Roseville Rail Yard Air Monitoring Project (RRAMP)

Second Annual Report
Review and Summary of Year 2 (2006) Data

Prepared for

Placer County Air Pollution Control District
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1. INTRODUCTION

The Roseville Rail Yard Air Monitoring Project (RRAMP) is being undertaken under the auspices of the Placer County APCD (PCAPCD), in cooperation with the Union Pacific Railroad (UPRR), Sacramento Metro AQMD, and USEPA Region IX. The purpose of the project is to monitor for diesel locomotive emissions from the UPRR's J.R. Davis Rail Yard, located in Roseville, CA. The monitoring segment of the study consists of intensive monitoring by PCAPCD in each of the summers in 2005-2007 (mid-July to mid-October). Laboratory support for the study is provided by the California Air Resources Board and the South Coast Air Quality Management District. This second interim report summarizes the results of an independent review conducted by the Desert Research Institute of the internal, spatial, temporal, and physical consistency of each data set obtained during the second year of the monitoring program. This report also provides an initial summary and analysis of the data. It is preceded by a similar report for the first year of the monitoring program (Campbell and Fujita, 2006).

1.1 Background

The characterization of a community's exposure to air pollutants is essential in assessing cumulative impacts to public health. An important part of such assessments is the identification and quantification of disproportionate impacts that may be experienced by certain communities due to their proximity to sources of hazardous air pollutants. At the request of the Placer County Air Pollution Control District (PCAPCD), the California Air Resources Board (ARB) initiated a risk assessment study in 2000 of diesel emissions from the Union Pacific Railroad's J.R. Davis Rail Yard, located in Roseville, CA. The results of this assessment study, released in October 2004 (ARB, 2004), concluded excess cancer risk levels between 100 and 500 in a million in the neighborhood immediately downwind of the rail yard and risk levels between 10 and 100 in a million for up to 155,000 people that reside in a larger urbanized area downwind of the facility. Based upon these findings and community concerns, the PCAPCD initiated the Roseville Rail Yard Air Monitoring Project (RRAMP) in 2005. The purpose of this three-year monitoring study is to measure the air quality impacts of emissions, primarily diesel, from the rail yard facility and effects of mitigation measures that are implemented at the facility during this three-year period.

The main objectives of the RRAMP measurement program is to determine the localized air pollutant impacts from the emissions at the UPRR facility and to determine if any trends can be detected as a result of emissions mitigations which UPRR has agreed to implement over the three-year period of RRAMP. The air quality monitoring segment of the study commenced in summer 2005 and consists of intensive monitoring in each of the summers in 2005-2007 (mid-July to end of September). Monitoring for the RRAMP consists of two upwind/downwind pairs of monitoring sites aligned as optimally as possible to wind direction which most persistently is perpendicular to the rail yard tracks. The field measurements that were made during summer 2006 are summarized in Table 1-1. The prevailing winds during the late night through early morning hours in the summer months coincide with the conditions that are most favorable for achieving the monitoring objectives for the study. The map in Figure 1-1 shows the locations of the two upwind (Pool and Vernon) and two downwind (Denio and Church) sampling sites. The upwind/downwind wind directions between the Vernon/Church and Pool/Denio pairs are 137

and 162 degrees, respectively. Meteorologic data was also collected at the Roseville AQMD monitoring station which is located East of the area shown in the figure at 151 N Sunrise Bl.

Meeting RRAMP objectives depend upon factors that may contribute to the variations and overall uncertainty in downwind/upwind differences in pollutant concentrations over a three year period. These factors include precision and accuracy of measurements (the main focus of this interim report), diurnal, daily, seasonal, and annual variations in meteorological conditions that affect transport and dispersions of emissions, spatial and temporal variations in activity patterns that can affect the concentrations measured at downwind locations under the same meteorological conditions, and the expected changes in emission levels due to the mitigation measures that will be implemented by UPRR during the 3-year study relative to overall measurement uncertainty.

1.2 Objectives of RRAMP Data Analysis

This report is the second of three annual reports that provide analyses of the RRAMP data. Data analysis effort for the first two annual reports consists of the following six tasks.

1. Provide additional review of the RRAMP monitoring data to identify possible outliers and other data inconsistencies.

2. Provide general descriptive statistics for each measured parameter.

3. Compare the RRAMP black carbon (aethalometer) and PM2.5 (BAM) measurements with Federal Reference Method (FRM) particulate data and determine degree of correlation among methods.

4. Examine the temporal variations in specific ratios of pollutants and characterize variations in contributions of aged versus fresh emissions and elemental carbon versus total carbonaceous particulate matter.

5. Perform statistical analyses to determine upwind/downwind differences in concentrations of black carbon and $PM_{2.5}$.

The final report at the end of the three-year monitoring program will include the following additional task.

6. Using BC and/or EC as surrogates to estimate the mass concentrations and associated uncertainties of diesel particulate matter (DPM) levels at the downwind monitoring sites.

7. Examine trends in black carbon and $PM_{2.5}$ concentrations over the three-year duration of the RRAMP and determine their statistical significance.

Table 1–1. Summary of RRAMP Measurements During Summer 2006. Filter samples were collected every third day for 7 hours (or alternating 7 and 24 hour samples at Church and Vernon).

	Denio Site					
	Wind Spd & Dir (hourly)	NO/NOx (hourly)	Aethalometer BC (5 minute)	EBAM $PM_{2.5}$ (hourly)	Teflon Filter for $PM_{2.5}$	Quartz Filter for TOR
monitoring period	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/16~10/14	6/16~10/14
total observations	2965	2952	35584	2965	41	41
valid observatrions	2963	2853	32820	2942	41	40
% valid	99.9%	96.6%	92.2%	99.2%	100%	98%

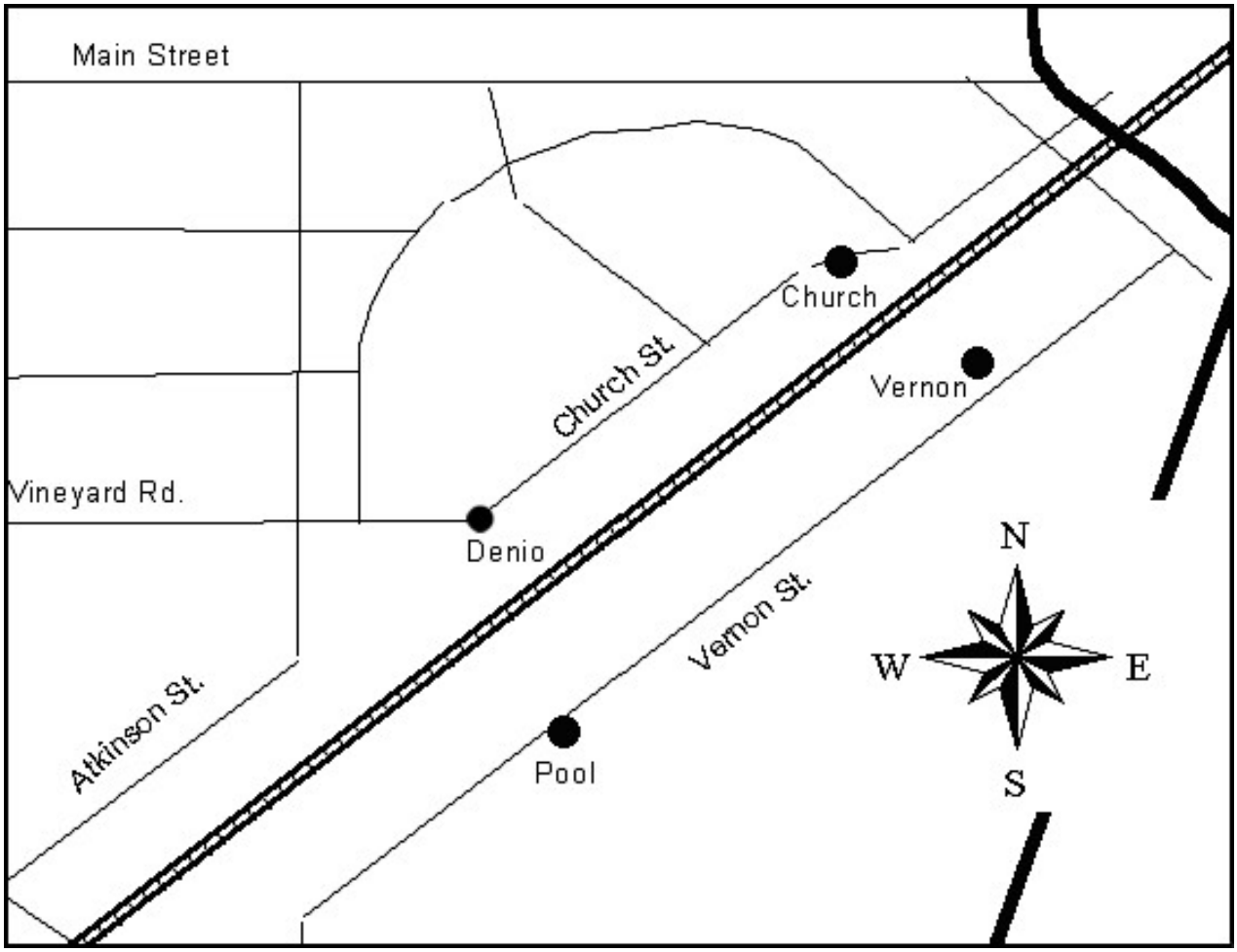
	Pool Site					
	Wind Spd & Dir (hourly)	NO/NOx (hourly)	Aethalometer BC (5 minute)	EBAM PM2.5 (hourly)	Teflon Filter for PM2.5	Quartz Filter for TOR
monitoring period	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/16~10/14	6/16~10/14
total observations	2965	2952	35584	2965	41	41
valid observatrions	2963	2906	34424	2638	41	41
% valid	99.9%	98.4%	96.7%	89.0%	100%	100%

	Church St. Site					
	Wind Spd & Dir (hourly)	NO/NOx (hourly)	Aethalometer BC (5 minute)	BAM PM2.5 (hourly)	Teflon Filter for PM2.5	Quartz Filter for TOR
monitoring period	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/16~10/14	6/16~10/14
total observations	2965	2952	35584	2965	42	42
valid observatrions	2965	2888	34106	2944	40	41
% valid	100.0%	97.8%	95.8%	99.3%	95%	98%

	Vernon St. Site					
	Wind Spd & Dir (hourly)	NO/NOx (hourly)	Aethalometer BC (5 minute)	BAM PM2.5 (hourly)	Teflon Filter for PM2.5	Quartz Filter for TOR
monitoring period	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/16~10/14	6/16~10/14
total observations	2965	2952	35584	2965	42	42
valid observatrions	2965	2926	33738	2941	40	41
% valid	100.0%	99.1%	94.8%	99.2%	95%	98%

	Roseville Met Tower						
	Wind Spd (m/s)	Std Dev. Of Wind Dir	Temp. @ 2m (F^0)	Delta of Temp. (F^0)	RH (%)	SR (W/m2)	Pressure (in/Hg)
monitoring period	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	7/15~10/15
total observations	2953	2953	2953	2953	2953	2953	2953
valid observatrions	2953	2953	2953	2953	2953	2953	2953
% valid	100.0%	100.0%	100.0%	100.0%	100%	100%	100%

Figure 1-1. Map showing locations of the two upwind (Pool and Vernon) and two downwind (Denio and Church) sampling locations. The bearing between the Vernon/Church and Pool/Denio pairs is 137 and 162 degrees, respectively.



2. EVALUATION AND VALIDATION OF RRAMP DATA

The determination of differences in measured parameters between the upwind and downwind sites requires a quantitative assessment of the relative precision between the paired samplers and measurement biases. Relative precision and bias were evaluated by examining the collocated sampler data collected before and after the summer sampling period, and accuracy was assessed by comparing time-averaged continuous sampler data with results from time-integrated filter methods. We also describe exceptional events and characteristics of the data that may affect the observed differences between paired measurements. The specific procedures described below were used to validate and analyze the continuous pollutant data and time-averaged filter-based FRM data. PCAPCD staff provided an initial review of the data by flagging suspect data due to sampler malfunctions or flow rates that were out of range. The validation checks performed by DRI checked the consistency of the data between sites and between pollutants at the same site. For consistency, these procedures will be applied to the data for all three years in the project final report. Appendix A describes the methods that were used during the summer 2006 measurement program and estimates of measurement precision and bias.

2.1 Aethalometer Black Carbon Data

The Aethalometer data is known to be strongly affected by electronic noise spikes which create exaggerated increases or decreases in individual measurements of light attenuation. Since the instruments estimate black carbon concentrations based on the slope of the change in attenuation, a single spike will produce two periods of inaccurate measurement. However, time-averaging those two periods together will negate the effect of the spike and give the correct value. Problems can occur when the time-averaged values do not contain a sufficient number of individual measurements to effectively cancel out the noise (this issue is discussed in the 2005 version of the aethalometer documentation provided by Magee Scientific). In this 2006 study the instruments were operated with the default 5-minute time constant, so each hourly average contains a maximum of 12 discrete measurements. Therefore, the probability of the two halves of a noise-related “bounce” in the signal being split between two hourly averages is 1:6.

Another issue is the periodic advancing of the filter tape to keep the optical attenuation in range of the detectors. When the tape changes there is a 15 minute gap in data collection and baseline shifting may occur. The instruments were operated with a preset tape advance schedule to minimize data loss per recommendation made in the first annual interim data review and analysis report. Overall, tape advance times varied slightly but were generally consistent starting at 5:25, 13:25, 21:25 and rarely occurred during the critical overnight hours except at Denio, where there were apparent tape advances at 1:35 from 7/29-8/7, and at Pool where an apparent tape advance occurred at 23:15 on 6/26.

The Aethalometers used in this study were dual wavelength instruments that simultaneously made measurements of the transmittance of the filter tape at 880 nm (Channel 1) and 370 nm (Channel 2) and converted them to black carbon concentrations using fixed mass absorption efficiency factors for each wavelength. All analysis of data presented in this report is for the data from channel 1, unless stated otherwise, since the longer wavelength is known to be absorbed more specifically by elemental carbon soot. The channel 2 data was used only for quality assurance purposes.

We calculated the incremental change in BC between successive 5-minute aethalometer measurements and prepared a histogram of the changes, then flagged pairs of data points that result in incremental changes that are clearly inconsistent with the overall distribution. Based on this analysis, we set criteria for flagging unrealistic spikes in data for further investigation. Basically this step involves making two passes through the data. The first pass involves an "eyeball" check to flag data that are inconsistent. Then a second pass through the data set is used to identify and flag potentially invalid data based on specific quantitative criteria developed to identify invalid data.

An algorithm was applied to the 5 minute averaged data to identify all 'bounces' (negative/positive pairs) and confirm that they did not overlap two different hourly averaging periods. In addition, we identified all values < -1 ug/m3 not associated with 'bounce'. These were eliminated from the data set along with unreasonably large spikes (>80 ug/m^3) and excessively negative values (<-10 ug/m^3). Data periods affected by this screening were: Vernon - 7/21-7/22 (all hours) and 7/23 (3 and 4 AM); Church - 7/22 (2, 3, and 4 AM).

We also examined all spikes (absolute change between successive 5 min values > 10 ug/m^3) not associated with 'bounce' to see if they were consistent with surrounding data and data from the other sites. Inconsistent spikes were flagged as questionable data (QD) and isolated spikes as local events (E). Finally, we removed all out-of-range flow, QD, and local Events from dataset before averaging by day or overnight period. A relatively small number of the more than 10,000 possible 5 minute data points for each site were flagged by this process, as shown in Table 2–1. After removing all invalid or suspect data points, we averaged the 5-minute BC data by hour, eliminating hours with less than nine (9) valid 5-minute observations (i.e., ≥75% data capture).

2.2 Application of Time and Wind Criteria

Based on prior data and analysis, it was decided that the evaluation of downwind-upwind differences in pollutant concentrations would be done on a restricted set of data adhering to the following criteria:

- Time period from 10PM to 5AM PST, when vertical mixing is limited.
- Wind speeds between 0.5 and 4 m/s (the maximum wind speed was increased from earlier criteria based on analysis of current wind data).
- Wind direction at downwind sites between 45 and 225 degrees (from general direction of rail yards).

After filtering out data for all measured parameters associated with hours that do not meet criteria for the time period of interest (2200 - 0500 PST) we compared wind data from all four sites. Scatter plots of hourly wind vector speeds comparing upwind/downwind pairs, upwind pair, and downwind pair are shown in Figure 2-1. Scatter plots indicate generally higher wind speeds at downwind sites, which is expected due to greater fetch. There were some exceptions, especially for the Vernon site where several of the highest hourly wind speeds were recorded. However the correlation between the two upwind sites Vernon and Pool is good, so no bias was indicated. Comparison of downwind and upwind pairs is generally about 1:1, except for wind speeds >2.5 m/s at Denio which exceed those measured at Church by as much as 1.5 m/s. A 20 to 25% bias in wind speeds measured by the two EBAMs used at Denio and Pool was apparent in

the pre and post-study period collocation data. To determine which instrument was responsible for the error we compared to the data from the pair of BAMs during the post-study collocation period, which showed excellent agreement for wind speed. Unfortunately, all 4 instruments were never operated at the same location so there is substantial scatter in the data shown in Figure 2-2, but it seems clear that the bias was due to a combination of the Denio instrument reading high while the Pool instrument read low. Since the mean wind speeds during the study period were 1.5 ± 0.03 m/s at both downwind sites it seems safe to assume this bias did not have a significant impact on the data selection.

The next step was to filter out data that do not meet criteria for wind speed (<1 m/s or >4 m/s at either downwind site). This is a wider range than the 1-5 mph (approximately 0.5 to 2.2 m/s) previously suggested for Year 1 data. Preliminary analysis of the wind data from 2006 indicated that a 5 mph (2.2 m/s) upper limit would exclude about 30% of the available data, as shown in Figure 2-3. As mentioned previously, data from year one will be reanalyzed based on a consistent set of criteria for the final report. Comparison of hourly wind direction at the four sites indicates that flow is still generally consistent across the rail yard at speeds up to 4 m/s (see Figure 2-4).

Next, hourly differences in wind direction for upwind/downwind pairs, upwind pair, and downwind pair were examined for evidence of bias. Based on comparison of wind directions measured at the four sites, there is an apparent bias in the wind direction data from Denio site, as shown in Figure 2-5 where the differences between the wind direction at Denio and the other sites converge towards a delta of about 35 degrees at higher wind speeds, rather than converging to 0-10 degrees as for the Church/Vernon and Pool/Vernon site pairs. Examining the wind data from the pre and post study collocation periods (the met data for each site was collected by the BAM and EBAM PM monitors) indicates that the instrument that had been located at the Denio site (EBAM 2237) was reading about 20 degrees high relative to the instrument used at the Pool site during the post study collocation period (see Figure 2-6). Bias during the pre-study periods and for the other pair of instruments was less significant (5 to 10 degrees).

Fortunately, these biases have little impact on the selection of data for upwind/downwind site comparison since the winds were consistently well within the range of interest during the overnight hours, as shown in Figure 2-4. Applying the wind direction and speed criteria described above to the overnight hourly wind data from the Church site resulted in elimination of 18% of the data from further analysis. All of the hours in this subset also meet the same criteria at the Denio site, regardless of whether or not we adjusted for the apparent biases in winds speed and direction at Denio. An additional 6 to 7 % of the overnight hours met the wind criteria at Denio, but failed on the basis of wind directions outside the specified range at Church.

2.3 Hourly Pollutant Data Distributions

Data distribution plots (histograms) were prepared for each parameter to look for data points that are clearly inconsistent with the overall distribution and flag as outliers.

NO and NO_x. Histograms in Figure 2-7 and Figure 2-8 show no outliers after removing two significantly negative data points from NO record at Pool (>-40 and >-100 ppb). NO at Pool was slightly below zero (-1 ppb) 34% of recorded hours. Similar values for NOx were recorded 3% of hours. Since no zero values were recorded at the downwind sites, it is not possible to say whether these periods of baseline shift also occurred there. As such, an uncertainty of 1 ppb will be assumed for the hourly measurements.

BC (Channel 1). Histograms in Figure 2-9 show no outliers (data was already screened at 5 min level).

BAM. Histograms in Figure 2-10 show no outliers, except a large spike ($PM_{2.5}$ = 343 μg/m^3) at Church Sept 15, 23:00. This spike falls within the period of the Ralston fire (9/5 to 9/17), so it was not used in our analysis.

2.4 Hourly Pollutant Time Series

Appendix B contains separate time-series plots of hourly data (filtered as per previous steps) for NO, NO_x, $PM_{2.5}$, BC (channel 1), and wind speed for all four sites. Additionally, NO, NO_x, and BC were plotted together since both NO and BC are expected to be largely due to local diesel emissions at the downwind sites. NO and BC generally track each other well. We examined these plots by month to look for inconsistencies in temporal patterns or inter-parameter relationships and flag questionable data, and used these plots to determine validity of outliers identified by the distribution analysis. If outliers were not consistent with data from related instruments or sites, or if other parameters indicate the occurrence of an exceptional event, they were flagged as invalid. The following data were either flagged as suspect or deleted.

- A period of unusually elevated NO was recorded at Pool from July 25 to 30. Further examination revealed that the data for this period were identical to that reported for the Denio site. In addition, temperature data from Pool NOx instrument indicate that the air conditioning/heating was not working. Data for Pool were deleted for this period.

- There was a period of continuously high NO at Church from Jul 27-29 that was not observed at any of the other sites. BC was not proportionately high during this period, but NO/NOx ratios were normal. These NO data were marked as suspect.

- At Denio on Sept. 7 and Sept. 26 large peaks in BC occurred (the one on Sept. 7 was the largest recorded – 11.8 ug/m3) without corresponding increases in NO, PM, or BC at other sites. The BC(1)/BC(2) ratios during these periods were unexceptional. Flagged as suspect.

- A large spike of $PM_{2.5}$ (161 ug/m3) was recorded at Denio on 9/29 22:00, with no corresponding increase in BC or at other sites. It was flagged as suspect.

- At Pool on Aug 3, 0:00, there was a large spike of $PM_{2.5}$ during one hour with no corresponding increase in BC or at other sites. Data were flagged as suspect.

- At Church, reported BAM $PM_{2.5}$ concentrations all equal 1.0 ug/m3 from July 12 – 16. This data was assumed to be due to a malfunction and deleted.

2.5 Related Pollutant Ratios

Additional QA procedures were applied by calculating hourly ratios of BC(1)/BC(2) (measurements using two different wavelengths from the same instrument), PM/BC(1), and NO/NO_x for each site. Appendix B contains separate time-series plots of hourly data NO/NO_x, PM/BC(1) and BC(1)/BC(2) ratio for all four sites.

NO/NOx ratios were consistent between sites, with similar averages at downwind sites and much lower averages at upwind sites. The maximum ratio is about 0.85 at all sites. No values greater than mean +2σ of all data existed (no values >0.88). BC/PM ratios were consistent between sites, with similar averages at downwind sites and much lower averages at upwind sites. Several unusually high hourly averages (BC > 50% of PM) were observed at the downwind sites, but all corresponded to period of low PM concentration (<20 ug/m3) and may be attributed to poor accuracy of BAM data at these levels where the measurement precision error is approximately 40% of the reported concentration. BC(1)/BC(2) ratios were higher at downwind sites (±2σ = 0.9 to 1.6) than typically observed for ambient data (0.8 to 1.2). BC(1)/BC(2) ratios at the Pool site were lower than elsewhere with many values between 0.4 and 0.8, possibly due to a greater influence of PM sources rich in high MW organic carbon such as on-road diesel vehicles or badly maintained cars to which channel 2 is more sensitive.

2.6 Collocation Data

Correlation plots of data from collocated samplers for pre- and post-study periods and regression statistics were used to estimate precision and identify the magnitude of possible biases between samplers. This analysis was used to estimate the uncertainty of the calculated upwind/downwind differences.

2.6.1 Collocated Aethalometer Black Carbon Data

Good agreement was observed between the Aethalometers used at Denio and Pool sites during pre-study collocation tests, as shown in Figure 2-11. The dashed lines show the range of residuals relative to the regression line, ±20%. Results were somewhat better for this pair of instruments during the post-study collocation, as shown in Figure 2-12, where the range of residuals is only about ±10%. It was demonstrated in the previous year's analysis that the errors are proportional to the measured concentration, rather than a consistent absolute variability. In order to quantify the range of errors, the relative differences between the two collocated instruments (relative error = difference in measured concentration between the two instruments divided by the average of the two measurements).

Although the statistically significant slopes of the regression lines suggest some small bias between the instrument pairs, averaging the biases from the pre- and post-study periods essentially eliminates the bias. In addition, the distribution of errors is always centered within 5% of zero. For these reasons we have chosen not to make any bias correction and allow small changes in the relative response of the instrument pairs to be accounted for by the precision uncertainty.

Figure 2-13 shows the distribution of relative errors during the pre- and post-study periods for the two Aethalometers used at the Denio and Pool sites. The histograms show that the relative errors assume a fairly steep normal distribution with the 95th percentile occurring at <20% relative difference. There was substantially higher relative error during the pre-study collocations, so these larger values of the 95th percentile error are used as the estimates of precision for the aethalometer data. As shown by the dashed lines in the regression plots, this may be somewhat overly conservative for very high BC concentrations, but accounts for the variance well throughout most of the range.

