Roseville Rail Yard Air Monitoring Project (RRAMP)

Third Annual Report
Review and Summary of Year 3 (2007) Data

Prepared for

Placer County Air Pollution Control District
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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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). A one year extension to include summer 2008 is currently planned, to compensate for the late start in monitoring at one of the site pairs in 2005. Laboratory support for the study is provided by the California Air Resources Board and the South Coast Air Quality Management District. This third 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 third 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 second year of the monitoring program (Campbell and Fujita, 2007).

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 was 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 was 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 mid-October). Monitoring for the RRAMP consisted 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 2007 are summarized in Table 1-1. The prevailing winds during the late night through early morning hours in the summer months coincided 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. Meteorological data was also collected at the Roseville AQMD monitoring station which is located east of the area shown in Figure 1-1 at 151 N Sunrise Blvd.

Meeting RRAMP objectives depends 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 third of three annual reports that provide analyses of the RRAMP data. Data analysis efforts for each report consists of the following five 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 $PM_{2.5}$ (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 $PM_{2.5}$.

This report also includes the following additional tasks.

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, NO, NOx, 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 2007. Filter samples were collected every third day for 7 hours.

	Denio Site					
	Wind Spd/Dir (EBAM)	NO/NOx (TECO-42)	Aeth BC (A330)	EBAM PM2.5 (2238)	Teflon Filter	Quartz Filter
monitoring period	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/17~10/15	6/16~10/14
total observations	2952	2952	34317	2952	41	41
count	2952	2951	33827	2952	36	41
%	100%	100%	98.6%	100%	88%	100%

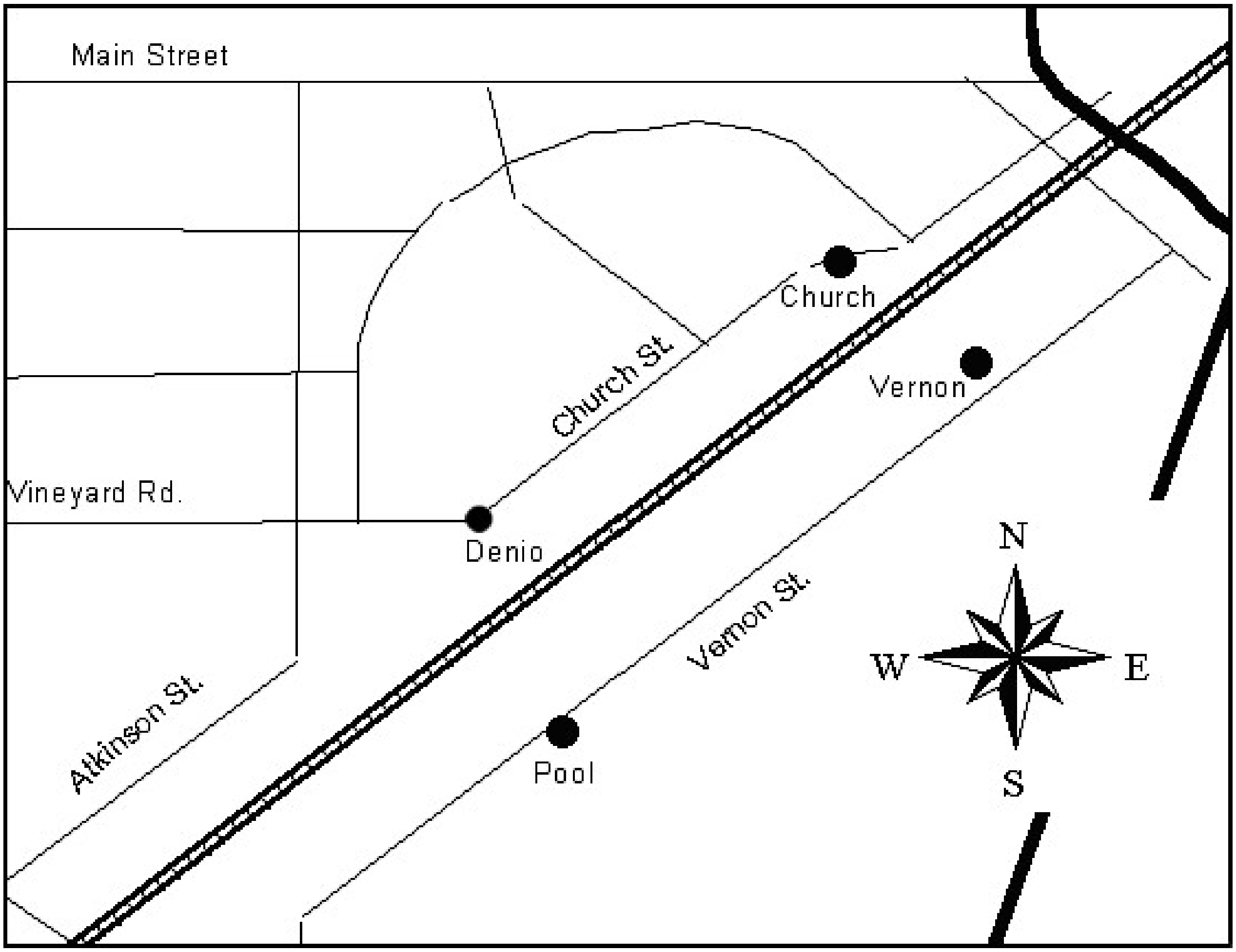
	Pool Site					
	Wind Spd/Dir (EBAM)	NO/NOx (TECO-42)	Aeth BC (A479)	EBAM PM2.5 (2237)	Teflon Filter	Quartz Filter
monitoring period	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/17~10/15	6/16~10/14
total observations	2952	2952	34317	2952	41	41
count	2952	2943	34105	2952	41	41
%	100%	99.7%	99.4%	100%	100%	100%

	Church St. Site					
	Wind Spd/Dir (EBAM)	NO/NOx (TECO-42)	Aeth BC (624)	BAM PM2.5 (4514)	Teflon Filter	Quartz Filter
monitoring period	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/17~10/15	6/16~10/14
total observations	2952	2952	34317	2952	41	41
count	2952	2946	33644	2952	41	41
%	100%	99.8%	98.0%	100%	100%	100%

	Vernon St. Site					
	Wind Spd/Dir (EBAM)	NO/NOx (TECO-42)	Aeth BC (623)	BAM PM2.5 (4515)	Teflon Filter	Quartz Filter
monitoring period	6/15~10/15	6/15~10/15	6/15~10/15	6/15~10/15	6/17~10/15	6/16~10/14
total observations	2952	2952	34317	2952	41	41
count	2952	2948	31198	2952	41	40
%	100%	99.9%	90.9%	100%	100%	98%

Data recovery from the Roseville AQM station met tower was near 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 2007 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 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. In general, tape advances did not occur during the overnight period of interest with the following exceptions:

- Tape advances occurred at Denio at 01:45 from 6/30 until 7/4, then at 02:15 until 7/9. There were none after that.
- Tape advances occurred at Pool at 19:55 from 8/3-9/4.
- Tape advances occurred at Church at 04:00 from 8/11-8/13, and at 04:40 from 10/1-10/3.
- Tape advances occurred at Vernon at 04:40 from 10/1-10/3.

These appear to be programmed, not due to tape loading, however no problems with system clocks were reported. Since these tape advances resulted in data loss during the primary time period of interest, we recommend that the cause of these unexpected tape advances be investigated to avoid future occurrences and to confirm that the problem did not affect the time signatures of the recorded data.

Concerns have been raised about a well-documented artifact that can occur in Aethalometer data due to non-linearity of the instruments response to increasing amounts of strongly light absorbing aerosol on the filter tape. In essence, the change in transmittance of the filter as light absorbing particles are collected on it is more rapid when the filter substrate is clean than when it has been 'soiled' by an accumulation of dark material. Since the instrument assumes a constant relationship between filter loading and the rate of change in transmittance, this can result in overestimation of the amount of BC when a clean filter spot is introduced, or underestimation when the filter is heavily loaded with BC. This problem is minimized by limiting the light attenuation that can occur on a single filter spot before advancing the tape, however it has been demonstrated that if the aerosol being collected is strongly light-absorbing, such as 100% fresh diesel exhaust or propane flame soot, significant under or overestimation of the concentration can occur for measurements with high time resolution. In ambient monitoring situations this problem is mitigated by two factors; first, the aerosol is typically not pure diesel exhaust or soot but also contains components that are not strongly light absorbing, and second, the data are averaged over sufficient time periods to cancel out the variations in sensitivity. Although several corrections for the non-linearity problem using the attenuation data recorded by the Aethalometers have been proposed in the literature, these were developed for carefully controlled aerosols in laboratory situations and may not be applicable to other situations unless one has detailed knowledge of the optical properties of the aerosol (Arnott 2005). Fortunately, a close examination of the 5-minute BC data from this study shows no indication that the filter loading effect was affecting the measurements, even during periods when the BC concentration was highest, as shown in Figure 2-1. Presumably, this is because there is substantial amounts of organic and/or non-carbonaceous material in the aerosol which do not strongly absorb light. Therefore, no attempt to correct the data was made.

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). No significant data periods were affected by this screening.

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. Only a relatively small number of the more than 10,000 possible 5 minute data points for each site were flagged by this process, and none were clearly determined to be invalid. The significant events are listed 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 analysis of prior data, 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).

Rather than repeat the extensive comparisons of wind data from the 4 sites conducted in previous reports, which verified the validity of the wind speed and direction criteria and also demonstrated that the wind patterns were similar at the upwind and downwind locations, for the current data set we chose to examine the wind data from the two collocated sampling periods conducted before and after the summer. Figure 2-2 and Table 2–2 show the correlation of the sampler pairs used during the summer. Based on this comparison, the precision of the wind speed (WS) and wind direction (WD) from collocated EBAMs is not very good. Precision of the EBAMs was ±25 degrees for WD. However, the wind rose in Figure 2-3**Error! Reference source not found.** shows that only about 1% of data was within 25 degrees of the min/max WD criteria so the errors should not affect selection of data for the downwind-upwind analysis. EBAM 2237 WS showed ~40% bias relative to 2238 in both pre and post periods. The scatter plots used to determine bias are shown in Figure 2-4 and Figure 2-5. Since 2238 and 4515 agree well in the post period when they were operated simultaneously at different downwind sites, and 4514 shows no consistent bias relative to 4515, we assume E2237 (used at Pool) to be incorrect. Since only wind data from the downwind sites is used to filter data this will have no impact on the downwind-upwind analysis. Some bias in unit 4514 (used at Church) is also indicated, but if we average pre and post collocation period results it is not significant since <5% of hours at Church are close enough to minimum or max WS criteria to be at risk of being incorrectly screened out due to the WS error.

Applying the wind direction and speed criteria described above for both downwind sites resulted in elimination of 14% of the data from further analysis.

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 2-6 and Figure 2-7 show no outliers. NO at Pool was zero or slightly below zero 44% of recorded hours. Zero values for NO were recorded 77% of hours at Vernon. Less than 2% zero values were recorded at the downwind sites.

BC (Channel 1). Histograms in Figure 2-8 show no outliers (data was already screened at 5 min level).

BAM. Histograms in Figure 2-9 show no outliers, except a value of $PM_{2.5}$ >100 μg/m^3 at Vernon on July 4. Due to potential local influence from fireworks, data from that night will not be used in our analysis. The histograms also show a change in the distribution shape above 40 ug/m3 at most sites. Further investigation revealed that this was due to a cluster of high values on Sept. 5 due to the Moonlight wildfire. Data from that night will also be excluded. EBAM measurements for 6 percent of hours at Denio were between 0 and -5 ug/m3 indicating a possible baseline drift. This will be corrected for in the collocated sampler analysis and comparison with filter sample data.

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.

- At Pool during 6/15 AM, all hourly average $PM_{2.5}$ values were reported as zero but the real-time EBAM values non-zero. Data were deleted.
- At Vernon on 7/22 at 0:00, a 31 ug/m^3 spike in $PM_{2.5}$ was recorded. No corresponding spike was observed in BC or at Pool. This appears to be a real, but localized event and is within the normal range of data observed at that site so it was not excluded.
- During the Moonlight Fire, on 9/5, all data are excluded. Aethalometer data is also flagged on 9/6, but there was no indication of fire influence in data.
- Large BC spike (12.6 ug/m^3) at Church on 10/1 AM. No proportional spike in NOx, but it also shows up in BAM data. Appears to be real.

- Smaller BC spike (5.7) at Denio on July 17, no corresponding spike at other sites or in NO. However, 5min data looks valid. Flagged as suspect.

- Elevated BC (1-2 ug/m3) was recorded at both upwind sites from 8/27-8/30.

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), $PM_{2.5}$/BC(1), and NO/NO_x for each site (NO/NOx ratios were only calculated when the hourly NOx was greater than 10 ppb). Appendix B contains separate time-series plots of hourly data NO/NO_x, $PM_{2.5}$/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 (0.66) and much lower averages (0.21) at upwind sites. The maximum ratio is about 0.86 at all sites, except for a few higher values at Church. All values were less than 1, and therefore physically reasonable, during the overnight period. At the Pool site, NO was slightly negative (-1 to -3 ppb) for about 8% of the hours for which ratios were calculated, but these values were not modified or excluded to avoid biasing the averages.

$BC/PM_{2.5}$ ratios were fairly consistent between sites, with similar averages at downwind sites (0.17 and 0.22) and much higher averages at upwind sites (0.4 and 0.9). Some unusually high hourly averages (BC > 50% of $PM_{2.5}$) were observed at the downwind sites, but all corresponded to periods of low $PM_{2.5}$ 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. The mean+2σ at all sites was below 0.50.

BC(1)/BC(2) ratios were slightly higher at downwind sites ($\pm 2\sigma = 0.9$ to 1.6) than typically observed for ambient data (0.8 to 1.2). BC(1)/BC(2) ratios at the Pool site were generally lower than elsewhere, as in the prior year, with a mean ratio less than 1, possibly due to a greater influence of $PM_{2.5}$ 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 2-10. The dashed lines show the range of residuals relative to the regression line, ±20%. Correlation was somewhat lower for this pair of instruments during the post-study collocation, as shown in Figure 2-11, due to the lower range of data but the range of residuals is again about ±20%. It was demonstrated in previous years' analyses 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).

Since slopes show a small, but statistically significant, difference from 1 and this difference does not change sign from pre- to post-study collocation, we can correct for that bias using the average of pre and post regression coefficients for each pair. However, the intercepts are not statistically significant so they will be considered to be zero (no absolute bias).

Figure 2-12 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. These values of the 95^{th} 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 best during the pre-study collocation, as shown in Figure 2-13 and Figure 2-14. Figure 2-15 shows that 95% of the relative errors are within 15-23%. We will use an average value of 20%, which is consistent with the pair, as the precision error estimate. The propagated errors for 7-hour and 24-hour averages shown in Table 2–3 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 7-hour nightime 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 18% 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+3.94 and Church*0.82+1.27) using the average of the pre- and post-study regression slopes and intercepts shown in Table 2–4. EBAM Data from post-study collocation period after 12:00 on 10/30 were excluded from this analysis due to apparent malfunctioning of unit 2238 (frequent 'dropouts' resulting in negative values) after a large concentration spike affecting both units, which might have been due to a power surge. The average coefficient of variance (CV) is also presented, along with the regression statistics, in Table 2–4 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 2-18 and Figure 2-21) 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 for hourly measurements as a fixed quantity (10.5 ug/m^3 for Denio/Pool and 8.8 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 2-16, Figure 2-17, Figure 2-19, and Figure 2-20) show that the majority of the scatter in the data set is accounted for by the precision error derived from the distribution analysis. Table 2–4 also 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 7-hour (2200 to 0500 PST) filter samples collected at the four sites were compared to the averages of corresponding data from the continuous $PM_{2.5}$ and BC instruments. All hourly data collected during the study period was averaged for the same overnight period (7 hours), eliminating 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 $PM_{2.5}$ versus BAM $PM_{2.5}$ (Figure 2-22 and Figure 2-24) and of filter EC versus aethalometer BC(1) (Figure 2-27 and Figure 2-28) were prepared. We used regression statistics to identify the magnitude of possible biases. The regression statistics are summarized in Table 2–5. The BAM $PM_{2.5}$ results were adjusted to match the FRM $PM_{2.5}$ 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 7 hour filters collected during nighttime hours there is no statistically significant difference in the site specific means, except for data from the Pool site. Regression analysis shows slopes significantly less than 1 for Vernon and Pool sites, but the correlations are poor due to the small range of values. Although the correlation between the FRM and BAM $PM_{2.5}$ concentrations at Denio and Vernon are fairly good, it is not advisable to apply site-specific corrections to the BAM data as the differences in slope and intercept are not statistically significant. Due to reported sampling errors for the BAM operated at the Pool site (the inlet heater was disabled for part of the summer) and the resulting poor correlation with the gravimetric filter data, we have substituted BAM $PM_{2.5}$ data from the other upwind site in the downwind-upwind comparisons to follow. Figure 2-23 shows that there is good agreement between the FRM filter $PM_{2.5}$ data collected at the two upwind sites for most days, except July 25 – 28th which will be excluded. Combining all data except one outlier on July 28 from Vernon yields a regression slope of 0.86 ± 0.06 and an intercept of 2.15 ± 0.50 (see Figure 2-24). 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 1.04, but it reduces the goodness of fit and conflicts with the apparent non-zero intercepts for the individual site data in Figure 2-22.

One outlier was removed from the data for this analysis; an unusually high value of gravimetric mass for the site (18.6 ug/m3) at Vernon on July 28. This filter measurement was well outside the range of other data from Vernon and inconsistent with data from the BAMs and FRMs at the other sites for that night. Data collected during the Moonlight fire and on July 4 were also excluded from this analysis since they are expected to be of atypical composition.

2.7.2 Filter Elemental Carbon Versus Aethalometer BC Concentrations

Prior to comparing EC from the TOR analysis of quartz filter FRM samples to the averaged Aethalometer BC data, the TOR data was reviewed and several observations were made. Unlike the samples collected in prior years, in 2007 all of the quartz substrates were pre-fired to reduce passive sampling artifacts in the OC fractions. Figure 2-25 shows a comparison of filter blanks collected using pairs of filters only one of which was pre-fired. Some of the filters were loaded into the FRM samplers for approximately 24 hours in the normal manner (labeled 'field blanks'), while others (labeled 'exposure') were simply exposed to ambient air in the instrument shelters. The figure shows that there is a very substantial increase in OC if filters are not pre-fired, and the artifact due to passive sampling is very variable. It should be noted that the range of OC measured from the non-prefired blanks is larger than the mean OC concentrations at any of the 4 sites. Based on this experiment, we feel that the 7-hr OC and TC data from previous years is not useable. TC data would be useful for assessing the fraction of $PM_{2.5}$ mass that is potentially resuspended crustal material from the railyard rather than direct emissions from locomotives. Fortunately, the blanks comparison indicates that the lack of pre-firing of the filters should have no effect on the measured EC so we may still be able to use those values from prior years for estimation of DPM as described below, which is the primary application intended for the TOR data.

Since the pre-fired filter blank values are fairly consistent (1.2 ± 1.2 for OC and 0.1 ± 0.4 for EC), we were able to use them for blank subtraction of the sample data. Figure 2-26 shows all of the filter EC measurements as well as the corresponding 7-hr overnight average BC from the Aethalometers. Although there are some noticeable differences between the EC and BC measurements, the differences between the methods are generally much smaller than the differences in concentration between the two upwind sites.

Although there is no statistically significant difference between the mean EC and BC for 7-hour data from the individual or combined sites, the regression analysis does indicate some biases (see Figure 2-27, Figure 2-28, and Table 2–5). For the 7-hour samples the regression results from the downwind sites were not significantly different. Correlation coefficients for the upwind sites were well below the level of significance so they are not included in the table.

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 $PM_{2.5}$ 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.

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 $PM_{2.5}$/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 2-29 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 and the slopes and intercepts are similar, but there seems to be some difference between the 2 site pairs at the higher concentrations. This could be due to some variation in the response of the Aethalometers (we only compared the instruments to their upwind/downwind counterparts in analyzing the collocation data). These site pair specific relationships will be used to adjust the calculated differences in downwind-upwind BC when estimating excess DPM concentrations.

Table 2–1. Anomalies in 5 minute black carbon data.

Site	Date	Max BC (ug/m3)	Description
Church	10/1	12.6	Not proportional to NOx but also shows up in BAM data. Appears to be real.
Denio	7/17	5.7	No corresponding spike at other sites or in NO. 5min data looks valid.
Pool and Vernon	8/27-8/30	1 to 2	Period of elevated BC relative to other parameters at upwind sites.

Table 2–2. Correlations between BAM collocated sampler wind speed and direction.

