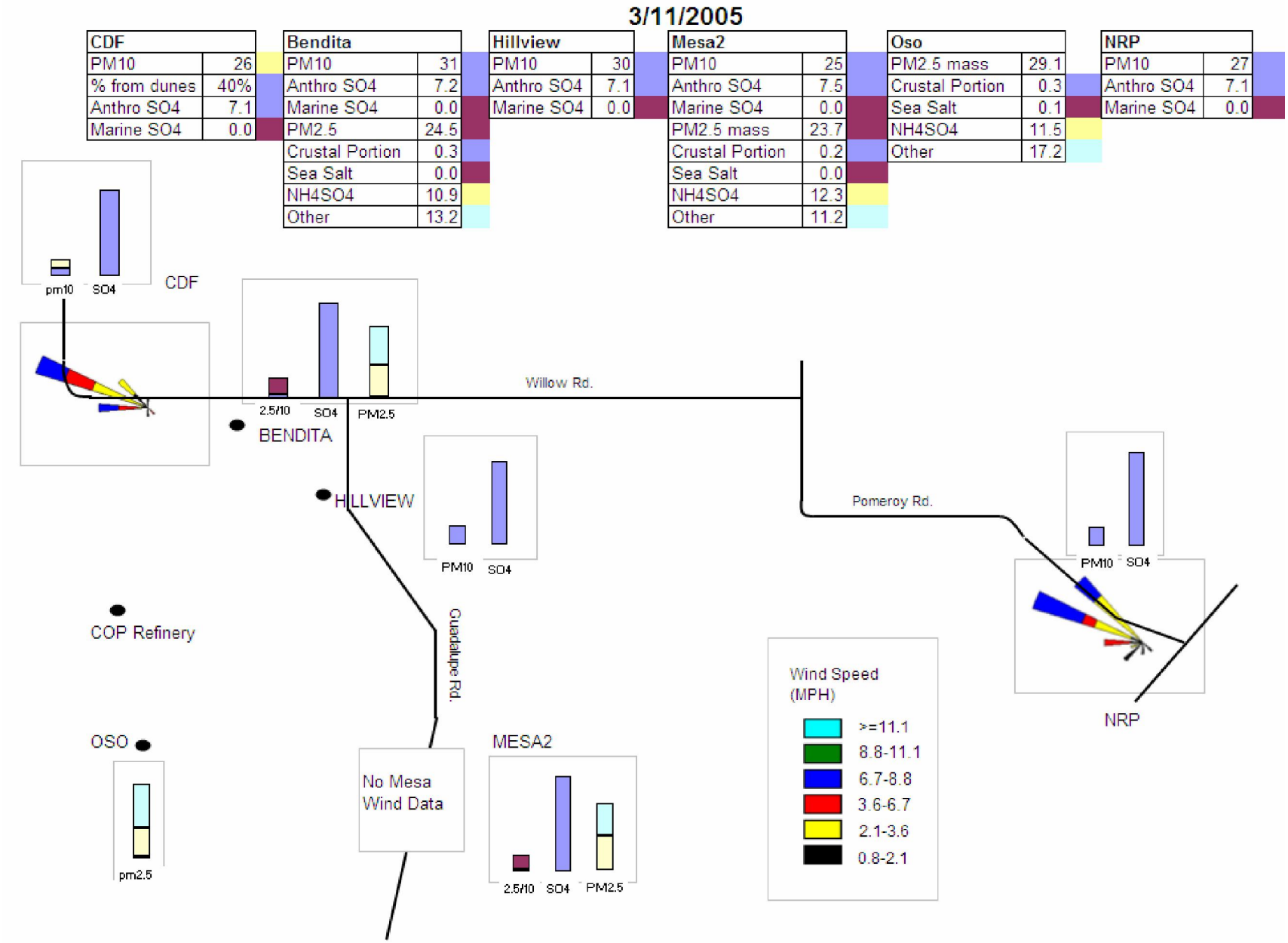


Figure B-11. 3/11/05