Agreement between the pair of instruments used at the Church/Vernon pair of sites was also good during the pre-study collocation, as shown in Figure 2-14 and Figure 2-15. Figure 2-16 shows that 95% of the relative errors are within 15%. The propagated errors for 7-hour and 24-hour averages shown in Table 2–2 are intended only to represent an estimate of the uncertainty of the aethalometer data in the time averages used for the subsequent downwind-upwind differential analysis. This estimate assumes that the measured concentrations during an averaging period are relatively constant. In practice, the propagated errors for each daily average will be calculated as:

$$\overline{\sigma} = \frac{\sigma\sqrt{\sum_{1}^{n} C_i^{\,2}}}{\sum_{1}^{n} C_i}$$

Where σ is the relative error, *C* is the measured concentration, and *n* is the number of measurements averaged.

2.6.2 Collocated BAM $PM_{2.5}$ Mass Concentration Data

Regression analysis revealed a small but significant bias of about 15% for each pair of BAM instruments which was consistent for both the pre- and post-study data periods. The data from the downwind sites was adjusted to account for this bias (Denio*0.82+0.37 and Church*0.88+1.98) using the average of the pre- and post-study regression slopes and intercepts shown in Table 2–3. The average coefficient of variance (CV) is also presented, along with the regression statistics, in Table 2–3 as a gauge of how precision varied between instrument pairs and collocation periods, but it is not useful as an estimate of precision in calculating the uncertainty of the downwind-upwind differences since it may be biased high due to the larger relative differences that occur at very low concentrations. The regression approach avoids this by weighting the higher concentrations more.

The distribution of differences in measured concentration between the collocated pairs of samplers after correcting for bias (Figure 2-19 and Figure 2-22) indicates that the error is random in nature and assumes an approximately normal distribution. This differs from the aethalometer where the error is proportional to measured concentration. From the error distribution we can estimate the precision for each pair at the 95% confidence level as a fixed quantity (11.5 ug/m^3 for Denio/Pool and 9.5 ug/m^3 for Church/Vernon (i.e., 95% of the observed differences between the collocated pair of instruments are less than the specified precision). The dashed lines on the regression plots (Figure 2-17, Figure 2-18, Figure 2-20, and Figure 2-21) show that the majority of the scatter in the data set is accounted for by the precision error derived from the distribution analysis. Table 2–3 shows the resulting errors 7-hour and 24-hour averages propagated as the root mean square of the hourly precision error:

$$\overline{\sigma} = \frac{\sqrt{\sum_{1}^{n} \sigma_i^{\,2}}}{n}$$

where *n* is the number of measurements used in the average and σ is the relative precision error.

2.7 Filter versus Continuous Data

The results of laboratory analysis of the 24-hour (midnight to midnight PST) and 7-hour (2200 to 0500 PST) filter samples collected at the four sites were compared to the averages of corresponding data from the continuous PM and BC instruments. All hourly data collected during the study period was averaged by 24-hr day and overnight period (7 hours), eliminating days with less than 18 valid hours, or nights with less than 5 hours of valid data for any parameter (i.e., ≥75% data capture). The date on which the overnight period began was used to designate that average. Correlation plots of FRM PM versus BAM PM (Figure 2-23 and Figure 2-24) and of FRM EC versus aethalometer BC(1) (Figure 2-25 and Figure 2-26) were prepared. We used regression statistics to identify the magnitude of possible biases. The regression statistics are summarized in Table 2–4. The BAM PM results were adjusted to match the FRM PM measurement results, by applying the best-fit regression coefficients for the aggregate data from all sites (shown in the Table in bold face type) to the BAM data.

2.7.1 Filter Gravimetric Mass Versus Continuous BAM Mass Concentrations

For the 24 hour filters there is no statistically significant difference between the site specific means of the averaged continuous and filter data, and regression analysis shows that the slope and intercept of the gravimetric vs. BAM least-squares linear fit are not significantly different from 1.0 and 0.

For the 7 hour filters collected during nighttime hours there is again no statistically significant difference in the site specific means.. Regression analysis shows slopes significantly greater than 1 for Church and Pool sites. Owing to the weak correlation between the FRM and BAM PM2.5 concentrations at Denio and Vernon (the correlation for Vernon is not statistically significant at the 95% level), it is not advisable to apply site-specific corrections to the BAM data. The weak correlations can be attributed to the relatively low concentrations experienced and the short sample time for the FRM filters. Good agreement between BAMs and FRM gravimetric mass has been observed in other studies where a larger range of concentrations were sampled (Chow, et al., 2006). Combining all data yields a regression slope of 1.13 ± 0.16 (not significantly greater than 1 at the 95% level) and an intercept of -2.16 ± 4.85. This regression equation was used to adjust the BAM data before performing the calculation of downwind-upwind differences. Forcing the intercept through zero for the combined data yields a slope of 1.00, but it reduces the goodness of fit and conflicts with the apparent non-zero intercepts for the individual site data in Figure 2-24. In practice, applying the combination of a slope slightly greater than 1 and a small negative intercept results in little change from the measured values with the range of data observed in this study ($PM_{2.5}$ = 1 to 40 ug/m^3 for the overnight averages at all sites).

Two outliers were removed from the data for this analysis; both were extreme values of gravimetric mass for the site (20.4 ug/m3 at Vernon on July 1 and 30.6 ug/m^3 at Denio on Oct. 5) and the difference between filter and BAM was well outside the range of other data. Data collected during the Ralston fire was excluded from this analysis, as well as the sample days when 24 hour filters were being collected at Church and Vernon in order to avoid biasing the combined regression towards the sites with more 7 hour samples.

The difference in the comparison results between the 24 hour and 7 hour sample groups may be due to the higher fraction of PM that is organic carbon (70% for 24 hour vs. 90% for 7

hour, based on mean ratio of uncorrected OC to gravimetric mass). Since the BAM can overestimate mass for aerosols with high organic content due to the increased fraction of hydrogen atoms in the material[1], the higher slopes observed for the 7-hour overnight samples could result.

2.7.2 Filter Elemental Carbon Versus Aethalometer BC Concentrations

Although there is no statistically significant difference between the mean EC and BC for either the 24-hour or 7-hour data from the individual or combined sites, the regression analysis does indicate some biases (see Figure 2-25, Figure 2-26, and Table 2–4). For the 24-hour samples collected at Church and Vernon there is a consistent slope indicating that the BC/EC ratio was about 0.7. The y-intercepts were not significantly different from zero. For the 7-hour samples the regression results were not significantly different, except at Church where the correlation was again very robust ($r^2 = 0.86$) and the slope was somewhat lower (0.53 ± 0.11 BC/EC).

The primary purpose of relating the Aethalometer BC measurements to filter EC, which is also an operationally defined parameter rather than a distinct physical material, is for the purpose of estimating the concentrations of diesel particulate matter (DPM) that are being contributed by the railyard to the area downwind. This estimation will involve several steps:

1. Determination of the characteristic ratio(s) of PM to EC in relevant diesel source emissions.
2. Characterization of the relationship between BC and EC for DPM in diesel dominated ambient air.
3. Estimation of the concentration of excess BC contributed by the source to the target area (downwind sites).
4. Conversion of BC concentrations to DPM using relationships derived in steps 1 and 2.
5. Validation of estimated DPM impact by comparison with information on local emissions patterns and activity.

In this process we assume that any increase in BC observed at the downwind sites relative to the upwind sites is due to fresh DPM emissions from the railyard area, therefore we may apply PM/EC ratios measured during locomotive load testing in step 1 above. This would not be appropriate for BC measured at the upwind sites, which is presumably from other sources and potentially modified during longer-range transport.

As such, it is only relevant to this process to try to convert the excess BC measured at the downwind sites to EC-equivalent concentrations so that we may use it to estimate DPM. Figure 2-27 shows the correlation between the difference in average overnight 7-hr BC between the upwind and downwind site pairs and difference in corresponding EC from the FRM filters (in other words, we compared the increase in BC and EC measured at the downwind sites relative to the upwind sites. The correlations are quite good, but there seems to be some difference between the 2 site pairs. This could be due to some variation in the response of the Aethalometers (we

[1] The beta-gauge method responds to the density of protons in the filter deposit and assumes a proportional number of neutrons to estimate mass concentration.

only compared the instruments to their upwind/downwind counterparts in analyzing the collocation data).

Table 2–1. Number of 5 minute aethalometer BC data points eliminated or flagged during the QA process. The full data set is composed of over 35,000 data points.

flag	Denio	Pool	Church	Vernon
Local Events	0	0	8	28
Negative	0	0	4	9
Outliers	0	0	3	7
Spikes	13	1	6	0

Table 2–2. Precision analysis of collocated Aethalometer data. Linear regressions use data from the sampler used at the upwind site as the independent (x) variable.

site pair	**Denio/Pool**		**Church/Vernon**	
Instrument IDs	**626/624**		**623/A479**	
Test Period	02/23/06-05/01/06	10/17/06-11/06/06	02/23/06-05/01/06	10/17/06-11/02/06
averaging period	1 hour	1 hour	1 hour	1 hour
mean BC (ug/m3)	1.92	2.41	1.62	1.98
regression				
r2	0.97	1.00	0.98	0.99
slope	0.957 ± 0.009	1.027 ± 0.003	0.980 ± 0.007	1.124 ± 0.004
intercept	0.05 ± 0.03	0.01 ± 0.01	0.02 ± 0.02	0.00 ± 0.01
relative difference				
mean	-1.2%	3.2%	0.5%	11.9%
2*stdev	23%	10%	28%	11%
skew	4.57	-1.71	9.06	-0.13
95% error estimates				
1 hr average	20%	10%	15%	17%
7 hr average	8%	4%	6%	6%
24 hr average	4%	2%	3%	3%

Table 2–3. Precision analysis of collocated BAM data. Linear regressions use data from the sampler used at the upwind site as the independent (x) variable.

site pair Instrument IDs	Denio/Pool E2237/E2238		Church/Vernon 4514/4515	
Test Period	05/01/06-05/24/06	10/16/06-10/31/06	05/25/06-06/12/06	10/17/06-11/06/06
averaging period	1 hour	1 hour	1 hour	1 hour
mean PM (ug/m3)	17.9	15.5	10.3	17.1
regression				
r2	0.72	0.67	0.75	0.86
slope	0.833 ± 0.045	0.805 ± 0.029	0.855 ± 0.047	0.911 ± 0.017
intercept	0.74 ± 1.97	0.00 ± 0.59	1.74 ± 1.26	2.22 ± 0.37
CV	32%	41%	43%	30%
average bias	**E2237**		**4514**	
multiply by	0.82		0.88	
add	0.37		1.98	
absolute difference	**E2237 - E2238**		**4514 - 4515**	
mean	4.94	5.55	3.29	4.00
stdev	3.90	4.43	2.97	3.33
skew	1.29	1.33	1.30	1.20
95% error estimates				
1 hr average	11.5	12.0	9.0	10.0
7 hr average	4.3	4.5	3.4	3.8
24 hr average	2.3	2.4	1.8	2.0

Table 2–4. Comparison of filter results and continuous sampler data. Linear regressions use FRM filter data as the independent (x) variable. Adjustments that were applied to data are highlighted in bold.

	number of samples	mean ± 2*stderr	mean ± 2*stderr	r^2	slope ± 2*stderr	y-intercept ± 2*stderr
24hr PM2.5		**Gravimetric**	**BAM**			
Church	19	12.4 ± 1.9	13.1 ± 2.3	0.70	1.00 ± 0.33	0.73 ± 8.62
Vernon	19	9.7 ± 2.2	11.9 ± 2.7	0.89	1.15 ± 0.20	0.50 ± 4.40
Both	38	11.1 ± 1.5	12.5 ± 1.8	0.79	**1.04 ± 0.18**	**0.88 ± 4.38**
24hr EC/BC		**EC**	**BC**			
Church	18	1.8 ± 0.4	1.5 ± 0.3	0.75	0.67 ± 0.31	0.36 ± 1.26
Vernon	18	1.1 ± 0.3	1.0 ± 0.2	0.73	0.66 ± 0.25	0.25 ± 0.65
Both	36	1.4 ± 0.2	1.3 ± 0.2	0.79	**0.70 ± 0.15**	**0.26 ± 0.51**
7hr PM2.5*		**Gravimetric**	**BAM**			
Denio	16	16.6 ± 2.6	16.1 ± 2.5	0.41	0.61 ± 0.40	5.92 ± 13.75
Pool	17	12.6 ± 3.2	12.4 ± 5.3	0.87	1.52 ± 0.31	-6.82 ± 8.50
Church	17	15.4 ± 2.7	16.1 ± 3.7	0.95	1.38 ± 0.16	-5.76 ± 5.23
Vernon	15	10.4 ± 3.0	8.4 ± 2.0	0.20	0.49 ± 0.33	3.91 ± 7.70
All	65	13.8 ± 1.5	13.4 ± 1.8	0.74	**1.11 ± 0.16**	**-1.82 ± 4.80**
7hr EC/BC*		**EC**	**BC**			
Denio	16	3.1 ± 0.8	3.3 ± 0.8	0.74	0.83 ± 0.30	0.65 ± 2.14
Pool	17	0.6 ± 1.5	0.8 ± 1.4	0.72	0.80 ± 0.26	0.32 ± 0.44
Church	17	2.8 ± 0.8	2.2 ± 0.5	0.86	0.53 ± 0.11	0.72 ± 0.70
Vernon	17	0.8 ± 0.3	0.7 ± 0.2	0.67	0.49 ± 0.18	0.34 ± 0.37
downwind - upwind difference (7hr) *		**EC**	**BC**			
ΔDenio-Pool	33	2.5 ± 0.6	2.5 ± 0.6	0.80	**0.92 ± 0.17**	**0.13 ± 0.71**
ΔChurch-Vernon	30	2.0 ± 0.6	1.5 ± 0.6	0.90	**0.55 ± 0.08**	**0.34 ± 0.29**

**Only data for nights when 7-hr samples were collected at all sites were used to calculate statistics shown.*

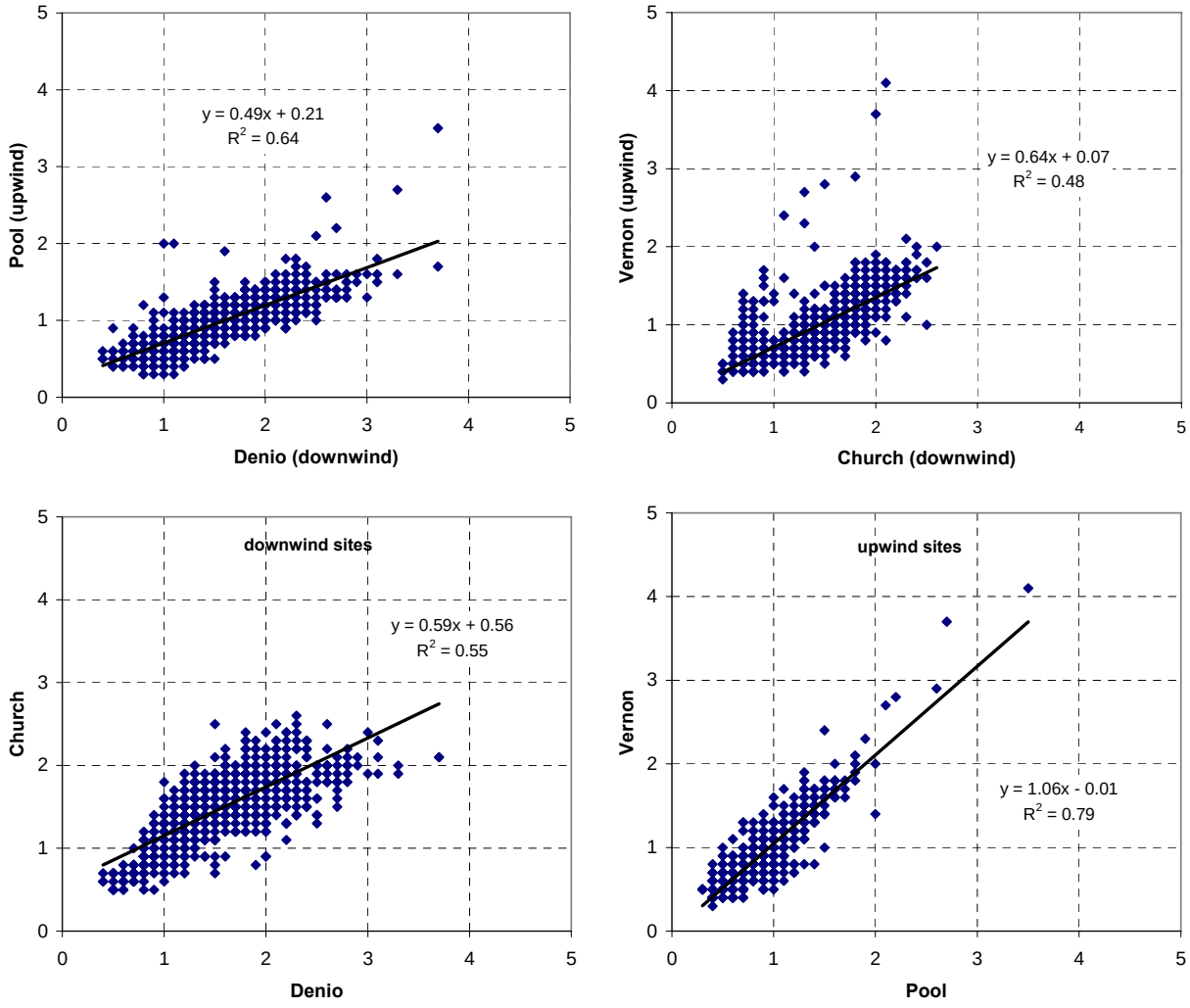


Figure 2-1. Comparison of hourly mean wind speeds (m/s) from 22:00-5:00 at site pairs.

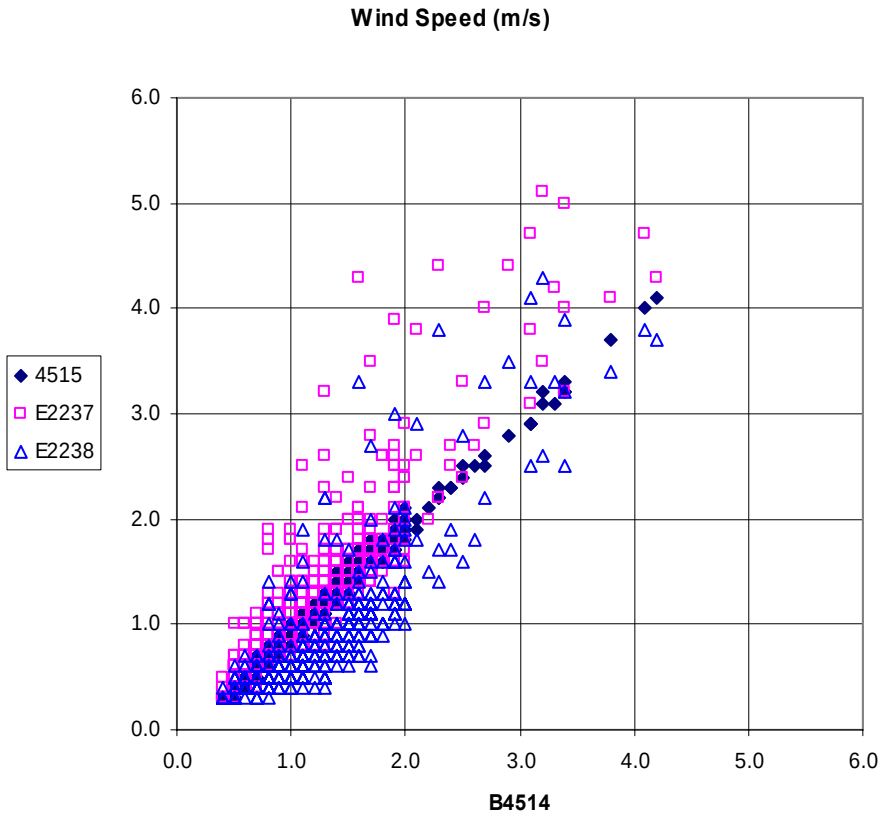


Figure 2-2. Hourly average wind speed (meters per second) from instruments collocated after the main study period. E2237 was used at Denio, E2238 at Pool, and 4515 at Vernon.

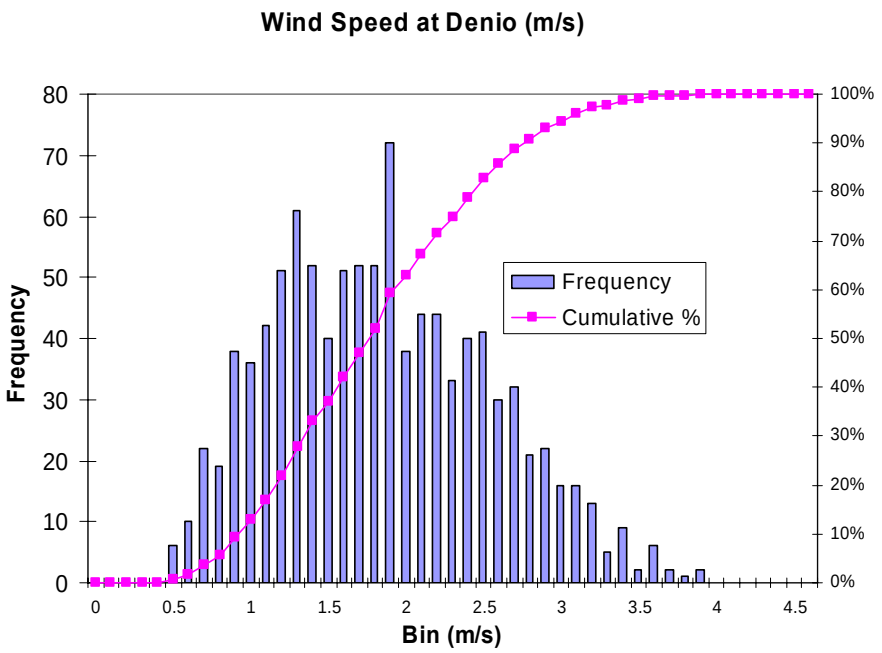


Figure 2-3. Distribution of hourly mean wind speeds (m/s) from 22:00-5:00 at Denio site.

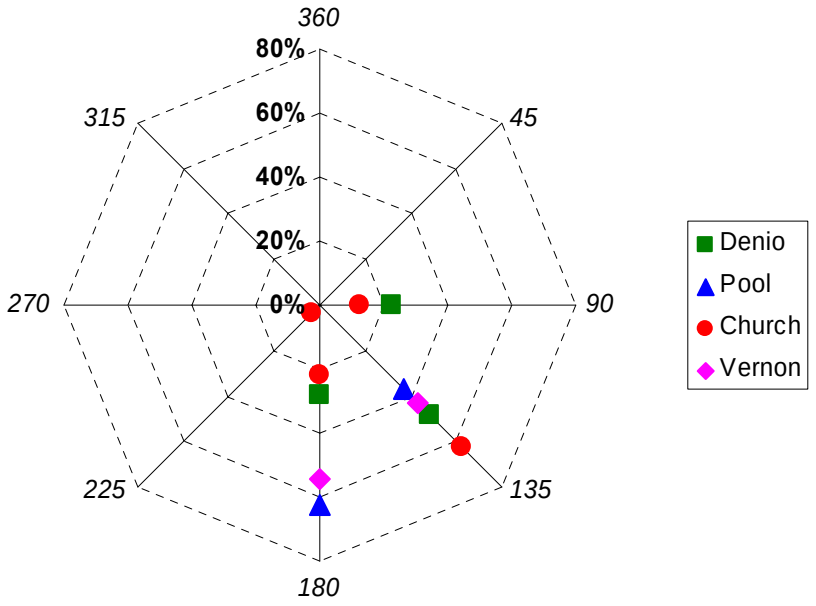


Figure 2-4. Frequency of hourly average wind directions at the four sites during overnight hours (22:00 to 05:00 PST). Wind directions have been rounded to the nearest 45 degrees. Only hours where winds were between 45° and 225° were used to determine downwind-upwind differences.