	WS (m/s)	r2	slope	intercept	precision	WD (deg)	r2	slope	intercept	precision
4514/4515	pre	0.94	0.93	0.25	0.30	pre	1.00	1.01	4.60	8.60
	post	0.91	1.08	-0.42	0.80	post	1.00	1.08	-0.42	10.10
	mean		*1.01*	*-0.09*	*0.55*			*1.05*	*2.09*	*9.35*
E2237/E2238	pre	0.98	1.42	-0.05	1.00	pre	0.85	0.98	19.65	-26.00
	post	0.88	1.39	0.07	0.90	post	0.97	1.00	9.23	25.00
	mean		*1.41*	*0.01*	*0.95*			*0.99*	*14.44*	*-0.50*

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

site pair	**Denio vs Pool**		**Church vs Vernon**	
Instrument IDs	**A330/A479**		**624/623**	
Test Period	05/16/07-05/30/07	10/29/07-11/16/07	05/16/07-05/30/07	10/31/07-11/16/07
averaging period	1 hour	1 hour	1 hour	1 hour
mean BC (ug/m3)	1.61	2.23	1.68	2.87
regression				
r2	0.99	0.96	0.99	0.96
slope	0.984 + 0.011	0.951 + 0.020	1.003 + 0.011	1.039 + 0.026
intercept	0.05 + 0.05	0.04 + 0.11	0.01 + 0.05	0.08 + 0.16
Multiply by	Denio 0.97		Church 1.03	
relative difference				
mean	3.7%	-2.6%	0.6%	8.0%
2*stdev	16%	21%	13%	23%
skew	1.23	0.86	0.44	0.77
95% error estimates				
1 hr average	20%	20%	15%	23%
7 hr average	8%	8%	6%	9%
24 hr average	4%	4%	3%	5%

Table 2–4. Precision analysis of collocated BAM data. Linear regressions use data from the sampler used at the downwind site as the independent (x) variable.

site pair Instrument IDs	Denio/Pool 2238/2237		Church/Vernon 4514/4515	
Test Period	05/29/07-06/10/07	10/22/07-10/30/07	05/10/07-05/31/07	10/22/07-11/11/07
averaging period	1 hour	1 hour	1 hour	1 hour
mean PM (ug/m3)	14.3	18.1	12.8	16.6
regression				
r2	0.71	0.62	0.67	0.84
slope	0.808 + 0.060	0.825 + 0.094	0.764 + 0.024	0.878 + 0.012
intercept	1.20 + 2.16	6.67 + 3.43	2.58 + 0.37	-0.04 + 0.26
CV	37%	31%	38%	27%
average bias	**E2238**		**4515**	
multiply by	0.82		0.82	
add	3.94		1.27	
absolute difference	**E2237 - E2238**		**4515 - 4514**	
mean	4.47	5.49	3.53	3.92
stdev	3.23	3.96	3.32	3.19
skew	0.81	0.93	2.87	1.09
95% error estimates				
1 hr average	10.0	11.0	9.0	8.5
7 hr average	3.8	4.2	3.4	3.2
24 hr average	2.0	2.2	1.8	1.7

Table 2–5. 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
7hr PM2.5		**Gravimetric**	**BAM**			
Denio	28	13.0 ± 1.9	13.5 ± 1.8	0.74	0.92 ± 0.20	0.51 ± 3.65
Pool	35	7.9 ± 1.2	11.8 ± 2.2	0.24	0.28 ± 0.30	4.61 ± 3.92
Church	34	11.4 ± 1.6	10.1 ± 1.3	0.83	1.08 ± 0.14	0.42 ± 2.27
Vernon	34	7.8 ± 1.2	5.6 ± 1.2	0.50	0.70 ± 0.25	3.88 ± 2.80
All	131	9.8 ± 0.8	10.1 ± 1.0	0.83	**0.86 ± 0.06**	**2.15 ± 0.50**
7hr EC/BC		**EC**	**BC**			
Denio	37	2.4 ± 0.5	2.0 ± 0.3	0.82	0.57 ± 0.09	0.64 ± 0.50
Pool	37	0.7 ± 0.2	0.5 ± 0.1	0.33		
Church	39	2.5 ± 0.5	2.5 ± 0.4	0.89	0.75 ± 0.09	0.58 ± 0.52
Vernon	39	0.9 ± 0.2	0.7 ± 0.2	0.26		
All	152	1.6 ± 0.2	1.4 ± 0.2	0.82	0.74 ± 0.06	0.22 ± 0.25
Difference in 7hr EC/BC; downwind - upwind						
ΔDenio-Pool	36	1.7 ± 0.09	1.5 ± 0.3	0.71	**0.48 ± 0.10**	**0.70 ± 0.48**
ΔChurch-Vernon	39	1.6 ± 0.1	1.8 ± 0.5	0.80	**0.71 ± 0.11**	**0.65 ± 0.55**
both pairs	75	1.7 ± 0.0	1.6 ± 0.3	0.73	0.60 ± 0.08	0.66 ± 0.38

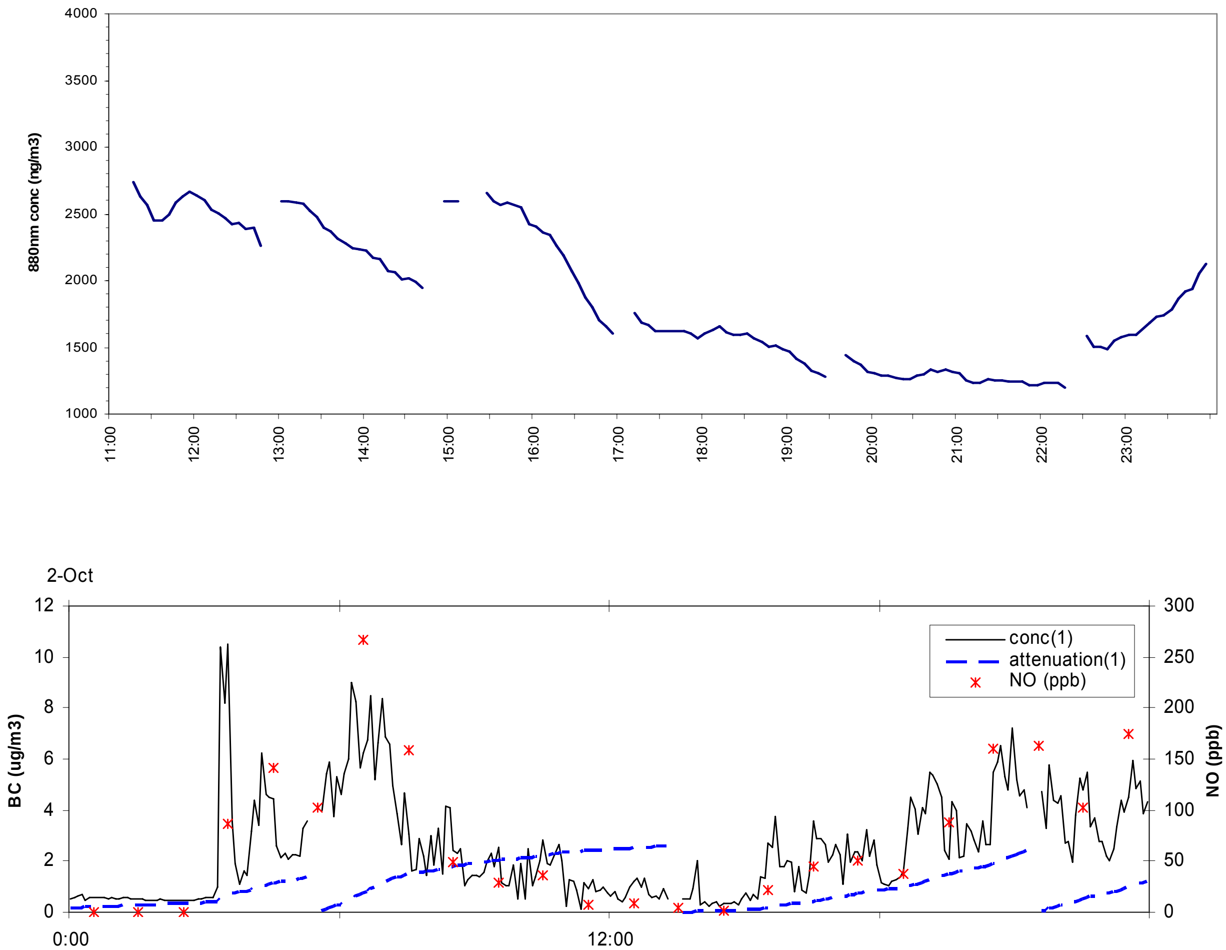


Figure 2-1. Time trace of 5-min BC data from Aethalometers. The upper chart shows an example of the filter loading effect – note the sharp increase in measured concentration after each tape change. The lower chart shows data from the Denio site during the day with the highest average overnight BC concentrations. Tape advances occurred during the gaps in the dashed attenuation line.

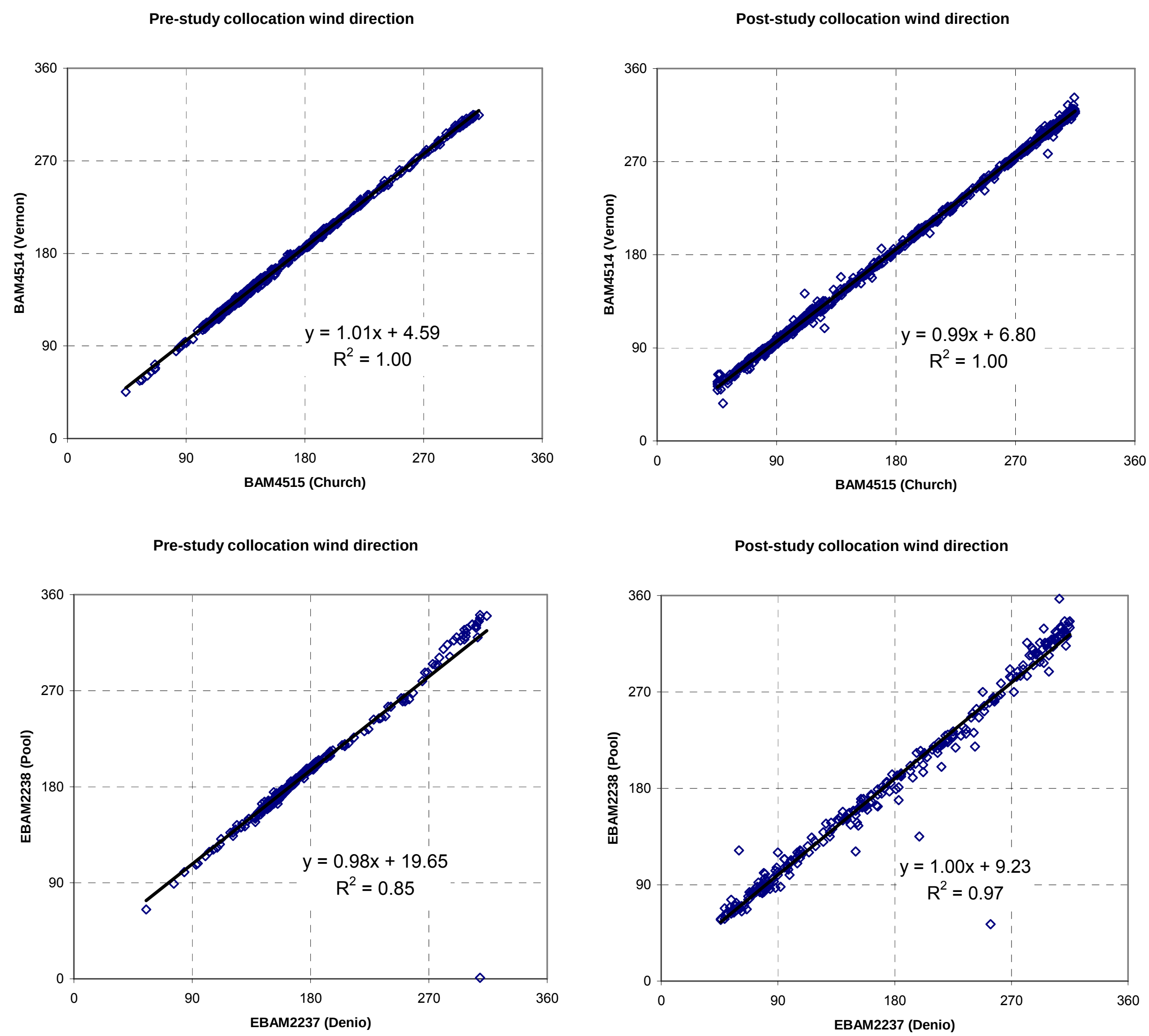


Figure 2-2. Comparison of hourly mean wind direction during collocation testing.

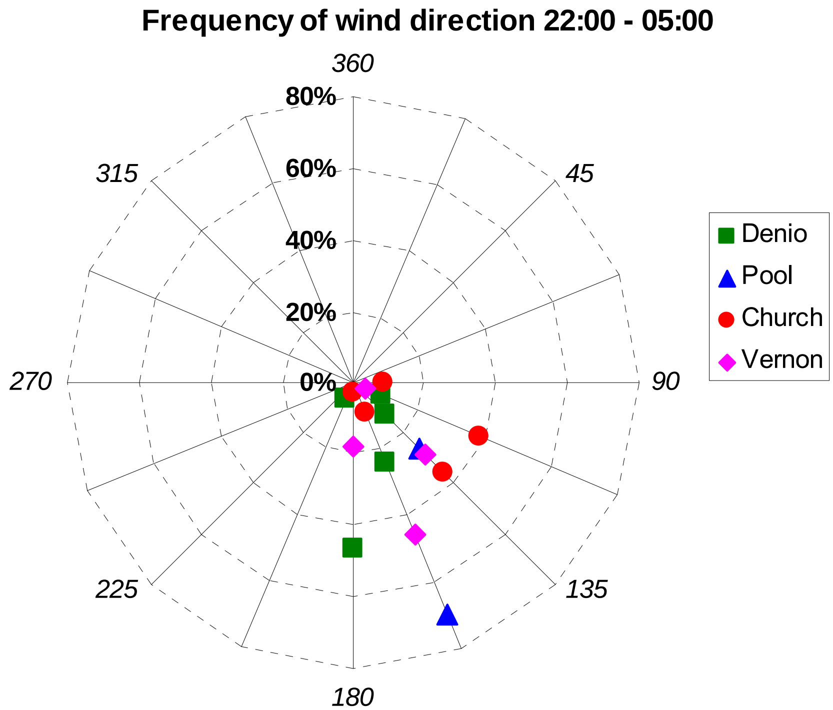


Figure 2-3. Frequency of hourly average wind directions at the four sites during overnight hours (22:00 to 05:00 PST). Wind directions have been rounded to the nearest 45 degrees. Only hours where winds were between 45˚ and 225˚ were used to determine downwind-upwind differences.

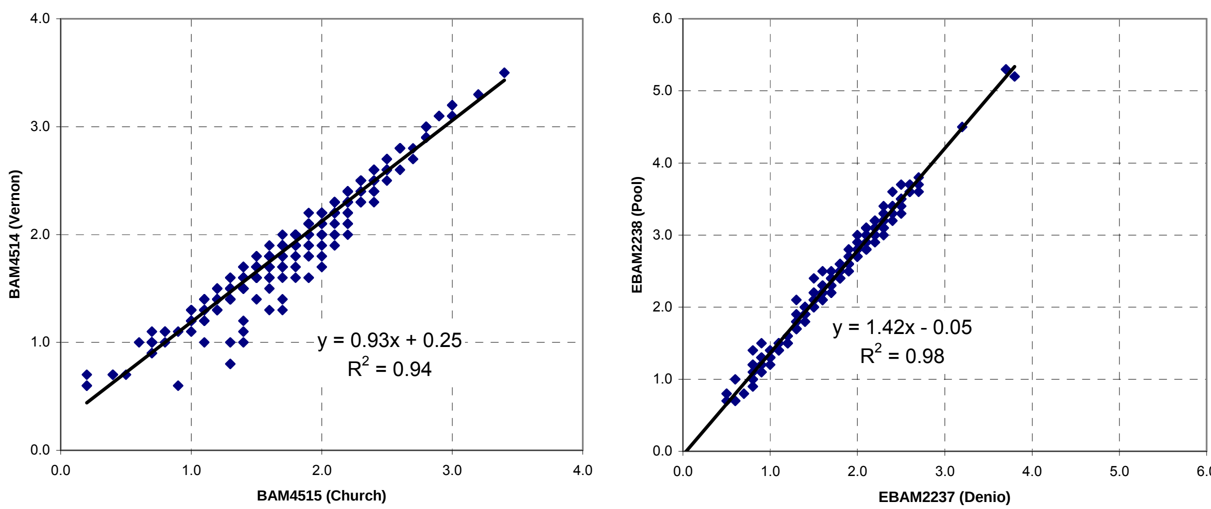


Figure 2-4. Comparison of hourly wind speed measurements during pre-study collocation.

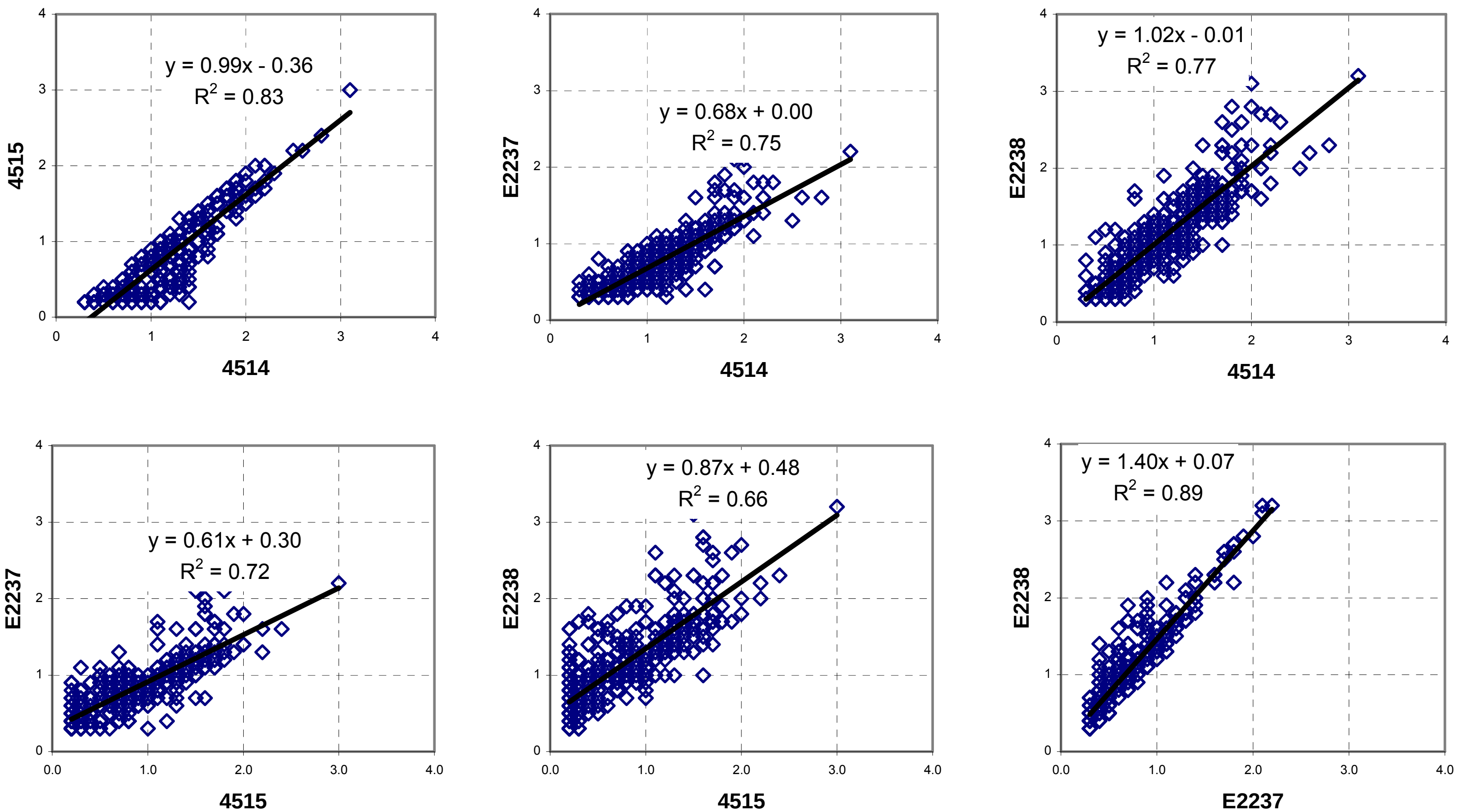
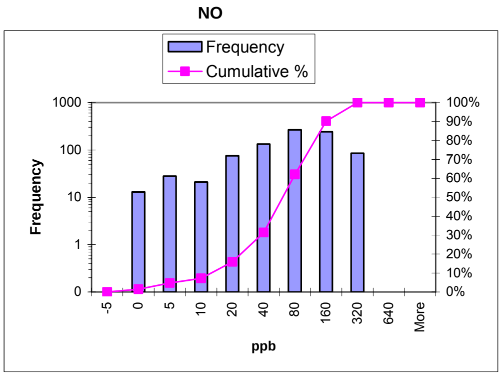


Figure 2-5. Comparison of hourly wind speed measurements during post-study collocation. E2237 and E2238 were used at Denio and Pool, respectively. 4514 and 4515 were used at Vernon and Church.

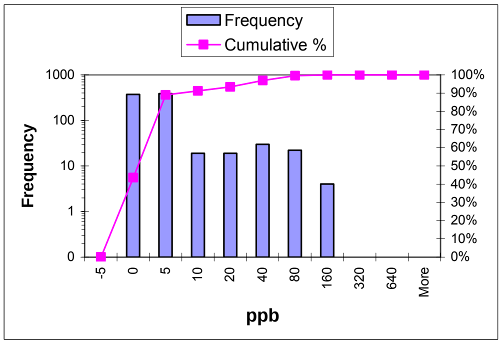
DENIO

Bin (< or =)	Frequency	Cumulative %
-5		0.00%
0	13	1.51%
5	28	4.76%
10	21	7.20%
20	75	15.91%
40	133	31.36%
80	264	62.02%
160	242	90.13%
320	85	100.00%
640		100.00%
More		100.00%



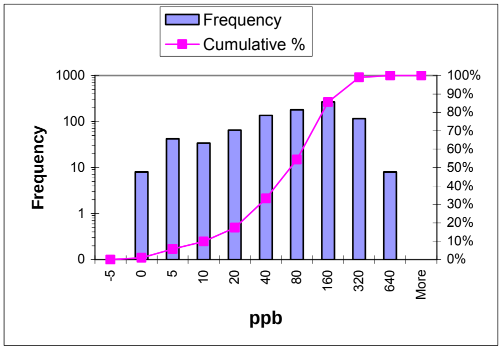
POOL

Bin (< or =)	Frequency	Cumulative %
-5		0.00%
0	372	43.56%
5	388	88.99%
10	19	91.22%
20	19	93.44%
40	30	96.96%
80	22	99.53%
160	4	100.00%
320		100.00%
640		100.00%
More		100.00%



CHURCH

Bin (< or =)	Frequency	Cumulative %
-5		0.00%
0	8	0.93%
5	42	5.83%
10	34	9.79%
20	65	17.37%
40	136	33.22%
80	181	54.31%
160	268	85.55%
320	116	99.07%
640	8	100.00%
More		100.00%



VERNON

Bin (< or =)	Frequency	Cumulative %
-5		0.00%
0	659	76.63%
5	96	87.79%
10	25	90.70%
20	27	93.84%
40	36	98.02%
80	16	99.88%
160	1	100.00%
320		100.00%
640		100.00%
More		100.00%

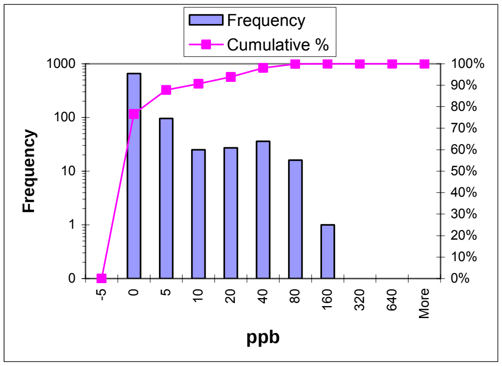
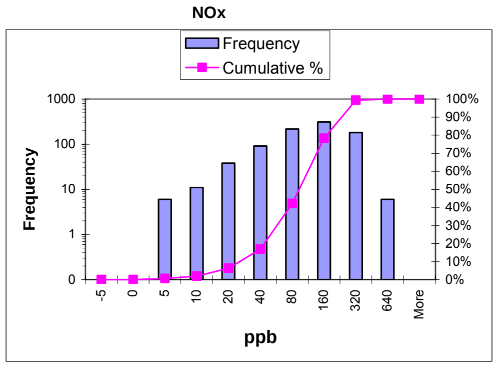


Figure 2-6. Histograms showing the frequency distribution of hourly averaged NO data at the four sites.

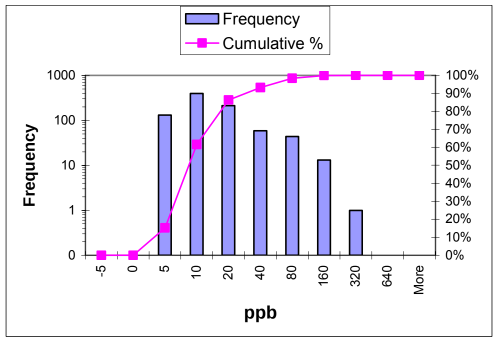
DENIO

Bin (< or =)	*Frequency*	*Cumulative %*
-5		0.00%
0		0.00%
5	6	0.70%
10	11	1.97%
20	38	6.39%
40	91	16.96%
80	217	42.16%
160	311	78.28%
320	181	99.30%
640	6	100.00%
More		100.00%



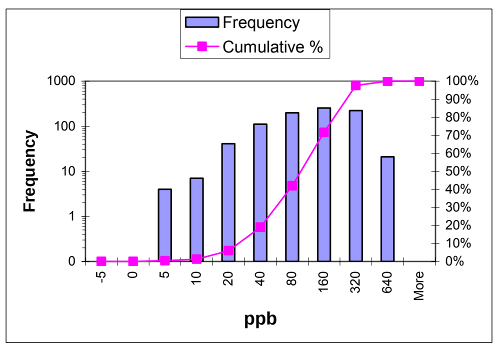
POOL

Bin (< or =)	*Frequency*	*Cumulative %*
-5		0.00%
0		0.00%
5	130	15.22%
10	396	61.59%
20	211	86.30%
40	59	93.21%
80	44	98.36%
160	13	99.88%
320	1	100.00%
640		100.00%
More		100.00%



CHURCH

Bin (< or =)	*Frequency*	*Cumulative %*
-5		0.00%
0		0.00%
5	4	0.47%
10	7	1.28%
20	41	6.06%
40	111	19.00%
80	197	41.96%
160	254	71.56%
320	223	97.55%
640	21	100.00%
More		100.00%



VERNON

Bin (< or =)	*Frequency*	*Cumulative %*
-5		0.00%
0		0.00%
5	229	26.63%
10	333	65.35%
20	165	84.53%
40	79	93.72%
80	46	99.07%
160	8	100.00%
320		100.00%
640		100.00%
More		100.00%

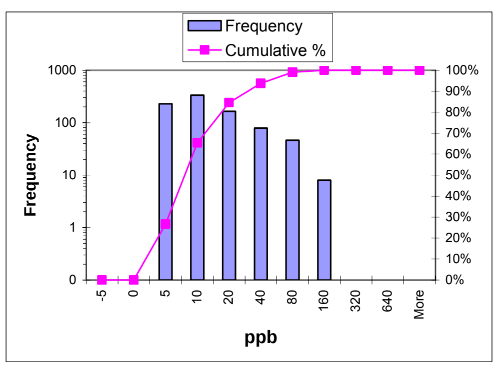
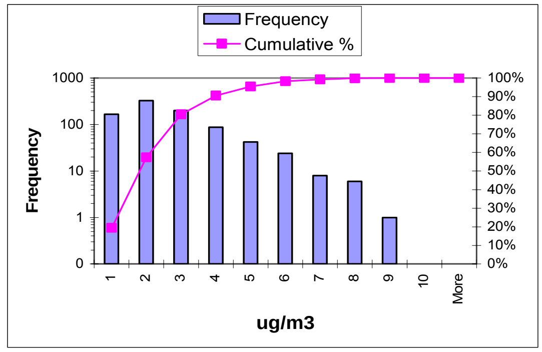


Figure 2-7. Histograms showing the frequency distribution of hourly averaged NOx data at the four sites.