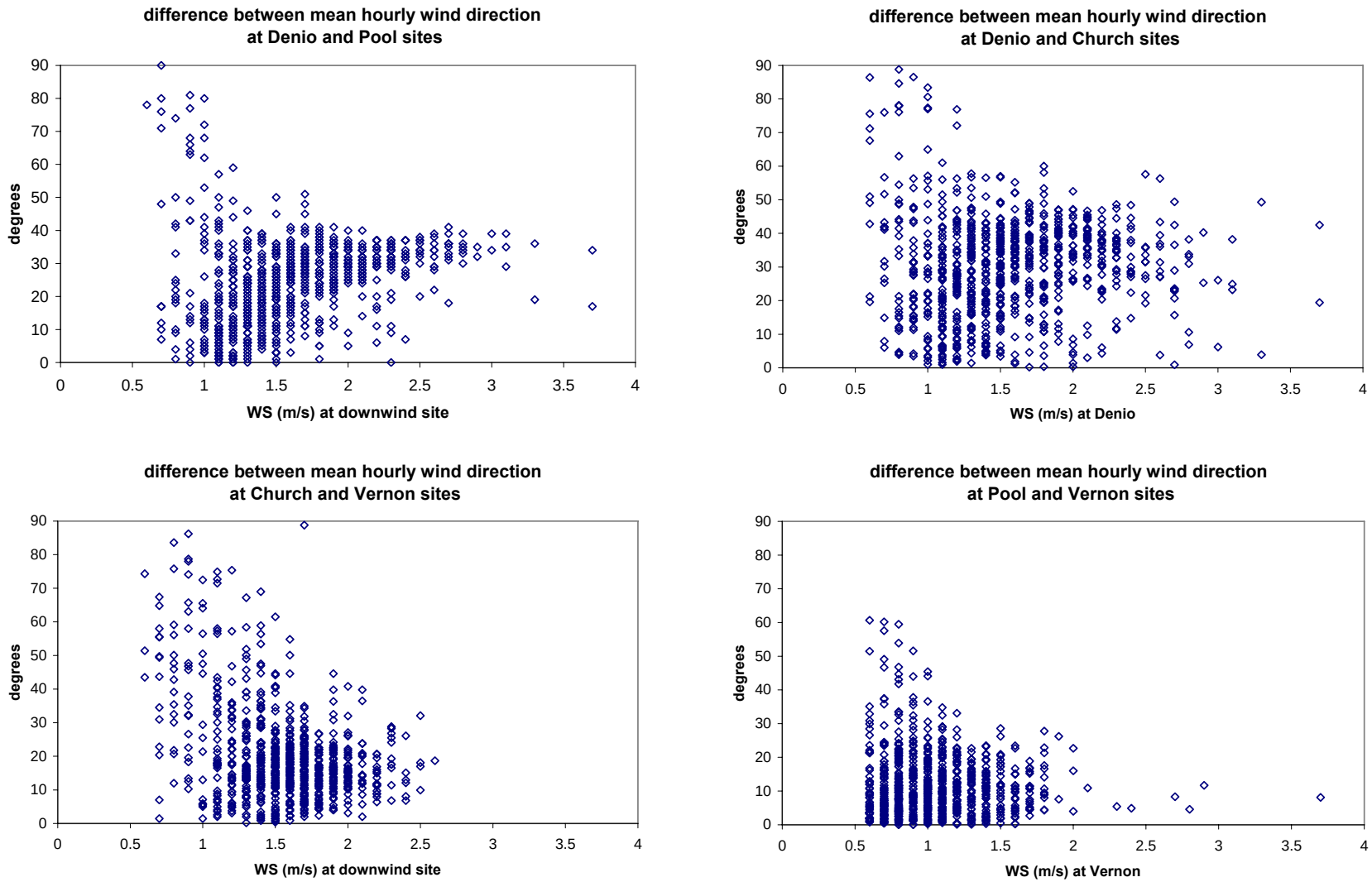


Figure 2-5. Differences in mean hourly wind direction between site pairs.

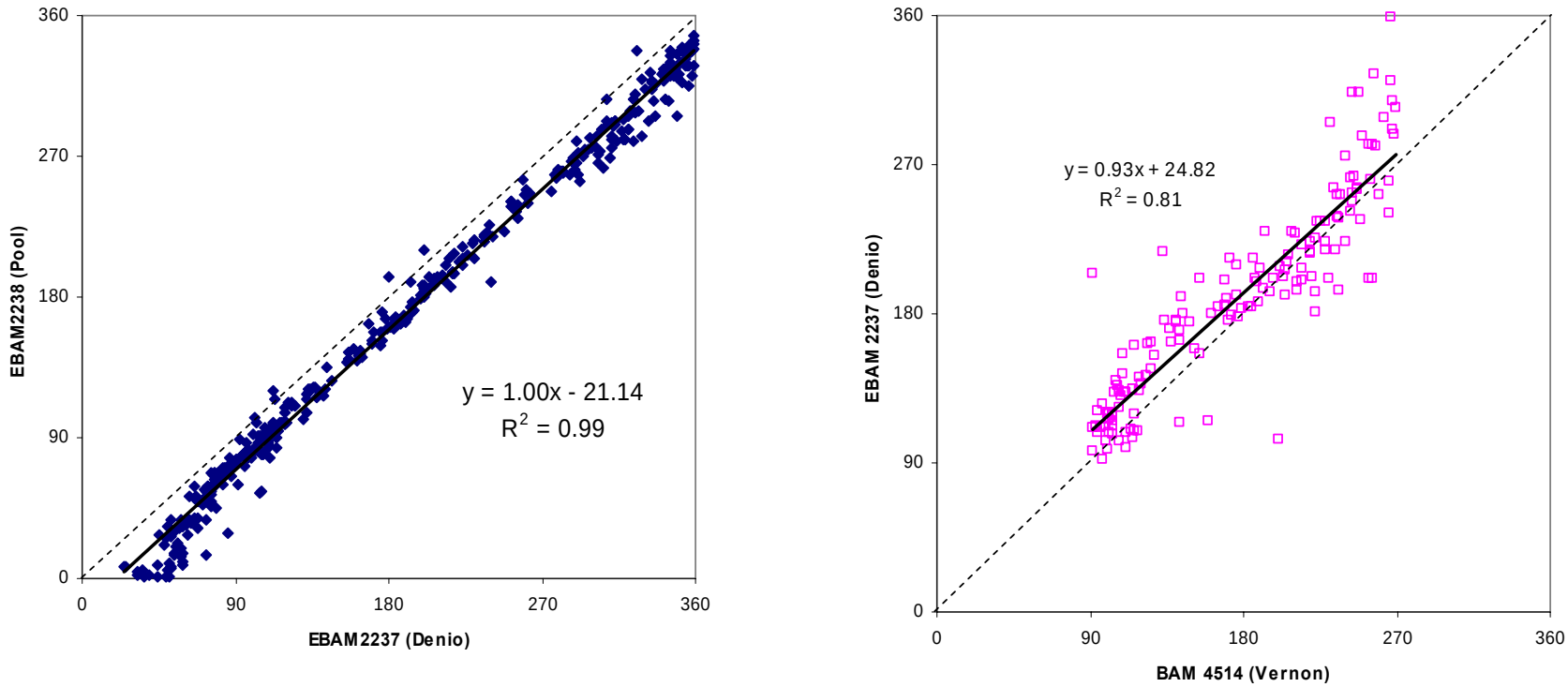
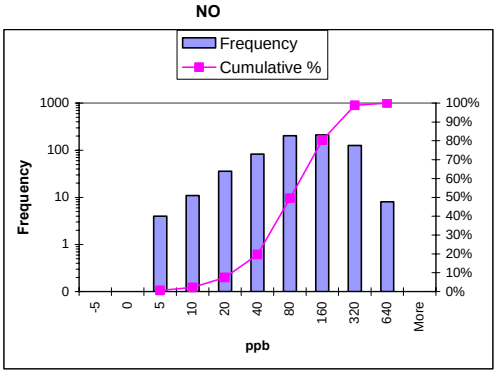


Figure 2-6. Hourly average wind direction (degrees) from instruments collocated after the main study period. BAM 4514 is believed to be accurate due to its excellent agreement with BAM 4515 during the collocation tests. The dashed lines representing a 1:1 relationship are included for comparison.

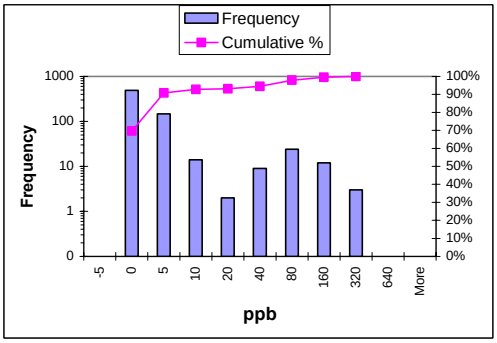
DENIO

Bin (< or =)	Frequency	cumulative %
-5		
0		
5	4	0.59%
10	11	2.20%
20	36	7.49%
40	83	19.68%
80	203	49.49%
160	210	80.32%
320	126	98.83%
640	8	100.00%
More		



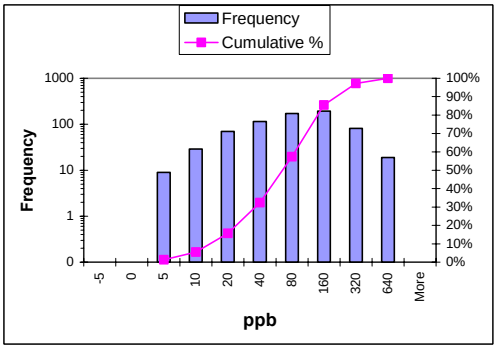
POOL

Bin (< or =)	Frequency	cumulative %
-5		
0	488	69.71%
5	148	90.86%
10	14	92.86%
20	2	93.14%
40	9	94.43%
80	24	97.86%
160	12	99.57%
320	3	100.00%
640		
More		



CHURCH

Bin (< or =)	Frequency	cumulative %
-5		
0		
5	9	1.31%
10	29	5.52%
20	70	15.70%
40	115	32.41%
80	172	57.41%
160	193	85.47%
320	81	97.24%
640	19	100.00%
More		



VERNON

Bin (< or =)	Frequency	cumulative %
-5		
0	648	92.57%
5	39	98.14%
10	4	98.71%
20	3	99.14%
40	4	99.71%
80	1	99.86%
160	1	100.00%
320		
640		
More		

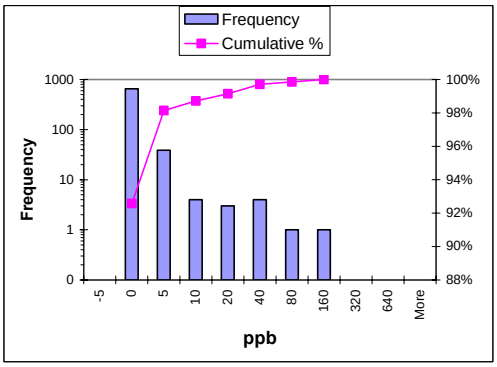
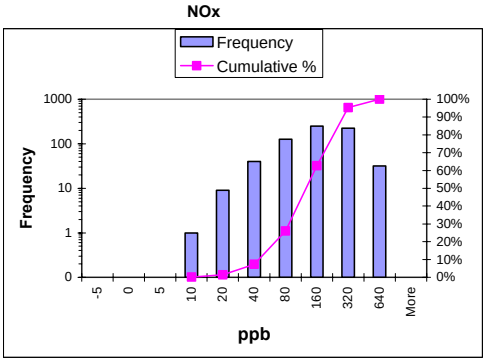


Figure 2-7. Histograms showing the frequency distribution of hourly averaged NO data at the four sites.

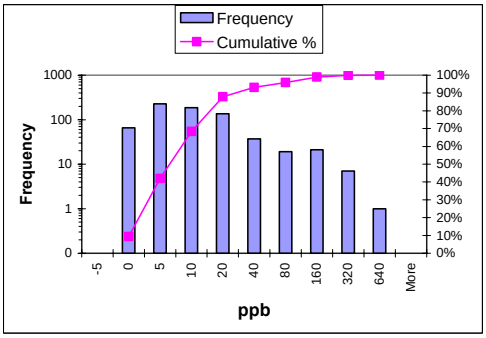
DENIO

Bin (< or =)	Frequency	umulative %
-5		
0		
5		
10	1	0.15%
20	9	1.47%
40	40	7.34%
80	127	25.99%
160	250	62.70%
320	222	95.30%
640	32	100.00%
More		



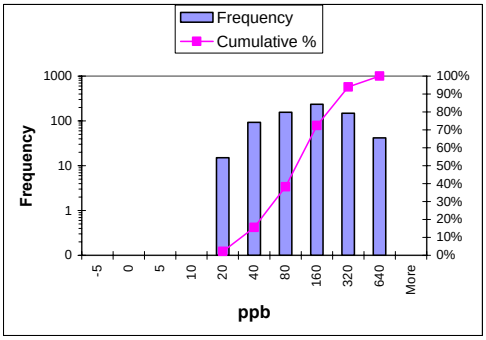
POOL

Bin (< or =)	Frequency	umulative %
-5		
0	66	9.43%
5	228	42.00%
10	185	68.43%
20	136	87.86%
40	37	93.14%
80	19	95.86%
160	21	98.86%
320	7	99.86%
640	1	100.00%
More		



CHURCH

Bin (< or =)	Frequency	umulative %
-5		
0		
5		
10		
20	15	2.18%
40	92	15.55%
80	156	38.23%
160	235	72.38%
320	148	93.90%
640	42	100.00%
More		



VERNON

Bin (< or =)	Frequency	umulative %
-5		
0	17	2.43%
5	247	37.71%
10	245	72.71%
20	149	94.00%
40	34	98.86%
80	6	99.71%
160	2	100.00%
320		
640		
More		

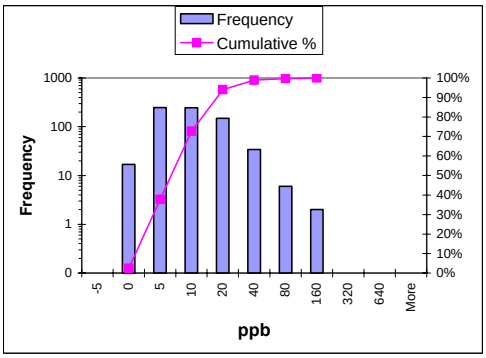
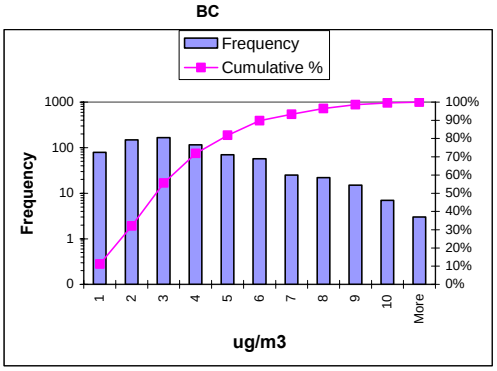


Figure 2-8. Histograms showing the frequency distribution of hourly averaged NOx data at the four sites.

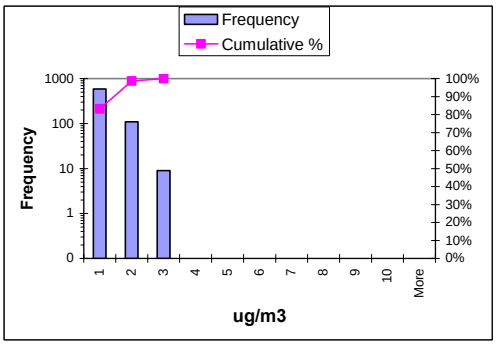
DENIO

Bin (< or =)	Frequency	cumulative %
1	79	11.17%
2	148	32.11%
3	166	55.59%
4	115	71.85%
5	70	81.75%
6	57	89.82%
7	25	93.35%
8	22	96.46%
9	15	98.59%
10	7	99.58%
More	3	100.00%



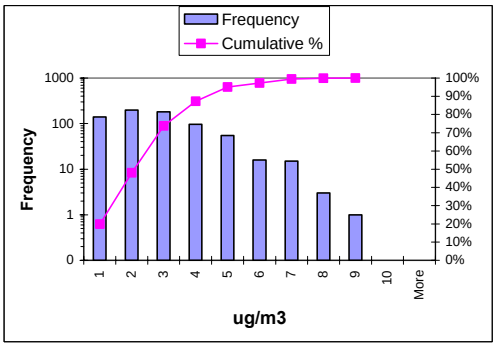
POOL

Bin (< or =)	Frequency	cumulative %
1	588	83.17%
2	110	98.73%
3	9	100.00%
4		
5		
6		
7		
8		
9		
10		
More		



CHURCH

Bin (< or =)	Frequency	cumulative %
1	140	19.80%
2	199	47.95%
3	182	73.69%
4	96	87.27%
5	55	95.05%
6	16	97.31%
7	15	99.43%
8	3	99.86%
9	1	100.00%
10		
More		



VERNON

Bin (< or =)	Frequency	cumulative %
1	616	87.13%
2	80	98.44%
3	11	100.00%
4		
5		
6		
7		
8		
9		
10		
More		

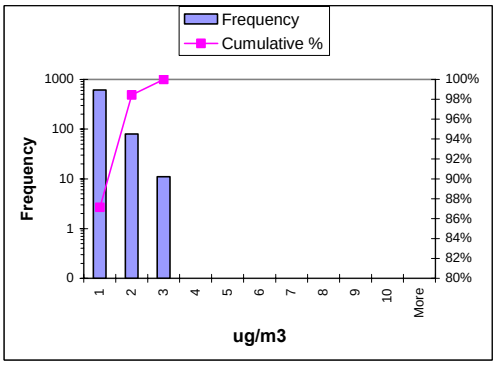
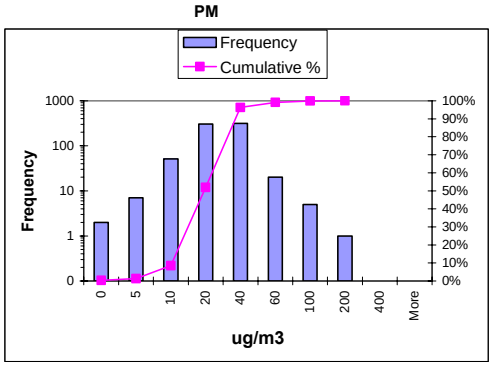


Figure 2-9. Histograms showing the frequency distribution of hourly averaged Aethalometer BC(1) data at the four sites.

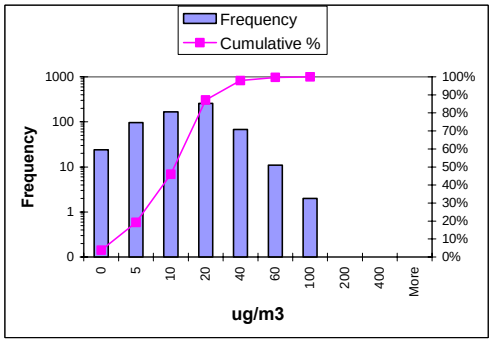
DENIO

Bin (< or =)	Frequency	umulative %
0	2	0.28%
5	7	1.27%
10	51	8.49%
20	307	51.91%
40	314	96.32%
60	20	99.15%
100	5	99.86%
200	1	100.00%
400		
More		



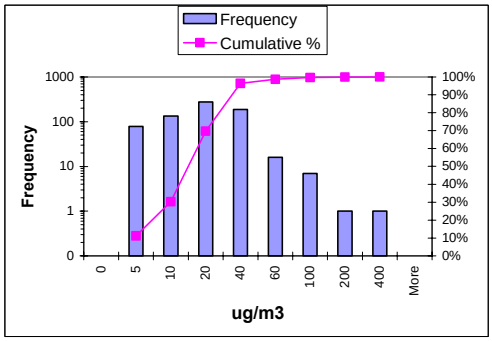
POOL

Bin (< or =)	Frequency	umulative %
0	24	3.83%
5	96	19.14%
10	168	45.93%
20	258	87.08%
40	68	97.93%
60	11	99.68%
100	2	100.00%
200		
400		
More		



CHURCH

Bin (< or =)	Frequency	umulative %
0		
5	78	11.14%
10	134	30.29%
20	276	69.71%
40	187	96.43%
60	16	98.71%
100	7	99.71%
200	1	99.86%
400	1	100.00%
More		



VERNON

Bin (< or =)	Frequency	umulative %
0		
5	161	22.90%
10	226	55.05%
20	268	93.17%
40	43	99.29%
60	5	100.00%
100		
200		
400		
More		

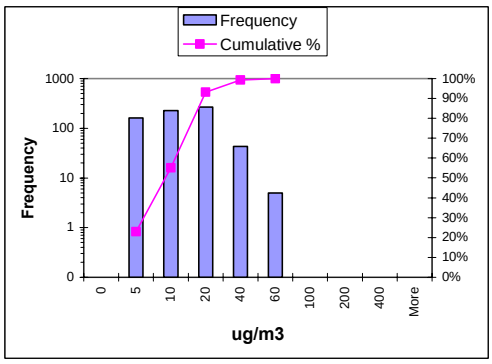


Figure 2-10. Histograms showing the frequency distribution of hourly averaged BAM PM2.5 data at the four sites.

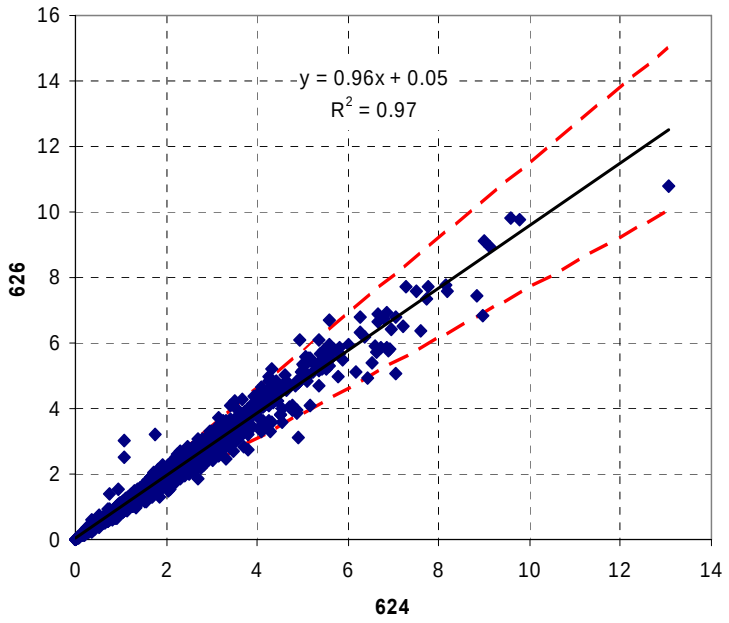


Figure 2-11. Correlation of hourly BC(1) (ug/m3) averaged data from collocated Aethalometers 02/23/06-05/01/06. Instrument 626 was later used at the Denio site, and 624 at Pool.

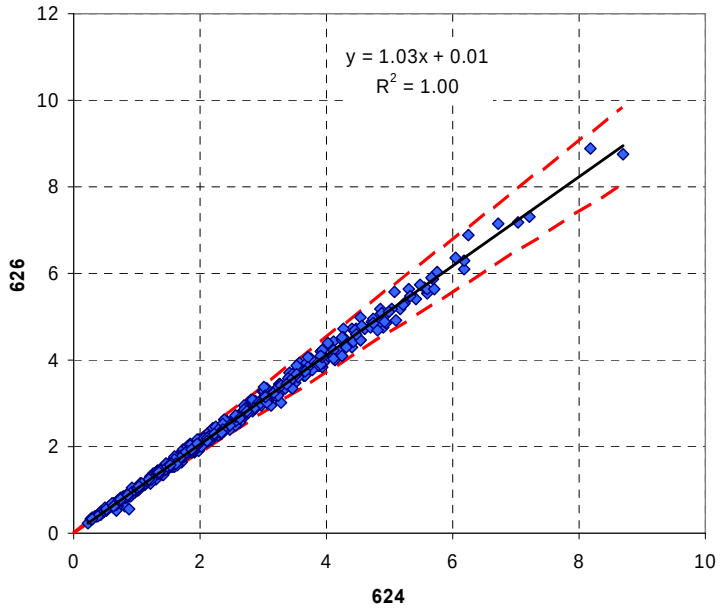
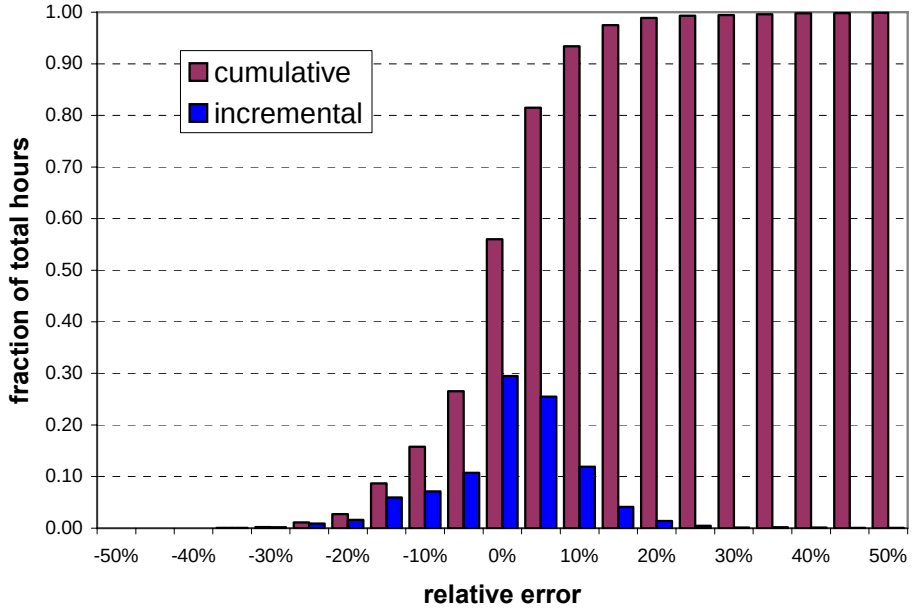


Figure 2-12. Correlation of hourly averaged BC(1) (ug/m3) data from collocated Aethalometers 10/17/06-11/06/06.

02/23/06-05/01/06

relative error	cumulative fraction
<5%	0.55
<10%	0.78
<15%	0.89
<20%	**0.96**
<25%	0.98
<30%	0.99
<35%	1.00
<40%	1.00
<45%	1.00
<50%	1.00
>50%	0.00



10/17/06-11/06/06

relative error	cumulative fraction
<5%	0.67
<10%	**0.94**
<15%	0.99
<20%	0.99
<25%	1.00
<30%	1.00
<35%	1.00
<40%	1.00
<45%	1.00
<50%	1.00
>50%	0.00

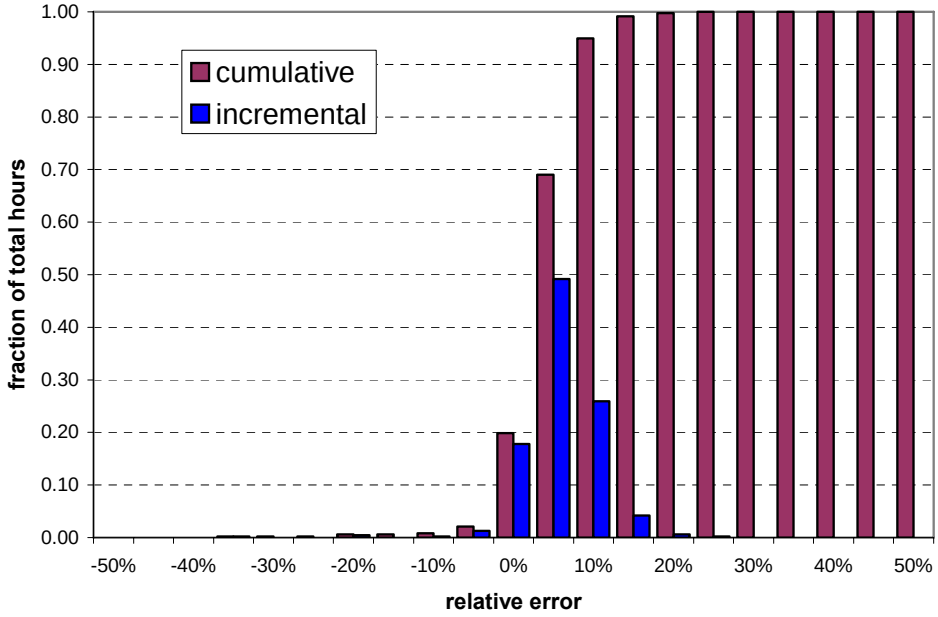


Figure 2-13. Relative difference between collocated Aethalometers used at Denio and Pool sites. Data are from hourly averages of channel 1 BC. Table gives distribution of absolute values of relative differences, with approximate 95th percentile in bold.

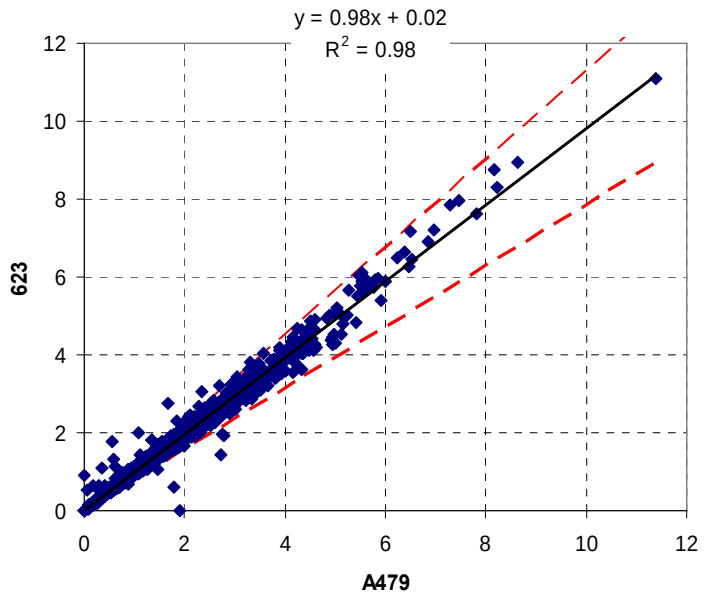


Figure 2-14. Correlation of hourly averaged BC data (ug/m3) from collocated Aethalometers 02/23/06-05/01/06. 623 was later used at Church and A479 at Vernon.

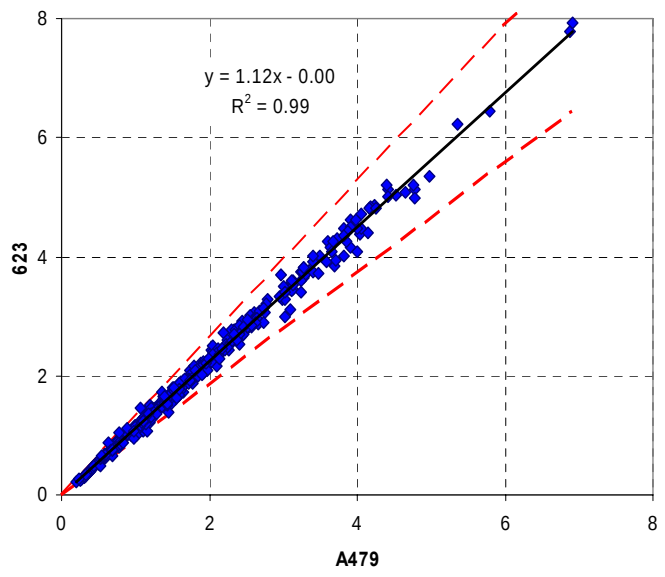
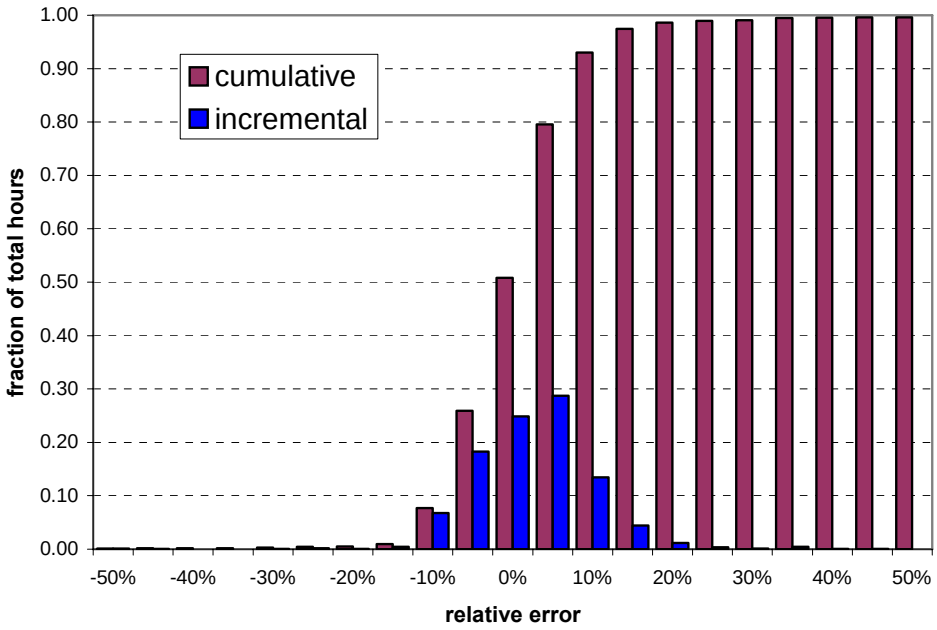


Figure 2-15. Correlation of hourly averaged BC data (ug/m3) data from collocated Aethalometers 10/17/06-11/06/06.

02/23/06-05/01/06

relative error	cumulative fraction
<0%	0.00
<5%	0.54
<10%	0.85
<15%	**0.97**
<20%	0.98
<25%	0.99
<30%	0.99
<35%	0.99
<40%	0.99
<45%	0.99
>45%	1.00



10/17/06-11/02/06

relative error	cumulative fraction
<0%	0.00
<5%	0.11
<10%	0.30
<15%	0.73
<20%	**0.97**
<25%	0.98
<30%	0.99
<35%	0.99
<40%	1.00
<45%	1.00
>45%	1.00

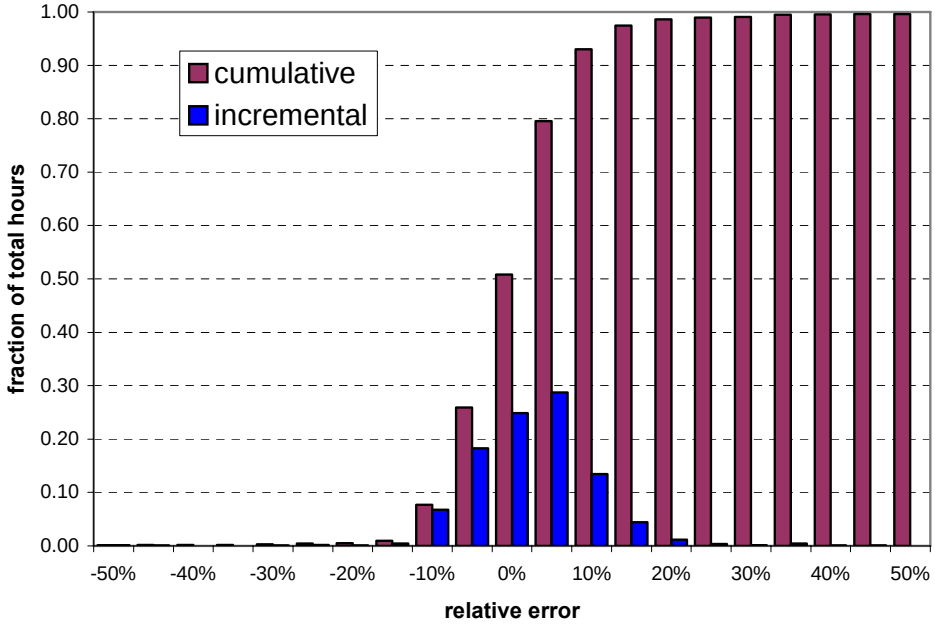


Figure 2-16. Relative difference between collocated Aethalometers used at Church and Vernon sites. Data are from hourly averages of channel 1 BC. Table gives distribution of absolute values of relative differences, with approximate 95th percentile in bold..

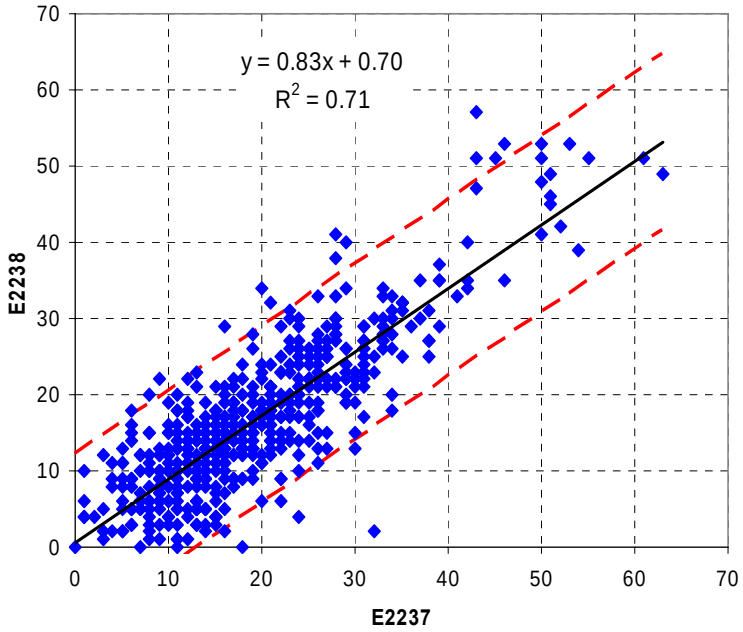


Figure 2-17. Correlation of hourly PM2.5 (ug/m3) averaged data from collocated EBAMs 02/23/06-05/01/06. Instrument E2237 was later used at the Denio site, and E2238 at Pool.

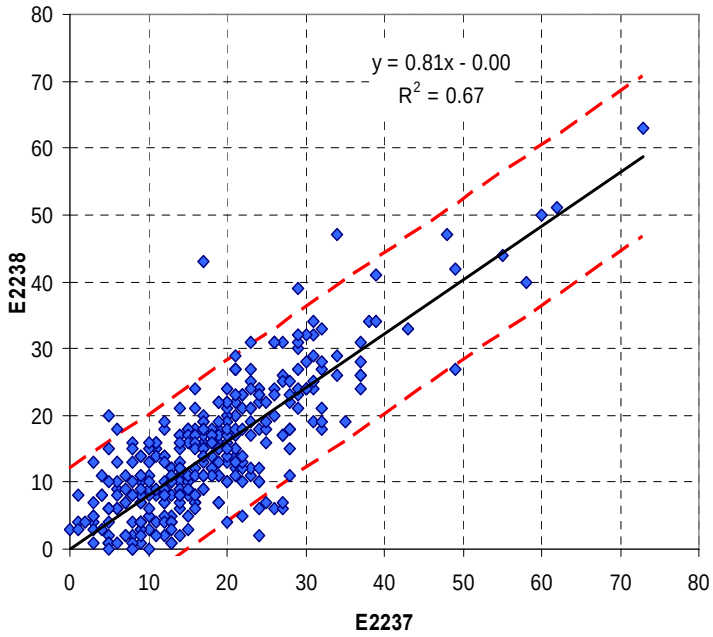
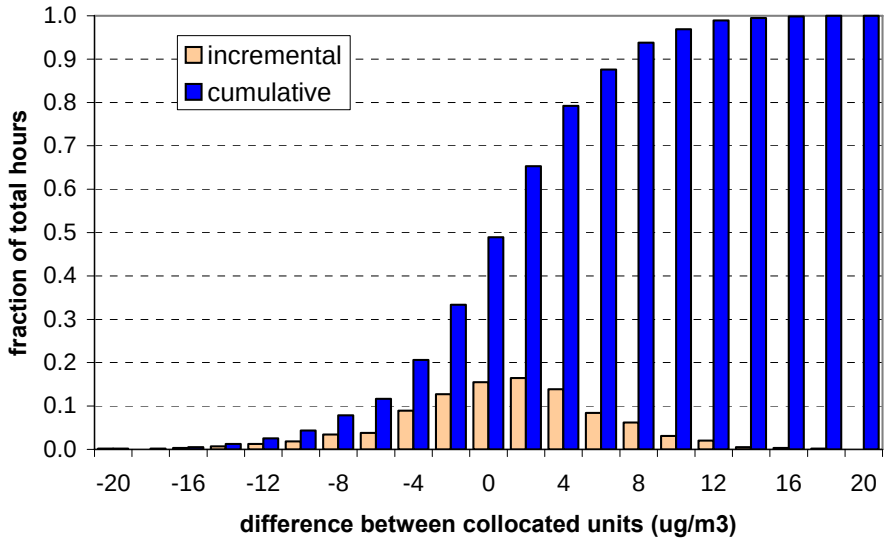


Figure 2-18. Correlation of hourly averaged PM2.5 (ug/m3) data from collocated EBAMs 10/17/06-11/06/06.

02/23/06-05/01/06

absolute error (ug/m3)	cumulative fraction
<2	0.32
<4	0.59
<6	0.76
<8	0.86
<10	0.93
<12	**0.96**
<14	0.98
<16	0.99
<18	1.00
<20	1.00
>20	0.00



10/17/06-11/06/06

absolute error (ug/m3)	cumulative fraction
<2	0.26
<4	0.51
<6	0.73
<8	0.85
<10	0.92
<12	**0.95**
<14	0.98
<16	0.99
<18	0.99
<20	1.00
>20	0.00

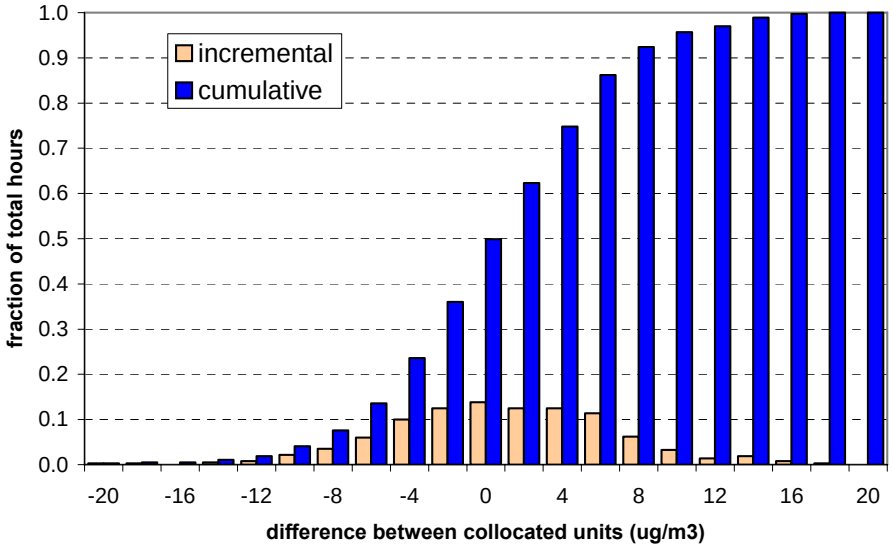


Figure 2-19. Difference between collocated EBAMS used at Denio and Pool sites. Data represented are hourly averages. Table gives distribution of absolute values of differences, with approximate 95th percentile in bold.

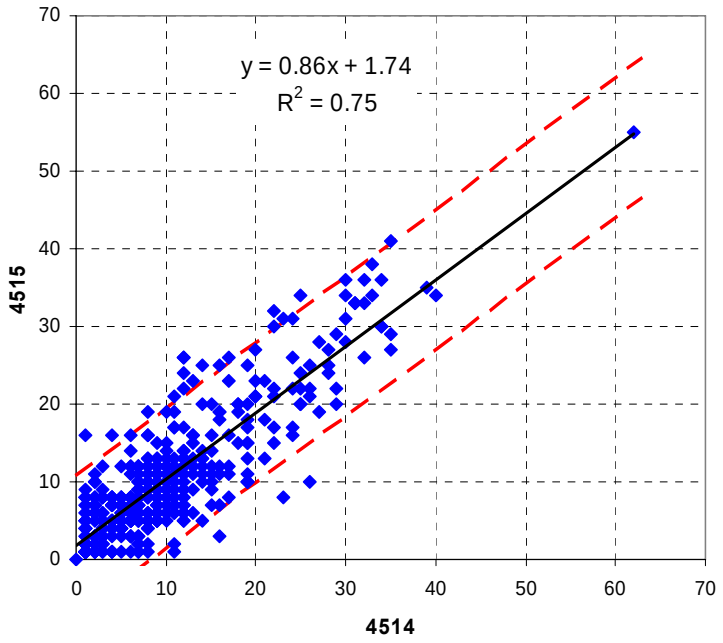


Figure 2-20. Correlation of hourly averaged data from collocated BAMs 02/23/06-05/01/06. 4514 was later used at Church and 4515 at Vernon.

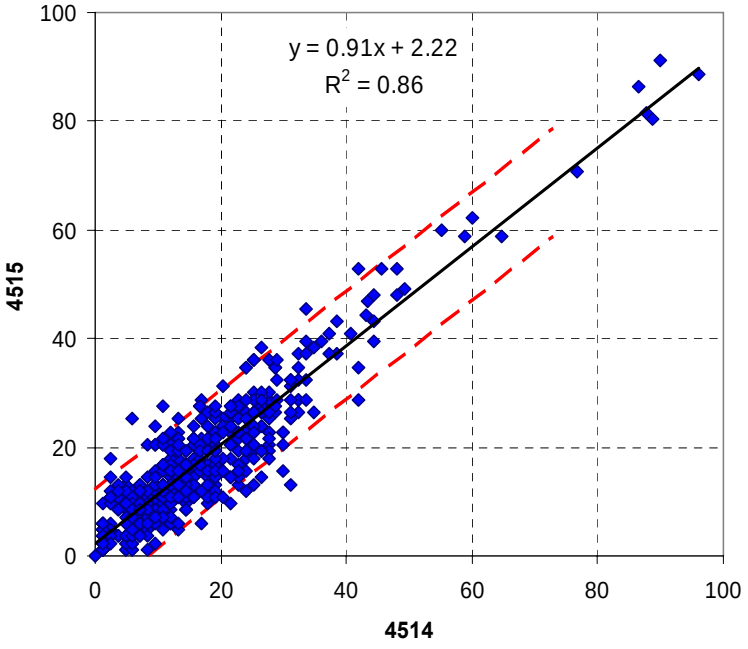
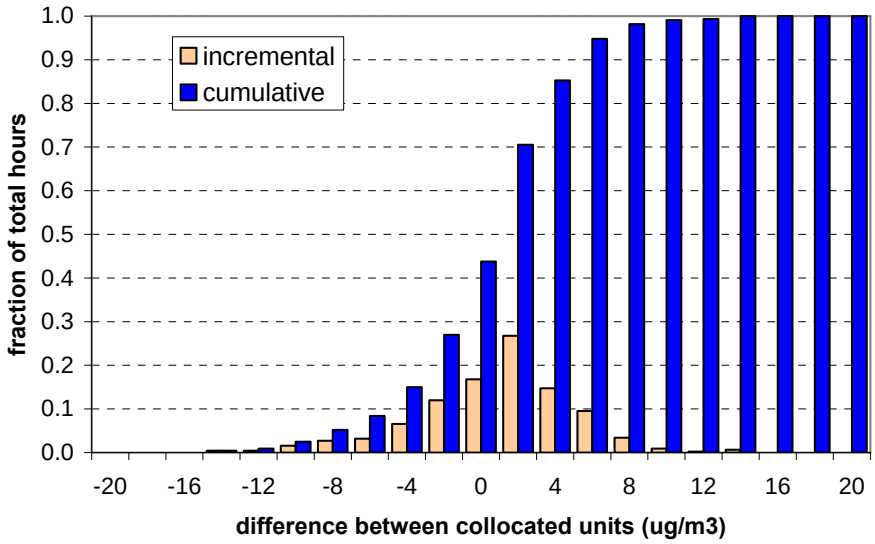


Figure 2-21. Correlation of hourly averaged data from collocated BAMs 10/17/06-11/06/06.

02/23/06-05/01/06

absolute error (ug/m3)	cumulative fraction
<2	0.44
<4	0.70
<6	0.86
<8	**0.93**
<10	**0.97**
<12	0.98
<14	1.00
<16	1.00
<18	1.00
<20	1.00
>20	1.00



10/17/06-11/02/06

absolute error (ug/m3)	cumulative fraction
<2	0.31
<4	0.59
<6	0.79
<8	0.90
<10	**0.95**
<12	0.98
<14	1.00
<16	1.00
<18	1.00
<20	1.00
>20	1.00

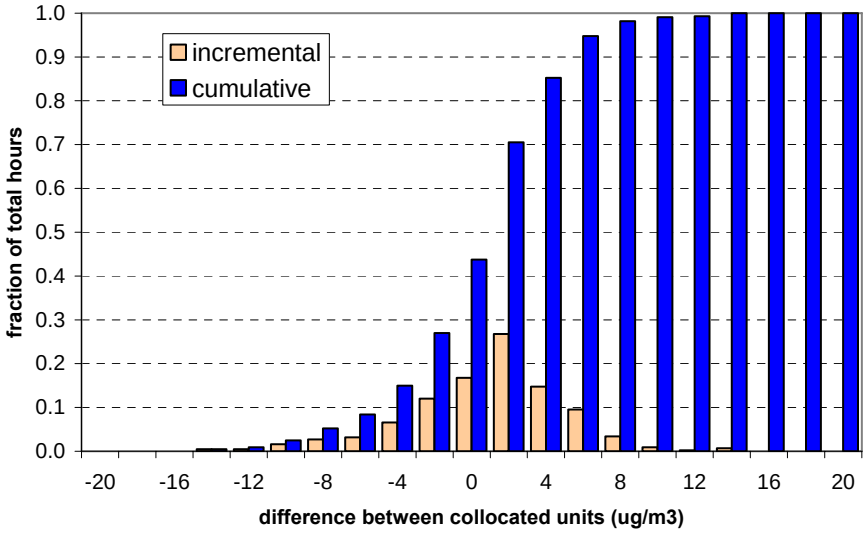


Figure 2-22. Difference between collocated BAMS used at Church and Vernon sites. Data represented are hourly averages. Table gives distribution of absolute values of differences, with approximate 95th percentile in bold.