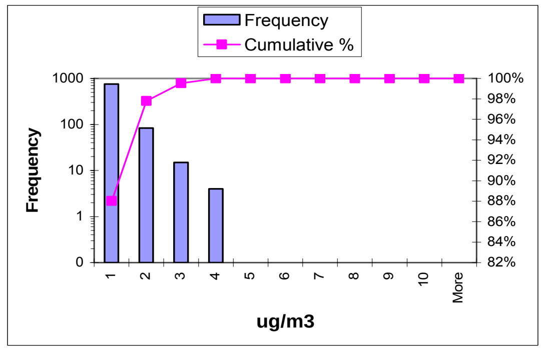
DENIO **BC**

Bin (< or =)	Frequency	Cumulative %
1	167	19.42%
2	326	57.33%
3	199	80.47%
4	87	90.58%
5	42	95.47%
6	24	98.26%
7	8	99.19%
8	6	99.88%
9	1	100.00%
10		100.00%
More		100.00%



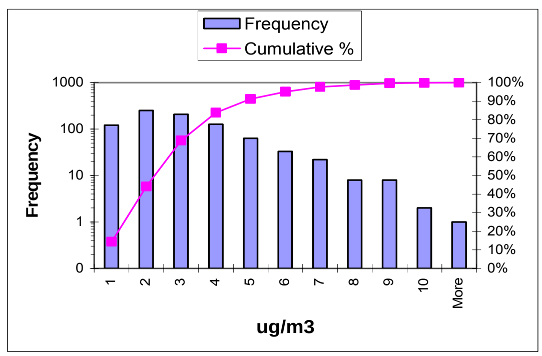
POOL

Bin (< or =)	Frequency	Cumulative %
1	757	88.02%
2	84	97.79%
3	15	99.53%
4	4	100.00%
5		100.00%
6		100.00%
7		100.00%
8		100.00%
9		100.00%
10		100.00%
More		100.00%



CHURCH

Bin (< or =)	Frequency	Cumulative %
1	121	14.30%
2	252	44.09%
3	209	68.79%
4	127	83.81%
5	63	91.25%
6	33	95.15%
7	22	97.75%
8	8	98.70%
9	8	99.65%
10	2	99.88%
More	1	100.00%



VERNON

Bin (< or =)	Frequency	Cumulative %
1	681	81.85%
2	115	95.67%
3	28	99.04%
4	5	99.64%
5	3	100.00%
6		100.00%
7		100.00%
8		100.00%
9		100.00%
10		100.00%
More		100.00%

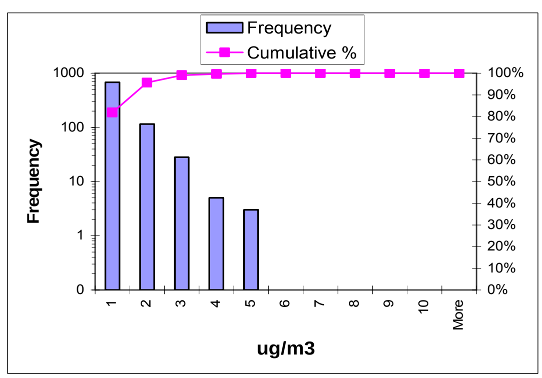
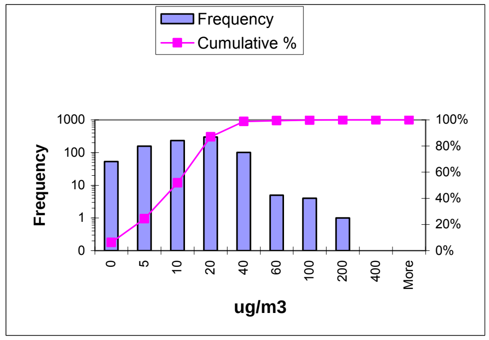


Figure 2-8. Histograms showing the frequency distribution of hourly averaged Aethalometer BC(1) data at the four sites.

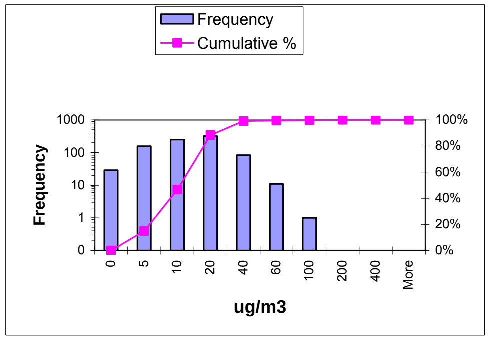
DENIO **PM**

Bin (< or =)	Frequency	Cumulative %
0	53	6.21%
5	156	24.50%
10	233	51.82%
20	300	86.99%
40	101	98.83%
60	5	99.41%
100	4	99.88%
200	1	100.00%
400		100.00%
More		100.00%



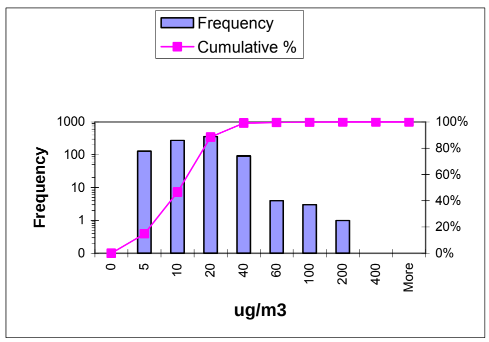
POOL

Bin (< or =)	Frequency	Cumulative %
0	29	0.00%
5	157	14.88%
10	251	46.63%
20	321	88.37%
40	83	99.07%
60	11	99.53%
100	1	99.88%
200		100.00%
400		100.00%
More		100.00%



CHURCH

Bin (< or =)	Frequency	Cumulative %
0		0.00%
5	128	14.88%
10	273	46.63%
20	359	88.37%
40	92	99.07%
60	4	99.53%
100	3	99.88%
200	1	100.00%
400		100.00%
More		100.00%



VERNON

Bin (< or =)	Frequency	Cumulative %
0		*0*
5	432	50.23%
10	305	85.70%
20	110	98.49%
40	5	99.07%
60	7	99.88%
100		99.88%
200	1	100.00%
400		100.00%
More		100.00%

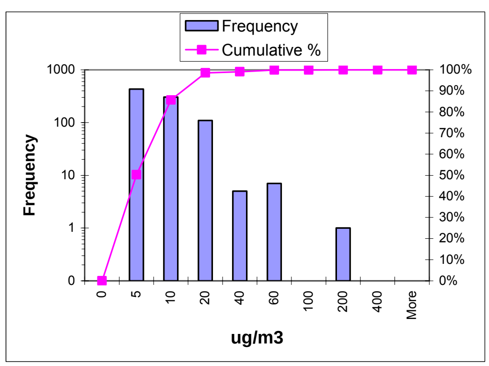


Figure 2-9. Histograms showing the frequency distribution of hourly averaged BAM $PM_{2.5}$ data at the four sites.

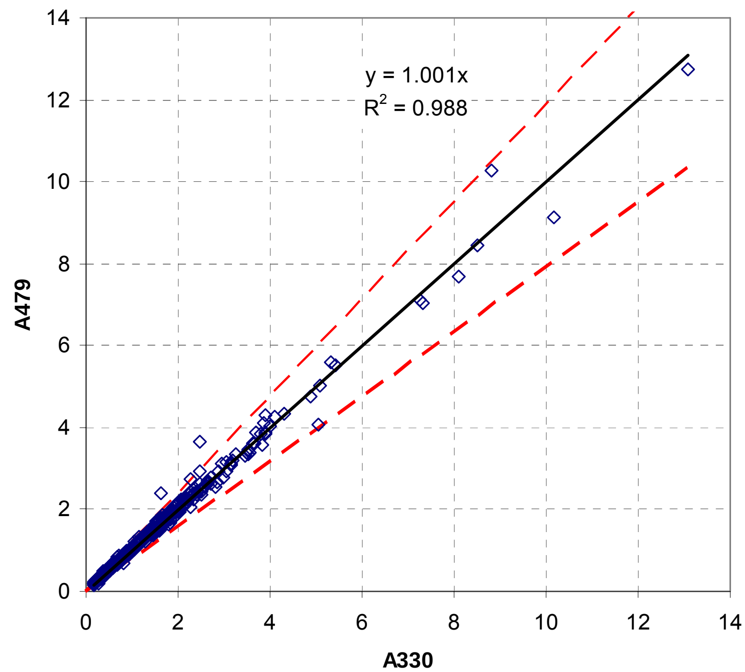


Figure 2-10. Correlation of hourly BC(1) (ug/m3) averaged data from collocated Aethalometers 05/16/07-05/30/07. Instrument A330 was later used at the Denio site, and A479 at Pool.

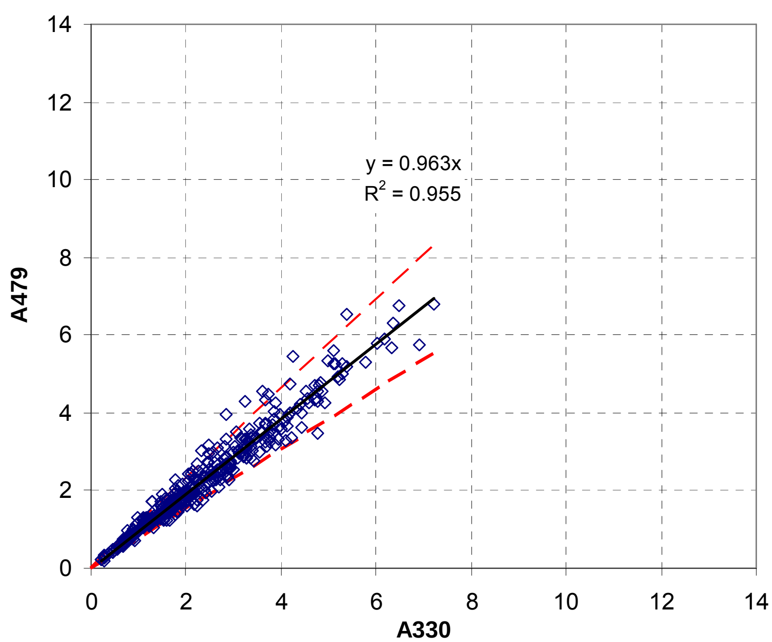
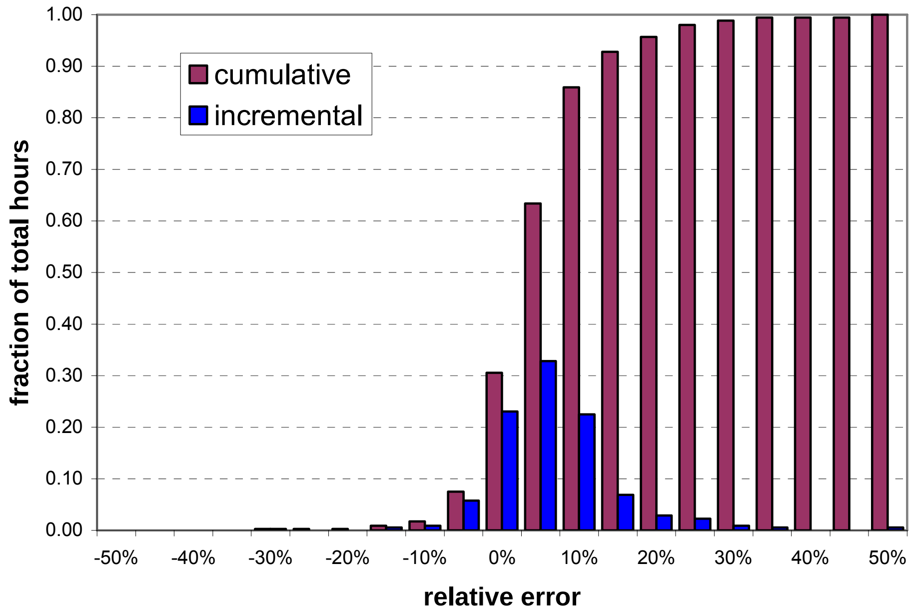


Figure 2-11. Correlation of hourly averaged BC(1) (ug/m3) data from collocated Aethalometers 10/29/07-11/16/07.

05/16/07-05/30/07

relative error	cumulative fraction
<5%	0.56
<10%	0.84
<15%	0.92
<20%	**0.95**
<25%	0.98
<30%	0.99
<35%	0.99
<40%	0.99
<45%	0.99
<50%	1.00
>50%	0.00



10/29/07-11/16/07

relative error	cumulative fraction
<0%	0.00
<5%	0.43
<10%	0.71
<15%	0.87
<20%	**0.96**
<25%	0.99
<30%	1.02
<35%	1.03
<40%	1.03
<45%	1.03
>45%	1.03

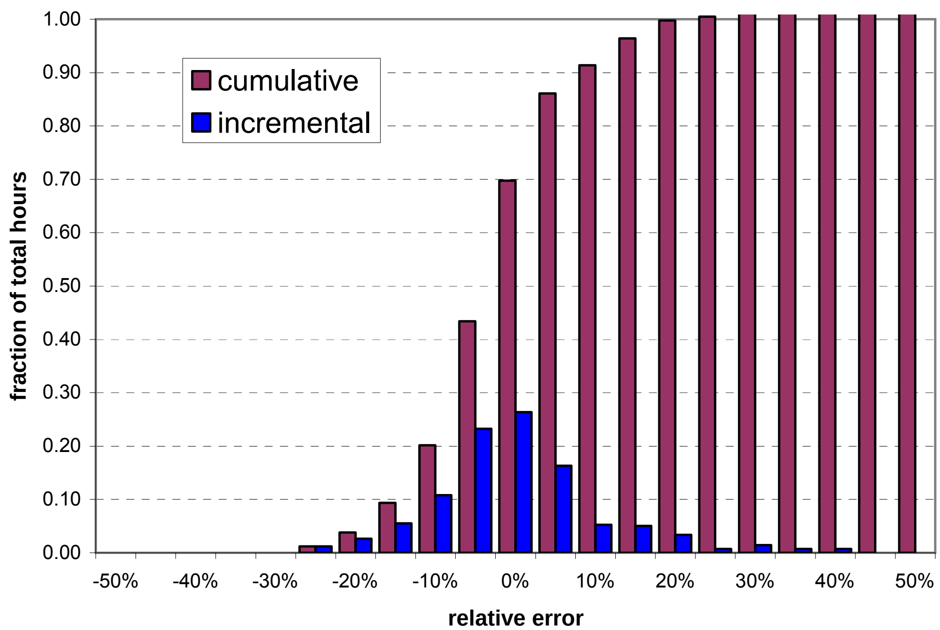


Figure 2-12. Relative difference between collocated Aethalometers used at Denio and Pool sites. Data are from hourly averages of channel 1 BC. Table gives distribution of absolute values of relative differences, with approximate 95th percentile in bold.

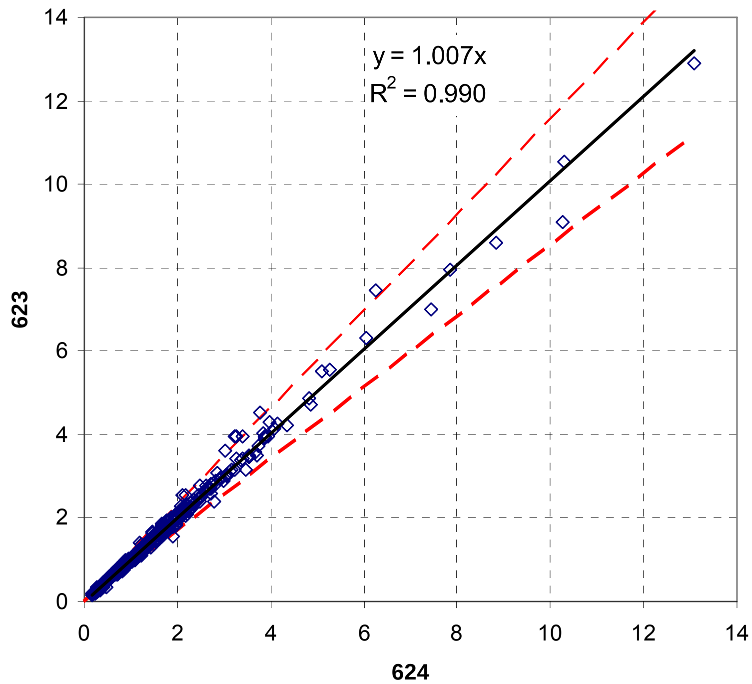


Figure 2-13. Correlation of hourly averaged BC data (ug/m3) from collocated Aethalometers 05/16/07-05/30/07. 624 was later used at Church and 623 at Vernon.

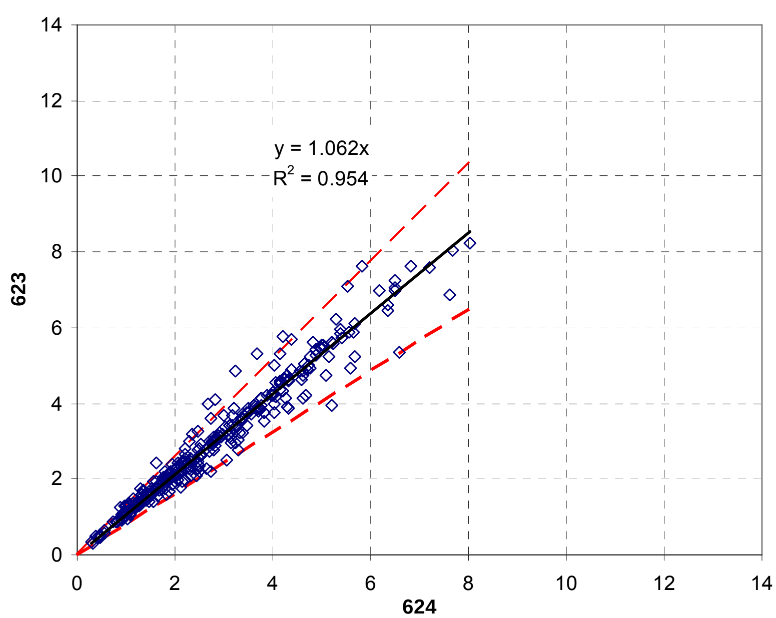
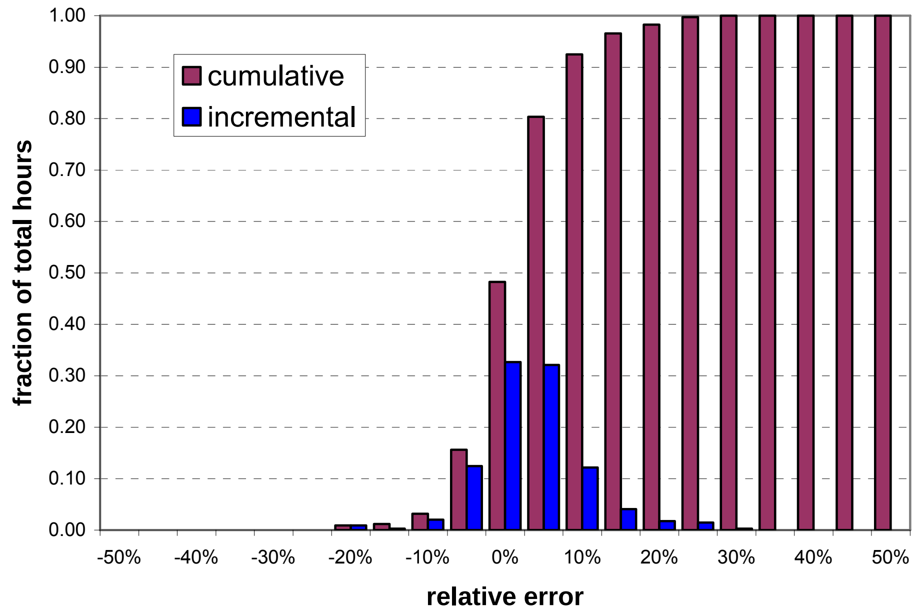


Figure 2-14. Correlation of hourly averaged BC data (ug/m3) data from collocated Aethalometers 10/31/07-11/16/07.

05/16/07-05/30/07

relative error	cumulative fraction
<5%	0.65
<10%	0.89
<15%	**0.95**
<20%	0.97
<25%	1.00
<30%	1.00
<35%	1.00
<40%	1.00
<45%	1.00
<50%	1.00
>50%	0.00



10/31/07-11/16/07

relative error	cumulative fraction
<0%	0.00
<5%	0.26
<10%	0.62
<15%	0.82
<20%	0.87
<25%	**0.92**
<30%	0.95
<35%	0.97
<40%	0.98
<45%	0.98
>45%	0.99

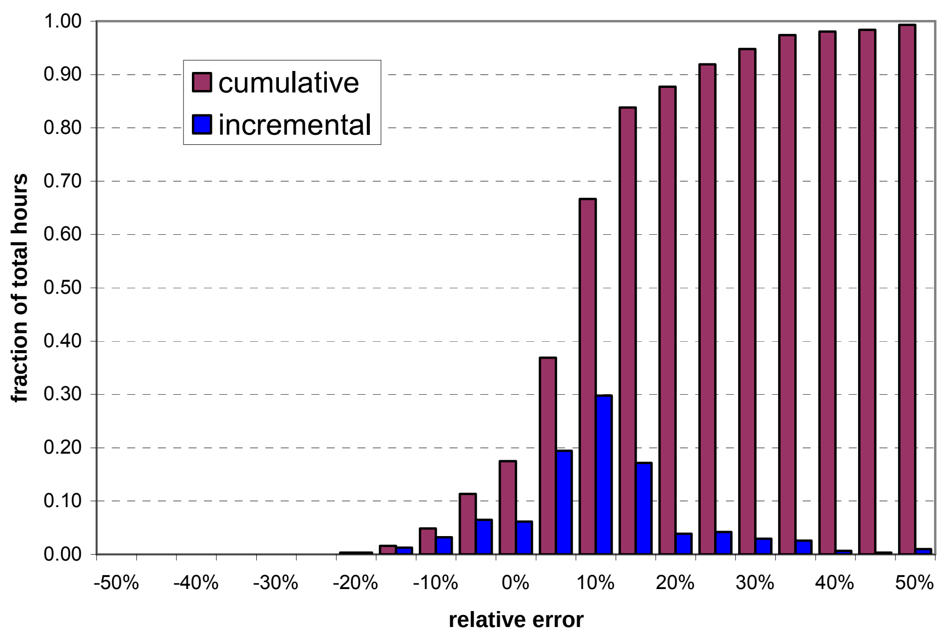


Figure 2-15. Relative difference between collocated Aethalometers used at Church and Vernon sites. Data are from hourly averages of channel 1 BC. Table gives distribution of absolute values of relative differences, with approximate 95th percentile in bold..