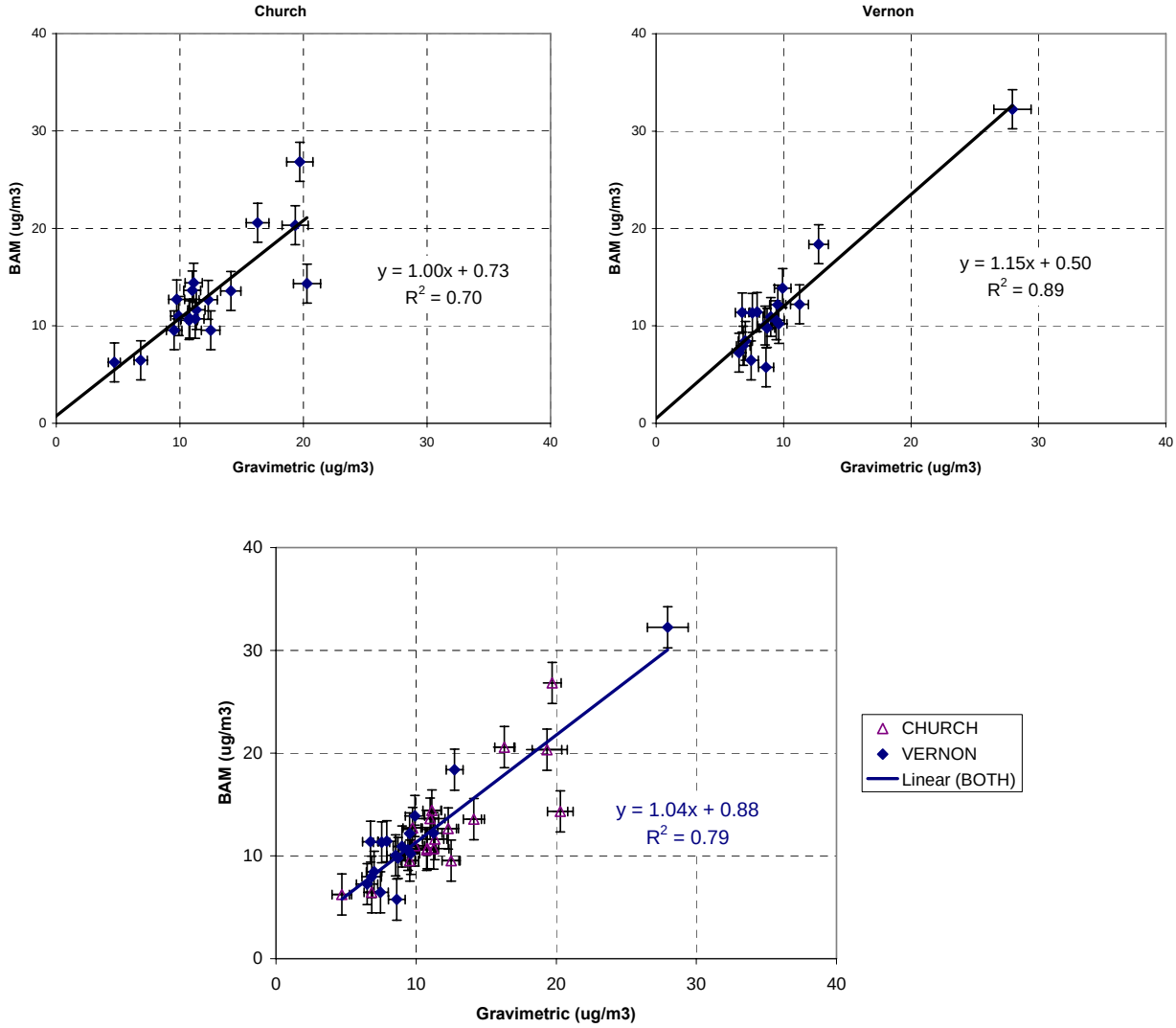


Figure 2-23. Correlation plots comparing average BAM PM2.5 to gravimetric mass from FRM filters for 24hr samples at 2 sites.

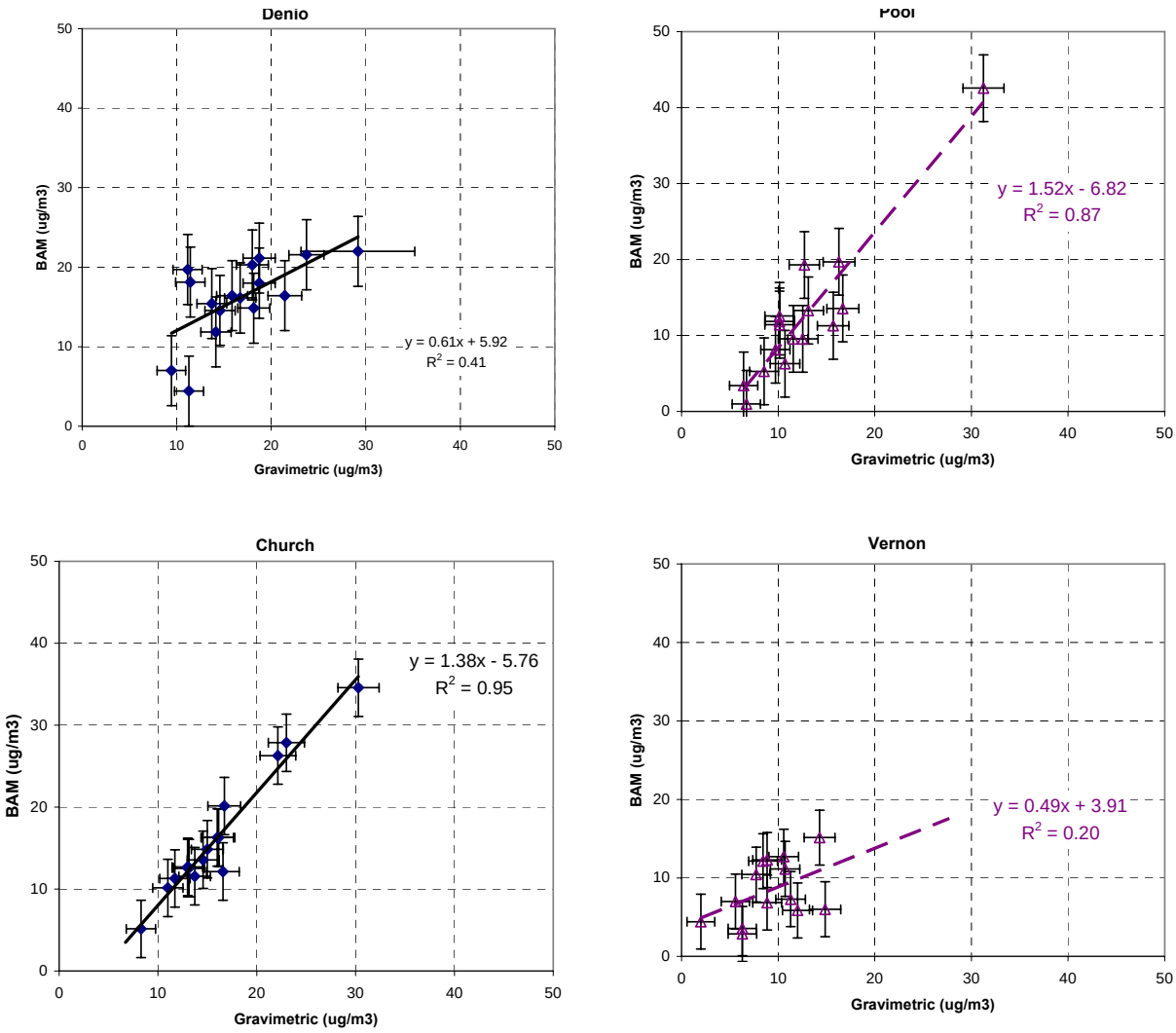


Figure 2-24. Correlation plots comparing average BAM PM2.5 to gravimetric mass from FRM filters for 7hr samples at 4 sites.

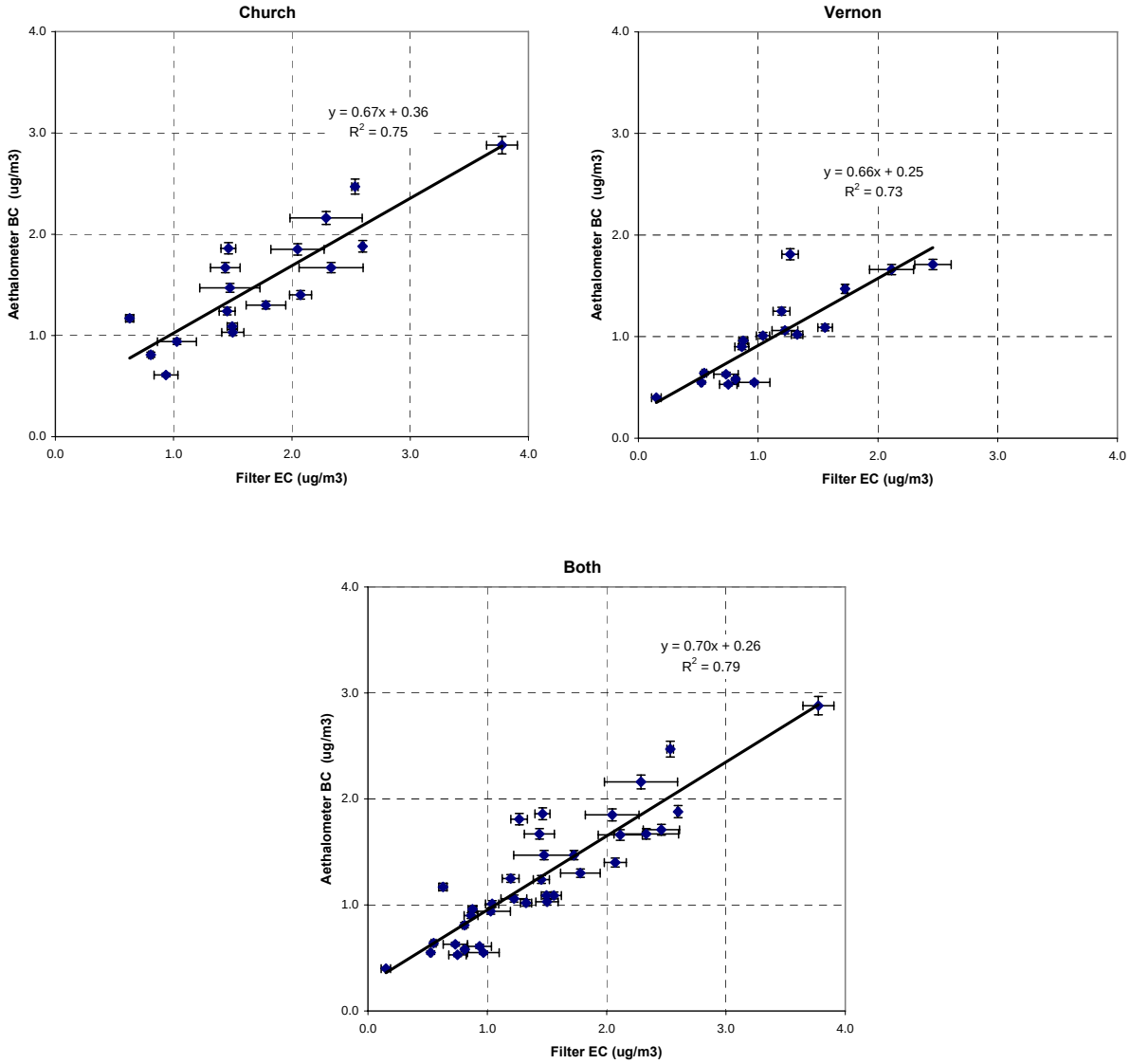


Figure 2-25. Correlation plots comparing average aethalometer BC(1) to elemental carbon from FRM filters for 24hr samples at Church and Vernon.

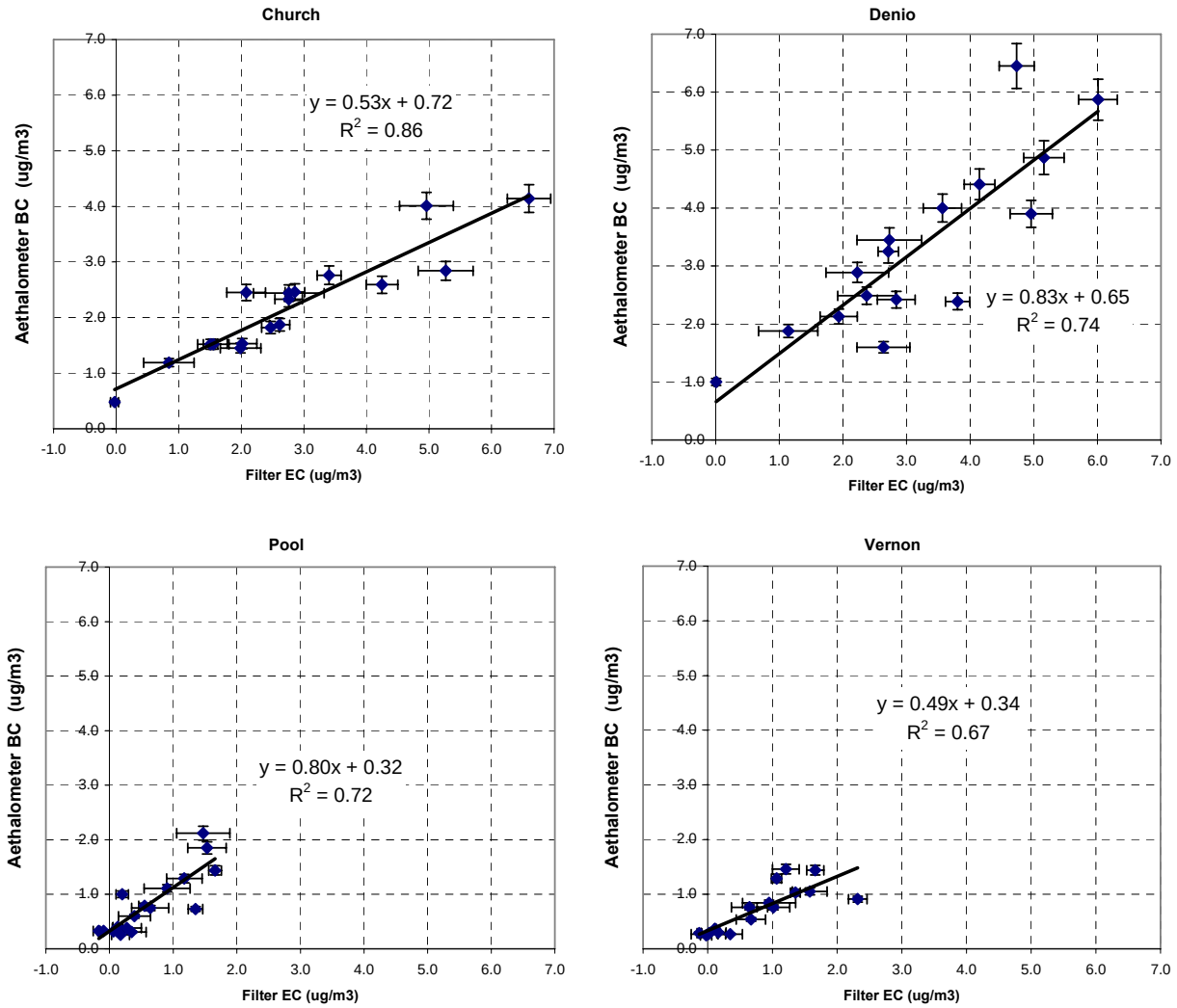


Figure 2-26. Correlation plots comparing average aethalometer BC(1) to elemental carbon from FRM filters for 7hr samples at 4 sites.

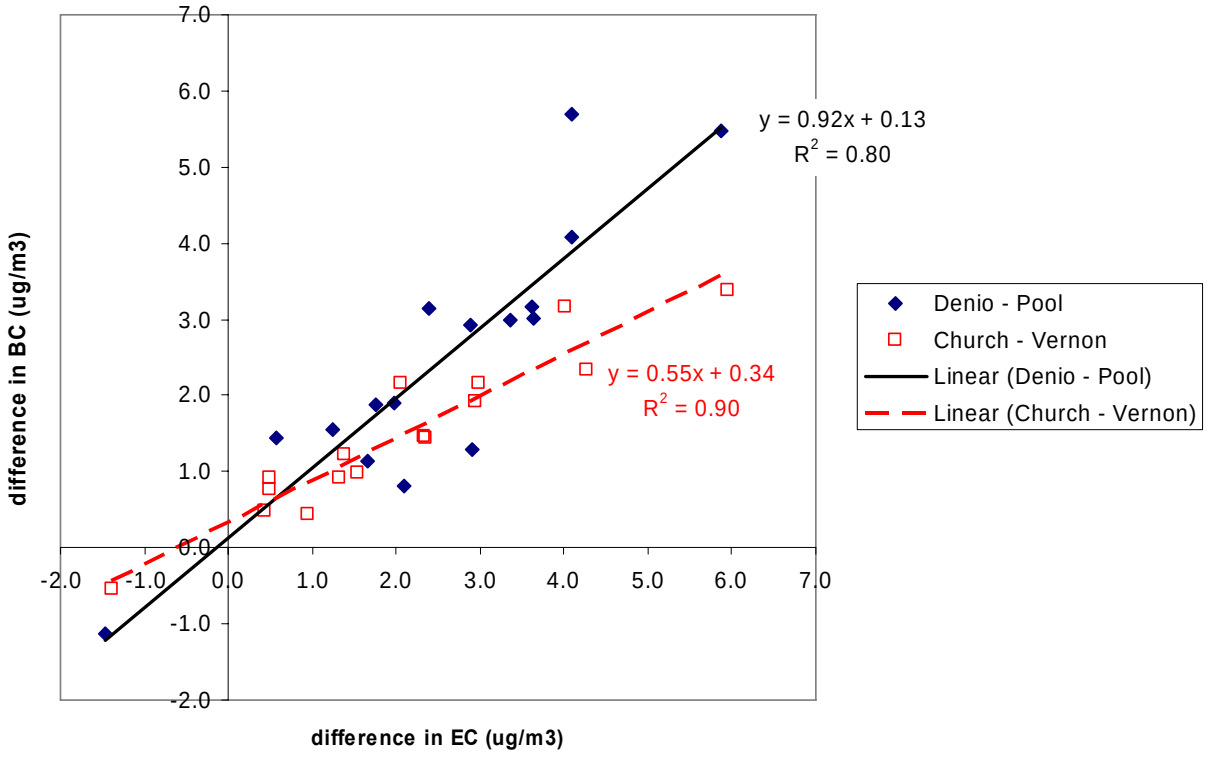


Figure 2-27. Correlation plot comparing difference in elemental carbon (EC) concentration from FRM filters between downwind and upwind sites to to difference in average Aethalometer black carbon (BC) for 7hr samples at 2 site pairs.

3. RESULTS

This section summarizes results of the analysis of RRAMP data to quantify the localized air pollutant impacts from the emissions at the UPRR facility. First we compared the mean diurnal variations in pollutant concentrations at the downwind and upwind monitoring sites. The purpose of these comparisons is to determine whether differences in diurnal patterns of rail yard emissions are detectable in the data. The mean pollutant concentrations were then determined for each monitoring site using the selection criteria for the downwind/upwind analysis. Differences in pollutant concentrations for the pairs of downwind and upwind sites were compared to the standard errors in the mean and propagated measurement uncertainties to address the hypothesis that differences in downwind and upwind pollutant concentrations are statistically significant.

3.1 Upwind/Downwind Differences

We examined the downwind minus upwind concentrations of NO, BC and $PM_{2.5}$ for the two pairs of upwind/downwind sampling locations in order to develop a basis for selecting appropriate subsets of the data that would be used to establish the impact of emissions from the rail yard on downwind pollutant levels. The locations of the two upwind (Pool and Vernon) and two downwind (Denio and Church) sampling sites are shown in Figure 1-1.

We calculated nightly downwind-upwind differences in PM, BC, NO, and NO_x concentrations for each site pair. Uncertainties of differences were calculated as the square root of the sum of the squares of the measurement error, using PM and BC measurement errors determined from the precision and accuracy analysis of the collocation data. NO and NO_x measurement errors are assumed to be consistent with the EPA reference method specifications. All statistics for these calculations are based on the filtered nightly average values.

Table 3-1 shows the means, standard deviations, and standard errors of the means for 7-hour average BC, PM2.5, NO and NOx concentrations collected between 2200 to 0500 PST at the four RRAMP sites. Mean downwind minus upwind differences in PM, BC, NO and NOx concentrations were calculated for each site pair for the entire study period excluding the time period of the Ralston fire. Significance of differences was determined from the standard errors of the means, pooled standard error of the differences, root mean squares of the measurement errors, and student's T-test. Using a 2-sample unequal variance (heteroscedastic) Student's t-test, these differences are all significant at above the 99% confidence level. The 2-sigma standard errors for the slope and intercept of linear regressions shown in Table 2–4 were included in the calculation of propagated analytical errors of the seasonal mean $PM_{2.5}$ values in Table 3-1. Descriptive statistics for the 24-hour daily average concentrations are also included in the table. Since the data used for the daily averages were not subjected to the same restrictions on wind speed and wind direction as the overnight (7-hour) averages there are a larger number of valid days included. Data from the period of the Ralston Fire (Sept. 5-17) were excluded from all seasonal averages.

The graphical displays of the downwind-upwind differences are shown in Figure 3-1. Note that the ratios of pollutant concentrations at the upwind relative to downwind sites are lowest for NO and are larger in increasing order for NO_x, BC and PM. [Ratios are not shown in Figure 3-1; they are addressed in Table 3-2. Suggest you include a Aethalometer showing the ratios.] The increasing ratios from NO to PM are consistent with larger contributions of urban

background to the measured PM and BC concentrations. Figure 3-1 also shows the differences between the two downwind and two upwind sites. These differences are small in comparison.

Table 3–2 lists the statistics for several key ratios that indicate the relative contribution of fresh emissions to the measured pollutant mix. Note that all of these ratios are higher at the downwind sites, particularly NO/NOx which is directly tied to proximity to fuel combustion sources. The higher BC/PM ratios are particularly indicative of diesel vehicle influence. Although the BC(1)/BC(2) ratios vary extensively at each site, the mean values are clearly higher at the downwind sites which is consistent with the greater specificity of the longer BC(1) wavelength to diesel soot. It is also instructive to note that these mean ratios are generally quite consistent for the two downwind sites, supporting the conclusion that both sites are subject to the same types of local influence.

3.2 FRM filter results

As discussed in Section 2.8, the analysis results from the FRM sampler filters collected every third day at each site may ultimately be used to relate the Aethalometer BC and continuous PM data to estimated diesel particulate matter concentrations. They may also prove useful for characterizing differences in the composition of the PM at the upwind and downwind sites by comparing the relative amounts of carbon constituents from the TOR analysis to each other and to the total PM measured by gravimetric analysis of the Teflon filters. Unfortunately, the quartz filters were not pre-fired prior to sampling to reduce the organic carbon artifact that results from absorption of volatile organic species by the filter material. Field blanks collected after the study period confirmed the significance of this artifact, as shown in Table 3–3. Note that there is a clear and consistent difference in composition between the two upwind sites and the two downwind sites.

Since only 4 field blanks were collected and they were not concurrent with the actual samples it is difficult to make a quantitative correction to the organic carbon data with any confidence, however, we may presume that the calculation of downwind – upwind differences in concentration for the paired sites will not be strongly affected by the high artifact levels since both samples should have similar blank levels. This seems supported by the comparison of the blank corrected EC/TC values in Table 3–3 to those in Table 3–4, which lists the elemental to total carbon (EC/TC) ratios and TC/PM ratios calculated using the differences in carbon and gravimetric mass measurements for the two site pairs. EC/TC ratios without blank correction are consistent for sites on the same side of the railyard and higher at the downwind sites, but still much lower than we would expect for an aerosol with a strong diesel exhaust component (source testing from diesel engines typically yields EC/TC ratios ≥ 50%). Subtracting the average field blank from the reported values increases the EC/TC ratios but they also become much more variable and the difference between the downwind and upwind sites is no longer clear. In contrast, EC/TC ratios for the downwind-upwind differences (Table 3–4, without blank correction) are quite consistent and high enough to be indicative of strong diesel influence. However, the TC/PM ratios are very inconsistent suggesting some disconnect between the two types of filter samples. The addition of more frequent field blank collection and some collocation testing of the FRM samplers next year may help explain the poor agreement between the gravimetric and TOR results and allow better characterization of the EC/TC ratios at the upwind sites.

Table 3–1. Means, standard deviations, and standard errors of the means for 7-hour (2200 to 0500 PST) and 24-hour (midnight to midnight PST) BC, $PM_{2.5}$, NO and NOx concentrations at the four RRAMP sites. The differences in mean concentrations between the two pairs of downwind and upwind sites (Denio-Pool and Church-Vernon) during the overnight period and pooled standard error of the differences are also shown.

Statistics	**BC (ug/m^3)**				**PM2.5 (ug/m^3)**				**NO (ppb)**				**NOx (ppb)**			
2200-0500 averages	Denio	Pool	Church	Vernon	Denio	Pool	Church	Vernon	Denio	Pool	Church	Vernon	Denio	Pool	Church	Vernon
average	3.24	0.59	2.36	0.54	16.9	12.1	16.9	10.2	98	0	93	0	143	8	133	8
stdev	1.48	0.29	1.08	0.30	4.4	4.8	6.5	3.6	55	2	69	1	71	5	84	5
n observations	84	88	88	87	88	83	83	87	84	81	85	87	84	81	85	87
sterr_mean	0.16	0.03	0.12	0.03	0.5	0.5	0.7	0.4	6	0	8	0	8	1	9	1
Downwind-Upwind																
avg delta	2.65		1.81		4.7		6.5		99		93		136		125	
sterr_delta	0.15		0.12		0.5		0.7		6		8		8		9	
T-test	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00	
propagated error	1.06		1.04		1.0		1.1		1.1		1.0		1.1		0.8	
Downwind and Upwind pairs	Denio - Church		Pool - Vernon		Denio - Church		Pool - Vernon		Denio - Church		Pool - Vernon		Denio - Church		Pool - Vernon	
avg delta	0.91		0.05		0.1		2.1		6		0		11		-1	
ster_delta	0.20		0.01		0.8		0.5		10		0.2		12		0.4	
propagated error	1.29		1.27		1.3		1.3		1.3		1.3		1.3		1.1	
	Denio	Pool	Church	Vernon	Denio	Pool	Church	Vernon	Denio	Pool	Church	Vernon	Denio	Pool	Church	Vernon
24 hr averages																
average	2.29	0.94	1.69	0.94	13.2	9.6	12.4	10.0	55	8	51	9	87	21	81	24
stdev	0.64	0.42	0.52	0.44	3.5	3.5	3.7	3.8	24	14	34	12	31	21	43	18
n observations	98	104	104	102	104	95	97	102	101	98	102	104	101	98	102	104
sterr_mean	0.06	0.04	0.05	0.04	0.3	0.4	0.4	0.4	2	1	3	1	3	2	4	2

*Data collected during the Ralston Fire (9/5 -9/17) are excluded. Data used to calculate overnight averages are limited to periods of typical wind flow.