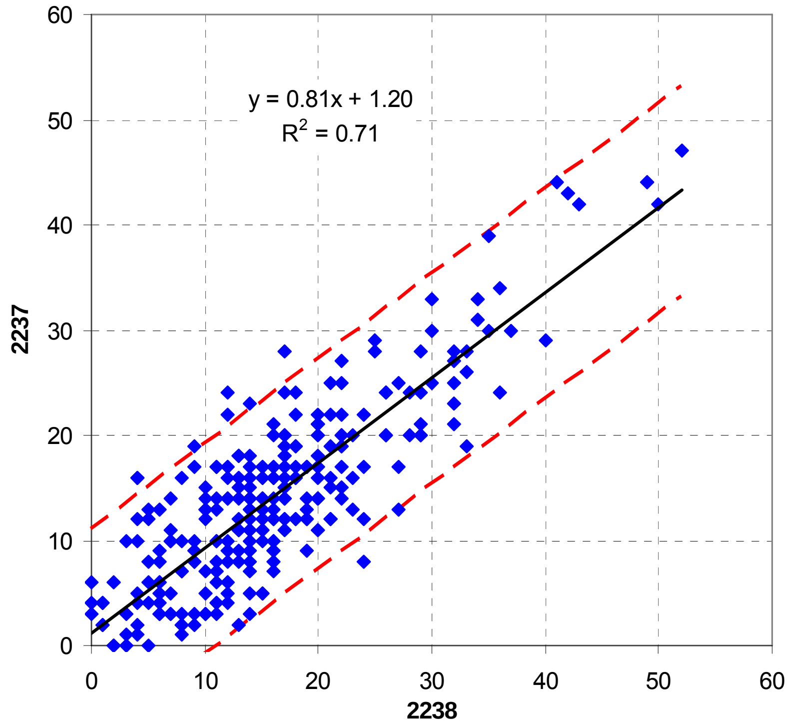


Figure 2-16. Correlation of hourly $PM_{2.5}$ (ug/m3) averaged data from collocated EBAMs 05/29/07-06/10/07. Instrument E2238 was later used at the Denio site, and E2237 at Pool.

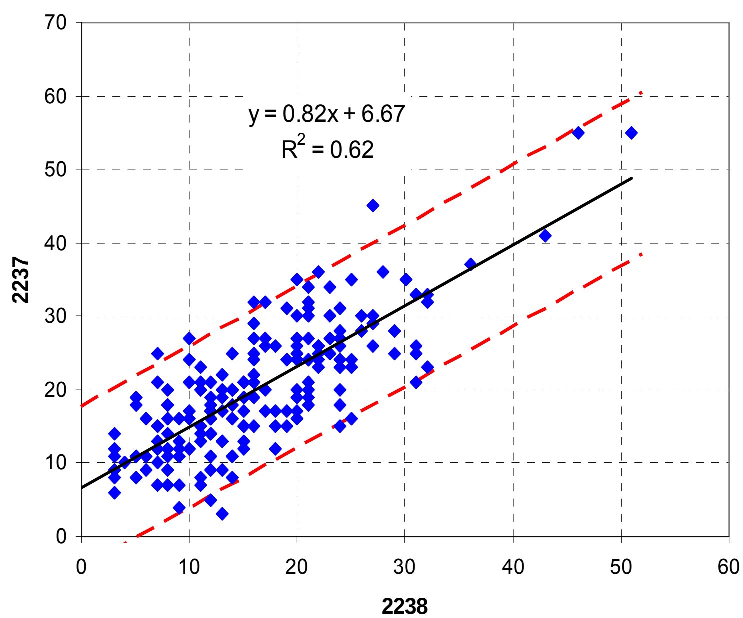
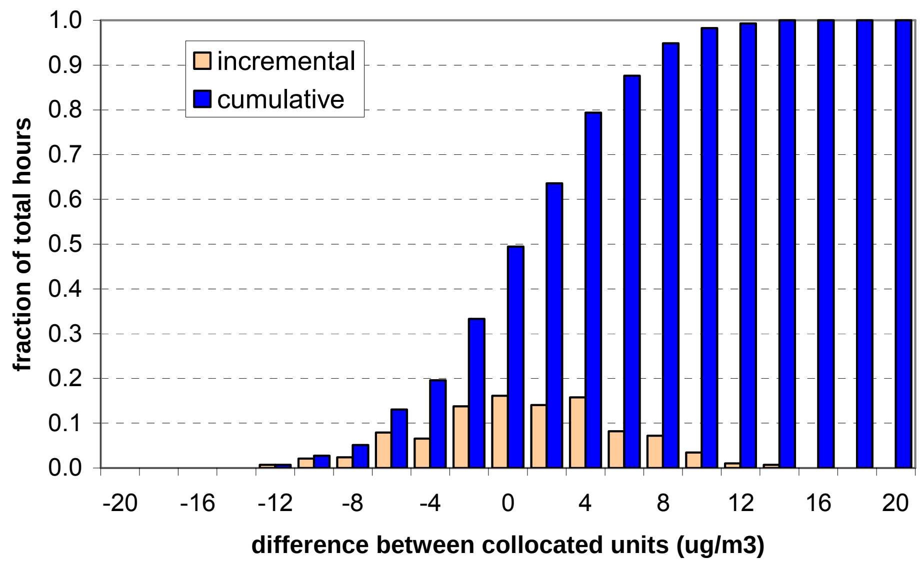


Figure 2-17. Correlation of hourly averaged $PM_{2.5}$ (ug/m3) data from collocated EBAMs 10/22/07-10/30/07.

05/29/07-06/10/07

absolute error (ug/m3)	cumulative fraction
<2	0.30
<4	0.60
<6	0.75
<8	0.90
<10	**0.96**
<12	0.99
<14	1.00
<16	1.00
<18	1.00
<20	1.00
>20	1.00



10/22/07-10/30/07

absolute error (ug/m3)	cumulative fraction
<2	0.35
<4	0.54
<6	0.71
<8	0.85
<10	**0.91**
<12	**0.97**
<14	0.99
<16	0.99
<18	1.00
<20	1.00
>20	1.00

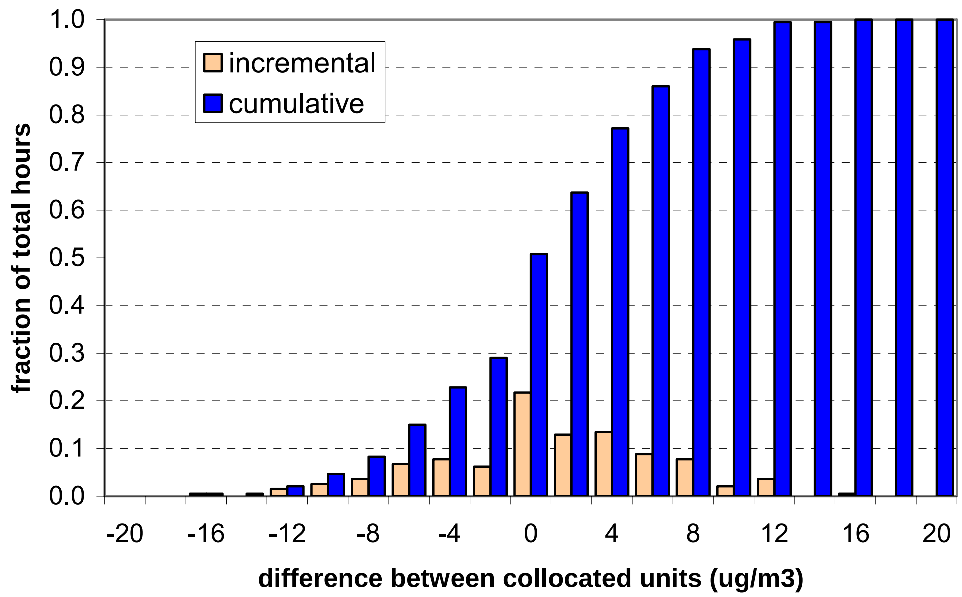


Figure 2-18. Difference between collocated EBAMS used at Denio and Pool sites after correcting for bias. Data represented are hourly averages. Table gives distribution of absolute values of differences, with approximate 95th percentile in bold.

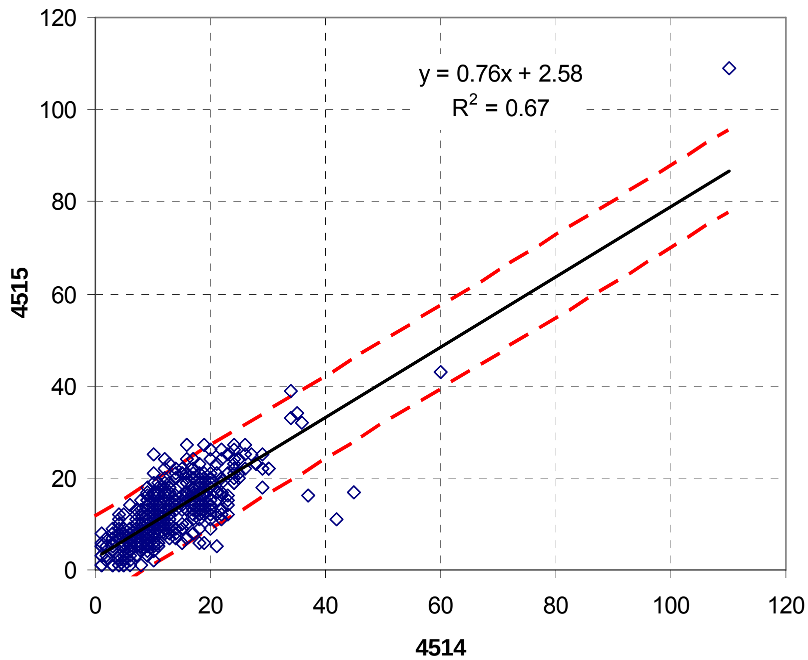


Figure 2-19. Correlation of hourly averaged data from collocated BAMs 05/10/07-05/31/07. 4514 was later used at Church and 4515 at Vernon.

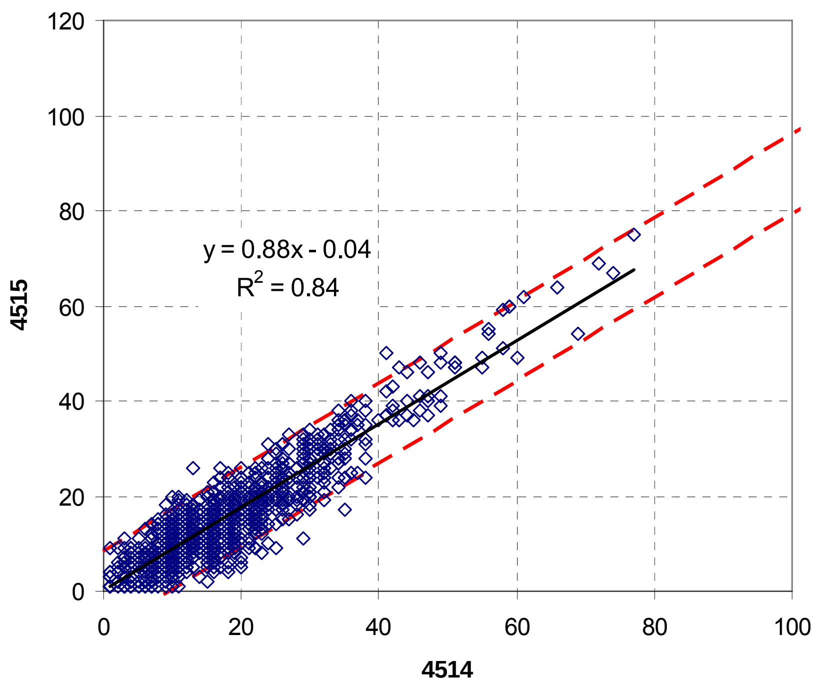
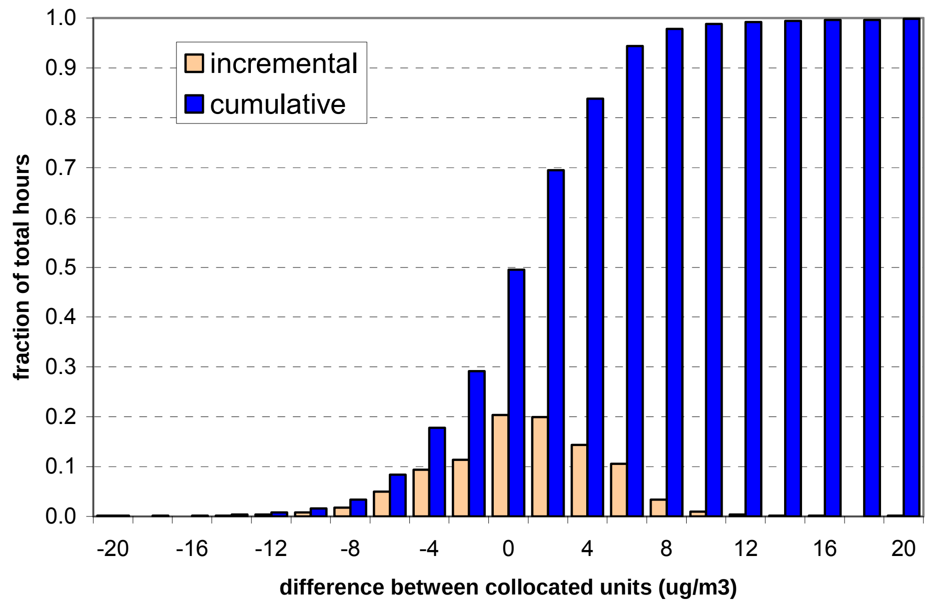


Figure 2-20. Correlation of hourly averaged data from collocated BAMs 10/22/07-11/11/07.

05/10/07-05/31/07

absolute error (ug/m3)	cumulative fraction
<2	0.40
<4	0.66
<6	0.86
<8	**0.94**
<10	**0.97**
<12	0.98
<14	0.99
<16	0.99
<18	0.99
<20	1.00
>20	1.00



10/22/07-11/11/07

absolute error (ug/m3)	cumulative fraction
<2	0.37
<4	0.64
<6	0.82
<8	**0.94**
<10	**0.98**
<12	0.99
<14	1.00
<16	1.00
<18	1.00
<20	1.00
>20	1.00

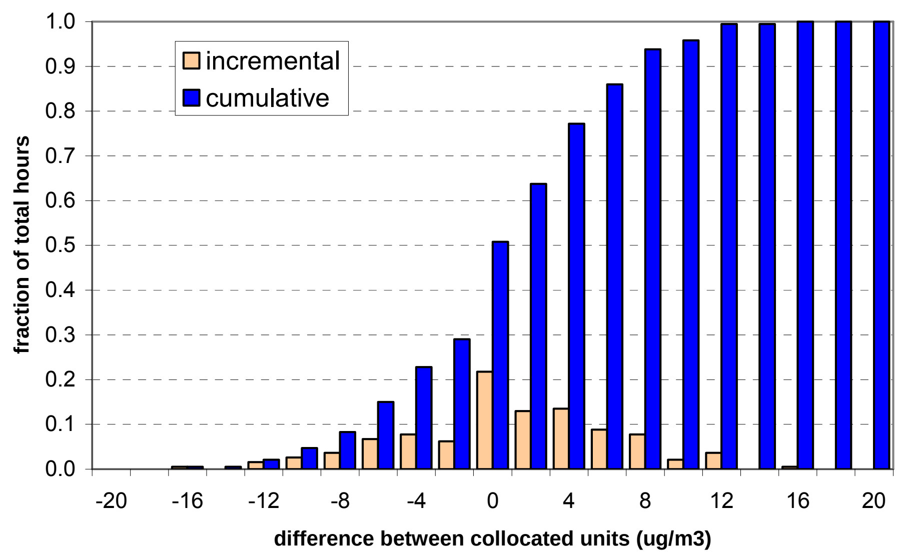


Figure 2-21. Difference between collocated BAMS used at Church and Vernon sites after correcting for bias. Data represented are hourly averages. Table gives distribution of absolute values of differences, with approximate 95th percentile in bold.

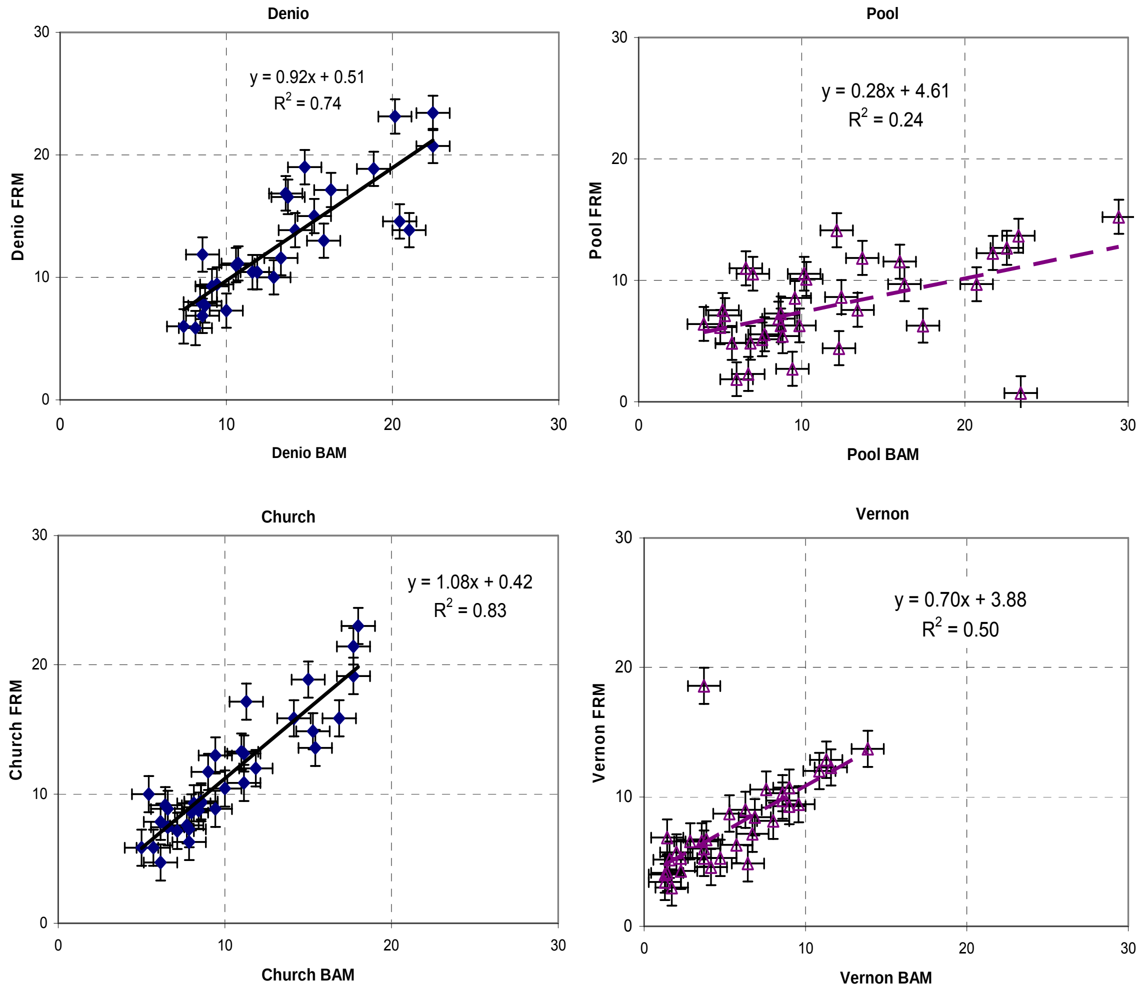


Figure 2-22. Correlation plots comparing average BAM $PM_{2.5}$ to gravimetric mass from FRM filters for 7hr samples at 4 sites. Note: Pool BAM was operating without inlet heater during most of the summer.

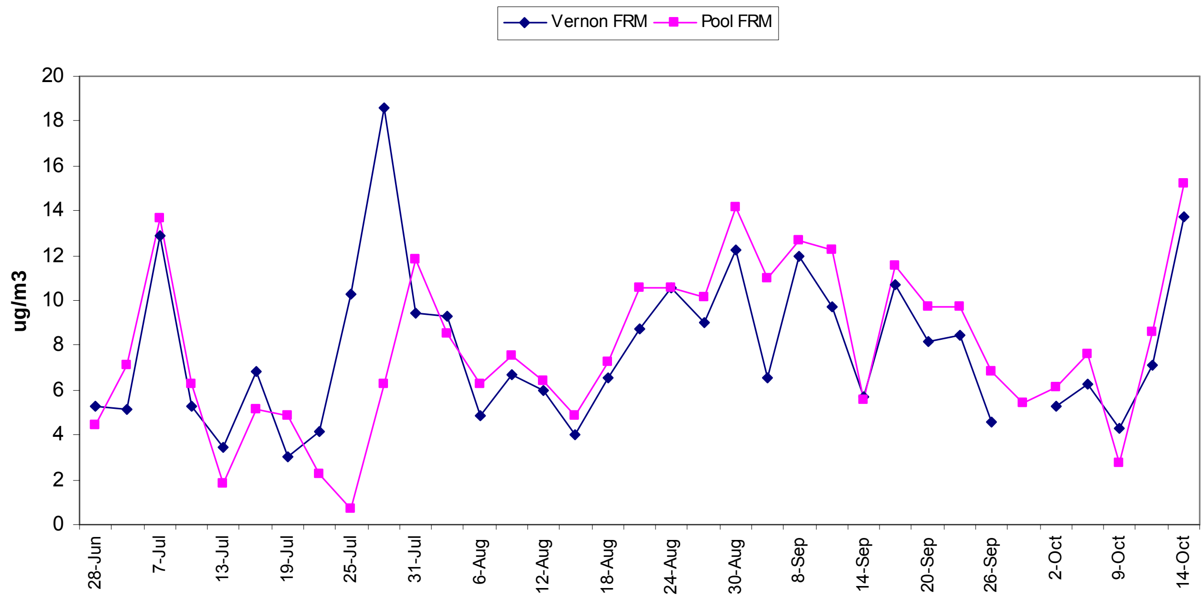


Figure 2-23. Correlation plot comparing FRM filter gravimetric mass concentrations at the two upwind sites during the summer.

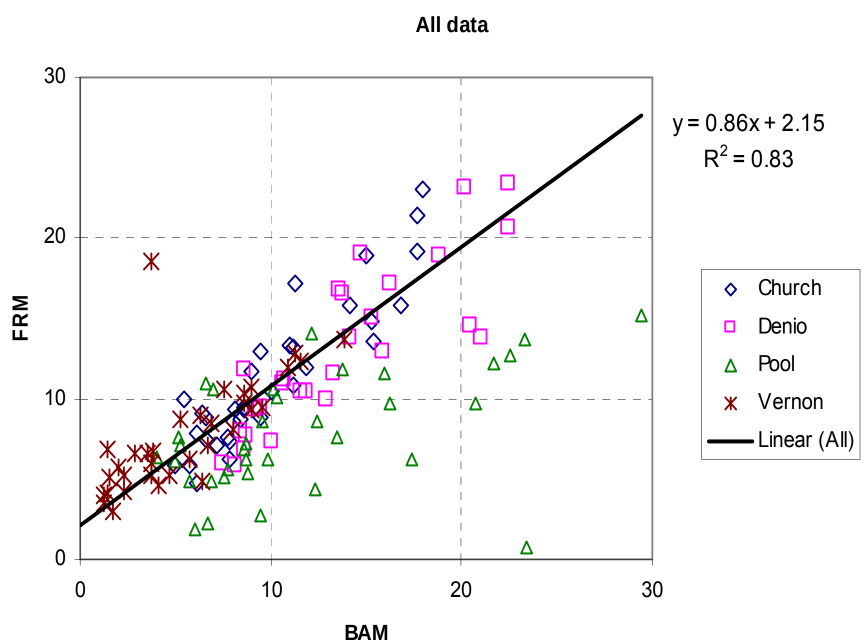


Figure 2-24. Correlation plots comparing average BAM $PM_{2.5}$ to gravimetric mass from FRM filters for 7hr samples at all sites. The regression line is plotted for all data except Pool and 1 outlier (Vernon, July 28).

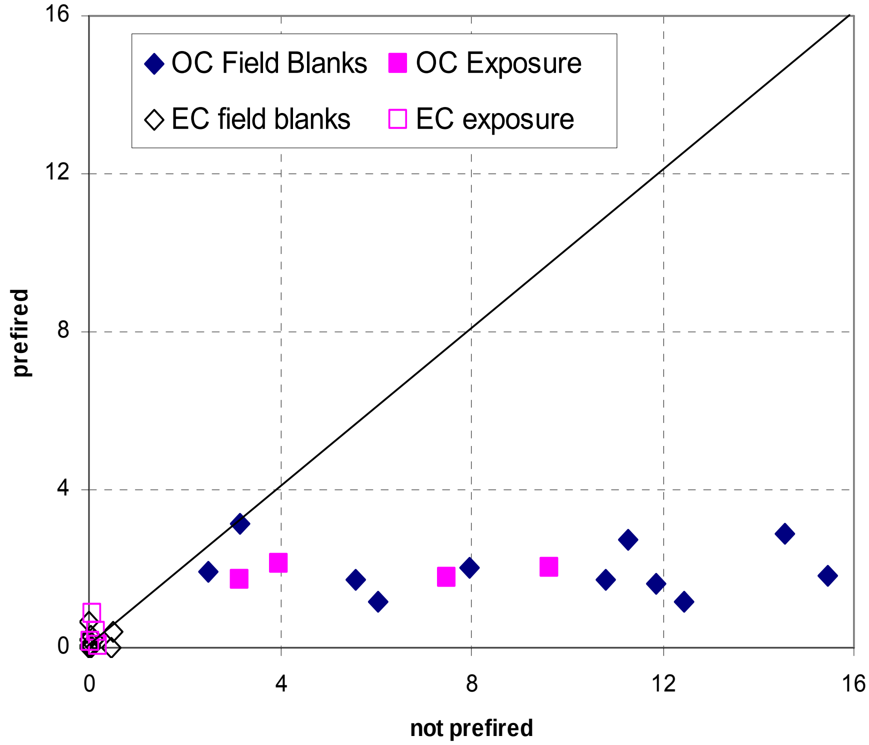
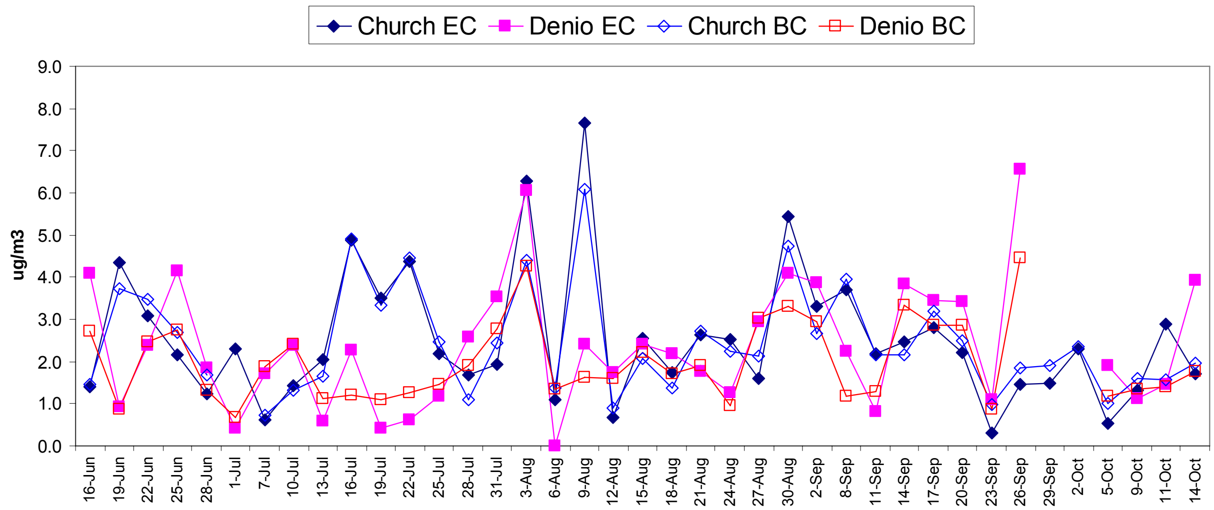


Figure 2-25. Comparison of prefired to unfired blank results. Units are ug/cm^2 carbon.



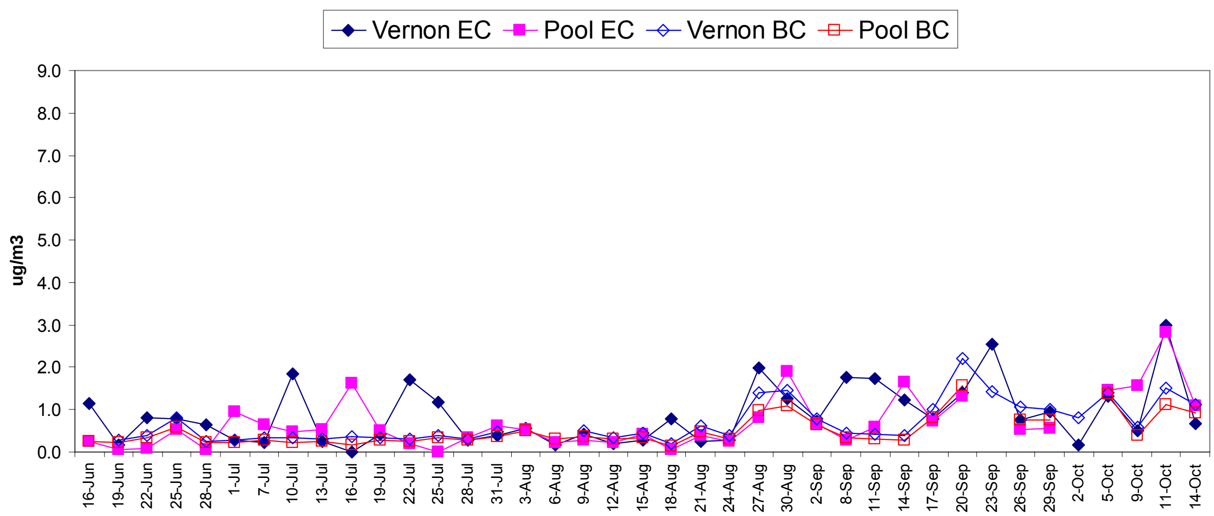


Figure 2-26. Time series plots of 7hr EC and BC at downwind (upper chart) and upwind (lower chart) sites.

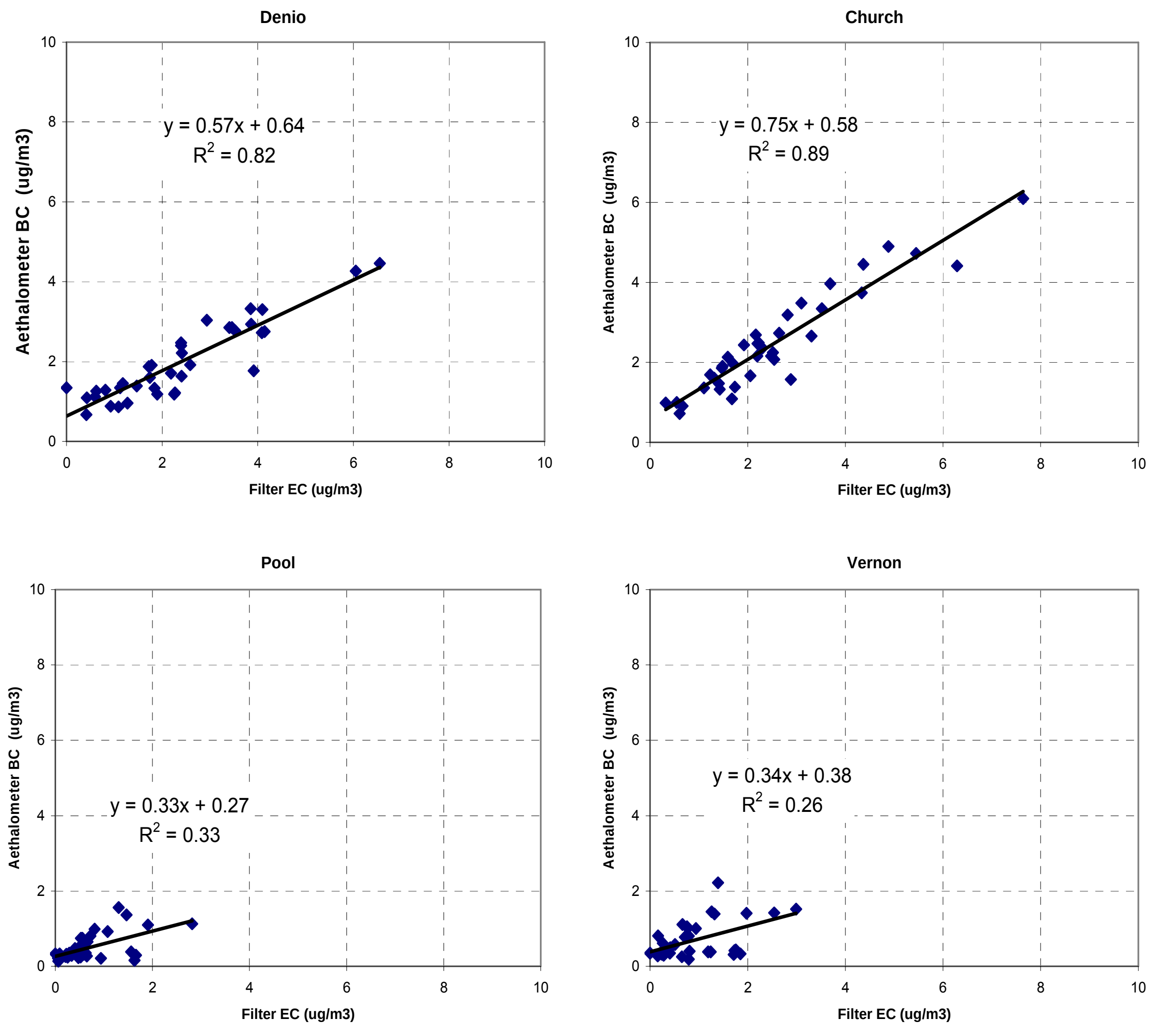


Figure 2-27. Correlation plots comparing average aethalometer BC (channel 1) to elemental carbon from FRM filters for 7hr samples at the 4 sites.

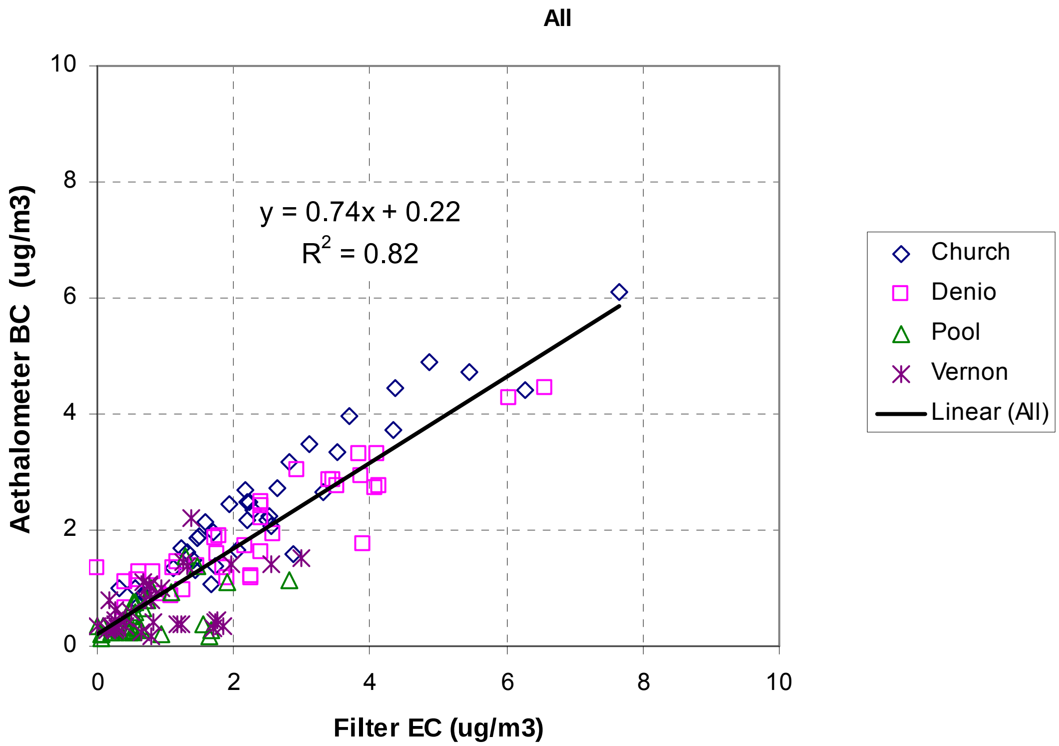


Figure 2-28. Correlation plots comparing average aethalometer BC(1) to elemental carbon from FRM filters for 7hr samples.

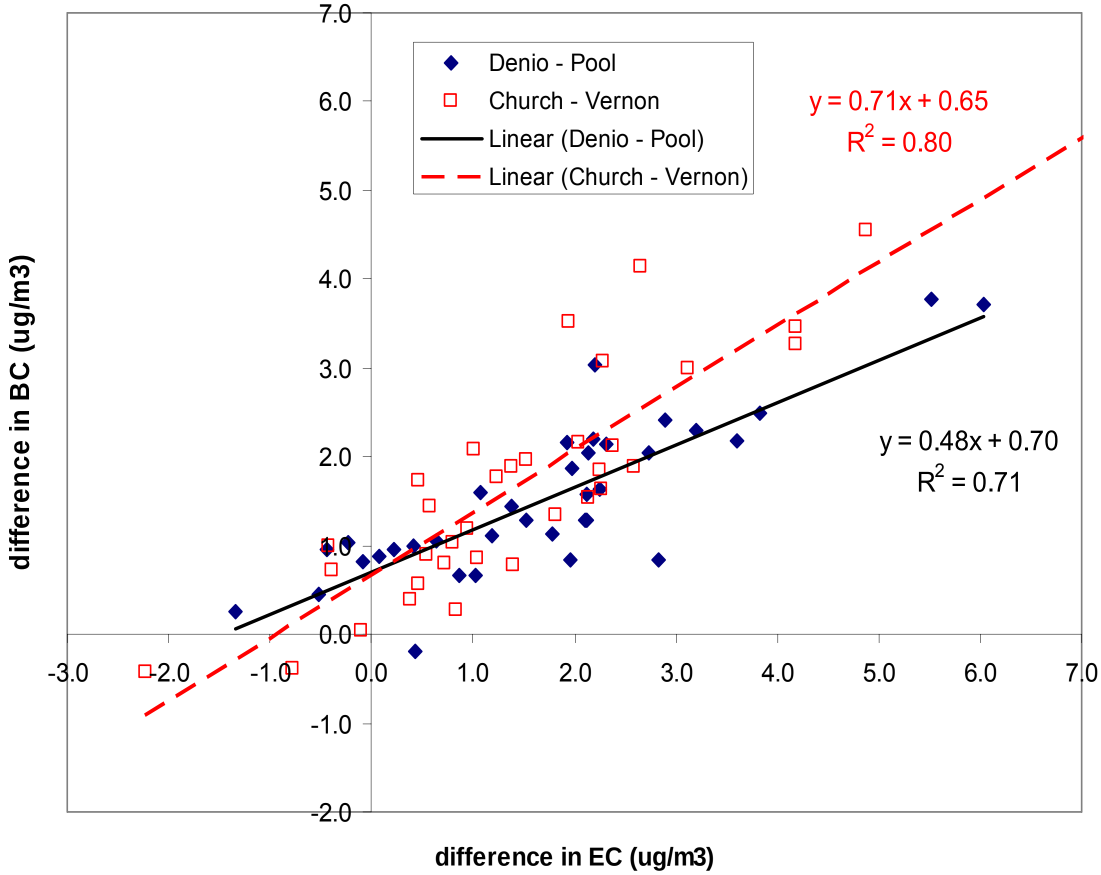


Figure 2-29. Correlation plot comparing difference in elemental carbon (EC) concentration from FRM filters between downwind and upwind sites to to difference in average Aethalometer black carbon (BC) for 7hr samples at 2 site pairs.

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, NOx, 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 $PM_{2.5}$, BC, NO, and NO_x concentrations for each site pair. For $PM_{2.5}$, the data from the Pool BAM was suspect so we substituted data from Vernon, adjusted for a small bias (12%) based on comparison of the FRM filter data gravimetric masses from the two upwind sites shown in Figure 3-1. Uncertainties of differences were calculated as the square root of the sum of the squares of the measurement error, using $PM_{2.5}$ 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, $PM_{2.5}$, NO and NOx concentrations collected between 2200 to 0500 PST at the four RRAMP sites. Mean downwind minus upwind differences in $PM_{2.5}$, BC, NO and NOx concentrations were calculated for each site pair for the entire study period excluding the time period of the Moonlight 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 2–5 were included in the calculation of propagated analytical errors of the seasonal mean $PM_{2.5}$ values in Table 3-1.

Figure 3-2 compares the mean BC, $PM_{2.5}$, NO and NOx concentrations at the four RRAMP monitoring sites and shows the downwind - upwind differences for the two pairs of sites (Denio-Pool and Church-Vernon). Differences between the two downwind and between the two upwind sites are also shown for comparison. Error bars are the standard errors of the means. The figure show that the pollutant concentrations at the downwind sites are largest in proportion to those at the upwind sites for NO (which is near zero upwind) and are progressively smaller for

NO_x, BC and $PM_{2.5}$. The decrease in downwind/upwind ratio from NO to $PM_{2.5}$ is consistent with larger contributions of urban background aerosol to the measured $PM_{2.5}$ and BC concentrations. Average concentrations of all pollutants were consistent between the two upwind sites. However, for the downwind site they were significantly higher at the Church than at Denio resulting in larger downwind – upwind differences for the Church – Vernon site pair.

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 $BC/PM_{2.5}$ 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.

Table 3–3 lists the means and 2-sigma standard errors for field-blank corrected TOR analysis results of the 7-hour overnight FRM filter samples. These are presented to give some indication of variation in aerosol composition between sites. The average concentrations of OC and EC are significantly higher at the downwind sites and the EC/TC ratio is also higher downwind, indicating greater relative contribution from diesel sources. $TC/PM_{2.5}$ ratios are also somewhat higher at the downwind sites, suggesting that secondary and crustal aerosols are in smaller proportion there.

3.2 Estimation of Diesel PM

As explained in Section 2.7.2, the amount of diesel PM impacting the downwind area can be estimated from the difference in measured BC concentrations between the downwind and upwind sites using observed relationships between $PM_{2.5}$ and EC in diesel exhaust and between BC and EC in this study. Unfortunately, we do not currently have applicable data on the $EC/PM_{2.5}$ ratio in diesel locomotive exhaust to use in this process. Data collected during the ALECS hood testing at the Roseville Railyards have not been reviewed to determine if they can be applied, and we have not located any other published emissions data from similar testing. Emissions from in-use diesel-electric switching locomotives were collected and published by CE-CERT recently (Sawant 2007), however they used the NIOSH protocol for the TOR analysis so the EC measurements are not directly comparable to those made with the IMPROVE protocol at Roseville since TOR analysis of diesel exhaust filter samples using several different analysis protocols has demonstrated that measured EC can be substantially lower with the NIOSH method.

The best available data set for estimating DPM is from the DOE/NREL Gas Diesel PM Split project (Fujita et al., 2007), in which emissions from 31 heavy-duty diesel trucks and 2 transit buses were measured during dynamometer load testing using a variety of driving cycles. In this study DRI collected the samples and did the TOR analysis using both the IMPROVE and NIOSH protocols so the compatibility of the measurement methods to the RRAMP study is well understood. Measured $PM_{2.5}/EC_{NIOSH}$ ratios for the diesel trucks and buses ranged from 1.1 to 12. These ratios are similar to those from the CE-CERT locomotive tests (1.4 to 8.0), supporting the use of the Gas Diesel PM Split ratios calculated from the IMPROVE TOR method to estimate DPM. The ratios of $PM_{2.5}$ to IMPROVE EC ranged from 0.9 to 3.3 for the various truck models and operating conditions, so we will choose a ratio of 2 ± 1 as the characteristic ratio of DPM to EC for diesel exhaust (i.e.; DPM = 2*EC). For comparison, the average ambient $PM_{2.5}$/EC ratio measured at the downwind sites was 6.2.

For the 2007 season, the DPM relationship can be extended to the average increase in black carbon (ΔBC) measured at the downwind sites using the correlation equations shown at the bottom of Table 2–5. However, for 2005 and 2006, when the quartz filters were not pre-fired and sufficient field blanks were not collected to characterize the large passive sampling artifact, it may not be accurate to rely on the observed relationships between ΔEC and ΔBC. For the prior years we will use the ΔEC to ΔBC correlation from the combined 2007 summer data from Table 2–5: ΔBC = 0.60[ΔEC] + 0.66. Combined with the characteristic $PM_{2.5}$/EC ratio discussed above, we estimated DPM for 2005 and 2006 as:

$$DPM = 2*[\Delta BC-0.66]/0.60$$

For 2007 we use site-specific relationships:

$$\text{Denio DPM} = 2*[\Delta BC-0.70]/0.48 \qquad \text{Church DPM} = 2*[\Delta BC-0.65]/0.71$$

3.3 Three-year trends

After reprocessing the data collected in 2005* using the same methods as for 2006 and 2007, we compare the resulting average values and downwind-upwind differences to look for indication of trends in the pollutant concentrations impacting the downwind area that may result from mitigation efforts in the railyard. Data from the Church and Vernon sites was only collected for about 1 month at the end of the summer in 2005, so the wind data from the Denio site was used to determine hours meeting the wind speed and direction criteria for that year. Table 3–4 and Table 3–5 show the mean overnight concentrations of each pollutant measured for each of the the three years as well as the mean downwind-upwind concentrations by year and relevant statistics. Figure 3-3 shows the mean values plotted for each site to make visualization easier. Table 3–6 shows the estimated diesel PM impacting the downwind sites, based on the calculation of DPM described above.

NO, NOx, and $PM_{2.5}$ show a decrease each year at Denio (Figure 3-3). Since there is no corresponding decrease in NO and NOx at Pool, it appears that reductions in the impact of the railyard concentrations at Denio are responsible for the decrease in NO. No decreasing trend in NO and NOx is evident for Church and Vernon, particularly if the limited amount of 2005 data is considered. Although $PM_{2.5}$ shows a consistent decrease each year, there is also a decrease at the upwind sites for 2007 so no clear trend in the impact of the railyard on $PM_{2.5}$ at downwind sites is indicated. No consistent temporal pattern is evident for BC at any of the sites. This is somewhat surprising since excess BC is expected to track excess NO at the downwind sites because they presumably originate from the same source. The lack of a decrease similar to that for NO may be an indication of variations in the composition of emissions from the railyard activities. Table 3–6 contains estimated mean overnight concentration of diesel PM from railyard

* The original analysis of the 2005 data focused on analysis of instrumental precision and evaluating statistical methods for calculating downwind – upwind differences. After discussing various options presented, the TAC and DRI agreed upon a standard protocol for analysis of data from all years.

activities impacting the two downwind monitoring sites based on the calculation described in section 3.2. Results are very similar for the two downwind sites for 2005 and 2007, and higher at Denio for 2006 however the difference is within the uncertainty. Given the large uncertainty in the estimation of DPM, it is not possible to discern any temporal trend in impact on the downwind area as shown in Figure 3-4.