Table 3–2. Means and statistics for hourly (2200 to 0500 PST) NO/NOx, BC/PM2.5, and BC(1)/BC(2) ratios at the four RRAMP sites. The standard deviation and 2-sigma standard errors of the means are included to indicate the significance of the differences.

	Denio NO/NOx	Pool NO/NOx	Church NO/NOx	Vernon NO/NOx	Denio BC/PM	Pool BC/PM	Church BC/PM	Vernon BC/PM	Denio BC1/BC2	Pool BC1/BC2	Church BC1/BC2	Vernon BC1/BC2
avg	0.65	0.13	0.63	0.05	0.17	0.05	0.15	0.06	1.24	0.85	1.21	1.03
min	0.15	-0.09	0.06	0.00	0.01	0.01	0.02	0.00	0.38	0.40	0.73	0.45
max	0.86	0.83	0.88	0.88	0.72	0.20	0.64	0.22	1.95	1.27	1.74	1.48
stdev	0.10	0.16	0.14	0.13	0.10	0.04	0.08	0.04	0.16	0.19	0.15	0.12
2*stderr	0.01	0.02	0.01	0.02	0.01	0.00	0.01	0.00	0.01	0.02	0.01	0.01

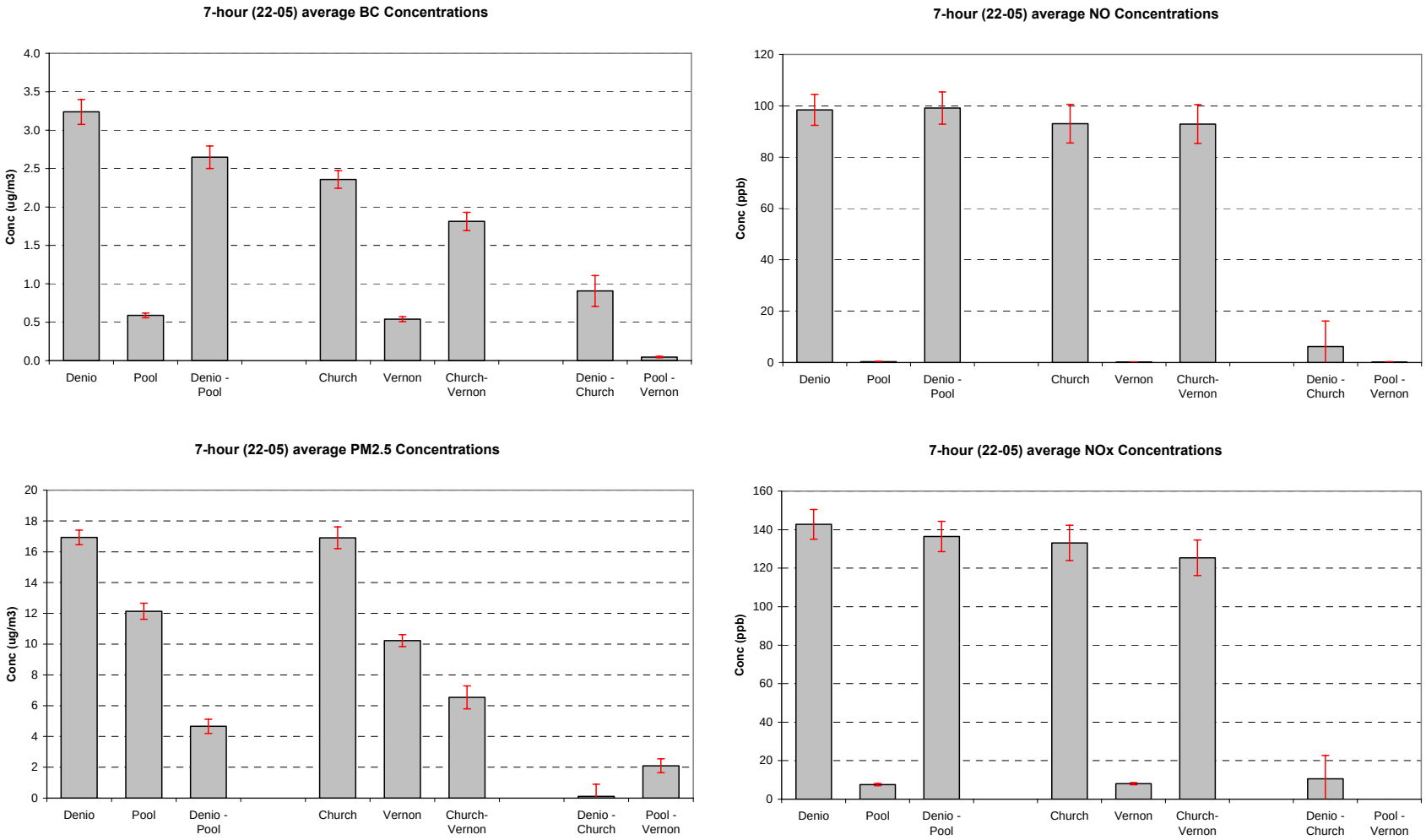
Table 3–3. Means and 2-sigma standard errors for TOR analysis results of the 7-hour overnight FRM filter samples.

	no blank subtraction			***blank subtracted***
	OC (μg/m^3)	**EC (μg/m^3)**	**EC/TC**	**EC/TC**
DENIO	12.6 ± 1.3	2.9 ± 0.4	0.18 ± 0.11	0.34 ± 0.36
POOL	9.3 ± 1.3	0.9 ± 0.3	0.08 ± 0.09	0.21 ± 0.27
CHURCH	11.1 ± 2.2	2.7 ± 0.7	0.19 ± 0.12	0.36 ± 0.27
VERNON	8.8 ± 2.2	0.9 ± 0.4	0.10 ± 0.12	0.40 ± 0.73
blanks	6.7 ± 0.8	0.3 ± 0.2		

Table 3–4. Elemental to total carbon ratios and total carbon to PM2.5 ratios for 7-hour overnight FRM filter samples. All values are calculated from the differences in concentration between downwind and upwind sites, without blank correction. The group mean and 2-sigma standard errors of the means are included to indicate the significance of the differences.

	EC/TC RATIO		TC/PM RATIO	
Date	**DENIO-POOL**	**CHURCH-VERNON**	**DENIO-POOL**	**CHURCH-VERNON**
06/19/06	0.34	0.63	0.75	0.61
06/25/06	0.35	0.23	0.91	0.15
07/01/06	0.31	0.44	-1.77	-1.17
07/07/06	0.36	0.39	0.90	1.22
07/13/06	0.34	0.50	1.22	-0.99
07/19/06	0.57	0.37		
07/25/06	0.33	0.24	1.11	
07/31/06	0.37	0.00	1.21	
08/06/06	0.27	0.25	1.64	
08/12/06	1.09	0.58	-0.82	0.53
08/18/06	0.34	0.36	-3.11	1.32
08/24/06	0.24	0.58	1.21	0.77
08/30/06	0.27	0.43	1.44	0.72
09/23/06	0.21	0.48	-4.42	-1.07
09/29/06	0.41	-0.05	2.87	-5.36
10/05/06	0.18	0.17	-4.85	2.11
10/11/06	0.28	0.13	1.36	-11.82
MEAN	0.37	0.34	-0.02	-1.00
2STDERR	0.10	0.10	1.15	2.08

Figure 3-1. Mean BC, $PM_{2.5}$, NO and NOx concentrations at the four RRAMP monitoring sites and differences of the two pairs of downwind and upwind sites (Denio-Pool and Church-Vernon). Differences between the two downwind and two upwind sites are also shown for comparison. Error bars are the standard errors of the means.



4. CONCLUSIONS AND RECCOMENDATIONS

This section summarizes the findings and conclusions from the evaluation and validation of the RRAMP data and analysis of the data. Several modifications to the field measurement protocol is suggested for consideration by the RRAMP Technical Advisory Committee.

4.1 Data Evaluation and Validation

- Collocated Aethalometers showed generally good agreement with no significant bias between instruments, but substantial variation (10-20%) on an hourly basis. Improved operating procedures adopted in the second year greatly improved data quality.

- The random error in 1-hour $PM_{2.5}$ BAM is still too large (±10 ug/m^3) to make comparisons of the hourly data feasible at the measured concentrations. BAM data contained frequent negative values indicating baseline drift. Collocated BAMs showed good agreement in measured $PM_{2.5}$ concentrations after averaging over periods of 6-hours or more.

- NO/NOx data contained some negative values which were removed. Numerous instances of slightly negative NO data were retained to avoid biasing the averages.

- BC/PM and NO/NOx ratios are consistently higher at the downwind sites, which is consistent with presence of fresh emissions.

- Averaged $PM_{2.5}$ data from the BAMs is not always well correlated with the corresponding filter gravimetric mass data, and shows some evidence of a slight positive bias at higher concentrations. Adjustments to the BAM data were made to account for this. The correlations are weakest for 7-hr overnight samples at Denio and Vernon where the range of concentrations measured was smallest.

- 24-hour averaged BC data from the Aethalometers is well correlated with the corresponding EC from filter samples. The BC/EC ratio is about 0.7, which is consistent with prior data.

- TOR and gravimetric mass results from the FRM samples are not always consistent. At this point we are unable to determine whether this is due to the presence of inorganic aerosol of local origin or the large organic carbon artifacts from the quartz filters. A more thorough QC process for the FRM samples should be implemented next year.

4.2 Data Analysis

- Overall, there is evidence of substantial impact on the downwind sites. There was a substantial increase in NO, NOx, and BC at the downwind sites relative to the upwind sites, with the largest differential for NO. The magnitude of the mean concentrations and downwind-upwind site deltas are somewhat different than those observed during the first

year of monitoring but the comparison may not be valid unless differences in sampling period and schedule are accounted for.

- The differences in mean concentrations between the two pairs of downwind and upwind sites (Denio-Pool and Church-Vernon) are all significant at above the 99% confidence level.

- Ratios of pollutant concentrations at the upwind relative to downwind sites are lowest for NO and are larger in increasing order for NO_2, BC and PM. The increasing ratios from NO to PM are consistent with larger contributions of urban background to the measured PM and BC concentrations.

- EC/TC ratios from the FRM filter samples are consistent with initial expectations and show a clear difference in aerosol composition between the upwind and downwind sites.

5. REFERENCES

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Chow, J.C., Watson, J.G., Lowenthal, D.H., Chen, L.W.A., Tropp, R.J., Park, K., Magliano, K.L., 2006. PM2.5 and PM10 mass measurements in California's San Joaquin Valley. Aerosol Science & Technology 40 (10), 796-810.

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APPENDIX A

Measurement Methods

APPENDIX A – MEASUREMENT METHODS

Measurements at each of the four RRAMP sites during summer 2006 consisted of continuous (hourly average) wind speed and wind direction, Aethalometer for black carbon, Beta Attenuation Monitors (BAM) for $PM_{2.5}$ mass, chemiluminescent NO/NOx analyzers. The four Aethalometers and four BAMs were co-located to assess measurement precision during a 2 week period prior to and after each intensive period. FRM $PM_{2.5}$ filter sampling was conducted every third day during the 2006 intensive monitoring period using a pair of samplers at each site, one loaded with Teflon filters for gravimetric mass analysis and the second unit loaded with quartz filters for carbon analysis. The FRM samplers were operated for 7-hour nighttime periods at Denio and Pool and for alternating 7-hour and 24-hour periods at Church and Vernon. Table 1–1 provides an inventory of the data collected during summer 2006. The data sets were compiled and quality assured by PCAPCD staff.

Aethalometer

The Aethalometer instrument continuously passes ambient air through a quartz-fiber filter tape. Light absorbing particles such as black carbon (BC) cause attenuation of a light beam incident on the tape. By assuming that all light-absorbing material is black carbon, and that the absorption coefficient of the black carbon is known and constant, the net attenuation signals can be converted into black carbon mass concentrations. The time resolution of the Aethalometer is on the order of a fraction of a minute depending on ambient black carbon concentration. Detection limit for the Aethalometer is $\sim 0.1\ \mu g/m^3$ black carbon for a one minute average.

Two models manufactured by Magee Scientific were used in this study. The rack-mounted AE-20 model at Denio and Pool sites, and the 'portable' model AE-42 at Church and Vernon. Both models measure attenuation at two wavelengths (880 nm and 370 nm) and have identical sample collection, detection, and software systems. Flow rates were set to 5 lpm for all units, and data was recorded at the default 5-minute time intervals. Data were collected at both wavelengths, but all black carbon data in the analyses are from the 880nm wavelength of the Aethalometer (channel 1) unless otherwise specified.

There are several operational features of the Aethalometer that can affect comparability of data from multiple instruments. Baseline measurements are made after each tape advance resulting in a 15 minute gap in the data. These tape advances can be set at fixed intervals or initiated automatically at set threshold opacity. The instruments were operated during RRAMP in the fixed interval mode resulting in 15-minute gaps that occur at predetermined times each day. Aethalometer data is also known to be strongly affected by electronic noise spikes which create exaggerated increases or decreases in individual measurements of light attenuation. Another factor that contributes measurement uncertainty is the effect of filter loading on light absorption measurements. The Aethalometer has been shown to overpredict BC concentrations on a fresh filter and underpredict BC concentrations on a loaded filter (Arnott et al., 2005). Arnott et al. found that the Aethalometer BC measurements correlate well with photoacoustic BC and thermal optical elemental carbon if the data are averaged over the full range of filter loading. All of the effects mentioned above can be minimized by averaging the data over longer intervals. This issue was addressed in detail in the Year 1 Annual Report.

Beta Attenuation Monitors

Beta rays (electrons with energies in the 0.01 to 0.1 MeV range) are attenuated according to an approximate exponential (Beer's Law) function of particulate mass, when they pass through deposits on a filter tape. Automated Beta Attenuation Monitor (BAM) samplers utilize a continuous filter tape, first measuring the attenuation through the unexposed segment of tape to correct for blank attenuation. The tape is then exposed to ambient sample flow, accumulating a deposit. The beta attenuation measurement is repeated. The blank-corrected attenuation readings are converted to mass concentrations, with averaging times as short as 30 minutes. Detection limit is ~ 5 $\mu g/m^3$ for a one-hour average.

Met One E-BAMs were used at the Denio and Pool sites. Manufacturer's specifications cite an accuracy of 2.5 ug for a 24 hour average, and a ± 3% accuracy in the volumetric flow rate. The BAM 1020 model, which has a specified accuracy of ± 8% for 1-hour measurements and ± 2% for 24-hour averages, was used at Church and Vernon. Cyclones with a 2.5um cut point were used on all units.

Nitric oxide (NO) and nitrogen oxides (NOx)

NO is continuously measured by the chemiluminescence nitric oxide-ozone method (OCM). This method is based on the gas-phase chemical reaction of NO with ozone. In this method ambient air is mixed with a high concentration of ozone so that any NO in the air sample will react and thereby produce light. The light intensity is measured with a photomultiplier and converted into an electronic signal that is proportional to the NO concentration. To measure NOx concentrations, the sum of NO and NO2 (nitrogen dioxide), the air sample is first reduced to NO by a heated catalyst (molybdenum or gold in the presence of CO) adding to the NO already present in the sample, then passes into the reaction chamber for measurement as described above. The NO_2 concentration is derived by subtracting the NO concentration measurement from the NOx concentration measurements. Four Horiba NOx instruments were used in the study. This instrument has a zero stability of 10 ppb in 24 hours and span drift of less than 1 percent.

Thermal Optical Carbon Measurements

Elemental carbon (EC) and organic carbon (OC) were measured by thermal optical reflectance (TOR) method using the IMPROVE (Interagency Monitoring of Protected Visual Environments) temperature/oxygen cycle (IMPROVE TOR). Samples were collected on quartz filters using Federal Reference Method (FRM) $PM_{2.5}$ samplers. A section of the filter sample is placed in the carbon analyzer oven such that the optical reflectance or transmittance of He-Ne laser light (632.8 nm) can be monitored during the analysis process. The filter is first heated under oxygen-free helium purge gas. The volatilized or pyrolyzed carbonaceous gases are carried by the purge gas to the oxidizer catalyst where all carbon compounds are converted to carbon dioxide. The CO_2 is then reduced to methane, which is quantified by a flame ionization detector (FID). The carbon evolved during the oxygen-free heating stage is defined as "organic carbon". The sample is then heated in the presence of helium gas containing 2 percent of oxygen and the carbon evolved during this stage is defined as "elemental carbon". Some organic compounds pyrolyze when heated during the oxygen-free stage of the analysis and produce additional EC,

which is defined as pyrolyzed carbon (PC). The formation of PC is monitored during the analysis by the sample reflectance or transmittance. EC and OC are thus distinguished based upon the refractory properties of EC using a thermal evolution carbon analyzer with optical (reflectance or transmittance) correction to compensate for the pyrolysis (charring) of OC. Carbon fractions in the IMPROVE method correspond to temperature steps of 120°C (OC1), 250°C (OC2), 450°C (OC3), and 550°C (OC4) in a nonoxidizing helium atmosphere, and at 550°C (EC1), 700°C (EC2), and 850°C (EC3) in an oxidizing atmosphere. The IMPROVE method uses variable hold times of 150-580 seconds so that carbon responses return to baseline values.

Because EC and OC are operationally defined by the method, the specific instrument used, details of its operation, and choice of thermal evolution protocol can influence the split between EC and OC (34). Visual examination of filter darkening at different temperature stages have shown that substantial charring takes place within the filter, possibly due to adsorbed organic gases or diffusion of vaporized particles. The filter transmittance is more influenced by within-filter charring, whereas the filter reflectance is dominated by charring of the near-surface deposit. TOR and TOT corrections converge in the case of only a shallow surface deposit of EC or only a uniformly distributed pyrolyzed organic carbon (POC) through the filter and diverge when EC and POC exist concurrently at the surface and are distributed throughout the filter, respectively, especially when the surface EC evolves prior to the POC. The difference between TOR and TOT partly depends on the POC/EC ratio in the sample (31). Thus, highly loaded source samples would yield similar EC values for TOR and TOT corrections, while lightly loaded source and ambient samples would typically yield different EC values. While EC values for TOR may tend toward higher EC due to underestimation of the POC correction, higher absorption efficiency of POC within the filter may tend toward lower EC values for TOT.

APPENDIX B

Time series plots of hourly data by month

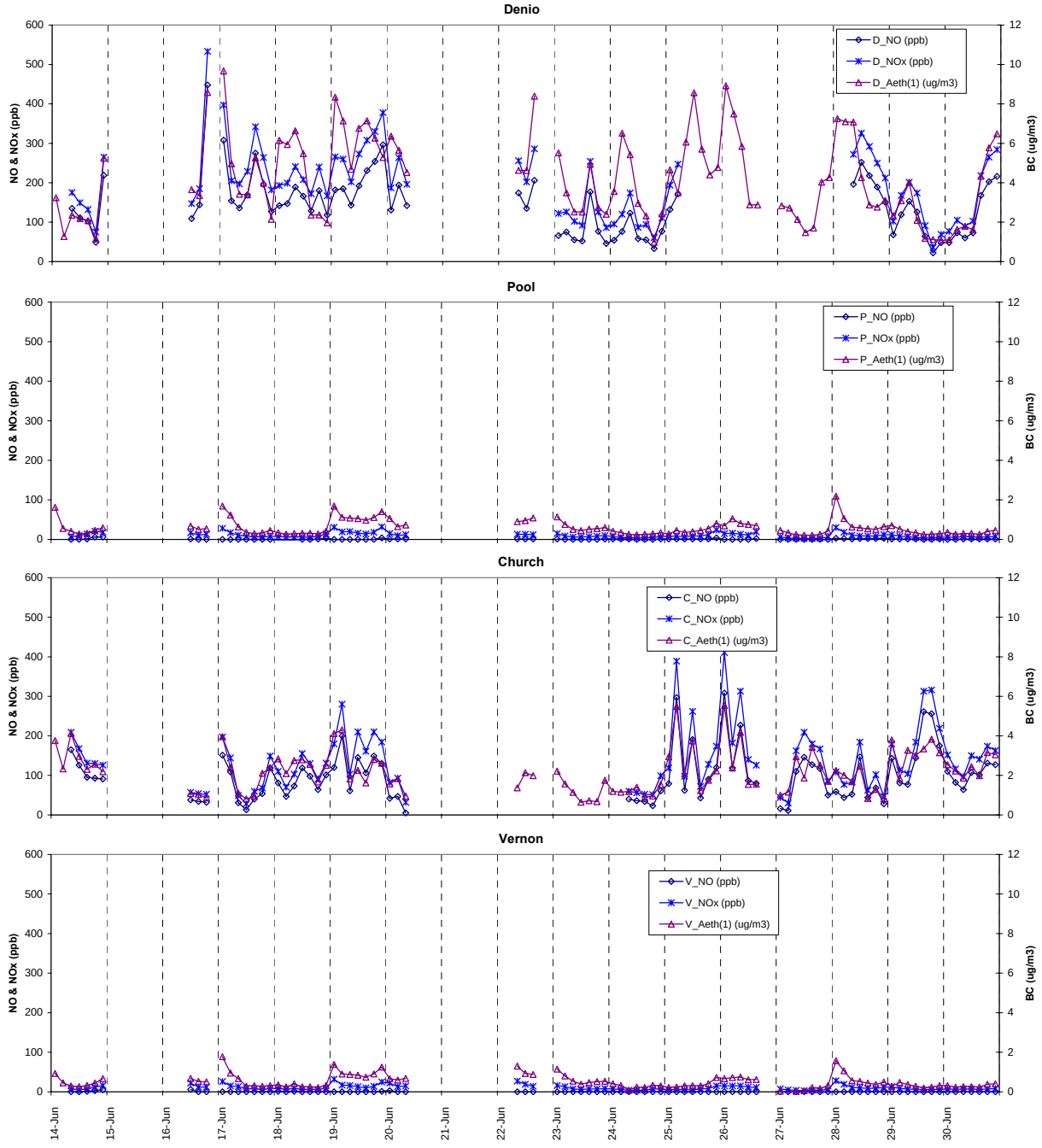

Figure 2. Hourly NO, NOx, and BC for June 2006

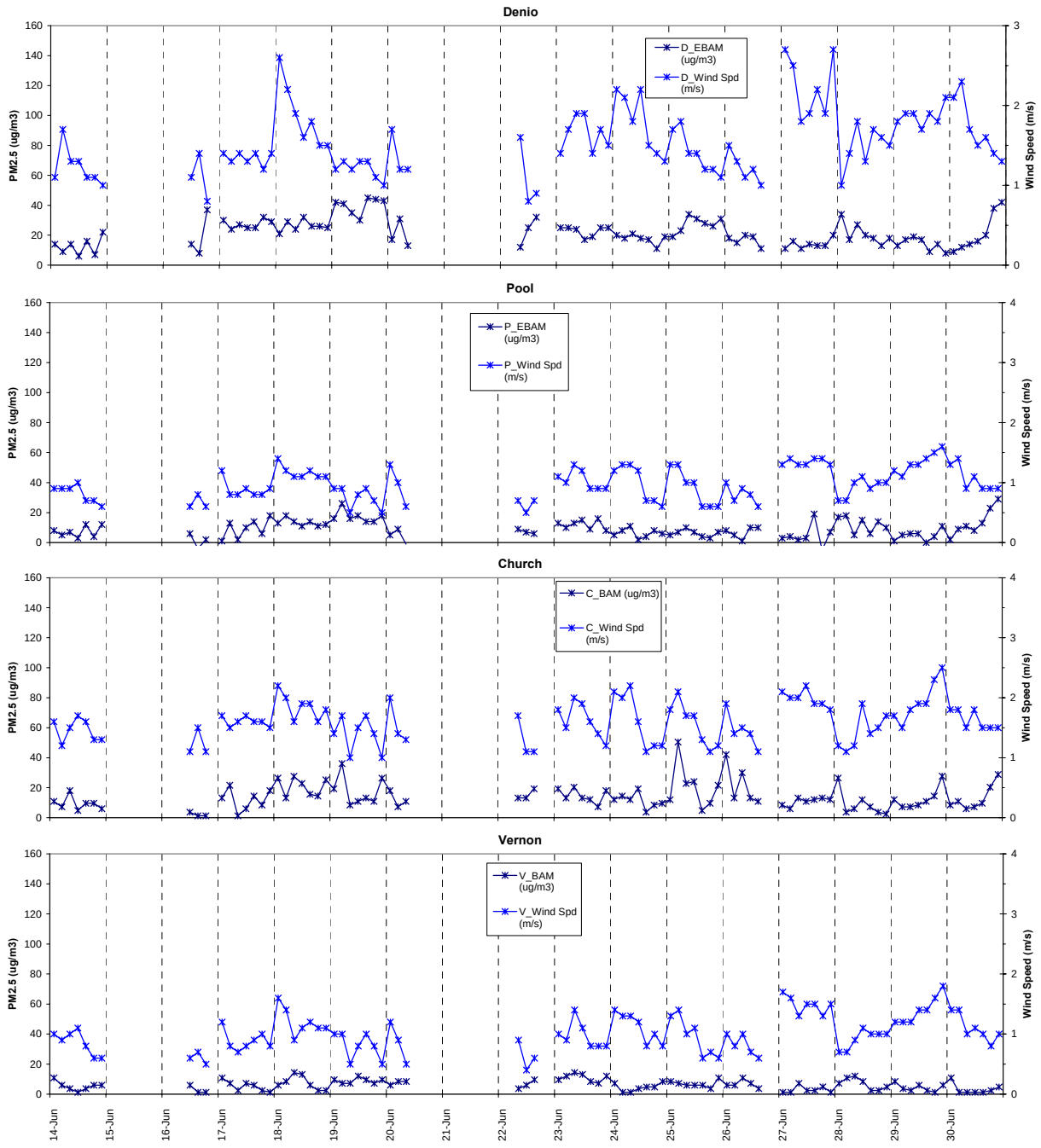

Figure 3. Hourly PM2.5 mass concentration and wind speed for June 2006.