Table 3–1. Means, standard deviations, and standard errors of the means for 7-hour (2200 to 0500 PST) BC, $PM_{2.5}$, NO and NOx concentrations at the four RRAMP sites during the 2007 summer monitoring season. 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	2.43	0.19	3.42	0.27	10.7	3.3	11.9	3.3	76	1	99	0	108	9	133	8
stdev	1.20	0.30	1.65	0.39	7.5	5.3	5.8	5.3	43	1	53	1	54	3	64	4
n observations	102	102	100	99	101	102	102	102	102	102	102	102	102	102	102	102
sterr_mean	0.12	0.03	0.17	0.04	0.7	0.5	0.6	0.5	4	0	5	0	5	0	6	0
Downwind-Upwind																
avg delta	2.24		3.20		7.5		8.6		75		99		98		124	
sterr_delta	0.11		0.16		0.4		0.5		4		5		5		6	
T-test	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00	
propagated error	0.96		0.99		1.0		1.0		1.0		1.0		1.0		0.8	
Downwind and Upwind pairs	Denio - Church		Pool - Vernon		Denio - Church		Pool - Vernon		Denio - Church		Pool - Vernon		Denio - Church		Pool - Vernon	
avg delta	-0.98		-0.07		-1.1		0.0		-23		1		-25		1	
ster_delta	0.20		0.02		0.7		0.0		6		0.1		8		0.1	
propagated error	1.19		1.20		1.2		1.2		1.2		1.2		1.2		1.1	

* The night of July 4 and the Moonlight fire (9/5) have been 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/$PM_{2.5}$, and BC(1)/BC(2) ratios at the four RRAMP sites during the 2007 summer monitoring season. 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/$PM_{2.5}$	Pool* BC/$PM_{2.5}$	Church BC/$PM_{2.5}$	Vernon BC/$PM_{2.5}$	Denio BC1/BC2	Pool BC1/BC2	Church BC1/BC2	Vernon BC1/BC2
avg	0.65	0.22	0.66	0.20	0.17	0.07	0.22	0.09	1.08	0.95	1.22	1.07
min	0.00	-0.25	0.05	0.00	0.00	0.00	0.02	0.00	0.46	0.49	0.54	0.51
max	0.92	0.86	0.94	0.86	0.88	0.39	0.76	0.39	1.38	1.31	1.70	1.39
stdev	0.13	0.24	0.16	0.24	0.12	0.06	0.12	0.08	0.11	0.17	0.17	0.14
2*stderr	0.01	0.03	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.02

** BAM $PM_{2.5}$ data from Vernon were used due to operational problems at Pool*

Table 3–3. Means and 2-sigma standard errors for field blank corrected TOR analysis results for the 7-hour overnight FRM filter samples collected during the 2007 summer monitoring season.

	OC (μg/m^3)	EC (μg/m^3)	EC/TC	TC/$PM_{2.5}$
DENIO	6.7 ± 1.0	2.4 ± 0.5	0.28 ± 0.13	0.56 ± 0.68
POOL	3.8 ± 0.5	0.7 ± 0.2	0.15 ± 0.16	0.45 ± 0.26
CHURCH	7.1 ± 0.9	2.5 ± 0.5	0.25 ± 0.13	0.79 ± 0.44
VERNON	3.9 ± 0.5	0.9 ± 0.2	0.17 ± 0.21	0.42 ± 0.31

Table 3–4. Average overnight summer BC and $PM_{2.5}$ concentrations by year 2005 - 2007.

BC (ug/m3)	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007
2200-0500 averages		**Denio**			**Pool**			**Church**			**Vernon**	
average	2.48	3.24	2.43	0.47	0.59	0.19	2.51	2.36	3.42	0.66	0.54	0.27
stdev	1.27	1.48	1.20	0.31	0.29	0.30	0.89	1.08	1.65	0.47	0.30	0.39
n observations	81	84	102	59	88	102	28	88	100	26	87	99
sterr_mean	0.14	0.16	0.12	0.04	0.03	0.03	0.17	0.12	0.17	0.09	0.03	0.04
Downwind-Upwind		**Denio - Pool**						**Church - Vernon**				
avg delta	1.97	2.65	2.24				1.80	1.81	3.20			
sterr_delta	0.17	0.15	0.11				0.19	0.12	0.16			
T-test	0.00	0.00	0.00				0.00	0.00	0.00			
propagated error	1.05	1.06	0.96				1.86	1.04	0.99			

PM2.5 (ug/m3)	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007
2200-0500 averages		**Denio**			**Pool**			**Church**			**Vernon**	
average	20.4	16.9	10.7	9.9	12.1	3.3	20.6	16.9	11.9	9.9	10.2	3.3
stdev	5.7	4.4	7.5	3.9	4.8	5.3	7.0	6.5	5.8	3.9	3.6	5.3
n observations	81	88	101	30	83	102	26	83	102	30	87	102
sterr_mean	0.6	0.5	0.7		0.5	0.5	1.4	0.7	0.6	0.7	0.4	0.5
Downwind-Upwind		**Denio - Pool**						**Church - Vernon**				
avg delta	10.5	4.7	7.5				10.8	6.5	8.6			
sterr_delta	1.1	0.5	0.4				1.5	0.7	0.5			
T-test	0.00	0.00	0.00				0.00	0.00	0.00			
propagated error	1.7	1.0	1.0				1.8	1.1	1.0			

Table 3–5. Average overnight summer NO and NOx concentrations by year 2005 - 2007.

NO (ppb)	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007
2200-0500 averages	**Denio**			**Pool**			**Church**			**Vernon**		
average	136	98	76	2	0	1	125	93	99	8	0	0
stdev	80	55	43	4	2	1	75	69	53	11	1	1
n observations	72	84	102	73	81	102	56	85	102	24	87	102
sterr_mean	9	6	4		0	0	10	8	5	2	0	0
Downwind-Upwind	**Denio - Pool**						**Church - Vernon**					
avg delta	134	99	75				123	93	99			
sterr_delta	10	6	4				19	8	5			
T-test	0.00	0.00	0.00				0.00	0.00	0.00			
propagated error	1.1	1.1	1.0				1.9	1.0	1.0			

NOx (ppb)	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007
2200-0500 averages	**Denio**			**Pool**			**Church**			**Vernon**		
average	188	143	108	17	8	9	169	133	133	21	8	8
stdev	99	71	54	11	5	3	89	84	64	18	5	4
n observations	72	84	102	73	81	102	56	85	102	24	87	102
sterr_mean	12	8	5		1	0	12	9	6	4	1	0
Downwind-Upwind	**Denio - Pool**						**Church - Vernon**					
avg delta	171	136	98				158	125	124			
sterr_delta	12	8	5				22	9	6			
T-test	0.00	0.00	0.00				0.00	0.00	0.00			
propagated error	1.1	1.1	1.0				2.1	0.8	0.8			

Table 3–6. Estimated mean overnight concentration of diesel PM from railyard activities impacting the two downwind monitoring sites in summers 2005 -2007.

	Denio			**Church**		
Diesel PM (μg/m^3)	**2005**	**2006**	**2007**	**2005**	**2006**	**2007**
2200-0500 averages	4.4 ± 2.2	6.7 ± 3.3	5.3 ± 2.7	3.9 ± 1.9	3.9 ± 2.0	8.5 ± 4.2

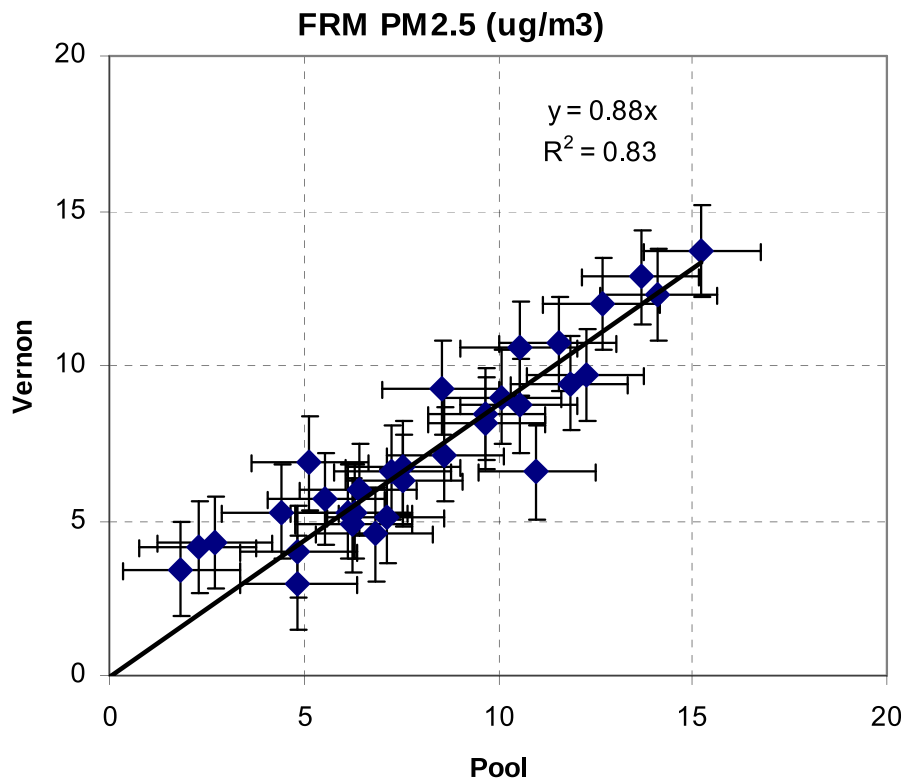


Figure 3-1. Comparison of the FRM filter data gravimetric masses from the two upwind sites

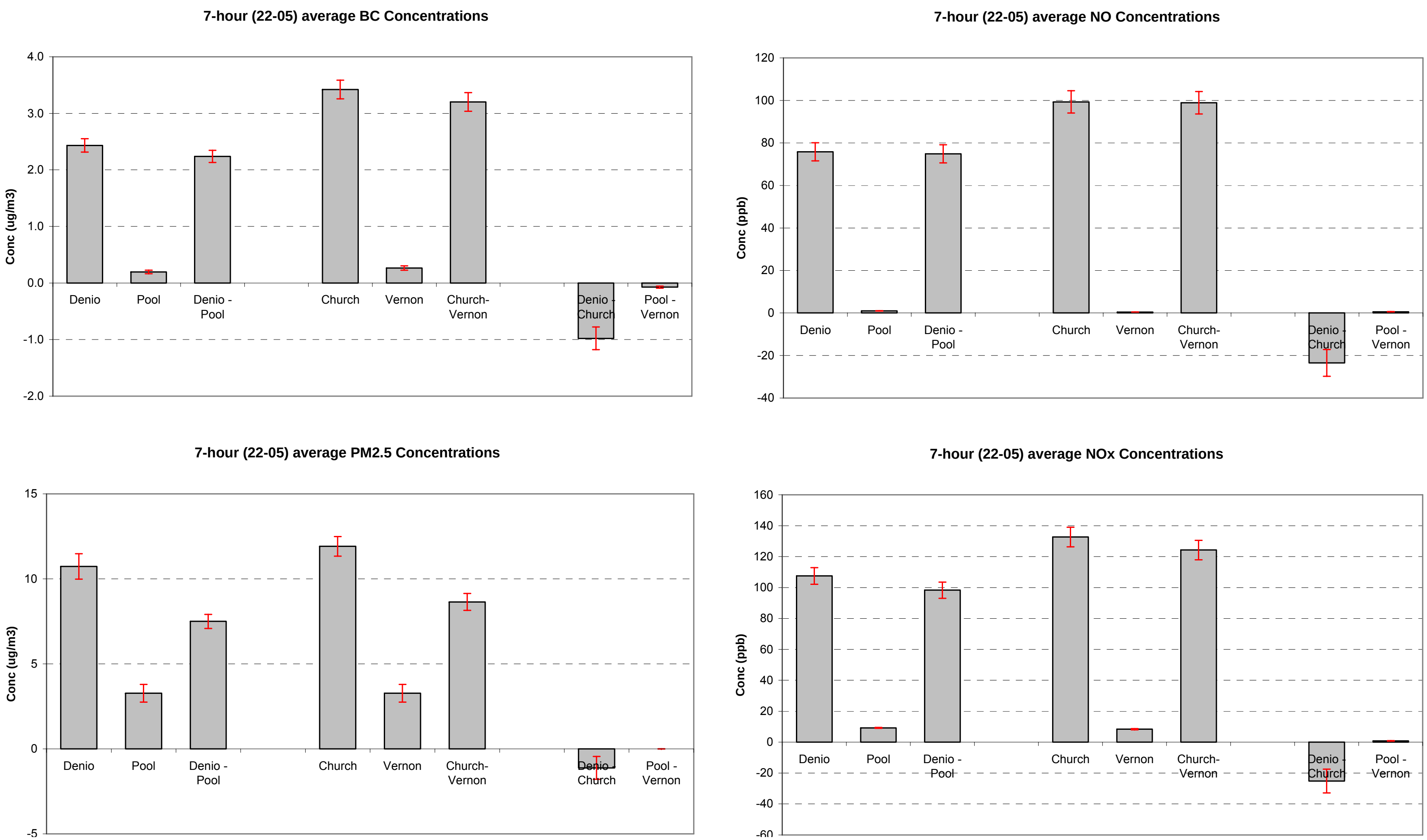


Figure 3-2. Mean BC, $PM_{2.5}$, NO and NOx concentrations at the four RRAMP monitoring sites and differences of the two pairs of downwind and upwind sites (Denio-Pool and Church-Vernon). Differences between the two downwind and two upwind sites are also shown for comparison. Error bars are the standard errors of the means.

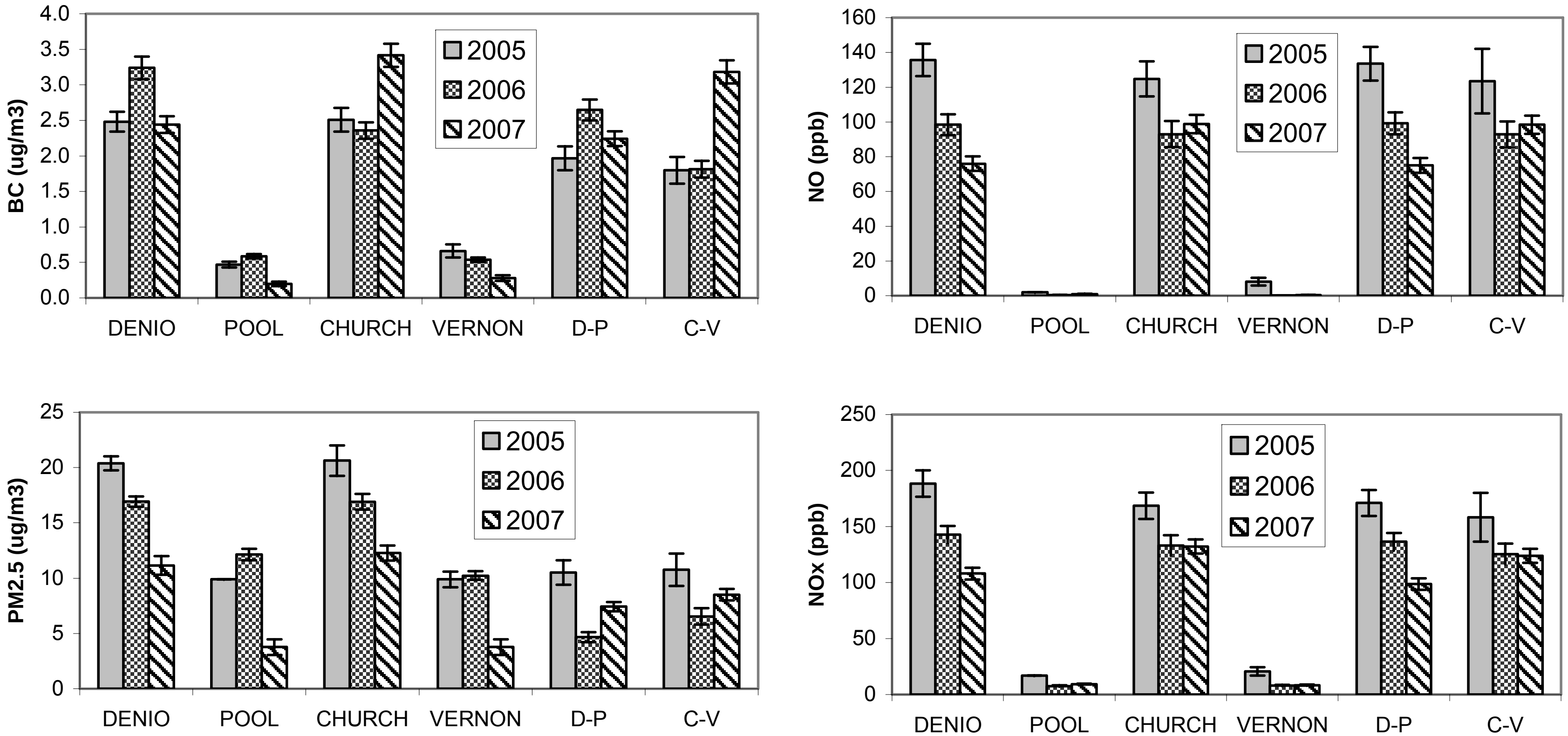


Figure 3-3. Mean BC, $PM_{2.5}$, NO and NOx concentrations at the four RRAMP monitoring sites and differences of the two pairs of downwind and upwind sites (Denio-Pool and Church-Vernon) for 2005 -2007. Error bars are the standard errors of the means.

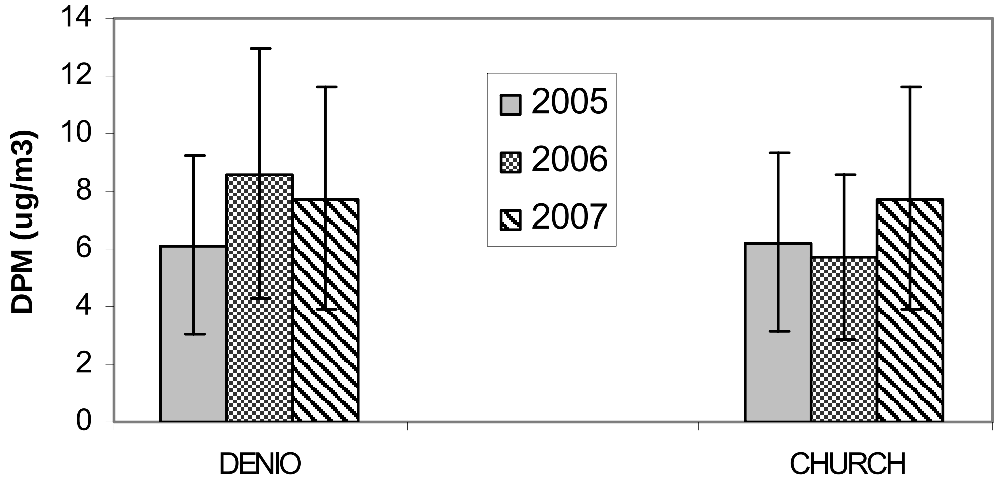


Figure 3-4. Estimated mean overnight concentration of diesel PM from railyard activities impacting the two downwind monitoring sites in summers 2005 -2007. Error bars are the uncertainty of the estimate.

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.

4.1 Data Evaluation and Validation

- Collocated sampler precision was comparable to that measured during the previous years, indicating that the performance is typical for the methods used.

- Pre-firing of the quartz filter substrates substantially lowered and stabilized the field blank values, allowing blank subtracted TOR results to be calculated for 2007.

- Even with pre-firing of the filters, the TOR results from the upwind sites were all at or below measurement uncertainty, so only the increase in measured EC at the downwind sites should be used to estimate DPM.

- Averaged $PM_{2.5}$ data from the BAMs is correlated with the corresponding filter gravimetric mass data for the downwind sites, but shows some evidence of a slight negative bias at higher concentrations. Adjustments to the BAM data were made to account for this. This relationship is different than that observed for the 2006 season, suggesting that the bias is due to measurement error rather than compositional effects on the BAM or volatilization of aerosol from the filters.

- 7-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.

4.2 Data Analysis

- Overall, there is evidence of substantial impact on the downwind sites. There was a substantial increase in NO, NOx, BC, and $PM_{2.5}$ 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 prior years 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_x, BC, and $PM_{2.5}$. The increasing ratios from NO to $PM_{2.5}$ are consistent with larger contributions of urban background to the measured $PM_{2.5}$ and BC concentrations.

- $BC/PM_{2.5}$ and NO/NOx ratios are consistently higher at the downwind sites, which is consistent with presence of fresh emissions.

- EC/TC ratios from the FRM filter samples are lower than in the previous year (but that may be a result of high blank EC concentrations in 2006) and clearly indicate a difference in aerosol composition between the upwind and downwind sites. $TC/PM_{2.5}$ ratios were also similar at sites on both sides of the railyard, as in 2006.

- Given the large uncertainty in the estimation of DPM (± 50%), it is not possible to discern if any variations in impact on the downwind area occurred from year to year. The application of more appropriate $PM_{2.5}/EC$ ratios to the calculation, when they become available, may reduce the uncertainties substantially but it is not expected to change the relative magnitude of the annual averages since the same BC data will be used.

5. REFERENCES

Arnott, W. P., H. Moosmüller, et al. (1999). "Photoacoustic spectrometer for measuring light absorption by aerosols: Instrument description." *Atmospheric Environment* 33: 2845-2852.

Arnott, W. P., K. Hamasha, H. Moosmüller, P.J. Sheridan and J.A. Ogren (2005). "Towards Aerosol Light Absorption Measurements with a 7-Wavelength Aethalometer: Evaluation with a Photoacoustic Instrument and 3-Wavelenght Nephelometer." *Aerosol Sci. and Technol.* 39:17-29.

Campbell, D.E. and E.M. Fujita (2005). Deployment of DRI Mobile Van in Support of the Roseville Rail Yard Air Monitoring Project. Final report submitted to Placer County Air Pollution Control District, Auburn, CA, May 6, 2005.

Campbell, D.E. and E.M Fujita (2006). Data Analysis on the Roseville Rail Yard Air Monitoring Project. Final report submitted to the Placer County Air Pollution Control District, Auburn, CA, March 15, 2006.

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.

Fujita, E.M., B. Zielinska, D.E. Campbell, W.P. Arnott, J. Sagebiel, L. Reinhart, J.C. Chow, N. P.A. Gabele, W. Crews, R. Snow, N. Clark, S. Wayne and D.R. Lawson (2007). Variations in speciated emissions from spark-ignition and compression ignition motor vehicles in the California's South Coast Air Basin. J. Air Waste Manage. Assoc., 57, p705-720.

Sawant A., A Nigam, J. W. Miller, K Johnson, and D. Cocker, III (2007). Regulated and Non-Regulated Emissions from In-Use Diesel-Electric Switching Locomotives. Environ. Sci. Technol.; 2007; 41(17) pp 6074 – 6083.