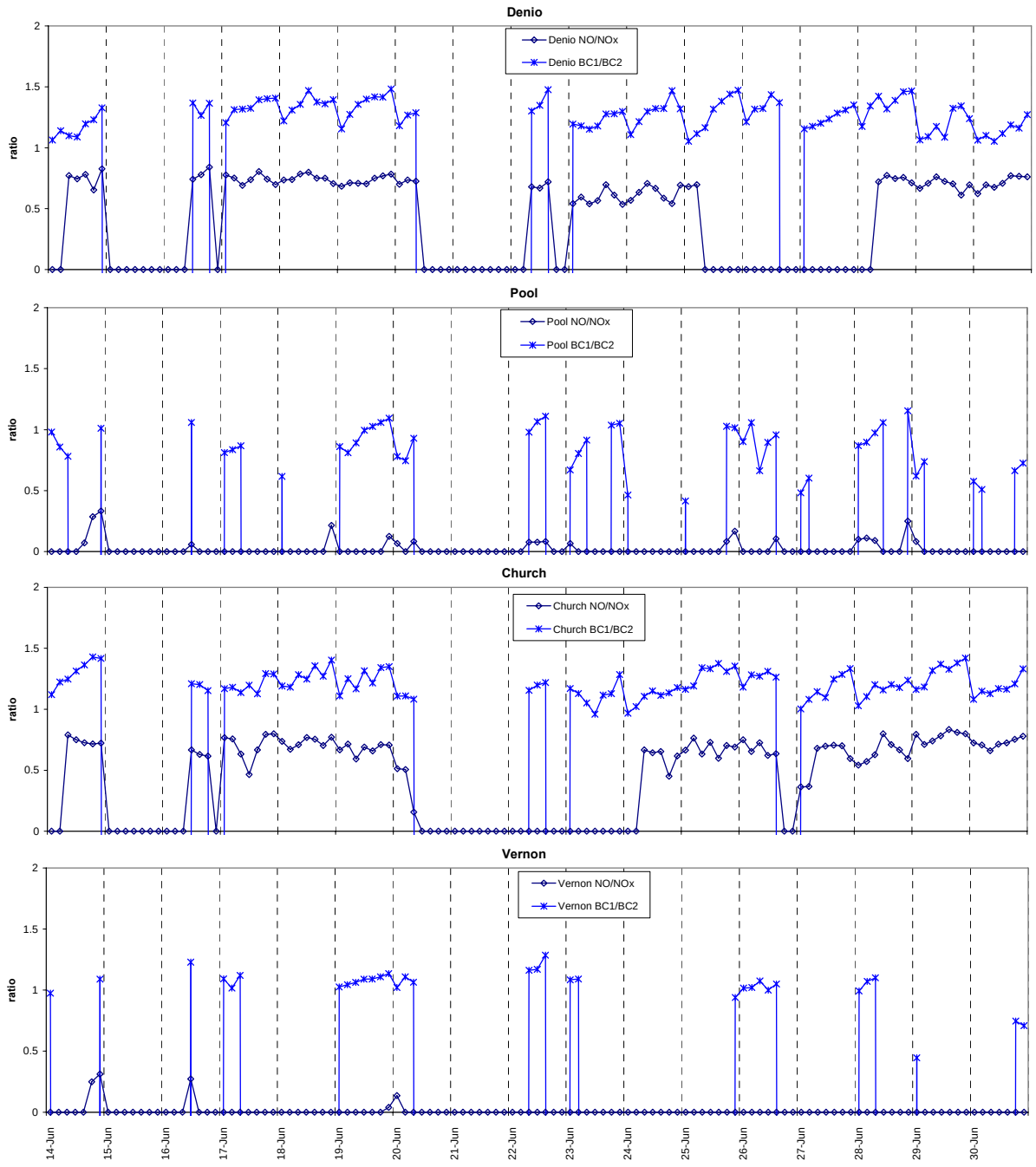

Figure 4. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for June 2006.

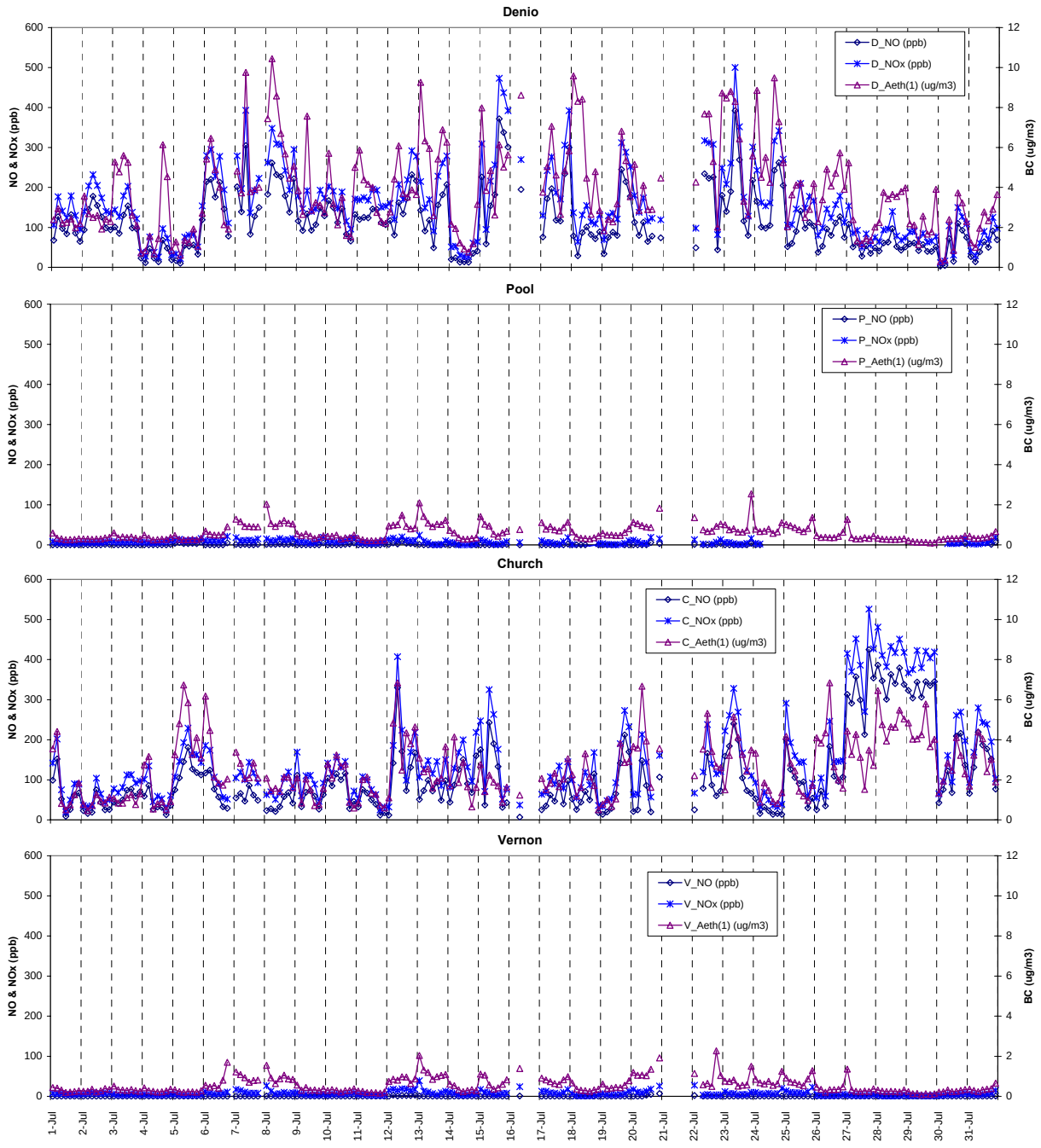

Figure 5. Hourly NO, NOx, and BC for July 2006

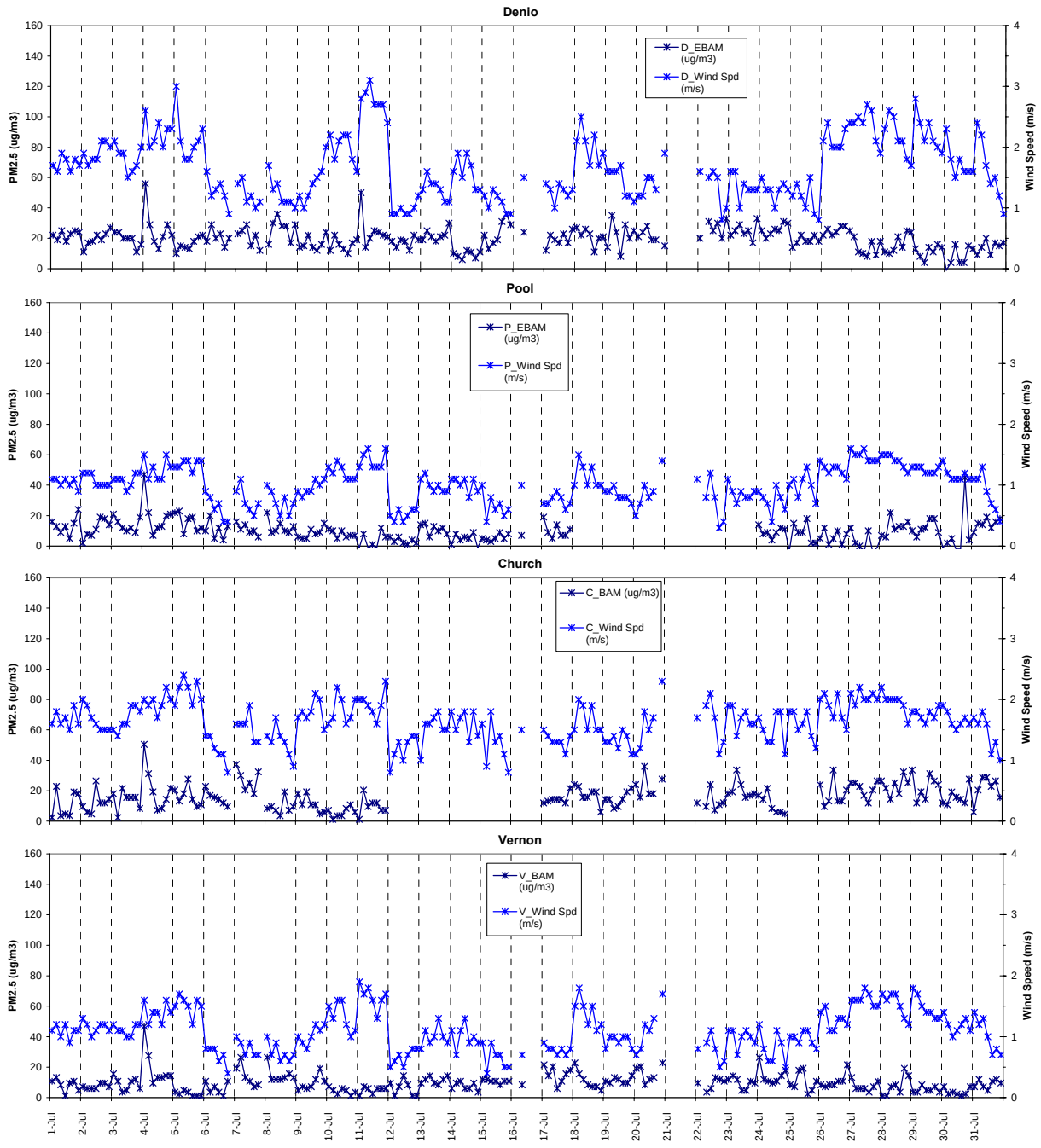

Figure 6. Hourly PM2.5 mass concentration and wind speed for July 2006.

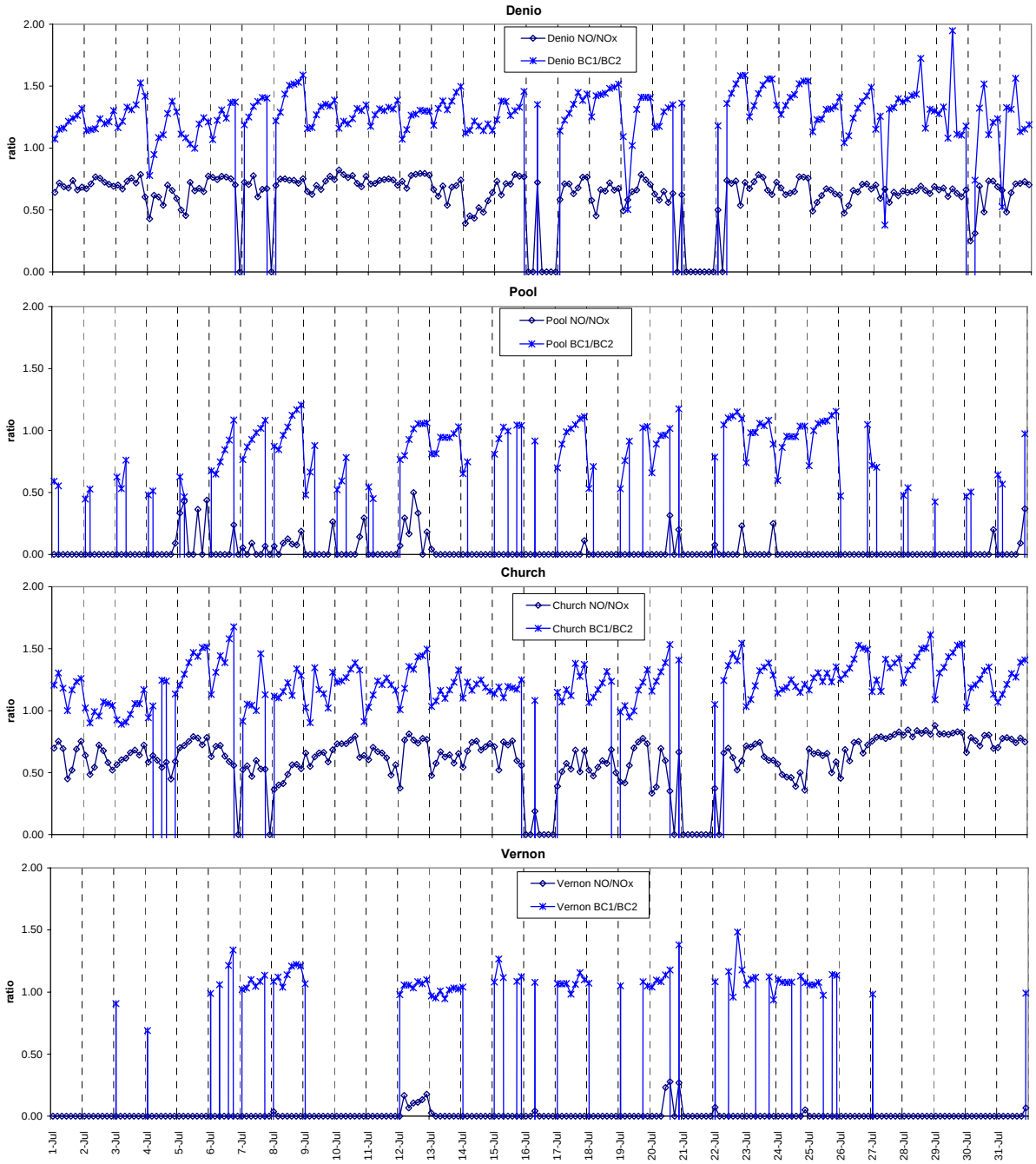

Figure 7. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for July 2006.

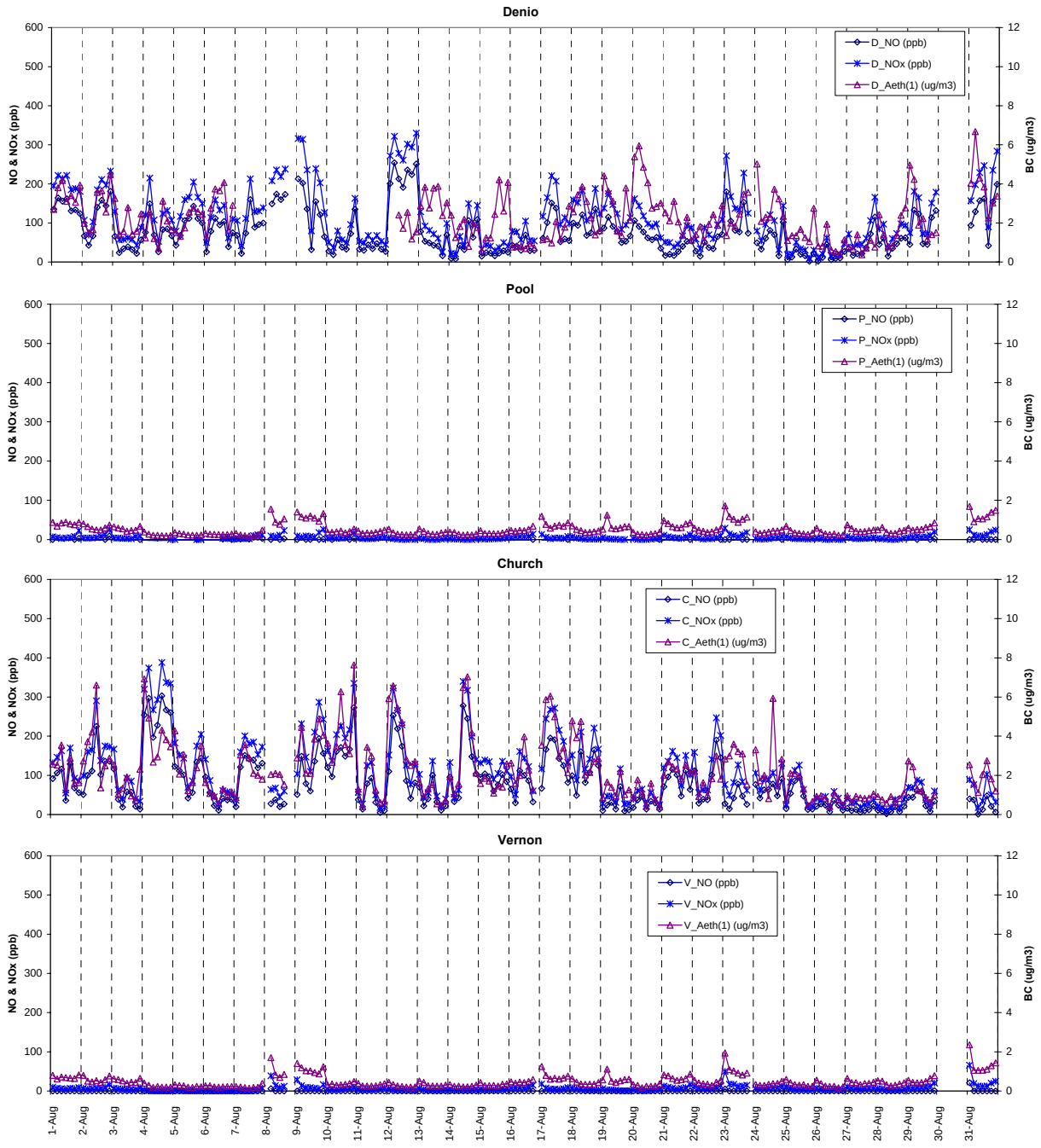

Figure 8. Hourly NO, NOx, and BC for August 2006

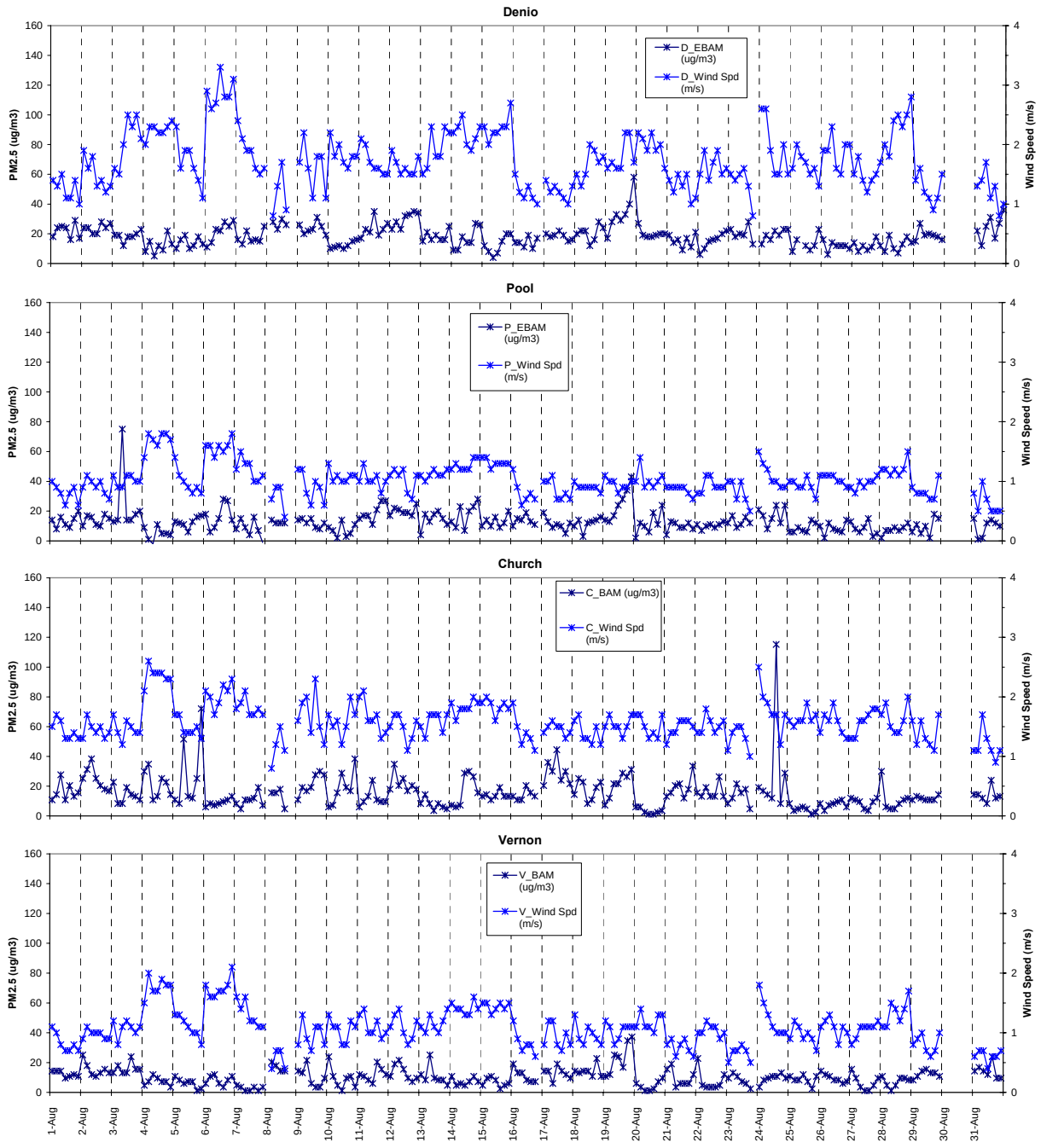

Figure 9. Hourly PM2.5 mass concentration and wind speed for August 2006.