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 ~ 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^{o}C (OC1), 250^{o}C (OC2), 450^{o}C (OC3), and 550^{o}C (OC4) in a nonoxidizing helium atmosphere, and at 550^{o}C (EC1), 700^{o}C (EC2), and 850^{o}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

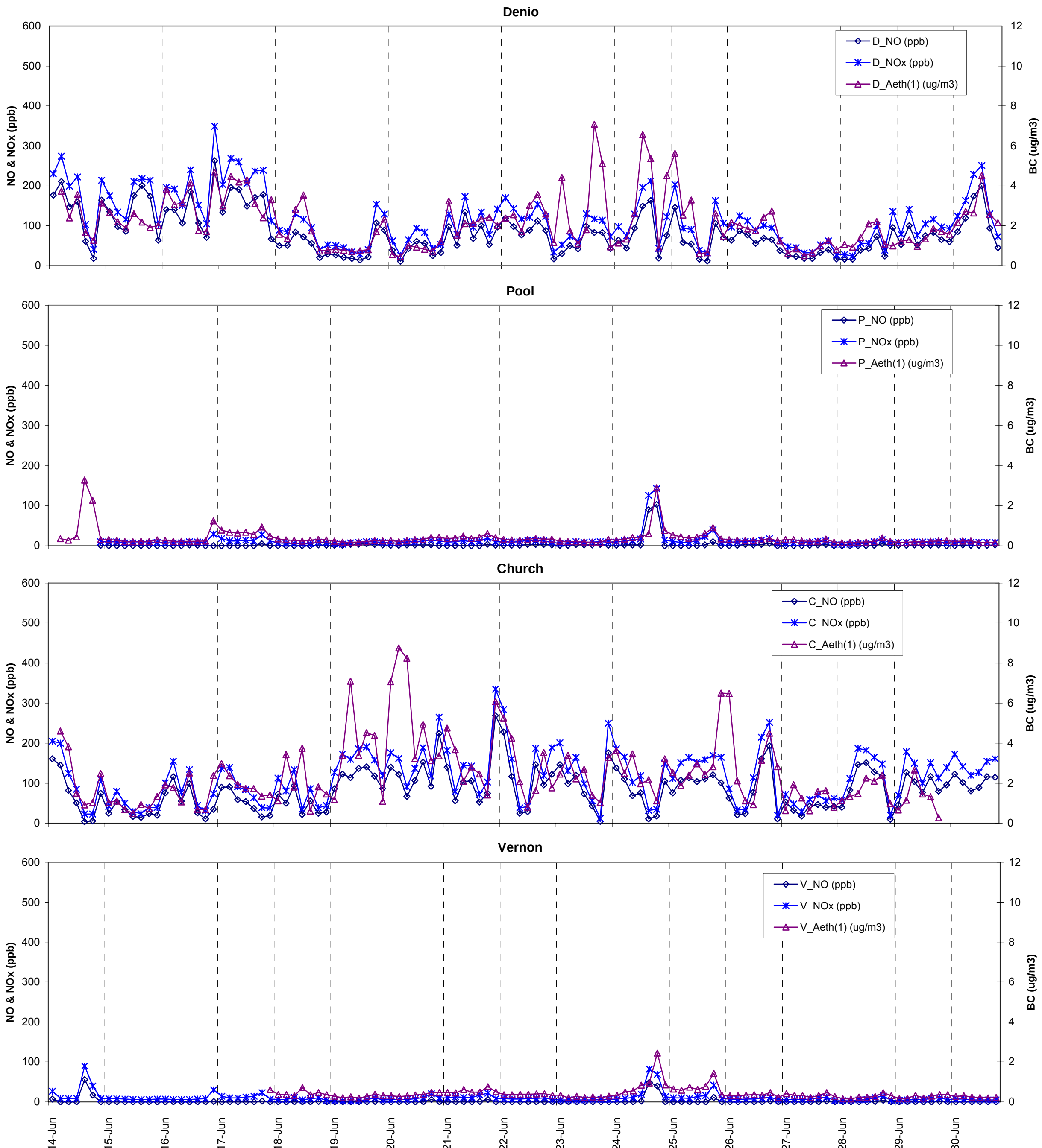


Figure 5. Hourly NO, NOx, and BC for June 2007

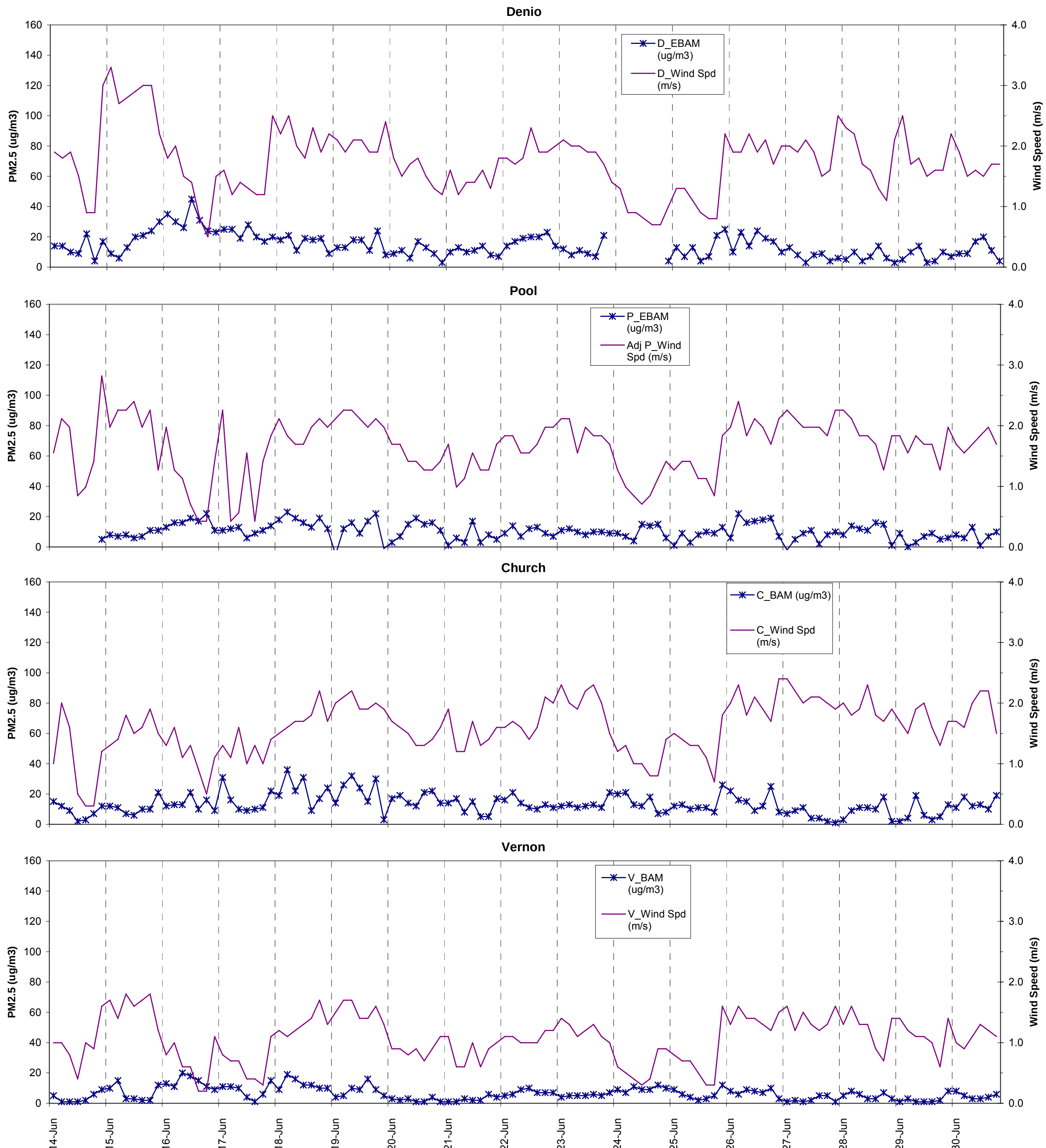


Figure 6. Hourly PM2.5 mass concentration and wind speed for June 2007.

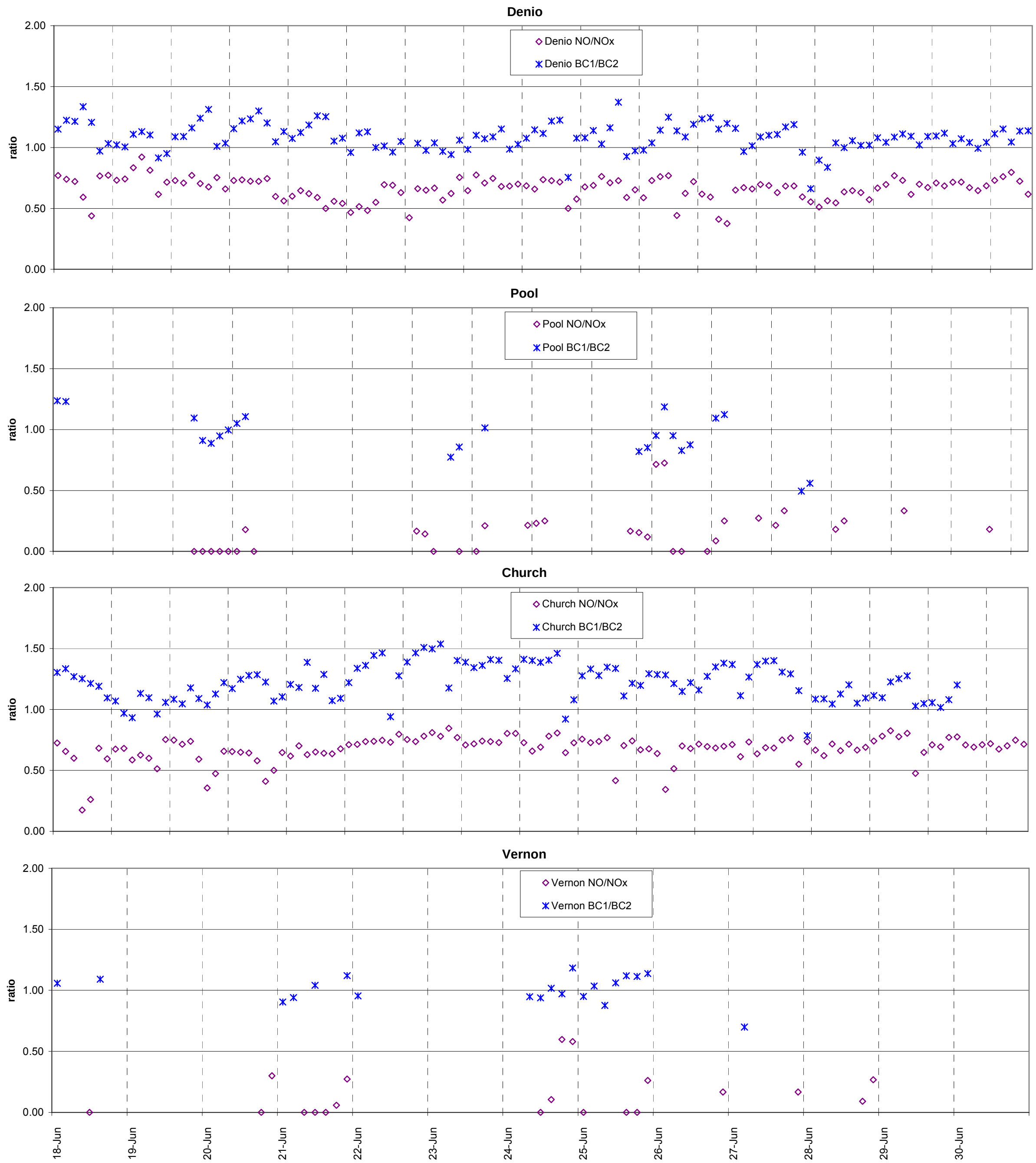


Figure 7. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for June 2007.

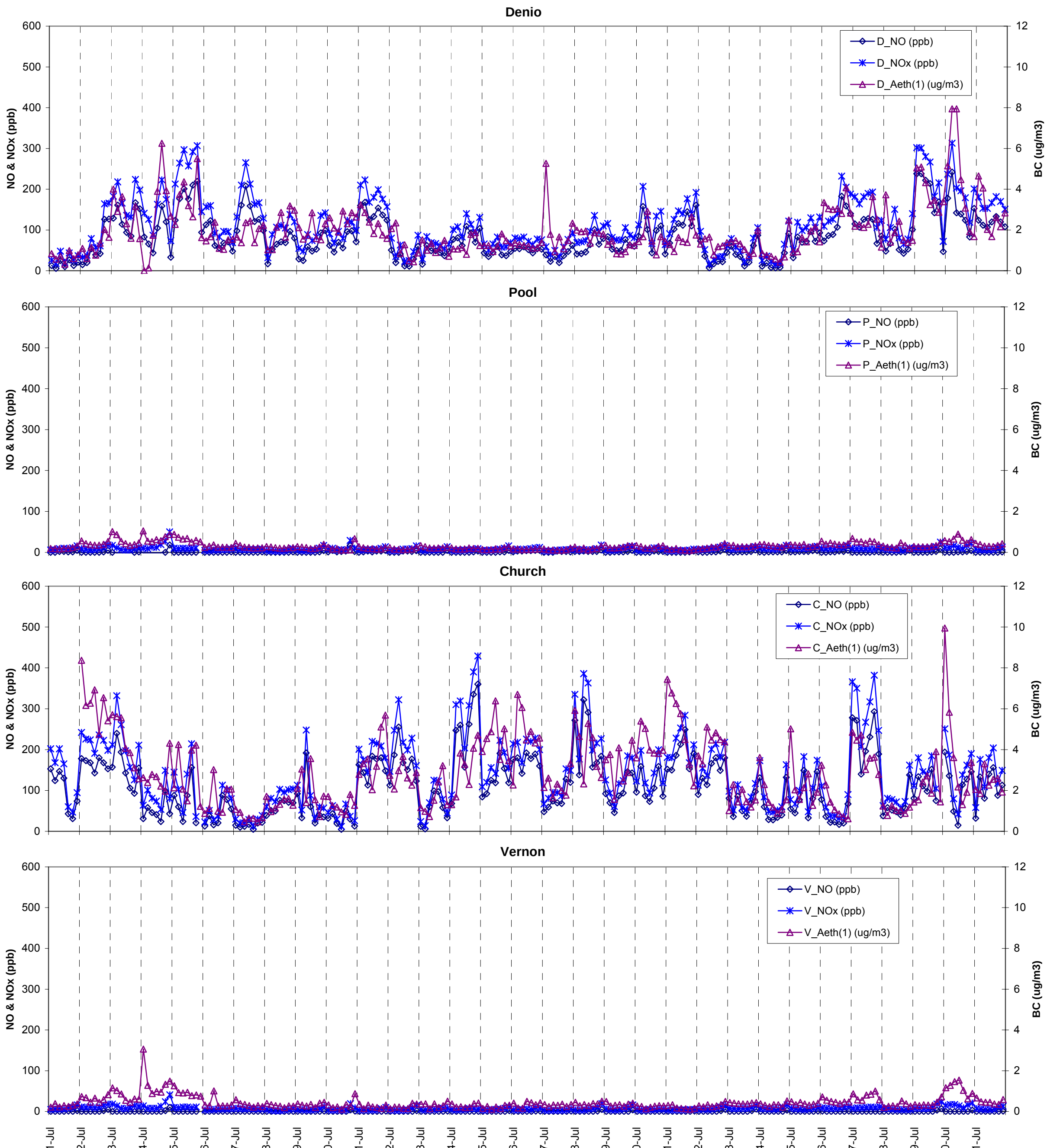


Figure 8. Hourly NO, NOx, and BC for July 2007

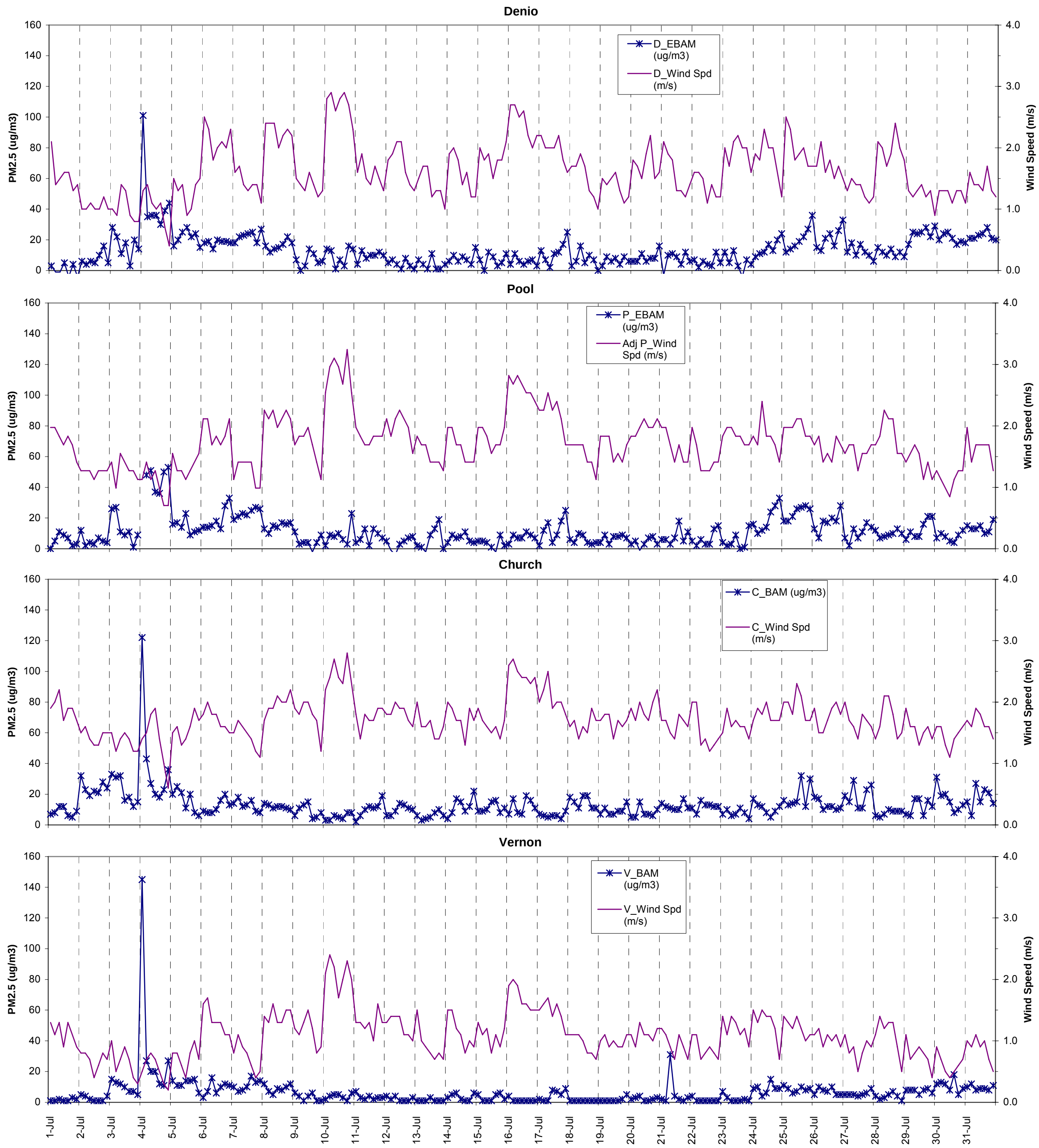


Figure 9. Hourly PM2.5 mass concentration and wind speed for July 2007.

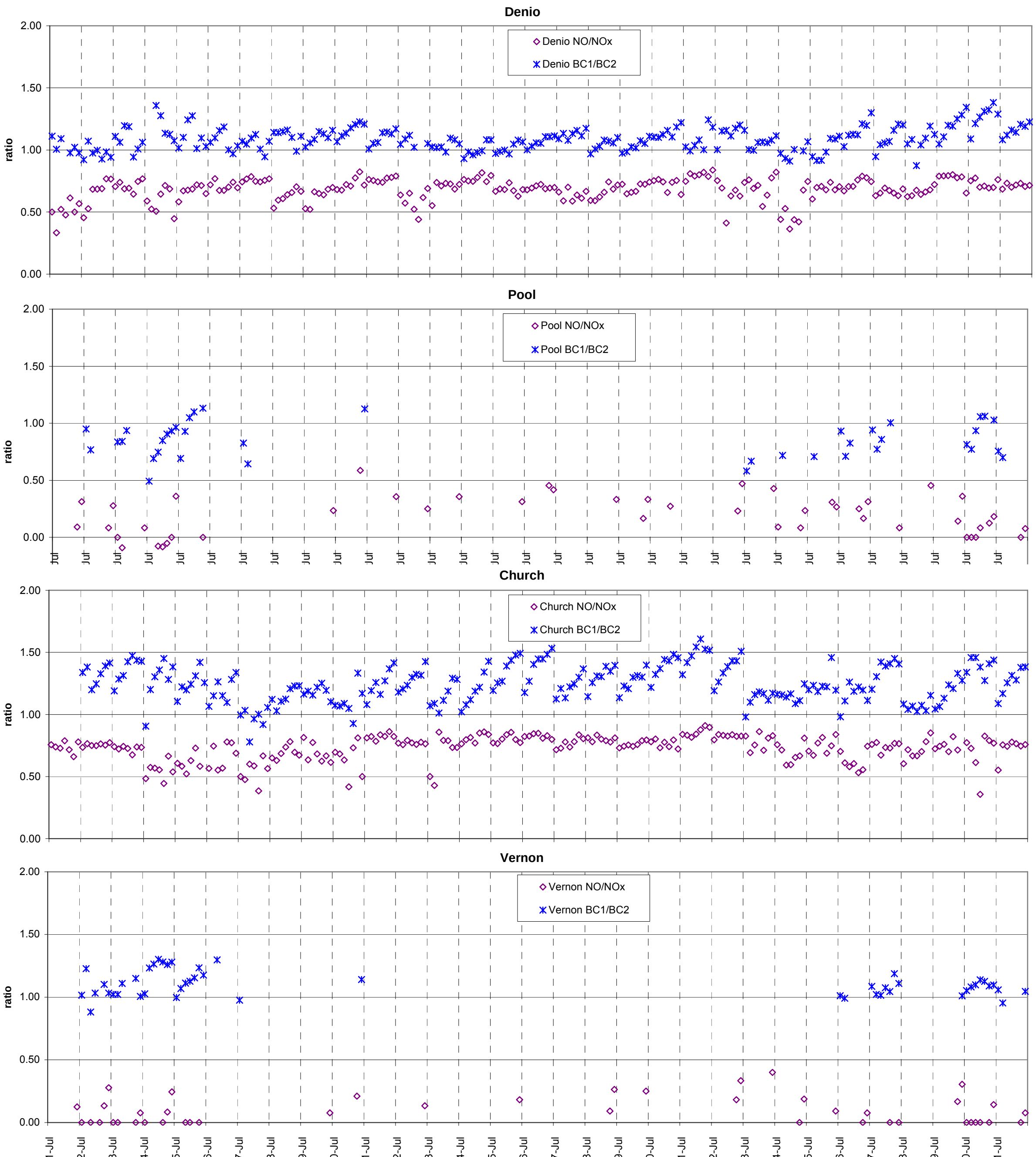


Figure 10. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for July 2007.