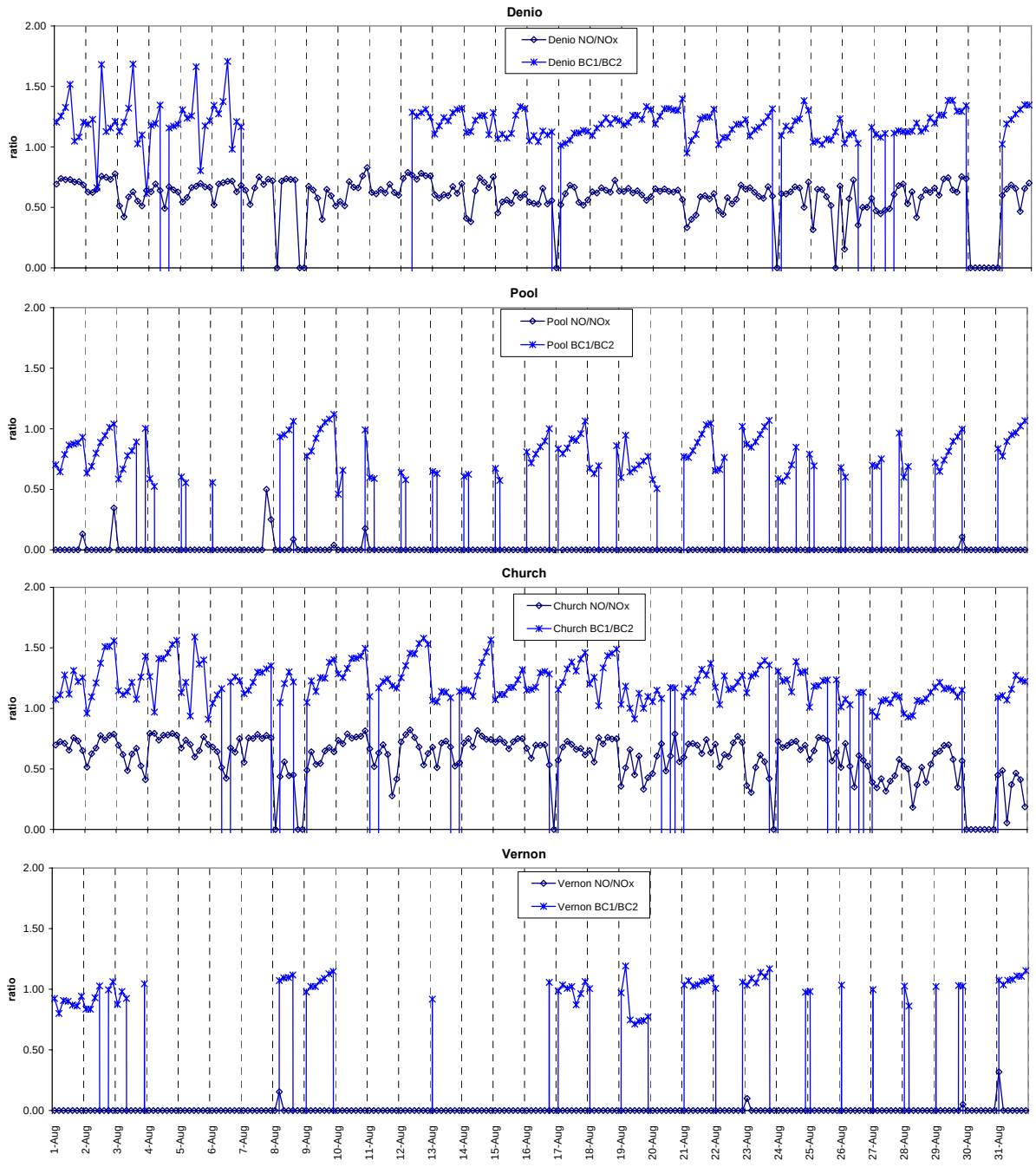

Figure 10. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for August 2006.

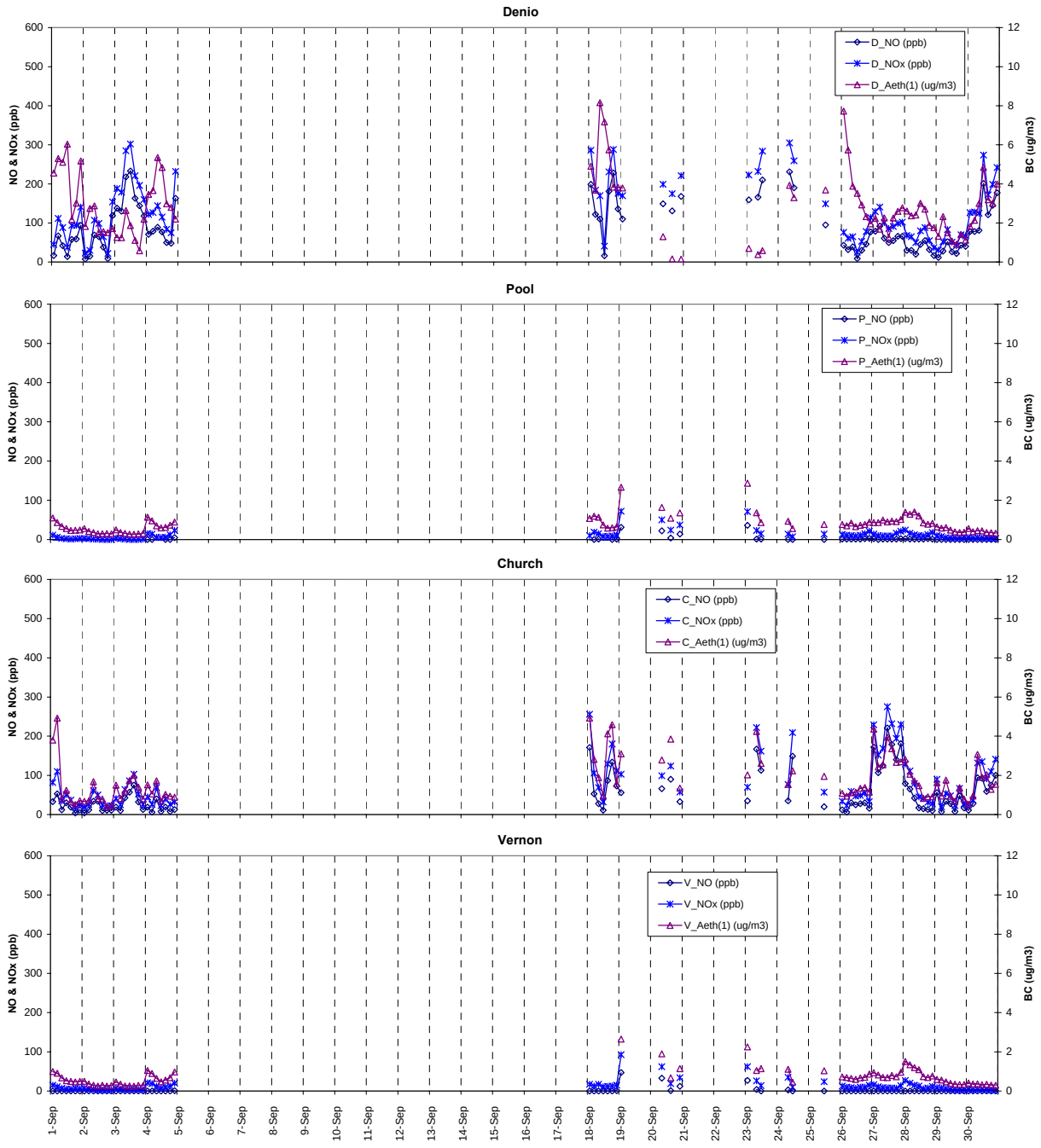

Figure 11. Hourly NO, NOx, and BC for September 2006

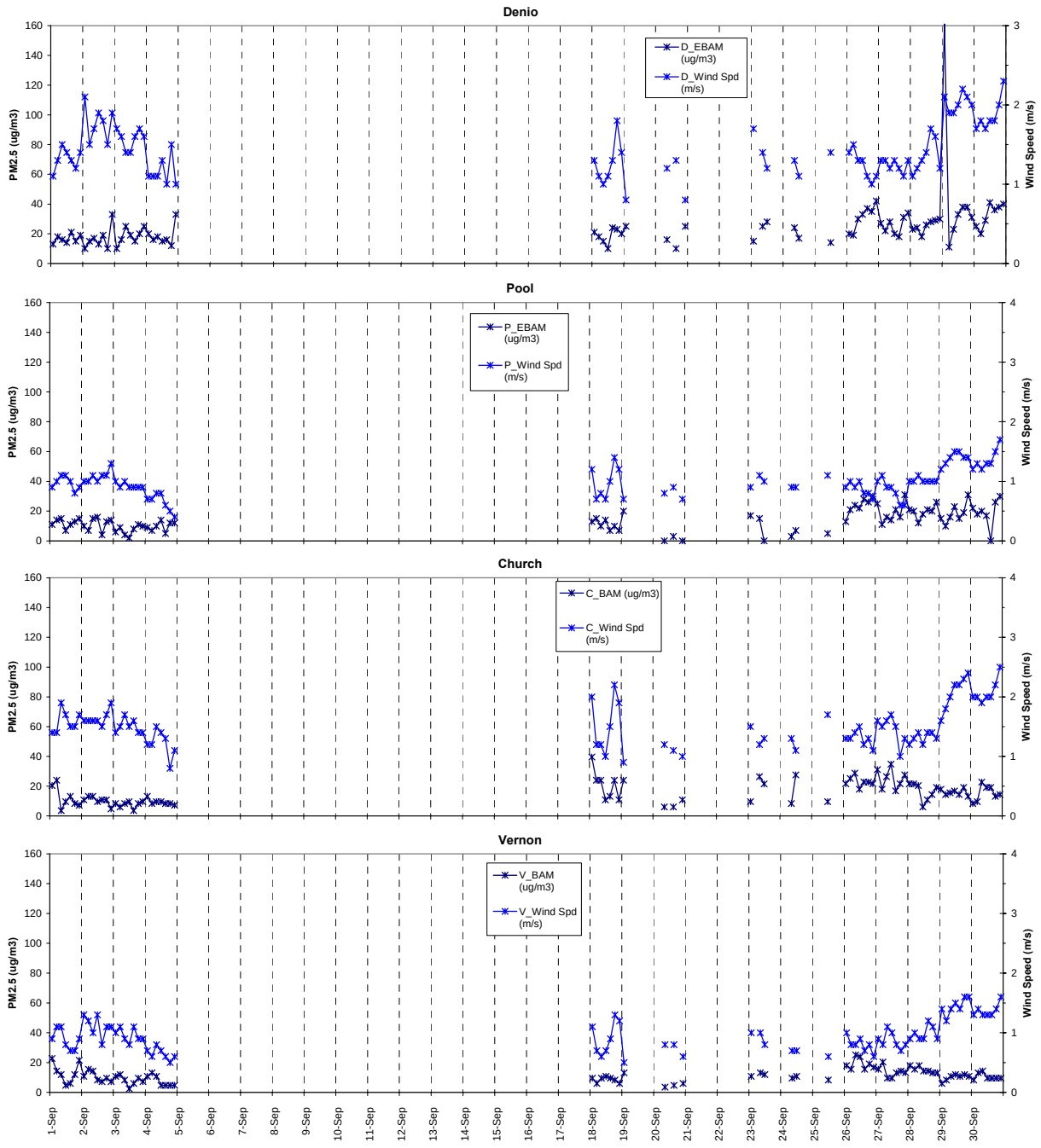

Figure 12. Hourly PM2.5 mass concentration and wind speed for September 2006.

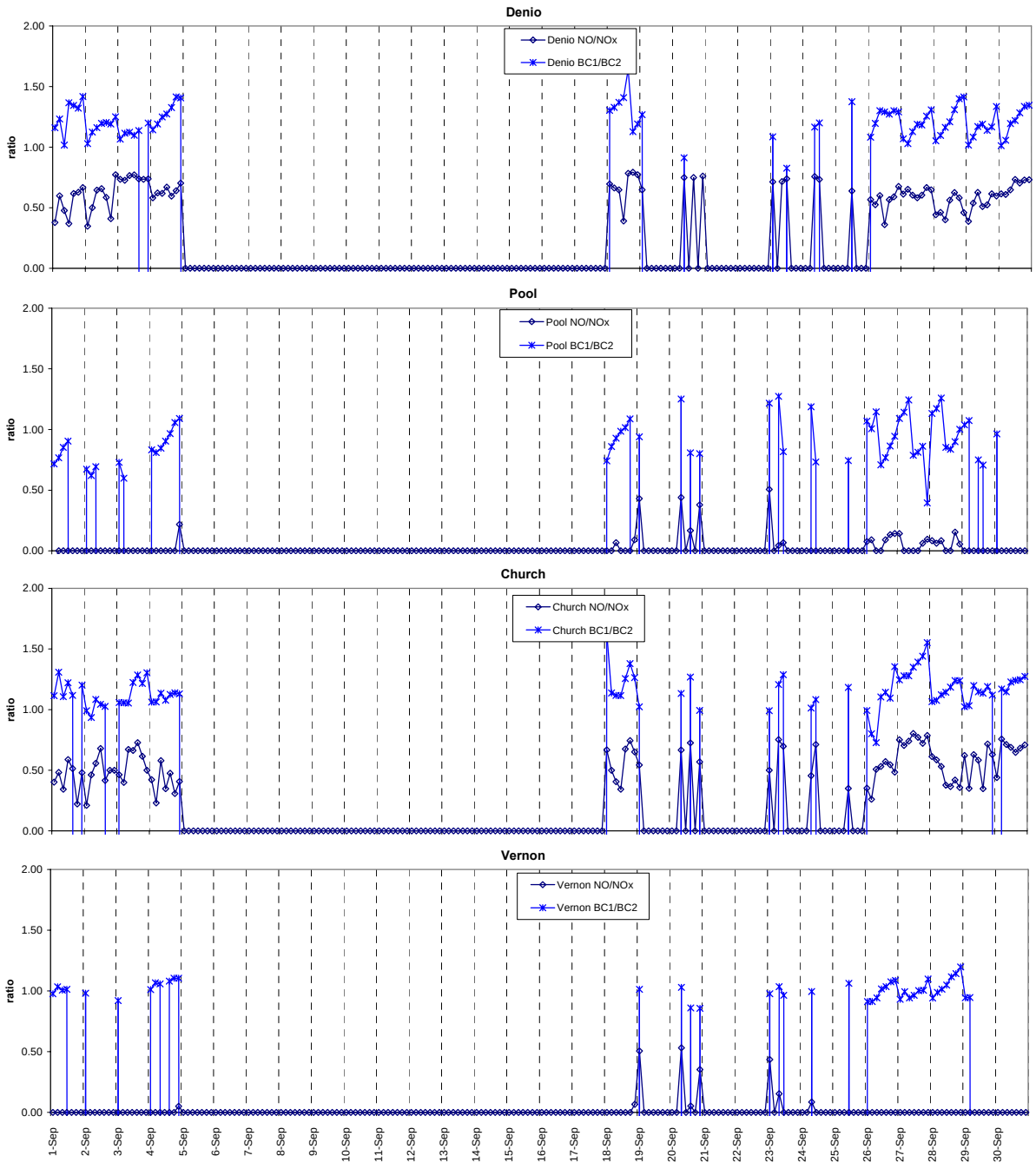

Figure 13. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for September 2006.

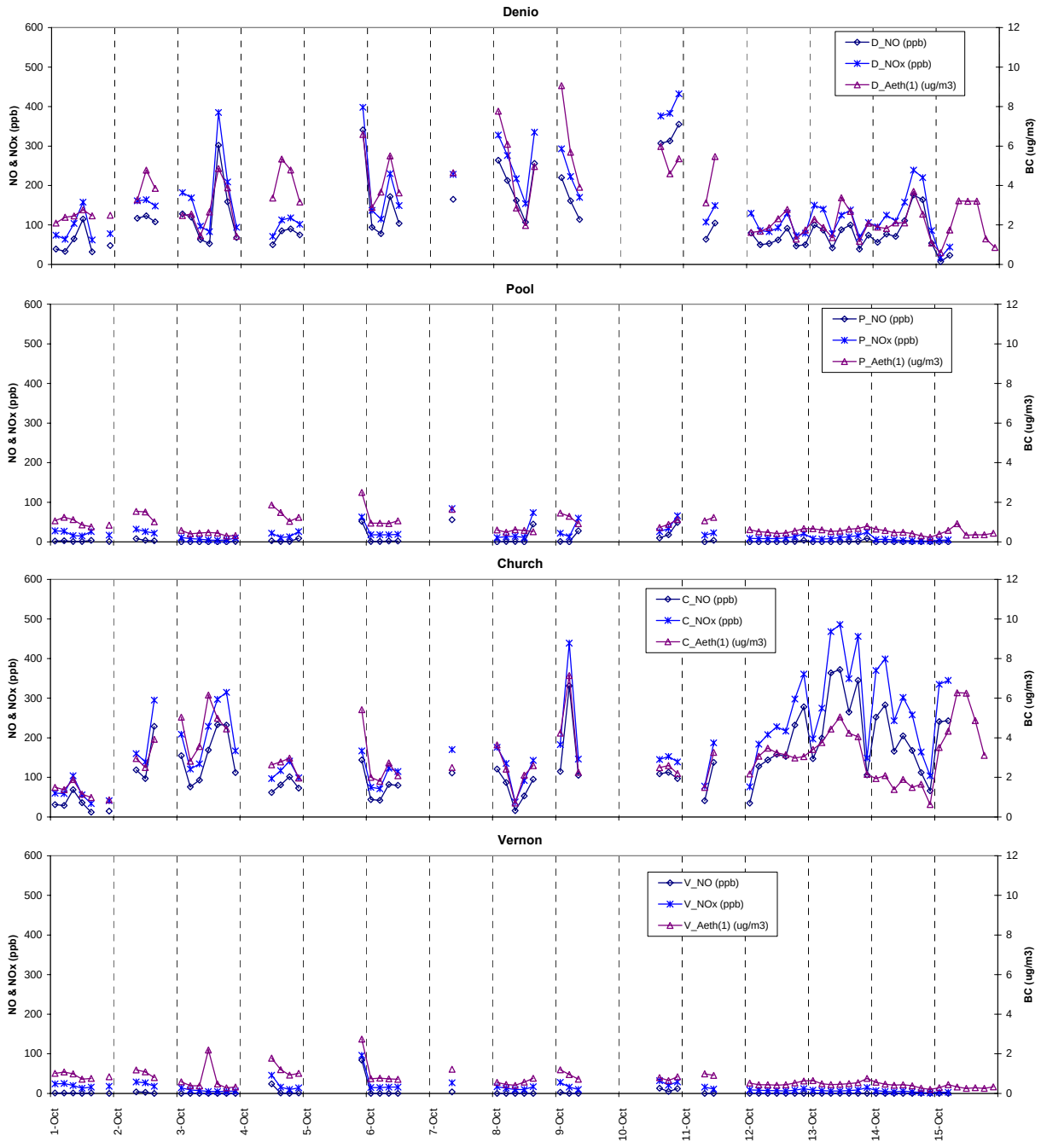

Figure 14. Hourly NO, NOx, and BC for October 2006

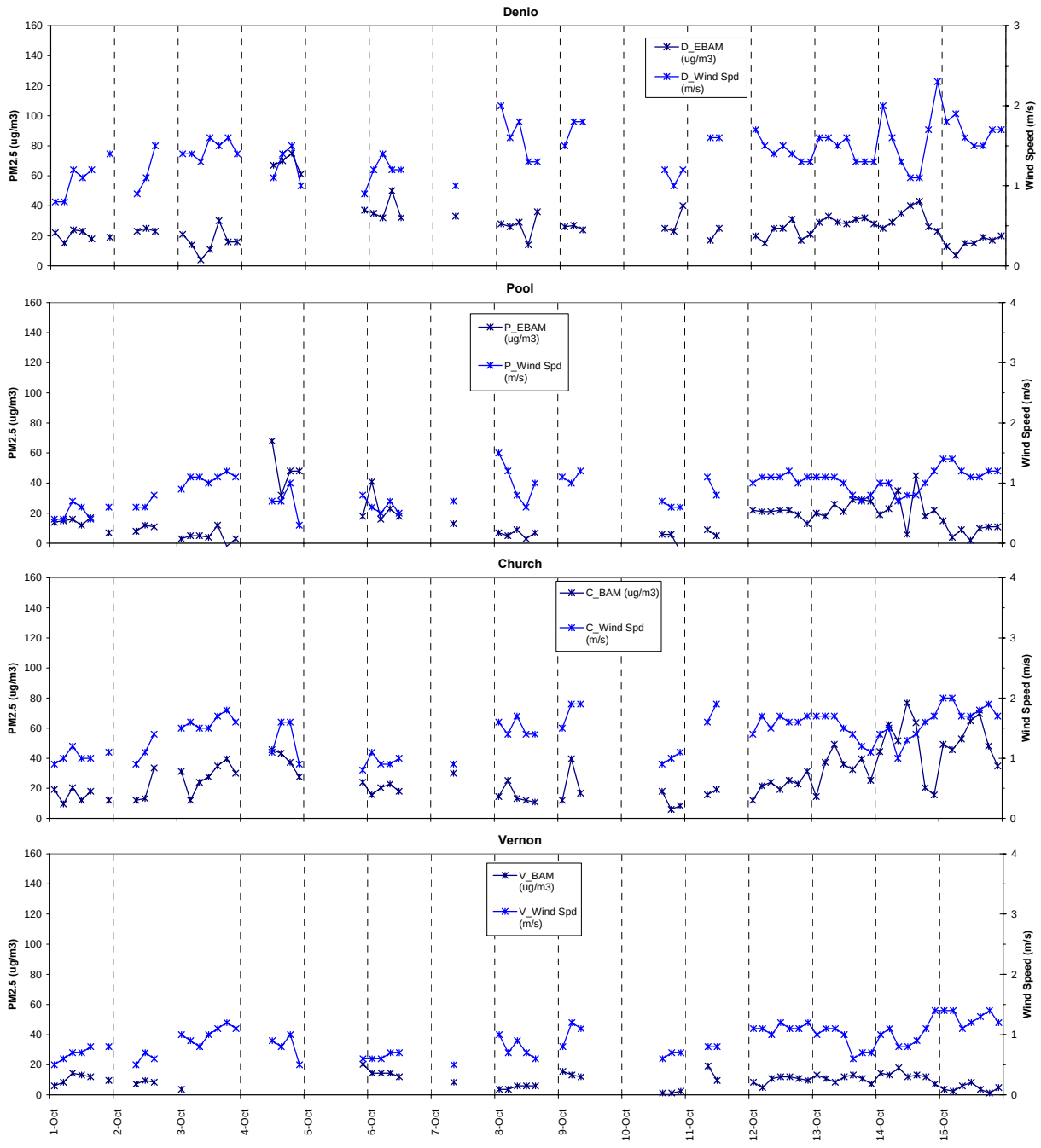

Figure 15. Hourly PM2.5 mass concentration and wind speed for October 2006.

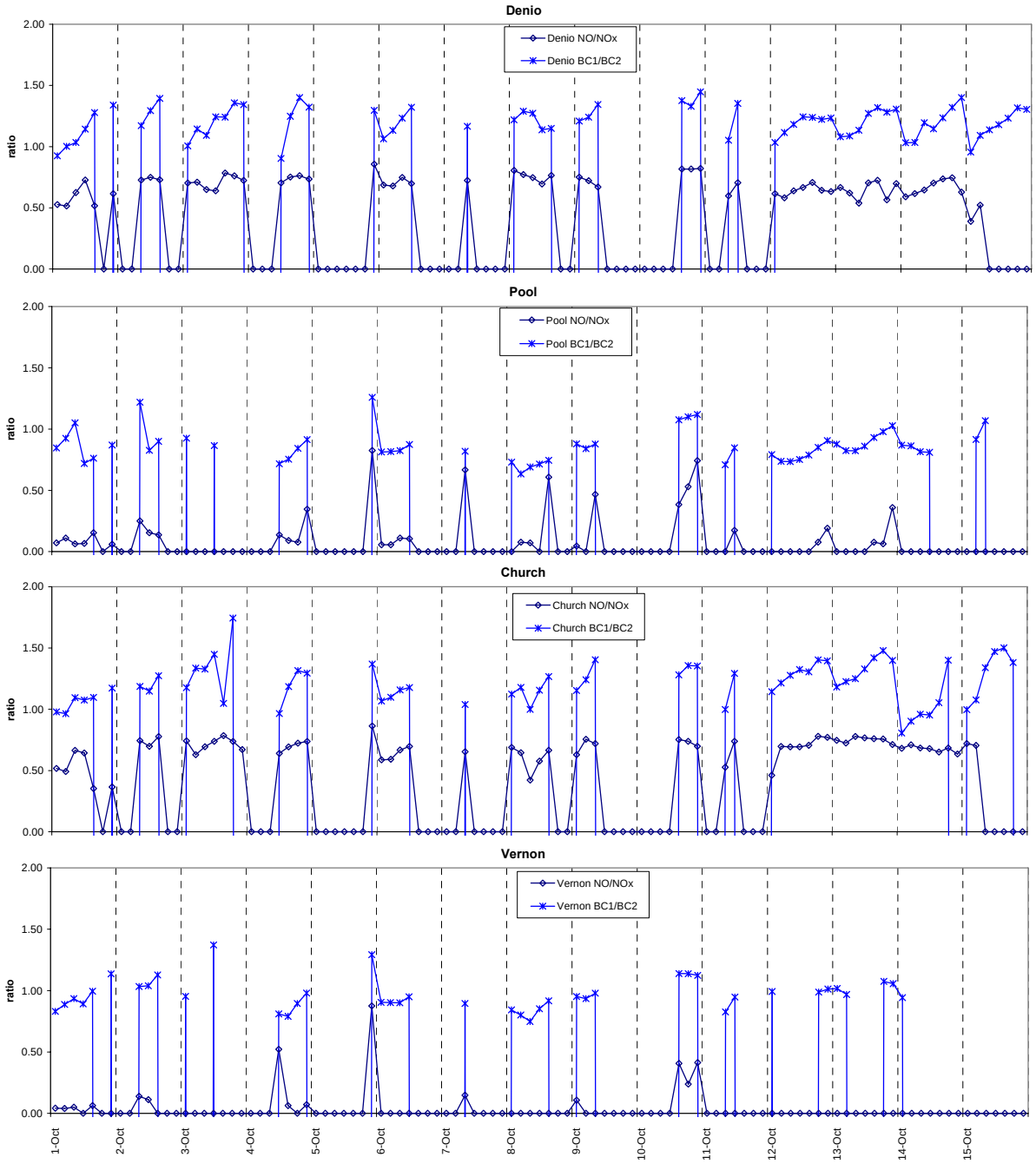

Figure 16. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for October 2006.