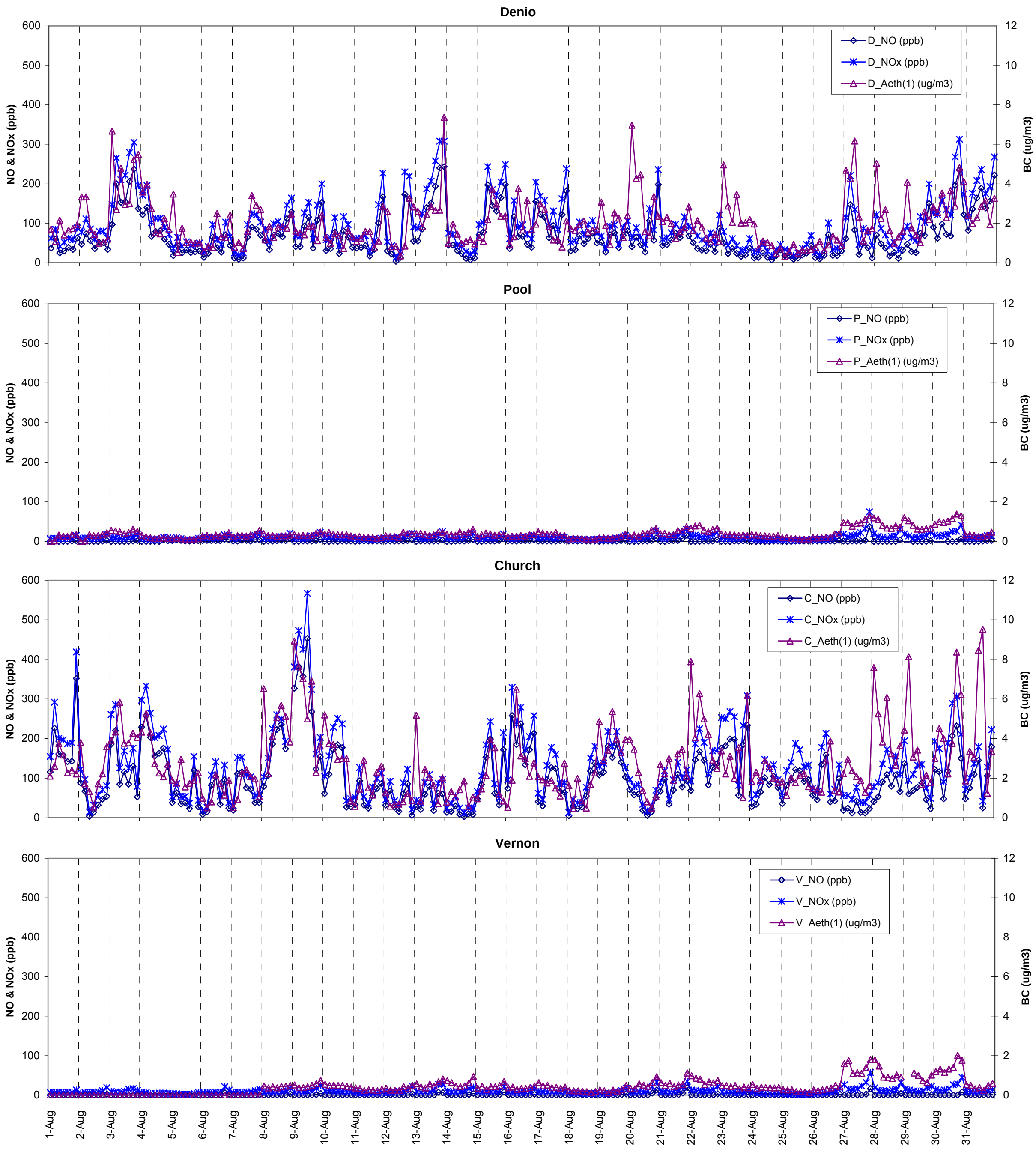


Figure 11. Hourly NO, NOx, and BC for August 2007

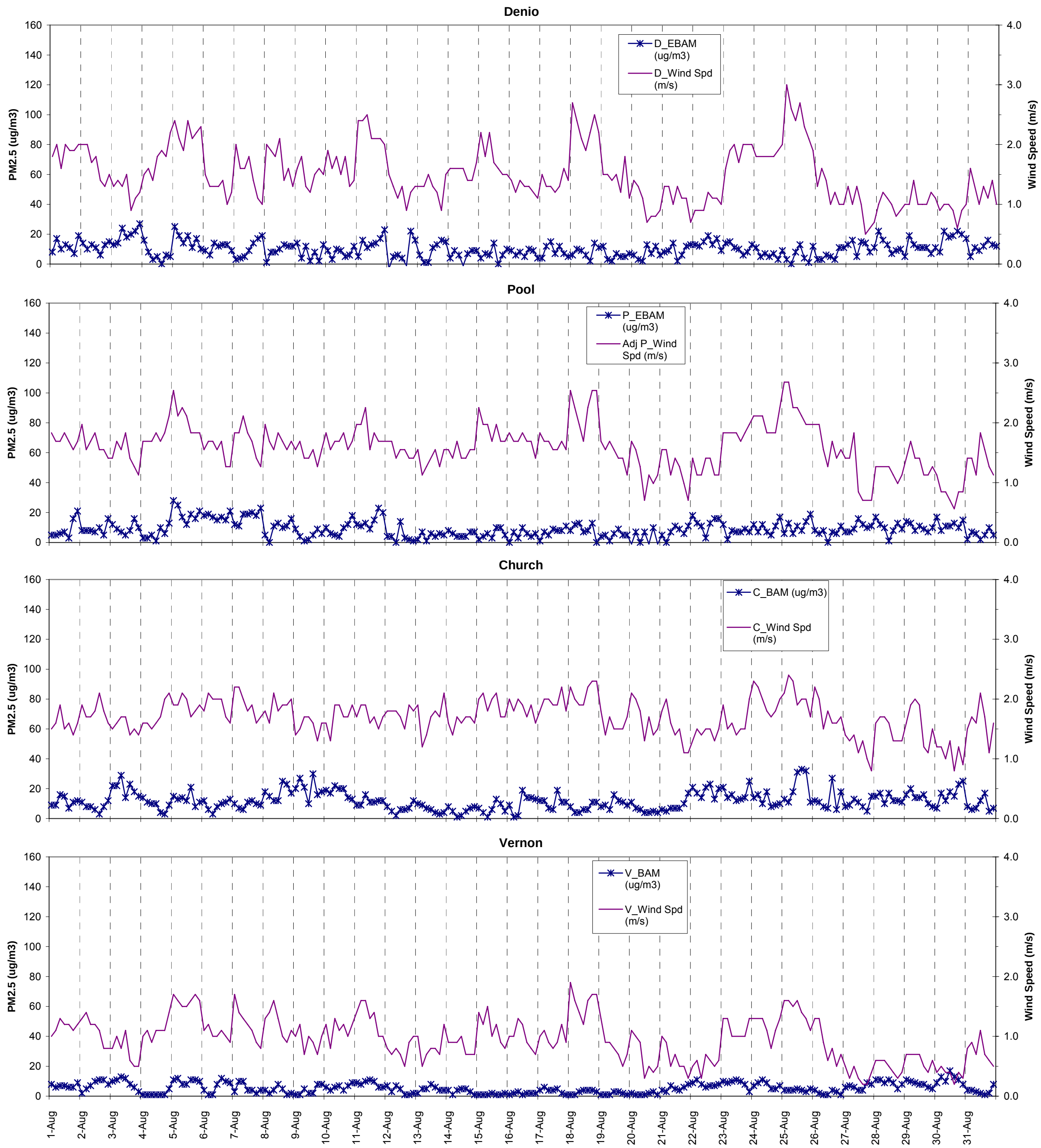


Figure 12. Hourly PM2.5 mass concentration and wind speed for August 2007.

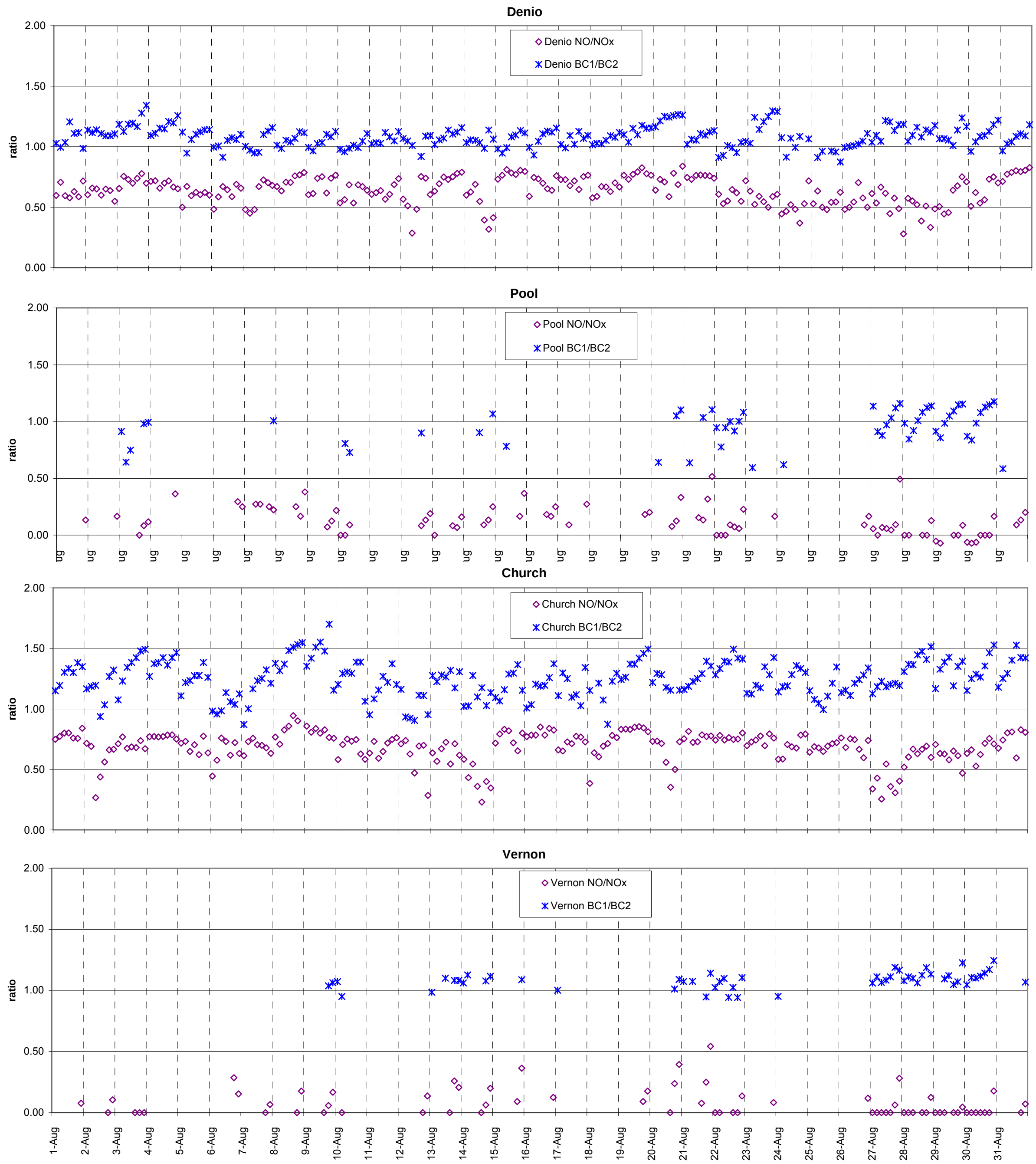


Figure 13. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for August 2007.

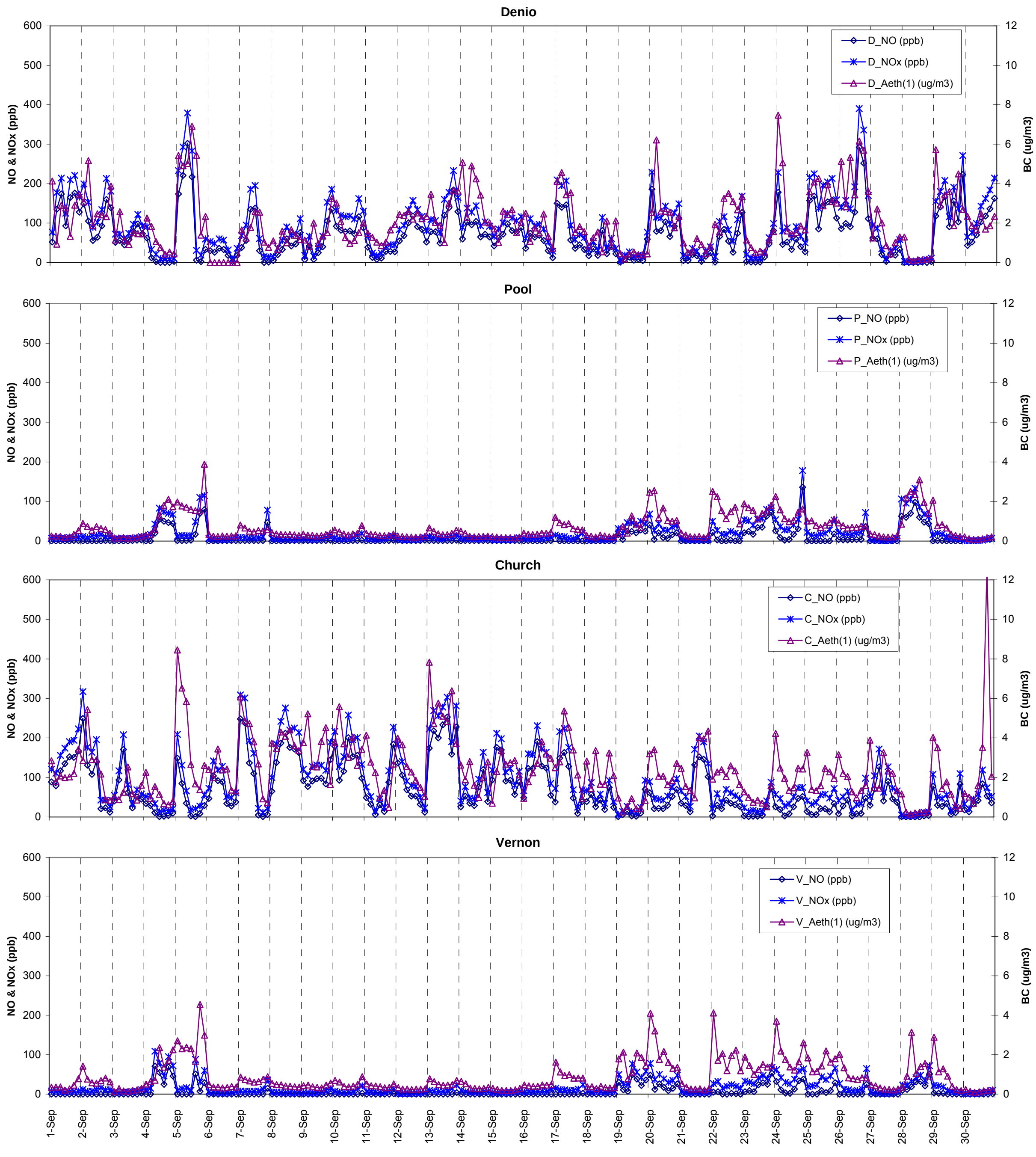


Figure 14. Hourly NO, NOx, and BC for September 2007

Figure 15. Hourly PM2.5 mass concentration and wind speed for September 2007.

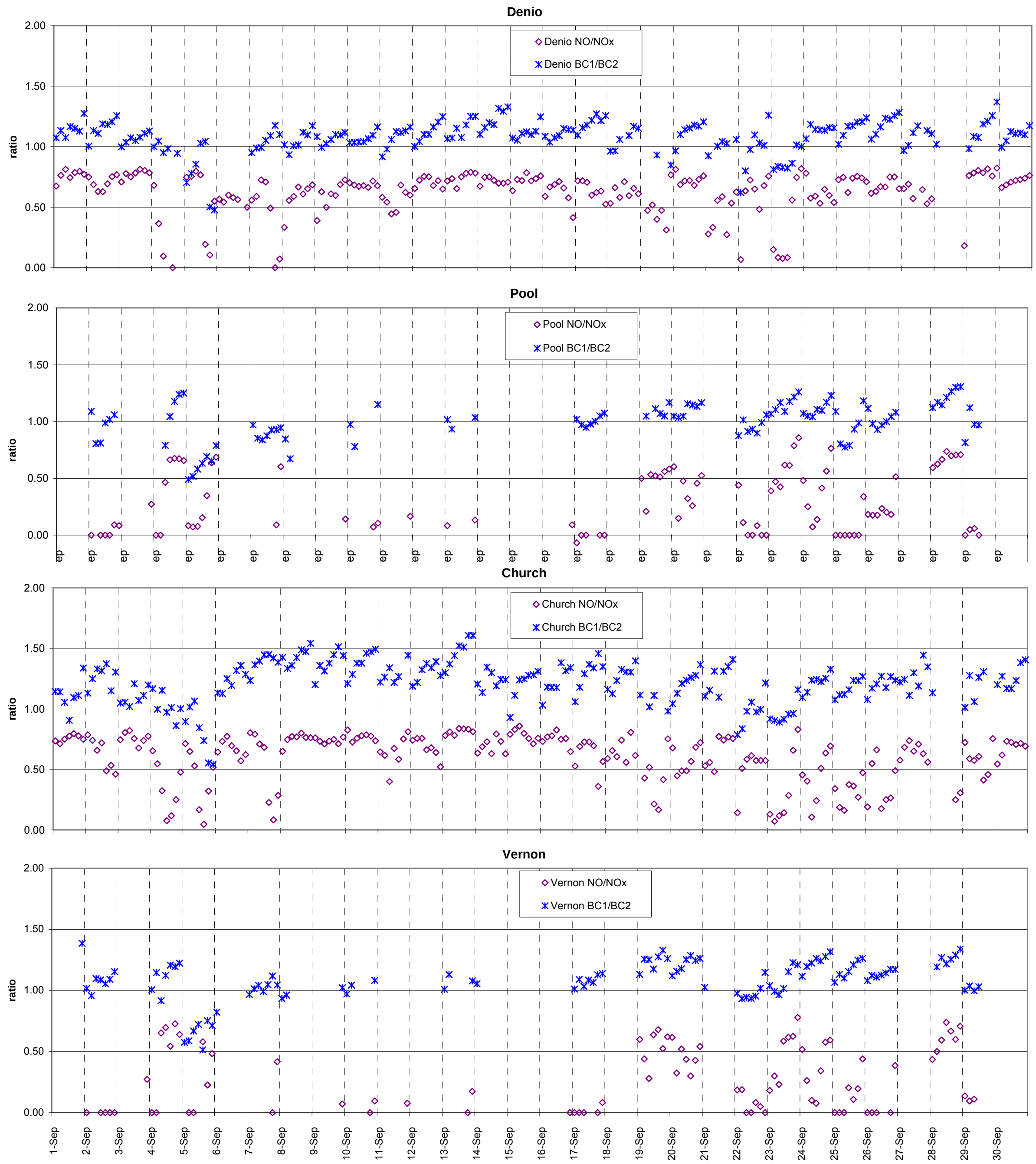


Figure 16. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for September 2007.

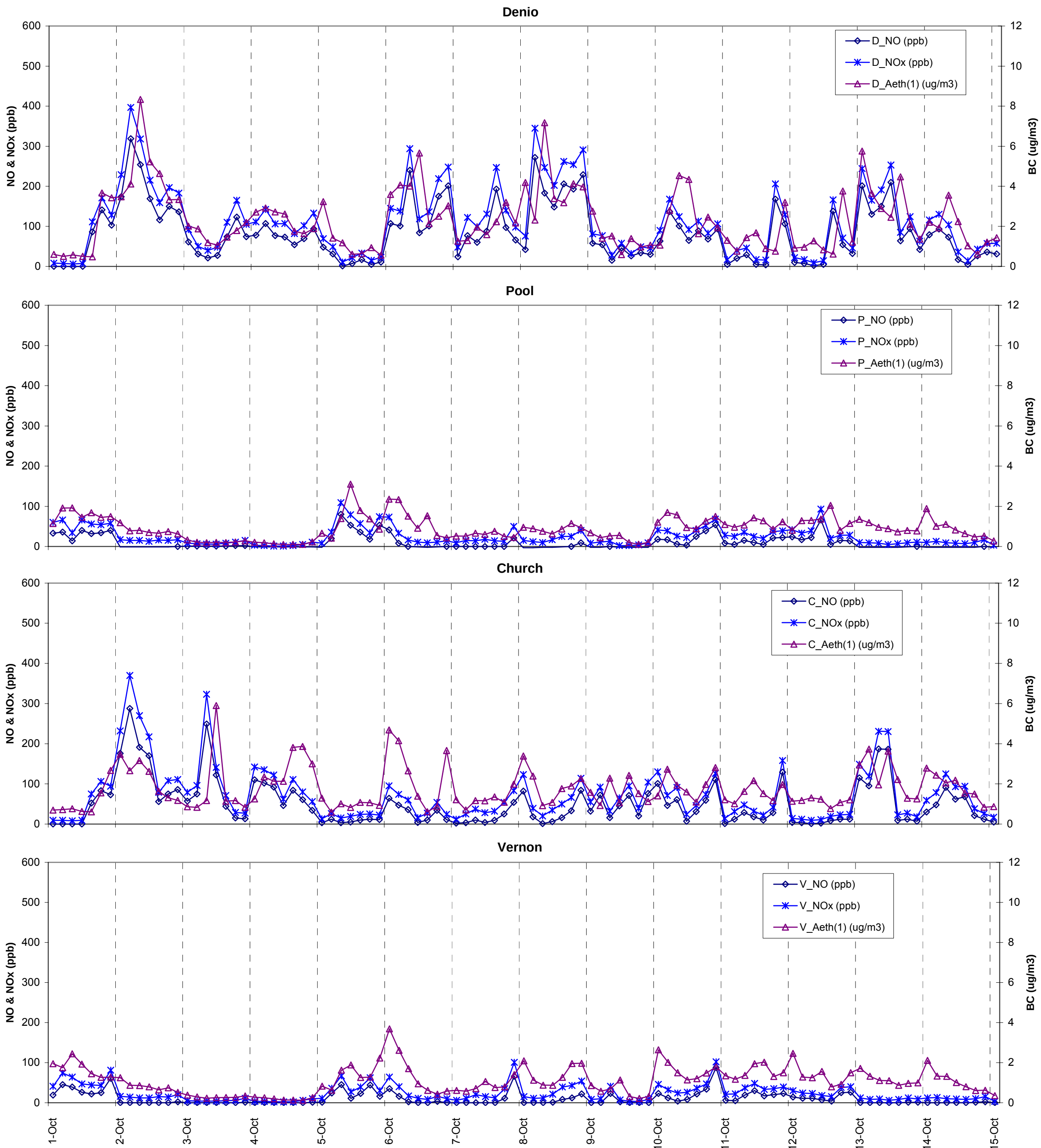


Figure 17. Hourly NO, NOx, and BC for October 2007

Figure 18. Hourly PM2.5 mass concentration and wind speed for October 2007.

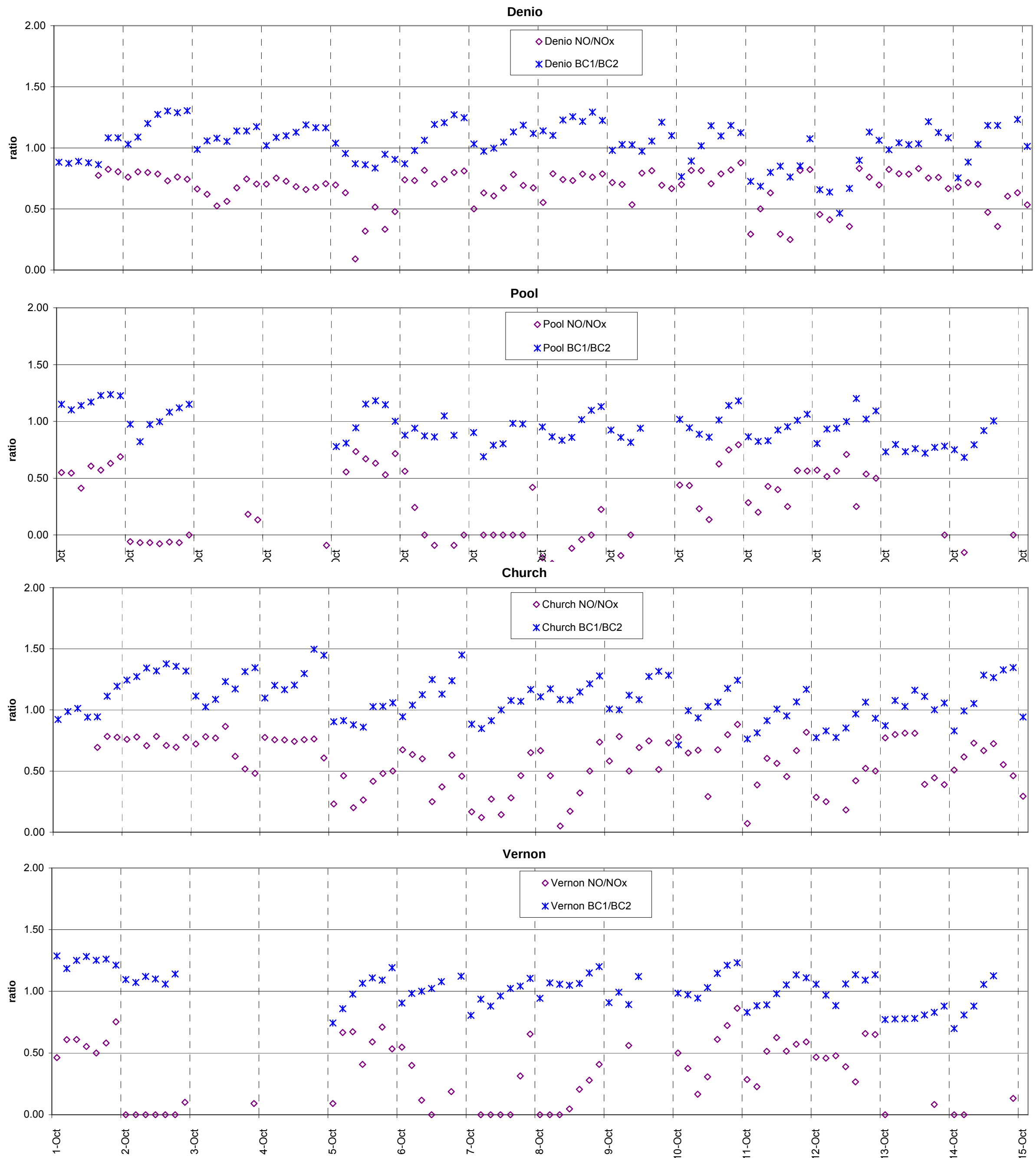


Figure 19. Hourly NO/NOx ratio and BC(1)/BC(2) ratio for October 2007.